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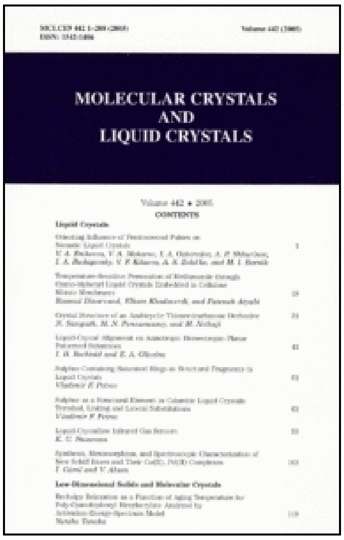

Molecular Crystals and Liquid Crystals

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Surface Tension of Liquid Crystals

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Abstract—The problem of finding the equilibrium shape of a small particle by the Wulff construction is reviewed briefly, with emphasis on its applications to liquid crystals. The proof of Wulff's theorem is stated in a concise mathematical form. Some typical equilibrium shapes of liquid crystalline drops are described. When there is orientational order of the molecules in the liquid crystal but no translational order, the equilibrium shape may be an ellipsoid or a tactoid; when there is translational order as well, the shape may have plane faces, possibly with sharp edges and corners. The formation of the stepped drop, goutte à gradins, is interpreted as analogous to the stepwise roughening of a flat crystal surface whose orientation does not occur amongst the boundary surfaces of the Wulff shape.

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As is well known, the problem of determining the equilibrium shape of a given quantity of material reduces mathematically to one of finding the condition for minimum surface energy. It was formulated over eighty years ago by Gibbs, and independently by Curie, and has since been investigated in great detail particularly in relation to the equilibrium shapes of crystals. It is the aim of this paper to review these ideas briefly and to discuss their applications to liquid crystals.

The surface tension of a liquid crystal may be expected to be anisotropic.[1] A solid crystal also has anisotropic surface tension, but there is an essential difference between the two cases.[2] The surface tension of a solid crystal (or the specific surface free energy, measured by the work done in creating a new surface) differs numerically from its surface stress (measured by the work done in deforming a surface). For a liquid crystal, on the other hand, these two quantities will be equal because of the inability of the medium to sustain a shear stress, except for short periods of time.[3]

Wulff's Theorem

The relation between the surface tension and the equilibrium shape of a small particle is determined by a theorem due to Wulff.[4] Proofs of this theorem were given by Hilton,[5] Liebmann[6] and Laue,[7] all of whom assumed the equilibrium shape to be a polyhedron and compared its surface energy with that of other polyhedra with slightly different face areas. However, these proofs are not strictly valid for liquid crystals, for the equilibrium shape may not be polyhedral. A general proof of the theorem was given by Dinghas[8] and extended by Herring,[2] who also discussed some applications to liquid crystals. The proof is restated below in a concise mathematical form.

Consider a body P_0 for which the surface tension γ is a function of the direction only, i.e. $\gamma = \gamma(\vec{n})$, and is defined as the specific surface free energy of any plane normal to $\vec{n}$.

If p is a point and π a plane not containing p, π divides the space into two half-spaces, one of which contains p. Define $\pi_{\vec{n}}(\lambda, p)$ as the plane normal to $\vec{n}$ at a distance $\lambda\gamma(\vec{n})$ from p, where $\lambda \geqslant 0$ is a scale factor. Let $S^{p}_{\pi_{\vec{n}}}$ denote the half-space containing p together with all points in $\pi_{\vec{n}}(\lambda, p)$. Then

$$W_\lambda(p) = \bigcap_{\vec{n}} S^{p}_{\pi_{\vec{n}}} \tag{1}$$

forms a convex body and is called the Wulff construction centred at p with scale factor λ. If v_λ is the volume of $W_\lambda(p)$, then $v_\lambda = \lambda^3 v_1$, where v_1 is the volume of the Wulff construction with scale factor 1.

Now, let $\vec{n}$ be an outward normal to the surface of P_0 at the point Q, and $W_\lambda(Q)$ the Wulff construction centred at Q. Clearly,

$$W_\lambda(Q) \subset S^{Q}_{\pi_{\vec{n}}}, \quad \text{for every } Q.$$

Define P_λ as the body whose surface is the envelope of all planes $\pi_{\vec{n}}(\lambda, Q)$ as Q varies over the surface of P_0. Therefore if

$$\overline{W} = \bigcup_{Q \epsilon P_0} W_\lambda(Q),$$

we have

$$\overline{W} \subseteq P_\lambda.$$

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If $\overline{V}$, V_0 and V_λ are respectively the volumes of $\overline{W}$, P_0 and P_λ,

$$\overline{V} \leqslant V_\lambda,$$

$$\frac{\overline{V}-V_0}{\lambda} \leqslant \frac{V_\lambda - V_0}{\lambda}. \tag{2}$$

It may be verified that if $W_\lambda(Q)$ is similar to, and with the same orientation as, P_0, $\overline{W}=P_\lambda$, $\overline{V}=V_\lambda$, and the equality sign holds in Eq. (2). But

$$V_\lambda - V_0 = \int_A \lambda\gamma(\vec{n})\,dA,$$

where dA is an element of area containing Q. Therefore,

$$\int_A \gamma(\vec{n})\,dA = \operatorname*{Lim}_{\lambda\to 0} \frac{V_\lambda - V_0}{\lambda}$$

$$\geqslant \operatorname*{Lim}_{\lambda\to 0} \frac{\overline{V}-V_0}{\lambda}. \tag{3}$$

We next invoke the Brunn-Minkowski inequality in the following form. Let P_0 and P be two bodies, one of which, say P, is convex. Select an arbitrary interior point 0 of P and call it the "centre" of P. Displace P to a new position without changing its orientation such that 0 coincides with a point p of space. In this position of P we denote it by $P(p)$. Consider the union

$$\overline{P} = \bigcup_{p\epsilon P_0} P(p).$$

If $\overline{V}$, V_0 and V are respectively the volumes of $\overline{P}$, P_0 and P, we have the Brunn-Minkowski inequality

$$\overline{V} \geqslant (V_0^{1/3} + V^{1/3})^3, \tag{4}$$

the equality sign holding only when P is similar to P_0. Taking $\overline{W}$ for $\overline{P}$, W_λ for P, we get from Eq. (4)

$$\overline{V} \geqslant (V_0^{1/3} + v_\lambda^{1/3})^3$$

$$= (V_0^{1/3} + \lambda v_1^{1/3})^3.$$

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We thus obtain, using Eq. (3)

$$\int_A \gamma(\vec{n})\,dA \geqslant \lim_{\lambda\to 0} \frac{(V_0{}^{1/3}+\lambda v_1{}^{1/3})^3 - V_0}{\lambda},$$

i.e.

$$\int_A \gamma(\vec{n})\,dA \geqslant 3V_0^{2/3}v_1^{1/3},$$

the equality sign holding only when $W_\lambda(Q)$ is similar to P_0. This proves that the Wulff construction is a body with minimum energy of the surface. The equilibrium shape of P_0 will therefore be geometrically similar to the Wulff construction.

The Wulff theorem may be stated simply as follows. Consider the polar plot of γ in which the length of the radius vector in any direction is proportional to $\gamma(\vec{n})$. If a plane is drawn normal to $\vec{n}$ at the end of every radius vector, then the body formed by all the points that can be reached from the origin without crossing any of these planes will be similar to the equilibrium shape.

We have assumed here that gravitational forces are negligible, an assumption which is valid for small drops. We have also ignored the possible variation of γ with curvature and the effect of the energies of the edges and corners.

Equilibrium Shapes of Liquid Crystalline Drops

A detailed calculation of the surface tension as a function of the orientation requires knowledge of the molecular distribution function and the potential of the intermolecular force in the liquid crystal. Not enough is known about these quantities for such a calculation to be carried out. It is however possible to determine qualitatively the general characteristics of the equilibrium shapes that are to be expected.

We shall consider first a liquid crystal in which there is orientational order of the molecules but no translational order (Fig. 1). Imagine a plane surface of the liquid crystal parallel to the long axes of the molecules. The atomic density will be greater for this plane than for a plane of any other orientation. We may therefore

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suppose that the specific surface free energy γ is least for this plane, because it is well known that the closest packed planes in crystals have the lowest surface energies. Similarly γ will be greatest for a plane normal to the long axes of the molecules. The polar plot of γ will, in general, vary smoothly between these two directions, and when the anisotropy is not large the Wulff shape will be of type 2(a) with the major axis parallel to the long axes of the molecules. Such a shape is indeed to be expected from purely physical considerations, for it may be regarded as an equilibrium between the tendency of a liquid to form a spherical drop and the orientational forces aligning the molecules approximately parallel to each other.

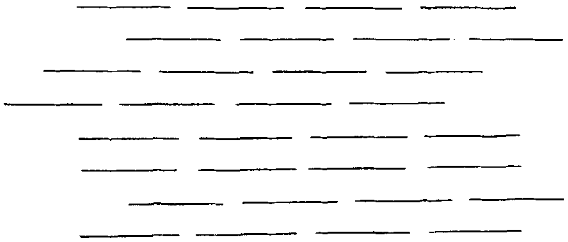

Figure 1. Molecular arrangement in nematic mesophase (idealized).

When the anisotropy is large, as is often likely to be the case with liquid crystals, it may be shown easily that not all orientations of the γ plot will occur in the boundary surface of the Wulff construction, which will therefore have sharp edges as illustrated in Fig. 2b. Such shapes, called tactoids, were observed in colloidal solutions by Zocher[9, 10] and in plant virus preparations by Bernal and Fankuchen.[1] The virus preparation used by Bernal and Fankuchen corresponded to the class RRD of Hermann's classification[11] of possible liquid crystalline systems. Two kinds of tactoids were formed, which they named positive and negative. Positive tactoids contained the liquid crystal in the isotropic liquid, negative tactoids vice versa. In both cases, they established by optical observations that the long axes of the molecules were approximately parallel to the major axes of the tactoids—as is to be expected. The shapes of the tactoids depended slightly on the size, the larger tactoids being

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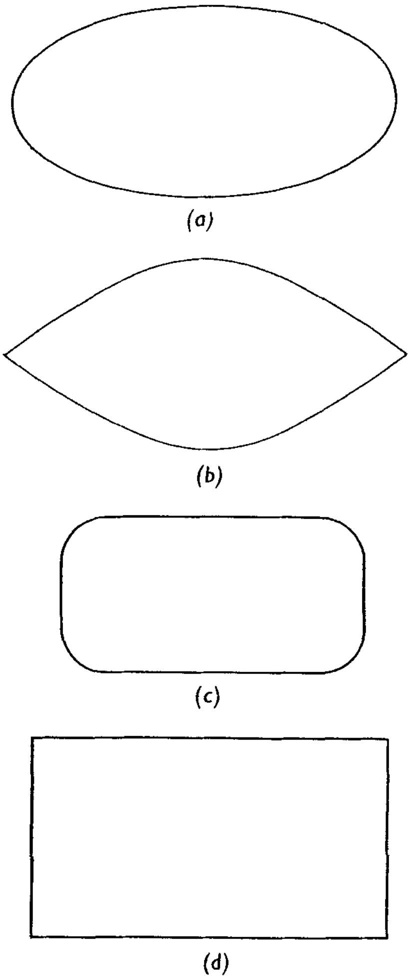

Figure 2. Equilibrium shapes of liquid crystalline drops.

more spherical than the smaller ones. That the tactoids were equilibrium forms was shown directly by the fact that they recovered their shapes when distorted. Bernal and Fankuchen gave an interpretation of the tactoids in terms of anisotropic surface tension. These shapes have also been discussed briefly by Herring.[2]

The view has been expressed in the literature that the equilibrium shapes of liquid crystals cannot have plane faces. This view would seem to be incorrect. As we shall see presently, when there is translational order of molecular arrangement in the liquid crystal plane faces are possible. The layer arrangement in a smectic mesophase is an example of translational order (Fig. 3). In this case, the problem of determining the equilibrium shape becomes analogous to that for a crystalline solid. The polar plot of γ for a crystal at absolute zero of temperature will exhibit a singularity in the form of a cusped minimum at every rational orientation.[12, 2] But at higher temperatures all the cusps, except a few in directions corresponding to low Miller indices (most closely packed planes), will be smeared out by thermal fluctuations. These few cusps will give rise to plane regions in the Wulff construction, and the equilibrium shape will be a polyhedron. Thus for a liquid crystal in which there is translational order of the molecules, the equilibrium shape may be expected to have plane regions. These planes may be joined by smoothly rounded surfaces as in type 2(c); but if the minima in the γ plot are sufficiently pronounced the planes may meet to form sharp edges and corners as in type 2(d). Distinctive polyhedral shapes have in fact been observed very recently by Balmbra, Clunie and Goodman,[13]† in an electron micrograph of a lyotropic mesophase formed by an aqueous solution of sodium 2-ethylhexyl sulphate.

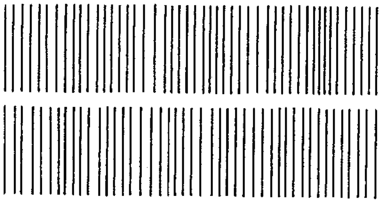

Figure 3. Layer arrangement of molecules in the smectic mesophase (idealized).

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† Paper presented by Dr. J. S. Clunie at this conference.

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Other shapes are also possible. For instance, the shape may have curved as well as plane regions and some sharp edges and corners. If the equilibrium shape is known, the γ plot may be derived, though, as will be clear from the earlier discussion, it can be done for all directions only for some shapes.

The Stepped Drop (goutte à gradins)

One of the consequences of Wulff's theorem is that a surface having an orientation which occurs in the boundary of the equilibrium shape is more stable than a hill-valley structure of the same mean orientation.[2] The converse result is also true, namely, that a plane surface with an orientation not occurring in the Wulff shape is unstable with respect to some hill-valley structure, and will break up into steps, providing, of course, the kinetic factors allow such a change to take place. Thus, for types (a) and (c) a plane of any orientation is stable, whereas for type (d) planes of all except a few discrete orientations are unstable. Type (b) forms an intermediate category with certain ranges of orientation stable, certain others unstable.

Let us now consider the stepped drop, goutte à gradins, discovered by Grandjean.[14, 15, 16] The familiar model for the smectic mesophase with the layer arrangement of rod-like molecules is shown in Fig. 3. The forces between the sides of the molecules are large, but those between the adjacent layers are relatively weak. This situation is obtained by the presence of strong dipole moments acting across the long axes of the molecules.[17] Therefore, owing to dipole–dipole reinforcement, the layer arrangement is energetically the most stable.

It will be seen from Fig. 3 that there are two singular directions (analogous to rational orientations in a crystal) for which γ will exhibit pronounced minima, and the cross-section of the equilibrium shape may be expected to be 2(d). In practice, however, the drop forms terraces. This remarkable phenomenon may be interpreted as the hill-valley configuration adopted by a plane surface which does not conform to the Wulff shape. The layer arrangement of molecules being the only energetically feasible one

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at that temperature, a smooth surface of arbitrary orientation, produced, let us say, by a deformation of the ideal equilibrium shape, will readily break up into steps whose heights are integral multiples of the molecular length (Fig. 4).

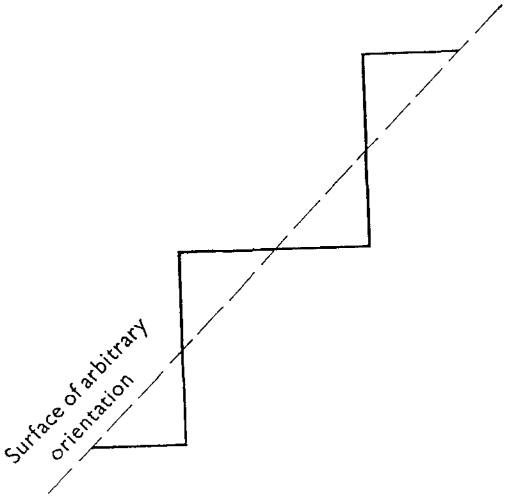

Figure 4. Formation of steps.

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