The Surface Tension of Solids

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By R. SHUTTLEWORTH*

H. H. Wills Physical Laboratory, University of Bristol

ABSTRACT. A distinction is made between the surface Helmholtz free energy F, and the surface tension γ. The surface energy is the work necessary to form unit area of surface by a process of division : the surface tension is the tangential stress (force per unit length) in the surface layer; this stress must be balanced either by external forces or by volume stresses in the body.

The surface tension of a crystal face is related to the surface free energy by the relation

$$\gamma = F + A(dF/dA),$$

where A is the area of the surface. For a one-component liquid, surface free energy and tension are equal. For crystals the surface tension is not equal to the surface energy. The standard thermodynamic formulae of surface physics are reviewed, and it is found that the surface free energy appears in the expression for the equilibrium contact angle, and in the Kelvin expression for the excess vapour pressure of small drops, but that the surface tension appears in the expression for the difference in pressure between the two sides of a curved surface.

The surface tensions of inert-gas and alkali-halide crystals are calculated from expressions for their surface energies and are found to be negative. The surface tensions of homopolar crystals are zero if it is possible to neglect the interaction between atoms that are not nearest neighbours.

§1. FUNDAMENTAL CONCEPTS

IN the study of capillarity the two concepts of surface tension and surface free energy are used. According to Millington (1945, 1947) the concept of surface tension was introduced by Cabeo (1629) and was stated more explicitly by Segner (1751). Theories that explain the surface tensions of liquids in terms of molecular forces have been advanced by Young (1805), Laplace (1806), Poisson (1830), Worthington (1884), Bakker (1928), Brown (1947), and Prandtl (1947). The concept of surface energy is more recent and was introduced by Gauss (1830). Rayleigh (1890) has shown that for the Laplace model of a liquid the surface tension and energy are numerically equal. Dupré (1869) by a general argument has shown that for a one-component liquid the surface tension and surface free energy must be equal.

Because the surface tension and surface free energy of a one-component liquid are numerically equal the two terms have tended to become confused and are often regarded as equivalent: this is not correct. Gibbs (1876) pointed out that for a solid they are not equal, and that the value of the surface tension in a particular crystal face can vary with direction. Recently Orowan (1950) and Nicolson (1950) have discussed the surface tensions of solids in detail, and Nicolson has calculated the surface tensions of some ionic crystals from the force constants of their ions.

In this paper the surface tension and the surface Helmholtz free energy are defined, and a thermodynamic relation between them is derived. The standard

* Now at Physics Department, University of Illinois, Urbana, U.S.A.

thermodynamic formulae of surface physics are reviewed, and it is found that the surface free energy appears in the expression for the excess vapour pressure of small crystals, and in the expression for the equilibrium contact angle between liquid and solid, but that the surface tension appears in the expression for the difference in pressure between the two sides of a curved surface. Surface energy is always positive: calculation shows that the surface tensions of inert-gas and alkali-halide crystals are negative whilst for homopolar crystals, for which it is possible to neglect the interaction between atoms that are not nearest neighbours, the tension is zero.

(i) *Surface Free Energy*

Consider a large one-component crystal in equilibrium with its vapour in a constant volume enclosure that is maintained at a constant temperature. If this crystal is divided into two parts by a plane whose indices are p and the two parts are then separated, the Helmholtz free energy of the system increases by an amount $A_p F_p$, where A_p is the increase in surface area, and F_p is defined as the surface Helmholtz free energy per unit area. During this process there will be no change in the number of atoms in each of the two phases, and if the separation is made by a reversible process the external work that is needed will equal the increase in the total free energy of the system.

When a crystal is large compared with atomic dimensions it is possible to neglect the edge and corner energies, and the total free energy of a system consisting of a crystal in equilibrium with its vapour is $N_1 F_1 + N_2 F_2 + \Sigma A_p F_p$, where N_1 and N_2 are respectively the number of moles in the crystal and the vapour ($N_1 + N_2$ is the total number of moles in the system), F_1 and F_2 are the free energies per mole of the crystal and vapour phases, and the summation is over all the crystal faces. The surface free energy is only a small correction to the total free energy of the system. For an isotropic material with a curved surface the surface free energy per unit area will be supposed independent of the curvature of the surface, in analogy with the neglect of the edge and corner energies of a crystal.

Although the densities of the two phases near the surface will vary from their value in the interior, the differences in density are small and occur only within a few interatomic distances of the surface, so that they may be neglected and N_1 and N_2 calculated from the volume of the phases on the assumption of constant density.

The surface free energy F_p will be a function of the volume strain of the crystal (e.g. strains produced by hydrostatic pressure). The free energy of the vapour F_2 will vary with the vapour pressure, and since the equilibrium vapour pressure of small crystals is greater than that of large crystals, F_2 will depend on crystal size. The free energy of the solid F_1 will vary with the volume strain in the crystal, and since the surface tension induces volume strains in the crystal (see (ii) below) F_1 will also depend upon crystal size. The variation of F_1 and F_2 is important only for small crystals.

Calculations of the surface energies of inert-gas and ionic crystals on the model of central forces between the atoms have been made by Shuttleworth (1949, to be referred to as I). Attempts to measure the surface free energy of mica were made by Obreimoff (1930) and Orowan (1933) based on the fact that mica can be split reversibly. A thin sheet of mica was partially split from a

thicker piece by means of a wedge and the distance between the wedge and the line of bifurcation measured. For a constant height of the wedge the spreading of the crack reduced the elastic energy of the thin mica sheet but increased the surface free energy; the equilibrium depth occurred when the sum of the two energies was a minimum.

(ii) *Surface Tension*

A direct conclusion from the elementary experiments of capillarity is that a liquid surface is in a state of plane stress—this point has been emphasized by Brown (1947). The stress in a liquid surface is known as the surface tension; in the present paper an attempt is made to widen the concept so that it can be applied to crystal faces.

The surface stress is defined analogously to stress in elasticity. Suppose a cut is made perpendicular to the surface of a body and extending only a short distance into it; then in order that the surface remain in equilibrium and no additional stresses occur in the volume of the crystal, it is necessary to apply external forces to atoms near the surface of the cut. Equal and opposite forces, which are in the plane of the surface, must be applied to the atoms on the two sides of the cut; the total force per unit length of cut is the surface stress that
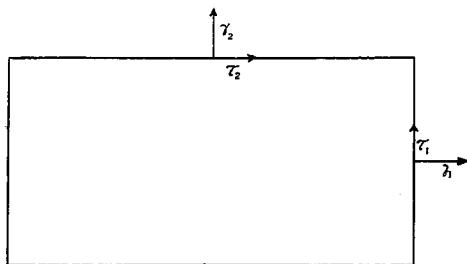
existed across the line of the cut. These forces, which are over and above any due to a volume stress, need only be applied to atoms that are within a few atomic distances of the surface. Because two new surfaces have been created to form the cut, it is also necessary to apply forces that are perpendicular to the old surface in order to preserve the equilibrium of the atoms, but the sums of these forces on the atoms on each side of the cut are zero and so do not affect the definition of the surface stress. This surface stress can be balanced either by external forces, e.g. the forces that must be applied to the edges of a plane soap film, or by a volume stress in the material below the surface, e.g. the hydrostatic pressure inside a drop. When the surface stress is balanced by external forces some rearrangement will occur of those atoms that are within a few atomic distances of the point of application of the force, but the surface stress is regarded as a macroscopic concept and this local rearrangement does not affect the definition.

In an isotropic material, such as a liquid, the surface stress is perpendicular to every line in the surface. In a crystal face the surface stress will in general have a shear component; the Figure shows the forces per unit length on an arbitrary rectangle in a crystal face. The condition that there should be no resultant couple rotating the rectangle is that the shear components τ_1 and τ_2

should be equal (cf. elasticity theory). Thus, in general, three numbers are sufficient to specify the surface stress at a point: the normal components γ_1 and γ_2 across two perpendicular directions and the shear components τ parallel to these directions.

When the stresses across two directions in a crystal face are known, the stress across a third direction can be obtained by considering the mechanical equilibrium of a triangle in the face with sides parallel to the three directions. It is then readily shown (see, for example, Timoshenko 1934) that it is always possible to find two perpendicular directions across which the shear stresses are zero. These two directions and the normal stress components across them are referred to as the principal directions and the principal stresses. If there is a line of reflection symmetry in a crystal face the shear component across this line must be zero and therefore this will be one of the principal directions. From the expression for the stress across any arbitrary line it can be shown that the sum of the normal stress components in any two perpendicular directions is equal to the sum of the two principal stresses (see also §3). The surface tension γ in a crystal face will be defined as half the sum of the two principal stresses, in analogy with elasticity where a third of the sum of the three principal stresses is defined as the hydrostatic pressure. The sign convention followed is in opposition to that for elasticity, and a tension stress will be taken as positive.

Since the surface stress must have at least the symmetry of the crystal face, one number (the surface tension) is sufficient to specify it when the face has a three-fold (or greater) axis of rotational symmetry. Then the normal stress components across all lines in the face are equal and all shear stresses are zero, so that the normal stress components are equal to the surface tension. This can be seen by considering any equilateral triangle in a face which has a three-fold axis of symmetry: by symmetry the stresses on each side must be equal and, since there must be no resultant couple to rotate the triangle, the stresses must be perpendicular to the sides (the same conclusion is reached for a four- or six-fold axis of symmetry by considering any square or regular hexagon in the surface). Now when the stresses across two directions in a crystal face are known the stress across any third direction is obtained from the equilibrium of a triangle whose sides are parallel to these three directions. Since the forces on two sides of this triangle are perpendicular to the sides and proportional to their length, the triangle of forces coincides with the triangle and the force on the third side is also perpendicular and proportional to its length. Hence the normal stress component is the same on all sides and the shear stresses are zero.

In a face-centred-cubic crystal the {111}, {100} and {110} faces have respectively six-, four- and two-fold axes of symmetry. The shear component of the surface stress will therefore be zero for the {111} and {100} faces, but not for the {110} faces.

A direct explanation of the surface tension of a liquid in terms of intermolecular forces is somewhat difficult. The conventional explanations (see, for example, Brown 1947) are based on the fact that the separations between the layers of atoms at the surface of a homopolar substance are greater than in the volume of the material (I). It is postulated that even in the surface layers the arrangement of the molecules of a liquid is isotropic, so that there is a corresponding increase in the separation of the atoms in directions parallel to the surface. This decrease in the density of molecules near the surface is equivalent to a negative pressure parallel to the surface; this negative pressure is identified as the surface tension.

A more immediate explanation of the origin of surface tension is possible for a crystal; for simplicity a crystal at $0°$ K. will be considered, and the forces between any two atoms will be supposed to depend only on their separation. If it is not possible to neglect the interaction between atoms that are not nearest neighbours, then the equilibrium separation of atoms in an isolated plane will be different from that in a three-dimensional lattice, since the number of non-nearest-neighbour atoms will be different in the two cases. The lattice constant of an isolated (100) plane of atoms of an inert-gas crystal is $0·643\%$ greater than that of the three dimensional crystal *. Lennard-Jones and Dent (1928) have shown that the lattice constant of an isolated (100) plane of ions of an alkali-halide crystal is about 5% less than that of the three-dimensional crystal. In order that an isolated plane should have the same spacing as that of the crystal it is necessary to apply external forces to the edges of the plane and tangential to it: the forces are compression for inert-gas crystals and tension for alkali-halide crystals. If the stressed plane is now moved towards the crystal, until it becomes the surface plane, the external forces needed to keep it with the three-dimensional lattice constant will be reduced. When all the atoms are on the positions they would occupy if no surface existed and they were in the centre of the crystal, then the tangential force it is necessary to apply to the surface plane is reduced to half of that which must be applied to an isolated plane. This state is not stable, for in equilibrium the distance between the outermost plane of atoms and the next is different from that in the centre of the crystal (I); when the surface plane takes up its equilibrium position this movement causes a further change in the tangential force which must be applied.

Similar, but smaller, tangential forces must be applied to successive planes in the crystal surface. The surface tension is the total force per unit length that must be applied tangentially to the surface in order that the surface planes have the same lattice spacing as the underlying crystal.

It is possible that the energy of a crystal face would be reduced if, instead of the surface atoms being uniformly strained so as to fit the underlying lattice, faults such as dislocations occurred periodically; this would also change the surface stress. However, Frank and van der Merwe (1949) have shown that dislocations do not occur spontaneously in the surfaces of inert-gas crystals.

In a complete treatment it would also be necessary to consider the difference in the thermal vibrations of the surface and interior atoms.

Nicolson (1950) has measured the surface tension of sodium chloride and magnesium oxide crystals. By means of x-ray diffraction he measured the change in lattice constant which the surface tension causes in small crystals that have {100} faces. Although the surface tension induces non-uniform stresses in cubes, he makes the approximation that the change in lattice constant is the same as would occur in an isotropic sphere. From equations (4) and (5) of § 3,

$$\Delta R_1/R_1 = -2\beta\gamma/3R_1, \qquad \ldots \ldots (1)$$

where $2R_1$ is now the cube edge and β is the compressibility. The reduction in linear dimensions of the cube, $-\Delta R_1$, is independent of R_1, $\Delta R_1/R_1$ is strain which is measured by x-rays. He obtains positive values for the surface tension.

Udin, Shaler, and Wulff (1949) find that when copper is heated to near its melting point it behaves as a viscous fluid; a thin wire, radius R_1, shortens

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* The lattice sums of an isolated (100) plane of an inert-gas crystal are $_2A_6''=0·5823$; $_2A_{12}''=0·06350$ (see I for their method of calculation).

because of the surface tension forces. They balance this force of contraction by means of weight hung at the end of the wire; when the strain rate is zero the weight downwards is equal to the surface forces $\pi R_1 \gamma$ upwards. They obtain a positive value (1,400 dyne/cm.) for the surface tension of solid copper. Since an infinitesimal stress causes plastic deformation the surface tension and surface free energy will be equal.

§2. THE RELATION BETWEEN SURFACE ENERGY AND SURFACE TENSION

A relation between the surface free energy and the surface tension of a crystal face can be obtained by an application of the principle of virtual work. Consider a crystal in which the surface tension is balanced entirely by external forces. If these are the only external forces that are applied to the crystal there will be neither stress nor strain in the volume of the crystal and any infinitesimal distortion will cause no change in the volume energy of the crystal; the work done by the external forces will be equal to the increase of surface energy. Suppose the crystal is deformed so that a square, of area A, in the crystal face is deformed into a rectangle whose sides are parallel to the square. An amount of work $\gamma_1 \, dA_1 + \gamma_2 \, dA_2$ must be done against the surface stress, where γ_1 and γ_2 are the components of the surface stress perpendicular to the sides of the square, and dA_1 and dA_2 are the increases in area in these two directions (for this kind of deformation no work is done against any shear component of the surface stress). Provided the deformation is reversible and occurs at constant temperature, the additional work is equal to the increase in the surface free energy of the square

$$\gamma_1 \, dA_1 + \gamma_2 \, dA_2 = d(AF). \qquad \ldots \ldots (2)$$

For an isotropic substance, or for a crystal face with a three- (or greater) fold axis of symmetry, all normal components of the surface stress equal the surface tension and equation (2) reduces to

$$\gamma = d(AF)/dA = F + A(dF/dA), \qquad \ldots \ldots (3)$$

where dA is the total increase in area. For such faces no work is necessary to change the shape of the surface if there is no change in area, since the shear components of the surface stress are zero; equation (3) is therefore true no matter what the manner of deformation of the surface. If the crystal face has not such high symmetry suppose it to be deformed by an equal stretch in all directions, $dA_1 = dA_2 = \frac{1}{2} \, dA$, so that for this particular kind of deformation equation (3) is still true since $\gamma = (\gamma_1 + \gamma_2)/2$.* The surface tension of any crystal face may therefore be defined as the work necessary to increase the area by unit amount by means of a reversible process of stretching which is the same in all directions. This work is additional to any which may be necessary to deform the volume of the crystal—if the initial volume strain in a crystal is not zero, work is necessary to deform the volume by even an infinitesimal amount.

In a solid, at least at low temperatures, the atoms are not mobile and after any deformation they preserve their relative positions: the total number of atoms in the surface remains constant and their separation changes. Then F is a function of area, the term dF/dA of equation (3) is not zero, and the surface tension and energy are not equal. As will be shown below, the terms F and $-A(dF/dA)$ are of the same magnitude.

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* This proves the invariance of the sum of the normal stress components on any two perpendicular lines, since $d(AF)$ does not depend upon the orientation of the square.

In order to derive a value of dF/dA for a one-component liquid it is convenient to consider a deformation in which the increase of surface area is brought about by a change of the shape of the liquid without a change of volume.   The molecules of a liquid are mobile, and in this deformation some are transferred from the centre of the liquid to form the new surface.   Since there is no change of volume stress the configuration of the molecules at the surface is not changed.   Thus F is not a function of area, dF/dA is zero and the surface energy is equal to the surface tension.   This argument is a generalization of Dupré's who considered the work necessary to extend a film of liquid.

If a new surface is suddenly produced in a viscous liquid (say, by the rapid extension of a filament, or by a fracture) then the surface energy and tension will not be equal, but will become equal as rearrangement of molecules between the surface and interior occurs.   The time for rearrangement will be greater the greater the viscosity.   In the calculation of the rate of deformation of a viscous liquid by surface forces, it is only permissible to assume that surface energy and tension are equal when it can be shown that rearrangement of the molecules at the surface occurs much more rapidly than does the relaxation of the shear stress in the interior of the liquid.

Although surface tension and surface energy have the same physical dimensions, the convention of expressing surface tension in units of dyne/cm., and the surface energy in units of erg/cm², will be followed.

§3. THE THERMODYNAMICS OF SURFACES

(i) *Difference of Pressure between the two Sides of a Curved Surface*

When a surface has zero curvature the surface tension can be balanced by external forces applied at the periphery parallel to the surface.   If, however, the surface is curved it is also necessary to apply normal pressures to each point of the surface.   For an isotropic material, Δp the normal pressure at a point is readily calculable in terms of the radii of curvature at that point.

Consider the mechanical equilibrium of an infinitesimal curvilinear square, of side δ, drawn in the surface.   Parallel sides of the square have the same curvature. The surface tension forces that act on the two pairs of sides of the square have components $\gamma\delta^2/R_1$ and $\gamma\delta^2/R_2$ parallel to the line drawn normal to the surface at the centre of the square; R_1 and R_2 are the radii of curvature of perpendicular sides.   The components of the surface tension that act perpendicular to the normal are equal and opposite on parallel sides.   The normal component of the pressure on the element of surface is $\Delta p\delta^2$; for equilibrium of the surface

$$\Delta p = \gamma(1/R_1 + 1/R_2). \qquad \ldots \ldots (4)$$

In the derivation of this formula it has been implicitly assumed that the radii of curvature are large compared with the depth to which the surface stress extends. Many textbooks obtain a similar formula, in which F replaces γ, by a method of virtual work, but they implicitly assume that dF/dA is zero.

The surface of a drop has no periphery and for equilibrium of the surface it is sufficient to apply a normal pressure Δp.   In a spherical drop this normal pressure can be produced by a uniform volume dilatation

$$\Delta V/V_0 = 3\Delta R_1/R_1 = -\beta\Delta p, \qquad \ldots \ldots (5)$$

where β is the compressibility.

(ii) *Vapour Pressure of Small Crystals*

Because of the greater proportion of surface to volume the total free energy per mole of small crystals is greater than that of large crystals and, if in the same enclosure, they evaporate and condense on the large crystals. Thomson (1871) considered the equilibrium of a liquid in a capillary tube and derived an expression that connects the vapour pressure, surface tension, and the curvature of a surface; this proof is not appropriate to a solid as it depends on the fact that the shear stress in the liquid must be zero. The same expression can be derived (see, for example, Guggenheim 1933) if it is supposed that in equilibrium the chemical potentials of the liquid inside and the vapour outside a drop are equal; Gibbs (1876) has shown that this is not true for a solid. Helmholtz (1886) derives a similar expression in which the surface free energy appears instead of the surface tension; he neglects the effect of the compression of the liquid by the surface tension. Helmholtz's proof can be modified to apply to crystals.

Wulff (1901) and Wells (1946) have pointed out that the vapour pressure of a crystal depends on shape as well as size. The condition that the total surface energy, $\Sigma A_p F_p$, is a minimum predicts an equilibrium shape for the crystal. For this shape the vapour pressures of all those faces that appear are equal. If the surface energies of all crystal faces are nearly equal, large numbers of faces will appear in equilibrium and the shape will be approximately spherical. If, however, a particular face has a much lower surface energy than any other, only faces of this form will occur in the equilibrium shape, although the surface area will be larger than that of a sphere. A thermodynamic treatment is appropriate only to crystals of the equilibrium shape.

Consider a one-component crystal in equilibrium with its vapour in a constant volume enclosure. When the surface tensions in the crystal faces are produced by external forces there is no volume strain in the crystal and the free energy of the whole system is $N_1 F_1 + N_2 F_2 + \Sigma A_p F_p$ where N_1 and N_2 are the number of moles in the crystal and the vapour, and F_1 and F_2 are the free energies per mole of the unstrained crystal and the vapour. If the external forces are reduced to zero, the surface tensions are then balanced by elastic strains in the crystal. The energy of the system decreases by an amount equal to the work done against the external forces as they reversibly decrease to zero; the net decrease arises from a decrease in surface energy and an increase in volume strain energy. An accurate estimate of this decrease can be made only for an isotropic spherical drop, for which the external forces are equivalent to an excess hydrostatic pressure Δp; from equation (5) the decrease is seen to be

$$\int_{\Delta p = 2\gamma/R_1}^{\Delta p = 0} \Delta p \, dV = -\tfrac{4}{3}\beta\pi R_1^3 \int_{2\gamma/R_1}^{0} \Delta p \, d(\Delta p) = \tfrac{8}{3}\pi\beta\gamma^2 R_1. \quad \ldots \ldots (6)$$

The total free energy of the system then becomes

$$N_1 F_1 + N_2 F_2 + AF - \tfrac{8}{3}\pi\beta\gamma^2 R_1. \qquad \ldots \ldots (7)$$

Here, for simplicity, it is supposed that only crystal faces of one form occur; F is the surface free energy, γ is the surface tension, R_1 is the distance of a crystal face from the centre of symmetry.

When the crystal is in equilibrium with the vapour the change of free energy on the transfer of dN moles from crystal to vapour is zero. The corresponding decreases in volume, area, and radius of the crystals are

$$dV = M \, dN/w; \quad dA = 2 \, dV/R_1; \quad dR_1 \simeq dV/4\pi R_1^2, \quad \ldots \ldots (8)$$

30-2

where w is the density of the crystal, and M is the molecular weight of the vapour. By equations (7) and (8) the equilibrium condition becomes

$$F_1 w/M + 2F/R_1 - 2\beta\gamma^2/3R_1{}^2 = w(RT \ln p)/M. \qquad \dots\dots (9)$$

The vapour is assumed to be a perfect gas, so that F_2, the free energy per mole, is $RT \ln p$ +terms that depend only on temperature, where T is the temperature and p is the pressure of the vapour. The ratio of the vapour pressure of a crystal with equivalent radius R_1 to that of an infinite crystal at the same temperature, is found by subtracting the corresponding equation from (9)

$$\frac{p}{p_\infty} = \exp \frac{2}{RT}\frac{M}{w}\left(1 - \frac{\beta\gamma}{3R_1}\frac{\gamma}{F}\right)\frac{F}{R_1}. \qquad \dots\dots (10)$$

When the compressibility or the surface tension is small this reduces to Thomson's expression; even for the smallest crystals the correction will never be more than a few per cent.

(iii) *Contact Angle*

When three liquid surfaces meet at a line, the condition of equilibrium is that the particles that form the line should be in equilibrium when acted on by the three surface tensions—Neumann's triangle. It is clear that Neumann's triangle is still appropriate when there are different pressures in each of the three liquids; and hydrostatic stresses are the only stresses that can occur in stationary liquids.

This argument cannot be used to calculate the contact angle between liquid, solid, and vapour, because the solid can support a shear stress and this stress contributes to the equilibrium of the particles at the line of contact. Thus a sheet of stretched rubber, whose edge is fastened to the solid, can be in equilibrium at any angle. If, however, the solid is assumed undeformable and the liquid incompressible, the contact angle can be calculated in terms of the three interfacial free energies. Then the equilibrium contact angle occurs when an infinitesimal displacement of the line of contact along the solid causes no change in energy of the system. This (see, for example, Shuttleworth and Bailey 1948) leads to the expression

$$F_{\mathrm{SV}} = F_{\mathrm{SL}} + F_{\mathrm{LV}} \cos\theta, \qquad \dots\dots (11)$$

where θ is the equilibrium contact angle the liquid makes with the solid and F_{SV}, F_{SL} and F_{LV} are the surface energies of the three interfaces.

§4. THE SURFACE TENSION OF INERT-GAS CRYSTALS

In I the surface energies of inert-gas crystals at $0°$ K. were calculated on the assumption that the forces between any two atoms depended only on their separation. The potential between two atoms at a distance r apart was supposed to have the simple form

$$\epsilon(r) = \lambda r^{-s} - \mu r^{-t} \qquad s > t, \qquad \dots\dots (12)$$

where the first term represents the short-range repulsive forces and the second term the longer-range attractive forces. U, the surface energy at $0°$ K., is entirely potential and for purposes of calculation was divided into two parts U' and U''; U' is the surface energy of a crystal face before any rearrangement of the surface atoms occurs, and while they occupy the same relative positions as they did when

at the centre of the crystal. When the stress perpendicular to the surface is relieved by movement of the surface atoms in this direction, the surface energy decreases by an amount U'':

$$U = U' - U''. \qquad \ldots \ldots (13)$$

For a (100) face of an inert-gas crystal the surface plane of atoms are separated from the next by a distance 2.54% greater than normal, and this makes U'' about 1% of U'. Inert-gas crystals are face-centred-cubic and U' and U'' are given by

$$U_p' = \{-B_s''\lambda a^{-s} + B_t''\mu a^{-t}\}/2\omega_p a^2, \qquad \ldots \ldots (14)$$

$$U_p'' = \{\Delta C_s''\lambda a^{-s} - \Delta C_t''\mu a^{-t}\}/\omega_p a^2, \qquad \ldots \ldots (15)$$

where $2a$ is the lattice constant, $1/\omega_p a^2$ is the number of atoms per unit area in the surface plane, B_s'', B_t'', $\Delta C_s''$ and $\Delta C_t''$ are lattice sums whose values depend on the crystal face. Equations (14) and (15) are appropriate even when $2a$ is not the equilibrium lattice constant, provided the lattice has been distorted by a uniform dilatation. During uniform dilatation each face is stretched uniformly and its area is proportional to a^2. For such a distortion equation (3) enables the surface tension of a face at $0°$ K., γ_0, to be calculated from the surface energy:

$$\gamma_0 = \frac{d(AU)}{dA} = \frac{1}{2a}\frac{d(a^2U')}{da} - \frac{1}{2a}\frac{d(a^2U'')}{da}, \qquad \ldots \ldots (16)$$

$$\gamma_0 = \gamma_0' - \gamma_0''. \qquad \ldots \ldots (17)$$

From equations (14), (15), (16), and (17)

$$\gamma_0' = \{\tfrac{1}{2}sB_s''\lambda a_0^{-s} - \tfrac{1}{2}tB_t''\mu a_0^{-t}\}/2\omega a^2_0, \qquad \ldots \ldots (18)$$

$$\gamma_0'' = -\{s\Delta C_s''\lambda a_0^{-s} - t\Delta C_t''\mu a_0^{-t}\}/2\omega a_0^2, \qquad \ldots \ldots (19)$$

where $2a_0$ is the equilibrium lattice constant when the external pressure is zero; it is remembered (I) that $\Delta C_s''$ and $\Delta C_t''$ were derived from the condition

$$\left\{\frac{d(\Delta C_s'')}{da}\lambda a_0^{-s} - \frac{d(\Delta C_t'')}{da}\mu a_0^{-t}\right\}\frac{da}{dc} = 0, \qquad \ldots \ldots (20)$$

where ca_0 is the distances of the surface plane of atoms from the plane below. The heat of sublimation per atom of a crystal at $0°$ K. is

$$\epsilon = \{-A_s''\lambda a^{-s} + A_t''\mu a^{-t}\}/2, \qquad \ldots \ldots (21)$$

where A_s'' and A_t'' are lattice sums. When the crystal is unstrained ϵ is a minimum with respect to the variation of a at the value $a = a_0$, and

$$sA_s''\lambda a_0^{-s} = tA_t''\mu a_0^{-t}. \qquad \ldots \ldots (22)$$

When λa_0^{-s} and μa_0^{-t} are eliminated from equations (18) and (19) by equations (21) and (22)

$$\gamma_0' = +\frac{st}{s-t}\frac{B_s''/A_s'' - B_t''/A_t''}{2\omega}\frac{\epsilon_0}{a_0^2} = G'(s,t)\frac{\epsilon_0}{a_0^2}, \qquad \ldots \ldots (23)$$

$$\gamma_0'' = -\frac{st}{s-t}\frac{2\Delta C_s''/A_s'' - 2\Delta C_t''/A_t''}{2\omega}\frac{\epsilon_0}{a_0^2} = G''(s,t)\frac{\epsilon_0}{a_0^2}. \qquad \ldots \ldots (24)$$

The attractive forces between inert-gas atoms are of van der Waals type for which $t = 6$. In Table 1, $G'(s, 6)$ is given for {111}, {100}, {110} faces and for values of s between 7 and infinity. Values of $B_s{}''$ and $A_s{}''$ for a range of s are given respectively in (1), and by Lennard-Jones and Ingham (1925). The tension γ_0' is negative in homopolar crystals and increases towards zero with increase in s (increase in hardness of the atoms).

The computation of $\Delta C_s{}''$ and $\Delta C_t{}''$ has been made (I) only for a (100) face for $s = 12$, $t = 6$; these values give $G''(12, 6) = -0.146$. For the {100} faces of such a crystal

$$\gamma_0' = -0.170\epsilon_0/a_0{}^2; \quad \gamma_0'' = -0.146\epsilon_0/a_0{}^2; \quad \gamma_0 = -0.024\epsilon_0/a_0{}^2. \quad \ldots\ldots(25)$$

The surface distortion makes a large and positive contribution to the surface tension. Values of γ_0', γ_0'' and γ_0, for neon, argon, krypton, and xenon crystals were calculated from equation (25) and are given in Table 2; the surface energy of a (100) face at $0°$ K. is included for comparison.

Table 1.   Variation of $G'(s, 6)$ with Crystal Face and 'Hardness' of the Atoms

s	7	8	9	10	11	12	∞
{111}	-0.382	-0.315	-0.273	-0.245	-0.225	-0.209	-0.110
{100}	-0.339	-0.272	-0.231	-0.204	-0.185	-0.170	-0.087
{110}	-0.332	-0.268	-0.229	-0.203	-0.184	-0.171	-0.088

Table 2.   The Surface Tensions of the (100) Faces of Inert-Gas Crystals

	ϵ_0 (10^{-14} erg/atom)	a_0 (A.)	γ_0' (dyne/cm.)	γ_0'' (dyne/cm.)	γ_0 (dyne/cm.)	U (erg/cm^2)
Ne	4·08	2·26	$-13\cdot6$	$-11\cdot7$	$-1\cdot9$	17·9
A	13·89	2·70	$-32\cdot4$	$-27\cdot8$	$-4\cdot6$	42·7
Kr	19·23	2·79	$-42\cdot0$	$-36\cdot1$	$-5\cdot9$	55·3
Xe	26·87	3·09	$-47\cdot8$	$-41\cdot1$	$-6\cdot7$	63·0

From equation (2) the compressibility of a crystal at $0°$ K. is seen to be

$$\frac{1}{\beta_0} = V_0 \left(\frac{d^2E}{dV^2}\right)_{V_0}, \quad\quad \ldots\ldots(26)$$

where E is the energy of a crystal volume V. For a face-centred-cubic crystal the volume and energy per atom are $2a^3$ and $-\epsilon$,

$$\frac{1}{\beta_0} = -\frac{1}{18a_0}\left(\frac{d^2\epsilon}{da^2}\right)_{a_0}. \quad\quad \ldots\ldots(27)$$

For inert-gas crystals, from equation (21),

$$1/\beta_0 = \{s(s+1)A_s{}''\lambda a_0{}^{-s} - t(t+1)A_t{}''\mu a_0{}^{-t}\}/36a_0{}^3. \quad\quad \ldots\ldots(28)$$

The proportional change in lattice constant of an isotropic sphere due to a tension in the surface is given by equation (1). For a crystal whose faces are all of the same form an approximate value of the lattice change is obtained by using the equivalent radius of the crystal. From equations (1), (17), (18), (19), (22) and (28)

$$\frac{\Delta R_1}{R_1} = \frac{6}{\omega(s-t)}\left\{\frac{B_t{}''+2\Delta C_t{}''}{A_t{}''} - \frac{B_s{}''+2\Delta C_s{}''}{A_s{}''}\right\}\frac{a_0}{R_1} \quad\quad \ldots\ldots(29)$$

and from equations (23) and (24)

$$\frac{\Delta R_1}{R_1} = -\frac{12(G'-G'')}{st}\frac{a_0}{R_1}. \quad\quad \ldots\ldots(30)$$

As s and t increase, the dilatation caused by the surface tension tends to zero more quickly than does the tension. When the values $G'(6, 12)$ and $G''(6, 12)$ for a (100) face are used, the proportional increase in lattice constant is $\Delta R_1/R_1 = 0.004a_0/R_1$; this is too small to be detected by x-rays, even in the smallest crystals. The increase in radius due to the volume dilatation is much smaller than the increase due to surface distortion ($0.0254a_0$).

In a homopolar crystal in which it is possible to neglect the forces between atoms that are not nearest neighbours, all components of the surface stress are zero at zero temperature and pressure. This is because in such a crystal the attractive and repulsive forces between nearest neighbour atoms are equal and opposite, so that the net force between all pairs of atoms in the lattice is zero. It is, therefore, not necessary to apply external forces in order that the surface atoms remain in the same relative positions as they had in the centre of the crystal. That γ_0' is zero is also clear from equation (23) for, when only nearest neighbour interaction is considered, B_s''/A_s'' equals B_t''/A_t''. If, however, the simple model of central forces between the atoms is not adequate, and account must be taken of the electronic distortion of the surface atoms, then γ_0'' will not be zero (Gurney 1947).

§5. THE SURFACE TENSION OF ALKALI-HALIDE CRYSTALS

In crystals of the alkali-halides the alkali and halide ions are arranged on alternate points of a simple-cubic lattice. The interatomic forces are: electrostatic, dipole–dipole, dipole–quadrupole and short range repulsive forces. Mayer (1933), and Huggins and Mayer (1933) give numerical values for the force constants. In (I) it was shown that U', the surface energy of an undistorted face at $0°$ K., can be written

$$U' = \{2B_e'''e^2a^{-1} + [B_6''(c_{++}+c_{--}) + 2B_6'c_{+-}]a^{-6} + [B_8''(d_{++}+d_{--}) + 2B_8' d_{+-}]a^{-8} - N''(1.25b_+^2 + 0.75b_-^2)\exp(-\sqrt{2}a/\rho) - 2N'b_+b_-\exp(-a/\rho)\}/2\omega a^2,$$

$$\ldots\ldots (31)$$

where a is the distance between adjacent alkali and halide ions. B and N are lattice sums given in I; c, b, d and ρ are the force constants. From equation (16)

$$\gamma_0' = -\{B_e'''e^2a_0^{-1} + 3[B_6''(c_{++}+c_{--}) + 2B_6'c_{+-}]a_0^{-6}$$
$$+ 4[B_8''(d_{++}+d_{--}) + 2B_8' d_{+-}]a_0^{-8} - (a_0/\sqrt{2}\rho)N''(1.25b_+^2 + 0.75b_-^2)$$
$$\times \exp(-\sqrt{2}a_0/\rho) - (a_0/\rho)N'b_+b_-^2\exp(-a_0/\rho)\}/2\omega a_0^2. \quad\ldots\ldots (32)$$

In Table 3 are given $_{100}\gamma_0'$ and $_{110}\gamma_0'$ the surface tensions of the {100} and {110} faces when there is no surface distortion; and the contributions of the various interatomic forces to $_{100}\gamma_0'$.

Table 3. The Contributions of the Various Forces to $_{100}\gamma_0'$ (dyne/cm.)

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI
Electrostatic	−309·0	−172·8	−144·9	−113·9	−198·3	−125·2	−107·9	−87·9
Dipole–dipole	−248·3	−238·7	−233·6	−228·5	−252·3	−209·3	−194·9	−181·8
Dipole–quadrupole	−35·3	−34·4	−33·4	−33·6	−33·3	−28·9	−26·4	−25·0
Repulsive	−1806·9	1087·3	946·0	794·6	1203·2	767·4	669·7	563·6
Total $_{100}\gamma_0'$	1214	641	534	419	719	404	341	269
$_{110}\gamma_0'$	1443	776	646	505	884	521	442	354

Dent (1929) has given numerical values of the contributions of the various forces to $_{100}\gamma_0''$ for sodium and potassium halides. Although her force constants are not the same as those used in this paper, her values have been used to calculate $_{100}\gamma_0''$ from equations (16) and (17). Since surface distortion is due almost entirely to the polarization of the surface ions in an electrostatic field that varies rapidly over their volume, the most important source of error is her assumption that the polarization of a surface ion is the same as it would be in a uniform field, whose value is equal to that at the centre of the ion. In Table 4 are given: $_{100}\gamma_0'$, $_{100}\gamma_0''$, $_{100}\gamma_0$, β (experimental) and ΔR_1 (from equation (1)) for sodium and potassium halides.

Table 4. The Surface Tensions of the {100} Crystal Faces (dyne/cm.)

	NaF	NaCl	NaBr	NaI	KF	KCl	KBr	KI
$_{100}\gamma_0'$	1214	641	534	419	719	404	341	296
$_{100}\gamma_0''$	1034	771	868	724	929	779	842	581
$_{100}\gamma_0$	180	−130	−334	−305	−210	−375	−501	−312
β (10^{-12} bar^{-1})	2·11	4·26	5·08	7·0	3·31	5·63	6·70	8·54
ΔR_1 (A.)	−0·03	0·04	0·11	0·14	0·05	0·14	0·22	0·18

Except for sodium fluoride the calculated surface tensions are negative. However, the crude model used to calculate $_{100}\gamma_0''$ may have introduced considerable errors, so that the net surface tension $_{100}\gamma_0$ is uncertain even as to sign. The values obtained for $_{100}\gamma_0'$ are in fair agreement with those of Nicolson (1950); in his calculation of $_{100}\gamma_0''$ he took account of the polarization of the surface ions, but neglected the effect of their displacement, which procedure gives values of $_{100}\gamma_0''$ only half those of Table 4. Nicolson's experimental values of $_{100}\gamma_0$ were positive.

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On the Temperature Dependence of Counter Characteristics in Self-quenching Geiger–Müller Counters

BY OM PARKASH* AND P. L. KAPUR†

* East Punjab University, Physics Department, Hoshiarpur (E. Punjab), India
† Delhi University, Physics Department, Delhi (India)

ABSTRACT. The effect of temperature on the counting rate–voltage characteristics of self-quenching Geiger–Müller counters with internal and external cathodes (in this paper denoted as counters Nos. 1 and 2) has been investigated within the temperatures ranging from 8° to 60° c.

It is found that the average counting rate remains independent of temperature (within the statistical error limits), and this constancy is better in the case of the external cathode counter than with the other. As counter No. 1 shows a greater increase in slope at higher temperatures, the rate appears to be greater at higher applied potentials. Further, it is noticed that the plateau decreases and disappears at lower temperatures in the case of counter No. 1, while counter No. 2 does not show this effect. This is partly explained by the formation of semiconducting paths between the central wire and the cathode, the discharges along which give rise to spurious counts in the case of counter No. 1, and the absence of these in the case of counter No. 2.

It is also observed that the slope of the plateau increases and the width decreases with rise of temperature in both cases, though the increase in slope is more marked with counter No. 1 than with counter No. 2. The increase in slope is probably due to the presence of a greater number of multiple discharges or spurious counts at higher-temperatures, an important point which is under study.

The investigation also brings about the advantage of the external cathode in the construction and design of G–M counters, especially when reliable observations are desired with a counter under widely changing temperature conditions.

§1. INTRODUCTION

FROM the general considerations of the theory of discharge mechanism in Geiger–Müller counters developed by Rose and Korff (1941), Ramsey (1940), and Montgomery and Montgomery (1940) we find that the counters of the internally quenched type, first introduced by Trost (1937), must show some change in their characteristics with temperature. According to this theory, the organic vapour causes quenching of the discharge by absorbing the photons,