Theory of the equilibrium shape of crystals

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(Submitted 21 April 1981)
Zh. Eksp. Teor. Fiz. **81**, 1141–1144 (September 1981)

It is shown that the equilibrium shape of crystals cannot involve angles. The possibility, in principle, of equilibrium twinning is noted. Certain electrocapillary effects at the surface of a liquid, similar to striction effects at the surface of a crystal, are discussed.

PACS numbers: 61.50.Jr, 68.10.Cr

1. In the literature one may encounter the statement that under conditions of thermodynamic equilibrium, the shape of crystals can involve edges. Andreev,[1] in an investigation of facet phase transitions, showed that onset of edges by a transition of the second order is impossible because of striction effects. On the other hand, phase transitions of the second order are impossible on the surface of crystals.[2] In such a situation, the question of the very existence of edges naturally arises.

Let the stability condition

$$\alpha+\alpha''_{\varphi\varphi}>0$$

where α is the surface energy, be violated within a certain interval $(\varphi_1<\varphi<\varphi_2)$ of variation of one of the angles that determine the orientation of a facet of the crystal surface. It is customary to suppose that this leads to the appearance of edges, at which stable facets φ_1 and φ_2 intersect. But as we shall see, a certain reorganization is possible at the surface, such that all facets within the interval (φ_1, φ_2) become stable. In fact, an arbitrary facet $\varphi_1<\varphi<\varphi_2$ can be built up out of stable facets φ_1 and φ_2 in the form of a periodic structure (see Fig. 1, case a). The sum of the energies of the facets φ_1 and φ_2 is independent of the period L and is, per unit length,

$$\alpha_0(\varphi)=(\alpha_1L_1+\alpha_2L_2)L^{-1}=[\alpha_1\sin\varphi+\alpha_2\sin(\varphi_0-\varphi)]\sin^{-1}\varphi_0$$

(we measure all angles from the facet φ_1). This part of the energy, on variation of φ from 0 to φ_0, satisfies the relation

$$\alpha_0+\alpha''_{0\varphi\varphi}=0.$$

Therefore the stability of the structure is determined by the sum of the strictional energy and the energy of the edges (A and B in Fig. 1, case a).

Striction originates because of the presence of surface tensions. In crystals, the surface tensions are determined by the surface-tension tensor $\beta_{\mu\nu}$ $(\mu,\nu=1,2)$.[3] The total strain energy is

$$^1/_2\int\sigma_{ik}u_{ik}dV+\int\beta_{\mu\nu}u_{\mu\nu}\,dS, \tag{1}$$

where u_{ik} is the strain tensor, σ_{ik} is the stress tensor, and $i,k=1,2,3$. The strains that occur correspond to a minimum of the energy (1); therefore in equilibrium, the energy (1) must be negative. By use of the equations of the theory of elasticity and of the boundary conditions,[3] the expression (1) can be reduced to the form

$$-^1/_2\int\sigma_{ik}u_{ik}\,dV, \tag{2}$$

as is natural, since the volume energy is quadratic and the surface energy linear in the strain tensor. The action of the surface tensions in our case reduces to forces **F** concentrated on the edges (see Fig. 1, case a). The energy (2) can be transformed to a surface integral

$$-^1/_2\int\sigma_{in}u_i\,dS$$

where u_i is the displacement vector. And since $\sigma_{in}=0$ everywhere except on the edges, this integral reduces to the sum

$$-^1/_2\sum_{n=-\infty}^{\infty}\mathbf{F}_n\mathbf{u}_n,$$

in index n enumerates the edges.

We restrict ourselves to consideration of the isotropic case, in which the surface-tension tensor reduces to the coefficients of surface tension β_1 on facet φ_1 and β_2 on facet φ_2. Furthermore, we shall suppose that the angle φ_0 is small; then the solution of the problem of elasticity theory simplifies considerably, since we may neglect the difference of the shape of the surface from a plane and may find the strains in the crystal, under the action of surface forces **F** (see Fig. 1, case b), by use of the results of §8 of the book of Landau and Lifshitz.[4] We shall show, for example, how to find the displacement u_z at the point B under the action of the z component of the force distribution **F**.

We first calculate the derivative $\partial u_z/\partial x$ on the surface in the interval between the points A and B [see Ref. 4, §8, formulas (8.19)];

$$\frac{\partial u_z}{\partial x}=\frac{1-\sigma^2}{\pi E}F_z\sum_n\int_{-\infty}^{+\infty}\left(\frac{nL-x}{[(nL-x)^2+y^2]^{3/2}}-\frac{nL+L_1-x}{[(nL+L_1-x)^2+y^2]^{3/2}}\right)dy$$

$$=\frac{1-\sigma^2}{\pi E}F_z\left\{-\frac{1}{x}-\frac{1}{L_1-x}+2\sum_{n=1}^{\infty}\left(\frac{x}{n^2L^2-x^2}+\frac{L_1-x}{n^2L^2-(L_1-x)^2}\right)\right\}$$

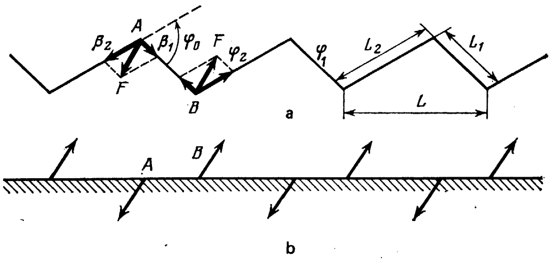

FIG. 1. a) Proposed corrugated structure of a crystal surface: $L_1=L\sin\varphi/\sin\varphi_0$, $L_2=L\sin(\varphi_0-\varphi)/\sin\varphi_0$, $F^2=(\beta_2-\beta_1\cos\varphi_0)^2+\beta_1^2\sin^2\varphi_0$; b) Distribution of forces of surface tension when $\varphi_0\ll1$ (surface almost plane).

0038-5646/81/090605-03$02.40

E is Young's modulus, σ is Poisson's ratio. The integral of this expression from $x=0$ to $x=L_1$ is

$$u_z(B)-u_z(A)=2u_z(B)=2\frac{1-\sigma^2}{\pi E}F_z\ln\frac{Lc}{a},$$

$$c=c(\varphi)=\frac{\varphi}{\varphi_0}\prod_{n=1}^{\infty}\left\{1-\frac{1}{n^2}\left(\frac{\varphi}{\varphi_0}\right)^2\right\}=\frac{1}{\pi}\sin\pi\frac{\varphi}{\varphi_0},$$

where the cutoff parameter a is a quantity of the order of the atomic distance. As a result of such calculations, we get the following expression for the total energy (3) per period:

$$-\frac{(1-\sigma^2)F^2}{\pi E}\ln\frac{Lc}{a}.$$

Adding to this the energy ε of the edges A and B, we get for the energy density

$$-\frac{(1-\sigma^2)F^2}{\pi EL}\ln\frac{cL}{a^*}, \tag{4}$$

where we have introduced the notation

$$a^*=a\exp\{\pi E\varepsilon/(1-\sigma^2)F^2\}.$$

The minimum of the energy (4) is attained at $L=ea^*c^{-1}$. The surface energy is then less than $\alpha_0(\varphi)$ by the amount

$$\frac{(1-\sigma^2)F^2c}{\pi eEa^*}\propto\sin\frac{\pi\varphi}{\varphi_0}$$

and satisfies the stability condition.

The formulas obtained are quantitatively applicable only if the period L of the structure is large in comparison with the atomic distance. As regards the qualitative result concerning the stability of the facets considered, it seems unlikely that the limitations assumed (isotropy and small angles φ_0) would be important.

2. As was established by Osheroff, Cross, and Fisher,[5] solid ^{3}He in the antiferromagnetic state is a tetragonal crystal. But in no case has it been possible to observe a single-crystal state, and it has been proved conclusively that each individual crystal divides into three domains, so that the C_4 axes of these domains are mutually perpendicular. The surface of He^3 crystals under these conditions should possess the quantum properties predicted by Andreev and Parshin[6] and detected in He^4 by Keshishev, Parshin, and Babkin.[7] In particular, He^3 crystals should acquire the equilibrium shape rapidly. Therefore the observed[5] splitting of He^3 crystals into domains is probably an equilibrium phenomenon. Specifically, if the energy of twinned boundaries is less than the surface energy, then for sufficient anisotropy of the surface energy a situation is in principle possible in which it is advantageous, by production of several twinned boundaries, not to exhibit at all, in the equilibrium shape, the portion of the facets with the larger energy.

3. As was shown earlier,[2] because of strictional effects, two-dimensional phase transitions of the first kind on the surface of crystals are impossible. It turns out that the existence of surface polarization (a double layer[8]) leads to the same prohibition on the surface of a liquid. In an isotropic liquid, the surface polarization is directed along the polar vector normal to the boundary. We assume that on the surface there exist two phases, differing, for example, with respect to the density of adsorbed atoms. Then the surface energies of the liquid in the two states coincide, but there is no reason for equality of the surface polarizations. Therefore an electric field is produced near the line of separation between the phases.

As an example, we consider a nonconducting liquid, and we neglect its polarizability. The electric energy density is

$$-\mathbf{PE}-\mathbf{E}^2/8\pi. \tag{5}$$

The polarization density $\mathbf{P}$ in our case is $\mathbf{n}p\delta(z)$, where $\mathbf{n}$ is the unit vector normal to the surface. In the electric field $\mathbf{E}$, we separate out the perpendicular part, representing $\mathbf{E}$ in the form $\mathbf{E}=-4\pi\mathbf{P}-\mathbf{e}$. Then the expression (5) splits into two parts: the first, positive part $2\pi\mathbf{P}^2$ simply renormalizes the surface energy; the second, negative part $-\mathbf{e}^2/8\pi$ is nonzero near the line of separation between the phases. To find $\mathbf{e}$, we note that the surface polarization leads to a discontinuity of the electric potential at the surface.[8] In our symmetrical case, we may choose on the two sides of the boundary potentials $2\pi p_1$ and $-2\pi p_1$ for the first phase, $2\pi p_2$ and $-2\pi p_2$ for the second. The electric field for such boundary conditions is known.[8] All that is important for us is that this field falls off slowly, as R^{-1}, with distance R from the line of separation between the phases. The energy

$$-\int\frac{\mathbf{e}^2}{8\pi}dV$$

diverges logarithmically, and therefore unlimited mixing of the phases is advantageous.

Any point defect (an impurity atom, for example) on the surface of a liquid changes the surface polarization. In other words, such a defect possesses an electric moment, whose order of magnitude is obviously $\varepsilon a^3/e$, where e is the charge of the electron and where ε is the coupling energy of the impurity with the surface. Therefore identical defects at distances large in comparison with atomic distances repel according to an R^{-3} law, i.e., the same as for elastic interaction of defects on the surface of crystals[9]; the order of magnitude of the energy of interaction of the impurities is the same in both cases: $\sim\varepsilon^2a^4/e^2R^3$.

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Translated by W. F. Brown, Jr.