The molecular mechanism of surface tension

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Introduction

There are often obscurities and fallacies in the teaching of surface tension at an elementary level and this is perhaps the reason why the subject is no longer fashionable. Many treatments (Shortley and Williams 1965, Nightingale 1949), present a diagram like figure 1 together with the statement that the unbalanced inward attraction on molecules in the surface layers causes the surface to be pulled in and to try to contract. Any bright pupil or student will point out that there are at least two serious difficulties with this explanation. First, the situation depicted is mechanically impossible if, as is often implied, it is supposed to represent statical equilibrium. Second, and more important, an inward attraction on surface molecules does not explain the tension *parallel to the surface* which is invoked in the usual explanations of simple
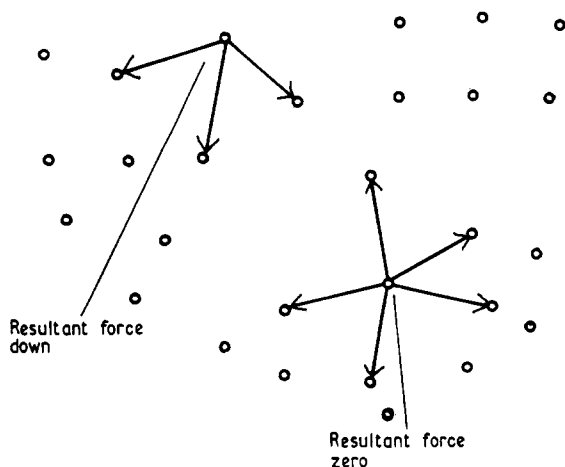

Figure 1   Diagram sometimes found in elementary texts purporting to explain surface tension.

phenomena involving bubbles, liquid in capillary tubes, etc.

Similar difficulties arise in trying to account for the existence of an angle of contact, θ, between liquid and solid surfaces in the presence of a gas. The offending diagram is shown as figure 2 (Starling and Woodall 1958, Nelkon and Parker 1968). Three forces are shown; they are the surface tensions γ_L, γ_s and γ_{LS} of the liquid/air, solid/air, and solid/liquid interfaces. However, it is not often made clear what the matter is on which these three forces act (is it a single molecule in the line of contact at A, a small mass of liquid and solid at A, or what?). Further, it is obvious that the three forces are not in statical equilibrium, and if figure 2 represented reality the matter on which the forces act would accelerate perpendicularly away from the solid surface! (The equilibrium of forces parallel to the solid surface is assumed, and indeed used, to calculate θ).

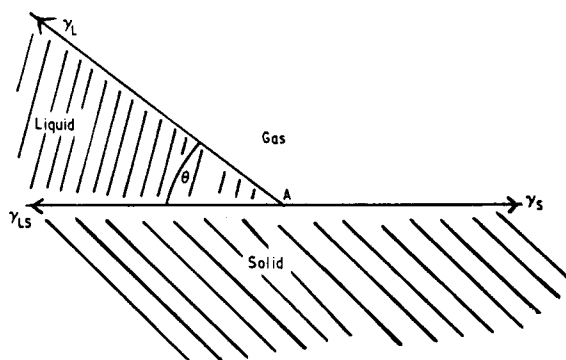In the short section 2 of this article we consider

Figure 2   Diagram sometimes employed in attempt to explain angle of contact.

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more carefully what happens to a molecule in the liquid surface; then, in the main part of the paper, section 3, we show how the tension parallel to the surface arises; finally in section 4 we attempt a consistent treatment of the angle of contact.

The inward attraction on surface molecules

There is in fact a net inward force on a molecule in the surface, but this is only one aspect of a *dynamical* equilibrium in which the *repulsive* forces acting on a molecule from its very near neighbours (figure 3) play a key role. For a molecule in the bulk liquid the resultant repulsive force from its near neighbours and the resultant attractive force from its farther neighbours are both zero, on the average. These resultants are not usually zero at any instant, however, and this causes the random heat motion. In the surface there is an unbalanced force on a molecule; it is directed inwards because the decreasing density in the surface layer implies that there are fewer very near neighbours to give an outward repulsive force. Thus, on the average, surface molecules accelerate inwards. This inward acceleration cannot continue down into the bulk because the descending molecules soon encounter the upward repulsive forces from the interior molecules. A helpful analogy is the behaviour of a large number of balls (surface molecules) bouncing elastically off the earth's surface (bulk liquid). The force acting on them, and the resulting acceleration, is downwards except for the brief periods when they encounter repulsive forces from the solid ground.

Similar arguments can be used to explain *surface energy*: in the bulk liquid a molecule has more attractive bonds joining it to its neighbours than one at the surface. To create new surface therefore, some bonds must be broken; this involves the doing of
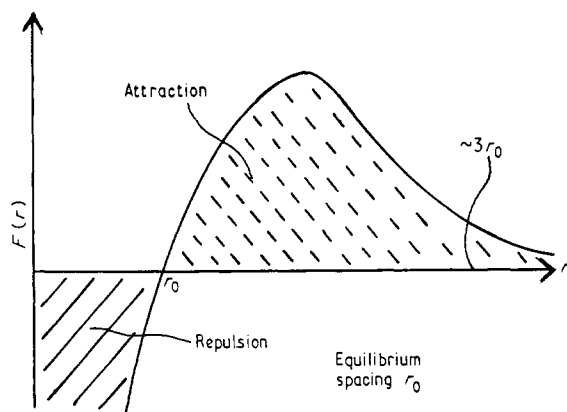
work, related to the positive shaded area in figure 3, which is called surface free energy if the surface is created reversibly and isothermally. There is a negative contribution to the surface energy, related to the negative shaded area in figure 3, due to the 'breaking' of repulsive 'bonds' from the very nearest neighbours, but this must be smaller than the contribution from the attractive forces, since otherwise the liquid would not cohere at all.

The tension parallel to the surface

The arguments just presented in section 2, which concerned themselves with the forces on, and energies of, single molecules, can be used to explain the tendency of liquid surfaces to contract. But the origin of the tension parallel to liquid surfaces is not explained. Indeed, it has been authoritatively stated that the notion of surface tension is a 'useful fiction' (Champion and Davy 1936) and that 'surface tension does not exist as a physical reality, and is only the mathematical equivalent of free surface energy' (Adam 1938). However, without using the concept of a tensile force parallel to the surface, it is very difficult to explain experiments involving static situations (for instance the support of a weighted movable wire by a soap film on a fixed frame), where no work is being done. (To explain these experiments using surface energy involves the principle of *virtual* work, which implies the existence of forces). It comes as something of a relief then, to read (Ono and Kondo 1960, Shoemaker *et al* 1970) that in recent research work not only is the existence of surface tension confirmed but its numerical value is also calculated from first principles — that is from the known intermolecular forces — and results are obtained which agree fairly well with experiment. These calculations imply a qualitative explanation of surface tension which does not seem to have been presented before.

The basic idea is that the component of fluid pressure directed parallel to the surface (we shall use the term 'pressure' loosely, to denote the normal component of the stress tensor) decreases and becomes negative — that is turns into a *tension* — in the region near the liquid surface. Thus surface tension is a macroscopic quantity like density, an average over times long compared with the mean interval between collisions, and cannot be understood by considering the forces on single molecules. There is no inconsistency in the concept of macroscopic quantities which vary substantially over intermolecular distances — the density, for example, must change rapidly but smoothly from its liquid to its gas value, and it is fairly well known that changes in the positions of macroscopic objects

Figure 3   Curve showing force $F(r)$ between molecules whose centres are separated by a distance r.

can be followed over fractions of atomic distances (Jones 1967).

In a fluid in equilibrium the pressure can be defined as the average normal force per unit area exerted by all the molecules on one side of a small imaginary test surface in the liquid on all those on the other side. The total pressure can be separated into two parts: the first is the kinetic contribution which arises because we are taking a time-averaged force and is due to the transport of momentum by molecules moving across the surface. In a perfect gas this is the only contribution to the pressure, but its value, given by

$$p_k = \rho k T \tag{1}$$

(where ρ is the number density of molecules at the point considered, k is Boltzman's constant and T is the absolute temperature) is the same in a liquid, because the velocity distribution of molecules is the same for a liquid in equilibrium as it is for a gas. The kinetic pressure is, of course, essentially positive. The second contribution to the pressure is important in a dense gas or a liquid; it is due to the time average of the static forces between molecules on opposite sides of the test surface (figure 4). This static force pressure, p_f is usually negative, since p_k is very much greater for a liquid than for a gas, so that attractive forces must dominate the repulsive forces in order to reduce the total pressure to the value externally applied. Only when the external pressure is very great is p_f positive; then the repulsive forces dominate the attractive ones, in order to help the kinetic pressure resist further compression. The total pressure is thus

$$p \quad = \quad p_k \quad + \quad p_f \tag{2}$$
$$\text{(usually} \quad \text{(always} \quad \text{(usually}$$
$$\text{positive)} \quad \text{positive)} \quad \text{negative)}$$

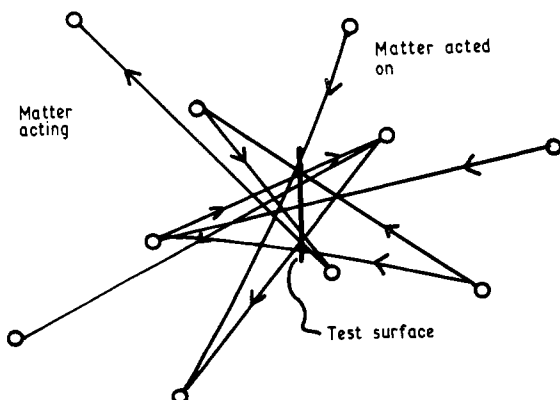In the bulk liquid and vapour the pressure has the same value, p_0, whatever the orientation of the test surface employed in its definition. Near the liquid surface, however, the tangential pressure p^t and the normal pressure p^n need not be the same, since there is no longer any symmetry of direction. But the fluid is in equilibrium, so that the forces on the opposite faces of a small cube must be equal and opposite (figure 5). This means that (apart from a cumulative downward increase due to gravity, which is negligible near the surface) the normal pressure must have the constant value p_0 right through the surface layer. The tangential pressure p^t, however, while being equal to p_0 in the bulk liquid and vapour, can and does vary in the surface layer.

To see this it is necessary first to understand how p^n can keep its constant value p_0 even though both its kinetic and static force contributions p_k^n and p_f^n vary with Z, a coordinate perpendicular to the liquid surface which increases in value into the vapour. From equation (1), the decrease in density with increasing Z means that p_k^n decreases; the corresponding increase in p_f^n from negative values to nearly zero, necessary to keep p^n constant (figure 6), occurs because there are fewer pairs of molecules attracting across the test surface as it nears the liquid surface. Now p^t will have the same kinetic part p_k^t as p^n but its static force contribution p_f^t will increase towards zero more slowly at first than p_f^n does; this is because the static force contribution comes mainly from molecules lying along perpendiculars through the test surface, so that the tangentially oriented test surfaces used to define p^n 'see' the depletion of molecules in the liquid surface before the normally oriented test surfaces used to define p^t (figure 7). If these two contributions to p^t are added (equation (2)), the resultant (figure 8) is not constant, but goes negative so that there is, in fact, a *tangential tensile stress* near the liquid surface, which even for rare gas liquids which cohere only weakly can amount to more than a thousand atmospheres. The
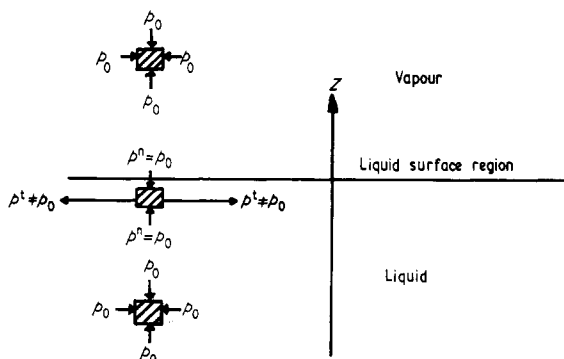

Figure 4   Origin of static force contribution to pressure.

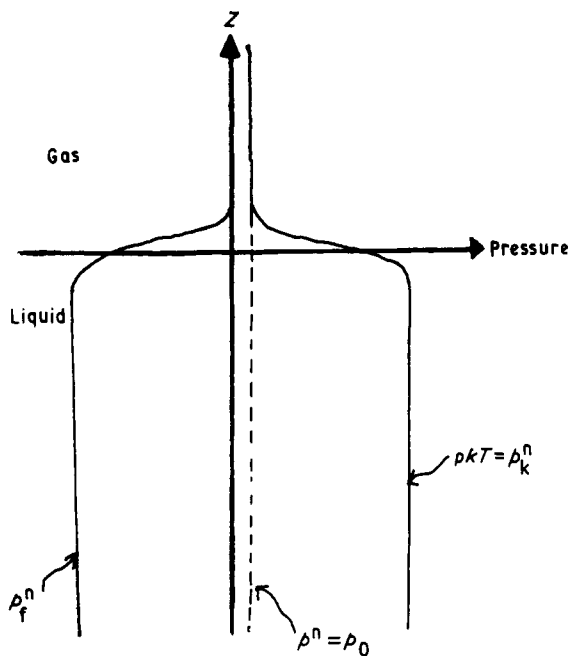*Figure 5   Equilibrium of elementary fluid cubes in liquid, vapour and surface.*
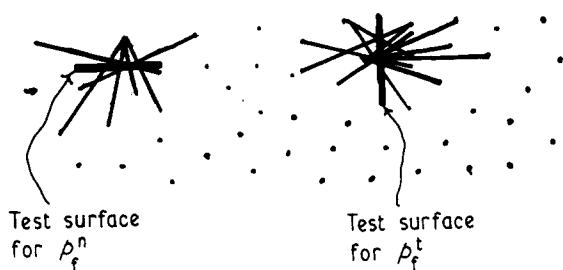
Figure 6   Contributions to normal pressure.

Figure 7   Greater number of interactions contributing to p_t^t than to p_f^n near liquid surface.
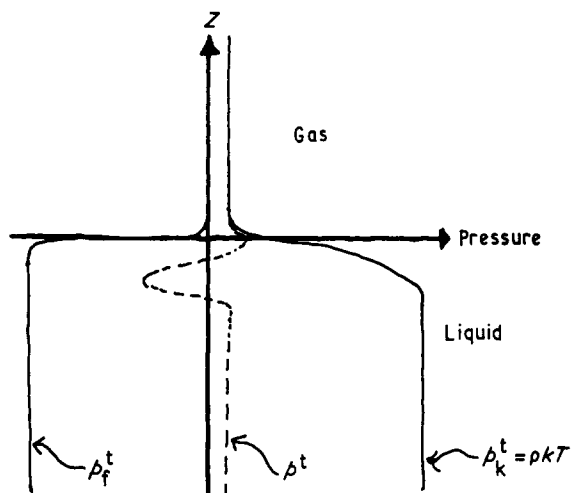

Figure 8   Contributions to tangential pressure.

surface layer of liquid, in contrast with the bulk, must possess rigidity in order to resist the shear stress that results from p^t differing from p^n; this is the basis for the statement appearing in older textbooks that liquids behave as if their surfaces are covered by an 'elastic skin'.

The *surface tension*, γ, defined in an elementary way as the total force exerted between the portions of liquid on opposite sides of a line of unit length in the surface, is simply the integral of the underpressure through the surface layer, i.e.

$$\gamma = \int_{-\infty}^{\infty} (p_0 - p^t(Z))\mathrm{d}Z. \qquad (3)$$

Any portion of a plane surface is in equilibrium under the action of the surface tension forces acting round its perimeter. To observe the effects of surface tension it is necessary either to have a curved surface as in bubbles, menisci, etc, where the unbalanced surface tension forces are equilibrated by excess pressure on the concave side, or to terminate the surface as in the wire-frame experiment mentioned earlier, where the unbalanced surface tension forces are equilibrated by the weight *mg*.

The surface tension of solids arises in basically the same way, but the details are considerably complicated by the possibility that the bulk stress may include shear components. At the interface between two liquids the behaviour of the tangential pressure is more complicated but if the liquids do not mix there is generally a net positive tension (figure 9).

The numerical calculations so far performed (Ono and Kondo 1960, Shoemaker *et al.* 1970) have employed the approximation of assuming that the fluid properties change suddenly from their liquid to their vapour values; that this procedure is unphysical is revealed by the fact that the resulting calculated normal pressure p^n is not constant through the surface.

The angle of contact

Consider the forces which act on a small mass of fluid ABC (figure 10) near the line of contact between liquid, solid and gas, which passes through A; BC must exceed the thickness of the surface layers. Only the *departures* from atmospheric pressure (which acts all round) will affect the statical equilibrium. These departures will be caused by the rest of the liquid and some solid near C, acting across BC, and by the solid acting across AC.

The force across BC consists of two parts: first, there is the liquid near B, which pulls with the usual liquid surface tension γ_L per unit length of line of contact. Second, there is the interfacial liquid and solid near C; in the 'wetting' case where the liquid is

strongly attracted to the solid we may reasonably expect its density to increase towards C, giving a *pressure* on BC near C (figure 9), whose total force per unit length of line of contact we call F. It is possible to obtain an expression for F by considering the tangential forces near C in the solid as well as in the liquid (figure 11), and assuming (dubiously), that the stresses in the solid are unaffected by the presence of the liquid. This leads to the result

$$F = \gamma_s - \gamma_{LS} \qquad (4)$$

where γ_s and γ_{LS} are the solid–gas and solid–liquid surface tensions. The third force to be considered is that exerted by the solid on the liquid above AC. Except for the region very near to A this will be just p_0 which acts all round and is irrelevant; near to A, however, the density decreases and there can be a net downward force X due to the diminution of the kinetic part of the pressure.

These three forces γ_L, F and X must be in equilibrium and, if the angle of contact is θ, resolving horizontally gives

$$\gamma_L \cos\theta = F = \gamma_s - \gamma_{LS} \qquad (5)$$

which is the usual formula, while resolving vertically gives

$$X = \gamma_L \sin\theta \qquad (6)$$

In the 'non-wetting' case, where the liquid is only weakly attracted to the solid, similar considerations apply but there is now a *tension F* near C, and the angle of contact is obtuse (see figure 11). The result (5) can also be derived using the concept of surface energy and the principle of virtual work (Poynting and Thomson 1947).

Conclusion

In this paper it has been shown that consideration of the condition of single molecules in the surface can provide an explanation of the tendency of liquid surfaces to contract, but that in order to understand the origin of the tensile tangential stress in the surface it is necessary to examine the variation of *averaged* quantities, namely pressure and density.

Because there really is a tensile force in liquid surfaces, ordinary statics can validly be used in surface tension problems: such explanations as, for example, 'the water in a capillary tube is held up by the surface tension forces acting round the rim of the meniscus' are perfectly correct, and need not be prefaced by any apologia to the effect that surface tension is merely a 'useful fiction'.

Acknowledgments
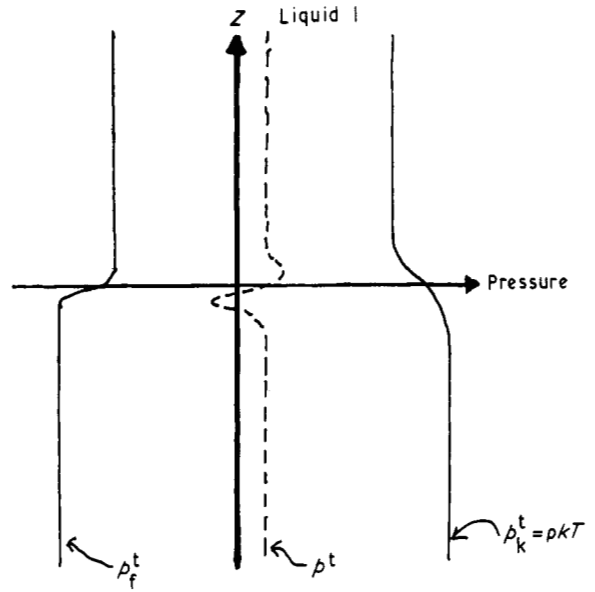
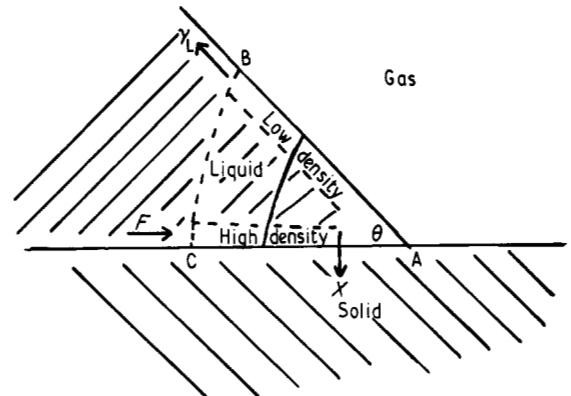*Figure 9* Contributions to tangential pressure at interface between two liquids.

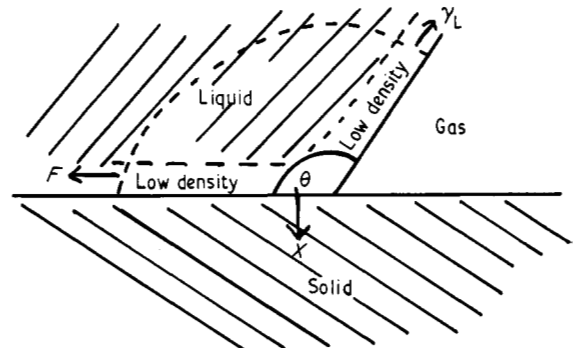*Figure 10* Forces on fluid near line of contact in 'wetting' case.

Figure 11 Forces on fluid near line of contact in 'non-wetting' case.

and the schoolteachers of Bristol for helpful discussions.

References

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Physics crossword

Clues across

1 Massive baryons (8)

5 Oh, wads may be total or partial . . . (8)

9 . . . though objects which are this may ruin that effect (8)

10 Very old medium for light (6)

12 Softening a stirred mole before fifty-one confused ten (9)

13 Through these old hardships to the stars (5)

14 Mangled rose may provide metals (4)

16 A monkey or the head of a church (7)

19 When so prejudiced the valve may in fact improve its performance! (7)

21 Little beginning for a big crystal or a mustard tree (4)

24 He gave his name to organ of hearing in a popular Ford car (5)

25 Generous gifts — big fools lose one (8)

27 Half way across the circle in the arm (6)

28 French photo-cell in the road? (8)

29 Mad mimers keep on the boil (6)

30 'Come and see these acidic products', said the spider (8)

Clues down

1 Ha, yell up to his faithful comet! (6)

2 Sip up the old mass — it goes to and fro (6)

3 In the country are the original robots and a little aluminium (5)

4 Sicknesses from a crazy Finnish bath with two different directions (7)

6 Bloody iron ore! (9)

7 Bounded by two planes I'd back two-thirds of a large church (8)

8 Belligerent antics which may conceal the realities of life? (3–5)

11 Suddenly changing voltage turns animals upside-down (4)

15 Give back — bounce like a ball? (9)

17 What 5 tends to do — sob in distress over successful treatments (8)

18 Domain of the peris (8)

20 Uninteresting, like a rainy day (4)

21 Employee who might be civil (7)

22 A German star at the back of the ship (6)

23 To mark the students fairly involves double secret service (6)

26 Treasure-house of electric charge is our Mother (5)

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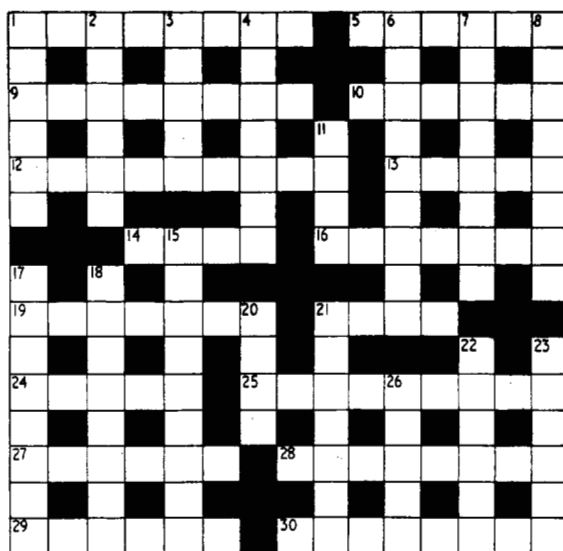
Competition

A prize of a £2 book token will be given for the first correct entry opened at the Bristol Editorial office on Wednesday, 24 March. Entries should be addressed to Crossword, *Physics Education*, IPPS, Netherton House, 23 Marsh Street, Bristol BS1 4BP.

The solution will be published in the May issue