Theory and Simulation of Freeze-Fracture in Cholesteric Liquid Crystals

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A theory of fracture in spatially varying anisotropic glass is developed to interpret electron micrographs of freeze-fractured surfaces of cholesteric samples. The expression for energy per unit area released by crack formation is $\gamma \propto [\mathbf{n} \cdot (1 + b\mathbf{Q}_1) \cdot \mathbf{n}]^{1/2}$, where $\mathbf{Q}_1$ is the traceless Landau tensor for unit order parameter and $\mathbf{n}$ is a unit vector normal to the crack surface. The two parameters of the theory are b, which is a function of the ratio of length to width of molecule, and a crack-precursor length. Contours closely matching those observed in the laminar cholesteric texture and in blue phase I are generated.

A thin sample of cholesteric or nematic liquid crystal between thin copper sheets can be quick frozen with jets of cold propane to form a glass with long-range order of molecular orientation. The glass retains the varying director orientation of the original liquid-crystal phase. The sample can be fractured by forcing the copper sheets apart, and the fracture-surface contour can be obtained from an electron micrograph of a platinum shadow replica.[1]

In order to interpret such micrographs we have developed a very simple theory of fracture in spatially varying anisotropic materials that gives results closely resembling our experimental observations. The theory is based on three hypotheses: First, that the crack contour is one which minimizes energy released over a precursor band of fixed breadth during each incremental advance of the crack. Second, that the energy of crack formation is proportional to the number of molecules intersecting the precursor surfaces. This is equivalent to saying that the binding-energy per molecule is independent of molecular orientation. Third, that each molecule occupies an ellipsoid-shaped volume, on average.

An ellipsoid of revolution with its nondegenerate axis parallel to the z axis, representing the average volume occupied by a molecule, may be defined in terms of the Landau tensor[2,3] for unit order parameter, $\mathbf{Q}_1$, as follows:

$$\mathbf{R} = a(1 + b\mathbf{Q}_1) = a \begin{vmatrix} 1 - \dfrac{b}{3} & 0 & 0 \\ 0 & 1 - \dfrac{b}{3} & 0 \\ 0 & 0 & 1 + \dfrac{2b}{3} \end{vmatrix}. \quad (1)$$

The anisotropy parameter b depends on the geometry of the molecule and its order parameter. It increases with increasing order parameter or geometrical anisotropy. Both a and b might vary spatially, particularly in a smectic liquid crystal, but in a cholesteric or nematic substance we believe that both a and b are approximately constant throughout the sample except that, in the neighborhood of the cores of disclinations, b quite suddenly approaches zero, which means that the cores are melted.[4-9]

If b is positive, then a crack normal to the major axis of the volume ellipsoid separates more molecules than a crack parallel to it, as illustrated in Fig. 1. If the angle between the major axis and the crack surface-normal $\mathbf{n}$ is θ, and if the ratio of major to minor axes of the ellipsoid is c, then the area of intersection of the ellipsoid with the fracture plane is proportional to

$$\rho = c/[1 + (c^2 - 1)\cos^2\theta]^{1/2}. \quad (2)$$

This is also illustrated in Fig. 1. If the energy γ required to separate a unit area of the two surfaces of the crack is proportional to the number of molecules separated, then it is inversely proportional to ρ. Although this would be most obvious if all ellipsoids were cut across their equators, it is true regardless of the level of the cut because of the similarity of all parallel cross sections of an ellipsoid.

It is easy to show that

$$\mathbf{n} \cdot \mathbf{R} \cdot \mathbf{n} \propto 1 + \left(\frac{3b}{3-b}\right)\cos^2\theta. \quad (3)$$

Thus, if we make the identity

$$c^2 - 1 = \left(\frac{3b}{3-b}\right) \quad \text{or} \quad b = \frac{3(c^2 - 1)}{(c^2 + 2)}, \quad (4)$$

we see that

$$\gamma \propto (\mathbf{n} \cdot \mathbf{R} \cdot \mathbf{n})^{1/2}. \quad (5)$$

Approximate expressions for the directional variation of Q_1 in the Grandjean texture and in blue phase I (BP-I) of cholesteric liquid crystals have been obtained from optical diffraction[7,8] and from theory.[5,9,10] Correspondence between results of present computations and experiments in the way described in this paper should reveal further details about the structure of these phases and of their disclinations.

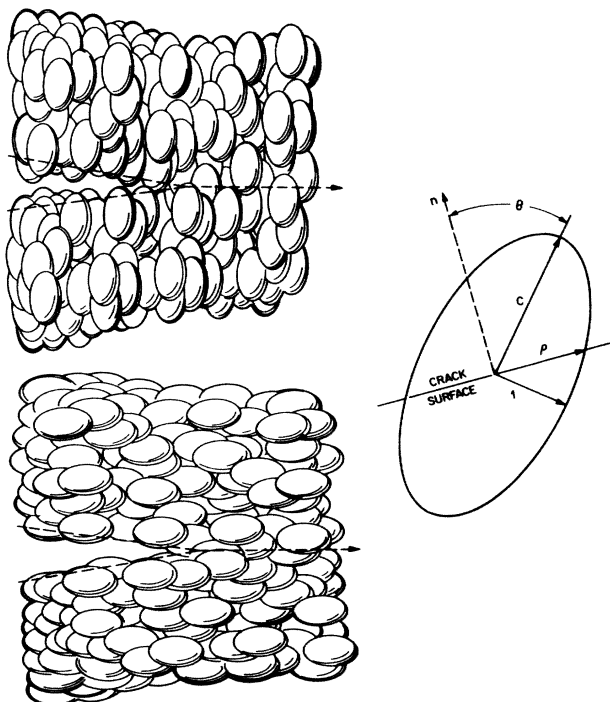Consider a rectangular coordinate system around a

FIG. 1. More molecules per unit area are separated if their major axes are normal than if they are parallel to the crack surface. A prolate spheroid with unit minor axis, tilted at angle θ with respect to crack-normal n, has cross section ρ that is inversely proportional to the number per unit area.

fracturing sample with stress in the z direction. Suppose that the crack front, which is the trailing edge of the precursor surface of breadth Δy, is, at any instant, a curve lying on the x-z plane. The energy released per unit distance by the advancing crack front is

$$\frac{\delta U}{\delta y} = \frac{1}{\Delta y} \int_y^{y+\Delta y} \int_0^w \frac{\gamma \, dx \, dy}{\mathbf{n} \cdot \mathbf{e}_z}, \tag{6}$$

for each incremental advance, δy, of the crack front. The term $\mathbf{e}_z$ is a unit vector parallel to the stress. Although the contour of the trailing edge of the precursor surface, which is the crack front at y, can no longer vary because the fracture is already complete there, the rest of the precursor is subject to some readjustment as the crack advances. Computations consist in minimizing the integral in Eq. (6) by readjusting the precursor contour after each incremental advance of the crack.

We developed a very direct and robust computational method for doing this minimization in order to avoid difficulty where there is an abrupt change in $\mathbf{R}$, or where the direction of the crack changes abruptly. (Standard calculus of variations fails at such discontinuities.) We adjust the value of z at each point on a net of points over the precursor ahead of the crack front, until the contribution to energy at that point is minimal. In this process we first scan a broad range of

values of z, pick that value giving lowest local energy, scan a small surrounding range, and then interpolate to find the minimum. When z at each point has been readjusted, a new value of $\mathbf{R}$ is computed there. This process is then repeated until no value of z changes by more than a preset value, usually less than 0.005 times the spacing in the net.

In the special case of uniform isotropic media, for which b is zero and $c = 1$, the contour of the precursor surface is that of a soap bubble with the same boundaries. The front line of the precursor is not defined before it is reached, and the boundary condition there is somewhat arbitrary. The effective width, Δy, of the precursor band that gives a good match between computed and observed profiles is affected somewhat by the choice of boundary condition at the leading edge of the precursor. The criterion we adopted is to assume that the curvature in the y direction is zero at the front. We found that another criterion, zero global curvature at the front as in a soap bubble, had about the same effect on the contours as use of a somewhat wider precursor band.

In our program the boundary conditions at $x = 0$ and $x = w$ may be periodic, they may be set at fixed z, or they may have zero curvature in the x direction to match the forward boundary condition. Periodic boundary conditions may bias the results if there is a tendency for the structure to twist the crack front overall. Fortunately such twisting diminishes as the width of the crack increases, and we may suppose that our crack fronts are much broader than a small region under examination. The computations shown were made with periodic side boundary conditions.

It is necessary to write an expression from which the tensor $\mathbf{Q}_1$ can be generated at any point in space because it cannot be known in advance where the crack front will be. Writing an analytic expression for $\mathbf{Q}_1$ is easy for the planar Grandjean texture but very difficult for any but the simplest models of the blue phases. For BP-I we have followed a procedure described earlier.[5,7,8] Starting with a simple first-order Fourier-Landau model,[10] we replace the tensor at any point with a uniaxial, unit–order-parameter tensor with the same principal-axis direction over most of space. We create isotropic cores along disclination lines in the isotropic model by setting $\mathbf{Q}_1 = 0$ when a second principal axis of the tensor from the Fourier-Landau model is more than about 0.2 times the largest positive axis. A number larger than 0.2 decreases the average diameter of the isotropic core. Realistic diameters[4-9] are too small to have an appreciable effect on our results with the low resolution of the present computations.

The electron micrographs of freeze-fractured cholesteric liquid crystals to be studied here, and the method by which they were obtained, were described previously by Costello, Meiboom, and Sammon.[1] The

material was a mixture of 60% 4-cyano-4'-(2-meth-yl)butylbiphenyl (CB15), with 40% E9 to lengthen its pitch. Both CB15 and E9 are British Drug House designations, and the latter is itself a nematic mixture. Figure 2 shows an electron micrograph of a freeze-fractured sample quick frozen from the ordinary planar chiral texture, together with a computed profile for $c = 3.5$ ($b = 2.4$) and Δy equal to 1/3 of the full-turn pitch of the cholesteric. Generally, longer precursors or smaller anisotropies generate smoother contours. We designate the angle between the chiral axis and the stress by Θ, and the angle between the chiral axis and the x,z plane by Φ. These computed profiles shown were done with $\Theta = 30°$ and $\Phi = 45°$. Because the sample orientation is uncontrolled, the direction of cracking with respect to stress and chiral axis, as well as c and Δy, must be estimated by trial and error to fit a particular region of a micrograph. Contours at other orientations were generated with the same Δy and c, and compared with other fracture contours to verify that the fit with these parameters is not orientation dependent. Equally good fits can be obtained with somewhat longer or shorter precursors if the anisotropy is also adjusted. The particular choices made here compare favorably with less uncertain parameters for BP-I.

Figure 3 shows a small region from a freeze-fractured sample of the same material quick frozen from the BP-I texture, together with a profile computed from a model with $c = 3.0$ and Δy equal to 0.3 times the unit-cell dimension. The crack starts at a line along the [1,0,0] axis, and the stress is normal to that line and to the [0,1,11] axis. Lateral shift in repeated profiles as crack rises through the unit cells, and diagonal mounds with a peak at one end, are critical features of the figure. The computed profile is an approximate mirror image of micrograph because we chose the wrong sign of chirality in the computations.

The edge of the crack profile is superposed on an illustration of 2×8 unit cells in Fig. 4. The model used has O^8 symmetry and has been designated as $O^8 -$ because of the choice of sign on the off-diagonal elements of the first-order term in its Landau expansion.[5,7,8,10] Although there are some fine details on the freeze-fracture picture that do not show on the model, the overall contours are quite similar. The experimental fracture probably did not move exactly parallel to the [1,0,0] axis, as assumed in the computa-
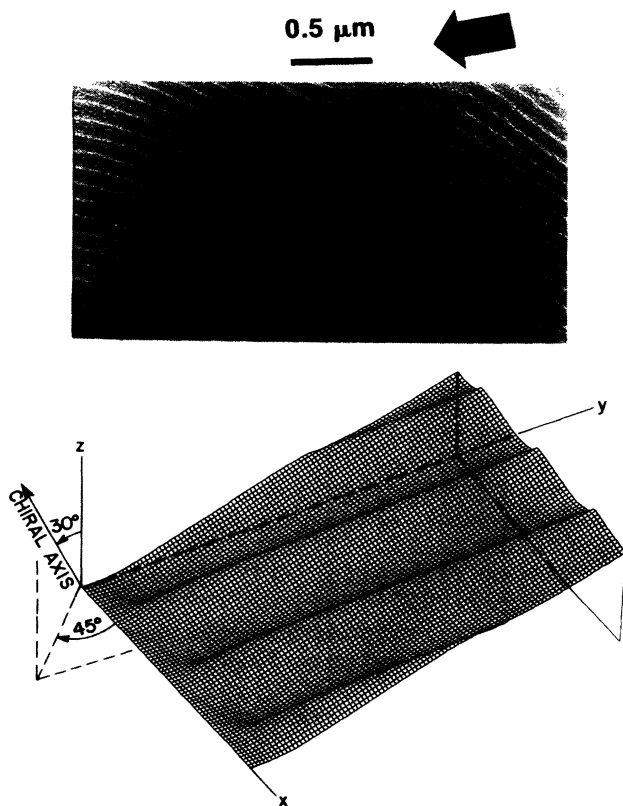

0.5 μm

FIG. 2. Top: Electron micrograph of freeze-fractured sample from the ordinary planar cholesteric phase. Arrow indicates azimuth of incident platinum. Dark areas have thicker platinum. Bottom: Three cycles of computed contour of fracture surface with chiral axis oriented at $\Theta = 30°$ and $\Phi = 45°$ with respect to x,y,z coordinate system of crack front and stress. Asymmetric sawtooth contour is critical feature for comparison.
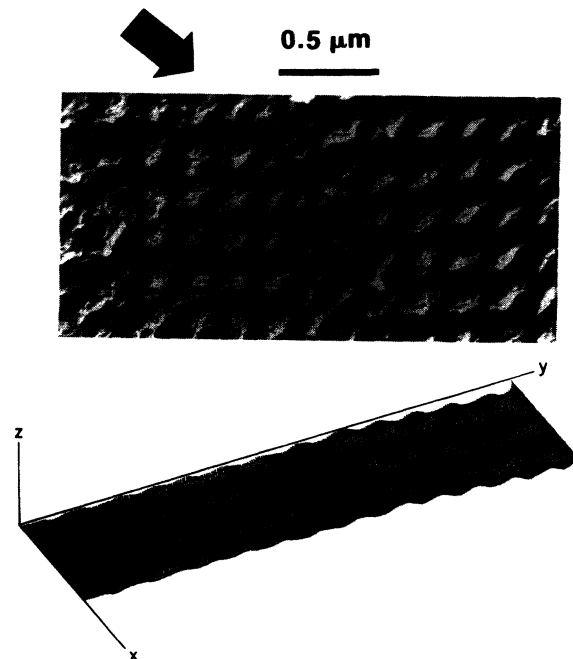

0.5 μm

FIG. 3. Top: Electron micrograph of cholesteric mixture freeze-fractured from BP-I. The surface shown is monocrystalline and slightly tilted from the [1,0,0] plane. Bottom: Computed contour based on the $O^8 -$ model of Refs. 5, 7, and 8 with stress normal to the (0,1,11) plane. The computed segment is three unit cells wide and eleven long. Computed profile is approximate mirror image of micrograph.
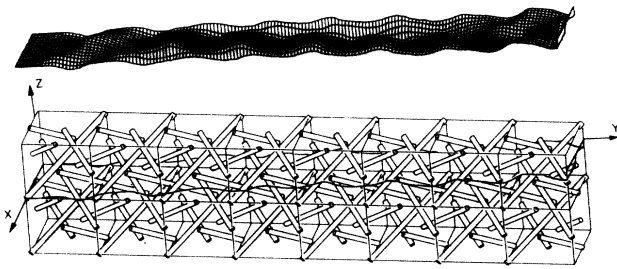
FIG. 4. Top: One cycle of crack surface through first eight unit cells; same orientation as in Fig. 3. Bottom: Sixteen unit cells of BP-I with edges of crack of same contour superposed. Rods show the location and approximate diameter of the isotropic cores that are presumed to exist at disclinations in O^8- symmetry.

tion of the profile.

Contours with values of c that are somewhat larger look very similar if the precursor length is increased accordingly. We are biased toward assuming the smaller value $c = 3$, not because the contours match our observations better, but because it seems like a more realistic number for the shape of the molecules. It is still somewhat larger than might be expected from the geometry and order parameter of the molecules. However, if we use a shorter precursor the height of the long ridges and valleys are too extreme with respect to the more local contours. There is also too strong a tendency for the contours to follow the $(0,0,1)$ planes, rather than to remain generally normal to the stress, so that it is hard to reproduce the observed climb through the unit cells illustrated in Fig. 4.

We failed in our attempts to fit the observed contours for BP-I using the tensor generated directly by first-order Landau theory.[10] Regions were encountered where the fracture energy γ was imaginary when a reasonable anisotropy c was used. Contours with sufficiently small b were unrealistically flat.

The precursor length of 0.3 times the unit cell dimension is about equal to 1/3 the pitch of the planar cholesteric phase of the same material. We chose this precursor length for the cholesteric phase to match that of BP-I partly because there is no evident reason that they should differ. Another reason is that a good fit is obtained with that value and with an anisotropy c that is slightly larger than in the bulk of the blue phase, away from disclinations. We expect this uniform order from numerical computations based on a free-energy function that is fourth order in Q_1, with a temperature-dependent first-order term, and third order in strain.[9]

This paper attempts to describe fracture in moderately anisotropic, spatially varying glassy materials in a way that is fast enough to be used repeatedly for testing different models of molecular orientation. Rigorous application of accepted principles of elastic fracture mechanics[11-13] to spatially varying anisotropic media seems completely impractical in the cases considered here. We have retained the concept of surface-energy minimization but the effects of elastic strain field and possible inertial effects are all swept into a single parameter, the empirical precursor length. (Precursors observed in metallic fracture are much larger, contain voids, and bear only superficial resemblance to the concept introduced here.) Despite gross simplifications we believe that the similarity between our computations and our observations indicates that the theory is sufficiently accurate to help in understanding the detailed structure of features observed in thermotropic cholesteric and nematic phases.

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[1]M. J. Costello, S. Meiboom, and M. J. Sammon, Phys. Rev. A 29, 2957 (1984).

[2]P. G. de Gennes, Phys. Lett. 30A, 454 (1969).

[3]C. Fan and M. J. Stephen, Phys. Lett. 25A, 500 (1970). (Q_1 is denoted by Δ there.)

[4]C. Fan, Phys. Lett. 34A, 335 (1971).

[5]M. Sammon, Mol. Cryst. Liq. Cryst. 89, 305 (1982). (Note: There are some typographical errors in the off-diagonal terms for O^8 symmetry here. They are correct in Ref. 10.)

[6]S. Meiboom, M. Sammon, and W. F. Brinkman, Phys. Rev. A 27, 438 (1983).

[7]D. W. Berreman, in Liquid Crystals and Ordered Fluids, edited by A. Griffin and J. Johnson (Plenum, New York, 1984), Vol. 4, p. 925. (Note: The generalized off-diagonal term of O^8 symmetry has different typographical errors here than in Ref. 5.)

[8]S. Meiboom, M. Sammon, and D. W. Berreman, Phys. Rev. A 28, 3553 (1983).

[9]D. W. Berreman, in Proceedings of the Eleventh International Liquid Crystal Conference, Berkeley, California, 1985 (to be published).

[10]H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A 28, 1114 (1983).

[11]A. A. Griffith, Philos. Trans. Roy. Soc. London Ser. A 221, 163 (1921).

[12]G. R. Irwin, J. Appl. Mech. 24, 361 (1957).

[13]K. Jagannadham and M. J. Marcinkowski, Unified Theory of Fracture (Trans Tech, Rockport, MA, 1983).
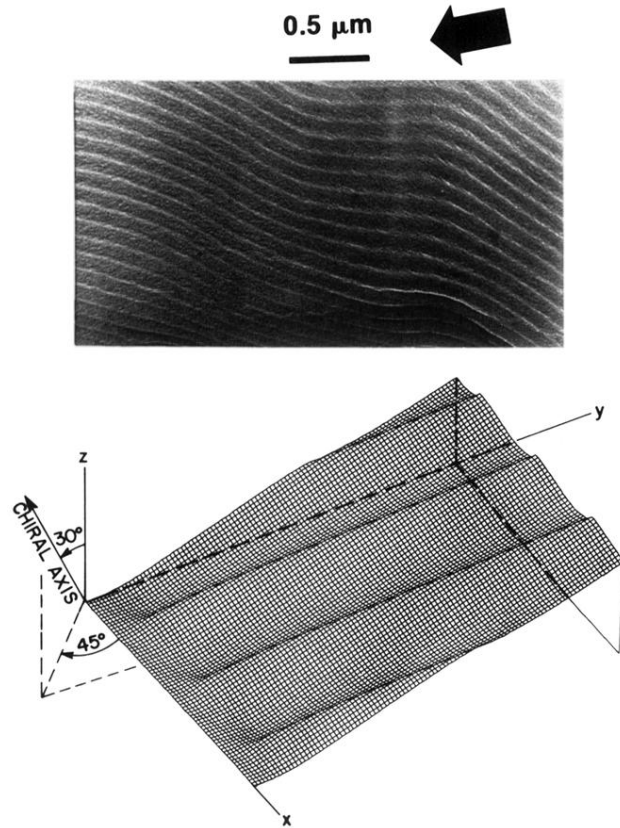
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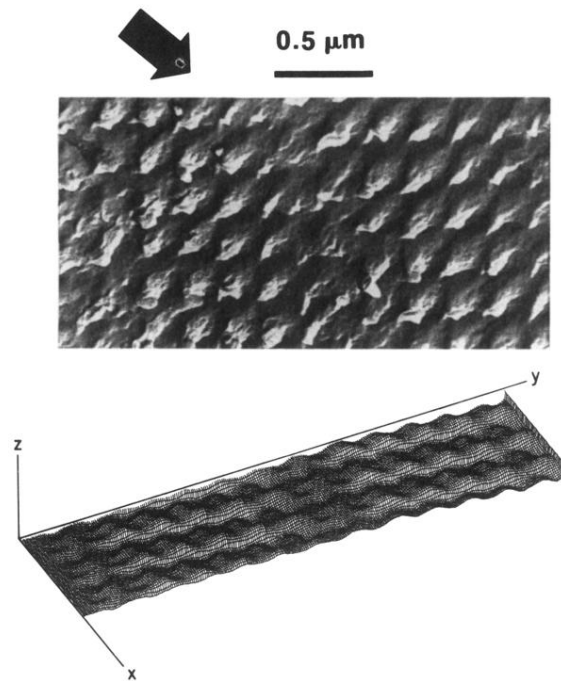
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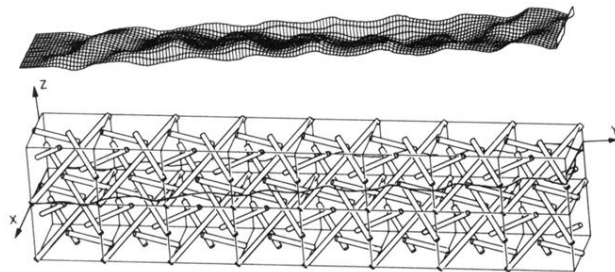
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