Pretransitional anomalies in the shear flow near a second-order nematic–smectic-*A* phase change

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Pretransitional anomalies in a shear flow near a second order nematic–smectic-*A* (*NA*) phase transition temperature T_{NA}, for liquid crystals (LC's), taking into account the fluctuations of the local smectic order parameter above the T_{NA}, are investigated. It is shown that the tumbling instability of the Couette shear flow for polar LC compounds, such as 4-*n*-octyl-4′-cyanobiphenyl (8CB), in the vicinity of T_{NA}, e.g., at a few tens of mK from T_{NA} in the nematic phase, occurs at any shear rate $\dot{\gamma}$.

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The theoretical description of dissipation processes in liquid crystals (LC's) is still an important issue [1–6]. Despite the fact that certain qualitative advances have been achieved in the construction of a molecular theory of the rheological properties of nematic liquid crystals (NLC's) in a shear flow far away from a nematic–smectic–*A* (*NA*) phase transition temperature T_{NA} [1–4], it is still too early to talk about the development of a theory which would make it possible to describe the rheological process in the vicinity of T_{NA}, e.g., at a few tens of mK from T_{NA} in the nematic phase [5–7]. Taking into account that the fluctuations of the local smectic order parameter (OP) above the second order *NA* phase transition gives rise to singularities in the elastic constants and the rotational viscosity coefficient (RVC) γ_1 [4,5], one should expect that shear flows will also demonstrate peculiarities in the vicinity of T_{NA} [6,7]. Indeed, when the director $\hat{\mathbf{n}}$, oriented in the shear *x*-*y* plane [*x*-*y* plane, defined by the liquid crystal flow (*x* direction) and the velocity gradient in the *y* direction; *z* is the vorticity axis], is disturbed and then allowed to relax, at temperatures far away from T_{NA}, one deals with a twofold result. First, the hydrodynamic torque,

$$\mathbf{T}_{vis}=\left[\frac{1}{2}(\gamma_1+\gamma_2\cos 2\theta\dot{\gamma})\right]\hat{\mathbf{k}}=[(\alpha_3\cos^2\theta-\alpha_2\sin^2\theta)\dot{\gamma}]\hat{\mathbf{k}}, \tag{1}$$

exerted per unit volume in a high shear flow vanishes when the director aligns at an equilibrium angle [1,2],

$$\theta_{eq}=\frac{1}{2}\cos^{-1}(-\gamma_1/\gamma_2)=\tan^{-1}(\sqrt{\alpha_3/\alpha_2}), \tag{2}$$

with respect to the direction of flow velocity $\mathbf{v}=\dot{\gamma}y\hat{\mathbf{i}}$. Second, the director continuously rotates in the shear plane. Here $\gamma_1=\alpha_3-\alpha_2$ and $\gamma_2=\alpha_3+\alpha_2$ are the rotational viscosity coefficients (RVC's), α_2 and α_3 are the Leslie coefficients, and $\dot{\gamma}$ is the shear rate. It is clear from this equation that if $|\gamma_1|>|\gamma_2|$ or $\alpha_3>0$ (because in practice, $\alpha_2<0$), no real solution for θ_{eq} exists. Physically, this means that in this case the director will tumble under shear flow of the nematic. Taking into account that both coefficients γ_1 and γ_2, as well as α_2 and α_3, are temperature dependent functions, one should expect that some LC materials undergo a transition from a laminar flow regime to a tumbling instability as the temperature decreases [7,8]. As temperature is reduced towards T_{NA}, the growth of pretransitional *SmA* fluctuations are expected to give rise to a novel torque $\mathbf{T}_{fl}$ on $\hat{\mathbf{n}}$, which alters the $\mathbf{T}_{vis}$. As results, for low shear rates $\dot{\gamma}\tau_m<1$, the equation for the balance of torques takes the form $\mathbf{T}_{vis}+\mathbf{T}_{fl}=0$, where $\mathbf{T}_{fl}$ is [7]

$$\mathbf{T}_{fl}=-\mathcal{A}\hat{\mathbf{n}}\times\hat{\mathbf{j}}=-\left[-\frac{\pi}{2}\frac{k_BT}{l^2\xi_{\parallel}}(\dot{\gamma}\tau_m)(\hat{\mathbf{n}}\cdot\hat{\mathbf{v}})+O((\dot{\gamma}\tau)^2)\right]\hat{\mathbf{k}}\cos\theta. \tag{3}$$

Here τ_m is a relaxation time along the director, $\xi_{\parallel}=\xi$ is the correlation length along $\hat{\mathbf{n}}$, $\hat{\mathbf{v}}=\mathbf{v}/|\mathbf{v}|$, and l is the layer spacing of the smectic layers. The physical origin of $\mathbf{T}_{fl}$ is due to the effect of shear flow on the fluctuation domains. This means that for a temporal fluctuation domain with $\hat{\mathbf{n}}\|\hat{\mathbf{v}}$, shear flow tends to tilt the layers, which changes the layer spacing and gives rise to the restoring torque $\mathbf{T}_{fl}$. In contrast, shear flow does not alter the internal structure of fluctuations with $\hat{\mathbf{n}}\perp\text{grad }v$ and $\hat{\mathbf{n}}\perp\text{grad }v$ and $\hat{\mathbf{n}}\perp\hat{\mathbf{v}}$ orientations. As a result, the effect of fluctuations, at the lowest order in $\dot{\gamma}\tau_m$, is reflected in a renormalization of γ_1 or α_3,

$$\overline{\gamma_1}=\gamma_1+\alpha_3^c;\quad \overline{\alpha_3}=\alpha_3+\alpha_3^c=\alpha_3+\frac{\pi}{2}\frac{k_BT}{l^2}\frac{\tau_m}{\xi}, \tag{4}$$

in Eq. (1), and the balance of torques take the form

$$\overline{\gamma_1}\frac{\partial\theta}{\partial t}+\frac{1}{2}(\overline{\gamma_1}+\gamma_2\cos 2\theta)\dot{\gamma}=\overline{\gamma_1}\frac{\partial\theta}{\partial t}+(\overline{\alpha_3}\cos^2\theta-\alpha_2\sin\theta)\dot{\gamma}=0. \tag{5}$$

Here α_3 and γ_1 are the bare values of the corresponding Leslie and rotational viscosity coefficients. It has been found,

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by applying dynamical scaling arguments [4], that the relaxation time τ_m of the order parameter is $\tau_m \sim \xi^{3/2}$, and the *SmA* correlation length $\xi = \xi_{\parallel}$ in the reduced temperature range close to the critical point is $\xi = \xi_0 t^{-\nu}$, where ξ_0 is the bare correlation length, $t = (T - T_{NA})/T_{NA}$, and $\nu = \nu_{\parallel}$ is the associated critical exponent. So, for low shear rates $\dot{\gamma}\tau_m < 1$, both $\overline{\gamma_1}$ and α_3^c diverge at T_{NA} as $\tau_m/\xi \sim t^{-\nu/2}$. Because $\alpha_3 < 0$ for temperatures far from T_{NA} in the nematic phase [9], this result predicts a sign change in $\overline{\alpha_3}$ in the vicinity T_{NA}. Taking into account that the critical contribution to the RVC α_3^c has been found, for instance, in the case of 4-*n*-octyl-4′-cyanobiphenyl (8CB), only in the reduced temperature range $0 < t < 10^{-3}$ (less than 306.7 K $[T_{NA}(\text{8CB}) = 306.5\text{ K}]$) [6], the presmectic behavior in shear flow should be expected at temperatures for the same t range.

It should be noted that the fluctuations of the local smectic order parameter above the second order *NA* phase transition give rise to singularities not only in the viscosities of the nematic but also in the elastic constants. In the hydrodynamic regime $q_s\xi \gg 1$, the behavior of the (total) bend deformation $\overline{K_3}$ can be written in the form [4,6]

$$\overline{K_3} = K_3 + K_3^c = K_3 + \frac{k_B T}{24\pi} q_s^2 \xi = K_3 + \frac{k_B T}{6} \frac{\pi \xi_0}{l^2} t^{-\nu}, \qquad (6)$$

where K_3^c is the critical contributions to the elastic parameter, $q_s = 2\pi/l$, l is the layer spacing of the smectic layers, ξ is the *SmA* correlation length along the director, τ_m is the relaxation time of the order parameter, and $t = (T - T_{NA})/T_{NA}$ is the reduced temperature. Taking into account that the flow alignment at temperatures close to T_{NA} is governed not only by hydrodynamic and fluctuating torques, but also by elastic torques [9], the equation for the balance of momentum takes the form $\mathbf{T}_{vis} + \mathbf{T}_{fl} + \mathbf{T}_{el} = 0$, or in the dimensionless form as

$$\frac{\partial \theta}{\partial \tau} + \frac{1}{2}\left[1 + \frac{\gamma_2}{\gamma_1}\cos 2\theta\right] - h(\theta)\frac{\partial^2 \theta}{\partial \overline{y}^2} - \frac{1}{2}h'(\theta)\left(\frac{\partial \theta}{\partial \overline{y}}\right)^2 = 0. \qquad (7)$$

Here $h(\theta) = (K_1 \cos^2\theta + \overline{K_3}\sin^2\theta)/(\overline{\gamma_1}\dot{\gamma}l^2)$, $h'(\theta)$ is the derivative of $h(\theta)$ with respect to θ, the coefficients K_1 and K_3 are the splay and bend elastic constants, respectively, the dimensionless time $\tau = \dot{\gamma}t$, and the dimensionless size $\overline{y} = y/l$, where l is the length of the smectic layers. Since the shear flow is normally obtained by displacing an upper horizontal glass plate with respect to a fixed lower glass plate, the possible smectic layering can be organized to be parallel to the boundary surfaces. As a result, the $\overline{y}$ is the dimensionless distance from the surface in the $\hat{\mathbf{j}}$ direction, with $\hat{\mathbf{j}}$ a unit vector directed perpendicular to the substrates and the smectic layers. Let us consider first the temperature region $-5 < \log_{10}(T/T_{NA} - 1) < -4$ close to $T_{NA} = 306.5$ K for 8CB. First of all, when the temperature $T \to T_{NA}$, e.g., at a few tens of mK from T_{NA} in the nematic phase, the bend deformation coefficient $\overline{K_3}$ and RVC $\overline{\gamma_1}$ both increase to infinity and the ratio $\lim_{T \to T_{NA}} \overline{K_3}/(\overline{\gamma_1}\dot{\gamma}l^2) \sim \lim_{t \to 0} O(1/t^{2\nu - 1})$. Measurements of the *SmA* correlation length ξ for 8CB, in the reduced temperature range close to the critical point, have been made by means of high-resolution x-ray scattering on the mass-density fluctuations [10]. It was found that in the reduced temperature range $-5 < \log_{10}(T/T_{NA} - 1) < -2$, $\xi = \xi_0 t^{-\nu}$, where $\xi_0 = 0.45$ nm is the bare correlation length, $\nu = 0.67 \pm 0.03$ is the associated critical exponent, and $l = 1.8$ nm. As a result, the fluctuation relaxation time τ_m and factor $q_s\xi$, for 8CB, grows between $\tau_m \sim 1$ μs and $q_s\xi \sim 18$ for $\log_{10}(T/T_{NA} - 1) \sim -2.0$ and $\tau_m \sim 1$ ms and $q_s\xi \sim 1800$ for $\log_{10}(T/T_{NA} - 1) \sim -5.0$, respectively.

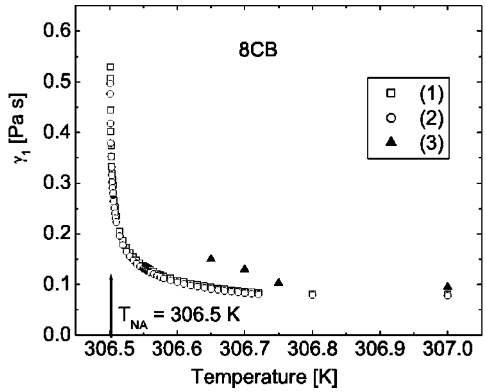

FIG. 1. The temperature dependence of the rotational viscosity coefficient $\overline{\gamma_1}$, calculated using Eq. (4) (symbols 1), Eqs. (4) and (8) (symbols 2), and measured values in Ref. [11] of $\overline{\gamma_1}$ (symbols 3), respectively. In both theoretical cases, the bare values of the RVC γ_1 have been calculated using Eq. (8) [6].

It should be noted that there is another description of the critical contribution to the RVC γ_1 or Leslie viscosity coefficient α_3, which, in the hydrodynamic regime $q_s\xi \gg 1$, takes the form [4,6]

$$\alpha_3^{cc} = \gamma_1^{cc} = \frac{k_B T}{4}\frac{\pi}{\xi_0}\sqrt{\frac{\rho_m}{K_1}}t^{\nu - 1}, \qquad (8)$$

where $q_s = 2\pi/l$, K_1 is the splay elastic deformation, and ρ_m is the mass density. So, the disturbing effect of the surface-induced fluctuating layer structure on the viscosity $\overline{\gamma_1}$ reflects in two different forms; first, when $\overline{\gamma_1}$ diverges at T_{NA} as $\sim t^{-\nu/2}$, and, second, when $\overline{\gamma_1}$ diverges as $\sim t^{\nu - 1}$. The temperature dependence of the γ_1^{cc} and $\overline{K_3}$ in the temperature range $-5 < \log_{10}(T/T_{NA} - 1) < -4$ has been calculated in Ref. [6]. The values of the RVC γ_1^c and γ_1^{cc} as the function of temperatures are presented in Fig. 1. It is found that the temperature dependence reflected in these two different forms gives, practically, the same values of the viscosity $\overline{\gamma_1}$. In both these cases, the bare values of the RVC γ_1 has been calculated using Eq. (8) [6]. Reasonable agreement is also observed between the calculated values and experimental results, which were obtained by dynamic light scattering method [11]. So, the pretransitional anomalies in $\overline{\gamma_1}$ and $\overline{K_3}$ should be expected at temperatures less than 306.7 K, $\lim_{T \to T_{NA}} \overline{K_3}/(\overline{\gamma_1}\dot{\gamma}l^2) \to 0$, and Eq. (7) leads to a nonstationary equation for $\theta(\tau)$, which can be rewritten as

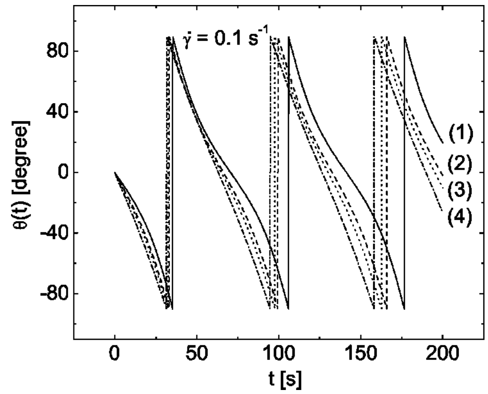

FIG. 2. Plot of the rotation of the director in the bulk 8CB sample under shear flow, characterized by an angle $\theta(t)$ given in Eq. (12), at four temperatures $\log_{10}(T/T_{NA}-1)=-3.20$ (curve 1); -3.67 (curve 2); -3.94 (curve 3); and -5.01 (curve 4). In all these cases the value of the shear rate is $\dot{\gamma}=0.1\ \mathrm{s}^{-1}$.

$$\frac{\partial\theta}{\partial\tau}+\frac{1}{2}\left[1+\frac{\gamma_2}{\gamma_1+\gamma_1^c}\cos 2\theta\right]=0, \tag{9}$$

where

$$\overline{\gamma_1^c}=\frac{\pi}{2}\frac{k_BT}{l^2}\frac{\tau_m}{\xi},\quad \text{where } \tau_m/\xi\sim t^{-\nu/2},\quad \text{or}$$

$$=\frac{\pi}{4}\frac{k_BT}{\xi_0}\sqrt{\frac{\rho_m}{K_1}}\,t^{\nu-1}. \tag{10}$$

From Eq. (9), the flow alignment angle $\theta(\tau)$ is easily derived from

$$-\int\frac{d\omega}{1+\kappa\cos\omega}=\tau+\tau_0, \tag{11}$$

where $\omega=2\theta(\tau)$, and $\kappa=\gamma_2/(\gamma_1+\gamma_1^c)$. In the vicinity of the second order phase transition temperature $-5<\log_{10}(T/T_{NA}-1)<-4$ (or $\sim$10 mK from T_{NA} in the nematic phase), the case $1>\kappa$, i.e., $\gamma_1+\gamma_1^c>\gamma_2$, is always realized, and Eq. (11) gives the solution for the tumbling flow in the nematic phase,

$$\theta(\tau)=-\tan^{-1}\left(\frac{\chi}{1-\kappa}\tan\frac{\tau\chi}{2}\right) \tag{12}$$

where $\chi=\sqrt{1-\kappa^2}$.

Calculations of the relaxation processes (Figs. 2 and 3), in the temperature range $-5<\log_{10}(T/T_{NA}-1)<-2$, close to $T_{NA}\sim 306.5$ K for 8CB, shows that under low shear rate flow $\dot{\gamma}=0.1\ \mathrm{s}^{-1}$ (Fig. 2) and $\dot{\gamma}=1.0\ \mathrm{s}^{-1}$ (Fig. 3), one has similar tumbling regimes, but with a different period Δt, in which the director executes a full cycle of rotation; in the second case Δt is $|\dot{\gamma}|$ times larger than in the first case. When the temperature $T\to T_{NA}$, e.g., at a few mK from T_{NA} in the nematic phase, the director tumbling in the shear flow is described by the equation

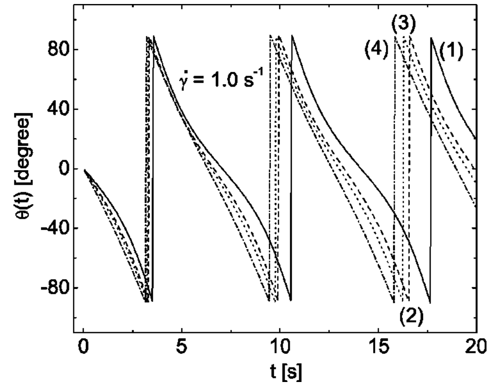

FIG. 3. The same as Fig. 2, but the value of the shear rate is $\dot{\gamma}=1.0\ \mathrm{s}^{-1}$.

$$\lim_{T\to T_{NA}}\theta(\tau)=-\frac{\tau}{2}=-\frac{\dot{\gamma}}{2}t. \tag{13}$$

Physically, this means that the shearing flow, at temperatures close to T_{NA}, always produces a tumbling regime, and the angular velocity of the director $\hat{\mathbf{n}}$ in the shear plane is a linear function of $\dot{\gamma}$.

Having obtained the function $\theta(\tau)$, one can determine the angular velocity $\omega(\tau)=\dot{\theta}(\tau)\equiv\partial\theta(\tau)/\partial\tau$ of the director $\hat{\mathbf{n}}$ in the shear flow as

$$\omega(\tau)=-\frac{\chi^2(1-\kappa)}{2}\left[(1-\kappa)^2\cos^2\frac{\tau\chi}{2}+\chi^2\sin^2\frac{\tau\chi}{2}\right]^{-1}. \tag{14}$$

Calculations of the absolute magnitude of $\omega(\tau)$ shows that under low shear rates $\dot{\gamma}=0.1\ \mathrm{s}^{-1}$ [Fig. 4(a)] and $\dot{\gamma}=1.0\ \mathrm{s}^{-1}$ [Fig. 4(b)], the angular velocity of the director $\hat{\mathbf{n}}$ in the shear flow is characterized by oscillating behavior of $|\omega(\tau)|$ with changing τ, and magnitudes of these oscillations vary between 0.2 and 0.8 s^{-1}, for both shearing regimes, and the range of these oscillations decrease with decreasing of the

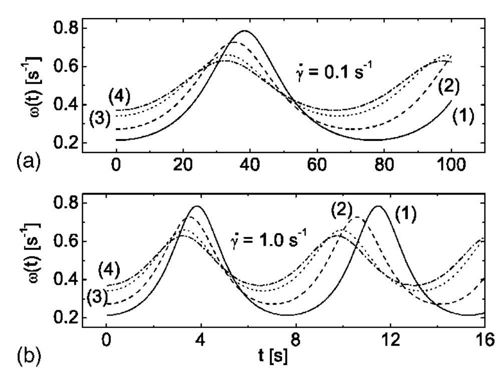

FIG. 4. (a) Plot of the angular velocity $\omega(t)$ of the director in the bulk 8CB sample under shear flow, calculated using Eq. (14), at the same four temperatures as in Fig. 2. In all these cases the value of the shear rate is $\dot{\gamma}=0.1\ \mathrm{s}^{-1}$. (b) The same as (a), but for the value of $\dot{\gamma}=1.0\ \mathrm{s}^{-1}$.

temperature towards T_{NA}. Note that according to Eq. (14) the temperature $T \rightarrow T_{NA}$, e.g., at a few mK from T_{NA} in the nematic phase, leads to $\lim_{T \rightarrow T_{NA}} |\omega(\tau)| = \frac{1}{2}$.

Based on these calculations we can conclude that the described tumbling instability of the Couette shear flow for LC compounds, when allowing fluctuations of the local smectic order parameter above the second order *NA*, occurs at any shear rate $\dot{\gamma}$. However, for temperatures far from T_{NA}, and under low shear rate flow, the director orientation in the bulk of the nematic phase is governed mainly by the elastic forces and shear flow always produces an alignment regime [6]. For temperatures far from the T_{NA} (in the case of 8CB, for $T > 307$ K), where the critical contributions $\gamma_1^{c,cc}$ to the viscous coefficient $\overline{\gamma_1}$ can safely be disregarded, we deal also with the tumbling instability of the flow under high shear rates, because the condition $|\gamma_1| > |\gamma_2|$ or $\alpha_3 > 0$ is realized for that compound. On the other hand, for 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) a molecule that has an extra oxygen atom compared to 8CB, $|\gamma_2| > |\gamma_1|$ is always realized [12] and the director, at least in the high shear flow, aligns at an angle θ_{eq} to the flow direction [6].

It should be also pointed out that the small chemical difference between the molecules 8CB and 8 OCB probably manifested itself only at temperatures far from T_{NA}. So, that difference between these compounds may lead to different flow dynamics in a high shear Couette flow, at temperatures far from T_{NA} [6].

It is important to stress that in the vicinity of the boundary surface the dynamics of nematic LC's is also dependent on the surface potential, which penetrates the bulk nematic over a distance λ_s up to ~ 3.0 μm [13], and gives an additional contribution to the torque balance equation which is largely temperature independent. But in the present study we are primarily focused on the shear flow far away over λ_s from the boundary surfaces, where influence of the surface forces is vanishingly small.

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