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Influence of the order parameter and of the director orientation on the surface tension of free nematic films

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A radial hydrodynamic flow in the nematic phase of free, suspended cylindrical films of 4-*n*-heptyl- and decyloxybenzoic acid and in 4,4′-di-*n*-heptyloxyazoxybenzene has been observed. The flow starts about 7°C before the phase transition into the smectic C phase. Under the same experimental conditions such a hydrodynamic flow is not established in free nematic films of 4-*n*-heptyl- and octyloxy-4′-cyanobiphenyl, 4,4′-dimethoxyazoxybenzene and *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline after the completion of the transition from the isotropic liquid to the nematic phase. The observed hydrodynamic flow is explained by a non-linear temperature dependence of the surface tension.

1. Introduction

We have attempted to elucidate experimentally the influence of molecular orientation and of the excess surface ordering on the nematic surface tension. We have generalized the results obtained by studying the nematic textures of free, suspended films of conventional liquid crystals. The observed hydrodynamic flow due to the Marangony effect [1] in the narrow temperature interval 110–115°C in the nematic phase of 4-*n*-octyloxybenzoic acid (OOBA) showed an anomalous temperature dependence of the surface tension [2]. Such an irregular behaviour has been observed elsewhere [3]. Some authors predict such a possibility in the context of a very general thermodynamic theory [4–6].

Here the results from the investigation of the nematic textures of free, suspended films of 4-*n*-heptyloxybenzoic acid (HOBA), 4-*n*-decyloxybenzoic acid (DOBA), 4,4′-di-*n*-heptyloxyazoxybenzene (HOAB), 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB), 4-*n*-heptyloxy-4′-cyanobiphenyl (7OCB), 4,4′-dimethoxyazoxybenzene (PAA) and *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline (EBBA), are given.

2. Experimental results

The free, suspended films were obtained in the same way as in [2]. Aluminium foil 50 and 20 μm thick have been used with a cylindrical hole of 1 mm diameter. The clean foil, 20 × 20 mm, and with the circular hole in the middle was placed in a thermostat on the microscope stage. Upon heating the foil to a temperature close to the transition into the isotropic phase, a small quantity of liquid crystal was spread over the foil near the side of the hole and, after melting, it was smeared over the hole with a glass plate. In this way films were obtained in the cylindrical hole with a desired thickness. The conditions

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in the thermostat were such that two types of temperature gradient were obtained. The first appears since the aluminium foil is in contact with the metal substrate of the thermostat from below and with the air from the upper side. In spite of its small thickness, there is a very small vertical temperature gradient ($<1°\mathrm{C\,mm^{-1}}$) across the film. The second appears, since a radial gradient ($\sim 3°\mathrm{C\,mm^{-1}}$) was created as the temperature of the film in contact with the aluminium foil is greater than that in the middle of the film. In films obtained in this way powder particles several microns in size, which float freely in the liquid crystal were especially involved.

The nematic textures were observed by polarized microscopy with a good thermalization on cooling when the transition from the isotropic liquid to the nematic phase is completed. The selected substances exhibit different phases below the nematic phase and possess various molecular orientations at the nematic–air interface.

2.1. *HOBA*

C 92°C S_C 98°C N 147°C I [7].

In our opinion the director is inclined at the free nematic surface and there is conical degeneration. In 40 μm thick HOBA films the same results as OOBA were obtained: after good thermostating, a stable nematic texture in the temperature interval ~140–105°C was observed. At about 105°C the hydrodynamic flow began. Observing the movement of the seeding particles in the film we were able to establish some definite regularities: the seeding particles move radially between the centre and the film perimeter; changing the focus of the microscope we established that on the surface the movement is accelerated from the centre to the perimeter, but in the bulk from the perimeter to the centre; the movement on the surface is faster than in the bulk, the hydrodynamic flow was observed in the temperature interval 105–100°C. The transitional texture begins at 100°C and the transition into the S_C phase was completed at 98°C.

2.2. *DOBA*

C 97°C S_C 125°C N 143°C I [7].

We established the same results as for OOBA and HOBA. Now the hydrodynamic flow begins approximately at 132°C and stops with the appearance of the transitional texture at ~126°C. In addition it was established that the seeding particles in HOBA move faster than in OOBA and DOBA and penetrate further into the bulk. Taking into account that the latent heat for the nematic–smectic C transition for HOBA is nearly one order greater than that for OOBA [8] it may be inferred that the observed hydrodynamic flow is not connected with the latent heat of this transition.

2.3. *HOAB*

C 74·6°C S_C 95°C N 124·3°C I [9].

On the basis of the observed texture we accept that the director is tilted at the nematic–air interface. After film temperature stabilization, a steady nematic texture was observed several degrees after the completion of the transition from the isotropic liquid to the nematic (at about 120°C). This condition was maintained to approximately 100°C. From this temperature near to the transition to the smectic C phase we observed a radial motion of the seeding particles in the nematic. By focal alteration of the microscope we have found that the particles accelerated from the centre of the film to its perimeter on the surface and in the bulk they slow up moving from the perimeter to the centre. The hydrodynamic flow on the upper free surface was independent of that on the lower surface if the film is thick enough [2]. The nature of the motion was the same as in OOBA, but it is weaker and the seeding particles penetrate less in the nematic film.

We must emphasize that hydrodynamic flow is observed in the nematic phase of HOBA, OOBA, DOBA and HOAB before the appearance of the transitional structure to the smectic C phase. It is easily seen in figure 1, that due to the radial temperature gradient, the transition texture is already generated in the film centre. At the perimeter, however, where the nematic phase is present, the radial hydrodynamic flow continues and this is clearly seen by the radial disclination lines.

We carried out an experiment with a 2:1 mixture of HOAB and *N*-(4-hexyloxybenzylidene)-4-*n*-butyloxyaniline. The mixture shows the microscopically defined transition temperatures on cooling:

$$\mathrm{C}\ 44^\circ\mathrm{C}\ \mathrm{S_C}\ 90^\circ\mathrm{C}\ \mathrm{S_A}\ 94^\circ\mathrm{C}\ \mathrm{N}\ 110^\circ\mathrm{C}\ \mathrm{I}.$$

The observation of a free, suspended film 40 μm thick shows that there is an intensive movement in the nematic after the transition from the isotropic phase was completed (see figure 2(*a*)). On very slow cooling this movement is suppressed gradually and at 97°C we observe a completely immovable nematic texture. The transition to the smectic A phase is very clear: at first a dark round spot, with crossed polarizers, appeared in the film centre where the temperature is lowest. The spot colour does not change on turning the microscope stage. This proves that in the dark spot the director is orientated perpendicular to the free surface (see figure 2(*b*)). Both, the smectic A in the middle and the nematic around it, are immovable. Gradually on lowering the temperature the transition N–$\mathrm{S_A}$ was completed over the whole film (see figure 2(*c*)). The transition to the smectic C phase begins at 90°C also in the middle of the film (see figure 2(*d*)) and during the transition the smectic layers created in the smectic A phase

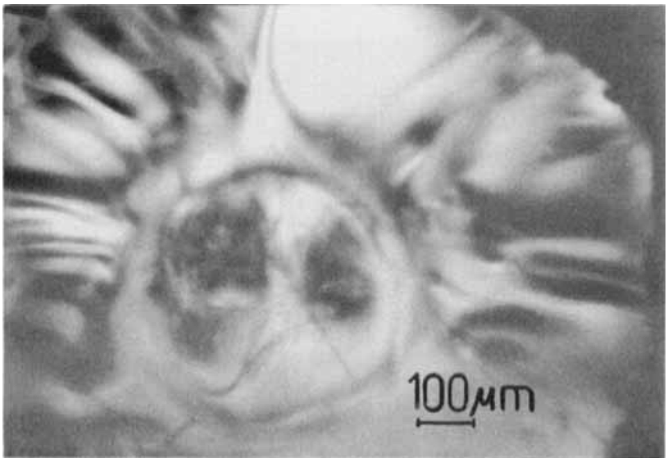
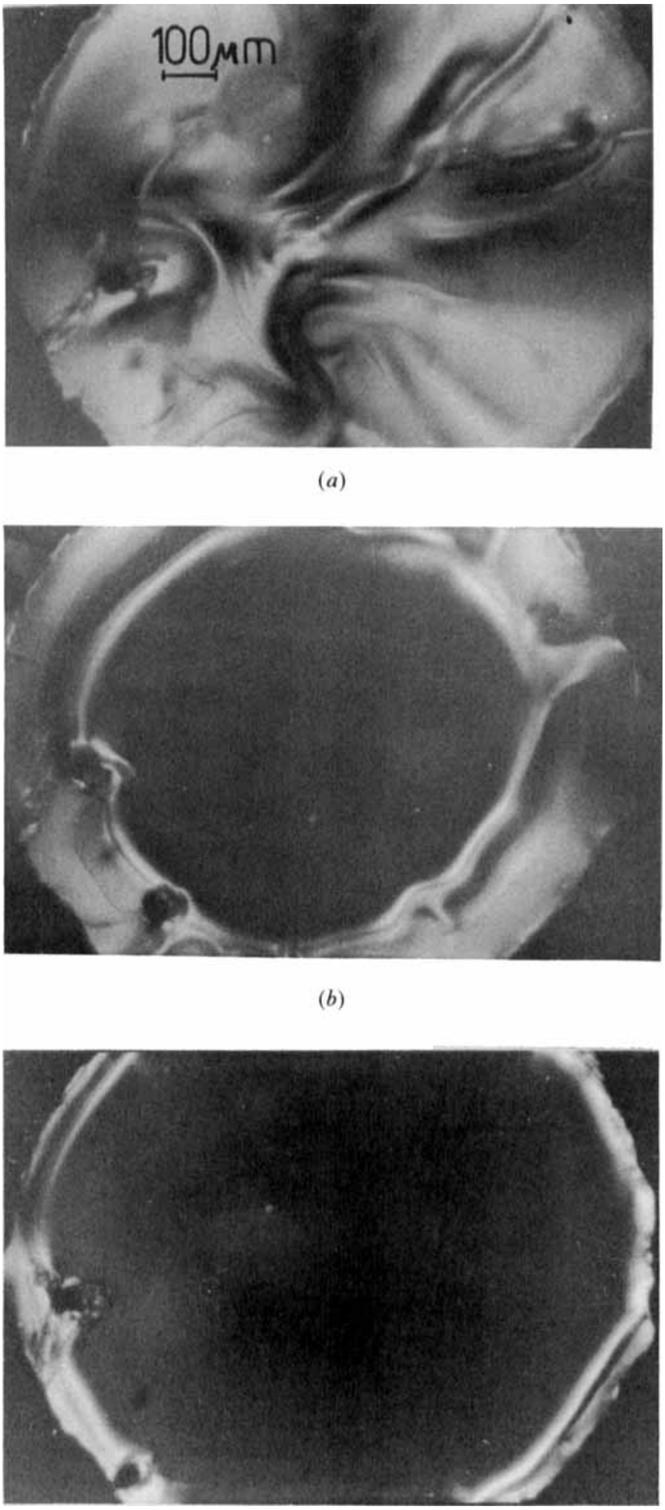


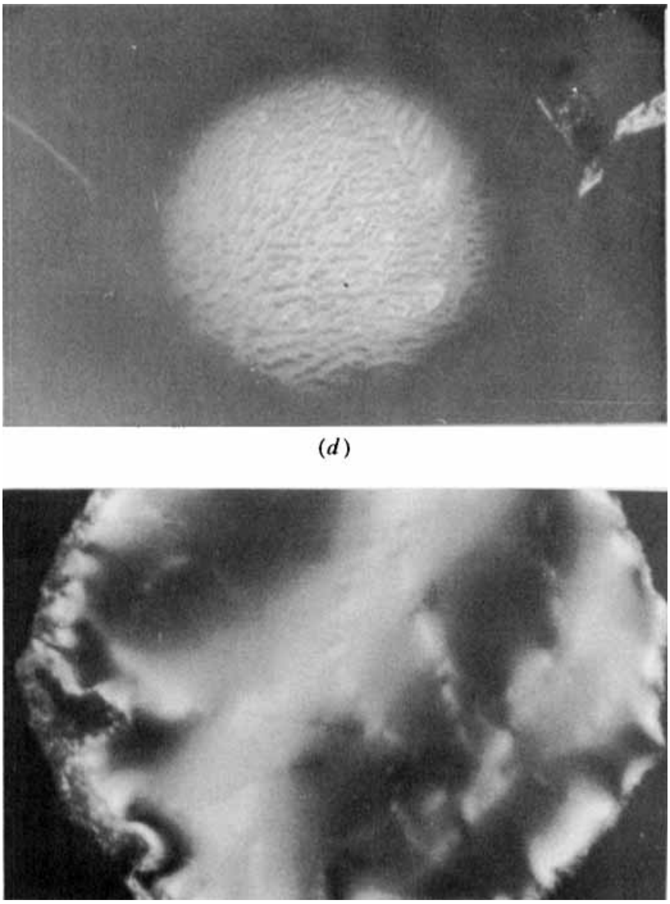
Figure 1. Optical texture of a DOBA free, suspended film 20 μm thick at the $\mathrm{S_C}$–N transition. In the nematic phase at the film's perimeter the hydrodynamic flow is indicated by radial disclination lines.



(a)

(b)

(c)



(e)

Figure 2. Optical texture of a free, suspended film 40 μm thick of a HOAB mixture. (a) Nematic at 106°C with radial disclination lines due to radial hydrodynamic flow; (b) phase transition S_A–N (in the film's middle–S_A, at the perimeter–N); (c) smectic A only; (d) S_C–S_A phase transition; (e) S_C at 84°C.

keep their parallel alignment to the free surface, as the director tilts. In the smectic C texture obtained again a movement of the seeding particles and change of texture which occasionally resembles a running wave can be observed. At 84°C the smectic C texture becomes immobile and this can be explained by the completed director tilt in the smectic layers (see figure 2(e)).

2.4. *8OCB*

C 54·5°C S_A 67·5°C N 80°C I. [10].

The molecules are perpendicular to nematic–air interface, which was clearly seen from the observed texture: at P⊥A the nematic texture is displayed as a dark field, which does not change on turning the microscope stage. We observed a completely stable texture throughout the whole nematic temperature interval. The seeding particles in the film are immobile even at and after the transition into the smectic A phase.

2.5. *7OCB*

C 53·5°C N 75°C I [10].

The director is orientated normal to the free nematic surface. As for 8OCB, we can observe a perfectly motionless texture throughout the whole nematic phase.

2.6. *PAA*

C 117°C N 135°C I.

The director lies on the free surface over the whole temperature interval of the nematic phase [11]. We have observed a completely stable schlieren texture typical for the planar director orientation. We note that the HOAB molecule has the same core as PAA, but possesses long chains which according to Parsons [12] give a quadrupolar interaction, besides polar, thus giving the possibility for a tilted director orientation on the free surface.

2.7. *EBBA*

C 36°C N 80°C I.

In the sample prepared on a 20 μm thick foil, after the transition from the isotropic to the nematic phase the director is oriented normal to the free surface: the microscope field is dark grey at P$\perp$A and it does not change on turning the sample. Since upon thinning, the film becomes blacker, there is some evidence that the surface director orientation partially influences the bulk order parameter and this influence extends to a given final depth. On further cooling the film brightens at about 63°C and remains the same until the phase transition to the crystal. In the film $\sim$15 μm thick we even observe a schlieren texture below 63°C. This indicates a considerable change in the surface director orientation. We wish to point out that, we do not establish any hydrodynamic flow throughout the whole nematic interval, including 63°C, but we observe very strong director fluctuations on the free surface at the same temperature.

3. Discussion

The observed hydrodynamic flow or Marangony effect [1] in OOBA, HOBA, DOBA and HOAB can be explained by assuming an anomalous surface tension increase with temperature [2]. The conventional liquid theories predict a linear surface tension–temperature dependence [13]

$$\sigma V^{2/3} = b(T_c - T),$$

where V is the molecular volume, T_c is the critical temperature for the liquid and b is a constant which is almost the same for all liquids. The experimental investigations on liquid crystals show that in the nematic phase having a long temperature interval the surface tension also decreases with temperature. Some authors have observed a discontinuity or a non-linear variation in $\sigma(T)$ at the nematic–isotropic transition [14–16]. The investigations of the surface tension in smectic phases are unfortunately not numerous and the results are inconsistent. The study of ethyl

4-((4-methoxybenzylidene) amino) cinnamate (EAC) established that $\sigma(T)$ does not change its slope at the S_A–N transition [15]. The investigation of 4-cyanobenzylidene-4′-*n*-octyloxyaniline (CBOOA) showed that the slope of $\sigma(T)$ changes its sign at S_A–N transition being negative in the nematic and positive in the smectic A phase [16].

The lack of hydrodynamic flow in the nematic phase of substances studied by us at temperatures $T - T_{S_CN} > 7$ K *is, most probably, due to a low value of the surface tension* temperature gradient $d\sigma/dT$, which is not enough to overcome the nematic viscosity forces and to provoke hydrodynamic flow. However, in the narrow temperature interval before the N–S_C transition, $d\sigma/dT$ must be considerable and as a result we observe a hydrodynamic flow or Marangoni effect. If a surface tension gradient is present, the effective tangential force is directed to the region with higher surface tension. The accelerated motion of the seeding particles shows that we have a higher surface tension at the film perimeter where the temperature is higher, i.e. $d\sigma/dT > 0$. We note that mass hydrodynamic flow is displayed in a narrow nematic temperature interval just before the transition to the smectic C phase, which gives us a reason to exclude the possibility that this flow is caused by any diffusion or convective forces.

To explain the non-linear surface tension temperature variation we consider the possible influence of two factors: (i) change of the free surface director orientation and (ii) the change of the order parameter.

According to Parsons' theory [5], built within the frame of Gips's formalism, the following expression for surface tension known as the Rapini–Papoular form [17] is, taking into account the surface orientation of the director:

$$\sigma = \sigma_1(S) + \sigma_2(S)\cos^2\theta, \qquad (1)$$

where S is the scalar order parameter

$$S = \tfrac{1}{2}\langle 3\cos^2\varphi - 1\rangle,$$

and φ is the molecular orientation with respect to the local director and a thermal average has been taken over the orientational states in the bulk, θ is the angle between the director and the surface normal, σ_1 is a function of the density ρ and S. σ_2 does not have a fixed sign; it may be positive or negative and it is connected with the nature of the molecule. So the following two possibilities result:

(i) $$\sigma_2 < 0 \quad \text{and} \quad \sigma = \sigma_1 - \sigma_2\cos^2\theta.$$

Then at $\mathbf{n}\parallel\mathbf{k}$ and $\theta = 0$, σ will have a minimal value $\sigma = \sigma_1 - \sigma_2$. At

$$\mathbf{n}\perp\mathbf{k} \quad \text{and} \quad \theta = \frac{\pi}{2}$$

σ is a maximum: $\sigma = \sigma_1$. If

$$0 < \theta < \frac{\pi}{2}$$

then $\sigma_1 - \sigma_2 < \sigma < \sigma_1$.

(ii) $$\sigma_2 > 0, \ \sigma = \sigma_1 + \sigma_2\cos^2\theta.$$

In this case at $\mathbf{n}\parallel\mathbf{k}$ and $\theta = 0$, σ will have a maximal value ($\sigma = \sigma_1 + \sigma_2$) and at

$$\mathbf{n}\perp\mathbf{k} \quad \text{and} \quad \theta = \frac{\pi}{2}$$

will reach a minimal value ($\sigma = \sigma_1$). If there is a tilted orientation we have $\sigma_1 < \sigma < \sigma_1 + \sigma_2$.

Now let us consider the case of HOBA. In the temperature range 140–105°C hydrodynamic flow was not observed and it may be assumed that the surface tension changes with temperature in the normal way as for the liquids: that is $d\sigma/dT < 0$ [13]. The experiment shows the onset of flow at 105°C which means that $d\sigma/dT$ changes its sign and σ decreases over the temperature range 105–100°C.

In HOBA, OOBA and DOBA most of the molecules are associated in dimers, which do not possess a dipole moment. A small quantity of these dimers dissociates into single molecules and these molecules actively display their dipolar forces on the surface and in this way, in general, they create a tilted director orientation. Upon cooling the number of monomers decreases and at temperatures near the transition into the smectic C we can assume, with a good approximation, mainly the presence of dimers. According to Parsons [12] this gives a possibility for a planar surface orientation. We can assume that over the temperature range 140–105°C in which the nematic texture remains fixed the surface director tilt θ is almost constant and large. Below 105°C for HOBA the tilt decreases, i.e. the director tilts until θ obtains a value near to the real tilt in the smectic C of about 45°. From equation (1) it is seen that if θ decreases σ can also decrease if $\sigma_2 < 0$.

The effect of the order parameter on the surface tension has been considered theoretically by Croxton [4]. According to its definition the slope of $\sigma(T)$ is proportional to the entropy surface excess

$$\frac{d\sigma}{dT} = -\Delta S.$$

In the approximations of the theory [4] this dependence is presented as

$$\frac{d\sigma}{dT} \sim \int_0^\infty [\rho(z)S^2(z) - \rho S^2 + \rho(z)\eta^2(z) - \rho\eta^2]\, dz, \tag{2}$$

where ρ is the density, S is the orientational order parameter and η is the translational order parameter in bulk far from the free surface ($z = 0$), but $\rho(z)$, $S(z)$ and $\eta(z)$ are the respective values near the nematic–air interface. For a classic nematic phase $\eta = 0$ and

$$\frac{d\sigma}{dT} \sim \int_0^\infty [\rho(z)S(z) - \rho S^2]\, dz.$$

For HOBA, OOBA, DOBA and HOAB, where we observe the Marangoni effect, we can assume that about 7°C above the nematic–smectic C transition there is a sufficiently large surface enhancement of the orientational order $S(z)$. In addition, a generation of smectic layers from the free surface is possible. This means that over a narrow temperature interval near T_{S_CN} a surface translational order parameter appears $\eta(z) \neq 0$ while in the bulk η may be zero or $\eta < \eta(z)$. From equation (2) it follows immediately that the slope of $\sigma(T)$ can assume positive values.

The behaviour of 8OCB, 7OCB and PAA indicates that their surface molecules have reached, in the nematic phase, a deep minimum of the free surface energy density. As the experiments demonstrate, the surface director has a fixed orientation throughout the whole nematic phase: normal for 8OCB and 7OCB and planar for PAA. The only possibility for the slope of $\sigma(T)$ to become positive is a large surface enhancement of the orientational order parameter $S(z)$. This is obviously not enough and we do not observe a hydrodynamic flow. Experimental studies of $\sigma(T)$ for PAA has really showed a monotonic negative slope of $\sigma(T)$ in the nematic temperature range 120–133°C [14].

Our investigation on 8OCB is in accord with the results obtained with ethyl 4-((4-methoxybenzylidene)amino)cinnamate (EAC) [15]. Here a continuous increase of the surface tension with decreasing temperature in the nematic and the smectic A phase was established. However it is in contradiction with the results obtained with 4-cyanobenzylidene-4′-*n*-octyloxyaniline (CBOOA) [16]. For this substance a positive slope of $\sigma(T)$ was found in the smectic A phase and $d\sigma/dT$ reverses its sign at the $\mathrm{N}-\mathrm{S_A}$ transition. To solve this discrepancy additional research is needed.

The assumptions for the influence of the free surface director tilt and of the order parameter on the surface tension is elucidated by observing free nematic films of EBBA. A director reorientation from normal to almost planar at 63°C is quite clearly established, i.e. at a point, which is 17°C below the nematic–isotropic transition and 27°C above the transition into the crystal. As it was already noted, in spite of the sudden change of the free surface director orientation, a hydrodynamic flow was not observed. Hence we may assume that there is no non-linear change of σ in this temperature range. To explain this fact we use Parsons' consideration [12] assuming that the molecule has a polar as well as a quadrupolar interaction and therefore two order parameters, namely quadrupolar Q and polar P. In this case the surface tension is given by

$$\sigma=\sigma_0+\tfrac{1}{2}\sigma_Q\cos^2\theta-\sigma_P\cos\theta, \tag{3}$$

where σ_0 is valid for a system without ordering. We denote the temperature 63°C by T_e. Then at $T_e+\Delta T$ we have $\cos\theta=1$, but at $T_e-\Delta T\cos\theta\sim0$, as $T\approx1°\mathrm{C}$ (see figure 3). From the dependence in equation (3) it follows that

$$\sigma_{T_e+\Delta T}=\sigma_0+\tfrac{1}{2}\sigma_Q-\sigma_P$$

and

$$\sigma_{T_e-\Delta T}\approx\sigma_0.$$

Taking the limit $\Delta T\to0$ gives

$$\sigma_{T_e+\Delta T}\approx\sigma_{T_e-\Delta T}$$

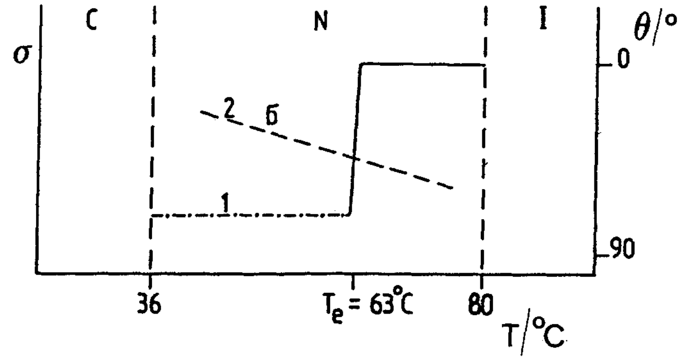


Figure 3. (1) Temperature dependence of the surface director tilt angle, $\theta(T)$ and (2) supposed temperature dependence of the surface tension, $\sigma(T)$ of an EBBA free film.

from which it follows that $\sigma_Q \approx 2\sigma_P$ near T_e. According to Parsons [12] the case $\sigma_P = \sigma_Q$ corresponds to a critical point, at which the fluctuation in the tilt angle θ diverges

$$|\theta_Q|^2 = \left|\frac{k_B T}{\sigma_P - \sigma_Q}\right|.$$

As was mentioned in the Experimental, for EBBA at 63°C we do not observe any hydrodynamic flow, but on focusing on the free surface a strong director fluctuation is established. This fluctuation means oscillations of the director **n** toward the surface normal or oscillation of the tilt angle θ.

4. Conclusions

We have observed a radial hydrodynamic flow in the nematic phase of free cylindrical films of HOBA, DOBA and HOAB beginning about 7°C before the transition into the smectic C phase and stopping with the appearance of a transitional structure about 2°C before the transition into the S_C phase. The hydrodynamic flow is explained by the presence of a non-linear surface tension change with temperature. There is a supposition that the anomalous temperature dependence of the surface tension is due to the surface enhancement of the orientational order $S(z)$ in comparison with that in the bulk nematic, to the appearance of surface translational order $\eta(z)$ [4] as well as to a change of the director tilt at the nematic–air interface near the S_C–N transition [12]. According to the experimental data we have found that the variation of only one of these factors is not sufficient. Hence the quite sudden change of surface director orientation in the nematic phase of the free EBBA film at 63°C is not accompanied with a hydrodynamic flow. Moreover the expected increase in the order parameter near the S_A–N transition in the 8OCB free film does not create a hydrodynamic flow, since the director is orientated normal to the film, $\theta = \text{constant} = 0°$.

We have observed the oscillation of the director surface tilt angle θ of free EBBA films at a critical temperature 63°C predicted theoretically by Parsons [12].

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