



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Physique

www.sciencedirect.com



Liquid and solid foams / Mousses liquides et solides

General introduction: Liquid and solid (materials, main properties and applications . . .)



*Les mousses liquides et solides : Introduction générale
(matériaux, propriétés principales et applications)*

Simon Zabler

Chair of X-ray Microscopy, LRM, University of Würzburg, Germany

ARTICLE INFO

Article history:

Available online 16 October 2014

Keywords:

Foams
Surfactants
Foam mechanics
Drainage
Coarsening
Metallic foams

Mots-clés :

Mousses
Mécanique des mousses
Drainage
Grossissement
Mousses métalliques

ABSTRACT

A general introduction about the diversity of foam structures is given with focus onto the structural, mechanical and dynamical properties at hand. Two classes of materials are addressed: liquid and semi-solid foams, on the one hand, solid foams, on the other hand. The latter can be subdivided into metallic, ceramic and organic foams, depending on the nature of the solid skeleton that supports the overall cell structure. Solid foams generally stem from the concept of mechanical light-weight structures, but they can just as well be employed for their large surface area as well as for their acoustic and thermal properties. Modern biomaterials use tailored ceramic or organo-ceramic foams as bone scaffolds, whereas hierarchically micro- and nanoporous structures are being used by chemistry to control catalytic reactions. Future materials design and development is going to rely increasingly on natural and synthetic foam structures and properties, be it food, thermal insulators or car frames, thus giving a promising outlook onto the foam research and development that is about to come.

© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

Cet article constitue une introduction générale à la diversité des structures que peuvent épouser les mousses, avec un coup de projecteur sur les propriétés structurales, mécaniques et dynamiques correspondantes. Deux classes de matériaux sont envisagées : les mousses liquides et semi-solides, d'une part, les mousses solides, d'autre part. Ces dernières se subdivisent en mousses métalliques, céramiques et organiques, selon la nature du squelette solide qui supporte la structure cellulaire globale. Les mousses solides dérivent généralement du concept de structures métalliques légères, mais elles peuvent tout aussi bien être employées pour leur grande surface accessible ou pour leurs propriétés acoustiques et thermiques. Les biomatériaux modernes utilisent des mousses céramiques façonnées ou des mousses organocéramiques comme charpentes osseuses, tandis que des structures hiérarchiquement micro- and nanoporeuses sont utilisées en chimie pour contrôler les réactions catalytiques. La conception de futurs matériaux ainsi que leur développement va de manière croissante reposer sur des structures et des propriétés de

E-mail address: szabler@physik.uni-wuerzburg.de.<http://dx.doi.org/10.1016/j.crhy.2014.09.005>

1631-0705/© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

mousses naturelles et synthétiques, qu'il s'agisse d'aliments, d'isolants thermiques ou de châssis d'automobiles, ce qui nous offre un aperçu prometteur de la recherche dans le domaine des mousses et des développements à venir dans un futur proche.

© 2014 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Definition, morphology and properties of foams

Foams can be broadly defined as a sub-category of the so-called cellular materials, i.e. as a two-phase mixture in which gas cells/pores are enclosed into a liquid, semi-solid or solid phase. Cellular materials in turn also comprise the inverse structure, i.e. in which solid or liquid particles are closely packed and surrounded by gas or liquid, as well as liquid–liquid mixtures that are known as emulsions. The structural, dynamic and mechanical properties of foams vary tremendously, whether they are liquid, semi-solid or solid foams, and so does their range of applications. Given the cellular nature of foams, their cell morphology is as important for their properties as are the properties of their individual components. Two types of morphologies are characteristic of foam cells: (1) spherical structures that are simply characterized by (a) the number distribution of radii, and (b) the distance distribution to the nearest neighbors; (2) polyhedral cells that are characterized by (a) faces or lamellas, which are curved thin films separating two neighboring cells, (b) plateau borders, which outline the skeleton of the liquid or solid structure, and (c) junctions of four borders each, the so-called vertices (cf. Fig. 1). In this text, we shall refer to foams as three-dimensional structures, keeping in mind that two-dimensional or quasi two-dimensional (e.g., wood) foams exist as

We encounter foams everywhere in our everyday life: Every plant on this planet is made of solid and/or semi-solid bio-foam, most insects build their hives in cellular arrangements, every car, plane and boat uses solid foams as structural components, every coffee we drink is tipped with a shiny cup of milk micro-foam which provides the unique sensation of fine latte art. Today, we know that even the universe itself has a cellular structure resembling that of foam [1].

2. Overview over liquid, semi-solid and solid foams

Most liquid foams owe their existence to *surfactants*, i.e. surface-active molecules that stabilize the thin intra-cellular films and reduce the surface energy of the phase boundary. In aqueous foams, these *surfactants* are generally hydrophilic on the one end, and hydrophobic on the other end, hence they have a natural tendency to form membranes in water–gas mixtures. Depending on the amount of liquid phase, these foams are referred to as dry foams (< 5% liquid) or wet foams (> 5%). Fig. 2 shows two transmission radiographs that illustrate the morphological difference between wet and dry foams.

When nanometer-sized solid particles are dispersed in the liquid and then the dispersion is mixed with gas, one speaks of semi-solid foams, the most common example being soap foam, but also many protein foams are being investigated for food applications, in which globular or micellar proteins act as stabilizing colloidal particles (e.g., milk foam); see the articles by Salonen and Fameau, and by C. Monteux, in this dossier. The effect of the particles is to stabilize (over time) the cellular structure by forming a network of semi-solid bridges or clusters inside the cell walls [2], while at the same time slowing down the liquid drainage (more information on dispersions stabilized by solid particles can be found in the article by Schmitt et al., in this dossier). In the case of cream foam, lipid molecules take that role, forming fat globules, which cluster in the cell walls when the air is whipped into the cream. Many metallic foams are being formed in the liquid or semi-solid state; nevertheless we treat them as solid foams referring to their technological use in this state. Polymer foams

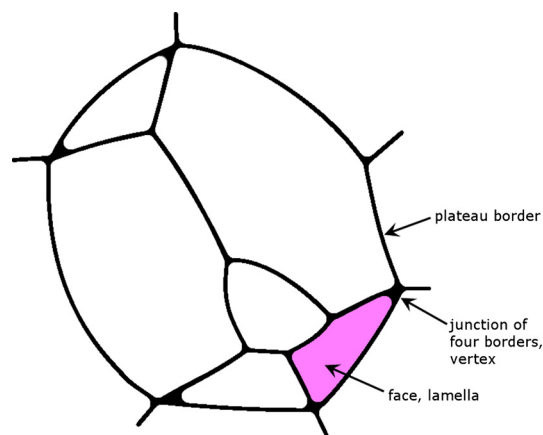


Fig. 1. (Color online.) Schematic drawing of a polyhedral pore in a three-dimensional dry foam.

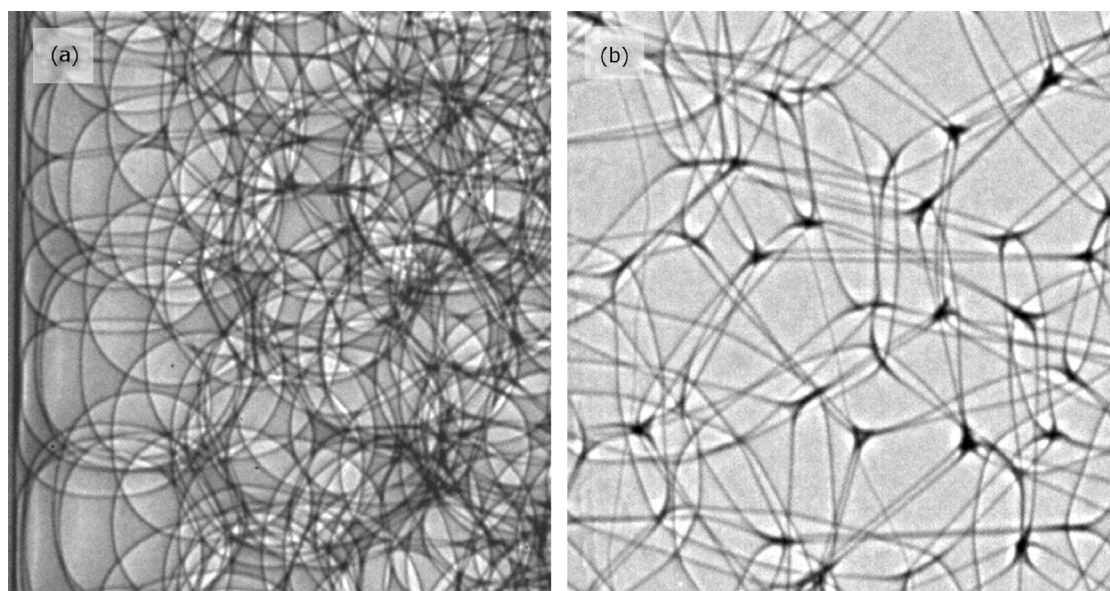


Fig. 2. Typical radiographic phase contrast images (taken at LRM, University of Würzburg, Germany) of (a) a wet, and (b) a dry detergent foam (courtesy of A. Meager).

which are—at least partially—made of hydrogels, hence comprising cell walls that can wet and dry, shall also count as solid foams, accounting for the elastic properties of their gel-like cellular structure. Wood, which is the most prominent example for such material, is generally used as solid structural foam, although in the green state it clearly shows the viscoelastic behavior of semi-solid foams.

Finally, solid foams are surely the most prominent application of solid cellular materials in structural mechanics. Their mechanical properties shall thus be discussed in length as well as their different fields of applications. Among metallic foams, aluminum is the most widely used base metal that can be foamed relatively cheaply on a large scale. The number of processing routes for metallic foams, some using foaming agents in powder mixtures, others using organic precursors are legion. Magnesium and titanium are now also being considered for foam structures and in certain applications, nickel-based metallic foams are being used. Ceramic foams are widely being produced for biomedical applications, often embedded in a polymer matrix. Finally, the extremely large number of solid polymer foams that are used on a large scale in construction and heat-shielding must be mentioned. Foaming of the latter is generally achieved in the liquid state above T_g .

3. Liquid foams and semi-solid foams

3.1. Materials and applications

Among the aqueous foams, mono-disperse foams, hence where all bubbles have about the same size, have attracted increasingly scientific interest, since they can be used to model the mechanics of closed packed crystals [1]. If no further stabilizer is added, the stability of the aqueous foam mostly depends on the amount and on the viscosity of the liquid and on the type of gas, i.e. on the diffusivity of the gas molecules in the liquid phase. The lower the latter, the more stable the foam. Typical ways of producing liquid foams are:

- blowing gas through a single nozzle into a liquid, and letting the bubbles rise to the surface where they form the foam. This method can produce mono-disperse foams if the gas flow is constant and relatively low. If, on the contrary, the gas flow is very high (the extreme case are aerosol sprays of cream and shaving foam), bubble formation is chaotic;
- blowing gas into the liquid through a porous plug, which is either at the tip of the nozzle (wash bottle) or at the bottom of the liquid reservoir. This method, which is called sparging, is useful for producing a very fine micro-foam defined by the very fine porosity of the plug;
- the nucleation of gas bubbles from a super-saturated liquid, e.g., by slowly evaporating or cooling the liquid until the point of saturation is reached. This method produces bubbles of a fairly homogeneous yet rather coarse size distribution (e.g., beer foam or soda). Since nucleation generally takes place at microscopic inhomogeneities in the container walls (e.g. beer glass), the structure of the resulting foam depends on the latter.
- shaking or beating the liquid. This method leads to a very broad bubble size distribution. For the case of egg white foam, the whipping has the additional effect of re-configuring proteins which then structure in thin layers forming stable cell walls. For the case of shaving cream (which is basically semi-solid soap foam), beating results in a very fine micro-foam, giving it its typical white color.

Applications range from food engineering to a variety of beauty and health products (e.g., shaving cream, shampoo and hair conditioner). Also in the chemical industry, liquid and semi liquid foams are used for controlling chemical reactions through larger surface areas. Fire extinguisher employ foam sprays for the very same reason.

3.2. Structural properties and measurement techniques

While for dry foams, the plateau borders form an outlined skeleton determining its viscoelastic properties, wet foams are characterized by the additional mobility of the pores as well as by convection in the liquid phase. All liquid and semi-solid foam structures are considered metastable, accounting for the collapse of the cellular structure which is driven by the thermodynamic principle of a minimum surface energy that is only achieved for one single flat phase boundary between the two phases, hence when no more bubbles exist. In every foam, this collapse takes place sooner or later. It occurs through known structural changes, i.e. drainage, coarsening and/or coalescence.

The morphology of liquid or semi-solid foams is described through a number of parameters, such as: pore size distribution, cell wall thickness, length of plateau borders, nearest-neighbor correlation. Depending on the pore size and the cell wall transparency of the foam, measuring the morphology can be very difficult. To assess the outcome of a foaming process, samples of liquid foams are spread and photographed on glass surfaces, thus reducing the morphological parameters to a two-dimensional extract of the foam, but also destroying part of the three-dimensional morphology of the real structure. The expansion rate during foaming is measured either mechanically and/or by video extensometers, the latter giving also limited information on the morphology of the foam, if it is transparent. True three-dimensional information on foam morphology, especially for foams that are not transparent, can only be measured by X-ray micro-CT, for which various examples exist [3].

3.3. Mechanical properties

Under shearing, liquid foams have a limited range of elasticity in which they behave like solids and are characterized by a shearing modulus G . For a complete overview of aqueous foam rheology, please refer to [4,5]. For detergent foam, G is of the order of a few hundred Pa, hence very low as compare to solids ($> 10^7$ Pa). Above the yield stress, the foam starts to flow, it behaves more like a liquid, which would be characterized by a certain viscosity η . Since η and G strongly depend on the amount of liquid phase, their magnitude can change, e.g., due to drainage. To be more precise, the elastic modulus and the yield stress scale with the Laplace pressure (surface tension/bubble radius) and both decrease with the amount of liquid inside the foam. As a rule of thumb, dry foams have a higher yield stress S_y than wet foams, but the actual pore size distribution might play a role as well. Both effects are summarized in the Herschel–Bulkley model [4]:

$$S = S_y + \dot{\epsilon}^n \eta \quad (1)$$

where S is the integral stress, $\dot{\epsilon}$ is the deformation rate, and n is an empirical exponent. For $n = 1$, the model reduces to the known Bingham law. To be more precise, the elastic modulus and the yield stress scale with the Laplace pressure (surface tension/bubble radius) and both decrease with the amount of liquid inside the foam. Under shear, the analogy to shear bands in solids can be observed in foams: avalanches of pores move and rearrange conjointly. Yet these analogies remain strongly debated in the community and are still not fully explained. Measuring η generally takes place in Couette and cone–plate viscosimeters, but also oscillatory measurements can be applied to extract the magnitude and phase of the shearing modulus, the latter being associated with energy dissipation. Yet, such measurements are only little informative about what is happening inside the structure, in particular when the latter is inhomogeneous, and topological rearrangements are likely to occur very early for the smaller pores. If oscillatory experiments are applied beyond the yield stress, a stress–strain hysteresis is observed, a typical characteristic of shear thinning. Another characteristic is creep deformation, which occurs for all viscoelastic materials, hence also for foams.

Shear thinning, viz. creep, comes into play when Eq. (1) is solved for the effective viscosity which is integral stress divided by strain rate:

$$\eta_{\text{eff}} = \frac{S_y}{\dot{\epsilon}} + \eta \dot{\epsilon}^{n-1} \quad (2)$$

The divergence of η_{eff} is an artifact of the simplified equation, and for very low strain rates creep takes place via coarsening of the foam structure, hence η_{eff} remains finite, even for $\dot{\epsilon} \rightarrow 0$.

3.4. Aging

The structural dynamics of liquid and semi-solid foams generally takes place in an irreversible manner: e.g., coarsening will cause small bubbles to shrink and larger bubbles to grow until the latter are so big that only coalescence or film rupture (collapse) can lead to a further increase in size. Drainage generally increases the probability for collapse, because growth and coarsening can less and less take place through the liquid phase [6,7]. For typical surfactant foam, coarsening and drainage take place over a couple of minutes, depending on the initial porosity (controlled by the initial bubble size)

and on the amount of liquid (plateau border cross section), then pore and foam collapse become the dominant processes. Nevertheless, the individual coarsening rates of very small pores can be relatively high in relation to their actual size. Pores that are smaller than 20 μm are likely to vanish within less than one minute, 200 μm pores in less than 10 min, thus inducing a re-arrangement and displacement of the larger pores. The observation of foam dynamics hence strongly depends of the level of detail that one wants to observe. Even the collapse of individual cell walls has been visualized in liquid aluminum foams, but such measurements are only possible with a very fast imaging system [8]. On the other hand, one coalescence event in chocolate mousse can be monitored over several hours [9].

Numerical simulation of liquid and semi-solid foam structures remains still very delicate. On the one hand, real foam structures display a large variety of cell sizes; on the other hand, a realistic simulation will have to include both linear elastic deformation and viscous flow, as well as irreversible structural changes such as cell collapse and coarsening. Two-dimensional models are much more common than three-dimensional simulations, because of their comparably low computational effort. Also Voronoi tessellation is used as a realistic start for such 2D computation, if no real measurement data is at hand. Each cell is thereby regarded as a polyhedral object with a certain inner gas pressure. The curvature of the cell edges is defined through the pressure difference of adjacent cells as well as by the $3 \times 120^\circ$ rule for the vertices. For example, coarsening may be introduced in this relatively simple model by introducing small changes in the cell sizes. Wet foams may be simulated by growing the cell edges and plateau borders through additional constraints. Models of three-dimensional foams exist, but they are much more demanding in terms of computational power, and validation with experimental data is often hard to come by. In particular, for coarsening scenarios, we obtain for the two-dimensional dry foam that the average cell diameter will grow with the square root of time:

$$\bar{d} \propto \sqrt{t - t_0} \quad (3)$$

whereby t_0 is the start time. The change of area over time for a polyhedral cell with n facets is given by Von Neumann's law for the dry foam:

$$\frac{dA_n}{dt} = \frac{2\pi}{3} \gamma \kappa (n - 6) \quad (4)$$

where κ is the permeability of one facet per unit of transverse length, and γ is a line tension, the equivalent to a surface tension in 2D. From Eq. (4) we can see that cells with a number of facets $n < 6$ will shrink, whereas cells with a number of facets $n > 6$ will grow. A cell with 6 facets will maintain its area until topological changes occur. An extension of Eq. (4) to three-dimensional foam has been proposed and shown experimentally to hold on average [1,2,7,10]. If coarsening theory has to be applied to a three-dimensional wet foam, most often the early work of Ostwald as well as those of Lifshitz, Slyzov and Wagner (LSW) are being cited [11,12]. Yet, the LSW model implies: (a) a constant liquid fraction (no drainage), (b) ideally dissolved particles in an oversaturated solution (and no close packing of gas bubbles), and (c) a spherical shape of the particles. The resulting rate equation for the particle radius R is:

$$\frac{dR}{dt} = \frac{K_{\text{diff}}^*}{R^2} \left(\frac{R}{R_c} - 1 \right) \quad (5)$$

where K_{diff}^* is the rate constant of the diffusive process. In analogy to the $n = 6$ case in Von Neumann's law, now there is a critical radius R_c for which the size of a particle remains constant, for $R > R_c$ the particles grow, approaching the asymptotic law $R \propto \sqrt{t - t_0}$, whereas for $R < R_c$ particles shrink, approaching the asymptotic law $R \propto \sqrt[3]{t - t_0}$. In reality, LSW theory has only been validated for certain 3D foams in terms of growth of the average cell diameter, not for individual cells.

4. Solid cellular materials/foams

4.1. Metallic foams (materials, mechanics, applications)

The motivation for metallic foams comes from the need to increase the specific strength or stiffness of a foam structure as compared to the bulk material, thus reducing weight in order to save energy. Depending on their production process, there are *open* metallic foams, and *closed* metallic foams. The latter are formed, as mentioned earlier, in the molten liquid phase where gas is either injected (*Alcan* line) into the melt, or added in form of a blowing agent (*Alporas* line), or the gas is set free by oversaturating the liquid (*Gasar* line). Very similar to the *Alporas* line is the *precursor* foaming during which a second material (e.g., TiH_2 or ZrH_2) is mixed and molten along with the metal, setting the gas free through a chemical reaction that takes place at a temperature slightly above the melting point of the base metal. Even though precursor foaming with TiH_2 as a blowing agent is the most common routine for producing aluminum foams, the precise chemical reactions that take place during the dissociation of TiH_2 have only been unveiled recently by in situ diffraction [13]. Open metal foams, on the other hand, are often produced by sintering organic–inorganic *templates*. During high temperature sintering, the organic phase evaporates, leaving only the sintered metallic network. Such spongy materials have properties that are much different from those of closed metallic foams, and have therefore different fields of application. Nevertheless, high melting temperatures make this process the only option to build porous material from many metals (e.g., Ni, Ti, Cu) or

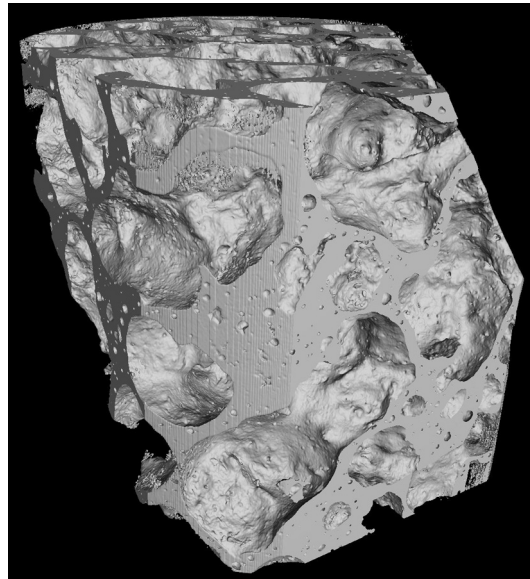


Fig. 3. 3D rendering of a solid magnesium foam (recorded at LRM, Würzburg, Germany; courtesy of Tobias Neum HZB, Berlin, Germany).

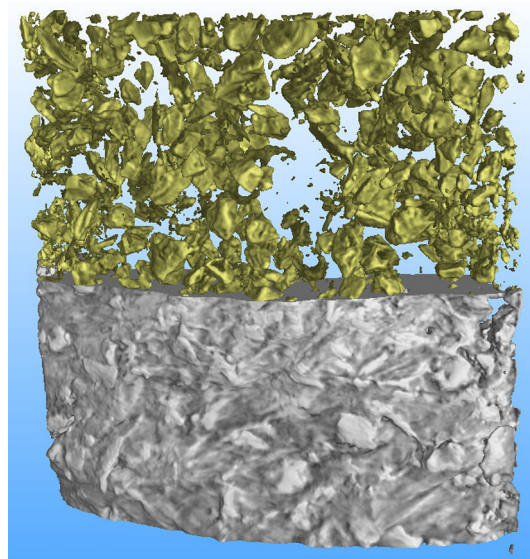


Fig. 4. (Color online.) High-resolution rendering of a single aluminum foam cell wall including the densely packed SiC particles that act as stabilizers in the foaming process (recorded at BAMline, Berlin, Germany).

ceramics [14–16]. Metal foaming has been invented as early as 1925 by M.-A. De Meller [17]. For a complete review on the history of metallic foams, the reader will refer to [18]. It is today a large-scale industrial process for a material with countless applications, many in the automotive industry.

In addition to aluminum, which may be called the “standard metallic foam”, other base metals are being considered for foaming, such as magnesium and zinc. Fig. 3 shows a micro-CT image of magnesium foam (courtesy of F. Garcia-Moreno, Helmholtz Berlin, Germany). The melting points of these metals are not too high, but the production process is still too expensive and experimental to allow for large-scale applications. As compared to soap or cream, the release of gas during precursor foaming is very rapid and the larger cells are relatively unstable, which is why, for aluminum foaming, the dispersion of solid particles (e.g., SiC, TiB or WC) into the melt has become an important way to control and stabilize the foam structure, very similar to the way soap stabilizes aqueous foams. An example of a single cell wall of aluminum foam with dispersed SiC particle is shown in Fig. 4.

The mechanics of metal foams is described and tested in the same way as for other solid structural materials, hence: stress–strain measurements, fatigue, impact and creep experiments [19]. Depending on the size distribution and shape of the pore structure, the samples have to be relatively large as compared to bulk metals. Density measurements are important in

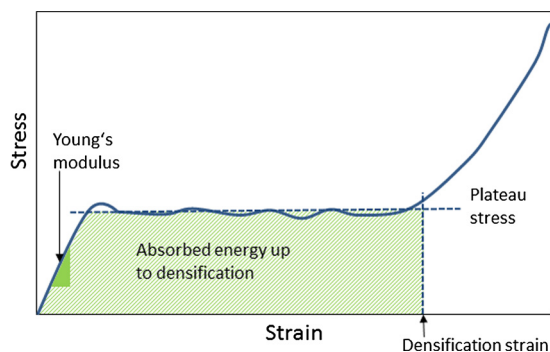


Fig. 5. (Color online.) Schematic stress–strain diagram for metallic foams, showing the large plasticity plateau until densification starts with a critical strain.

this manner in order to relate the force-vs-displacement measurements to local stress in the cellular structure. In particular, the dependency of the Young modulus of metal foams on the mass density is not linear, but follows a power law with an exponent of approximately 1.9 [1]. Failure has to be treated indeed in a different manner as compared to bulk metal samples. Typical failure modes are buckling (compression) and rupture (tensile) of cell walls. In fatigue experiments, unless high-resolution in situ X-ray methods are employed, crack nucleation and propagation can unfortunately not be studied on the whole sample. It is even likewise difficult to determine the onset of failure. Most often, these are microcracks in single cell walls, which are described and explained through the known deformation of thin sheets. Very similar to the case of sintered ceramics, fracture and failure of metal foams is strongly influenced by small defects, which can be a higher concentration of oxide particles or a particular strong curvature in the cell wall structure. The cell size distribution, on the other hand, has been shown to be not of much relevance to the mechanical properties. Hence, very inhomogeneous foams with a large variety of cell sizes shows the same bulk properties as completely mono-sized foam of the same density. Stress–strain curves do not feature a very high yield, but extended stress plateaus that mark the important property of metallic foams to absorb a lot of energy until the structure is too dense to deform by bending the cell walls only (cf. Fig. 5). Energy absorption would be maximized if yield in the cell walls and plastic flow of the material were to occur under the same load; yet in reality the cell walls yield almost immediately when stress is applied, then they bend and buckle, giving rise to the extended stress–strain plateau.

Metallic foam sandwiches or foamed tubes have a structural advantage over bulk material in bending as well as in compression, and are therefore used in constructions where such load applies, whereas in tensile load they do not permit weight reduction, be it stress or stiffness-controlled applications. For energy uptake under impact, their isotropic structure makes metallic foams an ideal material for shell applications. Other areas of application make use of their metallic properties which make them very good heat dissipaters as well as electric conductors [20]. Also the acoustic properties (sound damping) of metallic foams play an important role in their use as a structural material. Until today no standard corrosion tests are being applied to metallic foams, although they are likely to be more vulnerable to crevice corrosion because of their cellular structure.

4.2. Ceramic foams (materials, mechanics, applications)

Ceramic foams have become very popular since they are being used frequently as biomaterials, most often as the so-called scaffold materials. Hereby, the foam structure is used as a scaffold in which—once the implant is inside the body—the voids are filled by a growing structure, generally bone. Using ceramic foams as bone scaffold has a three-fold use: first, the porous interface between the implant and the living matrix is favorable for osteoblasts to attach to the scaffold, even more if the surface has been treated to promote this attachment; second, if the scaffold is re-absorbed, as is the case for tri-calcium phosphate (TCP), the cell walls can provide the ingredients for the formation of new bone; and third, if the scaffold is permanent, its effective Young modulus can be made match the modulus of bone, thus avoiding stress shielding and the risk of bone-resorption, which is a core problem with bulk metallic implants. Nevertheless, since most applications of permanent implants are stress limited, bulk metals (Ti, Zr, Au, Pt) or bulk ceramics (Al_2O_3 or ZrO_2) are the preferred choice. Yet, their surface is often treated (e.g., by corundum sand-blasting and/or electrochemical etching), so that it becomes a thick foam-like junction between the bulk implant and the surrounding bone.

Recently, the sintering of ceramic foams from nanobeads has been proposed to create a so-called hierarchical porosity with pores on two or more length scales. Such a process is important when several specific properties must be united: e.g., a high specific surface for catalytic reactions that are carried out on the foam support, as well as high mechanical strength and large permeability, hence a low tortuosity, as required for filtering (e.g., of liquid metal) and sorption applications. While polyurethane or polystyrene (PS) particles are often used to make the template for the macro-porosity, the tri-block co-polymer P123 can be used to direct the mesoporous structure on the top of the macro-pores in the same production process. For a review, see Colombo et al. [21]. Sol-gel methods have also been proposed to create ceramic foams of nanoscale porosity.

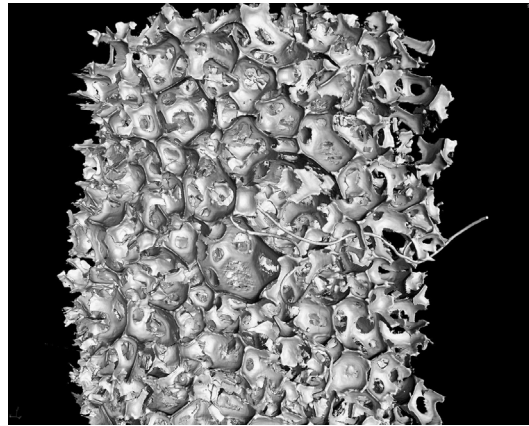


Fig. 6. 3D rendering of a polyurethane foam (recorded at LRM, Würzburg, Germany).

The production of ceramic foams from pre-ceramic polymer templates is the reason why these foams have—in most cases—an open cell structure [22]. In a similar way to bulk ceramics, the strength and toughness of ceramic foams strongly depend on their production process and can be spoiled by a very small concentration of microscopic flaws or inhomogeneities. Mixing the ceramic powder with the polymer template is generally done in a liquid suspension, which leads to additional problems if the ceramic is hydroscopic and structural changes are induced during dehydration of the suspension. Recently ceramic foams made of alumina (Al_2O_3) and hydroxyapatite (HAp) were created through mixing and foaming with a protein solution, using bovine serum albumin as well as whey proteins as a dispersing agent, followed by sintering. Such foams can be used as bioreactor for cultivating human stem cells [23]. For more information on ceramic foams, refer to [24,25].

In comparison to metal foams, ceramics have a higher yield, but hardly an extended stress–strain plateau, because of the low fracture toughness of the ceramic sponge. One of the few methods to make closed cell ceramic foams so far is the direct foaming of SiOC followed by pyrolytic reduction to SiC foam [22]. Closed cell foams display a higher strength as compared to open cells.

4.3. Organic/polymer foams

Polymer foams are by far the most frequently used solid foam in modern society. Polyurethane and polystyrene are known examples that are used for impact protection as well as for thermal insulation in packaging and construction, respectively. PS and PU foams usually have large (millimeter size) polyhedral closed cells (cf. Fig. 6). Polymer foams also play an important application in the biomedical sector: cell cultivates on freeze structured and dried gelatin foam has been proposed as material for cartilage scaffold [26]. In production, foaming is directed by a blowing agent, which is blend with the monomer, and which—upon heating—liberates a gas (that can be fluorocarbons, CO_2 or N_2), thus creating the foam. The engineering of blowing agents is somewhat more challenging than in the case of metal foams. When the gas is released the polymer must flow, hence temperatures must be some tens of degrees above T_g , the glass-transition temperature, typically in the range of 150–250 °C. Foaming can be followed by thermal and/or chemical reactions during which the polymer is further hardened (e.g., UV light). Spray foaming is also not uncommon for polymers. Crispy chocolate is an example for solid polymer foam in modern food industry.

Concerning their mechanical properties, polymer foams show a large variety: e.g., carbon foam which is created through heat treatment of polymer foam is rather stiff and brittle, whereas foams made from elastomers are a highly elastic material, used for beds. Making foams from thermoplasts results in a material that has a certain linear elastic response. Beyond the yield, plastic deformation causes the well-known stress–strain plateau, i.e., the cell walls buckle until finally compaction begins when the available pore space has been closed.

4.4. Natural foams

Most natural foams can be classed as polymer foams although many contain water in the cell walls (natural hydrogels) and/or in the pores. They can be organic–inorganic compounds, as it is the case for trabecular bone, which is built of fibrous collagen and hydroxyapatite crystals. The foaming of dough is also a semi-natural phenomenon that takes place in the semi-solid state and is converted into solid foam (bread) upon baking. Natural sponge is obviously natural open cell foam that is showing an entirely elastomeric response to mechanical stress. Wood is the classic anisotropic foam made from hexagonal long cells (tracheids) that are used for water transport and to bear mechanical load. A 3D rendering of wet pinewood is shown in Fig. 7 (courtesy of J. Dittmann, University of Würzburg, Germany).

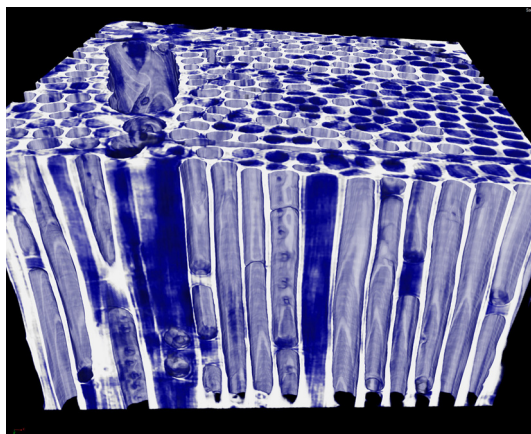


Fig. 7. (Color online.) 3D rendering of a wet pinewood cell structure (courtesy of J. Dittmann, LRM, Würzburg, Germany). The blue color indicates water which for some cells fills the structure, the white color indicates the cell walls. Measurements were done at the ID19 beamline, ESRF, Grenoble, France.

5. Outlook & summary: latest innovations and future of cellular materials

Clearly, among the many processing routes for liquid, semi-solid, and solid foams, the development of biological scaffolds by using functionalized surfaces is the most innovative and promising way. Using nanopowder processing routes, micellar precursors and grain refiners, in order to create high-strength, solid hierarchically tailored foams, comes along with the very common use of these additives in new materials' processing for bulk metals and ceramics. They are most promising for energy applications, in which foams are already being widely used: as gas filters, heat exchangers, diffusion and reaction layers. The number of foam applications in the energy sector is strongly increasing: even aerogels (a nanoscale foam) made of SiO_2 have been proposed for high-efficiency photovoltaic applications. Also, much remains to be done for the simulation and theory of liquid foam dynamics in the future.

References

- [1] D. Weaire, S. Hutzler, *The Physics of Foams*, Oxford University Press, Oxford, UK, 1999.
- [2] A. Eggert, M. Müller, F. Nachtrab, J. Dombrowski, A. Rack, S. Zabler, High-speed in-situ tomography of liquid protein foams, *Int. J. Mater. Res.* 105 (7) (2014) 632–639.
- [3] J. Lambert, Extraction of relevant physical parameters from 3D images of foams obtained by X-ray tomography, *Colloids Surf. A* 263 (2005) 295–302.
- [4] R. Höhler, S. Cohen-Addad, Rheology of liquid foams, *J. Phys.: Condens. Matter* 17 (2005) R1041–R1069.
- [5] N.D. Denkov, S. Tcholakova, K. Golemanov, K.P. Ananthpadmanabha, A. Lips, The role of surfactant type and bubble surface mobility in foam rheology, *Soft Matter* 5 (2009) 3389–3408.
- [6] A. Saint-Jalmes, Physical chemistry in foam drainage and coarsening, *Soft Matter* 2 (2006) 836–849.
- [7] S. Hilgenfeldt, S.A. Koehler, H.A. Stone, Dynamics of coarsening foams: accelerated and self-limiting drainage, *Phys. Rev. Lett.* 86 (20) (2001) 4704–4707.
- [8] A. Rack, et al., On the possibilities of hard X-ray imaging with high spatio-temporal resolution using polychromatic synchrotron radiation, *J. X-Ray Sci. Technol.* 18 (2010) 429–441.
- [9] S. Zabler, C. Fella, A. Dietrich, F. Nachtrab, Michael Salamon, V. Volland, T. Ebersperger, S. Oeckl, R. Hanke, N. Uhlmann, High-resolution and high-speed CT in industry and research, in: *Developments in X-Ray Tomography VIII*, 17 October, 2012, in: *Proc. SPIE*, vol. 8506, 2012, 850617.
- [10] J. Lambert, R. Mokso, I. Cantat, P. Cloetens, J.A. Glazier, F. Graner, R. Delannay, Coarsening foams robustly reach a self-similar growth regime, *Phys. Rev. Lett.* 104 (2010) 248304.
- [11] L. Radtke, P.W. Voorhees, *Growth and Coarsening*, Springer, 2001.
- [12] D.J. Durian, D.A. Weitz, D.J. Pine, Scaling behavior in shaving cream, *Phys. Rev. A* 44 (12) (1991) R7902–R7905.
- [13] C. Jimenez, et al., Metal foaming studied in-situ by energy dispersive X-ray diffraction of synchrotron radiation, X-ray radiography and optical expandometry, *Acta Mater.* 15 (3) (2012) 141–148.
- [14] D.C. Dunand, Processing of titanium foams, *Adv. Eng. Mater.* 6 (6) (2004) 369–376.
- [15] T. Dillard, et al., 3D quantitative image analysis of open-cell nickel foams under tension and compression loading using X-ray microtomography, *Philos. Mag.* 85 (19) (2005) 2147–2175.
- [16] N.G. Wadley, Cellular metals manufacturing, *Adv. Eng. Mater.* 4 (10) (2002) 726–733.
- [17] M.-A. De Meller, Produit métallique pour l'obtention d'objets laminés, moulés ou autres, et procédés pour sa fabrication, French Patent No. 615,147, 1926 (1925).
- [18] J. Banhart, Light-metal foams—history of innovation and technological challenges, *Adv. Eng. Mater.* 15 (3) (2013) 82–111.
- [19] J. Banhart, et al., Deformation characteristics of metal foams, *J. Mater. Sci.* 33 (1998) 1431–1440.
- [20] A.G. Evans, et al., Multifunctionality of cellular metal systems, *Prog. Mater. Sci.* 43 (1999) 171–221.
- [21] P. Colombo, C. Vakifahmetoglu, S. Costacurta, Fabrication of ceramic components with hierarchical porosity, *J. Mater. Sci.* 45 (2010) 5425–5455.
- [22] J. Grosse, et al., Morphological characterization of ceramic sponges for applications in chemical engineering, *Ind. Eng. Chem. Res.* 48 (2009) 10395–10401.
- [23] A. Berthold, et al., Biocompatible porous ceramics for the cultivation of hematopoietic cells, *J. Mater. Sci.* 18 (7) (2007) 1333–1338.
- [24] L. Montanaro, et al., Ceramic foams by powder processing, *J. Eur. Ceram. Soc.* 18 (1998) 1339–1350.
- [25] J.R.G. Evans, et al., Microstructure of ceramic foams, *J. Eur. Ceram. Soc.* 20 (2000) 807–813.
- [26] R. Zehbe, et al., Three-dimensional visualization of in vitro cultivated chondrocytes inside porous gelatine scaffolds: a tomographic approach, *Acta Biomater.* 6 (6) (2010) 2097–2107.