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# Liquid surface physics

**Key indexing words**
detergents
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surface energy
surface tension
wetting agents
water repellents

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## Basic facts

Molecules near the surface of a liquid in contact with a gas or another liquid are in a different environment from those in the bulk. By a mechanism whose details are only gradually being understood this causes the pressure that generally exists in the bulk liquid to give way to a large *tensile stress* in the region near the surface molecules, **1.** The total force with which the liquid on one side of a 1 cm line in the surface pulls the liquid on the other side is the *surface tension.* To extend the surface, work must be done against this tension, so that each unit area of surface can be said to possess a *free surface energy*, whose units and magnitude are the same as for surface tension. The energy and tension approaches are equally valid, and the type of problem determines which it is more convenient to use. Numerical values, measured in dyne-cm$^{-1}$, range from tens (rare gas liquids) to thousands (liquid metals in air).

## Liquid-gas systems

**Pure liquids** Surface tension forces tend to form liquid volumes into spheres, since this shape has the lowest surface energy. This tendency dominates over gravity forces in the case of small volumes, which is why thin jets and sheets of liquid break up into droplets. Industrial spraying techniques for paint, oil, insecticides, etc, involve the production of such jets and sheets.

**Liquid mixtures** Here the components with lowest surface tension are adsorbed in the surface layers to minimize the total surface energy. If the surface is disturbed, the resulting increase in tension caused by the exposure of the deeper layers with different composition tends to restore the surface to its former shape, provided the liquid is sufficiently viscous to prevent the exposed layer being instantly replenished with adsorbent from the bulk.

This self-healing property is called the *Marangoni effect.* Pure liquids do not show it, and can never form stable films, bubbles, froths, foams and other structures with large surface area. The polygonal films, separated by gas, that foams are made of must satisfy two conditions because

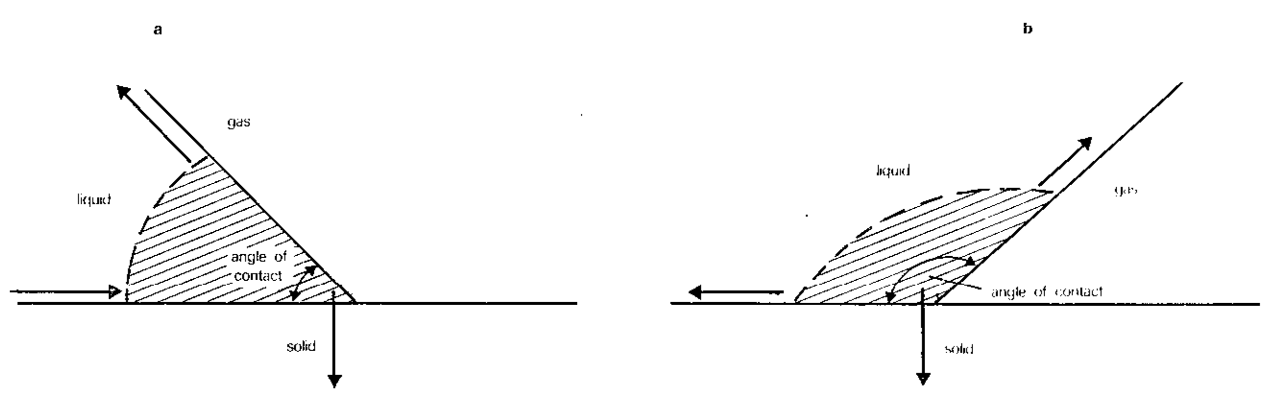
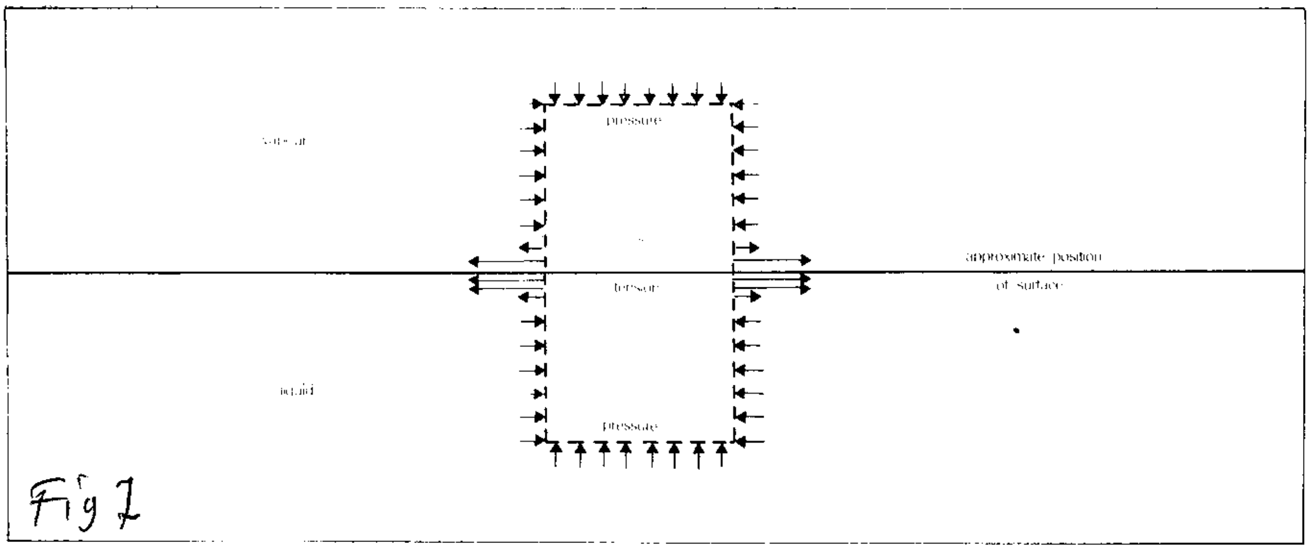


Fig 2

1 Diagram of the forces acting on elements of liquid and vapour near the surface where the bulk pressure of the liquid gives way to a tensile stress



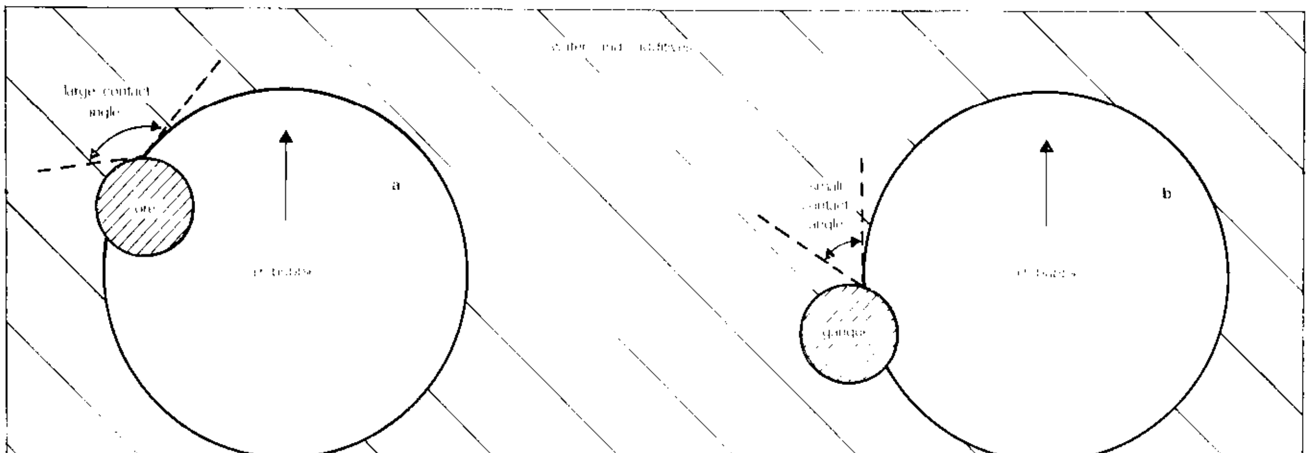
**2** The forces acting on a liquid (shaded) near a solid/gas boundary. On the left the condition of wetting; on the right that of non-wetting

of surface tension requirements: three films must meet at 120° at each edge, and four edges must meet at each corner. The resulting structure is light, has considerable mechanical strength, and contains a large amount of immobilized gas. Because of this, foams are widely produced industrially for such varied purposes as heat insulation, fire-fighting, sound-insulation and life-jackets (where the foam is solidified, as in the case of polystyrene), and shaving soap. *Frothing agents* are surface-active additives which help to stabilize bubbles, films and foams. Examples are pine oils and saponins.

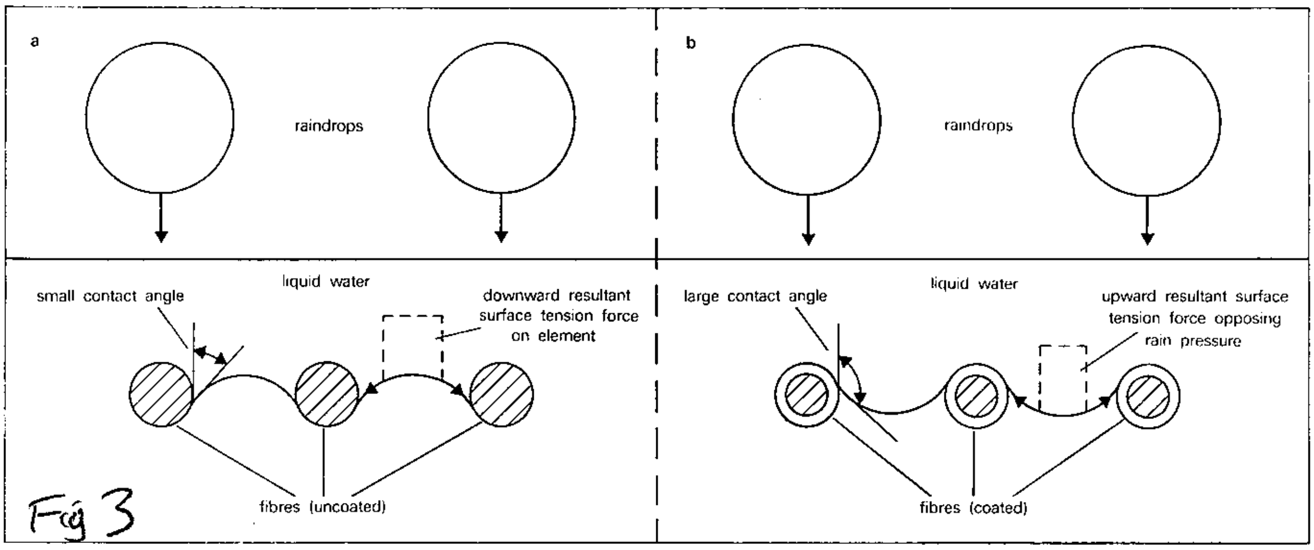
**Emulsions** are dispersions of one immiscible liquid in another. They are analogous to droplet systems if there is only a small amount present of the disperse phase, and resemble foams if the continuous phase is reduced to a system of films. The inversion of emulsions, where the two phases exchange roles, is exemplified by the turning of cream into butter. In metal-cutting processes it is desirable to have oil for lubrication and water for cooling at the same place, and an emulsion is the simplest way of realizing this. Many other industries, including tanning, paper-making and road-making, use emulsions for key processes. In addition, foods (eg milk) often take the form of emulsions, probably because this aids digestion.

## Liquid surfaces near solids

**Angle of contact** The forces which act on a small portion of fluid near a solid-gas boundary are not yet understood in detail. However,



**3** The penetration of rain into fibres depends to a large extent on the contact angle for the surface. A non-repellent surface (left) has a downward resultant; a repellent one (right) an upward one

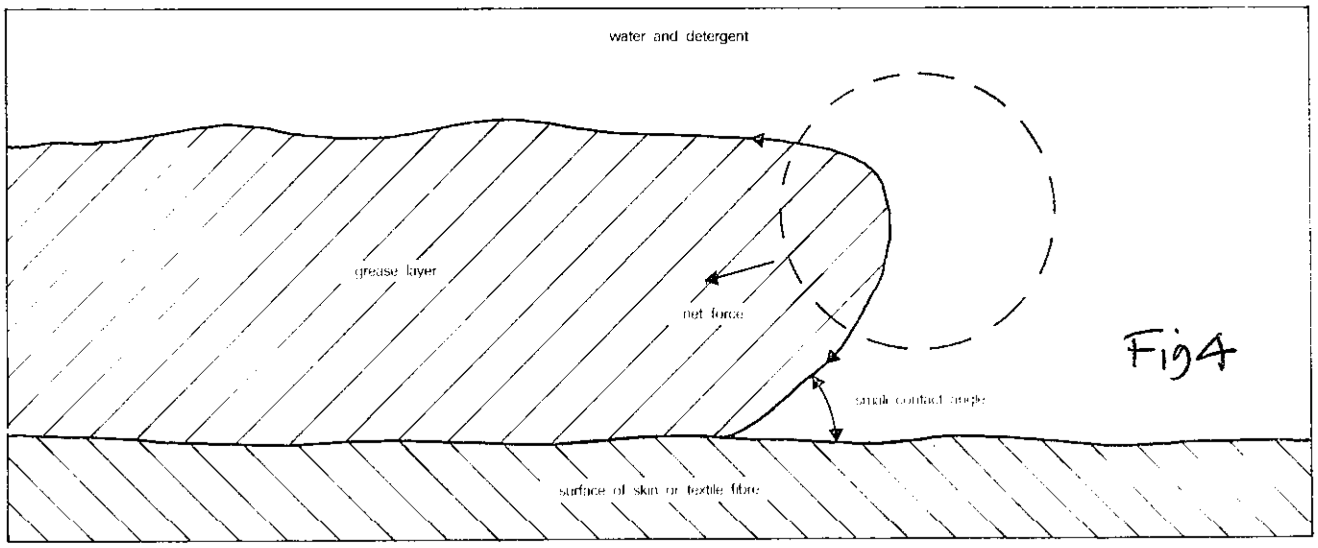


4 Solutions of detergents and soaps give a small angle of contact, and the resultant surface tension forces the solution under the grease layer, which is then removed by mechanical agitation

the arrows in **2** represent the action of easily-identifiable molecular processes. The experimentally-measurable effect of these forces is the angle of contact. This is acute if the liquid adheres to the solid more strongly than it coheres to itself (the case of wetting, **2a**) and obtuse otherwise (the case of non-wetting, **2b**). The angle of contact is a notoriously variable quantity, affected principally by contaminants in any of the three phases, and by whether the line of contact is advancing or receding over the solid.

**Water-repellency** If the angle of contact is large, liquids tend to form into small droplets, rather than as a continuous film, on a smooth surface. If the dropwise condensation of steam in a boiler is assisted by coating the surface with promoters such as grease, fatty acids, wax, etc, then the rate of heat transfer between steam and coolant is increased by a factor of two or three. The contact angle for ink on writing paper must exceed 90° to prevent the ink 'feathering' into the pores of the paper, and it must be less than 110° to prevent lines of ink gathering into droplets. These requirements are achieved by sizing—coating the paper fibres with minute droplets of rosin.

Many surfaces (eg textile fibres, skin, building materials) are not smooth, but have a complex pore or fibre structure. These can be made waterproof by a continuous coating of, for example, rubber, but such treatments render the surface impervious to air and water vapour as well as liquid water. Materials which can 'breathe', that is, those which



5 Froth flotation relies on the different action of the air bubbles on ore and gangue particles. Ore enters the bubbles and is carried upward; the gangue is excluded and drops down

restrict the passage of liquid water only, can be made by coating the pore and fibre surfaces with silicones or paraffin wax. These treatments result in a large contact angle, so that the small liquid menisci in the capillary spaces are convex into the material, and can exert a restraining force against, for instance, external rain pressure, **3**.

In addition to a large contact angle, the optimum conditions for water-repellency include fine, closely-spaced pores or fibres, and large liquid surface tension (the agent used to coat the fibres must therefore not contaminate the liquid). The water pressures that can be resisted by these treated materials are often increased by the entrainment of small air bubbles during processing; ducks' feathers are examples.

**Wetting** It is often necessary to produce intimate contact between a liquid and a solid surface. This implies that the contact angle must be as small as possible. Thus sprays of fertilizer or insecticide used in agriculture must include a wetting agent to counteract the natural water-repellency of leaf or insect structures, and paints and dyes must be treated to enable them to spread smoothly over the surfaces to which they are applied. Metals are seriously weakened by liquids which wet their grain boundaries and spread along them. Thus bismuth renders copper brittle, liquid gallium disintegrates aluminium, and hot shortness in steel is caused by the melting of sulphides. Fatty acids added to lubricants ensure that the two surfaces to be separated are well wetted. For adhesives to produce strong bonds it is necessary that there be no dry spots where the surfaces to be joined are not wetted. The success of epoxy and phenolic resins depends on the attraction between their polar hydroxyl groups and the ionic surfaces of the oxide films that cover most metal surfaces.

Solutions of detergents and soaps in water have small angles of contact with the surfaces of skin or textile fibres. The resultant surface tension forces, **4**, cause the cleaning solution to squeeze under and displace grease layers, which are then removed by mechanical agitation. It is not clear whether the production of lather helps or hinders the washing process. Liquid solder will not wet greasy metal surfaces, so these are first cleaned with fluxes. The resulting metal surface, covered with flux, is easily wetted by the liquid solder.

**Froth flotation** The widely used process of froth flotation makes use of both wetting and repellency to separate valuable ore materials from useless 'gangue'. The mixture is ground to a powder and covered with water through which a froth of air bubbles is blown. The air-water-mineral contact angle is larger for the ore than for the gangue particles. If it is obtuse, then the particles tend to be enclosed within the bubbles and lifted to the surface, whereas if the contact angle is acute the bubbles tend to exclude the particles and leave them behind, **5**. Frothing agents are added to the water to increase the stability of the bubbles. To increase the difference in contact angle between ore and gangue, collectors (eg xanthates for sulphide minerals and long-chain amines for oxide minerals) are added. Further separation of the different kinds of ore can be achieved by adding traces of activators (eg copper sulphate for zinc sulphide) or depressants (eg cyanides to suppress zinc and iron sulphides).

## Theory and experiment

A unified scheme of physical explanation for many biological phenomena and industrial processes is possible with the aid of the simple concepts of surface tension and energy, adsorption, and angle of contact. In the field of surface chemistry a vast body of knowledge has been built up concerning the types of compound which can be used for wetting and frothing agents, collectors, etc. This empirical knowledge, however, lacks a detailed theoretical understanding. In fact, as far as surface tension is concerned the only fundamental progress that has been made at a molecular level has been calculations for rare gas liquids, where the molecules are spherical and monatomic, and interact according to simple laws. Even in this work it has been found necessary to make drastic assumptions about the structure of the interface.

## Some centres of research or further information

University of Bristol
Imperial College, London University
University of Lancaster

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