

## Elastic properties of crystal surfaces

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The general properties of the surface stress tensor, describing elastic properties of crystal surfaces, are determined. The boundary conditions are obtained for the bulk stress tensor on the surface of a crystal of arbitrary shape. The elastic interaction between point and line defects on crystal surfaces is considered.

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It is well known that the thermodynamic properties of a liquid surface are governed entirely by one quantity which is the work done in reversible changes of the surface area. As pointed out long ago by Gibbs,<sup>1</sup> in the case of a solid we have to distinguish the work done in forming the surface and in deforming it. Thus, in describing the properties of crystal surfaces we have to introduce not only the surface energy but also the sur-

face stress tensor. We shall determine the general properties of this tensor and find the boundary conditions replacing in our case the familiar Laplace formula for the capillary pressure.

In the second section we shall consider the elastic interaction of surface defects over distances which are large with the atomic separations. As in the case of

bulk defects, the problem can be solved without postulating any models about the microscopic structure of defects.

## 1. SURFACE STRESS TENSOR

We shall consider a plane boundary of a crystal. A small elastic deformation  $u_i$  alters the surface energy by

$$-\int f_\mu u_\mu dS_0, \quad \mu=1,2 \quad (1)$$

(integration is carried out over an undeformed surface);  $f_\mu$  are the surface forces which have only tangential ( $\mu=1$  or  $2$ ) components because the normal surface forces vanish simply as a consequence of the third law of mechanics. As in the case of the bulk forces (see, for example, §2 in Ref. 2), the surface force  $f_\mu$  can be represented by a divergence of a certain symmetric vector:

$$f_\mu = \partial \beta_{\mu\nu} / \partial x_\nu, \quad \mu, \nu=1,2.$$

Substituting in Eq. (1) and integrating by parts, we obtain

$$\int \beta_{\mu\nu} u_{\mu\nu} dS_0, \quad (2)$$

where  $u_{\mu\nu}$  are the tangential components of the usual strain tensor.

In the general case of a crystal of arbitrary shape the correction to the surface energy is also of the form given by Eq. (2), where the indices  $\mu$  and  $\nu$  for each point on the surface correspond to a coordinate system in a tangential plane. Thus, the surface energy of a deformed crystal is given by

$$\int (\alpha + \beta_{\mu\nu} u_{\mu\nu}) dS_0; \quad (3)$$

here,  $\alpha$  is the surface energy density of an undeformed crystal. It is natural to call  $\beta_{\mu\nu}$  the surface stress tensor. It is important to note that, in general, all the components of this tensor differ from zero and have the same order of magnitude as  $\alpha$ . In the case of a surface which have a symmetry axis higher than twofold, we have  $\beta_{\mu\nu} = \beta \delta_{\mu\nu}$ , where  $\beta$  is the surface tensor coefficient. In the case of a liquid, the quantity  $\beta$  is identical with the surface energy  $\alpha$  (Ref. 1) and Eq. (3) has the usual form

$$\int \alpha (1 + u_{\mu\mu}) dS_0 = \int \alpha dS.$$

We shall regard as undeformed such a homogeneous state of a crystal which corresponds to an external pressure  $p$  in the absence of the capillary effects. Thus, the strains in a crystal are governed entirely by the surface stress tensor. The conditions for a mechanical equilibrium on the surface reduce to vanishing of the sum of the bulk and surface forces:

$$\begin{aligned} \sigma_{nn} + \beta_{11}/R_1 + \beta_{22}/R_2 + p &= 0, \\ \sigma_{\mu n} &= \frac{1}{R_1} \frac{\partial \beta_{\mu 1}}{\partial \varphi_1} + \frac{1}{R_2} \frac{\partial \beta_{\mu 2}}{\partial \varphi_2}, \end{aligned} \quad (4)$$

where  $\sigma_{ik}$  is the stress tensor;  $n$  is the index of the normal to the surface;  $R_1$  and  $R_2$  are the principal radii of curvature;  $\varphi_1$  and  $\varphi_2$  are the angles measured in the planes of the principal normal cross sections. It is interesting to note that the pressure in an isotropic

solid can be higher or lower than the external pressure.

It follows from the system (4) that there are always inhomogeneous stresses in a crystal which is in mechanical equilibrium with a liquid. This is also true of a phase equilibrium. The corresponding condition<sup>1</sup> (see also Ref. 3) is now

$$F_0 + p + \left( \alpha + \frac{\partial^2 \alpha}{\partial \varphi_1^2} \right) \frac{1}{R_1} + \left( \alpha + \frac{\partial^2 \alpha}{\partial \varphi_2^2} \right) \frac{1}{R_2} = \frac{\mu}{v_0}, \quad (5)$$

where  $F_0$  is the free energy per unit volume of an undeformed crystal;  $v_0$  is the atomic volume of such a crystal;  $\mu$  is the chemical potential of the liquid. The stresses given by Eq. (4) should strictly occur also in the condition for a phase equilibrium but only in the next approximation with respect to  $1/R$ . In this connection it is essential to stress that all the relationships given above represent essentially only the principal terms of an expansion in a small parameter  $a/R$ , where  $a$  is the interatomic distance.

## 2. ELASTIC INTERACTION OF SURFACE DEFECTS

It is known (see, for example, Ref. 4) that the field of elastic strains far from a bulk point defect (which may be a vacancy, an interstice, or an impurity) can be calculated by introducing the point distribution of forces of the type

$$F_i = A_{ik} \frac{\partial}{\partial x_k} \delta(\mathbf{r}), \quad i, k=1,2,3;$$

where  $\mathbf{r}$  is a three-dimensional radius vector (it is assumed that the defect is located at the coordinate origin);  $A_{ik}$  is some symmetric tensor; the total force and the moment of forces of such a distribution vanish. It is clear that similar defects on a crystal surface should be described by the point distribution of the surface forces:

$$f_\mu = A_{\mu\nu} \frac{\partial}{\partial x_\nu} \delta(\rho), \quad \mu, \nu=1,2, \quad (6)$$

where  $\rho$  is a two-dimensional radius vector in the plane of the boundary; the defect is located at a point  $\rho=0$ ;  $A_{\mu\nu} = A_{\nu\mu}$ . If we know the field of elastic strains caused by the forces of Eq. (6) (see §8 in Ref. 2), we can easily calculate the elastic interaction energy of such defects. It is found that in the case of an isotropic solid the "isotropic" defects ( $A_{\mu\nu} = A \delta_{\mu\nu}$ ) repel in accordance with the law

$$U(\rho) = \frac{1-\sigma^2}{\pi E} \frac{A^2}{\rho^3},$$

where  $E$  is the Young modulus and  $\sigma$  is the Poisson ratio. The same result was obtained by Lau and Kohn<sup>5</sup> in a microscopic theory. In the general case of an arbitrary symmetric tensor  $A_{\mu\nu}$  we can expect repulsion or attraction governed by the same law  $U \propto \rho^{-3}$ .

Surface defects need not have zero total moment. We shall consider an elementary step (Fig. 1). We shall select a certain large-radius region around the step. At the points 1 and 2 this region is acted upon by capillary forces equal to, per unit length of the step, to the surface tension coefficient  $\beta$  (for simplicity, we shall assume that  $\beta_{\mu\nu} = \beta \delta_{\mu\nu}$ ). These forces create a moment  $\beta a$  directed along the line of the step. The quantity  $a$  is

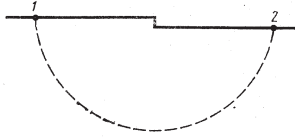


FIG. 1.

the interatomic distance in the direction along the normal to the surface, whereas the height of the step at large distances is equal to  $a$  irrespective of its short-range structure and of the structure of the surface itself.

Internal stresses should compensate this moment. We can describe them macroscopically by introducing the following linear distribution of the force normal to the surface:

$$f_n = \beta a \frac{\partial}{\partial x} \delta(x). \quad (7)$$

The  $x$  axis lies in the plane of the boundary and it is directed at right-angles to the line of the step. In addition to the distribution (7), the step—like any other line defect—has also certain linear distribution of forces of the (6) type with zero total moment:

$$f_x = f \frac{\partial}{\partial x} \delta(x). \quad (7a)$$

Using (7) and (7a), we find that the interaction of two identical steps should be repulsion in accordance with the law

$$U(x) = \frac{2(1-\sigma^2)}{\pi E} [f^2 + (\beta a)^2] \frac{1}{x^2}$$

(per unit length of the step), where  $x$  is the distance between the steps. Steps of different sign differ by the direction of the moment and, therefore, the energy of the interaction between them is

$$U(x) = \frac{2(1-\sigma^2)}{\pi E} [f^2 - (\beta a)^2] \frac{1}{x^2},$$

i.e., we can have attraction or repulsion.

Kinks in steps are point defects which have to be described by introducing a moment, in addition to the distribution (6). In this case the moment has two components in a plane perpendicular to the line of the step. The tangential component is of the same origin as the moment of the step itself, whereas the component normal to the surface is created by the forces of linear tension. The interaction energy of the kinks depends on the distance in accordance with the law  $\rho^{-3}$ , and we can have both attraction and repulsion. This should be allowed for investigations of the equilibrium shape of a crystal because attraction between identical kinks makes the surface unstable in a certain range of its orientation (compare with Ref. 6).

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<sup>2</sup>L. D. Landau and E. M. Lifshitz, *Teoriya uprugosti*, Nauka, M., 1965 (*Theory of Elasticity*, 2nd ed., Pergamon Press, Oxford, 1970).

<sup>3</sup>C. Herring, in: *Structure and Properties of Solid Surfaces* (ed. by R. Gomer and C. S. Smith), University of Chicago Press, Chicago, 1953, p. 5.

<sup>4</sup>A. M. Kosevich, *Osnovy mekhaniki kristallicheskoj reshetki* (*Fundamentals of Crystal Lattice Mechanics*), Nauka, M., 1972.

<sup>5</sup>K. H. Lau and W. Kohn, *Surf. Sci.* 65, 607 (1977).

<sup>6</sup>L. D. Landau, *Sobranie trudov* (*Collected Works*), Nauka, M., 1969, p. 119; *Sbornik posvyashchennyj semidesyatiletiju akad. A. F. Ioffe* (*Collection of Papers on the Seventieth Birthday of Academician A. F. Ioffe*), Izd. AN SSSR, M., 1950, p. 44.

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