Temperature Dependence of Flow Alignment in Nematic Liquid Crystals

Ch. Gähwiller
Physics Department, F. Hoffmann–La Roche and Company, Ltd., Basle, Switzerland
(Received 17 April 1972)

The temperature dependence of the flow alignment angle has been measured in two nematic liquid crystals, *p'*-methoxybenzylidene-*p*-*n*-butylaniline and *p*-*n*-hexyloxybenzylidene-*p'*-aminobenzonitrile. For both compounds this angle reaches a peak value at the nematic-isotropic transition point. Experimental evidence is reported for the first time that flow alignment does not occur over the entire mesophase of certain nematics.

In a nematic liquid crystal the long axes of the rodlike molecules align, apart from small fluctuations, in a common direction. This preferred orientation, the director, depends upon several factors such as boundary conditions at the surface, externally applied fields, or shear flow. So far it has been observed that the director always aligns nearly parallel to the direction of flow in the absence of other orienting forces.[1] This flow alignment appears to be a stable configuration characterized by zero torque density. In terms of the hydrodynamic theory of Ericksen[2] and Leslie[3] it can be shown that the torque acting on the director vanishes if the angle θ_0, between director and direction of flow, is such that

$$\tan^2\theta_0 = -\kappa_2/\kappa_1 . \quad (1)$$

Here κ_1 and κ_2 are shear torque coefficients having the dimensions of a viscosity; they are related through the Parodi-Onsager relation,[4]

$$\eta_1 - \kappa_1 = \eta_2 - \kappa_2 , \quad (2)$$

to the main viscosity coefficients η_1 and η_2[5] (η_1 and η_2 are the apparent viscosities measured when the orientation of the molecules is parallel to the shear gradient or to the direction of flow, respectively). Because of the rodlike shape of the molecules we have $\eta_1 > \eta_2$. It follows from the entropy-production inequality[3] that κ_1 is positive. This implies that the sign of κ_2 must be negative for flow alignment to occur. The condition $\kappa_2 < 0$ has generally been assumed in discussions about stability conditions of shear flow in nematics.[6,7] The magnitude of the shear torque acting on the molecules is expected to depend largely upon the shape of the molecules[8] as well as on their mutual interaction.

In this Letter we present the first direct determination of the flow-alignment angle θ_0 made on nematic compounds. The measurements were done on *p'*-methoxybenzylidene-*p*-*n*-butylanaline (MBBA) and on *p*-*n*-hexyloxybenzylidene-*p'*-aminobenzonitrile (HBAB). These two compounds were chosen for their negative and positive dielectric anisotropy, respectively.[9,10] In the case of HBAB we find for the first time that flow alignment does not occur over the entire mesophase of a nematic liquid crystal.

We used the following experimental procedure to study flow alignment: A flow cell was built of two parallel glass plates separated by Mylar spacers. The nematic was made to flow through the rectangular cross section by means of a slight pressure difference. Prior to assembly the glass surfaces were "rubbed" parallel to the direction of flow. A laser beam shone perpendicularly through the cell which was placed between crossed polarizers. Initially the orientation of the nematic was kept uniformly parallel to the direction of flow with a magnetic field applied in this direction. As this field was turned off the molecular orientation changed to a flow-alignment configuration. The direction then made an angle θ_0 relative to the flow direction with the exception of a thin layer halfway between the glass plates and of two adsorption layers at the cell walls. Theoretical estimates indicated that these layers were at most a few micrometers thick and could be ignored compared to the cell thickness of approximately 350 μm. Only very small shear rates up to 50 $\sec^{-1}$ were applied in order to avoid the formation of disclinations. As the orientation of the molecules varied from $\theta = 0$ to $\theta = \theta_0$, the optical path difference Γ between the ordinary and extraordinary components of the incident polarized light changed by an amount $\Delta\Gamma$. Hence the transmitted light intensity oscillated, passing through a minimum each time Γ equaled an integral number of wavelengths.

For a small angle θ_0 we have

$$\Delta\Gamma \cong \tfrac{1}{2} n_e d (n_e^2/n_0^2 - 1)\tan^2\theta_0 , \quad (3)$$

where n_0 and n_e are the ordinary and extraordinary refractive indices, respectively, and d the

cell thickness. From the measurement of $\Delta\Gamma$ we can therefore determine θ_0. Reproducible values within 5% were obtained for $\Delta\Gamma$. They were independent of the applied shear rate, hence confirming the existence of the zero-torque condition of flow alignment and justifying the neglect of the three transition layers just mentioned.

Figure 1, curve *a*, shows the alignment angle θ_0 as a function of temperature measured over the entire nematic range for MBBA. θ_0 is found to rise steeply from a value of 5° at room temperature up to 17.5° just below the nematic-isotropic transition point ($T_c = 43.0$°C). In the isotropic phase there is a weak flow alignment of the elongated molecules,[11] the preferred orientation being at an angle of 45° with the direction of flow. Recently, Helfrich[12] discussed a phenomenological relation between the flow alignment angle θ_0 and the degree or order, S, in weakly ordered nematics. Near the clearing point, where S is smallest, the molecules have a large degree of freedom with respect to their parallel orientation and may rotate even around their short axes as in the isotropic phase. Hence the same mechanism, which in shear flow tends to orient the molecules at 45° in the isotropic phase, contributes to some extent to the flow alignment in the nematic phase. This contribution decreases with decreasing temperature as the degree of order becomes larger.

Flow alignment has been shown to occur[8] in an idealized nematic constituted of ellipsoidal molecules of constant and equal orientation which collide elastically with each other. This model seems adquate to describe qualitatively flow alignment of MBBA well below the clearing point. The torque exerted on each ellipsoid has a negative sign if the long axis makes an angle smaller than θ_0 with the direction of flow. But if the actual shape of the molecule departs substantially from the assumed ellipsoid, this torque turns out to be positive for all orientations of the molecules with respect to the velocity gradient.

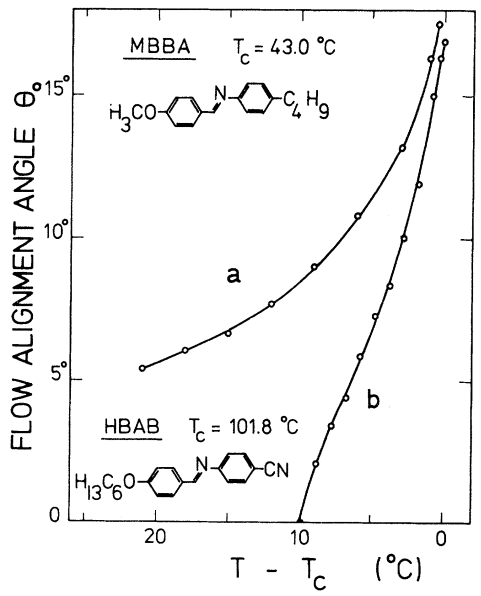

FIG. 1. Flow alignment angle θ_0 as a function of temperature for MBBA (curve *a*) and HBAB (curve *b*).

Similar values for θ_0 are found in HBAB near its clearing point $T_c = 101.8$°C (Fig. 1, curve *b*). However, compared to MBBA, θ_0 falls off much more rapidly with decreasing temperature and becomes equal to zero at $T = 91.8$°C. As the temperature is lowered past this critical point, the flow turns abruptly from a uniform configuration into many irregular rotating domains over the entire volume. Even if the shear rate is reduced by a factor of 50, no uniform alignment can be observed below 91.8°C. Only when a magnetic field of a few kilogauss is superimposed on the shear is the flow free of turbulence and can reproducible values for $\Delta\Gamma$ be measured. Exactly the same behavior is also observed with another nematic compound.[13] Hence HBAB is, to our knowledge, the first representative of a new class of nematics for which no uniform alignment of the molecules can be achieved with shear flow over a certain temperature range. Phenomenologically this means that the coefficient κ_2 in Eq. (1) becomes positive below $T = 91.8$°C in HBAB.

The different response to shear flow found in HBAB compared with MBBA is particularly striking if we consider that the two molecules are similar in both size and chemical structure (Fig. 1). We suggest that the permanent dipole-dipole interaction, which is unimportant for MBBA, is crucial for the disappearance of flow alignment in HBAB.

In MBBA the component of the permanent dipole moment in the direction of the molecule's long axis has about the same value as in *p*,*p*′-dimethoxyazoxybenzene (PAA), i.e., ~1 D. For PAA, which like MBBA has a negative dielectric anisotropy, the dipole-dipole interaction was shown not to contribute appreciably to the interaction energy of the molecules.[14] In the case of HBAB, however, there is a large contribution to the dipole moment (~4 D) associated with the C≡N bond, and the total permanent moment in the direction parallel to the long axis of the molecule is at least 5 D. The dipole-dipole interaction energy

in HBAB is therefore of the order of kT. It is high enough for two neighboring molecules to attract each other, the strongest attraction occurring when their C≡N bonds are antiparallel and side by side.

In terms of the hard-ellipsoid model previously discussed, we may visualize this attraction by the formation of a rigid pair of ellipsoids. Because of its "bumpy" contour, such a pair placed in a shear field is likely to feel a torque of positive sign even if it is oriented parallel to the direction of flow. Provided the ratio of paired to total number of molecules is high enough, this positive contribution to the torque acting on a small volume element will compensate the negative contribution from the unpaired molecules. If this picture is correct, flow alignment would not be possible.

Clearly, more detailed considerations are necessary to ascertain the existence of paired molecules in HBAB or, alternatively, to show how the dipole-dipole interaction affects the short-range correlation between the molecules in such a way that flow alignment disappears when the degree of order becomes larger than a critical value. In this respect it would be interesting to compare the temperature dependence of the order parameter S for MBBA and HBAB, or to look for a dispersion in the dielectric constant of HBAB at very low frequencies.

The author would like to thank W. Helfrich and D. Schmidt for many helpful discussions and A. Boller and H. Scherrer for the careful synthesis of the liquid crystals.

[1]R. S. Porter, E. M. Barall, and J. F. Johnson, J. Chem. Phys. 45, 1452 (1966).
[2]J. L. Eriksen, Arch. Ration. Mech. Anal. 4, 231 (1960), and Phys. Fluids 9, 1205 (1966).
[3]F. M. Leslie, Quart. J. Mech. Appl. Math. 19, 357 (1966).
[4]O. Parodi, J. Phys. (Paris) 31, 581 (1970).
[5]We have $\kappa_1=-\alpha_2$, $\kappa_2=\alpha_3$, $\eta_1=\frac{1}{2}(\alpha_4+\alpha_5-\alpha_2)$, $\eta_2=\frac{1}{2}(\alpha_4+\alpha_6+\alpha_3)$, where the α's are the viscosities introduced by Leslie (Ref. 3).
[6]J. L. Ericksen, Arch. Ration. Mech. Anal. 23, 266 (1966).
[7]F. M. Leslie, Rheol. Acta 10, 91 (1971).
[8]W. Helfrich, J. Chem. Phys. 50, 100 (1969).
[9]D. Diguet, F. Rondelez, and G. Durand, C. R. Acad. Sci., Ser. B 271, 954 (1970).
[10]M. Schadt, J. Chem. Phys. 56, 1494 (1972).
[11]See, e.g., J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).
[12]W. Helfrich, J. Chem. Phys. 56, 3187 (1972).
[13]A 1:1:1-molar mixture of HBAB with *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile and *p*-*n*-octanoyloxybenzylidene-*p'*-aminobenzotrile (RCA U. S. Patent No. 3 597 044).
[14]S. Chandrasekhar and N. V. Madhusudana, Acta Crystollogr., Sect. A 27, 303 (1971).

Self-Consistent Pair Potential in an Inhomogeneous Superconductor

J. Bar-Sagi* and C. G. Kuper
Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel
(Received 27 March 1972; revised manuscript received 17 May 1972)

de Gennes's equations for the Bogoliubov amplitudes in an inhomogeneous superconductor are solved in a simple geometry with the use of a one-parameter *Ansatz* for the pair potential. The solutions are used to determine the parameter self-consistently. In the limit $T\to T_c$, the results agree with the Ginzburg-Landau theory, but the present method is applicable at all temperatures $T<T_c$.

At any temperature $T<T_c$ in a superconductor, the pair potential Δ is given[1] by

$$\Delta(\vec{r})=V\sum_n u_n(\vec{r})v_n^*(\vec{r})[1-2f(E_n)], \tag{1}$$

where $f(E)$ is the Fermi-Dirac distribution, V is the strength of the interaction, E_n are the quasiparticle energies measured from the Fermi energy E_F, and $u_n(\vec{r})$ and $v_n(\vec{r})$ are the Bogoliubov[2] amplitudes. In a pure crystal with no magnetic field, they obey[1]

$$E_n\hat{\varphi}=\{-\sigma_z[(\hbar^2/2m)\nabla^2-E_F]+\sigma_x\Delta(r)\}\hat{\varphi}, \tag{2}$$

where $\hat{\varphi}$ is the spinor (u_n, v_n), σ_x and σ_z are Pauli matrices, and m is the effective mass of a Bloch