

# 1 Basic principles and concepts

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Thoughts without content are empty, intuitions without concepts are blind.

Immanuel Kant, Critique of Pure Reason, B25, 1781.

## 1.1 Introduction

Foams can exist in the wet, dry or solid state and can be seen almost everywhere, in the home, in the surrounding natural environment and in numerous technological applications. In fact they are prevalent, and it is almost impossible to pass through an entire day without having contact with some type of liquid or solid foam. They have several interesting properties which enable them to fill an extremely wide range of uses; for example, they possess important mechanical, rheological and frictional characteristics which enable them to behave similar to solids, liquids or gases. Under low shear, wet (bubbly) foams exhibit elastic properties similar to solid bodies, but at high shear, they flow and deform in a similar manner to liquids. On the application of pressure or temperature to wet foams, the volume changes proportionately, and this behavior resembles that of gases. Interestingly, it is the elastic and frictional properties of wet foams which lead to their application in personal hygiene products such as body lotions, foaming creams and shaving foams. While shaving, foam is applied to the skin and the layer on the blade travels smoothly over the surface, reducing the possibilities of nicking and scratching. Another example is their use as firefighting foams, where properties such as low density, reasonably good mechanical resistance and heat stability are required in order to be effective in extinguishing gasoline fires. Essentially, they act by covering the flames with a thick semi-rigid foam blanket. The low density allows the water in the foam to float even though it is generally denser than the burning oils. The chemical composition and mechanical properties of these types of foams can be varied to optimize the firefighting utility.

Foams are also found in many food items, either in finished products or incorporated during some stage in food processing. They primarily provide texture to cappuccino, bread, whipped cream, ice-cream topping, bread, cakes, aerated desserts, etc. Surprisingly, several novel types of food foams have been recently produced from cod, mushroom and potatoes, using specially designed whipping siphons powered by pressurized gas with lecithin or gelatin as alternative foaming agents to replace egg and

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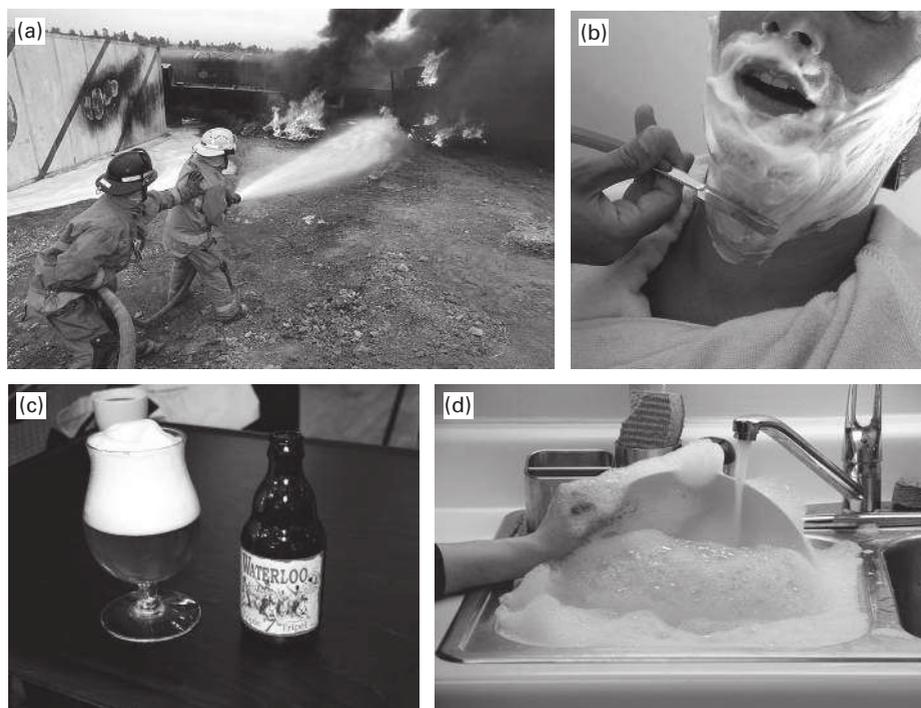
creams (1). Several modern architectural designs and works of art have also been manufactured from bubbles and foams, and they are also used for entertainment purposes. Foam and bubble exhibitions frequently take place at the Science Museum, London, where young children are enclosed within soap bubbles and foams. In fact, it has been reported that 50 children were packed inside a soap bubble which became a world record (2). Foams play an important role in evolution, particularly in the insect and animal world. For example, while female frogs lay eggs they also secrete a fluid which is whipped up into foam by the male frogs, and this robust foam protects the eggs by becoming a shield against the physical and biological environment.

Foaming also occurs in cleaning and detergency which is utilized in cleaning factories, shops, offices, machines, factories, cars, workshops, garages, floors, etc. In many of these applications, it is important to optimize the extent of foaming. This has been achieved by manufacturers synthesizing new types of low-foaming non-ionic chemical detergents. However, in some applications where customers prefer to see some foam, small amounts of special foam-producing substances were included in their product as foam improvers, boosters or foam stabilizers. During the 1950s and 1960s, wet detergent-based foams were well known to cause major problems when discharged into streams and rivers. They were often odorous, and when rivers flowed over weirs, the foams frequently increased in height and were frequently blown into neighboring environment. However, over the past 50 years, more effective biodegradable (green) surfactants (soft detergents) have been developed which considerably reduced foaming.

Often wet (bubbly) foams have been formulated to perform specific functions such as decontamination control (e.g. for cleaning materials inside nuclear reactors) and in oil-recovery, agriculture and beverages such as Guinness stout, where the foam head must remain stable during pouring and consumption. In addition, the method of generating foam is dependent on the application and requirements of the foam. In Fig. 1.1, four different everyday foams are shown. While firefighting and shaving cream foams are produced by release of gas under pressure, the bubbles in Guinness foams are produced by fermentation, and detergent foams are produced by entrapment of air during agitation.

In most cleaning operations, the foaming performance is not necessarily related to the volume of the foam or stability, although different applications may require different amounts of foam with an abundance of foam usually preferred in body-cleaning products. However, this is not the situation for washing machines where vigorous agitation occurs and foam volume needs to be minimized. Foams can often cause problems in commercial processes such as in paper-making and distillation where over-production of wet foams leads to loss of efficiency and downtime in plant production. Under these circumstances, it is often necessary to add antifoamer, defoamer or foam breakers (3).

Foams are also capable of immobilizing large volumes of air and combining lightness in weight with strength and elasticity, and these properties are critical in their use in many well-established industrial processes such as froth or foam flotation. This is one of the largest and most important industrial uses of bubbles and wet foams which have been

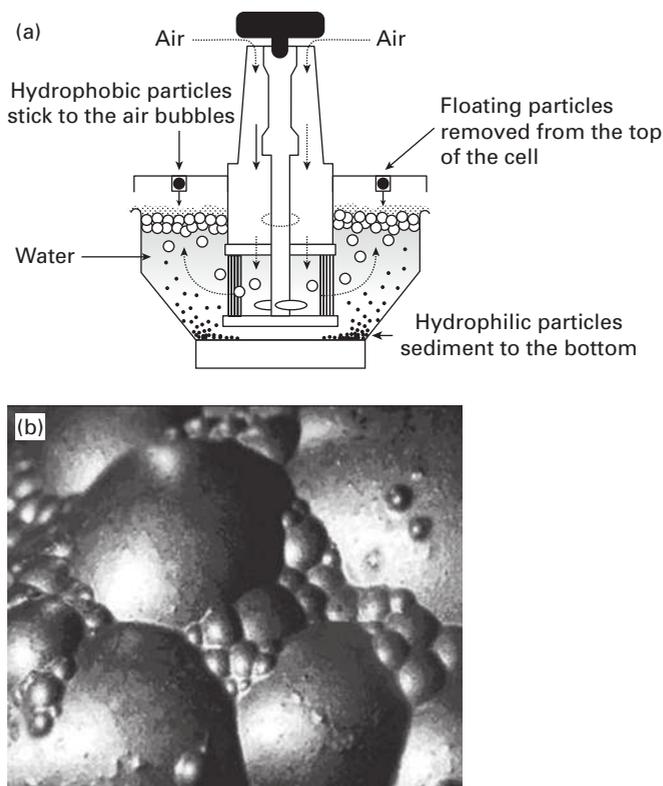


**Fig. 1.1** Applications of wet foams. (a) Firefighting foams act to cover or blanket out the flames (prevent air reaching the fire) and must remain stable at high temperatures. (b) Shaving foams are designed to give rheological flow properties (similar to an elastic solid). (c) Beer foams such as Guinness are stabilized by a protective film of proteins which define the texture and enhance the flavor and retain their stability until the beer is consumed. (d) Detergent foams (in dishwashing) are stabilized by low molecular weight synthetic surfactants.

used for more than 100 years. During the extraction of mineral ore, it is necessary to separate the particles by flotation so that the more valuable hydrophobic ore particles (sulfides of copper, zinc, gold, etc.) adsorb at the foam interface and remain suspended by capillary forces while the less valuable hydrophilic particles (usually silicates) sink in the liquid (4). The amount of ore that can be separated for a given amount of liquid is directly proportionate to the surface area of the foam (bubbles), and huge masses of ore can be easily processed using relatively small volumes of water. Figure 1.2(a) shows a schematic drawing of a foam or froth flotation cell, and Fig. 1.2(b) shows a typical foam of froth.

The terms “foams” and “froths” which can be considered as weakly stabilized foams are often used interchangeably, but in industry a three-phase system (a gas–water macrocluster with dispersed particles) is considered a froth, and a structure containing only the gas and liquid phases is considered a foam. The link between the stability of a flotation froth and flotation performance has been investigated both in the plant and in the laboratory by using a modified froth stability test column (5). In this test, a gas is continuously sparged into a foaming solution, and simultaneously froth collapses at its free surface occurs. When the rate of froth collapse equals

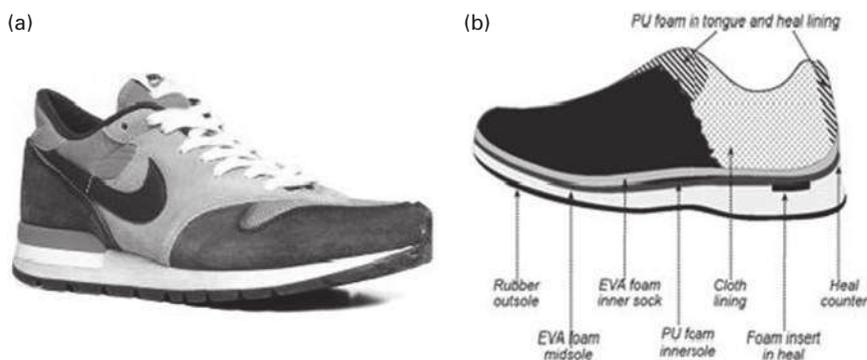
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**Fig. 1.2** (a) Schematic representation of a flotation cell and (b) the froth of foam with particles attached to the bubbles. Flotation of mineral particles is the largest industrial application of bubbles and foams. The process involves the separation of the more valuable minerals such as copper, zinc and lead from the less valuable silicates. Billions of tons of ore are treated annually using this technology.

the rate of generation of fresh froth, an equilibrium height is attained. The equilibrium foam height, divided by the superficial gas velocity, is used as a measure of froth stability. From these studies, it was found that the variations in flotation performance are directly related to changes in froth stability. In addition to mineral processing, froth flotation has also been successfully used in other separation processes such as the treatment and recycling of effluent, proteins, plastic wastes, etc. The flotation process is also extremely important in the deinking of waste paper (6) and enabling recycling of about 30% of paper. Foams also play an important role in the extraction of residual oil from porous rocks (7).

Although this text is mostly limited to wet foams, it is also important to note that solid polymeric foams (which are usually oil based and are usually manufactured from wet foams) are generally considered as a specific group of material foams. They can be classified as rigid, semi-rigid, semi-flexible or flexible depending on cellular morphology, composition and other physical characteristics. They are manufactured with a specific range of properties, achieved by controlling the degree of crystallinity

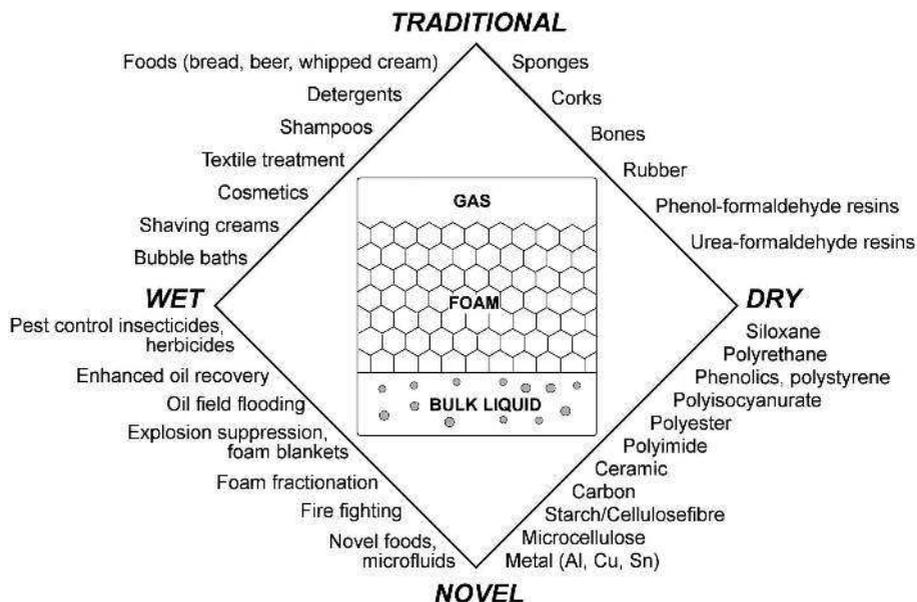


**Fig. 1.3** Running shoe showing some of the important foam polymers which are used as components.

and the extent of cross-linking of the polymeric framework. Close-cell material foams contain cells that are permanently trapped (isolated). In other cases where the cells are open or connected to neighboring bubbles by gas channels, both gas and solid may be considered to exist as continuous phases. However, only closed-packed structures are regarded as true polymer foams, and these products are more expensive to manufacture therefore, the cells are filled with special gases to improve insulation. Self-skin foams are frequently found, for example, in shoe soles and mattresses and are often manufactured with high-density skins and low-density cores. Open cells have networks or channels which allow air to flow (e.g. polyurethane seat cushion).

Their properties are extremely dependent on the method of preparation and manufacturing particularly during the solidification. Most close-cell foams have fairly rigid structures, but open-cell foams have been developed which are generally more flexible. Originally, foamed rubber and phenol-formaldehyde and urea-formaldehyde resin foams were developed in the early 20th century followed by more specific foam polymers such as polyurethane (PU), polystyrene (PS), ethylene-vinyl acetate (EVA) and polyvinyl chloride (PVC). Many specialized polymer foams have been developed for the consumer market, and these have been utilized in numerous applications in recent years. For example, a considerable amount of research and development has been invested in foams for lightweight running shoes where low mass is needed to reduce the energy consumption of the athlete. Figure 1.3 shows the cross-section of a pair of trainers, indicating the different sections and major foam components.

Several foam component parts such as the rubber innersole and the foam midsole compression which is molded from EVA copolymer are used to provide cushioning or control torsion of the foot. The foams have been developed to withstand compression and bending loads caused by feet. PU foams have been used as an alternative to EVA for midsoles, but the density of PU is higher although the compression is lower. The shoe components are bonded together so that adhesive action of the foam is important. Different gases are often used in these types of foams. For example, Nike's large bubbles contain  $\text{SF}_6$  gas as an insert in the main foam. Another recent development is the memory foam footbed. Most major shoe manufacturers show their design innovations on websites. A background on the polymer/structural properties relationships is given



**Fig. 1.4** In the figure, along the lower right side, Cellulose fibre Important traditional and novel applications of wet and dry foams.

by Mills 2005 (8), while information on the application of foams has been published on several websites (see, e.g., [www.foamstudies.bham.ac.uk](http://www.foamstudies.bham.ac.uk)).

Polymer foams are also widely used in boats, aircraft furnishing, cycle helmets, etc. and are manufactured from a variety of plastics and polymers. They are also used as light-weight cellular engineering materials which require a high strength to weight ratio, for space applications and have been used as core material in sandwich-structured composites. The combination of low weight and unique elastic properties are ideal for packing and cushioning, and polyurethane is used in the manufacture of seat covers and chairs whereas foamed polystyrene is used as take-out boxes, trays in restaurants, coffee cups in cafes, seat cushions, car seats, car bumpers and thermal or sound insulations. In addition to polymers, rigid dry foams may be produced from metal, glass, concrete and ceramics, and these have found widespread application in, for example, domestic insulators, air conditioners and reinforcements. They are used for thermal insulating, vibration damping and for acoustic absorption. Following the introduction of material foams, the principles governing the more advanced technology has become fairly well established, and it has become possible to match the effective properties such as stiffness or rigidity, strength, compression to the cellular architecture. Overall, both wet and dry foams cover a wide range of both traditional and novel applications, and many of these have been summarized in Fig. 1.4.

Novel and potential application of foams are frequently reported in the daily press. For example, an expanding foam has recently been developed that could be pumped into bodies of wounded soldiers to reduce internal bleeding (9). The technique involves injecting two chemicals into the badly injured soldier's abdomen which react to generate a rapidly expanding foam which solidifies and seals the injuries in the body organs,

preventing the loss of blood. This gives sufficient time for the soldier to be taken to a field hospital where the foam can be easily removed by surgeons. It is also shown as a potential bone substitute. Bone has a compact surface with a cellular core and is composed of both mineral substances and tissues. The bone tissues are made up from cells, fat and natural polymers (such as polysaccharides, collagen, polyphosphates, etc.). Recent developments in synthetic foam technology have led to the production of cellular materials from starch-based (biodegradable) polymers and polyethylene (bio-inert) polymers as possible replacements for bones (10). Syntactic dry foams have also been developed containing hollow particles such as glass ceramic and polymer spheres embedded in a matrix material. In the literature, numerous separate texts have been published covering specific types of polymer foams – for example, polyurethane or polystyrene foams.

## 1.2 The physics and chemistry of foams and foaming

Although foams have been shown to be extremely useful from the industrial viewpoint, they have, in addition, unique academic appeal within the physical chemistry, physics and biophysics communities from a scientific viewpoint and have served as useful models for numerous investigations over several centuries. Foams have been studied extensively within both universities and industrial laboratories. Foams are extremely complex systems, and early fundamental studies by Thomas (11) showed a basic relationship between soap foams and the cellular structures of plants and animals. This approach has led to a deeper understanding of natural processes through which many biological systems emerge. Also similar structural features have been revealed during grain growth in metallurgical systems (12). Within the physics community, a strong emphasis has been placed on the mechanics, film permeability, rheological properties (such as the variation in elasticity with gas fraction) and the structural rearrangements occurring as the bubbles become less spherical and more highly packed during the transition from wet to dry foam. In fact, it is the liquid content and geometry (surface area, bubble size and size distribution, shape (compaction) and order/disorder which are considered to be important parameters to consider, since these can lead to a fundamental understanding into the relationship between the scaling and structure. Most of the pre-1999 studies dealing with basic static and quasi-static properties of dry foams have been well described in the classic book by Weaire and Hutzler, entitled *The Physics of Foams* (13). More recently, Drenckhan and Saint-Jalmes presented a historical perspective entitled *The Science of Foaming* from a physicist viewpoint (14).

Physicists and mathematicians have been contemplating the structure of foams over a considerable period of time, often focusing on idealized ordered foams. However, ordered foams are not very diverse and collectively contain only a few kinds of cells, whereas real foams are disordered and contain a variety of shapes. Many theoretical computer simulations have been carried out over the past 20 years, using the Surface Evolver (15) to compute the evolution and equilibrium structures of foams, and this has

been found to enhance the understanding of real foams physics. The Surface Evolver is an interaction program which can be used to derive a minimal energy surface or to model the process of evolution of a surface which is shaped by surface tension and other energies such as gravitational energy, squared mean curvature, etc. The program evolves the surface toward minimal energy by a gradient descent method. It is also necessary to introduce user-defined surface integrals or knot energies. For example, computations on the equilibrium microstructure of soap films with random structure and with a wide range of cell-sized distributions have been reported (16).

For many experimental foam studies, physicists need a convenient highly reproducible sample which was assumed to be stable for extended time periods. Plateau (17) used a soap solution to produce thin films and foams but had difficulties in achieving sufficient stability. Later, formulations were improved by the addition of glycerin which raised the viscosity and retarded the evaporation of water, and since then many different types of chemical recipes have been described which produce highly stable foams. Strong (18) has published a long list of formulations for preparing foams with extremely long lifetimes. Over the past 50 years, numerous experimental studies have been carried out by physicists based on a stable foam system: a commercial shaving cream (Gillette foam regular) is produced by an aerosol method. This is a complex mixture, comprised of an aqueous solution of mixed ionic surfactants (triethanolamine and stearic acid) which is supersaturated with hydrocarbon gases. On release of the contents, the bubbles are generated from solution with the surfactants adsorbing at the bubble interface which stabilizes the foam. This system produces nearly spherical bubbles (with 20–30-micron diameter and a gas fraction of about 0.92) which are highly stable for more than 24 hours with negligible drainage within this period due to the high viscosity. More recently, the physics community has shifted toward the dynamic rather than the static nature of wet foams, and many studies have been documented which involve the creation and manipulation of relatively small, discrete and equal volume-sized bubbles which have a tendency to self-order under confinement while producing crystalline and microfluidic foam structures (19). Such monodispersed foam systems have been shown to have many useful applications in areas such as templating, colloids and granular systems.

However, for the physical chemist most of the attention has been focused on the mechanisms involved in stabilization and destabilization and the surface-active materials (which may be chemicals, polymers, particles or mixtures) in wet foams and their role in their assembly in the interfacial layers. Numerous papers and several books have been published on foam generation, stabilization, antifoaming/defoaming and foam films (20). It has been shown that the both dynamic and equilibrium surface tension and interfacial rheology play important roles in defining the foaming characteristics and overall structure of the foam. Wet foams are, in reality, stabilized by a huge range of different types of surface-active agents that adsorb at the interface and reduce the free energy or tension. Hence, from the chemical aspects, it is the adsorption kinetics and type and amount of surface-active agent at the gas and liquid interfacial which play an intricate role in the generation of foam. Collapse and instability usually involves film

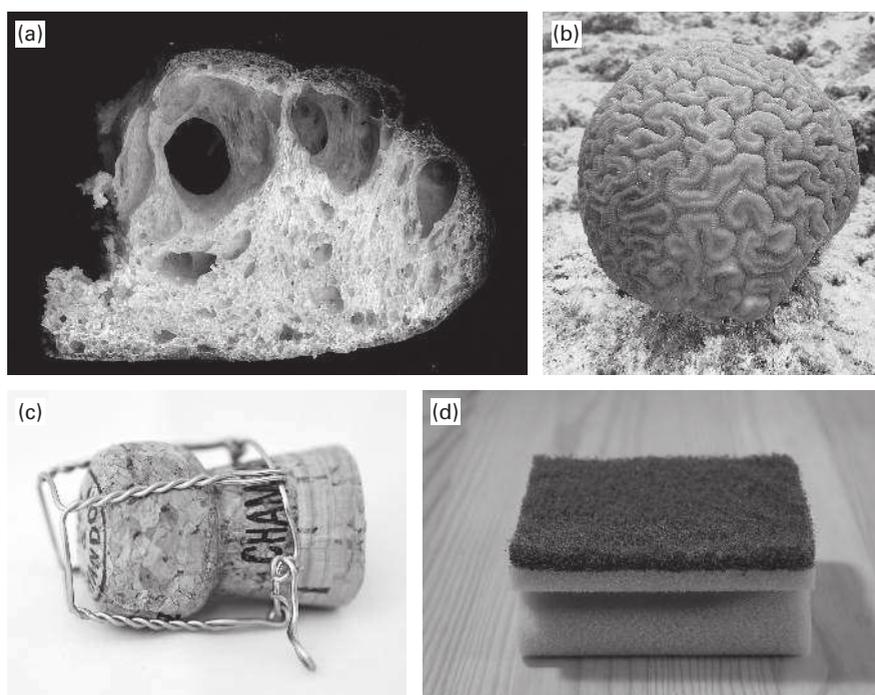
rupture and frequently depends on the sensitivity of the chemical composition and structure of the adsorbed film. Stability is more dependent on the viscoelasticity properties and the repulsive interaction between the film lamellae. In fact, changing the concentration of the surfactant or the introduction of alternative surfactants (antifoamers or foam boosters) or mixtures enhances or reduces the generation and stability of the foam.

### 1.3 The wetness and dryness of foams

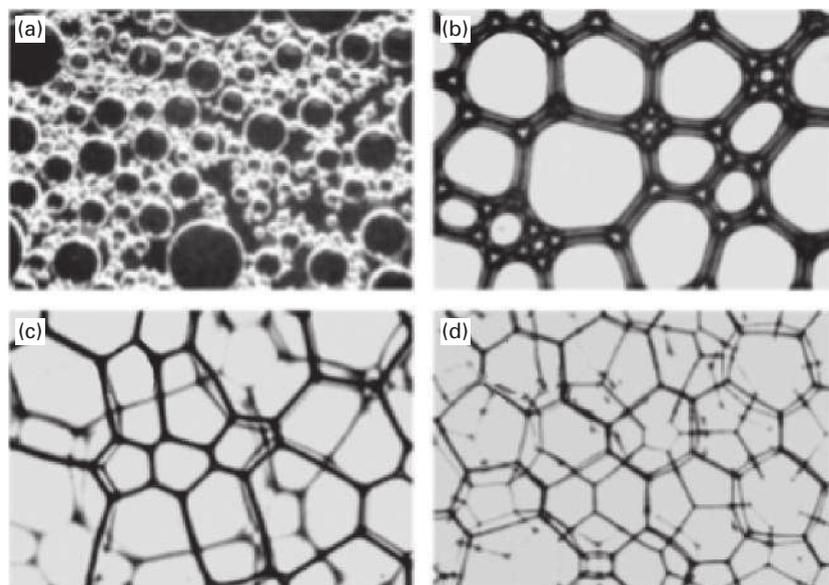
Foam properties depend on the gas fraction in cases where they contain low volumes of gas, and the bubbles that are spherical are usually referred to as bubbly liquids or bubbly foams. At high gas content, they are no longer spherical and thus behave as solids with a high shear modulus. Under these circumstances, elastic energy is required to shear the network. In his classic text in 1973, Bikermann (21) defined wet foams as systems where the volume of gas is much lower so that they can be called an agglomeration of gas bubbles, and this state occurs where the bubbles are separated from each other by thin liquid films. Each bubble is so closed that it has no gas-filled channels which can connect between neighboring bubbles. However, more generally, the system could be wet or dry, and in cases where a connection exists and there is a continuous gas phase, it is considered as an open foam structure. Cork, wood, coral and sponges are dry natural foams, whereas with bread (a man-made foam) the yeast produces small bubbles which grow into a close-cell structure (Fig. 1.5). However, if the bread is allowed to rise excessively, it develops into a dry open-cell structure with the spaces interconnected by threads of paste. Generally, a rigid dry foam system is usually regarded as a special class of dry foam produced by an irreversible chemical process.

The evolution toward dry foam proceeds by the reduction of water from the system, and it is usually caused by liquid drainage under gravity and by the suction produced by the pressure gradients that exist between regions of different curvature (capillary suction). Overall, wet foams may essentially be regarded as naturally evolving non-equilibrium systems, consisting of a collection of coarse polydispersed gas bubbles, packed into a smaller volume of liquid. In the case of pure water, the bubbles usually burst but in the presence of a sufficiently high enough concentration of surfactant, the liquid drains away gradually and the curved bubble surfaces are gradually transformed into characteristic irregular polyhedral foam cells bounded by thin soap films with almost plain surfaces of contact. The transitions in structure which occur from wet to dry foam systems are illustrated by the two-dimensional (2D) scheme in Fig. 1.6.

Generally, the liquid fraction of a foam is defined by the ratio of the volume of liquid to the total volume of the foam. Aqueous foams typically contain as much as 95% gas and 5% liquid, with the aqueous phase consisting of 99% liquid while the remaining 1% is the vital surface-active ingredients (typically a chemical surfactant). In general, the structure and dynamics of foams are determined by the amount of gas in the system, and the ratio of gas to liquid is defined as the foam number or wetness. However, the liquid



**Fig. 1.5** Common types of dry foams. Bread exhibits a close-cell structure, but coral, cork and synthetic sponges show open-cell structures.



**Fig. 1.6** Schematic 2D representation of a wet and dry foam with different volume fractions. (a) Very wet non-drained foam consisting of non-interacting bubbles; (b) wet foam partially drained with interacting bubbles causing deformation; and (c) further drainage causes lamellae to further thin and swell in the Plateau borders. (d) Finally, a well-drained foam. Dry foam consisting mostly of gas phase entrapped in polyhedral cells separated by thin films with thickness  $<100$  nm. Note curvature of some bubbles walls owing to unequal internal pressures. The nature of the thin film has been subject to intense study. From ref (22).