

Chapter 10 Surfaces

Relationships across and between surfaces are a large part of the interaction of materials with their environment, as contrasted with the more 'internal' mechanical properties upon which we have so far concentrated. Many dental materials function in a specialized environment, the mouth, being a biological as opposed to a purely physical or chemical context. Even so, if these interactions are to be understood, the physics and chemistry of surfaces must first be explored. It is the purpose of this chapter to introduce the fundamental concepts and illustrate their relevance to dental applications.

*The major surface interaction of interest is the **wetting** of a solid by a liquid. The importance of surface energy or, equivalently, surface tension is stressed, as well as the relevance to cracking in solids.*

*It is the energetic considerations of wetting that drive the movement of liquids over surfaces, in particular the phenomenon of capillarity. When this driving force is combined with the limitation to flow provided by viscosity, we obtain a measure to describe the **penetration** of fluids into spaces. This is of great importance to the proper functioning of topical treatments such as fluoride products as well as fissure sealing and etching for bonding purposes.*

*True **adhesive dentistry** depends on the attainment of chemical bonding across the interface, and the nature of this is discussed. Hydrogen bonding is both a benefit and a nuisance, depending on the context, but control of the outcome again depends on understanding the process. However, there are many difficulties in achieving an adhesive bond, and some of the chemical approaches that have been tried, and their deficiencies, are also discussed.*

Surface energies are involved in many other areas: the setting expansion of gypsum products, the investing of wax casting patterns, oxides on amalgam and casting alloys, as well as soldering and porcelain. It is the pervasiveness of these effects and their influence on the success of dental procedures of so many kinds that demands an understanding of the basic principles.

B.W. Darvell. Chapter 10 - Surfaces, in: B.W. Darvell (Ed.) Materials Science for Dentistry (Tenth Edition), Woodhead Publishing. 2018, pp. 292-336.

It has been suggested that dentistry is very largely concerned with interfaces: the adhesion of plaque, the retention of full dentures, the cementation of devices, the application of fissure sealants and fluoride treatments, and so on; all depend on the properties and behaviour of tissue and other surfaces. Thus, in order to understand the effects and processes of dental procedures and treatments, their successes and failures, it is necessary to consider surface chemistry and physics. This will then guide the selection of designs and treatments in many contexts.

§1. Wetting

Whilst restorative dentistry is needed (which will be so long as tooth tissue continues to be lost through caries or trauma), the repair of developmental defects is attempted, or even cosmetic changes are desired by the patient, the retention of the restoration is of central interest. Hence, the search for direct restorative or cementation materials that are truly adhesive in dentistry is based on ideas such as the desirability of restorations being permanent, or at least as long-lived as possible, and orthodontic appliances being firmly held for as long as is required. This begs the question of what actually constitutes adhesion. In the circumstances, it is probably better to drop the use of the word adhesion, at least for the time being, and instead to discuss the nature of the bond between two substances. The use of the term 'specific adhesion' has been used to emphasize the difference between purely mechanical and purely chemical effects. But apart from the gross mechanical retention afforded by dovetail joints and similar undercuts in restorations, as exemplified by amalgam or a partial denture framework utilizing clasps, it is not really that clear-cut a distinction in practical dentistry. The reason for this is that to obtain mechanical interlocking of the roughness of tooth tissue on a microscopic scale, whether or not etched by, say, a resin-based restorative material, the wetting of the one by the other is an essential prerequisite.

•1.1 Contact angle

The fundamental effect of interest is the degree or ease of wetting, and this is conveniently studied through measurements of the **contact angle** exhibited by the fluid material on the substrate (Fig. 1.1). This is defined as the angle included between a plane tangent to the surface of the liquid and a plane tangent to the surface of the solid, both being at a point on their line of contact, measured through the liquid. It can be seen that liquid drops may exhibit a variety of extents of spreading on a surface (see, for example, water on wax or alcohol on glass). The greater the tendency of the liquid to wet and spread, the smaller the contact angle, until it vanishes when perfect spreading is observed. It is now necessary to explain how this comes about, and what the physical driving forces are that underlie this behaviour.

It has already been said that in order to fracture a solid material work is done in creating the two new surfaces (1§7): there is a characteristic amount of energy required per unit of area of new surface, and this is called the surface energy, γ (J/m^2). This is no less true for liquids. A raindrop in free fall always tends to assume a perfectly spherical shape, as this is the one unconstrained surface that minimizes the surface area, and hence the total surface energy, for a given volume. Any system will, of course, tend towards a state of minimum total energy: this is a thermodynamic requirement. Because the water is fluid, and the droplet can therefore change shape, a mechanism exists for this minimization to occur. Thus, work has to be done on the raindrop by the friction of the air in falling to disturb it from its spherical shape. Likewise, droplets of one liquid in another, such as an emulsion (8§4.1), tend to become spherical – viscosity and time permitting.

•1.2 Surface tension

One physical interpretation of this tendency of liquids to change their shape spontaneously after a disturbance is the concept of surface tension (Fig. 1.2) where the apparent surface skin of the liquid is attributed to the difference in the number of molecules mutually attracted by molecules at different positions. Simplistically, this mutual attraction of molecules explains

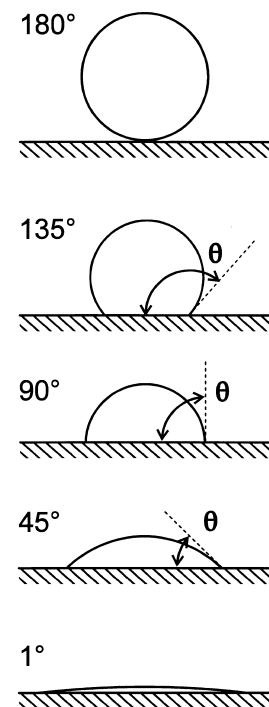


Fig. 1.1 Liquids may exhibit a variety of contact angles on solid substrates. (Note that the drawings do not represent constant drop volume.)

the tendency to minimize surface area because this also minimizes the number of ‘unbalanced’ molecules at the surface.

Surface tension, also given the symbol γ , is expressed as a force per unit length (N/m) (that is, a **line stress**), but since a joule is defined as 1 N.m (force \times distance acted over), surface energy and surface tension can be seen to be entirely equivalent: $\text{J/m}^2 = \text{N.m/m}^2$. It is just the conceptual approach that differs, one’s point of view, so to speak. (Note that the surface energy here is understood to be *specific* rather than *total*.) Hence, the work done in extending a surface, counting both sides of the film (Fig. 1.3), is identical to the work done creating the same area by splitting a column of liquid (Fig. 1.4), again counting both new surfaces:

$$E_{\text{new area}} = 2A\gamma = 2Ld\gamma = Fd \quad (1.1)$$

$(F = 2L\gamma)$

Surface tension may be measured directly as the force required to extend a film (Fig. 1.3) but more usually by a method equivalent to that shown in Fig. 1.5, *i.e.* by pulling on an object attached to a liquid surface and measuring the force required.

•1.3 Interfacial energy

So far we have discussed the fluid as if it were in vacuum, unaffected by any gas molecules above its surface. Indeed, when we consider the surface energy of a solid, we take it for granted that we are working in air at ‘normal’ temperature and pressure. Solids usually have entirely negligible vapour pressures (iodine is a notable exception, 0.31 mm Hg at 25 °C), so the composition of the air is unaffected. This is not, in general, the case with liquids. They will be more or less volatile, having appreciable vapour pressures, so that the ‘air’ must have some proportion of the vapour present. But the attraction from molecules in any vapour from the liquid tends to balance the forces acting on surface molecules of the liquid from within it. This is why we must refer to such systems at equilibrium, *i.e.* with saturated vapour, if any measurements of surface tension are to be meaningfully accurate and reproducible.

In other words, if γ_s is the surface tension of the solid against a vacuum, and γ_{sv} is the value equilibrated against some vapour, then $\gamma_s > \gamma_{sv}$. There are in fact adsorbed molecules on that surface, although not necessarily a full layer, and the extra energy for the surface against a vacuum can be explained as the work required to remove those adsorbed molecules.

In fact, the mere existence of a liquid surface depends on the attractive forces operating between the dense liquid and its much less dense vapour, and indeed any other gas molecules present, this force being less in total magnitude than between the molecules of the liquid. The implications of this may perhaps be seen when a liquid substance is raised above the critical temperature (at the critical pressure): the otherwise clear boundary between liquid and vapour simply ceases to exist as the densities of the two phases become indistinguishable.

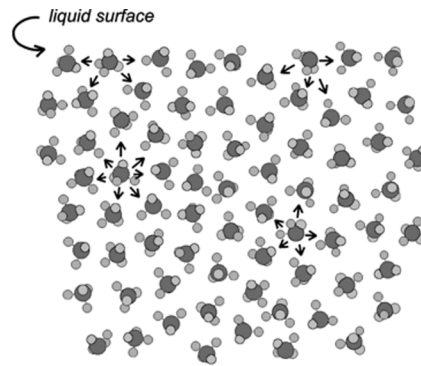


Fig. 1.2 Surface tension may be viewed as arising from unbalanced attractive forces on molecules at the surface in comparison with those in the bulk.

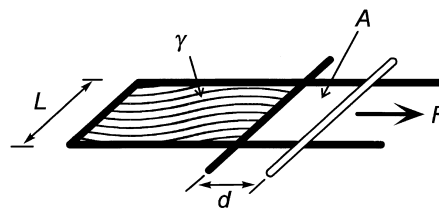


Fig. 1.3 Film extension (as for a soap film on a wire frame) ...

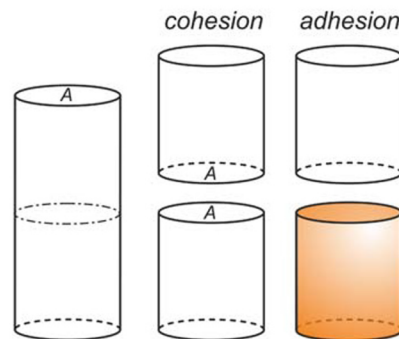


Fig. 1.4 ... and column splitting are equivalent in that both create new surface – which requires work to be done. The separation of adherent materials is similar.

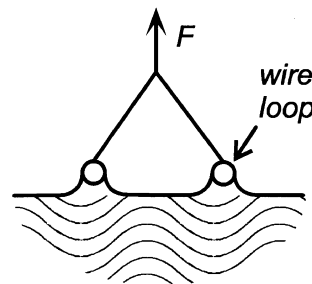


Fig. 1.5 One means of measuring surface tension directly.

Because there is no surface, there is then no surface tension. It has in fact diminished steadily to zero as the temperature is raised.

Similarly, any other liquid in contact with the first will have its own cohesive forces acting, and there will also be some interaction between the molecules of the two liquids. Since the second liquid will usually be very much denser (more compact) than the vapour of the first (*i.e.* the molecules more numerous per unit volume), even quite weak interaction between the two liquids leads to a generally lower **interfacial** energy, as it is now called, than either of the individual liquids' surface energies when in contact with their vapours.

•1.4 Energy minimization

So it is with a liquid on a solid: very often there will be a lower interfacial energy between the liquid and the solid than between the liquid and its vapour. There is then a tendency for the liquid to spread on the solid – which is energetically favourable. However, this spread necessarily implies a change in the surface area of the liquid against the vapour – which needs to be allowed for because the total liquid-vapour surface energy there is changed. There is also the decrease in the area of the solid against the vapour of the liquid to take into account.

We shall consider the simple case of a liquid drop on a plane, uniform¹, homogeneous², rigid, isotropic³ solid surface, but the results are extendable (with some effort) to other conditions. We know first that the shape of the liquid-vapour interface must be a spherical cap (Fig. 1.6) because, for any given liquid-solid interfacial area, this is the shape that minimizes that surface. We derive this as follows: a sphere is the closed surface of minimum area. The two parts cut off by an intersecting plane must also each be of a minimum area for the fixed intersection line since if either were not it implies that their sum, the original spherical surface, was not at a minimum in the first place. It follows then that the liquid-solid interface is a circular disc, since any section through a sphere gives a circle.

A sense of the nature of the variations in the interfacial areas as a drop spreads can be gained from Fig. 1.7. In order to understand this and its consequences, an equation for the total energy, E_{TOT} , of the system must be written. This takes the form of the sum of the product of the surface area A of an interface with its specific surface energy, γ , for each of the interfaces present:

$$E_{TOT} = A_{sv}\gamma_{sv} + A_{sl}\gamma_{sl} + A_{lv}\gamma_{lv} \quad (1.2)$$

where the subscripts *s*, *l* and *v* refer to solid, liquid and vapour respectively and the pairs identify the interface in question. It is this sum that must be minimized for thermodynamic equilibrium.

By the application of a little geometry, it can be shown that the minimum in equation 1.2 is obtained for the spherical cap whose contact angle θ is obtained from

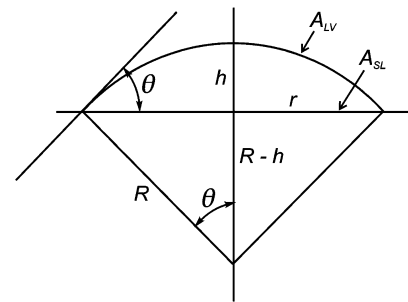


Fig. 1.6 Geometry of a drop on a plane surface.

Geometry of the drop (Fig. 1.6)

$$V = \pi h^2(3R - h)/3$$

$$R = h/(1 - \cos \theta)$$

$$A_{lv} = 2\pi Rh$$

$$r = R \sin \theta$$

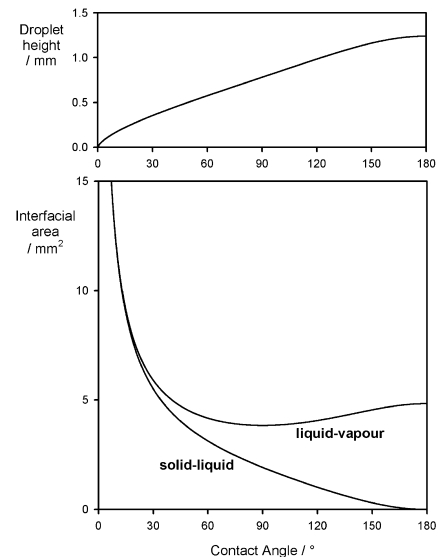


Fig. 1.7 Variation in droplet height (top) and the liquid interfacial areas (bottom) as a function of contact angle for a unit volume droplet (1 mm^3) (see Fig. 1.6). The minimum for the liquid-vapour plot occurs at $\theta = 90^\circ$. The maximum for both interfacial areas corresponds to a monomolecular layer; for water that would be about 2 m^2 (2§2.5). The solid-vapour curve is the complement of that for solid-liquid with respect to the original solid area (which is arbitrary).

¹ *e.g.*, if crystalline, only one crystal plane showing.

² single phase

³ *e.g.*, not drawn polymer or edge-on layer-structure crystal

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1.3)$$

This is called the **Young equation**. This result is on the assumption that the solid surface is ideal in the sense that the surface energy is constant from point to point. Even if it were not, the thermodynamic minimization must still occur, but the geometry becomes much more complicated and our ability to calculate a solution is somewhat impaired. Gravity, too, is ignored in equation 1.3, but for small drops the flattening that this causes, due to hydrostatic head, can safely be ignored. In addition, it is assumed that viscosity does not play a role, and that dissolution of the substrate – and of the liquid in the substrate – can be ignored. That is, all kinetic aspects have been allowed to equilibrate or are negligible. Despite all this, the general principle of the minimization of the total energy still stands as the driving force for the adjustments in shape that are observed when any liquid drop is placed on any surface. Systems of relevance to dentistry include fissure sealants into crevices, mercury on silver amalgam alloy, investment slurry on wax, and so on.

It is possible to deduce from equation 1.3 what conditions are required to promote wetting or non-wetting, depending on the application and the intention. Low surface tension liquids clearly will wet more effectively, and particularly if they are on high energy solid surfaces, aided by a strong interaction between the liquid and the solid to lower that interfacial energy. Conversely, low surface energy solids (such as polytetrafluoroethylene, ‘ptfe’ or ‘Teflon’) will be difficult to wet, and high surface tension liquids, such as mercury and other molten metals, do not wet most surfaces, and in particular not ceramics.

•1.5 Force balance

Given that we found an equivalence between surface energy and surface tension above, there is an alternative approach to the solution of this problem based on the surface tensions which are operating.

In any given surface (at equilibrium), the surface tension acting on one side of an arbitrary line drawn on that surface must be exactly balanced by the identical tension on the other side – the line stresses are necessarily identical. But if a drop of liquid is placed on a surface a line is established that disrupts that balance. The **contact line** or **three-phase line** (the ‘TPL’) is the boundary line along which solid, liquid and vapour meet simultaneously. Consider, for example, the view from the solid: the solid-vapour interface no longer exists on one side of that line, and it is replaced there by a solid-liquid interface whose interfacial tension is in general different from that of the solid-vapour interface. Across that contact line is therefore an imbalance. Equally, from the point of view of the liquid, part of the liquid-vapour interface has been replaced by that of the solid-liquid. There is again an imbalance of tensions across the contact line, but this time generally at some arbitrary angle. Because of these unbalanced forces acting on the line, the line must move, and it will move until the resultant of all three forces, F_{Σ} , is precisely zero in the plane of the solid surface at the contact line. This force-vector approach (Fig. 1.8) leads to the following straightforward equation being written down directly:

$$F_{\Sigma} = \gamma_{sl} - \gamma_{sv} + \gamma_{lv} \cdot \cos\theta = 0 \quad (1.4)$$

each term having a magnitude and a direction. This can be seen to be only a rearranged version of equation 1.3, and thus equally well expresses the thermodynamic result at equilibrium.^[1]

It should be clear from this that contact angle is not, in fact, just a property of the liquid itself at all, but a *geometrical* consequence of the particular values that the three interfacial energies have for a given system (and these, of course, vary with temperature). In other words, it is not an independent, intensive physical constant but a behaviour dependent on all local circumstances that influence any element of the system. Again, it is a property of the combination of the particular solid, liquid and gas phases – composition, constitution and structure, as appropriate.

In Fig. 1.8 it might be noticed that there is an additional force component, normal to the surface, of $\gamma_{lv} \cdot \sin\theta$, that is left apparently unbalanced. To see why the complementary downward force does not appear in equation 1.4, consider the situation of a drop of a liquid A floating on immiscible liquid B (Fig. 1.9). Here there

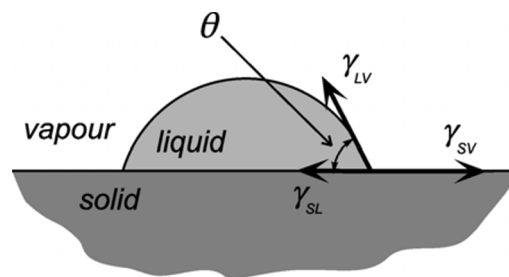


Fig. 1.8 The force vectors which may be considered to act at the contact line of a drop on a solid surface.

are again three interfaces to consider, but the force balance is complete because of the deformation of the surface of liquid B. Liquid A has two spherical section surfaces of different radii of curvature. In other words, in Fig. 1.8, the solid surface cannot deform (measurably), so the downward balancing force of $-\gamma_{lv} \sin \theta$ has no bearing on the calculation: the three-phase line can only slide in the plane of the solid surface. The normal forces still exist, but are accounted for by equilibrium elastic deformation of the solid (but which is usually far too small to be of any importance). (The ‘vapour’ in Fig. 1.9 must, of course, be saturated with respect to both liquids for thermodynamic equilibrium to be attained.)

Consideration of equation 1.4 will show that there are circumstances when no real value of θ can cause the sum to be zero. Thus, if

$$(\gamma_{sl} + \gamma_{lv}) < \gamma_{sv} \quad (1.5)$$

then F_{\perp} is negative (limiting $\cos \theta = +1$), which means a net tension pulling the contact line over the unwetted solid surface. This corresponds to **perfect wetting** and is accompanied by spontaneous spreading, the limit presumably being a monomolecular film. On the other hand, if

$$\gamma_{sl} > (\gamma_{sv} + \gamma_{lv}) \quad (1.6)$$

then F_{\perp} is positive (limiting $\cos \theta = -1$), and the contact line would be driven to retreat across any already wetted surface until the contact area, the solid-liquid interface, vanishes.

These conclusions can also be seen in the equivalent equation 1.3 where quite clearly it is very easily possible to construct ratios whose values lie outside of the range $[-1, +1]$. This is not an indication of the failure of the theory, but rather an illustration of the fact that the intermediate condition of **partial wetting**, $-1 \leq \cos \theta \leq +1$, is a rather special occurrence (Fig. 1.10). This observation reinforces the remark above that contact angle is not in any way a property of the liquid but a characteristic of the system as a whole.

A further point may be made here. Sometimes the word ‘wetting’ is interpreted as only applying to complete wetting, *i.e.*, if and only if $\cos \theta = 0^{\circ}$. However, noting that the interaction of liquid with solid that leads to any adhesion (Fig. 1.4), that is, lowering the energy of the system, means that some adsorption has occurred: this is wetting. Thus it is only for $\theta = 180^{\circ}$ that there is no wetting. Care must be taken to distinguish between the dynamic, physical process of the spreading of a liquid on a solid and the thermodynamic driving force for this that derives from a chemical interaction across the interface. ‘Partial’ wetting is still wetting.

•1.6 Critical surface tension

There are considerable difficulties with measuring individual solid interfacial tensions, and it is certainly easier to measure contact angles. But, in the region of perhaps most interest, θ approaching 0° , the determination of angles is difficult and an indirect approach is sometimes of value. For a given substrate, θ is measured for a series of homologous liquids (the aliphatic alcohols for example, or the paraffins themselves). The surface tensions of the liquids are independently measurable by other means (Fig. 1.5), and $\cos \theta$ is then plotted against γ_{lv} (Fig. 1.11).

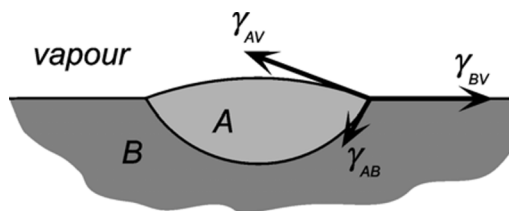


Fig. 1.9 The force vectors which may be considered to act at the contact line of a drop floating on another (immiscible) liquid (gravity-free).

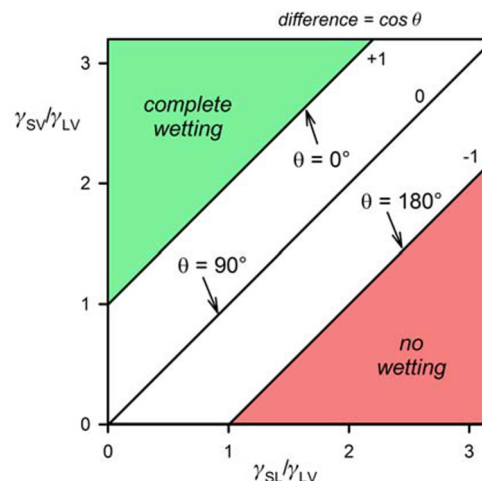


Fig. 1.10 Regions arising from the Young equation. By scaling the γ_{sv} and γ_{sl} values, and plotting the contours of constant difference, the intermediate partial wetting condition is seen to be a special occurrence.

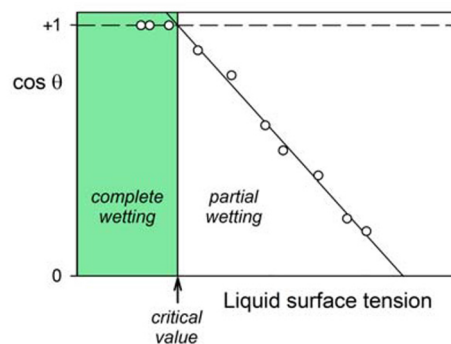


Fig. 1.11 Plot to determine critical surface tension.

This is known as a **Zisman plot**. The plotted points tend to fall on a straight line and an extrapolation can be made to estimate the **critical surface tension**, the value above which full wetting will not occur, and below which spontaneous spreading will be observed – for that substrate. Necessarily, this approach has to be used with caution because the result only applies to a similar liquid, one whose chemical interaction with the substrate is similar to that of the others of the test series.

•1.7 Work of adhesion

The necessity of counting *both* new surfaces in crack formation, film extension and so on can be demonstrated using the above results. The **reversible work of adhesion**, W_a , is the work required to separate the liquid from the solid (Fig. 1.4), and is given by:

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \quad (1.7)$$

(using the interchangeability of surface tension and surface energy). This equation is to be read as saying that for each unit of area of solid-liquid interface that is separated (*i.e.*, removed), one unit of area of each of solid-vapour and liquid-vapour is created. Now, from equation 1.4,

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cdot \cos\theta \quad (1.8)$$

Substitution from 1.8 in 1.7 gives:

$$W_a = \gamma_{lv}(1 + \cos\theta) \quad (1.9)$$

known as the **Young-Dupré equation**, which applies to any system where chemical changes do not occur on wetting. But if we imagine now that the same liquid is substituted for the solid substrate, we have of course $\theta = 0^\circ$, $\cos\theta = +1$, so that

$$W_c = 2\gamma_{lv} \quad (1.10)$$

In other words, the work done on joining together – or creating – two identical liquid surfaces is precisely twice the surface energy (ignoring sign). This is usually then referred to as **cohesion**, Fig. 1.4, hence the change of subscript to ‘c’. The result necessarily applies by extension to solids also, and serves to illustrate the reason for existence of the work of fracture previously discussed.

The difference between the work of adhesion of a liquid on a solid and the work of cohesion of that liquid

$$W_a - W_c = \gamma_{lv}(1 + \cos\theta) - 2\gamma_{lv} \quad (1.11)$$

is often given the (quite misleading and erroneous) name **spreading coefficient** (or **parameter**), the equation reducing to:

$$S_{eq} = \gamma_{lv}(\cos\theta - 1) \quad (1.12)$$

where the subscript ‘eq’ is specifically to indicate the equilibrium condition, that is when droplet spreading (or retraction) is complete. S_{eq} is, of course, not a coefficient, as it has the same dimensions as γ_{lv} (neither is it properly a parameter, *i.e.* a controlling dimensionless value in a mathematical expression). Strangely, as the term in parenthesis has a maximum value of zero (for complete wetting), minimum value -2 , S_{eq} might be better viewed as a measure of the thermodynamic driving force (*i.e.* change of energy) for *non*-spreading or, in the surface tension sense, the line stress tending to drive the TPL *back* from a fully-spread, complete wetting state.⁴

Comparison of equations 1.9 and 1.12 then shows that

$$W_a = -S_{eq} \quad (1.13)$$

which is reasonable in the sense that one refers to the work of forming the solid-liquid interface, the other to its removal. S_{eq} is therefore not an independent measure of anything, just a complementary view of the same wetting phenomenon (indeed, equation 1.12 may also be found referred to as the Young-Dupré equation).

The above discussion depends on the existence of an equilibrium TPL. However this does not apply to fully-immersed systems – there is no contact angle (they are always fully wetted unless there are bubbles – §9.2). Here, we can see that the (specific) **work of immersion**, is given straightforwardly just by:

⁴ Confusingly, this is sometimes defined with the opposite sign, $S \geq 0$. This would make sense if the sign of the energy change on joining bodies is defined to be negative.

$$W_{\text{imm}} = \gamma_{\text{sv}} - \gamma_{\text{sl}} \quad (1.14)$$

where the solid is imagined first to have been equilibrated against the vapour. If this condition is not allowed, as is normal, say for adding a dry powder to a liquid (although adsorbed water is likely always to be present, 2§2.5), then the vapour subscript of γ_{sv} needs to be very carefully considered and perhaps another value defined and used. The emphasis on contact angles in connection with fully-immersed systems such as implants is therefore seen to be misplaced.

•1.8 Boundary layer

Reference was made to the existence of a boundary layer on a filler and the effect that this has on viscosity (4§9.2). It is now possible to see that since wetting implies a lowered interfacial energy, the molecules forming that layer are by definition in a more stable position than those further away: they are adsorbed to the filler. They do not exchange with the bulk of the liquid so readily, and are more organized because they are constrained to be a two-dimensional entity, following the surface of the other phase. Indeed, depending on the strength of the binding to the substrate, the boundary layer may be described as a two-dimensional liquid or even crystal-like (indeed, for water it is probably ice-like for at least two layers^[2]). The ordering this represents may therefore have an influence on the next nearest neighbours, and so on, so that the effective thickness of the boundary layer may be several molecules thick, depending on the strength of interactions between molecules. The hydrogen bonding (§4) of water is clearly important in this context, and comparison may be made with the template effect of polysaccharides (7§8.2). The variation in behaviour between fillers as to their effect on viscosity can therefore be seen to depend in part on the chemical nature of the surface as well as surface area and matrix chemistry.

•1.9 Roughness

The calculations above involving surface energy implicitly assume that the respective surfaces are smooth – perfect geometrical planes and spherical caps. In such cases the specific surface energy is appropriate because the actual area of the interface enclosed by the relevant boundaries is exactly the area of the ideal delineated shape. For liquids, this is a perfectly acceptable assumption and – while flow can occur – inevitable thermodynamically to minimize area. However, real solid surfaces are rough, having a true surface area perhaps as much as two or three times the apparent size. Clearly, it is the true area of interface that must be used in the calculation of energy in equation 1.2, for both solid-liquid and solid-vapour. It is obvious that doubling the area inside a perimeter is numerically the same as doubling the specific surface energy (*i.e.*, the work of formation):

$$2A_{\text{sv}} \times \gamma_{\text{sv}} = A_{\text{sv}} \times 2\gamma_{\text{sv}} \quad (1.15)$$

Thus, if the areal roughness factor, r , is given by:

$$r = \frac{\text{actual area}}{\text{delineated area}} \quad (1.16)$$

then equation 1.2 becomes

$$E_{\text{TOT}} = rA_{\text{sv}}\gamma_{\text{sv}} + rA_{\text{sl}}\gamma_{\text{sl}} + A_{\text{lv}}\gamma_{\text{lv}} \quad (1.17)$$

such that equation 1.3 becomes:

$$\cos \theta_r = \frac{r(\gamma_{\text{sv}} - \gamma_{\text{sl}})}{\gamma_{\text{lv}}} = r \cos \theta \quad (1.18)$$

where θ_r is sometimes called the **Wenzel angle**. That is, the right hand side of the Young equation (1.3) is multiplied by the roughness factor. In other words, since the cosine function has the form shown in Fig. 1.12, the effect of roughness is to magnify the effect of the gain or loss of energy occurring in replacing the sv interface with the sl: if this is favourable (positive), it becomes more so; if not (negative), it is made worse^[3] (noting again the meaning of

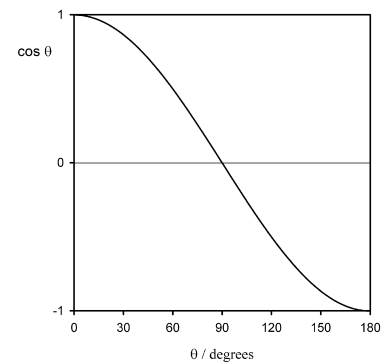


Fig. 1.12 Graph of the cosine function.

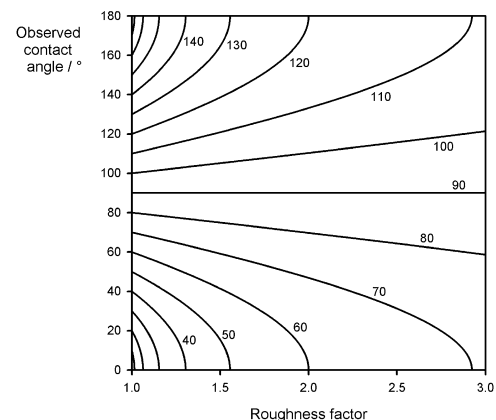


Fig. 1.13 Effect of roughness factor on observed contact angle. The contours are labelled with the value of the contact angle on a smooth surface. Thus, for roughness factor $r = 1$, observed angle = smooth surface angle.

values >1 or <-1 , Fig. 1.10). The effect is illustrated in Fig. 1.13. For a ‘perfect’, flat surface, contact angle of 90° (when $r = 1$), there is no change, but if there is any better wetting than this on a smooth surface, a rough surface improves it, and this can be quite dramatic for even a modest value of roughness factor of 1.5, where complete wetting (and thus spreading) is observed for a ‘smooth’ contact angle of about 47° . Conversely, droplets would roll cleanly off a surface with $r = 2$ for $\theta = 120^\circ$. It is a combination of microscopic texture and the waxy surface of many leaves that allows raindrops to be shed from them so easily (the ‘lotus effect’), and likewise from the treated fabric of raincoats. We can therefore amplify earlier remarks by saying that contact angle is a geometrical consequence of the particular liquid, solid and solid surface texture, and clearly not a material property in any sense.

•1.10 Levelling

One manifestation of the spontaneous tendency to minimize the surface area of a liquid is **self-levelling**. That is, a rough or wavy surface will become smooth, even in the absence of gravity effects. This is seen very clearly in paint, where brushmarks tend to disappear while the paint is still fresh enough to be just viscous (and not appreciably elastic), and in flamed wax (16§2.6). The same thing drives the smoothing of a fractured glass surface at a high enough temperature (so-called ‘flame-polishing’ – really flow when above the T_g ; cf. 25§4.6), and can be seen to a lesser extent in freshly mixed dental cements, filled resins, and so on, depending on whether there is a yield point, time allowed, and the radius of curvature.

•1.11 Experimental considerations

It may seem that the experimental determination of contact angle is a straightforward matter, but a number of factors must be borne in mind for meaningful results. Firstly, it has been emphasized that the equilibrium state that is the goal has to be with respect to the vapour of the liquid. More specifically, it has to be the saturated vapour if the thermodynamic conditions are to be met. Failure to achieve this not only affects the interfacial energies concerned, but might lead to appreciable evaporation of the liquid. If this liquid is itself a solution, then its concentration must change, and with it the interfacial energies. Secondly, any dissolution of the substrate, or components of it, changes both liquid and solid, including the roughness of the latter (§1.9). Even slightly soluble substances could have significant effects. Thirdly, the liquid should not dissolve in the substrate, for example, water in polymers. Testing polymeric materials as used in the mouth implies that they are saturated with water. Each of these can give time-varying behaviour. In addition, the presence of surface-active substances in the solution, such as glycoproteins in saliva or other body fluids, means that the true substrate surface is coated (almost instantly) and obscured such that what is tested is the chemisorbed (multi-molecular) layer instead. This is a quite different matter since this will tend to be chemically similar for a given solution no matter what substrate is underlying. Indeed, the adsorption of other active contaminants from the air means that the testing of truly clean surfaces is a serious challenge, while testing with liquids other than water is problematic in view of the near-universal presence of an adsorbed water layer (2§2.5).

Physically, observations of contact angles may be affected by electrostatic charges, especially where the substrate is not an electrical conductor. Such charges, which reside on the surface (as required by Coulomb repulsion) must – by that same repulsion – tend to increase the area of those surfaces, driving spreading. This is effectively the same as lowering the surface tension. Such charges can arise in a variety of ways, most commonly through the **triboelectric effect**, but also through chemical processes.^[4] Such effects must be avoided for accurate measurements.

Another field in which interfacial energy is of considerable importance is, as mentioned above, that of fracture. In particular, the Griffith criterion for cracking (1§7) depends on that work of formation. Thus, in any experiment in which crack formation and growth is involved, the environment of the new surface is critical. Effectively, as was discussed there, the strength of a brittle material depends on whether or not the test object is immersed, and in what kind of fluid. Obviously, for materials seeing service in the mouth, saliva is the principal medium of interest, but it is conceivable that foodstuffs and drinks might provide a sufficient change of conditions to permit cracking under otherwise survivable stress. For other types of material, variation in humidity might be important in affecting the value of the critical stress. It should go without saying that any attempt to measure a work to failure, or the toughness of a material (including fracture toughness, K_{Ic} [29§5.2]), should also be under a realistic service environment in all respects (including temperature) if meaningful values and comparisons are to be obtained (equation 1§7.2). Indeed, any process in practice that depends intrinsically on the formation of new surface, such as tearing, machining, cutting and abrasion, will also depend on the interfacial energy (see also 20§2.7), and thus the environment.

§2. Capillarity

Surface tension has another important manifestation which has many implications in dentistry: that of **capillary rise** or **capillarity** (Fig. 2.1). The same forces that cause the boundary of the liquid to move on the solid when this is horizontal, adjusting the position of the contact line, may also be observed to operate on vertical surfaces. The lens-like surface of water in a glass tube (such as a burette) – the **meniscus**, and the curved edge around the liquid in a cup should be familiar phenomena. It is this curvature that causes capillary rise. However, to demonstrate this, another system must first be examined.

•2.1 Droplets and bubbles

Consider a spherical droplet of radius r (Fig. 2.2). For any line segment drawn on a liquid surface, the total force acting on it is given by the product of its length and the line stress due to the surface tension of the liquid. Thus, if the line is a meridian (*i.e.*, a full circle from pole to pole) on a droplet, length $2\pi r$, the total force F acting on it is given by

$$F = \gamma \cdot 2\pi r \quad (2.1)$$

(We can drop the subscripts 'lv' when this interface is understood.) This generated force is acting in the sense of minimizing the area overall, and thus can be seen to be squeezing the contents of the droplet. It must therefore act over the entire cross-section (area = πr^2), so the increase in pressure, ΔP , inside the drop with respect to the outside is given by:

$$\Delta P = \frac{F}{\pi r^2} = \frac{2\pi r \gamma}{\pi r^2} = \frac{2\gamma}{r} \quad (2.2)$$

which is known as the **Laplace equation**.

For a droplet, the (excess) pressure is positive (compressive) in the liquid, and this is taken to define the curvature, $C = 1/r$, of the drop's surface to be positive (Fig. 2.3, left). This point is important because it establishes the sense of the pressure difference in any system. Thus, in a bubble of gas in a liquid, which can be represented by the same diagram, Fig. 2.2, the pressure in the gas of the bubble is higher than the pressure in the liquid by the amount given by equation 2.2. From the point of view of the liquid, the curvature of the interface is negative (curving away from the observer), so the pressure in the liquid is relatively negative *with respect to the gas*. We could change the viewpoint, and just as accurately say that from the point of view of the gas the surface curvature is positive (wrapping around the observer), and that therefore the pressure in the gas is higher than that in the liquid (Fig. 2.3, right). In brief, the pressure is relatively higher on the concave side, towards the centre of curvature, because the energy minimization requires that interfacial area to be minimized: whether bubble or droplet, it is 'trying' to shrink.

This effect is not insignificant: very small bubbles will have very high pressures (Fig. 2.4). Put simply, it is merely the curvature of the boundary that generates the pressure difference across the interface. In other words, it is of no consequence what lies either side of the boundary, the physical effect and its sign is the same. It is only the magnitude of the effect that depends on the surface energy of that interface.

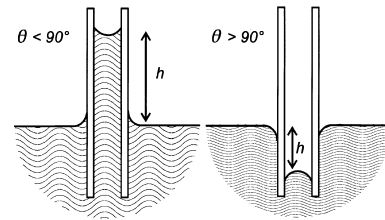


Fig. 2.1 Capillary rise and depression.

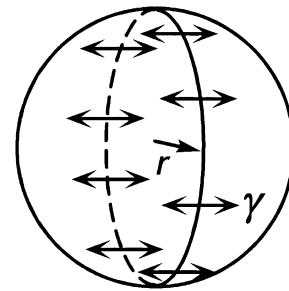


Fig. 2.2 The forces acting on a meridian of a liquid drop.

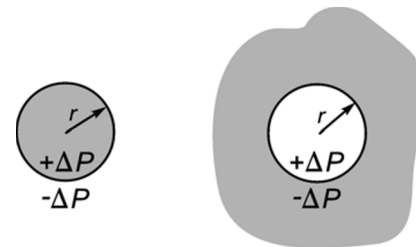


Fig. 2.3 Pressure differences across droplet (left) and bubble (right) surfaces.

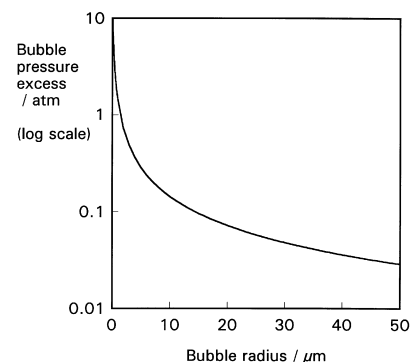


Fig. 2.4 Dependence of the Laplace pressure difference in a bubble on its size. Water at 20°C.

In passing, we can observe that a soap bubble has two boundary surfaces, an inner and an outer, either side of the liquid soap solution. There are therefore two contributions to the excess pressure inside the bubble, which is very nearly double that of the single surface value because the two radii are very similar, since the soap film is thin. Of course, the mere fact that a bubble has to be blown (Fig. 2.5) shows that a pressure difference is involved.

In deriving equation 1.3 we noted that a spherical surface has minimum area and therefore minimum energy. We can obtain a further view of what this means by considering the curvature. If the curvature of the surface of an unconstrained droplet or bubble varied from point to point across the surface, that is, not spherical, then the pressure just beneath the surface would accordingly vary. This is not an equilibrium condition. Pressure differences within a fluid mean that flow must occur in response, in order to eliminate all gradients (we are ignoring the effect of gravity here). Thus, the curvatures become everywhere identical and the surface is spherical.

•2.2 Capillary

The surface of the liquid-vapour interface in a circular capillary, the meniscus, can be viewed as sliced from a bubble (dotted in Fig. 2.6), a spherical cap. Now the tension forces in the liquid-vapour interface at the circular boundary are not balanced by forces in the same kind of surface, but rather by those at the contact line with the solid wall of the capillary tube. The total force acting at the meniscus in the direction of the axis of the tube is given by:

$$F = 2\pi r\gamma \cdot \cos\theta \quad (2.3)$$

Dividing by the cross-sectional area of the tube, πr^2 , the pressure difference across the meniscus is therefore given by:

$$\Delta P = \frac{2\gamma}{r} \cdot \cos\theta \quad (2.4)$$

This is known as the **capillary pressure**. This equation reduces to equation 2.2 when $\theta = 0^\circ$, *i.e.*, when the meniscus is hemispherical, and to zero when $\theta = 90^\circ$.

If the capillary is standing vertically in a large container of liquid with $\theta < 90^\circ$, *i.e.* as measured on the material of the capillary, and supposing that the meniscus in the tube is level with the flat liquid surface outside (Fig. 2.7), it can be seen that there is an imbalance of pressures: immediately beneath the meniscus pressure must be low because of equation 2.4, but equally the pressure immediately beneath the surface of the liquid outside the tube is atmospheric because the curvature there is zero. Hydrostatically, this condition is obviously disallowed, and the pressure difference forces the liquid up into the capillary until the pressure in the capillary at the same level as the outside surface is also atmospheric. This means that there is then a column of liquid of height h great enough to balance the reduction in pressure due to surface tension (Fig. 2.1, left):

$$\Delta P = -h\rho g \quad (2.5)$$

where ρ is the density of the liquid and g is the local gravity (the height in this sense is a negative depth, measured from the level of the outside liquid, to match the negative curvature of the meniscus). This situation may be compared with that in a closed tube (Fig. 2.8).

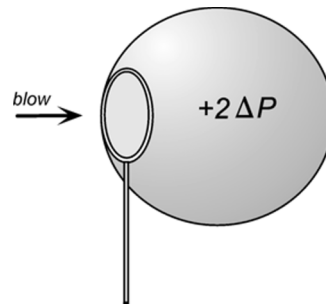


Fig. 2.5 Blowing a soap bubble requires that the pressure inside is greater than outside, but it also has two surfaces.

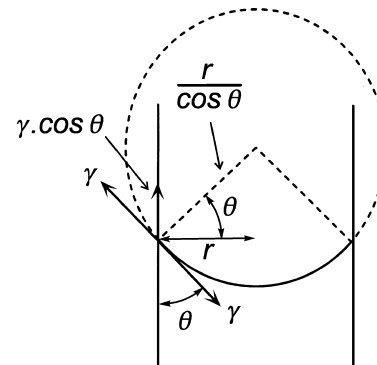


Fig. 2.6 A meniscus in a capillary.

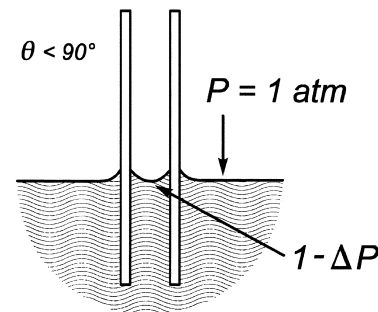


Fig. 2.7 The hydrostatically disallowed situation of a curved meniscus in capillary level with the outside liquid.

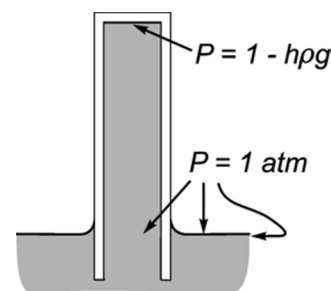


Fig. 2.8 At the top of the column of liquid in a closed tube, the weight of the liquid causes a pressure reduction.

The reduction in pressure at the top of the tube is precisely that due to the weight of the liquid column.

At equilibrium, the pressures calculated from equations 2.4 and 2.5 must be numerically equal:

$$h\rho g = \frac{2\gamma}{r} \cdot \cos\theta \quad (2.6)$$

so that the pressure difference inside the capillary at the level of the outside liquid is precisely zero (as required by hydrostatics).^[5]

The same situation applies in a Torricellian **barometer**, mercury in a closed-end glass tube (Fig. 2.9). Since there is a vacuum in the space above the mercury (ignoring the mercury's vapour pressure, Fig. 28§6.1), the pressure just inside the surface of the liquid must also be zero because the height of the column balances atmospheric pressure. That is, it is the pressure of the atmosphere driving the liquid up the tube, not the vacuum 'dragging' it up. The same effect would be obtained if the tube were open at the top and it reached into space, when the pressure in it, above the liquid, must fall to (very near!) zero. This therefore demonstrates that it is the pressure difference between points just in the liquid beneath the two surfaces (*i.e.* inside and outside the tube) which drives the capillary climb in an open tube, such as on the left in Fig. 2.1.

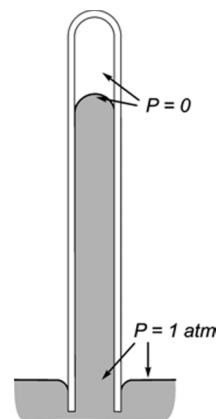


Fig. 2.9 In a mercury-in-glass barometer the height of the column balances atmospheric pressure.

On the other hand, if $\theta > 90^\circ$, there will be a depression of the liquid surface in an open capillary because of the positive curvature of the meniscus (Fig. 2.1, right). The height, h , would then have a negative value. The pressure just beneath the meniscus must then be higher than atmospheric by equation 2.5, and is of course identical to the pressure at the same depth outside the capillary, which is the hydrostatic condition. For the barometer, the actual height of the column is in fact slightly less than would ordinarily be expected simply because of this depression effect due to the positive curvature meniscus, which opposes atmospheric pressure slightly. Thus a slight correction is necessary to allow for the effect of the diameter of the tube (which is deliberately quite large to keep the effect small).

These phenomena can also be viewed as being driven by the imbalance in forces at the contact line, as was done above in the lead up to equation 1.4, with the weight of the liquid column 'hanging' on the contact line. Naturally enough, at $\theta = 90^\circ$ exactly there will be neither capillary rise nor depression and the meniscus will be quite flat, curvature zero. (As an aside: for certain of the polymers now used for cheap chemical volumetric ware such as burettes and pipettes, instead of glass – which has $\theta < 90^\circ$ for aqueous solutions – the meniscus is almost completely flat, $\theta \approx 90^\circ$, making reading somewhat easier.)

Clearly, with low contact angles the equalization of pressures draws more liquid from the mass, but if this reservoir is not present, a hydrostatic negative pressure is developed within the liquid and does not disappear. Thus, if we consider a liquid droplet placed beneath a supported microscope slide cover slip such as in Fig. 2.10, the tendency to spread at the TPL boundary on each glass surface (to increase the area of the wetted interface) the drop is placed under a negative pressure. The area of the interface with the air is minimized simultaneously, accounting for the strange shape of that surface.

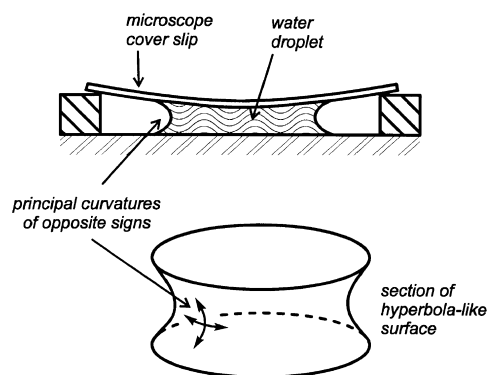


Fig. 2.10 The reduction in pressure in a drop can bend a cover-slip.

It may be noticed that the curvature of the liquid-air surface is negative in the radial planes, while the curvature in the other sense (*e.g.* the horizontal plane at the 'waist') is positive; this is an **anticoncave** surface. Without derivation, we can note that for all situations equation 2.2 may be generalized to take account of both

curvatures (which are measured in orthogonal directions, at any point on the surface, all orientations having the same net result):

$$\Delta P = \gamma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (2.7)$$

When $r_1 = r_2$ this is of course the same as equation 2.2. Equation 2.7 is read as saying that, at equilibrium, the sum of curvatures on a free liquid surface is everywhere constant if the pressure in the liquid is to be uniform. If the sum of curvatures is positive, then the pressure is greater inside as a result (Fig. 2.11) (as it must be with a **synclastic** surface, *i.e.* both curvatures positive). On the other hand, if the sum is negative, the pressure is correspondingly negative. This is the situation shown in Fig. 2.10. Here the negative curvature outweighs the small positive curvature so that the sum is indeed negative. The term in parenthesis in equation 2.7 may be called the **total curvature** of the surface.⁵ It follows that if the total curvature varies from place to place on a (gravity-free) liquid surface then the system is not at equilibrium: there must be a pressure gradient, and flow must follow.

Note that in the kind of system shown in Fig. 2.11 (a non-wetting droplet squeezed between two plates), the definition of the Young contact angle (equation 1.3) does *not* apply because the geometry of the system is constrained. Here, what appears to be the contact angle is not a function of properties of the solid and liquid but a geometrical consequence of the system. Thus the included angle at the TPL in this kind of case is *not* the Young contact angle. This can be seen in Fig. 2.11 where the “contact angle” at the TPL is clearly not that of mercury on glass ($\sim 130^\circ$ ⁶ [6]). To emphasise the point, as the plates are squeezed together, the disk becomes thinner, the radius of curvature must increase, so the ‘wall’ of the sphere section gets flatter, and the apparent contact angle approaches 90° .

This kind of wetting effect (Fig. 2.10) also accounts for the close adhesion of wet microscope slides, and partly for the retention of full dentures (§9.10). Notice that the strength of such a bond in shear is negligible because the ‘adhesive’ is a fluid (those microscope slides slip about quite freely), but in tension it can be appreciable. Capillary forces, therefore, lead to the retention of fluid in fine crevices and, conversely, when saliva is removed from these sites, drive the flow into them of fissure sealants, topical fluoride preparations, resin bonding agents, cements and similar materials.

Such forces also account for decreased expansion of setting gypsum products (2§5), the coherence of wetted porcelain powders (2§2.1), and many other such phenomena. Thus, in the case of plaster and the like, the reduction in volume of the liquid as setting proceeds causes the loss of gloss. But this means that the liquid surface is now locally curved. This in turn means that the pressure inside falls, so opposing crystal growth pressures. This applies in all systems where such a phenomenon occurs (Fig. 2.12; 14§6.3, 17§6.1).

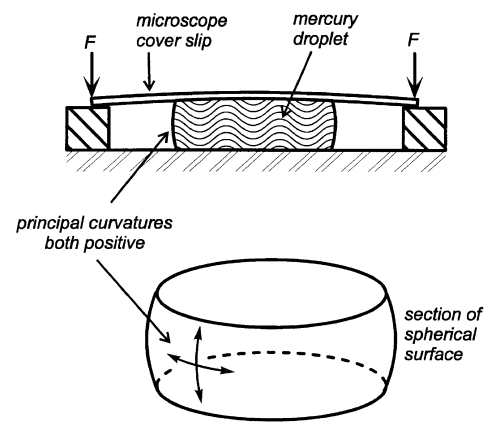


Fig. 2.11 A mercury droplet must be squeezed between the slip and the slide to deform it from a full sphere (doubly-truncated), although the surface remains ‘spherical’, with the two curvatures identical in value. The pressure due to the curvature is exerted on the glass.

It should be noted that the use of the ‘radius of curvature’ in equation 2.7 for the situation of a drop between two surfaces does not, in general, mean that a normal cross-section of the liquid surface is an arc of a circle. This is true in only a few special cases. It especially is not true if the Young contact angle (equation 1.3) is non-zero. Serious errors in calculations result from making that assumption. Curvature is a local property of a line on a surface representing the rate of change of slope at that point in a given direction.

Hydrostatic pressure within a drop means that at the (gravitational) bottom the total curvature is greater (more positive) than at the top. This results in distortions from the ideal shapes of such drops, and although the geometry of the drop is greatly complicated by this, the physical principles are not altered. We ignore gravity effects completely here only to simplify the picture.

⁵ Differential geometers do not like this physics usage of the term, which they define as either half the sum (= mean curvature, H), or as the product of the two reciprocals (= Gaussian curvature, K), depending on context. The point is here, as always, is to check definitions and symbols to ensure that the correct formulation is being used, no matter the context. ‘Total’ here is more logical.

⁶ That this is not 180° is attributable to van der Waals forces: §3.3, §3.4. Small droplets will cling to many surfaces (even in the absence of electrostatic effects due to charging).

•2.3 Capillary flow

Of course, the above remarks are based on equilibrium conditions and, since these would be achieved only through the flow of the fluid, its viscosity, η , would be expected to be a controlling factor in the rate of attainment of equilibrium. Dentistry is concerned about such behaviour because it controls the effectiveness of such treatments as the use of fissure sealants, infiltration of lesions,^[7] topical fluoride, etchants, bonding agents and, to a lesser extent, impression materials and cements.

Flow in tubes was dealt with in 4§11, where the force applied was external. Poiseuille's Law can again be used to deal with the situation where the force arises from wetting, *i.e.* as at equation 2.3, but now where the length of the tube filled varies with time, applying the same force-balance method. The rate of penetration of a fluid into a horizontal capillary (Fig. 2.13) can thus be calculated. The capillary is considered to be placed horizontally so as to eliminate gravitational effects, and penetration must continue indefinitely. We then have, from equation 4§11.4:

$$\frac{dx}{dt} = \frac{\Delta P r^2}{8\eta x} \quad (2.8)$$

where ΔP , the driving force, is given by equation 2.4 and x is the distance travelled by the meniscus of a Newtonian liquid into the capillary of radius r .^[8] This may be integrated with respect to time to give:

$$x^2 = \frac{r\gamma \cdot \cos\theta}{2\eta} \cdot t \quad (2.9)$$

which means that $x \propto \sqrt{t}$ (Fig. 2.14).⁷

We can understand the process in the following terms. The wetting of the tube wall creates a meniscus that generates a force, given by equation 2.3, acting to draw the liquid into the tube. This force creates a shear stress at the interface between the liquid and the tube that essentially depends on the area of the interface, $2\pi rx$. The wetting force is constant, and so therefore is the pressure difference across the ends, but the length is increasing, so the pressure gradient declines as the interfacial area increases with time. Therefore the shear strain rate decreases as does the shear stress, *i.e.* the meniscus velocity, or equivalently the bulk or volumetric flow velocity, decreases with time.

•2.4 Penetrativity

If we separate the 'external' variables and the physical constants of the system we obtain the following relationship:^{[9][10]}

$$\frac{x^2}{rt} = \frac{\gamma \cdot \cos\theta}{2\eta} \quad (2.10)$$

The expression on the right-hand side has been called the **penetration coefficient** for the system (also, **coefficient of penetrance**), but **penetrativity** is the preferable term. It has the units of m/s. Notice that this is

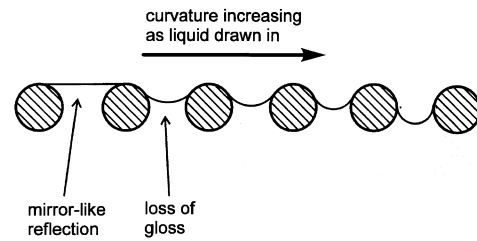


Fig. 2.12 For a setting gypsum product, loss of gloss indicates the generation of a negative pressure inside the mass due to the curvature of the liquid surface.

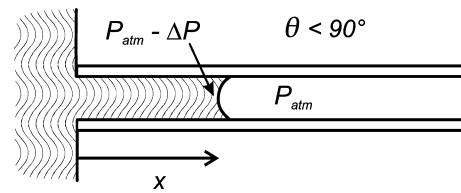


Fig. 2.13 Flow into a horizontal capillary, such as is used for blood collection, is driven by the advance of the contact line, which lowers the pressure behind the meniscus with respect to that in the fluid at the entrance, thereby causing flow.

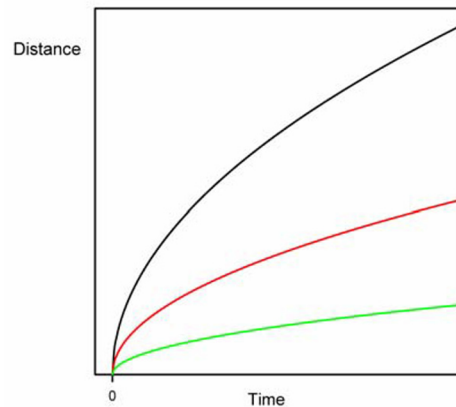


Fig. 2.14 Shape of the penetration curve for a wetting liquid into a uniform open capillary for penetrativity (§2.4) values in the ratio 100 : 25 : 4.

⁷ This is an approximation as clearly any such flow must be 'undeveloped' (see 4§11). Nevertheless, experimentally it is a fair fit. In addition, the initial supposedly infinite velocity, when $x = 0$, which is physically impossible, because mass and acceleration are ignored, is overlooked for convenience. Likewise, pinning (§9.6) is ignored. Experimentally, measurements would best be taken when the flow has settled down somewhat, *i.e.* the flow approaches the 'developed' condition.

defined for the whole system, *i.e.* including the substrate and gas phase, and not just for the test liquid because of the presence of $\cos \theta$, which represents the interaction of solid and liquid under the given atmosphere. As might be expected, the flow rate is inversely proportional to the viscosity. Clinically, the behaviour of interest would be how fast such penetration into crevices and capillaries might occur, as this would control the effectiveness of treatments, or rather the time which must be allowed for adequate completion of the process. In practice, the slope of a plot of the square of the distance travelled against time would be measured and, scaled by the capillary radius, this is proportional to the penetrativity.

It is worth noting that the numerator of the right-hand side of equation 2.10, $\gamma \cdot \cos \theta$, represents the thermodynamic driving force (the scaled line-stress) for the system, while the denominator represents the kinetic limitation (the viscosity). That is, this system is a good example of the trade-off so often encountered in dental materials: the compromise between the goal and the path, between ideality and reality, or between expectation and practical outcome. We may compare this with a rearrangement of equation 4§3.5:

$$\dot{\gamma} = \frac{\tau}{\eta} \quad (2.11)$$

– the shear strain rate (the flow) is given by the ratio of shear stress to viscosity: drive over retardation.

On the assumption that a transparent capillary material could be found such that the same contact angles would be formed with the test materials as would occur with, say, enamel, then direct comparisons of the penetrativity can be made without first having to obtain surface energy and viscosity data. That assumption may not be capable of realization, but some clinical correlation remains possible with, for example, glass capillaries. However, such a test system is capable of yielding much more information if the material, such as a self-cured fissure sealant, is in the process of setting (although this is of diminished interest with the current almost exclusive use of light-cured materials). However, it is still important to know how long to wait before the use of the curing light to allow adequate penetration.

•2.5 Working time

A self-curing material undergoing a process of cross-linking will show an increase in viscosity with time. However, as the network becomes extensive, the capacity for flow will be lost as the material is now rubber-like (see Fig. 6§4.7). Penetration ceases. Whether or not the setting reaction is anywhere near completed, the existence of the network is sufficient to stop flow under the small forces which are operating.

On this basis it will be seen that, for such materials, the penetrativity will be insufficient as a figure of merit for comparison of brands, for the ‘working time’ may be so short as to negate an apparent advantage, or short enough to override a seeming disadvantage (Fig. 2.15). Equally, the effect of delay in placement can also be judged, as the working time must be measured from the start of mixing (as with all materials). A vertical displacement of the plotted curve, so that its intersection with the abscissa indicates the actual time of placement, will indicate this directly because, of course, the working time is unaffected by placement if there is no change in temperature.

The implication of this is that the use of ‘command-set’ materials, *i.e.* light-cured resins, will avoid this problem. Nevertheless, it is still essential that time be allowed for penetration to occur.

•2.6 Bubbles

It is worth mentioning again the extreme sensitivity of polymer viscosity to changes in temperature (3§3) as well as molecular weight. It is obvious that much variation in either of these can drastically change the behaviour of the material. However, it is not enough merely for the penetrativity to be high and setting time to be long. Unlike the experimental system described above, the spaces into which sealants and bonding agents

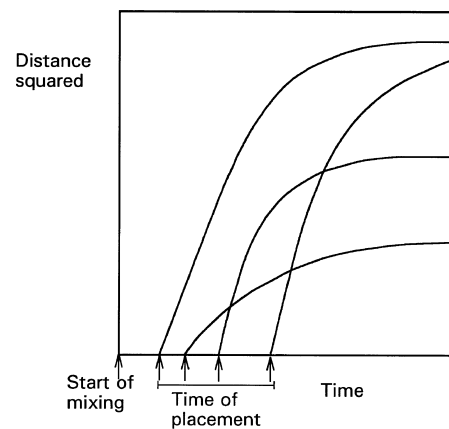


Fig. 2.15 Penetration plots to show working time effects for materials such as self-cure fissure sealants having a variety of setting behaviours.

are intended to go will be blind, *i.e.* closed at one end (§2.10). There will be nowhere for the air to go. For large fissures it is possible to place the fluid material at one end and allow the flow to fill the space gradually. This is not possible with small scale irregularities, and in particular with the pores of etched enamel. The air will be compressed because of the pressure difference across the meniscus which is driving the penetration. As a result the air tends to dissolve in the resin, but in any case the penetration rate will be decreased, and the extent may be substantially reduced. Sufficient time must therefore be allowed for air dissolution in the process of penetration of etched surfaces.^{[11][12]}

Clearly, there must only be air in these places, as water could not be displaced or dissolved. Careless placement of sealants on rough surfaces may easily trap bubbles (Fig. 2.16). This may be difficult to avoid. It reduces the total area of contact, but also detracts from the mechanical keying effect which resists shear forces. Such bubbles are also flaws in the Griffith sense (1§7).

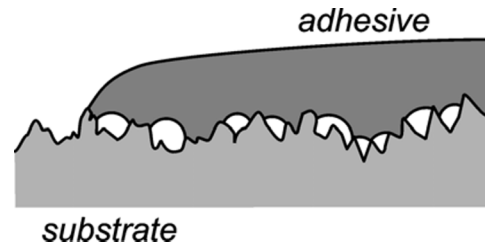


Fig. 2.16 Air may be trapped in roughness under an applied material.

Notice that the roughness effects described in §1.9 will apply here, so that if the resin is inherently going to wet the substrate, a rough etched surface, or even one that has simply been prepared with a rotary cutting instrument, will allow better wetting and spreading. The point is that it must be allowed to do so spontaneously, rather than simply covering the surface and thereby trapping bubbles.

●2.7 Contamination

It should be clear that flow driven by wetting is an important aspect of many dental systems. Because of this, the effects of contamination should not be forgotten. Contaminants of interest are nearly all of the kind that would reduce wetting. Thus, lubricating oil from a handpiece is potentially a serious problem,^[13] although the usual copious water spray may help to reduce the severity of this. Not so with the air used for drying surfaces prior to the application of bonding agents, cements or fissure sealants. This is one reason why oil-free compressors are (or should be) used to supply air for dentistry: a fine oil mist is always produced by oil-based compressors that cannot adequately be removed by filtration. Similarly, traces of wax or petroleum jelly in the wrong place will diminish if not destroy the intended effect. Even finger grease, which cannot be entirely removed by normal washing (nor is it desirable to try), is enough to spoil wetting. As a matter of principle, no surface which has been prepared for bonding, whether by etching (such as Maryland bridges or enamel), grit-blasting, or degreasing with detergent or solvent, should be touched by anything else prior to the bonding agent.

It should be noted that silicone oils and greases, which are commonly found in so-called barrier creams for hands and certain types of release agent used in dental technology, are particularly difficult to remove and should be avoided carefully. Of course, it is these very properties that make silicones suitable for those applications where wetting is not desired. Contamination from silicone impression materials (which always leave oily residues) is also to be avoided in critical contexts, as would be the inert oil used as the vehicle for the lead dioxide in polysulphide rubber. There are many sources of contamination. Care and forethought are therefore required to avoiding spoiling work.

●2.8 Penetration by plastic materials

There are two issues to be addressed in considering the delivery of a material to a site: getting it there and keeping it there. These are conflicting demands and compromise again is inevitable. It is apparent that wetting and viscosity affect delivery, but often a product is supplied in a viscous form to prevent it running away – out of a tray or off the tooth. Clearly, in this case, penetration is necessarily slow and it may be so slow that it is ineffective. Indeed, some products are plastic – they show a distinct yield point (4§7.3). It should now be clear that unless the wetting force (equation 2.3) is enough to exceed the yield point for the cross-section, nothing will happen. There will be no penetration. It is difficult if not impossible to force such materials into crevices and other small spaces when no seal can be made to allow the pressure to be raised. Thus, it is inevitable that topical fluoride products, for example, with a yield point (4§7.12) will not reach the target in pits and fissures without special effort, if at all. Likewise, impression materials will not record the necessary detail of embrasures, gingival margins and cavity line angles. Accordingly, it is usual first to apply light-bodied impression materials directly to the sites of principal interest with a syringe, relying on the pressure required to cause flow to drive the materials into the important features, before seating the filled tray. Flow requires a pressure gradient: fast enough flow requires a great enough excess pressure over the yield point.

●2.9 Penetration of porous bodies

If instead of a single capillary (§2.3) a porous body is considered, it is found that the penetration of a (Newtonian) liquid has exactly the same relationship, that is, distance travelled depends on the square root of time elapsed. The progress of such an experiment may be followed by weighing so that we may write, after correcting for the liquid density:

$$\frac{V}{A} = S.t^{1/2} \quad (2.12)$$

where V is the volume of liquid absorbed, A the cross-sectional area of the body being tested, and S is thereby defined as the **sorptivity**, the tendency to absorb liquid by capillarity (units $\text{m}\cdot\text{s}^{-1/2}$).^[14] Obviously, the porosity has to be continuously connected for this to work. Equally, the same general influences of interfacial energy, contact angle and viscosity must be involved as providing the driving force and the retardation for the process. What is not known is the scale factor. While a bundle of capillaries could be treated simply by a natural extension of the ideas of §2.3, normally the channels in a porous body are convoluted, irregular in cross-sectional shape and area, merging and diverging (typically) in a random manner. Thus, we need to consider the average behaviour assuming only that the body is similar in its porosity from place to place. The penetrativity is a property of the solid-liquid combination (as is contact angle itself, §1.5), and thus remains the same. All that is left is the effective scale factor representing the average porosity, r_{eff} , so we can write (either measuring the distance travelled directly or calculating it – making sure that evaporation does not affect the result):

$$x^2 = \frac{r_{\text{eff}}\gamma\cos\theta}{2\eta}.t \quad (2.13)$$

as at equation 2.9. Thus, from the right-hand side of equation 2.12, the sorptivity is then given by:

$$S = \sqrt{\frac{r_{\text{eff}}\gamma\cos\theta}{2\eta}} \quad (2.14)$$

so that if the penetrativity were known, the porosity can be characterized, but in any case the behaviour of the liquid in that body has been characterized by S . It can therefore be seen that coarse porosity leads to rapid absorption, as does improving the wetting ability of the liquid on that solid.

This behaviour is seen in the absorption of the solvent in thin-layer and paper chromatography. Contexts of dental interest include the initial absorption of water by a gypsum product powder (2§8.1), monomer in acrylic powder, glass into an alumina body (25§9.3), bonding resin into etched tooth tissue, including exposed collagen, fluids into endodontic paper points (27§2.2), water into a filter paper used to dry porcelain powder during build-up (25§2.1), and soaking a dental stone model. The latter three are not critical, perhaps, but there is an aspect of some importance for others.

Because the porosity in such bodies is generally random, and has a range or spectrum of characterizing values on the local scale, however these are defined, r_{eff} is in fact an overall average derived experimentally. Locally, however, penetration may proceed at varying rates, depending entirely on local conditions – including variation in surface energy. The absorption front, the ‘position’ of all the individual menisci in the absorption direction, may be far from planar (Fig. 2.17). The absorption front becomes irregular, and because the tortuosity of the path of wetting in the porosity may cause the path to turn back on itself, it may then enclose bubbles which cannot be swept out. That is, because the tendency is for the front at any moment to advance in a direction normal to itself, and because this direction is subject to randomization as the path taken locally, at the level of the single channel, deviates randomly (in a kind of “drunkard’s walk”), it may meet itself, closing off regions of a random range of sizes and shapes. In other words, the volume fraction of liquid absorbed will not attain the volume fraction of the porosity. In the case of investments and gypsum products, while soaking the powder like this is beneficial in removing a large volume of air, it cannot be complete and vacuum mixing remains necessary (18§1.2). The embedding of porous bodies in resin for microscopy, likewise, cannot in general be perfect, and the same applies with infiltrated ceramics (25§9.3), where remaining flaws might be critical.

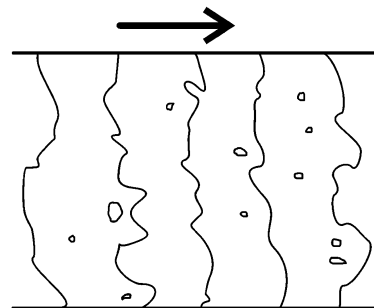


Fig. 2.17 The absorption front for a liquid in a porous body may be very irregular, and even cut off regions leaving trapped air.

In a system such as dried enamel, rehydration will occur by such a process. Accordingly, some air may remain trapped. However, in this case, the Laplace bubble pressure helps to drive the dissolution of that air. **Henry's Law** says that the solubility of a non-reacting gas is proportional to the partial pressure, and the bubble pressure is necessarily greater than that of the surroundings. This establishes a concentration gradient between the air dissolved adjacent to the bubble and the air outside, and this drives the diffusion of the dissolved air out of the imbibed saliva. As the air dissolves so the bubble shrinks, and this raises the bubble pressure further, accelerating the process. After a while, the enamel will be completely bubble-free. This effect would have to be allowed for in any quantitative work on the mineralization of enamel, where imbibition of sections with special dense solutions ('Thoulet's solutions') and fluorescent dyes is involved. Such dissolution may be of some value in contexts such as air bubbles trapped in denture base acrylic, although this must be distinguished from porosity generated by boiling monomer (5§2.6, 25§4.4).

It will be noticed that there is a parallel between the superficial roughness described at §1.9 and the internal character of a porous body. Indeed, any section will be rough in that sense. Accordingly, we can predict that the wetting internally will be affected in a similar manner so that if the smooth surface value of θ is $< 90^\circ$, penetration will be enhanced, and *vice versa*.

We can extend these ideas to cover various other circumstances. For example, the penetration of a liquid between two rough surfaces. If these surfaces are placed close together it will be equivalent to a thin slice through a porous body, and the path that the liquid takes will again be convoluted and may pinch off bubbles. Some examples might be soldering (22§1.2), fissure sealing, and even casting metals into an investment mould in very thin sections.

•2.10 Penetration of closed capillaries

While the penetrativity (§2.4) and the sorptivity (§2.9) may be a useful means of characterizing liquids and solids in open systems, in dentistry at least there are other types. Very often, closed capillaries or porosity is relevant, and this leads to another complication: rising pressure in the closed space now also opposes the flow.

Boyle's Law, for a fixed mass of (ideal) gas, says

$$PV = \text{constant} \quad (2.15)$$

at fixed temperature. So, in Fig. 2.18, the original gas trapped in the full length L of the closed capillary has a pressure given by:⁸

$$P_t = \frac{P_{\text{atm}} \pi r^2 L}{\pi r^2 (L-x)} = \frac{P_{\text{atm}} L}{L-x} \quad (2.16)$$

Thus the 'excess' pressure generated over the ambient pressure is then:

$$P_{\text{atm}} \frac{L}{L-x} - P_{\text{atm}} = P_{\text{atm}} \left(\frac{L}{L-x} - 1 \right) = P_{\text{atm}} \frac{x}{L-x} \quad (2.17)$$

and this must be subtracted from the surface tension-generated driving pressure, ΔP , in equation 2.8 because it is opposing the flow:

$$\frac{dx}{dt} = \left(\Delta P - P_{\text{atm}} \frac{x}{L-x} \right) \frac{r^2}{8\eta x} \quad (2.18)$$

Obviously, flow stops when the two pressures are equal:

$$\Delta P = P_{\text{atm}} \frac{x}{L-x} \quad (2.19)$$

Unfortunately, the integral solution of equation 2.18 is

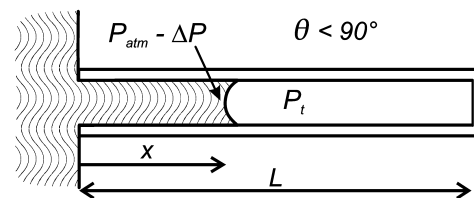


Fig. 2.18 Flow into a closed horizontal capillary is opposed by the compression of the included gas.

Compression of a gas raises its temperature, and this should be taken into account in a full analysis. However, because the volumes in the dental context are very small and the compression not rapid, very little heat is generated, and this may be rapidly dissipated through the relatively large surface area of a narrow capillary. Equilibration is therefore fast. The approximation of a constant temperature is therefore satisfactory for this discussion.

⁸ The volume of the meniscus sphere segment has been ignored for simplicity.

complicated and cannot be written explicitly for x as a function of t . However, it can be handled numerically, and an example of the form of the plot is shown in Fig. 2.19. From this it is clear that the trapped gas is a serious impediment to the penetration, as might be expected. But, of course, cylindrical capillaries would be unusual in practice, although dentinal tubules might provide a reasonable approximation. More common might be a tapered tube (Fig. 2.20), as is implied by the shape of the resin tags formed in etched enamel. The effect here is even more marked (and the integral even more complicated), as the excess pressure as in equation 2.17 then depends on $[L/(L-x)]^3$, and the flow comes to halt substantially sooner (Fig. 2.19). For effective penetration, one has to rely on the dissolution of the trapped gas (by Henry's Law, §2.9), which would take a relatively very long time.

Equating ΔP from equations 2.4 and 2.19, and rearranging, we get:

$$\gamma \cdot \cos \theta = P_{\text{atm}} \frac{x}{(L-x)} \frac{r}{2} \quad (2.20)$$

This is the actual driving force, expressed as the line stress (N/m), for the spreading of the liquid on that particular substrate; this is then a meaningful emergent property of the system. This might allow the direct use of tooth tissue substrates (with a drilled hole), where penetrativity could not be measured (§2.4).

The conceptual treatment can be extended to cover closed porous bodies (§2.9), although it is much harder to deal with the flow rates, using the effective pore size. In any case, the net result is that despite good wetting, one cannot expect porous structures to imbibe applied fluids very well unless they are vented. The trapping of gas may be accidental or unavoidable, but the limitations this represents to the outcome need to be recognized. This is why care must be taken to add powder to liquid in many dental materials so that air is not trapped. In the case of gypsum materials, a short wait for such soaking-in to occur is also recommended.

Further extension of these ideas can be made for casting metals (18§3.3 *et seq.*) where contact angles are unfavourable – no wetting, casting pressure needs to be generated, gas needs to escape, and cooling is occurring. Indeed, they are applicable to any system which involves the moulding of a fluid or semi-solid material into a constrained space which entails gas being trapped: filled resins (Chap. 6), impression materials (Chap. 7), cements (Chap. 9), and so on.

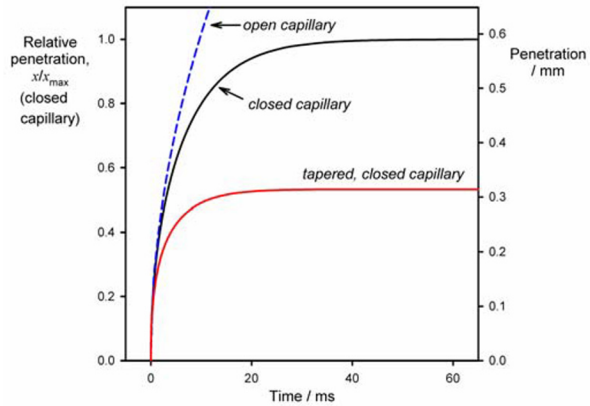


Fig. 2.19 Flow into a closed horizontal capillary is opposed by the compression of the included gas. If that capillary is also uniformly tapered to a point, the reduction in penetration is even more marked. ($r = 1 \mu\text{m}$, $L = 1 \text{ mm}$, $\eta = 1 \text{ mPas}$, $\gamma = 72 \text{ mNm}$, $\theta = 0^\circ$)

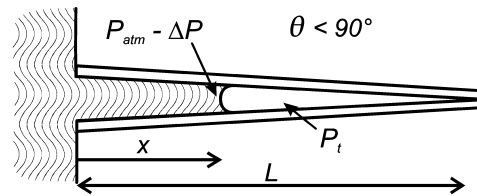


Fig. 2.20 Flow into a conically-tapered, closed horizontal capillary.

§3. Aspects of Chemical Bonding

So far only vague references to the attractive forces between molecules have been made. But to understand how bonding in the macroscopic sense may be achieved or improved, it is necessary to consider the mechanism of bonding at the atomic or molecular level.

The strength of chemical bonds is measured by the energy required to break them (Fig. 3.1). The **covalent** bonds that hold molecules together are very strong, typically about ten times more energy being required to break them than the **electrostatic** forces holding ionic materials together (Fig. 3.2). But there is a range of bonding from the weak to very weak collectively referred to as due to **van der Waals forces** (Fig. 3.3). These are the forces that hold many condensed, that is solid or liquid, materials together. Liquid air and paraffins are good examples. There is no chemical reaction between the molecules (that is, no formal bonds are formed), but their mutual attraction holds the liquid together, preventing it flying apart or boiling. The strength of the bonds is measured in these simple cases by the boiling points of the components. When enough energy is provided, the molecules escape. The origins of surface energy or surface tension in terms of these forces is obvious, but the forces themselves need some explanation.

•3.1 Ions

The inverse square law measures the force of attraction between two (assumed point-like) ions:

$$F = \frac{q_1 q_2}{d^2} \quad (3.1)$$

where d is their separation and q the charge (Fig. 3.2). When the charges are dissimilar in sign, the force is negative, meaning tension or attraction. This is the basis of the **electrostatic** bonds of ionic crystals.

•3.2 Dipoles

The same law applies to molecules which are polar through what are known as **Keesom** forces. That is, due to differences in the electronegativities of the constituent atoms, the electrons are not shared evenly but slightly displaced, revealing some of the nuclear charge on some atoms, and placing a net negative charge on others. If the overall effect is that the centre of the negative charge does not coincide in space with the centre of the positive charge, there is said to be a **permanent dipole** (Fig. 3.3). Dipoles interact in the same way as ions (that is, electrostatically), although more weakly because the effective charges are less, but also because each charge of one dipole interacts with each charge of the other, and two of the interactions are attractive while the other two are repulsive. It obviously depends on the relative orientation of the two dipoles whether the net effect is attractive or repulsive, but in liquids at least molecules and side groups are capable of rotation and reorientation to achieve a state of minimum energy, which means that if possible there will be a net attractive force. It does not require that the molecule has an overall dipole from such effects. Polar side-groups or substituents, such as hydroxyl or carboxyl, will act in the same way on their own account to strengthen intermolecular forces.

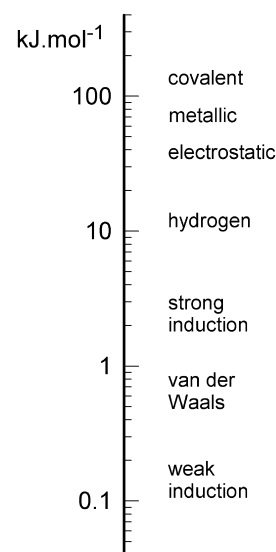


Fig. 3.1 The scale of chemical bond energies. Note that each type has a substantial range of values, and that these ranges overlap considerably.

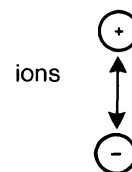


Fig. 3.2 Ionic solids are held together by electrostatic molecular interaction.

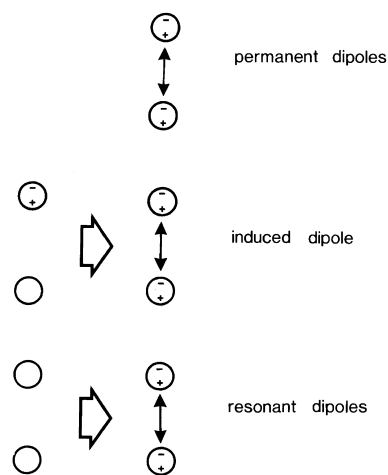


Fig. 3.3 Van der Waals types of molecular interaction.

●3.3 Induced dipoles

The electron ‘cloud’ around molecules and atoms is not rigid. Under the influence of the electrostatic field of a nearby ion or dipole it is capable of distortion. That is, the electron density distribution may become altered. The relative amount of distortion under a given influence is referred to as the **polarizability** of the molecule or atom. The effect is to create a new or **induced dipole** from the originally non-polar molecule. The forces between the inducing ion or dipole and the induced dipole, known as **Debye** forces, are about as strong as permanent dipole interaction forces, but because the induced dipole is induced, the closest poles are necessarily of unlike charge and attraction is always the net result.

●3.4 Resonant dipoles

Electrons can (simplistically) be viewed as orbiting the nucleus, and so at any instant there is a dipole. Over a period of time the average charge separation is of course zero, so that there is no net dipole, but the instantaneous dipole can be seen to oscillate. While a dipole exists it can induce another dipole in an adjacent molecule, which is itself oscillating. If these oscillations are in step, and the tendency will be for them to become so because this reduces the energy of the system, the attractive forces of adjacent dipoles will be operating, although there is no permanent dipole or ion being present. These dipoles are said to be **resonant** and the attraction is in fact stronger than with the other dipole interactions. These interactions are known as **dispersion** or **London forces**.

●3.5 Minimum energy

The forces themselves do not determine stability, but the resultant energy of the system. The energy of attraction (E_a) depends on how close the two molecules or atoms are and the magnitudes of the charges on the ions or of the dipoles. Clearly, however, there is some limit to how close atoms may get, as strong repulsive forces may be expected to develop as the electron clouds begin to overlap due to the mutual repulsion of like charges (Fig. 3.4). The energy of the system will tend to be lowered by closer approach due to the attraction forces, but also tend to be increased as electron cloud overlap increases. The net effect is the sum of the two energy changes. These two energy terms depend on different powers of the separation d , understood to be the internuclear distance:

$$E_a \propto d^{-1} \quad (3.2)$$

$$E_r \propto d^{-n}, \quad n \sim 5 - 12 \quad (3.3)$$

where E_r is the corresponding repulsion energy (the value of n depends on the atoms involved and their chemical state, that is, the kind of bonding involved). The resultant energy curve goes through a pronounced minimum at an ‘equilibrium’ separation d_0 .

Because of thermal vibration, the actual separation varies over a small range. As energy is supplied (*i.e.* the temperature is raised) so the oscillations increase in magnitude until complete separation occurs (d very large). E_{\min} (Fig. 3.4) can thus be viewed as the activation energy for the dissociation, as well as the stabilization energy for the association. Note also that the atoms must approach one another very closely for the attractive forces to be effective, only one or two atom diameters. This kind of treatment can be given for all atom-atom interactions of the van der Waals and electrostatic types, but similar behaviour is seen for covalent and metallic bonds as well. Ion-ion interactions can thus be seen as one extreme of a continuous range of strengths of such interactions. But there is another type of association as strong as those between ions which is of great importance biologically, in general chemistry as well as in many dental materials, *i.e.* the hydrogen bond (§4).

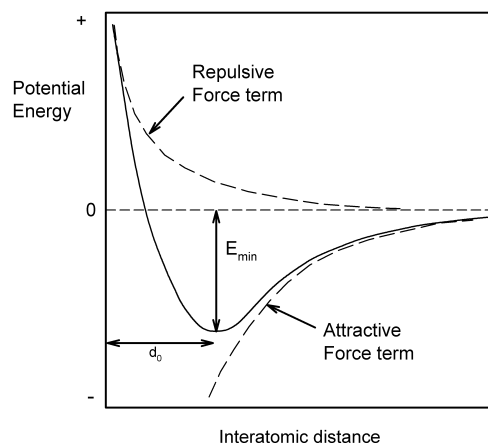


Fig. 3.4 The variation with distance of the potential energy of a system of two atoms due to attractive and repulsive forces between them. [NB: Schematic only – not at all to scale.]

●3.6 Origin of strength

While considering bonding in this way, we can also identify the origin of the strength of materials. Solid and liquid materials are held together by the forces acting between atoms and molecules and it is evident that these forces must be overcome if rupture of the material is to occur. Obviously, this has happened when a material has been heated enough to supply the energy corresponding to the bond energy. Thus, the melting point and heat of fusion of a substance are related to the depth of the energy well, E_{\min} . To consider mechanical strength requires an alternative viewpoint. We may consider a diatomic molecule as a model system. The bond between the two atoms may be considered to act as a kind of spring, and we can plot the force acting when that spring has been compressed or stretched (Fig. 3.5). This curve in fact represents the slope of the potential energy plot for the bond (*i.e.* as in Fig. 3.4):

$$F = \frac{dE_p}{dd} \quad (3.4)$$

If there is no applied force (and ignoring molecular vibration), the separation of the two atoms is represented by its equilibrium value, d_0 . It can be seen that the force rapidly becomes very negative when the bond is compressed, but on stretching it goes through a clear maximum. Thus, starting at d_0 and pulling, the separation will increase steadily as the force is increased, but as soon as the separation reaches the value corresponding to the peak the bond must break as now it has become an unstable system (the slope is zero at that point) and the force cannot be sustained (*cf.* the load-control test of 1§3.1).

Now we can see that the work of bond rupture, the area under the curve, is equivalent to the work to failure described earlier (1§4), at least for brittle materials. This follows since that area is the integral from d_0 to the maximum (Fig. 3.5), and the force curve was obtained as the differential (slope) of the potential energy curve. It can also be noted that the tangent 'spring constant' or stiffness of the bond, K (1§2; *i.e.*, underlying the modulus of elasticity), is given in turn by the slope of that line:

$$K = \frac{dF}{dd} = \frac{d^2E_p}{dd^2} \quad (3.5)$$

Several other things may be noticed in the force-separation plot. Firstly, Hooke's Law (1§2) can be seen to be an approximation that holds good only over a very small range. This corresponds to the observation that when the strain is large, deviations from linearity in the stress-strain curve can be more easily detectable (this does not apply in polymers at temperatures above the T_g because other mechanisms are operating, 3§4). Collapse of the bond corresponds to the point at which the stiffness is zero, that is, at the peak. Secondly, the maximum relative separation, in terms of separation/ d_0 (which is defined in the same way as extension ratio, 7§2.1), is actually quite small, but it is this strain that is the controlling, limiting factor for the 'strength' of a material. Thirdly, it is clear that bond failure cannot occur in compression: if the compressive force were large, one would expect shear to occur – if not exactly aligned in the direction of force application, one atom would slip to one side (*cf.* 1§6.3), and thermal agitation ensures that this always happens. Fourthly, the general tendency for strengths to decrease as temperature increases can be understood by noting that thermal energy is equivalent to the work done mechanically in stretching a bond (*e.g.* Fig. 14§7.2), and that the force required to rupture an already stretched bond must then be that much less. Fifthly, the modulus of elasticity of a material is also expected to decline steadily with temperature.

Since real materials on a macroscopic scale consist of very many molecules (or in a metal, atoms), it is clear that many bonds must be broken to fracture a real object. A simple calculation would consist of counting how many bonds were involved (of the order of $10^{13}/\text{mm}^2$), and multiplying the force accordingly – assuming

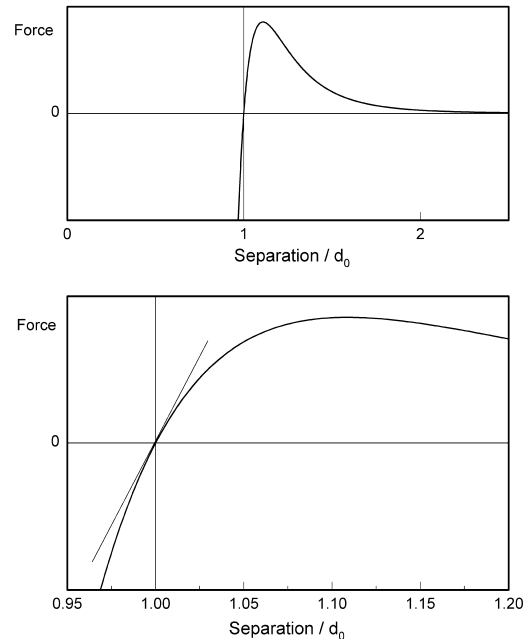


Fig. 3.5 Force acting in a diatomic molecule as a function of separation. The lower graph is an expanded view of part of the upper.

that they were all loaded uniformly. The reason that this is quite inadequate was explored in 1§7, where structural defects are seen to play a crucial role in real materials. Nevertheless, the arguments here can be seen to set an absolute upper limit to the strength attainable under any circumstances in the Griffith sense (equation 1§7.3), and to show how materials can show spring-like deformation.

•3.7 Thermal expansion

Whilst considering the chemical bond, we can usefully consider one aspect – thermal expansion. In a graph such as Fig. 3.5, for simplicity the atoms may be treated as if static, but of course, as explained in §3.5, they will be oscillating between the limits represented by the curve, according to the vibrational energy. As will be appreciated, the vibrational states of a bond are discrete or quantized (Figs. 6§5.2, 6§5.4), that is, only particular values of energy are possible, although there are very many such levels. Near the bottom of the energy well, the curve is very close to a simple parabola in shape, so the vibrating bond may be treated as a simple harmonic oscillator, to a first approximation. That is, it behaves like a Hookean spring (Fig. 1§2.1), with no loss of energy due to damping. The velocity is then zero at the extremes (all potential energy – hence the curve of Fig. 3.4) and at a maximum at the midpoint of the vibration (all kinetic energy) – very similar to the behaviour of a perfect pendulum (1§10.1). The midpoint then represents the ordinary, low temperature bond length, d_0 (§3.5). At progressively higher vibrational energy levels, the shape of the curve departs more and more from the simple parabolic. The midpoint therefore tends to move away from the low-energy d_0 value, increasing steadily (Fig. 3.6), and so the average bond length increases – which means that the atoms are, on average, moving further apart. Of course, not all bonds of a given kind have the same energy at a particular temperature, but rather the occupancy of the various vibrational energy levels follows a Boltzmann-type distribution (see Fig. 3§3.2). Even so, as the temperature is raised, so the mean of that distribution moves to higher values, and therefore so must the mean bond length, averaged over all such bonds in the body. In other words, the body is seen to exhibit thermal expansion.

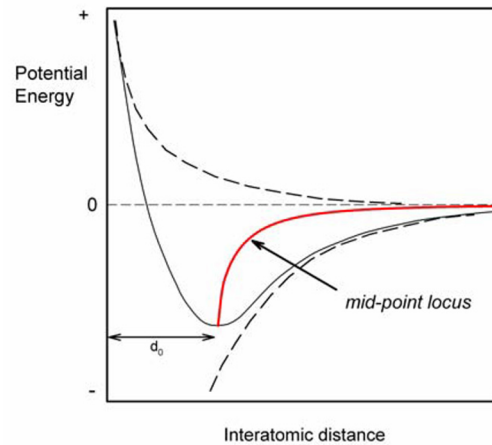


Fig. 3.6 The mid-point of the potential energy curve represents the average separation at a given energy. The locus of these point therefore represents the thermal expansion curve for the system. [NB: Schematic only.]

The same argument applies to all kinds of bond, whether covalent, ionic, metallic or van der Waals. In the latter case, the forces required are low and the bonds ‘soft’, so that greater thermal expansion coefficients are observed for materials such as small molecule liquids, waxes and organic polymers (Fig. 3§4.14). Giant molecules, fully covalently bonded, the best example being diamond, have low coefficients because van der Waals bonding is not involved. Other materials, with a mixture of bonding types and stiffnesses, show intermediate values. The differences in bond character affect the depth and shape of the potential energy curve. Broadly, the deeper it is, the lower the thermal expansion tends to be because the mid-point locus (Fig. 3.6) is near-vertical at ordinary temperatures.

The ideas of the energy to break a bond and thermal dissociation are therefore seen to be complementary, similar to the complementarity of the load and strain views of the mechanical breakage of a bond (§3.6). It is also clear that any bond must break at a high enough temperature. In addition, the escape of a molecule from a surface (whether liquid – evaporation, or solid – sublimation), can be seen as simply the realization of this breakage event for van der Waals bonding.

•3.8 Bond lability

In discussing matters such as bond length and strength it is easy to fall into the trap of thinking in terms of static systems. But, as made clear in §3.7, bonds are not of fixed length: atoms oscillate about a mean position. That is, all bonds are dynamic, and not just in simple stretching but in bending as well. Even this is simplistic. While at given temperature we can state what the average vibrational energy of a bond is, in fact over all such bonds there will be a distribution of values of the Boltzmann kind (*cf.* 3§3.3), as indicated above – some will be low but, more importantly, some will be high. Thus, because of this high-energy tail to the distribution,

there is a chance that any bond may break spontaneously at any temperature. However, at a low enough temperature this chance may be entirely negligible and materials and substances will appear to be quite stable. Of course, a broken bond may reform promptly, and nothing will appear to have occurred. We can see immediately, then, that bond-breaking is an activated process. Vapour pressure – molecules overcoming van der Waals forces – has a clear basis in this probabilistic view: the higher the temperature, the higher the rate of bond breaking and the higher the number of molecules in the gas phase at equilibrium:



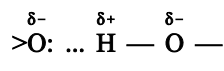
Equally, diffusion and creep (1§11) depend on bonds being broken, at least for a short time, for the movement to occur; these are activated processes (equation 3§3.3). Likewise, bond exchange in impression materials (7§11.3), whether these are covalent or hydrogen bonds, will occur at a rate dependent on the temperature. Of course, in such cases nothing seems to happen except when a load is applied and distortion results, but we talk about such bonds as being more or less **labile** – subject to being broken.

In this sense, all reactions and processes where bonds are to be broken can be seen to be activated and thus show a rate dependant on temperature. Thus the strength of a material is itself temperature-dependent as the thermal energy fluctuation is superimposed on the energy of the mechanically-stretched bond.

It should be noted that there is considerable confusion in some places over what is meant by the “strength” of a chemical bond, confusing at least three distinct aspects. The first is the chemically-meaningful bond energy – the work to failure, E_{\min} in Fig. 3.4 (*alias* the work of formation); the second is the load at which collapse occurs, the peak value in Fig. 3.5 – the force required to break it; while the third is the stiffness, the spring constant (sometimes called the force constant), as shown by the tangent to the force-separation curve. These are parallel to the ideas of toughness (1§4), failure stress (1§3.2), and elastic modulus (1§2.1), respectively, which are indeed quite distinct even if in common speech they may be confused or conflated. (We can also draw a parallel with the confusion of impact ‘strength’, 1§10.3.) While there may be a correlation between these values – a large value in one tending often to be associated with a large value in another, this does not mean that they are interchangeable. Primarily, this is because of the complexity of bonding: the nature of the molecular orbitals involved, that is, their three-dimensional shape; their polarizability (and so their dependence on their intra- and inter-molecular environment); as well as the mere fact that bonds are not independent – deformation changes the intramolecular environment, which changes the molecular shape, at least locally. In fact, in some contexts **bond length** (d_0) is taken as an inverse measure of bond strength, without specifying what is meant by strength, while **bond order** (essentially measuring how many pairs of electrons are involved) is an altogether separate idea, although the two are often inversely correlated. Accordingly, great care is required to determine which aspect is in fact under discussion when the term “bond strength” is used.

§4. The Hydrogen Bond

When hydrogen is attached (covalently) to strongly electronegative atoms, oxygen and (to only a slightly lesser extent) nitrogen being the ones of prime importance in the present context, it tends to acquire a small positive charge. That is, a local molecular dipole is produced. The same electronegative atoms acquire a negative charge by virtue of their electronegativity, their ‘electron-withdrawing’ power. When lone-pairs are available on others of these kinds of atom, a bond of the form:



is possible.^[15] These **hydrogen bonds** are responsible, for example, for the dimerization of acetic acid (Fig. 4.1), the extraordinarily high boiling point and heat of vaporization of water (Figs 4.2, 4.3), the network structure of polysaccharide gels (7§7, 7§8), the complex tertiary structure of proteins (27§3), the viscosity of poly(acrylic acid) (9§8.2), as well as the strength of dry cellulose (7§7, 27§2), and so on. The structure of ice (which is tridymite-like for the normal type, Ice I_h,^[16] – see Fig. 17§2.12) is all due to hydrogen bonds.^[17]

Hydrogen bonds have energies of about 4 ~ 40 kJ/mol, depending on the circumstances, and so are not quite as strong as typical covalent bonds (see Fig. 3.1).^[18] However, the frequent appearance of hydroxyl groups and oxygen or nitrogen means that hydrogen bonds can occur in very many circumstances, often with several per molecule. Note that it is the total energy of the association which determines the stability of the system.

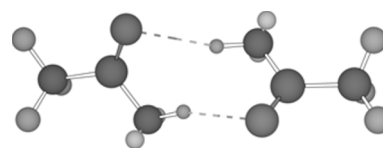


Fig. 4.1 Hydrogen bonding in acetic acid dimer.

Notice also that hydrogen bonds are specific, between particular atoms, rather than general as with van der Waals forces. This confers a spatial stability and directional (or steric) properties to any structure involving them. This, of course, is crucial in the case of the secondary and tertiary structure of proteins.

As a result of this ready formation of hydrogen bonds, water will adsorb strongly on very many polar surfaces containing appropriate groups, as well as dissolve in polymers such as poly(methyl methacrylate). Indeed, the polymers called nylon all contain many amine and carbonyl groups which are so readily solvated by this mechanism that they are unusable as denture base materials (Fig. 3§6.1), the plasticizing effect of the water so absorbed being excessive. A further point is that under normal circumstances polar surfaces and other high energy surfaces tend to be covered by a monolayer of water molecules, and the higher the water vapour pressure in the air, the more complete will this layer be. Obviously, we are not ordinarily aware of this, but potentially it represents a source of interference with the otherwise expected surface chemistry and physics.

It is apparent from previous remarks that any interface between a solid and a liquid with a contact angle less than 180° has a lower energy than the 'clean' solid surface. Clearly then, any material which is adsorbed does so because of the consequent lowering of the interfacial energy, *i.e.* due to the **heat of association**. Hydrogen bond formation will make a major contribution to such energy lowering, when it is possible.

§5. Dental Adhesives

Solids may be broadly classified by their surface energies:

- High surface energy, associated typically with high melting point, hard, inorganic materials, *i.e.* where strong intermolecular forces operate, *e.g.* tooth enamel, porcelain, metals.
- Low surface energy: usually associated with low melting, soft, organic materials, *i.e.* with weak intermolecular forces, *e.g.* protein, polymers (such as acrylics).

The adsorption of proteins into the polar surface of hydroxyapatite is thus energetically favourable and liable to be very stable (*cf.* §1.11).^[19] Such a film, commonly known as **acquired pellicle** when on enamel, and which may be very thick in molecular terms, will prevent other larger molecules which are designed to interact with the hydroxyapatite surface from doing so. Even so, for displacement to occur by small molecules, a further reduction of the interfacial energy must be associated with wetting by the incoming compound (*i.e.* a smaller contact angle). Such displacement does not occur in practice.

Consequently, for bonding metallic or ceramic devices to enamel, a major consideration is the cleanliness of the surfaces. Grit blasting (20§4.1) metallic items will remove much contamination, whereas the firing process is likely to burn off any organic contaminant on a porcelain restoration. It is then important to avoid subsequent contamination of those critical surfaces by contact with fingers or from other sources. Tooth surfaces must be cleaned thoroughly ('prophylaxis') to rid tooth surfaces of protein films, and subsequent contact with saliva scrupulously avoided. The contrast with the contamination discussed in §2.7 is that adsorbed protein may

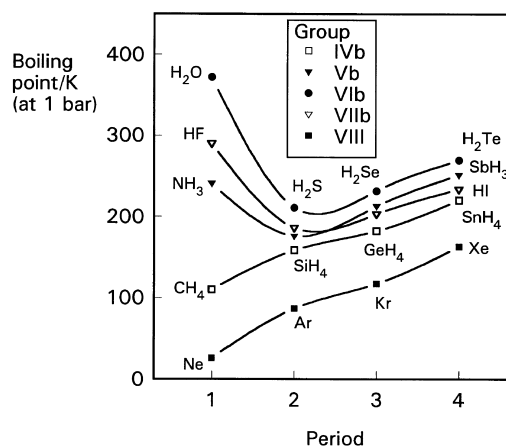


Fig. 4.2 The boiling points of the hydrides. The effect of hydrogen bonding in water, hydrogen fluoride and ammonia is clear.

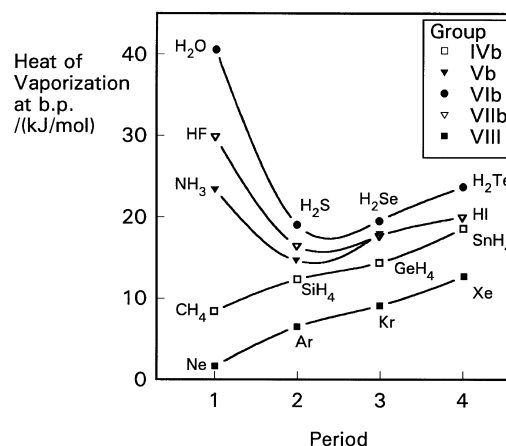


Fig. 4.3 The latent heats of vaporization of the hydrides. The hydrogen bond contributes about 30 kJ/mol in the case of water.

not reduce the wetting obtained with hydrophilic materials because they are so polar. However, they will prevent any intended mechanical key from being so effective because the protein layer will be mechanically weak, hydrolyse in the long term, and prevent altogether any intended covalent or coordination bonds to structural components from forming.

Polymeric 'adhesives' relying on hydrogen bonds may then bond sufficiently well to enamel thus cleaned and dried. However, due to the water absorption of such polymers, water soon becomes available at the interface by diffusion through the solid if not through the enamel itself (which, of course, is not impermeable), even if perfectly excluded initially (which is unlikely). Consequently, bonds between such surfaces can never be entirely satisfactory in the long term because the water will compete with the polymer. Other methods must be used for a strong bond. Various special **coupling agents** have been proposed but many have failed to perform satisfactorily clinically, if indeed any improvement could be detected otherwise.

•5.1 Silanes

Alkoxy groups on silicon are readily hydrolysed by water to the corresponding hydroxysilane (Fig. 5.1), which in turn can condense (water being eliminated) with hydroxy groups on other materials (*cf.* condensation silicone impression materials' setting reaction, 7§6.1). If the hydroxy group is on the surface of a solid, as for example ionically-bound hydroxyl in the surface of tooth enamel hydroxyapatite, the net effect is the 'grafting' of the silane onto the surface. If the silane also carries other reactive functional groups, such as vinyl or methacrylate, further reactions can then attach polymer chains at these sites, thus effecting a chemical bond of the bulk polymeric restoration or fissure sealant through to the tooth. Theoretically, the use of a methoxysilane, for example, can obtain the bond along with the elimination of adsorbed surface water molecules. Again, though, clinical results have been disappointing, possibly because the attachment site density (number of bonds per unit area) has been too low. Clearly, since the weakest link in the chain is the bonding of the silane oxygen to the substrate, dissolution of that substrate will free the link, as well as hydrolysis of the link itself (*cf.* Fig. 25§8.1). As was pointed out, water is available at such interfaces, and the exact layout of the hydroxyapatite crystal surface, ion by ion, cannot be expected to be maintained indefinitely.

•5.2 Coordination bonds

Chelation of metal ions by carboxylic acids has been mentioned in the contexts of alginate impression materials, and polycarboxylate and glass ionomer cements (Fig. 9§8.1). Because these are multiple coordination bonds, great stability may be achieved. These effects are also apparent on ions residing in the surface of a solid, and moderately good bonds with polyacrylates to enamel have been achieved. Indeed, this was the rationale behind the invention and development of those cements. Metal ions in oxide films such as are found on stainless steel and cobalt-chromium alloys are also susceptible to this action, leading to the usefulness of polycarboxylate cements for orthodontic bracket bonding, and the need for care in cleaning up when using stainless steel instruments with such cements.

§6. Enamel & Dentine Etching and Bonding

As the surface area of the substrate is important for providing a sufficient number of bonding sites, and while mechanical retention still has to be relied on for many systems, etching is used as a surface pre-treatment. This was first found to be useful on tooth enamel. The action of the acid solutions used is twofold:

- (1) by removing contaminants from surfaces inaccessible to prophylaxis, the surface energy may be raised;
- (2) the etching rates of different sites in the enamel structure may be greatly different, resulting in deep etch pits or pores being created; this is **differential etching**.

If the bonding material can flow into these pits before setting, many 'tags' may key the material to the surface and so resist shearing, although the resistance to tension normal to the plane of the substrate may not be improved very much in the absence of a more specifically chemical bonding. This approach is used for filled-resin restorations and fissure sealants in particular. However, the presence of the particulate filler in the restorative materials will inhibit the effect by blocking the pores and increasing the viscosity. Usually, then, an unfilled 'primer' resin would be used first, on top of which is placed the filled material.

●6.1 Dentine

Dentine presents rather different problems, however. It comprises a large proportion of low surface energy, hydrolysable, protein. Although sophisticated methods can actually graft polymeric materials onto the protein molecule using, for example, trialkyl boranes (which are thought to generate free radicals on proteins) (*cf.* 6§1), the poor mechanical strength and biological instability of protein does not permit good permanent bonds to be achieved. Chelating acids offer some chance of a bond but the exposed proportion of hydroxyapatite is very low and, since etching will remove this material and not the protein, the position can only deteriorate with this procedure. It is also quite impossible to dry the surface of dentine without damage to the pulp as the latter provides a good continuous supply to the surface film via the tubules.

Dentine bonding thus depends on several factors combined to achieve the best results, although whether they are yet – or can be – satisfactory in the long term remains to be determined.^[20] The factors are:

- mechanical key,
- interpenetration of structures, and
- specific bonding.

Mechanical key probably remains dominant, but it depends on penetration of dentinal tubules rather than a differentially etched structure as in enamel. This is problematic in that all that is needed here is the clearance from the tubules of the smear layer and debris plugs due to the preparation of the cavity by rotating instruments. Going further means the removal of structurally-important hydroxyapatite. Thus, the acidic agents used for this are described (erroneously) as ‘conditioners’ rather than etchants, but it must be recognized that the chemistry of the system takes no notice of the dentist’s intentions and etching necessarily does occur. What matters is controlling the extent of that etching; calling it a different name does not change the action (see 9§5.17).

Secondly, by a proper design of polymer in terms of viscosity and hydrophilicity, the exposed protein matrix resulting from the etching of the dentine that does occur may be infiltrated by the resin to create a composite structure called the ‘**hybrid layer**’ which is structurally continuous with the underlying dentine through the protein fibrils and appears to be important to achieving a strong interface.^[21] This may be valuable in providing a gradual transition in mechanical properties, specifically modulus of elasticity, from the unfilled resin through to the unaltered dentine. However, the stability of the protein has yet to be proved in these circumstances.

The third factor, **specific bonding** refers to covalent bonds between the molecules of the adhesive and some structural molecule (such as a protein) of the substrate. Such bonding is, of course, important in the same sense that a composite’s matrix must be bonded to its core to be effective (6§2.9): stress transfer. There are many proprietary versions of attempts to achieve this, and it is as yet unclear which is to be preferred. Even so, it appears that there is no firm evidence that these bonds are formed, at least, not in significant numbers. Despite this uncertainty, non-specific bonding, in the sense of wetting, perhaps aided by hydrogen bonds, can go some way towards achieving the necessary condition. This failure to attain covalent bonds does not, however, affect the importance of the principles which must be followed for bonding between tooth and resin to be effective, *i.e.* to have sufficient strength to be functional. In any case, since the substrate molecules to which the bonding must be made are themselves rather labile and subject to hydrolysis, the long term prospects for a reliable bond are poor.^[22] Indeed, enzymes called matrix metalloproteinases (MMPs) are present in dentine and odontoblasts and appear to be active in degrading the attachment to dentine, especially if this has been treated with acids or acidic bonding materials. Water in any case cannot be excluded from any site since it can diffuse through the materials involved; it does not require a gap to be present.

The chemistry of adhesives on the market changes rapidly, and in particular the presentation in terms of the numbers of preparation steps and their intentions. Given that at each stage there is a compromise, and that pressure of time is commonly overriding (sustaining the use of ‘self-etching’ adhesives^[23]), here as elsewhere attention to detail is essential for the best outcome.^[24] Even so, the longevity of such systems is likely to be affected by water sorption and hydrolysis.^[25] Some of the principal systems are used as illustrations here.

●6.2 Cyanoacrylate

In addition to the simple methacrylates and their numerous bis-GMA and other variants, as used in filled restorative resins, fissure sealants based on other reaction systems have been proposed. The cyanoacrylates, which have attained considerable fame (or maybe notoriety) as instant ‘super-glues’ on the domestic market, are characterized by their polymerization being initiated by water (Fig. 6.1).^[26] The cyano- group is so very

electrophilic that some net positive charge is apparent in the terminal vinyl carbon, which thus becomes susceptible to attack by as weak a base as the hydroxyl ion or even water. The carbanion so formed can go on to attack other vinyl groups at the same site, thus effecting polymerization. This is therefore an **anionic addition polymerization chain reaction**. The parallel with the methyl methacrylate polymerization (5§1) should be clear.

The reaction with adsorbed surface water molecules is, of course, both the polymerization initiation step and advantageous for bonding in that it removes a barrier to polymer-substrate interaction. Since proteins have hydroxyl and carboxyl side groups (some five amino acids have -OH groups, two have a second carboxyl group, and even one with -SH), bonding to and initiation by them of cyanoacrylate polymers is possible. Such a reaction can be seen to have **grafted** the polymer onto the substrate molecule by forming a covalent bond to it, which is necessarily quite strong, bearing in mind that the strength of the union of the two parts depends on the areal density of such bonds. Hence, some true bonding to the protein matrix of enamel and dentine, as well as fingers, is possible. The rate of chain termination is rather high so that only thin films polymerize successfully, limiting clinical application, although their low viscosity allows good penetration.

Hydrolysis of the polymer is also a problem, especially with the lower alkyls (R = methyl, ethyl). The strong electron-withdrawing power of the cyano and carboxylate groups on the same chain carbon atom leaves this with a positive charge, weakening the bonds of the backbone chain and thus leaving them vulnerable to attack by hydroxide, so-called **nucleophilic attack** (Fig. 6.2). It is only with the butyl ester that the hydrolysis rate is low enough for it to be used effectively as a medical tissue adhesive (presumably by providing a sufficiently polarizable source of electron density). The tensile strength and abrasion resistance of these materials is also poor, although some improvement might be expected with cross-linked systems or the addition of a filler.^[27] So, despite the clinical successes observed with, for example, six-monthly reapplications, usage has waned. However, as an adhesive for dry service it has its uses, and variants are used industrially for vibration-proofing nuts and bolts, for example.

•6.3 Polyurethane

Polyurethanes (6§4.9, 6§7.5) have also been much discussed in the context of fissure sealants. Isocyanates react with alcohols to produce a so-called urethane (Fig. 6.3). Clearly, with di-isocyanates and polyhydric alcohols, cross-linking with polymerization can occur, leading to a solid material. If water reacts with the isocyanate group, instant decarboxylation occurs to yield an amine and CO₂ (*i.e.* when R = H in Fig. 6.3). This reaction is used in the manufacture of polyurethane foam. The amine this forms can, however, then react with further isocyanate to form a substituted urea; again a cross-link or chain growth in the polymerization is possible.

An advantage of this system is therefore the elimination of surface adsorbed water, permitting the closer interaction of the polymer with tooth enamel. If it is only adsorbed water that is present, the small amount of gas produced probably just dissolves in the polymer. If there were larger quantities of water present either the urethane would be used up so that no little or no polymerization reaction is possible, or the CO₂ produced would appear as bubbles and compromise the strength of the interface. It is presumed that the reactive hydroxyl group could be on biological macromolecules, when some specific bonding is in theory possible, again grafting the polymer onto that substrate.

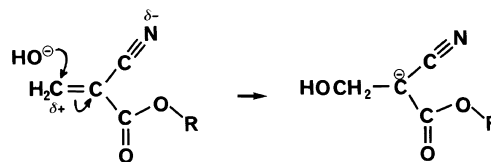


Fig. 6.1 Initiation of polymerization in cyanoacrylates. (R = methyl, ethyl, propyl, butyl, ... *etc.*) Water itself is also nucleophilic enough to initiate polymerization.

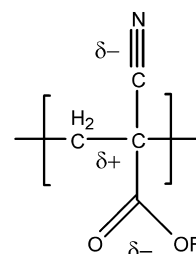


Fig. 6.2 The electron withdrawing power of the substituents leaves cyanoacrylate polymers open to nucleophilic attack.

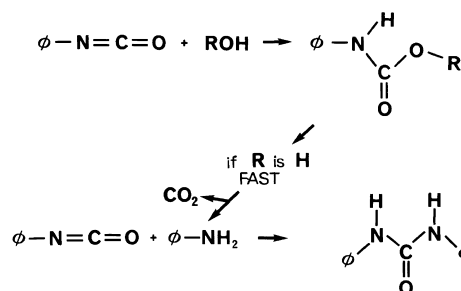


Fig. 6.3 Reactions of the urethane group. The CO₂ elimination occurs if pH > ~7.

Unfortunately, the materials which have been tested in this class proved unsuitable clinically, with very low retention rates. This may be linked to the ease with which urethanes are hydrolysed: commercial polymer products in many applications survive well if kept dry, but even high humidity can initiate a catastrophic depolymerization. Clearly, this behaviour was not taken into account in connection with the service conditions of fissure sealants: wet and warm. This would also apply to any specific bonds formed to proteins and other tissue elements.

●6.4 Bis-GMA

Pit and fissure sealant systems based on bis-GMA-methacrylate polymers (6§4.3) seem to be the most effective currently. Certainly, vinyl-type polymers are not capable of being hydrolysed – there is only a carbon-carbon backbone. But whether or not the methacrylate ester (see Fig. 6§4.4) linkage is hydrolysed at a clinically-significant rate is not known, although such a reaction is feasible. It would be a possible contributory factor to the long-term breakdown of both filled-resin restorations and sealants. However, it should also be remembered that free-radical polymerizations represent an equilibrium between monomer and polymer (5§2.7) so that bonds may break spontaneously and the chain ends be subject to entropic recoil and stress relaxation (7§2.2); slow degradation is then inevitable, especially if any leaching occurs. Nevertheless, no matter what type of material is used, etching remains essential for mechanical retention as covalent chemical bonds have not yet been achieved with the desired stability.

Light-activation offers most working time, but other systems based on chemical activation are successful. The use of glass ionomer cements as fissure sealants has been investigated, and indeed is showing much promise, and this may well achieve prominence in time, largely due to their good adhesion to enamel. The advantage may be that if ion mobility at the tooth surface causes a bond to be broken, it is capable of reforming, unlike typical coupling agents. One drawback is the poor penetration obtained because being a paste initially, with a high filler loading, the viscosity is very high. They therefore require some small sacrifice of tooth material to ensure retention.

§7. Fluoride

The wetting of enamel surfaces is no less important for topical fluoride applications to be successful than for bonding purposes. This is, in fact, of little difficulty as all systems are aqueous and water readily adsorbs to enamel, making the ion-exchange mechanisms required straightforward. The general aim of fluoridation is the replacement of a proportion of the hydroxy groups in hydroxyapatite by fluoride, on the grounds that fluorapatite is less soluble than hydroxyapatite, so reducing caries susceptibility. However, there is some doubt about the truth of this, with a number of side reactions occurring, such as the formation of calcium fluoride.

●7.1 Sodium fluoride

In a concentration of about 2% this was extensively used early on, but the ion-exchange ‘activity’ is relatively low and repeated applications are essential. The solution is at about pH 8.

●7.2 Stannous fluoride

This substance is said to be more effective, requiring fewer applications. The effect may be partly due to the formation of some tin salts on the surface, but it is mostly due to the low pH (~2!) of the solution, which gives it its unpleasant taste. This is due to the extensive and immediate hydrolysis of the salt:



Some dissolution of hydroxyapatite must follow in such an acid treatment. Further reactions in the solution result in the precipitation of various stannous oxide hydrates (which are of complicated and variable composition), leaving essentially a dilute solution of hydrofluoric acid. Oxidation of Sn^{II} to Sn^{IV} also occurs readily in contact with the oxygen of the air and in the light, so that the overall stability of the system is poor. Decreased activity in the fluoride-treatment sense is said to follow this. The solution should therefore be made freshly before use. So-called ‘stabilized’ solutions have been sold, but their composition and relative effectiveness is not presently known.

●7.3 APF

As indicated above, low pH seems to be advantageous for topical fluoride treatments, but it also necessarily causes dissolution of the enamel. The tendency to dissolve can be opposed by using a solution with a high concentration of phosphate to prevent this ion being removed from the surface. This cannot be done simply with stannous fluoride solutions because of the insolubility of tin phosphates. However, so-called 'Acidulated Phosphate Fluoride' (APF) materials incorporate fluoride ion in a solution of orthophosphoric acid. Such a solution may have a pH ~3. Commonly, these solutions are presented as a very viscous solution for easier manipulation. These are usually described as gels and to be thixotropic. However, they are not gels in the chemical sense, having no stable, three-dimensional network structure (see 7§8), but are simply solutions of substances such as sodium carboxymethylcellulose which in low concentration produce very high viscosity (27§2.3). Neither are they thixotropic, but are probably only plastic, showing a definite yield point (see 4§7.3).

The need for wetting by and a high penetrativity (§2.4) for these materials should be apparent, but it is a curious contradiction, apparently not recognized, that the treatment that is meant to deliver fluoride ions to caries-susceptible sites (which perhaps are the least accessible) is attempted with a material that has very poor penetration.

The rationale for the formulation of APF was apparently that the phosphate present would suppress the dissolution of the enamel, despite the low pH. Strangely, the original data show the opposite effect.^[28] Indeed, such phosphate is associated with very strange solubility behaviour.^[29]

●7.4 Surface energy effects

The incorporation of fluoride ions into the enamel surface results in a change in surface chemistry. Primarily, this exchanges hydrogen bonds of the type S-O-H...O= for S-F⁻...H-O- (where S is the solid substrate). Thus there will be strong interaction with water, as opposed to, say, carboxyl groups. This might make subsequent treatments with 'adhesive' materials more difficult or less successful. Certainly, anything that relies on the presence of hydroxide ions in the surface for coupling or other reactions must be compromised. Indeed, it is recognized that care has to be taken to avoid using fluoride-containing abrasive pastes prior to such procedures. Even so, reduction in surface energy has been cited as one reason for lower caries incidence by reducing the adhesion of plaque, although it does not necessarily follow that the surface energy falls. What is certain is that the nature of interactions will change.

This effect has to be carefully distinguished from that of the reduced solubility of tooth tissue as a result of fluoride treatment. It is believed that a common reaction is the formation of CaF₂ under normal conditions, and possibly other low-solubility substances. Fluorapatite, where the hydroxyl ion is substituted by fluoride ion does not form very readily except possibly at the very surface, or in the very long term through solution-mediated recrystallization. Even so, the net effect is believed to be an increased resistance to acid dissolution. Since this is not a matter directly of a surface energy effect (because of the primary facts of the relevant chemical equilibria), it cannot be claimed that dental caries – or even deliberate etching for restoration retention – is affected by other than a change in solubility or rate of dissolution.

This is not to say that there is no contribution at all from surface energy. Small crystals are more soluble than large ones, essentially because the larger **specific surface area** of small particles (area per unit mass) provides a greater driving force for dissolution, *i.e.* the lowering of the energy of the system on dissolution is greater. This is the underlying reason for the recrystallization of finely divided excess solid in a saturated solution to a few large crystals, given enough time. Related issues are discussed in connection with metal nucleation (11§2.2), grain growth (11§4.1), corrosion (13§6.3) and electrolytic polishing (20§5).

§8. Surfactants

Control of wetting is important in a number of areas, specifically when it is initially or ordinarily poor and needs to be much improved for a process to be effective. Examples are the wetting of wax patterns on being invested, and the pouring of hemihydrate slurries for casting models in elastomeric impressions.

●8.1 Oil and water

Water molecules interact so strongly with each other through the formation of hydrogen bonds that if

a non-polar molecule, such as a paraffin, is introduced into a body of water, the energy of the system is raised. This is because some hydrogen bonds are prevented from forming because the paraffin molecule is in the way. A second paraffin molecule would have the same effect. But if the two molecules were side by side there would be less disruption of hydrogen bonds than if they were separate. In effect, the introduction of a non-interacting molecule into water creates a small cavity. That cavity has a surface, so the total surface area of the water is increased, therefore the total surface energy is raised. Putting the two non-polar molecules together lowers the surface area of the cavity required to contain them. Even better, if the paraffin molecules were moved outside the body of water, the interface with the water is now minimized, therefore the energy of the system is minimized. This is what accounts for the spontaneous separation of oil and water.

•8.2 Amphiphiles

A molecule which is paraffin-like at one end and polar at the other presents an interesting problem in energy minimization. Clearly, the polar part would lower the energy of the system by being solvated, but the hydrocarbon part would be better separated from the water. The solution to this is to have the molecules arranged in **micelles**, near-spherical groups where all the polar parts are outside, interacting strongly with the water, while the non-polar parts are inside, gathered together (Fig. 8.1). Such molecules are called **amphiphilic** – hydrophilic at one end, hydrophobic at the other.^[30] Such micelles can take a variety of forms depending on concentration, but are typically spherical at modest values. Note that their formation is so energetically-favourable that the true solubility of such substances is ordinarily very low indeed. In other words, the concentration of fully-separated or isolated single molecules of an amphiphile in water is very small. Spherical micelles typically contain ~100 molecules, but depending on the compound and the conditions it may vary from a few to thousands.

If then a paraffin molecule is introduced, it would still raise the energy of the system if it were placed so as to be surrounded by water. But if it were placed inside a micelle, surrounded by the paraffinic tails of the amphiphilic molecules, no such disruption of water-water interactions occurs, except for that due to the small increase in the volume of the micelle (Fig. 8.2). It is therefore energetically favourable for the oil molecule to be surrounded by a coat of the amphiphile, not because of any significant interaction between the non-polar molecules but because disruption of polar interactions is avoided. Increasing the amount of oil in the system leads to small droplets, coated by the amphiphile, dispersed in the water. This action therefore stabilizes oil-in-water **emulsions**, and the action is said to be one of **solubilization** of the oil. However, this does not form a true solution, even after much agitation, and the result is probably best described as a **colloidal emulsion**. So long as there is sufficient amphiphile present, subdivision of the droplets increases the amphiphile-oil interfacial area, and thus lowers the overall energy.

•8.3 Detergents

Such amphiphilic molecules are the soaps and other detergents. Thus, sodium stearate is a typical soap: $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^- \text{Na}^+$ – the long paraffin tail is a very clear feature. There are several other types of detergent, mostly designed to be more “soluble” in water than soaps, and which in one way or another are designed to improve on the efficiency of the interactions. Such substances are therefore effective in **degreasing** surfaces prior to some treatment which depends on a clean substrate – such as bonding – when the use of organic solvents would be inappropriate.

There is one consequence of using such molecules which has wider implications. Any molecule which finds itself at the surface of the water will also be able to contribute to the energy minimization by sticking its tail out of the water – out of the surface.^[31] Thus, the surface of an aqueous solution of a detergent tends to be

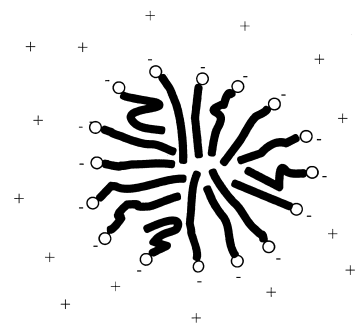


Fig. 8.1 A micelle of amphiphilic molecules.

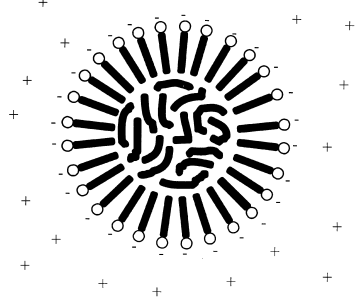


Fig. 8.2 The non-polar oil is in the lowest energy position surrounded by the amphiphile micelle.

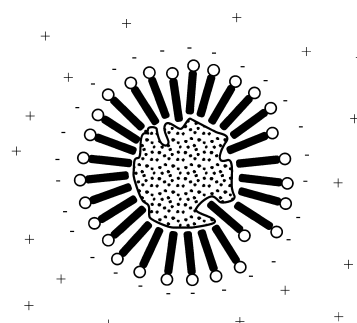


Fig. 8.3 Dirt is better suspended when the adsorbed surfactant presents a hydrophilic surface to the water.

a monolayer of the detergent molecules, ionic heads in the water – solvated, non-polar tails pointing out (Fig. 8.3). The water is thus covered by a low-energy layer. In other words, the surface tension of the liquid body is lowered. This means that on many surfaces the contact angle is reduced, even to zero. Detergent solutions therefore spread well. This wetting also applies to dirt, particulate contamination that may well be oily or otherwise poorly wetted by water. Consequently, such dirt is readily suspended in the aqueous phase and removed (Fig. 8.4). The detergents are broadly described as surface active agents or **surfactants**. Note that the properties of the water itself have not been changed by the presence of the detergent.

The lack of wetting and spreading of water and simple salt solutions on non-polar surfaces leads to the problem of air bubbles being trapped when plaster slurries are cast against hydrophobic impression materials (such as silicone rubbers, 7§6) or investment against wax casting patterns. In the latter case, a surfactant solution (commonly called a **debubbler**) is normally applied to the surface of the impression or pattern, and then dried in order to leave a film which will be wetted by the slurry (Fig. 8.5). That is, the wax or impression material itself is no longer ‘seen’ by the water.

●8.4 Non-ionic detergents

The basic type of general surfactants is ionic, that is, the molecule dissociates in solution into two ions. the charged amphiphilic part and, typically, a small ion. Soap (§8.3) is an **anionic** detergent; there are also **cationic** detergents. Increasingly now, **non-ionic detergents** are being used. These may be selected because they do not foam as much, are less toxic, or are not as strong in their action, so permitting a wider range of applications, particularly in biological contexts. A typical example group are the *n*-alkyl polyglycol ethers, $\text{CH}_3(\text{CH}_2)_{n-1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$. It can be seen that such a molecule remains amphiphilic: there are still the paraffinic and water-solvatable regions (*cf.* the behaviour of polyether impression materials, 7§5). Clearly, with this type of chemistry the balance between the hydrophilic and hydrophobic parts may be tuned by adjusting chain length, so enabling control of the properties.

§9. Wetting in Practice

Although a number of situations have been discussed above, there are some further aspects that need to be explored in order to assess the importance of wetting in dentistry. It is necessary to give some thought to the practicalities, that is, the actual situations in which a liquid is in contact with a solid.

●9.1 Types of context

Wetting situations for dentistry can be grouped into just four classes:

1. mixing, as of the liquid and powder components of cements, acrylic, plaster and silver amalgam;
2. penetration of small spaces, as in fissure sealants, bonding agents, solder and impression materials;
3. immersion;
4. prevention.

The first class depends much on mechanical intervention (Chap. 15), but while the second depends on the spontaneous movement of the three-phase line (TPL), and therefore in this sense depends on contact angle through the penetrativity (§2.4), there is generally required to be an excess of the liquid available so as to fill the spaces. Immersion speaks for itself, but it must be recognized that contact angle is then irrelevant.

Thus, there is no instance in dentistry where a small, metered droplet is placed on a surface with the specific intention that it spread spontaneously to cover that surface (that is, other than for experimental purposes). In all practical instances, an excess of the liquid is provided, mechanical intervention is common to spread it (*i.e.* with a implement of some kind, such as a spatula or brush) and, if necessary, excess is subsequently removed.

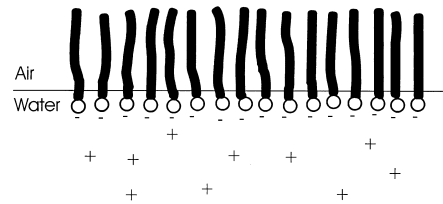


Fig. 8.4 The surface of the water carries a monolayer of the detergent molecules.

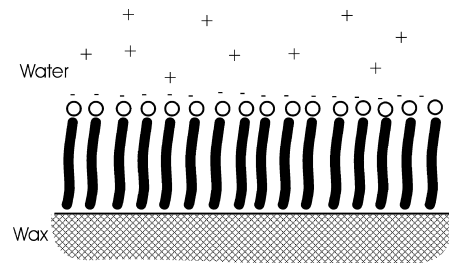


Fig. 8.5 Wax patterns and hydrophobic impression materials can be wetted when they are first coated with a surfactant.

Coating like this is in effect immersion. Examples include treating a wax pattern with surfactant solution, veneering porcelain-on-metal, silane treatment, and simply cleaning an object with a detergent solution, such as hands or hand instruments. Even if a small drop is used, such as of an adhesive or primer, spreading is secured by the approximation of the parts or the use of an implement, not through the action of unbalanced forces at the TPL. Contact angle as such, therefore, is again quite irrelevant as a concept or measure of goodness of wetting in such contexts, and the emphasis it is given misplaced. All that is required, in fact, is that the work of adhesion, W_r (§1.7) be non-zero for there to be an interaction between the two components (even if this can be expressed in terms of θ ; equation 1.9). Of course, it might be argued that in some situations the larger is W_r the better, such as when there is a change of state of the liquid to solid and retention is important. However, the key here is that a liquid with any value of contact angle $\theta < 180^\circ$ on a given substrate can fully wet that surface when it is present in excess: molecular-level contact is obtained. In other words, wetting occurs of any body in any liquid on immersion irrespective of contact angle, provided only that it is $< 180^\circ$, and it is not a function of substrate surface energy or liquid surface tension – only the strength of the interaction is affected, and that has no bearing on subsequent chemistry (such as for silanes). This means that, further to the discussion of §2.5, we have to be very careful in what we mean when we talk about wetting.

•9.2 Bubbles

Even so, there is a circumstance in the context of immersion where contact angle is important. When excess liquid is applied, such as casting an investment slurry around a pattern, or instruments are placed in an ultrasonic bath, air bubbles may be stuck to the surface. The analysis of this situation (Fig. 9.1), is exactly the same as for the droplet (Fig. 1.8) except that liquid and vapour are interchanged. It is necessary to bear in mind that contact angle is measured through the liquid: the Young equation (1.3) still holds, which can be seen from a consideration of the force vectors – there is symmetry. This means that for $\theta > 0$, such bubbles are stable, and unless the air dissolves (which would take a relatively long time), mechanical means would be required to dislodge them. Remembering that the contact angle will be large on low-energy surfaces such as oily or greasy contaminants, bubbles will tend to stick in such areas, hence the problems with investments on wax patterns (§8.3).

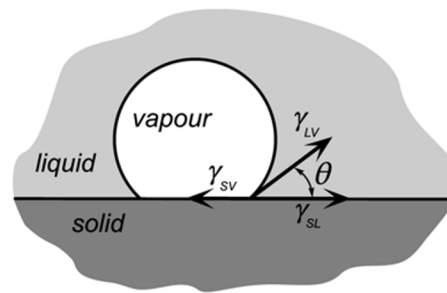


Fig. 9.1 Force vectors acting at the three-phase line of a bubble on an immersed solid surface.

One can understand the system through a small thought experiment. Consider such a bubble at equilibrium (Fig. 9.1) in, say, pure water. Now lower the surface tension of the liquid, *i.e.* the value of γ_{lv} , such as by adding an alcohol or detergent, which then diffuses to a uniform concentration, so that the forces now acting tend to move the TPL under the bubble, reducing the contact area, A_{sv} . This process continues with each addition. When the critical value is reached (Fig. 1.10), $\theta = 0$ – and the bubble detaches from the surface. This can be seen quite clearly to occur in a physical experiment of this type: adhering bubbles spontaneously separate from the surface.

•9.3 Oil

A similar analysis applies when a surface is coated with oil or grease (Fig. 9.2), with the exception now that one has to recognize the existence of two contact angles, through the oil (θ_o) and through the water (θ_w) (depending on one's point of view), but these are, of course, complementary angles: $\theta_o + \theta_w = 180^\circ$, and their cosines have equal magnitudes but opposite signs: $\cos(180 - \theta) = -\cos(\theta)$ (Fig. 1.12), both indicating the net force balance – there is no contradiction. Now, if the same kind of thought experiment as in §9.2 is conducted, lowering the interfacial tension γ_{ow} by the addition of a detergent (with an effect as in Fig. 8.5), so that θ_w decreases, then the TPL again tends to move under the drop, with the contact area A_{so} decreasing, ultimately leading to the release of the droplet from the surface. Simple observation shows that this occurs, although it might not be very rapid because it involves the flow of the oil or grease, whose viscosity will

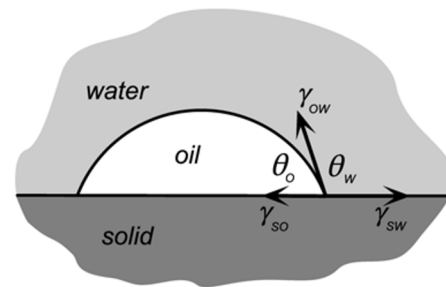


Fig. 9.2 Force vectors acting at the three-phase line of an oil droplet on an immersed solid surface.

play its part. Of course, raising the temperature must lower that viscosity and speed up the process, regardless of the changes that must occur in all interfacial energies: hot water is better for washing the dishes.

A similar situation arises when taking impressions of wet tooth surfaces: the TPL involves water (or saliva), tooth enamel and the impression material. Broadly, the system will look like that of Fig. 9.1 (with the impression material in the place of the bubble) because the wetting by the saliva is better. It is generally thought that this is problematic, especially for silicones (7§6) so that consequentially ‘hydrophilic’ materials have been produced. However, it is clear that the wetting must be substantially better than by water for spreading to occur (even if the spreading force resulting from the lack of equilibrium was enough, given the high viscosity of the material). That is, on a wet surface the water or saliva is still favoured in terms of contact angle (Fig. 9.3). While the aqueous liquid may be displaced, it is clear that this must be a mechanical action rather than a physical wetting and spreading process. Indeed, detail would not be reproduced when the impression material may ride over liquid in depressions (boundary later separation may be facilitated by that liquid – see 23§10.2). Thus, any suggestion that ‘hydrophilic’ silicone materials can displace water because of that property is in error. Nevertheless, the pouring of the model (*i.e.* dental stone slurry) in that material may be better. Such considerations apply to all impression materials, but for aqueous systems such as alginate and agar (7§8, 7§9) it is clear that they cannot be much better than saliva, if at all. The consequence then is that the contact angle is around 90° , and this must represent the limit for any attempt to improve the hydrophilicity. That is, no better than on a dry hydrophilic surface, if the behaviour shown in Fig. 9.3 (top) is indicative. The point here is that hydrophilicity is irrelevant: affinity for the substrate surface is what matters. Only if this is higher than that of water can active water displacement possibly occur. Active spreading still remains a problem if the viscosity is high, and impossible if the material has an appreciable yield point (*i.e.* plastic, 4§7.3).

●9.4 Other geometries

As has been stressed in §1, contact angle is not a material property in any sense whatsoever but arises from the geometrical requirements dictated by the energy minimization (equation 1.2), or equivalently the force balance (equation 1.4). It is generally defined in the context of an isolated drop on a plane substrate, which despite its common use for teaching and experimental purposes is a special case – very few practical examples are encountered. The case of a meniscus in a circular capillary was found to satisfy the exact same condition of the Young contact angle (§2.2). In these two special cases the liquid surface is a spherical cap. There are other cases where the gravity-free solution can be easily derived and shown to have the same expression (equation 1.3) for a simple surface shape, for example the “semi-infinite” filling between infinite parallel plates (Fig. 9.4). Here the constancy of curvature arises from the circular section of the liquid surface in the plane normal to the plates and the zero curvature in the direction along the meniscus; it is cylindrical.

The constancy of curvature is a strong requirement: as explained above: if it is not, the Laplace pressure differences must cause flow to occur until equilibrium is reached (bearing in mind that we have, for convenience, ignored gravity). We found this for a non-wetting drop pressed between two plates (Fig. 2.11). Thus, in the case, for example, of a droplet on a rod (Fig. 9.5), that droplet might (simplistically) be assumed to have a spherical surface. But this would then mean that the TPL does not show a fixed value of θ along its length

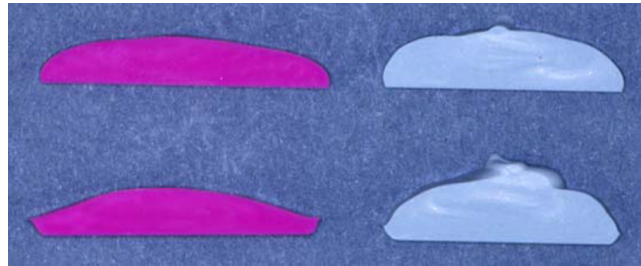


Fig. 9.3 Diametral sections of blobs of ‘hydrophilic’ silicone impression materials extruded onto (top) a dry hydrophilic surface, and (bottom) the same surface with a film of water present. The difference in contact angle is plain. Photo: Tom Smethurst

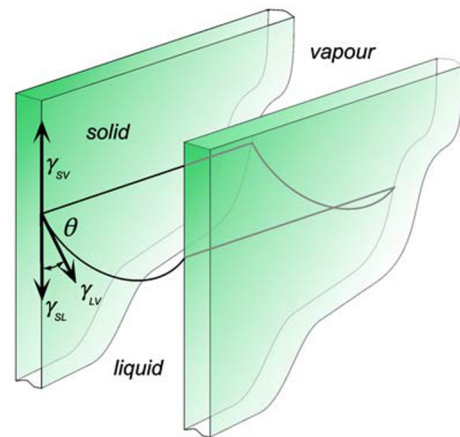


Fig. 9.4 Force vectors acting at the three-phase line of a liquid between infinite parallel plates.

according to the Young equation, varying from a maximum at point **a** to a minimum at point **b**, for the circumstances drawn here. This, then, is a contradiction: it cannot be (if the TPL is free to move), and so the equilibrium surface cannot be exactly spherical. Thus, in general (see box, 8§3.3), sphericity of the droplet surface is not required. There are many complex surfaces of constant curvature. There is a further difficulty.

●9.5 Non-homogeneity of surface energy

We have been assuming a number of conditions (§1.4) to keep the discussion simple, although we have noted briefly the effect of contamination (§2.7). However, most of the materials used in dentistry are composite, *i.e.*, of more than one phase, or polycrystalline, such as metals. Clearly, the surface energy can be expected to vary between phases in any system, but even the mosaic of crystal sections presented at metal surfaces (Fig. 1§2.12) have different surface energies because of the differing arrangements of atoms, as shown for example by reactivity variation (Fig. 12§2.5) and the variety of crystal growth habits (2§7.5). Indeed, even grain boundaries are different enough to matter here, being higher energy because they are disordered.

In principle, it is easy to deal with heterogeneity of this kind in calculating the energy balance (equation 1.2) by taking the area-weighted arithmetic mean (a mixture rule) and inserting this, much as a modified value was used for a rough surface (§1.9). Unfortunately, this ignores the fact that the force balance (§1.5) must also be satisfied at every point along the TPL. While these views are equivalent for homogeneous systems, it clearly is a bad assumption for polyphase materials.^[32] Essentially, if the contact angles differ but are fixed on each phase, there is a discontinuity in the liquid surface at the boundary, which is impossible. The shape of the surface in the vicinity of the boundary thus becomes very complex to maintain the constancy of the Laplace pressure; contact angle must vary smoothly and continuously around the TPL. Sphericity, again, is impossible. There is yet another difficulty.

●9.6 Pinning

In discussing roughness (§1.9) we ignored the local variation of contact angle in exactly analogous fashion: the total interfacial areas were calculated for the energy balance, but the local requirement for force balance was ignored. Obviously, local contact angle varies on a rough surface (Fig. 2.14), and again the actual liquid surface shape near the TPL must be very complex. The problem that emerges may be seen from Fig. 9.6. A very small displacement of the TPL causes the contact angle to vary depending whether it is an “uphill” (θ_u) or “downhill” (θ_d) location. Assuming that the true value lies between them, the one is being driven forwards, the other backwards. Depending on how steep the surface is locally, and especially if it is a sharp roughness, this can result in a considerable force being required to cause the TPL to advance or retreat, according to net energy balance demands. The roughness can be at a very small scale indeed, and not necessarily visible, for this to operate. Effectively, these surface tension-derived forces may not be great enough to overcome the effective activation energy barrier for movement, and the TPL gets stuck: it is said to be **pinning**. The same behaviour occurs on polyphase surfaces, even if atomically smooth. Contamination, such as by a minute amount of grease, or microscopic particles, have the same effect. It can readily be seen by the highly asymmetric shape of raindrops on windows, and their jerky, irregular movement. However, on an oiled surface, which is molecularly smooth (§1.10), the droplets are more nearly spherical and move steadily. In fact, if it were not for pinning, a droplet on a plane surface would immediately start to roll off if that surface were tilted at all.

This behaviour is quite general, whether due to roughness, heterogeneity or contamination, so general that there are many reports of “advancing” and “retreating” angles (Fig. 9.7), a behaviour known as **hysteresis**.^[33]

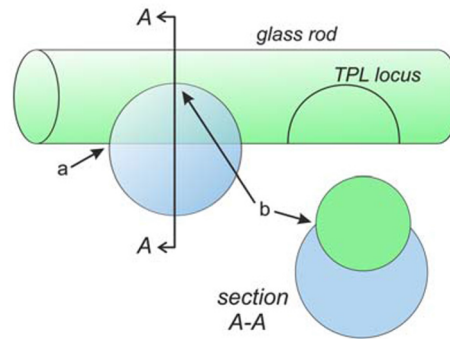


Fig. 9.5 A droplet on a rod: the contact angles at **a** and **b** clearly would be different if the droplet had spherical segment surface.

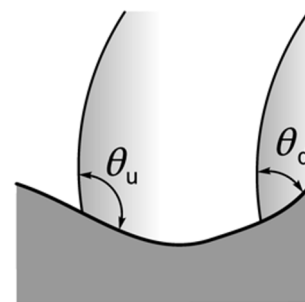


Fig. 9.6 A droplet on a rough surface would show locally-varying contact angle over microscopic displacements if the droplet has a perfectly spherical surface.

Unfortunately, it is often not recognized that such angles are artefacts and do not represent a clear thermodynamic property of the system.^[34] However, the behaviour of a pinned TPL is such that it appears to have a (line) shear strength, with the same dimensions and therefore units as surface tension (N/m) – sometimes (badly) described as ‘friction’. If the force acting is great enough, whether through the effects of gravity, intervention through some instrument or tool, a blast of air, or other agent, then it will move, otherwise not. This is therefore a **metastable** state, unaffected by small (enough) perturbations. Thus, the mere fact of a favourable contact angle under ideal conditions cannot be taken to imply that wetting (*i.e.* spreading) will occur spontaneously. The remarks at §1.11 must then be extended to take into account these other interferences. It is this behaviour that for all $\theta > 0^\circ$ causes water droplets to cling to even vertical ‘smooth’ surfaces, and even to leave behind a thin film, against which, of course, the contact angle is zero. Again, were the activation energy for movement zero, which is the same as saying that the shear strength of the TPL is zero, *i.e.* no pinning, all droplets of all liquids would be shed immediately. (One can measure the **roll-off** or **slide angle** of the droplet on the substrate for such systems as a measure of hydrophobicity which takes into account pinning. Effectively, it is a measure of the component of the weight of the droplet in the plane.) Likewise, one may observe that an evaporating droplet may not see the contact area shrink (Fig. 9.8) until the force vector imbalance becomes too great, when the TPL may jump substantially. In practical terms, for dentistry, steps must be taken to intervene to obtain the desired outcome in many systems, whether this be the removal of drops (such as by a towel or absorbent paper, where by implication wetting and capillarity are favourable, 27§2.1), or the full wetting of a surface by spreading.

By symmetry, similar remarks apply for bubbles in liquids (§9.2). Pinning can be seen clearly enough in carbonated drinks in a glass. It complicates the pouring of models and casting investments, and is another reason why the vibration for shear-thinning (4§7.9) is beneficial, along with the use of ‘debubblizer’ (§8.3): providing the activation energy for TPL movement and thus the dislodging of bubbles. Likewise, oil droplets may need some encouragement to move, even with detergent.

●9.7 Drying for bonding

For resin-bonding of restorations (§6), especially to dentine, there is considerable debate as to how wet or dry the substrate should be, and what other conditions are required. Part of the debate concerns the wetting of the prepared tooth surface by the bonding agents, and their penetration into the etched surface and demineralized collagen. As has been discussed above (§2.3, §2.4), capillarity and penetration depend in part on the surface tension of the applied material and the contact angle exhibited on the substrate.

One means of achieving better wetting is to include in the applied mixture substances of low surface tension, such as ethanol or acetone, where a small proportion can mean a large drop in the surface tension of the mixture (Fig. 9.9).^{[35][36]} Thus, water absorbed or desorbed from the substrate does not interfere substantially with the treatment, at least, while such substances are present. The lower viscosity caused by the presence of such diluents also assists the spreading and penetration of the bonding agent, although,

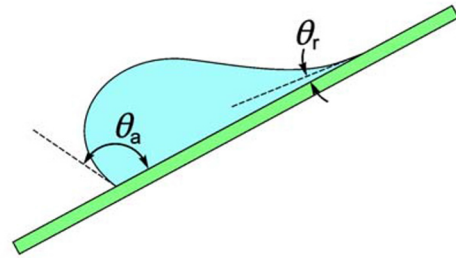


Fig. 9.7 Contact angles observed on a pinned drop: a “advancing”, r “retreating”. They may be grossly different, as shown here, and observed commonly for raindrops on window panes.

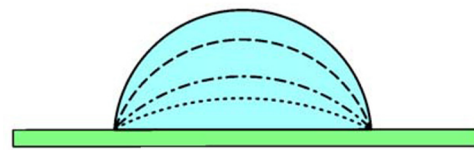


Fig. 9.8 A drying droplet may not show the expected retreating TPL but keep a nearly constant outline for some time, because of pinning.

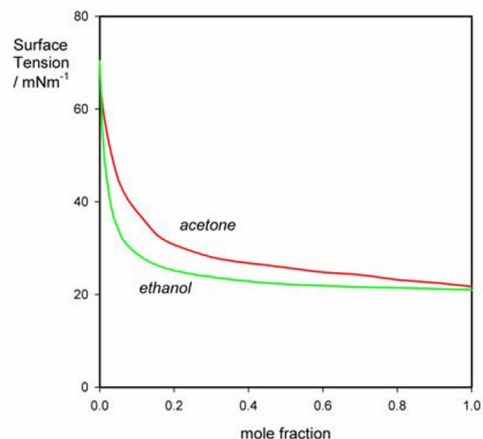


Fig. 9.9 Small proportions of water-miscible solvents such as acetone and ethanol reduce the surface tension of the mixture with water substantially, giving better wetting and spreading.

of course they should not remain and steps are taken to evaporate then, usually just by an air stream. The problem then is that any water in solution from the substrate tends to be left behind, incorporated as droplets in the resin, its boiling point being higher, and therefore its vapour pressure lower (see Clausius-Clapeyron equation, 5§2.1).

In this context, it has sometimes been claimed that acetone is a “drying” agent, and that this is because it forms an azeotropic mixture with water, in essence claiming that the evaporation of the acetone ‘assists’ or ‘encourages’ the evaporation of the water. Neither of these claims is true.

An **azeotrope** is a “constant-boiling” mixture, meaning that the composition of the vapour is the same as that of the liquid. This means that there is a minimum, called the **azeotropic point**, in the **dew curve** (where liquid would first appear on cooling the mixed vapours), and this is where it coincides with the **bubble curve** (where bubbles would first appear on heating, assuming nucleation), which is also at a minimum (Fig. 9.10). The behaviour can be traced using an isothermal tie-line in the liquid-vapour field on the left-hand side of the azeotropic point: the composition of the vapour is richer in ethanol than the liquid. On the other hand, if the initial mixture has more than this proportion of ethanol, then in complementary fashion the vapour is of a lower proportion of ethanol than the original liquid.

However, the phase diagrams are, of course, maps of closed systems at equilibrium. In a typical distillation process, which is ‘open’, the vapour is condensed and then effectively repeatedly redistilled, meaning that from the left, the ethanol concentration in the successively condensed liquid would rise, but only to approach, not exceed, the azeotropic composition. (A stepwise sequence similar to that shown in Fig. 12§1.8.) Conversely, from the right, it would fall. Thus, in this sense, then, a small quantity of water would be boiled off from an excess of ethanol because it is an azeotropic system. Distillation of such a high-ethanol liquid would, in an equilibrium system, approach the azeotropic point from the right.

Even so, this only applies at the temperatures attained during distillation at atmospheric pressure (1 bar). As the total vapour pressure is lowered, that is, for equilibration occurring at lower temperatures, the azeotropic point moves rightward and has vanished by 66 mbar, when the b.p. for ethanol is around 21 °C and that for water is about 38 °C. At open-mouth temperature, therefore, it cannot be expected that even if a large amount of initially pure ethanol were used (*i.e.* no water), effective drying of water adsorbed on the substrate could not occur: no preferential ‘encouraged’ evaporation of water then occurs, even with a jet of air to keep the sum of the vapour pressures low in the vicinity of the liquid surface (which of course cools the system even more, 30§5). Such behaviour is also affected by the other substances present.

For acetone-water, however, there is no azeotrope at 1 bar (Fig. 9.11), hence the ‘not true’ remark above, although it is known that at higher pressures ($> \sim 1.4$ bar) such behaviour does occur. Thus, the equilibrium vapour is always richer in acetone, and water gets left behind preferentially. In fact, boiling behaviour is altogether irrelevant in considering the effects of solvents on water in the present context of evaporation at, say, 20 ~ 37 °C; azeotropes are of no value here. Indeed, the equilibrium phase diagrams are of no help at all (remembering that they are thermodynamic statements). What are important are the relevant rates of evaporation.

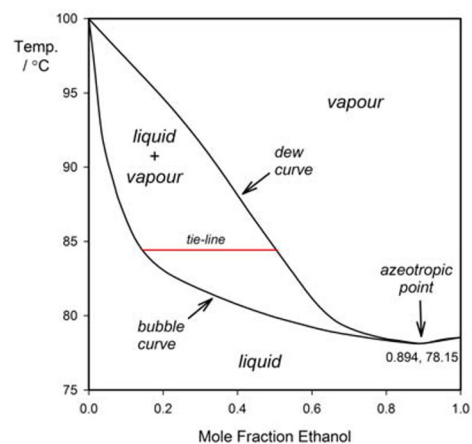


Fig. 9.10 Partial phase diagram for ethanol-water at 1 bar (see Fig. 2§12.1 for the lower-temperature portion). (Above the azeotropic point the two curves are too close together to resolve properly in this diagram, but there is a gap. The behaviour is parallel to that on the left-hand, low-ethanol side.)

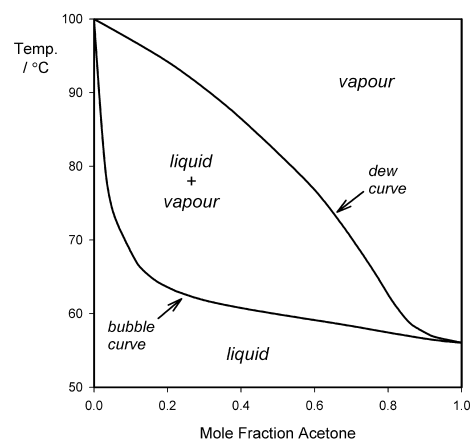


Fig. 9.11 Phase diagram for acetone-water at 1 bar.

Unfortunately, it is not just a simple matter of comparing vapour pressure curves calculated from the Clausius-Clapeyron equation, it requires a bit more elaboration because in such systems, where there is marked hydrogen bonding, 'ideal' behaviour (*i.e.* following **Raoult's Law** for the sum of vapour pressures) does not occur. The activities of the components in the liquid vary in non-independent fashion, not strictly proportional to concentration, hence their vapour pressures are not proportional either. Thus the **partition** (§3.1) between liquid and vapour phases needs to be examined, but also the kinetics of escape need to be considered since it is not a closed system in practice. This partition is portrayed in so-called **x-y** vapour-liquid equilibrium diagrams. Those for acetone-water and ethanol-water at 35 °C are shown in Fig. 9.12 (they do not vary much with modest changes of temperature). Here it is clear that the vapour pressures of the acetone and ethanol are both much greater than would be expected, which suggests that they would be readily lost from an open system, leaving the water concentrated in the liquid. Indeed, it is known that the lower boiling component, in general, has the greater escaping tendency, *i.e.* evaporates faster. This can be seen clearly for ethanol-water (Fig. 9.13).^{[37][38]}

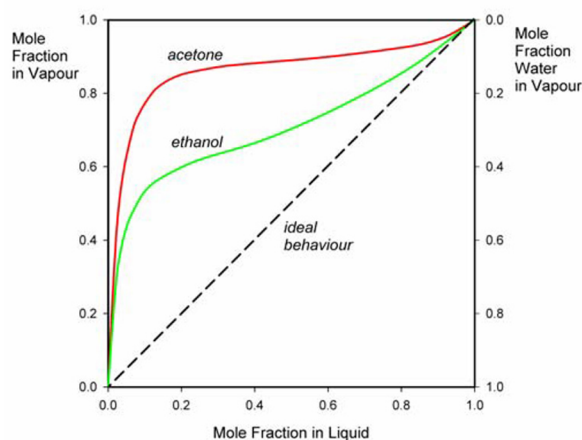


Fig. 9.12 Vapour-liquid equilibrium diagrams for acetone-water and ethanol-water at 35 °C. Note the complementary values for the mole fraction of water in the vapour, as read from the right-hand ordinate. For an azeotrope, the curve crosses the ideal line; here, neither does, so water cannot be 'driven off'.

It is clear from that figure that the ethanol is lost steadily until it has disappeared completely before 14 s have elapsed, well before the water itself had evaporated. Water, however, was initially absorbed from the air before its evaporation commenced. In fact, it is a common observation that if a film on, say, a glass surface of some such pure and initially water-free solvent is allowed to evaporate, tiny droplets of water remain; there is no "drying" effect, but on the contrary, water is deposited. The same can be expected to occur for acetone, only more strongly. This simple demonstration is enough to negate the wishful thinking. In fact, water absorption in the high humidity of the mouth can be expected to occur far more rapidly as well, compounding the problem. Thus, it is not a meaningful treatment to wash a surface to be bonded with acetone (or any similar solvent) and let it dry naturally. In fact, it is very difficult to keep such solvents water-free: mere exposure of the contents of the bottle to the air is enough for water to be absorbed (at any non-zero humidity). In any case, absolutely dry ethanol and acetone are expensive, but clearly quite pointless in the context.

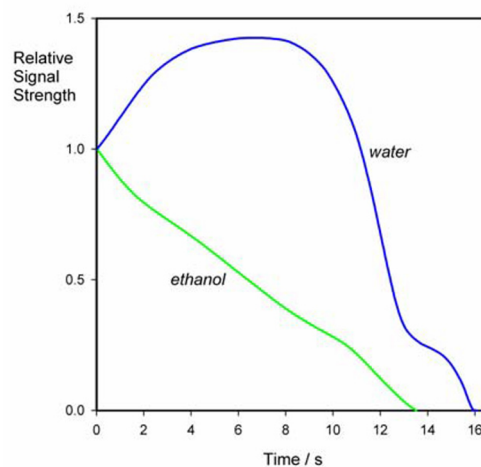


Fig. 9.13 An evaporation experiment for a 50 µL drop of 99% ethanol-water in air at 50 %RH, 25 °C and 1 bar, using an "IR microscope".

However, the avidity of such hydrophilic solvents for water is such that if one is placed in excess on a wet substrate (such as dentine), water will migrate – partition – from the substrate into the bulk of the solvent, a diffusive process.⁹ If then, before it is able to evaporate, it is removed in bulk, as liquid, by blotting or being displaced by a blast of air (that is, not allowing much evaporation to occur), then that water will have been at least partially removed. This, then, is a dilution mechanism of relative dehydration. Indeed, 99% ethanol is sold

⁹ A similar process is used in histology for dehydrating tissue, using 'ascending' concentrations of ethanol, from 30 to 100%, with the bulk simply decanted after each step. The sequence is used to avoid osmotic distortion of the tissue, but it takes time, 15 min ~ 24 h per step, because the partitioning is a diffusive process.

for just this purpose as a dental product. Of course, if the hydrophilic solvent is present in a prepolymer resin mixture, water will be absorbed in the same way, but without the means of removal, as mentioned above.

It should also be recognized that such solvents will also migrate by diffusion into the substrate dentine. Apart from any potential biological effects, this would mean that complete evaporation is not immediately possible. Remnant solvent diffusing back out could be involved at the interface with the bonding agent and also the resin.

●9.8 Marangoni effects

Solvents such as acetone and ethanol are sometimes said to be “water chasers” and to “displace” fluids in dentinal tubules and the water suspending the collagen fibrils exposed by acid-etching. This is a misinterpretation at best. The primary question would be one of to where such fluid could be displaced, ignoring miscibility: there is no space for this to occur, and quite obviously such water does not get ‘ejected’ from the system, like oil (§9.3). As indicated above, the water would be dissolved in the solvent, at the same time as the solvent dissolves in the water, and the mixture then occupies the whole space. Bulk removal would leave a remnant of the mixture in the collagen, tubules and the etched topography, from where evaporation would result in the same outcome as above: loss of the more volatile component first, then the water, more slowly.

This kind of remark may arise from observations of what are called **Marangoni effects**, which can indeed produce strange behaviour, due to surface tension gradients in imperfectly mixed systems. Noticing the large surface tension difference between water and solvent (Fig. 9.9), it can be seen that bringing the two liquids together will result in a large mismatch at the junction surface. Accordingly, there will be dramatic movements of the liquids because of the imbalanced forces, the water tending to be pulled back by its greater surface tension. The values change continuously as they each diffuse into the other (which occurs quickly), with corresponding continued movements, until equilibrium is attained at uniform composition. However, this can only occur in an open system with a free surface containing the liquid junction. Nothing like this can occur in a closed tubule or etch pit: the water has nowhere to go.

Of course, if solvent is evaporating unevenly from the surface of a mixture with water, then the imbalanced forces will again cause visible movements, but tending to concentrate the water locally rather than displacing it from the site of concern. This is the reason for the phenomenon of “tears of wine”.^[39] Alcohol solutions wet glass better than water – the contact angle is smaller – so they tend to climb higher up the side of the glass. However, the rapid change of concentration by the preferential evaporation of the alcohol from the thin film (Fig. 9.12) leave a liquid with higher surface tension, that therefore ‘rounds up’ into tears which then fall back down into the bulk liquid. Similar dramatic movements can be observed on a powder-sprinkled water surface, or one with scattered oil droplets: adding a drop of detergent or an alcohol, with the concomitant low surface tension, causes the particles or oil to rapidly withdraw from that point, as the surface area of the high surface tension pure water is minimized.

●9.9 Cassie’s Law

At §9.5, mention was made of the effect of non-homogeneity of surface energy. We can expand on this by extending equation 1.2 for a drop on a plane composite surface with solid phases s1 and s2:

$$E_{\text{TOT}} = A_{s1v}\phi_1\gamma_{s1v} + A_{s1l}\phi_1\gamma_{s1l} + A_{s2v}\phi_2\gamma_{s2v} + A_{s2l}\phi_2\gamma_{s2l} + A_{lv}\gamma_{lv} \quad (9.1)$$

where ϕ is the area fraction of the phase ($\Sigma\phi_i = 1$), and which after the usual manipulation reduces to:

$$\begin{aligned} \cos\theta_c &= \phi_1 \frac{(\gamma_{s1v} - \gamma_{s1l})}{\gamma_{lv}} + \phi_2 \frac{(\gamma_{s2v} - \gamma_{s2l})}{\gamma_{lv}} \\ &= \phi_1 \cos\theta_1 + \phi_2 \cos\theta_2 \end{aligned} \quad (9.2)$$

This is known as **Cassie’s Law**,^[40] which is a type of mixture rule (*cf.* 6§2.1, 6§2.6). (Obviously, this does not depend on the shape, size or distribution of the second phase in the first.) It has the obvious extension for more than two phases, and for the roughness(es), if any, of the individual phases as at equation 1.18. However, this can only be an approximation because, as noted above, the liquid-vapour surface cannot be exactly spherical everywhere, or – equivalently – the TPL cannot be circular, for a continuously varying value of contact angle. Nevertheless, it appears to be a workable approximation, assuming that the scale of the structure, the grain size of the various solid phases, is small in comparison with the size of the droplet (which is the usual condition for all such mixture rules).

If the second phase is in fact vapour (*i.e.* the droplet lies on a porous or highly irregular surface; Fig. 2.14), where the contact angle is taken to be 180° ,¹⁰

$$\begin{aligned}\cos\theta_c &= \phi_1 \cos\theta_1 + \phi_2(-1) \\ &= \phi_1 \cos\theta_1 + (1-\phi_1)(-1) \quad (9.3) \\ &= \phi_1(\cos\theta_1 + 1) - 1\end{aligned}$$

What this means is that if the effective (solid) surface area of the porous body is small, the apparent contact angle can be driven to near 180° even if θ_1 corresponds to reasonable wetting (Fig. 9.14).^[41] Thus, going further than the conclusions of §1.9, highly-sculptured surfaces can exhibit very high apparent (*i.e.* viewed macroscopically) contact angles^[42] because the geometry prevents spreading, despite apparently adequate ‘flat surface’ contact angles. This seemingly paradoxical behaviour – superhydrophobicity – can be seen in many contexts: droplets of water may not soak into paper towels, or will just sit on many other fabrics, even without special treatment, and in particular mixing liquids on powders may not immediately soak in (Fig. 9.15) (similar effects can be seen with raindrops in the dust). However, such systems may only be metastable, because once spreading starts (whether by some diffusive process or pinning being overcome by an external force), the wetted system does not undo – it is not a reversible process.

Now, a comparison between the ‘Wenzel’ behaviour on a rough surface (§1.9) (which involves wetting all of the enclosed surface) and the superhydrophobic Cassie Law effect shows that the critical value for the contact angle, when the energy minimization for the two equations (1.14, 9.3) gives the same apparent contact angle, is given by:

$$\cos\theta_{\text{crit}} = -\frac{1-\phi_1}{r-\phi_1} \quad (9.4)$$

In other words, the superhydrophobic behaviour is shown when the flat surface value, θ , gives a Cassie value greater than this:

$$\cos\theta_c < \cos\theta_{\text{crit}} ; \theta_c > \theta_{\text{crit}} \quad (9.5)$$

This is shown in Fig. 9.15, where for various values of the roughness factor, r , the critical value is plotted on top of the contours of Fig. 9.13.

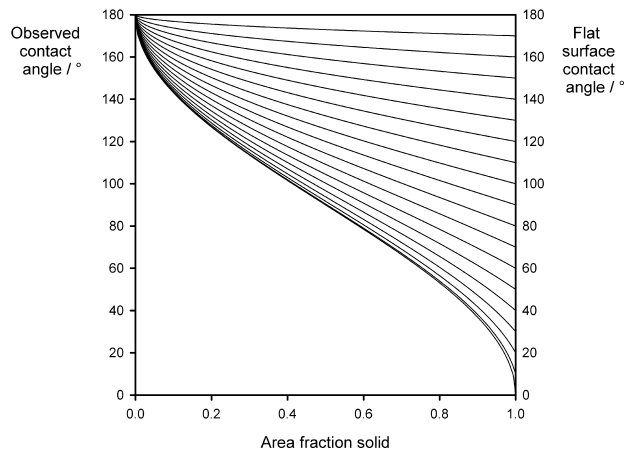


Fig. 9.14 The apparent contact angle of a liquid on a porous or highly-sculptured surface. First choose the line for the contact angle that the liquid gives on a flat surface (right-hand ordinate scale), then read off the observed contact angle for the given area fraction being wetted. Note that even well-wetting systems appear able to be made ‘superhydrophobic’.

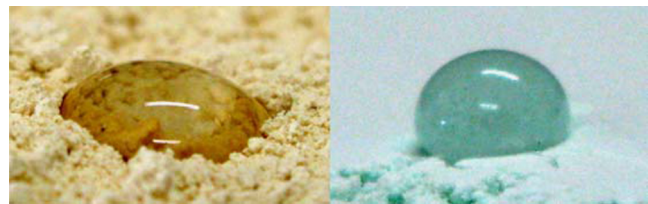


Fig. 9.15 Droplets may rest on the rough surface of a powder even if wetting is expected. Left: water on dental stone; right: water on alginate impression powder.

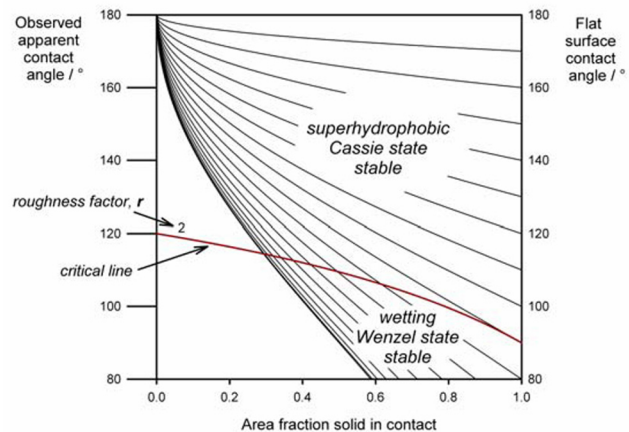


Fig. 9.16 The upper half of the graph of Fig. 9.14 with the critical angle of equation 9.4 plotted for roughness factor 2. Above the critical line, the drop rests on the roughness; below it and the whole surface inside the contact circle TPL is wetted.

¹⁰ This is an approximation as the work of separation of a gas is not zero in the sense of Fig. 1.4; there must still be intermolecular van der Waals forces to overcome. Nevertheless, as vapour densities are typically very low in comparison with solids and liquids, at ordinary temperatures and pressures, the approximation is good enough for the present purposes.

We can try a thought experiment to see how this works. Consider a droplet being lowered gently onto the rough surface with, say, roughness factor 2 (Fig. 9.16). It is necessary to trace along the contour for the appropriate “flat surface” contact angle (right-hand axis labels) from the $(0, 180^\circ)$ point (top left-hand corner), which line defines the system in hand. The initial contact is with very little solid, so ϕ_i is small, and this therefore corresponds to the superhydrophobic Cassie state. As the droplet is lowered, the contact area fraction will increase to the actual value for the substrate. (Remember that we start with a spherical droplet, and any contact is of zero area. Distortion to a spherical segment, lens-like shape is required to obtain increasing contact area – work has to be done in departing from the spherical shape, §1.1. Gravity provides the driving force for this.) If this point now lies above the critical line, it will be stable in that condition. If it is not, and it has crossed to the other side, the liquid is obliged to wet the whole of the roughness inside the contact circle (assuming that bubbles can escape).

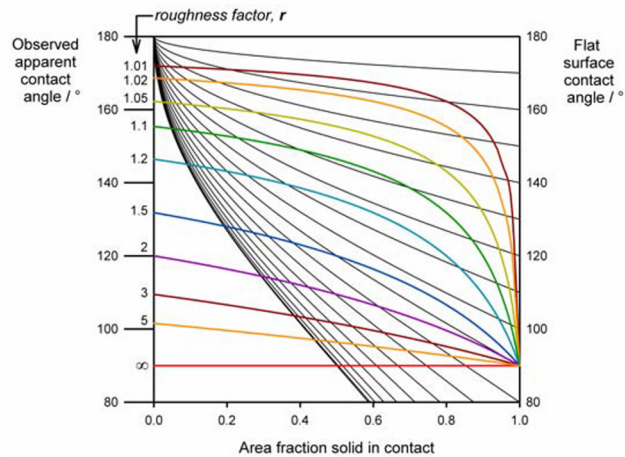


Fig. 9.17 Critical line variation with roughness factor. Very small contact areas on even low-roughness surfaces can allow metastable ‘superhydrophobic’ behaviour to be observed.

The effect of varying roughness can now be seen in Fig. 9.17: identify the flat surface contact angle to choose the correct line, determine the area in contact, and examine that point with respect to the critical line for the relevant roughness.

However, if there is any pinning – which generally seems inescapable – a metastable superhydrophobic state may easily be attained, even to the extent of falling below the $r = \infty$ line, where thermodynamically it is disallowed without that restraint on spreading. In this context, the effect of gravity matters, as the weight of large drops may force the contact area to be large enough to cross the critical line, while very small drops may survive, at least for a while. (An extreme example of this is shown by mercury porosimetry: the liquid can be pumped into any connected porosity in any material against the effects of surface tension by a sufficiently large external pressure.)

In dentistry, such behaviour is frequently seen when powder-liquid systems have to be mixed. The first contact may result in a powder-covered droplet that does not get absorbed by the mass, or the liquid simply sitting on the powder (Fig. 9.15), until some mechanical intervention disturbs the metastable state of the system or reaction changes its description. Such effects are possibly part of the process described in §2.6.

●9.10 Denture base retention

A subject in which wetting behaviour is of some interest is that of the retention of acrylic (PMMA) full denture bases. It is, of course, true that were there to be no wetting, no force would be needed to be applied to separate the denture from saliva and there would be no retention (Fig. 2.11). Acrylic does, however, wet with water, although this is not particularly good, and some efforts have been made to modify the material. Firstly, however, anything done to the polymer itself to improve wetting would increase its water sorption and therefore it would be plasticized and less stiff. Secondly, coatings may be applied which wet better. However, the wetting with saliva is much better than with water. This is due to the proteins and mucopolysaccharides present which adsorb to the acrylic rapidly and fairly strongly (multiple hydrogen bonds but through a covalent backbone, as with polycarboxylic acids: 9§6, 9§8). But, in so doing,

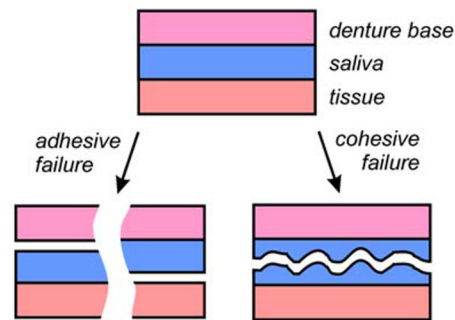


Fig. 9.18 Neither interfacial separation (adhesive failure), nor rupture of the liquid film (cohesive failure) can occur.

they create a surface which is more wettable: a condensed, multimolecular film of hydrophilic substances that then wets much better than the underlying acrylic, indeed the contact angle may be zero. Such a film is laid down very rapidly on contact with saliva, and on any coating, so that what is presented to the liquid saliva is always much the same.^[43] (Of course, it then becomes possible for a **biofilm** to develop: a microbiological ecosystem, but this remains perfectly wettable.) Thus, interfacial failure by a simple separation of denture and saliva, *i.e.* adhesive failure, does not occur (Fig. 9.18). This strength is therefore quite adequate and its insufficiency can be discounted as a factor of any importance. Likewise, the tensile strength of water (of the order of 70 MPa^[44]) is sufficient for cohesive failure not to occur, although any bubbles present may give the appearance of much lower apparent strength.

Disregarding mechanical devices such as clasps, screws and clips, or even magnets, there are only two mechanisms available for retention as such of a plain acrylic denture. The first is gravity, where the weight of the lower denture may hold it in place, but clearly this is of no help for an upper denture. The second is surface tension, depending on just the same pressure reduction as occurs between two plates (Fig. 2.10), providing that there is indeed a meniscus. A fully-immersed system cannot provide any retentive force (Fig. 9.19), only resistance to movement through the viscosity of the medium at low velocity. At high enough separation rate Stokes' Law-dependent drag becomes noticeable. If we consider only the effect of the viscosity of the liquid between such plates (and assume that they remain parallel and aligned), the **Stefan** equation^[45] shows that the velocity depends on the cube of the separation, h , for a given force:

$$-\frac{dh}{dt} = \frac{8Fh^3}{3\pi\eta R^4} \quad (9.6)$$

where R is the radius of the circular plates. After integration and rearrangement, we get:

$$\frac{1}{h} = \sqrt{\frac{1}{h_0^2} + \frac{16Ft}{3\pi\eta R^4}} \quad (9.7)$$

This gives plots as in Fig. 9.20. From this simplified¹¹ model we can deduce several things. Firstly, while breakaway when it occurs is extremely abrupt – the system collapses – the initial separation is very slow, meaning that there is an effective retention simply because the gap is narrow. An unsupported upper denture can therefore be expected to appear to remain stably in place for some appreciable time. Secondly, the better the fit, *i.e.* the smaller the initial gap, the longer it will take before breakaway occurs. Not only does this mean that the better the denture is made the better it will be retained, but the consequence of biting, which ‘seats’ the denture, squeezing out saliva, is to ensure that the gap is returned to a minimum. Thirdly, raising the viscosity of the medium in the gap can increase the time required for breakaway

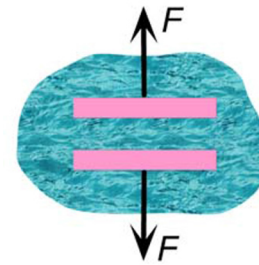


Fig. 9.19 No forces are acting on a fully-immersed system to oppose separation except those due to flow into the gap (ignoring Stoke's Law drag; *cf.* equation 4§10.1).

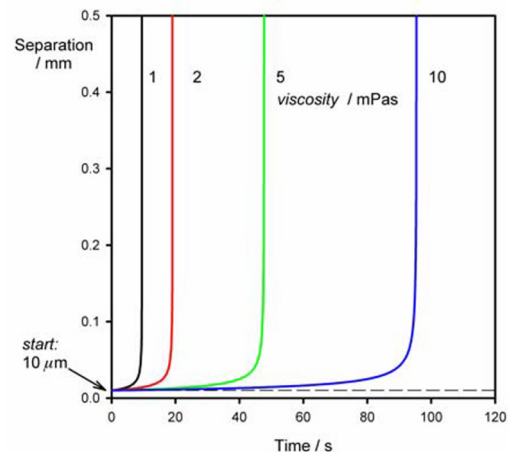


Fig. 9.20 The separation of parallel plates with a filled gap is quite abrupt, and depends on the viscosity of the fluid. The effect of increasing the initial separation gap can be seen by moving the time ‘0’ to the right to correspond to the chosen value. (calculated for $R = 30$ mm, $F = 0.5$ N) Viscosity of water: 1 mPas.

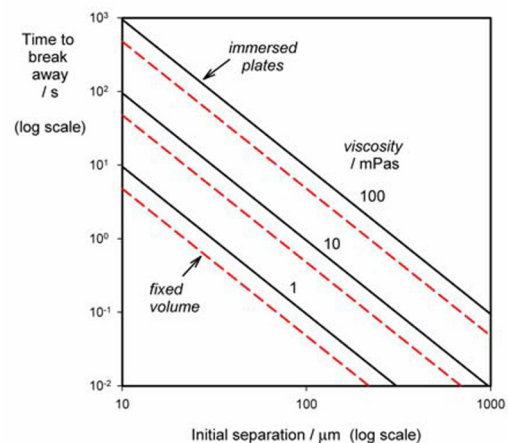


Fig. 9.21 Breakaway time varies as the inverse square of the initial separation and the viscosity of the liquid. (Other conditions as for Fig. 9.20.)

¹¹ Again, the inertia of the fluid is ignored – it is treated as massless – and therefore the acceleration is also ignored, for simplicity.

substantially. This is the basis of the action of many denture ‘fixatives’ or ‘adhesives’, given that they wet (adhere to) both mucosa and acrylic. The effect of gap and viscosity on breakaway time for immersed plates is illustrated in Fig. 9.21 (solid lines). However, it is not often the case that one’s mouth is completely full of liquid.

Thus, if the plates are not completely immersed, but simply have the gap filled by a fixed volume of liquid, then of course as separation occurs air is admitted to the space. Since the viscosity of air is about 0.02 mPas at ordinary temperatures, negligibly low compared with that of water, 1 mPas, we can expect the retardation of separation to be diminished. The equivalent equation to 9.7 for this case (which ignores the air) is:

$$\frac{1}{h} = \sqrt[4]{\frac{1}{h_0^2} + \frac{128\pi Ft}{3V^2\eta}} \quad (9.8)$$

where V is the initial liquid volume between the plates, filling the space. This means that breakaway occurs about twice as quickly and more abruptly (Fig. 9.22; Fig. 9.21 – dashed lines). Otherwise, the breakaway behaviour is similar to that in the immersed plates case (Fig. 9.20). This kind of behaviour is the cause of what is commonly referred to as ‘suction’, and is an everyday kind of observation when trying to separate wetted surfaces. However, this ‘suction’ must be seen as an **emergent** effect, a reaction to the applied force because of the difficulty of the liquid flow – there is nothing going on otherwise in an undisturbed system.

What has been ignored in that last scenario is the effect of surface tension. That is, as the liquid surface is drawn into the edge of the plates, the meniscus curvature generates a lowering of the pressure (Figs. 2.4, 2.10). This would be appreciable at small separations. However, at the separations where breakaway is prompt (Figs. 9.21, 9.22), the contribution would be negligible. This is assuming that there is no relatively deep reservoir of saliva in contact with the margins – which is unlikely. However, there are two topographical factors that promote retention: the enclosure of the ridge by the flanges, and the compliant seal occasioned by the soft tissue on the buccal surface (Fig. 9.23). The first means that the gap on the flanks of the ridge changes much more slowly than the displacement so the viscous retardation persists better, while the second means that the path for fluid ingress is possibly more limited. Of course, the weight of the lower denture tends to retain it in place, whilst the upper suffers that permanent force. Essentially, the better the fit, the better the physics of the system provides retention.^[46]

Such a system is not static, but is instead subject to intermittent forces, both tending to seat and tending to remove. It is therefore more appropriate to consider the response of the system to stress pulses (Fig. 4§2.1). The liquid between the denture and the tissue, saliva, is close to Newtonian in behaviour at low shear strain rates, and therefore the Stefan equation probably provides a suitable working model over small displacements, at least as far as the main dependencies are concerned. Once breakaway is approached, collapse is prompt. Of course, the variation in the size of the denture between wearers is relatively small, so the principal controlling factor then becomes saliva viscosity.

Unfortunately, fit cannot be retained for very long, no matter how well the denture is made, because of the biological changes in soft and hard tissue that occur. Accordingly, materials described as ‘denture fixatives’ or ‘adhesives’ are sold. These are intended to provide a highly viscous, sticky layer between the soft tissue and the denture base that also adheres to both. A common type of formulation includes a proportion of zinc oxide as a supposedly benign filler (9§3.2) in a mineral oil or aqueous carrier. The difficulty arises when reapplication

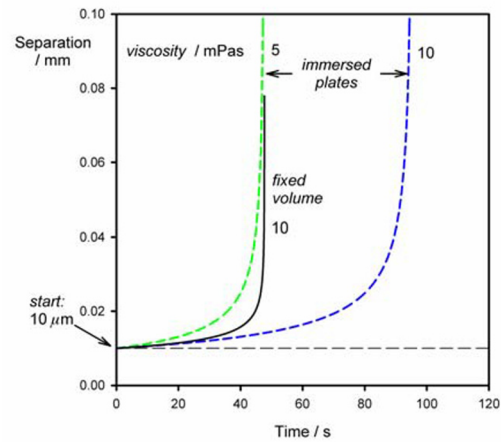


Fig. 9.22 If the gap contains only a fixed volume of liquid, the separation occurs earlier and more abruptly. (Other conditions as for Fig. 9.20.)

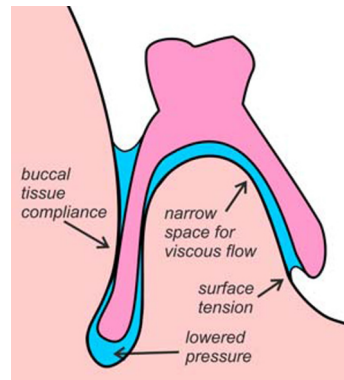


Fig. 9.23 The main factors promoting denture retention.

several times a day is required because the denture fit is so poor that retention is even then inadequate, noting that the lost material is being swallowed. While such ingestion in small amounts (*i.e.* used as directed) has no apparent ill consequences, over a long period excessive consumption may result in a zinc-induced copper deficiency which has been associated with a number of problems (30§5).^[47] Alternative formulations including substances such as carboxymethylcellulose (27§2.3) and copolymeric polycarboxylates (*cf.* Fig. 9§8.4) may be used that offer no such risks.

●9.11 Separating agents

Other than the direct blocking of porosity, preventing mechanical interlock, that mould sealants are intended to achieve (7§13), there is a group of materials whose purpose is to prevent wetting and adhesion. There are several aspects to this. Mechanically, if a coating remains liquid then no rigid interconnection can develop unless undercuts are severe. Physically, if a surface offers a large contact angle with the material to be overlain, then even on a moderately rough surface a full conformity will not be achieved (Fig. 2.14). Chemically, the complete avoidance of covalent and chelation (9§6.2) bonding, and the minimization of other interactions (Fig. 3.1), means that the work of adhesion (§1.7) is minimized. In particular, reaction with the moulded material must be avoided. If the mould is disposable, effects on that side are of lesser importance providing that dimensions are preserved accurately. Accordingly, thin coatings such as mineral or silicone oil, petroleum jelly, waxes (16§1.2) (perhaps applied in an evaporating solvent) and polytetrafluoroethylene (PTFE) may be used for many combinations of materials. Care must be taken in every case to ensure that contamination of important surfaces by these materials does not occur – silicones are especially problematic as they spread easily, are difficult to remove, and interfere with bonding even in very small amounts that are essentially undetectable by ordinary means.^[48] There are ways of removing silicones, but these are slow and hazardous,^[49] ill-suited to a dental context. While the reaction of Fig. 7§6.4 can be reversed by strong base or strong acid, this is not a practical proposition.

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