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# Nonparabolic Dendrites of a Smectic Phase Growing into a Supercooled Nematic.

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**Abstract.** – The interface of a growing smectic phase in a supercooled nematic liquid crystal was studied. A change in the morphology and the side-branching activity was observed with the undercooling. Nonparabolic dendrites with faceted dissymmetric tips were found for small undercooling. The equilibrium shape of the smectic germ was a rectangle. A drifting of the smectic objects was observed. The starting tip velocities obey the scaling relation $v_s \sim \Delta^4$.

Dendritic crystal growth has intensively been studied theoretically [1-4]. A summary of recent developments focusing on the interplay between the macroscopic thermal driving force and the microscopic interfacial dynamics is given in the review article of Ben-Jacob [5]. There are several excellent experimental studies on pure substances which form dendrites during the phase transition. Measurements on ice, metals, succinonitrile, cyclohexanol, krypton etc. are known [6-9].

Dendritic growth of *liquid-crystal* phases has also been observed for a certain range of supersaturation in columnar structures constructed of disclike molecules [10, 11]. One-component, thermotropic liquid crystal of rodlike molecules show dendrites very rarely. The smectic-*A* nucleating in the isotropic or nematic phase yields focal conic defects and forms the well-known «batonnets» [12]. Dendrites of a smectic-*B*–smetic-*A* interface were observed in a directional solidification experiment [13]. Dendritic smectic germs nucleating spontaneously in the nematic phase have only been reported in [14].

The special features of a smectic-nematic interface compared to a crystal growing into its melt are:

both phases being fluids, the material parameters (*i.e.* heat diffusivity) have similar values on the two sides of the interface,

both phases are anisotropic,

some of the relevant material parameters (*i.e.* surface tension, heat diffusivity, capillary length) are several orders of magnitude different from those of metals or organic crystals [15].

The interface between a growing smectic phase and a supercooled nematic one was studied on a pure, one-component liquid crystal 4-$n$-butyl-$N$-[4-($p$-cyanophenyl)-benzylidene]-aniline (1) which exhibits a 1st-order nematic-smectic phase transition at $T_{NS} = 87.4\,°C$. The smectic phase was not classified by X-ray diffraction. Textural observations exclude the phase to be $S_A$ which is a two-dimensional fluid and indicate it to be another—more ordered, crystal-like in the plane of the layers—orthogonal smectic phase (presumably $S_B$). Preliminary observations about three distinct morphologies (dense branching, dendritic and planar front) were published earlier [14]. In this work we report about detailed studies of the dendritic regime only.

A cell of $10\,mm \times 10\,mm \times 5\,\mu m$ was prepared with the nematic director oriented perpendicular to the glass plates. This homeotropic alignment ensures a geometry which provides an analogy in case of two-dimensional pattern growth between the nematic-smectic phase boundary problem and the crystallization from isotropic melt as far as anisotropy is concerned, since only the growing phase is anisotropic in both cases.

The sample temperature was controlled in a hot stage with an accuracy of 0.02 °C. The growth process was observed in a polarising microscope equipped with a CCD videocamera. The images were recorded and fed into a PC for digital analysis with spatial resolution of $512 \times 512$ and 256 grey scaling for each pixel.

The sample was thermostated above $T_{NS}$ in the nematic phase, then it was supercooled and the interface of the growing smectic germ was studied. A range of the dimensionless undercooling $\Delta = c_p(T_{NS} - T)/L$ between 0.06 and 0.26 was investigated (here $c_p = 1590\,J/kg\,K$ is the specific heat and $L = 10^4\,J/kg$ is the latent heat (2), $\Delta$ is determined with an accuracy of $\pm 0.005$) and a striking change in the morphology as well as in the side branching activity was observed.

Figures 1*a*)-*f*) show a series of patterns of approximately the same size (they fit into a circle with radius $\approx 200\,\mu m$) grown at different values of undercooling. The nucleation of the smectic phase was spontaneous, and both the location and orientation of the germs were random. We followed the growth process of one nucleus (a second one can be seen in the bottom left corner of fig. 1*f*)). The time passed from the moment of nucleation (pattern age) is shown in the pictures. For the lowest undercooling (fig. 1*a*)) it took more than one hour for the pattern to grow while at the highest undercooling (fig. 1*f*)) the process lasted a few seconds only. The growing smectic objects were not rigidly attached to the glass plates, they could float in the nematic.

The optical axis of the nematic phase is perpendicular to the plane of the pictures (homeotropic alignment) providing the black background between crossed polars. The smectic patterns are also optically homogeneous; we detected total extinction of them if the crossed polars pointed along the bisectrices of the main branches. The direction of the slower optical vibrations («slow» axis) which corresponds to the higher refractive index in the plane of the patterns is the bisectrix lying approximately along NW-SE. By assuming the orthogonality of the smectic phase the «slow» axis coincides with the director (average molecular orientation) as well as with the smectic-layer normal. Thus the director of the smectic phase and that of the nematic one (*i.e.* alignment inside and outside of the pattern, respectively) makes an angle of 90 degrees everywhere along the boundary. In fig. 2 the images of the smectic germs have been rotated by digital processing in order to achieve the same director alignment for all of them.

The number of the main branches (without any exception) was always 4. For large

(1) The substance was synthesized by S. Arora, LCI Kent State University.

(2) The calorimetric data of the substance were measured by J. Szabon.

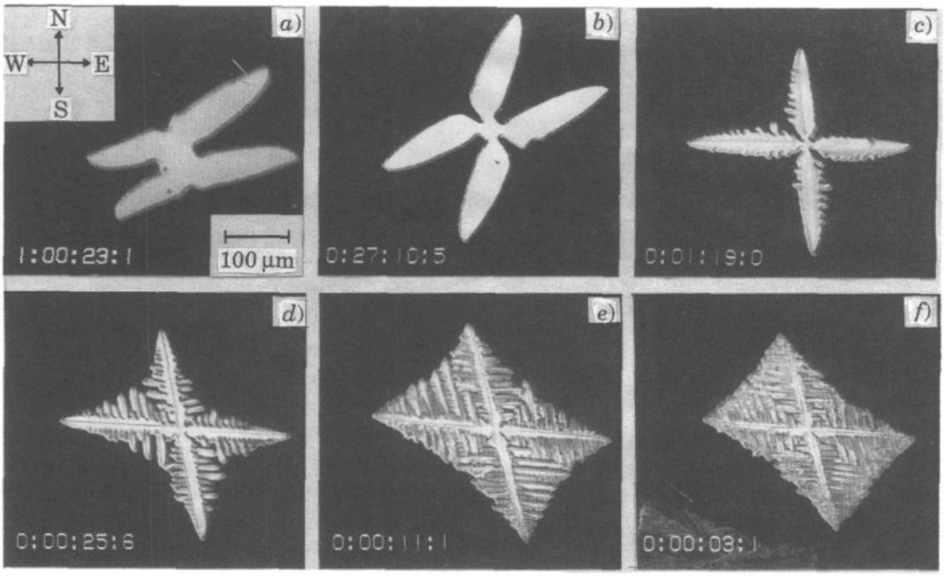


Fig. 1. – Microscopic images of smectic-liquid-crystal dendrites growing into a homeotropically aligned nematic phase at different values of the dimensionless undercooling $\Delta$. *a*) $\Delta = 0.064$, *b*) $\Delta = 0.096$, *c*) $\Delta = 0.143$, *d*) $\Delta = 0.159$, *e*) $\Delta = 0.191$, *f*) $\Delta = 0.255$. The sample was placed between crossed polars pointing along NS and WE. The age of the smectic pattern is given in the pictures in «hours : minutes : seconds : tenths of seconds».

undercoolings the branches made an angle of 70° with each other which did not change during the growth, resulting in straight branches (see fig. 1*e*),*f*)). For $\Delta = 0.159$ and 0.143 the angles were 76° (fig. 1*d*)) and 87° (fig. 1*c*)), respectively. At a further decrease of the undercooling (fig. 1*a*),*b*)) the main branches started growing—similarly to fig. 1*c*)—towards NS and EW but the normal velocity of the tips changed its direction during the growth. The process is demonstrated in fig. 3*a*) for $\Delta = 0.096$. The contours were obtained by digital processing of the microscope images taken at six subsequent moments. Thus the angle between the director of the growing smectic germ and the normal tip velocities depends on undercooling and time; in the particular case of orthogonal branches (fig. 1*c*)) this angle is 45°.

The slowly growing deformed dendrites (fig. 1*a*), *b*)) are nonparabolic, the branches are not symmetric with respect to the normal velocity of the tips. Side branches are lost, the surface becomes smooth and faceted. The straight sections of the boundary (see fig. 1*a*) and

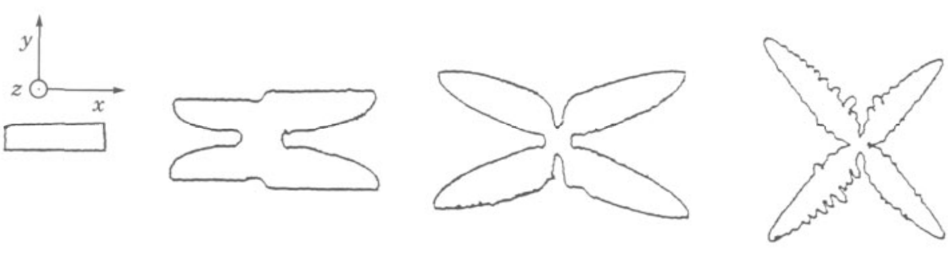


Fig. 2. – Contours of the smectic germs grown at different undercooling. The rectangle on the left-hand side corresponds to the equilibrium conditions. The smectic layers are parallel to the $(x, y)$-plane, the smectic director lies along $y$. The nematic director (alignment outside of the germ) is parallel to $z$.

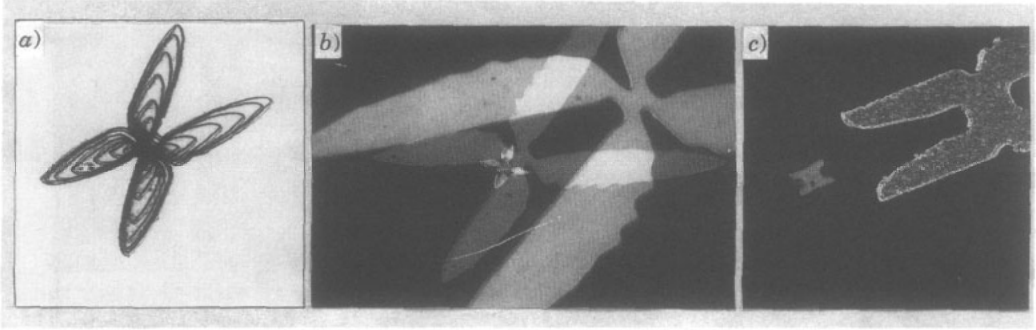


Fig. 3. – Growth of the nonparabolic dendrites. Microscopic images taken at subsequent moments were digitally processed and copied into one picture. *a*) The six contours correspond to pattern ages: 31 s (the smallest), 1 min 17 s, 6 min 45 s, 13 min 11 s, 19 min 43 s and 27 min 11 s (the largest), $\Delta = 0.096$. *b*) Drifting of a dendrite. The three images were taken at 1 min 54 s (the smallest), 30 min 54 s and 3 h 4 min 36 s, $\Delta$ is the same as in *a*). *c*) Drifting of a dendrite. The two images were taken at 4 min 34 s and 3 h 20 min 36 s, $\Delta = 0.064$.

3*c*)) are parallel with each other and with the smectic layers. We have also observed the equilibrium shape of the smectic germ, which turned out to be a rectangle bordered with very sharp and straight edges (see fig. 2). This equilibrium shape provides another argument for the orthogonality of the smectic phase. The longer edge of the rectangle lies in the plane of the smectic layers, while the shorter one is parallel with the smectic director. When the equilibrium germ starts growing, the shorter edge becomes concave (see fig. 3*c*)).

A peculiar effect was observed in the long-time behaviour of the nonparabolic dendrites. At the beginning of the growth process the «butterfly»-like objects had two symmetry axes along the bisectrices of the main branches. After some time—which depended upon undercooling but was typically 20 minutes—the symmetry with respect to the axis parallel to the smectic director was broken and the branches became longer on one side than on the other (see fig. 1*a*),*b*)). Further on, the smectic body drifted along the preserved symmetry axis (parallel to the smectic layers) towards the side of the longer branches. In order to

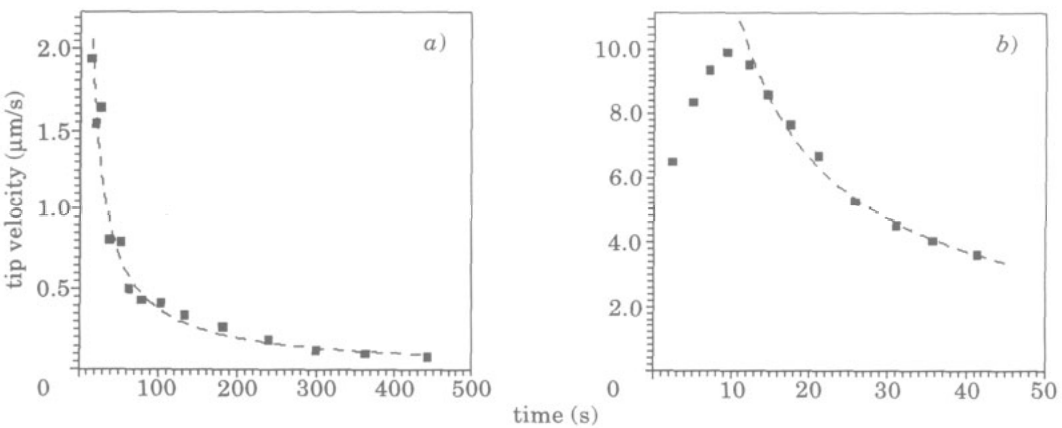


Fig. 4. – Experimental time dependence of the tip velocity for different undercoolings. The dashed lines correspond to a fit of $v \sim t^{-\alpha}$. *a*) $\alpha = 0.92$, $\Delta = 0.096$; *b*) $\alpha = 0.83$, $\Delta = 0.175$, for large undercooling the first few points should be omitted due to the effect of the thermal inertia.

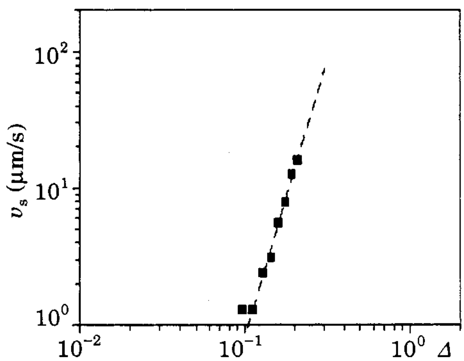


Fig. 5. – Logarithmic plot of the starting tip velocity $v_s$ *vs.* undercooling. The dotted line corresponds to $v_s \sim \Delta^4$.

demonstrate this effect, we copied three pictures on top of each other which were taken with large time intervals at the same undercooling as in fig. 3*a*). The result is shown in fig. 3*b*). A similar picture is presented in fig. 3*c*) for $\Delta = 0.064$ with two images showing a young and an aged pattern. The measured drift velocity was somewhat smaller than the vectorial average of the normal velocities of the four tips. This average velocity is obviously zero in symmetric dendrites. Thus the drift seems to be correlated with the asymmetry of the dendrites, *i.e.* the inequality of the length of the pattern boundary on the two sides.

The velocity of freely moving tips was measured as a function of undercooling. A slowing-down was detected which could be fitted with a power law $v \sim t^{-\alpha}$, where $\alpha$ was in the range of $0.62 \div 0.92$. The characteristic time dependence of the tip velocity is demonstrated in fig. 4*a*),*b*) for a low and a high undercooling. Since the thermal inertia of the system does not allow one to realize a steplike temperature change, for large $\Delta$ the power law applies only after a few seconds (fig. 4*b*)). The velocity of the tips shortly after nucleation (the starting velocity $v_s$ measured at a germ diameter of 20 μm) obeyed the scaling relation $v_s \sim \Delta^4$ [3]; data are shown in fig. 5.

We conclude that dendrites growing at large undercooling on a smectic-nematic interface behave similarly to those on a crystal-melt boundary. For low undercooling we detected some unique features in the liquid-crystal system, like nonparabolic tips and drifting of the germ. The understanding of these effects needs a more detailed quantitative study and remains unexplained at present.

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