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Abstract
Recent research related to foam drainage is surveyed with emphasis on the influence of interfacial rheology. Active research directions are highlighted and the possible impact of these studies on macroscopic rheology is indicated.

1. Introduction

Foams and emulsions are well known to scientists and the general public alike because of their everyday occurrence (Prud'homme and Khan 1996, Weaire and Hutzler 2000). Foams are common in foods and personal care products such as creams and lotions, and foams often occur, even when not desired, during cleaning (clothes, dishes, scrubbing) and dispensing processes. Polymeric foams are used in cushions and packing and structural materials (e.g. Gibson and Ashby 1999). Glass, ceramic, and metal foams (e.g. Ashby *et al* 2000) can also be made, and find an increasing number of new applications. In addition, mineral processing utilizes foam to separate valuable products by flotation. Finally, foams enter geophysical studies of the mechanics of volcanic eruptions.

During foam production the material is in the liquid state and fluid can rearrange while the bubble structure stays relatively unchanged. The flow of liquid relative to the bubbles is called *drainage*. Generally, drainage is driven by gravity and/or capillary (surface tension) forces and is resisted by viscous forces. We shall denote the volume fraction of liquid in the foam by ϵ, which is the fundamental 'density' variable in drainage studies. For example, for solid foams the relative density $\epsilon = \rho_{\text{foam}}/\rho_{\text{solid}}$, which is the ratio of the foam's density to the density of the solid material from which it is made, is an important parameter for characterizing the mechanical response.

When the liquid volume fraction is small, say $\epsilon < 5\%$, the foam structure is polyhedral, with Plateau borders (channels) where three faces, which separate the bubbles, meet, and

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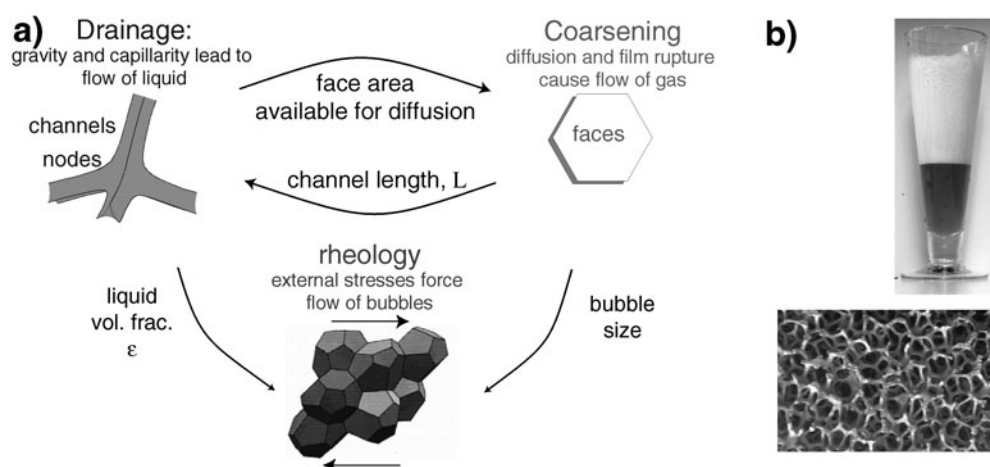
Figure 1. The coupling of dynamical processes in (liquid) foams. (a) As the foam drains, the amount of liquid separating the bubbles changes, which affects the rate of diffusion of gas from bubble to bubble. Also, as the foam coarsens, the bubble size grows and the drainage rate increases. The mechanical response of the foam when sheared depends on the amount of liquid in the foam and the bubble size. (b) Liquid drainage in a glass of wheat beer; the image of a solid aluminium foam clearly illustrates the channel structure of Plateau borders.

vertices or nodes where four borders meet[4]. We need the relationship of ϵ to the typical Plateau border radius r, channel edge length L, and face thickness h_{face}, which is well approximated by $\epsilon = \delta_\epsilon r^2/L^2 + \delta_n r^3/L^3 + \delta_f h_{\text{face}}/L$, where the δ_i are geometrical constants that can be evaluated once a model structure for the foam cells is chosen. Generally, we only utilize the first term, $\epsilon \approx \delta_\epsilon r^2/L^2$, which is an excellent approximation for dry foams (for a foam made of tetrakaidecahedral kelvin cells, $\delta_\epsilon \approx 0.171$).

1.1. The interrelation of structure, mechanics, and dynamics

Foams in their liquid state are metastable, and continually evolve on multiple length scales. In addition to drainage, coarsening simultaneously occurs, either because of diffusion of gas across films from bubbles of high pressure to bubbles of low pressure, or because faces become thin and unstable, and rupture; both processes result in continual growth of the average bubble size. Also, foams can be sheared or driven by a pressure gradient through a channel. Both coarsening and the response of the foam to deformation (i.e. rheology) depend on the liquid volume fraction and thus are coupled to drainage (figure 1). In some circumstances this coupling can be exploited to learn about individual processes in a foam (e.g. for coarsening and rheology see Cohen-Addad *et al* (1998)).

In this paper we summarize ideas surrounding the 'foam drainage equation' and discuss experiments illustrating the impact of bubble-scale interfacial rheology on drainage. Recent research directions are also described. We close with remarks on how this work may have an impact on the understanding of the macroscopic rheology of foams.

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[4] These fundamental coordination numbers in foams were found in the 19th century by the Belgian scientist Joseph Antoine Ferdinand Plateau.

2. The foam drainage equation: Darcy's law applied to a foam

Over the past decade much progress has been made with respect to quantifying drainage in foams. Generally, the measurements are made on scales larger than individual bubbles, so a continuum or coarse-grained approach is appropriate. It is convenient to work in terms of the liquid volume fraction ϵ and the average liquid velocity v in the channel-like network that makes up a foam; for this introductory derivation, we consider a monodisperse foam. The form of the 'foam drainage equation' follows from the continuity equation $\frac{\partial \epsilon}{\partial t} + \nabla \cdot (\epsilon v) = 0$ with the relative velocity $v = \frac{k}{\mu}(-\nabla p + \rho g)$, of liquid and bubbles, owing to pressure gradients ∇p and gravitational (or other) body forces ρg in the liquid, given by Darcy's law, where ρ is the liquid density and k is the permeability of the foam (dimensions length squared). As we discuss in more detail below, k depends on channel length L, liquid volume fraction ϵ, the interfacial mobility of the surfactant, and perhaps other variables. Characterizing k is the most important aspect of writing averaged equations of this type. It is expected on dimensional grounds that $k \propto L^2$, which is a reasonable estimate (not accounting for the ϵ dependence), though the bubble size dependence can be more involved, as k depends on surface rheological parameters as well. For the models summarized here, the average channel length L is the only geometrical quantity characterizing the bubbles.

Since the bubble pressure p_0 is expected to be approximately constant, then with γ denoting the interfacial tension, the liquid pressure $p = p_0 - \gamma/r$, and using the above we find

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \left(\frac{\rho g}{\mu} \epsilon k(\epsilon) \right) - \nabla \cdot \left(\frac{\gamma \delta_\epsilon^{1/2}}{2\mu L} \frac{k(\epsilon)}{(\epsilon)^{1/2}} \nabla \epsilon \right) = 0, \tag{1}$$

which we refer to as the foam drainage equation. This equation has been compared with experiments for one-dimensional (Verbist *et al* 1996, Cox *et al* 2000, Koehler *et al* 1998, 2000) and limited two-dimensional configurations (Koehler *et al* 2001); much insight can be obtained from other studies of nonlinear convective-diffusion equations. There are generalizations to account for changes in container shape (Saint-Jalmes *et al* 2000), which requires keeping track of the local number density of channels, for macroscopic foam flow during drainage (Grassia *et al* 2001), for simultaneous coarsening where the average bubble size changes with position and time (Hutzler and Weaire 2000, Hilgenfeldt *et al* 2001), and for incorporating higher-order terms in the $\epsilon(r, L)$ relation (Neethling *et al* 2002). Nevertheless, making quantitative predictions using (1) requires knowledge of the permeability, which means understanding microscale processes on the scale of individual bubbles and Plateau borders.

Some areas of research involving drainage are summarized in table 1. Topics discussed in the previous paragraph are indicated, but the table also includes investigations for:

  (i) modifying the rheology of the interstitial liquid by adding polymer;

 (ii) understanding the interfacial rheology of the surfactant system, which sets boundary conditions for the local fluid flow;

(iii) understanding the impact of polydispersity (the above discussion was based on a monodisperse foam); and

(iv) the effect of phase change with simultaneous drainage (e.g. manufacturing a solid foam).

Addressing these questions quantitatively requires understanding the permeability k.

Table 1. Themes of research in the foams community (with representative references).

Rheology/surfactants	Drainage and 'something'	Other
Interfacial rheology/Marangoni	2D, 3D drainage; foam expansion	Container shape[a]
Bulk rheology (e.g. added polymer)[b]	Drainage and coarsening	Particulate additives
Polydispersity	Drainage and phase change[c]	Convective instabilities[d]
Concentration of surfactant	Drainage during bulk flow	Foams in porous media

[a] Saint-Jalmes *et al* (2000).
[b] Safouane *et al* (2001).
[c] An example is in metal foams (e.g. Cox and co-workers).
[d] Hutzler *et al* (1998), Vera *et al* (2000).

3. Mobility of interfaces

3.1. Isolated films

There is a growing literature on the rheological response of surfactant layers (e.g. Brooks *et al* 1999, Langevin 2000) and the dynamical response of a soap film (e.g. Chomaz 2001). The mechanical response depends on the chemical state of the interface, e.g. the molecular weight and structure of the surfactant, and kinetic coefficients for interfacial adsorption/desorption. Consequently, the interfacial (and bulk) rheology should be adequately modelled to assess the dynamical response of foams.

In studies of surfactant and soap films, properties such as the surface shear and extensional viscosities are measured. Some systems have a Newtonian surface rheology, while others are viscoelastic (e.g. Edwards *et al* 1991), and the variation of the surface tension is reported as a function of the surface concentration of surfactant and the rate of change of interfacial area. Moreover, transport processes, such as diffusion of surfactant from the bulk to the interface, and subsequently processes of adsorption/desorption to/from the interface (e.g. Langevin 2000), can influence the dynamical response. For both thin films and foams there is a strong correlation between the interfacial rheology and stability, with higher surface viscosities generally leading to improved stability (e.g. Prins (1999); for further references see Edwards *et al* (1991)).

3.2. Drainage in foams: macroscopic measurements

Three types of experiment have been useful (e.g. Verbist *et al* 1996)): forced drainage where fluid is continually added to a foam and a wetting front moves with constant velocity $v(\epsilon)$; free drainage where a nearly uniform foam is made and then allowed to drain, with ϵ varying in space and time; and pulsed drainage where an injected volume is observed to spread. Results of forced drainage experiments with the washing-up liquid Fairy were in good agreement with the prediction $\mu v/(\rho g L^2) = K_1 \epsilon$, where K_1 is a constant. The results are consistent with a model wherein the permeability is controlled by viscous resistance in the Plateau borders ('channel-dominated flow').

Later, forced drainage experiments with the washing-up liquid Dawn gave results in agreement with $\mu v/(\rho g L^2) = K_{1/2} \epsilon^{1/2}$. This result can be rationalized if the dominant contribution to the flow resistance occurs in the nodes where the Plateau borders intersect (Koehler *et al* 1999), which is referred to as 'node-dominated flow'.

Forced drainage results consistent with these two distinct behaviours have been reported where large-molecule surfactants (e.g. the protein BSA) are close to the channel-dominated limit while small-molecule surfactants are close to the node-dominated limit. Durand *et al* (1999) reported forced drainage experiments with foams made with SDS–dodecanol solutions
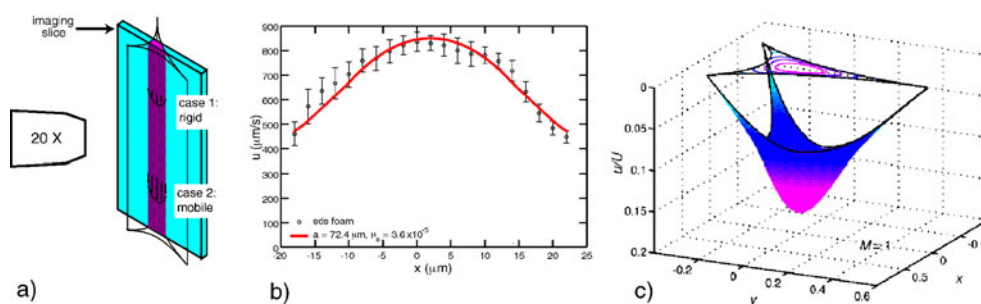
Figure 2. (a) The experimental configuration for confocal imaging of the flow in a single Plateau border. (b) The velocity profile across a Plateau border during drainage where the symbols show measurements and the solid curve is based on a model of flow along the channel with transverse shearing of a surfactant film. (c) A three-dimensional view of the numerically computed velocity profile when the interfaces exhibit flow due to interfacial mobility (Koehler *et al* 2002).

(This figure is in colour only in the electronic version)

and linked the different responses to the interfacial rheology: previous experiments with soap films (e.g. Mysels *et al* 1959) established that dodecanol enhances the surface viscosity and elasticity. Later Koehler *et al* (2000) performed forced, free, and pulsed drainage experiments with SDS foams and found that the results were well described by the node-dominated model.

3.3. Forced drainage in foams: microscopic experiments

Koehler *et al* (2002) reported confocal microscopy experiments on particle tracking in individual Plateau borders. A foam made with the large macromolecule BSA had velocities at the channel surfaces that were very small (essentially no slip), while a small-molecule SDS foam exhibited significant interfacial velocities (figure 2). The results were interpreted with a channel-scale flow model (Leonard and Lemlich 1965) where the degree of interfacial motion was calculated self-consistently by including surface shear transverse to the flow direction.

3.4. Microscopic models: from Leonard and Lemlich to the present

The above results illustrate that flow at the individual bubble scale controls the macroscopic drainage rates. Thus, it is of interest to characterize the microscale flow processes that vary with surfactant type and concentration, bubble size, bulk rheology, etc. Such research began with Leonard and Lemlich (1965), who studied axial flow in a Plateau border and included resistance for surface shear of a surfactant film. Research with this model continues, including improved numerical simulations with correlations (Nguyen 2002) and asymptotic analysis (Koehler *et al* 2002, and in preparation). Attributing a surface shear viscosity μ_s to the interfacing introduces the dimensionless mobility $M_L = \mu L/\mu_s$ into the functional determination of the permeability k. The influence of Marangoni stresses is also under investigation (M Loewenberg personal communication 2002, Durand and Langevin 2002). (M Loewenberg personal communication 2002, Durand and Langevin 2002). Durand and Langevin introduce a mobility parameter accounting for Marangoni stresses, $M_M = \mu D_s/(EL)$, where $E = -\Gamma\, d\gamma/d\Gamma$ is the surface elasticity, D_s is the surface diffusivity, and Γ is the surface concentration. These different models indicate the coupling of bubble size (through L) and interfacial rheology, which is an active area of research (e.g. Saint-Jalmes *et al* 2002, Carrier *et al* 2002).
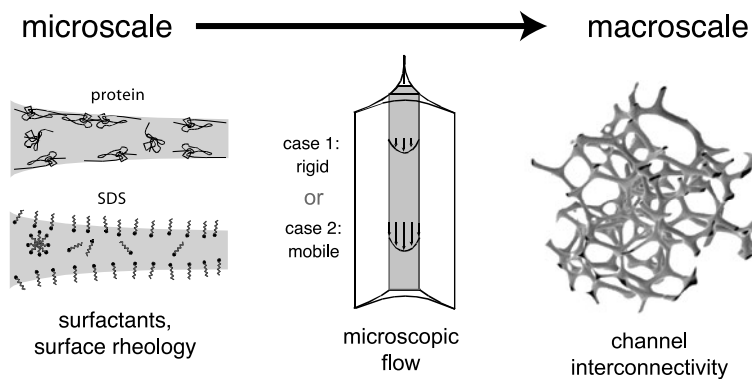
Figure 3. A schematic diagram of the surfactant film, which dictates interfacial mobility and the microscopic flow, and the subsequent coupling to macroscopic drainage.

4. Macroscopic modelling: the network model of the drainage process

There is evidence that the chemical and structural characteristics of a foam influence the rate of drainage (section 3), as is illustrated schematically in figure 3. Thus, a predictive macroscopic theory should incorporate the most important effects, which may include (i) channel and node resistances, while (ii) treating bulk and surface rheologies and surfactant transport dynamics, which may include (iii) Marangoni stresses and (iv) possible viscoelastic response (e.g. a yield stress). Other effects that are potentially important are (v) finite liquid volume fractions, (vi) the role of suspended particles, and (vii) polydispersity.

As a macroscopic model of flow through a foam treats the channel-like network as a series of resistances, the effective permeability k has the form $k^{-1} = \sum_{i=1}^{N} k_i^{-1}$ where each of the k_i represents a distinct source of dissipation (e.g. surface viscosity). Recognizing channels and nodes, as above, we can write $L^2 k^{-1} = K_{\text{channel}}^{-1}(M_L, M_M, \epsilon) + \epsilon^{-1/2} K_{\text{node}}^{-1}(M_L, M_M, \epsilon)$ where analytical arguments suggest that the dimensionless prefactor K_{channel} is strongly dependent on the mobility factor M_L, while K_{node} is only weakly dependent on M_L. These ideas lead to a 'phase diagram' for characterizing the permeability (Koehler *et al* 2002, in preparation).

For more generality in considering how micro-physical processes influence the permeability (or other aspects of foam mechanics), we consider a functional relation among the variables, such as $f(k, \epsilon, L, \mu, \mu_s, \gamma, E, \rho g, D, D_s) = 0$, where D is the bulk diffusivity of surfactant. Via dimensional arguments (i.e. the Buckingham–Pi theorem), there is then a relation among $9 - 3 = 6$ dimensionless variables, in addition to ϵ, i.e. $k/L^2 = f_1(\epsilon, \mu L/\mu_s, D_s \mu/(EL), D/D_s, \rho g L^2/\gamma, E/\gamma)$; other variables include concentration above the CMC, kinetic parameters for adsorption/desorption, and, if the kinematics requires it, distinguishing surface shear and dilational viscosities. This approach may be useful when considering rheology as discussed next.

5. Summary

5.1. Interfacial rheology and the influence on foam rheology

The macroscopic rheology of foams and emulsions is studied widely (e.g. Kraynik 1988); both shear and extensional motions are of interest. Nevertheless, many questions remain,

in particular on the dynamical response and the relationship of the dynamical response to the basic physical parameters characterizing the foam.

In an oscillatory small-amplitude shear experiment, the complex modulus G (proportionality of stress to strain) is reported as a function of frequency. Elementary dimensional arguments indicate that the elastic modulus $\mathrm{Re}(G) = G' = \mathrm{O}(\gamma V^{-1/3})$ where V is the bubble volume. A yield stress is also observed. These properties, essentially characterizing the static response, are largely *independent* of the constituents that make up the foam (e.g. Hemar and Horne 2000), at least at small frequencies (strain rates), other than setting the value of surface tension and having an impact on the process that leads to the bubble size.

The loss modulus $\mathrm{Im}(G) = G''$, which indicates the effective viscosity of the foam, is typically 6–10 times smaller than G' and is less well understood (e.g. Cates and Sollich 2000). Here the dissipative processes in the foam establish the magnitude and time dependence of the effective viscosity, and the interplay of macroscopic deformation, microscopic deformations, and interfacial transport and rheology are not yet sufficiently well understood to provide a quantitative characterization of the rheological response. Considerations of the influence of the interfacial rheology, and the manner in which they may have an impact on quantitatively macroscopic rheological measurements, have been considered by Buzza *et al* (1995), Hemar *et al* (1995) and Edwards and Wasan (1996); a quantitative understanding and a comparison of theory and experiment are lacking here. Rheology measurements can also be obtained from capillary, and other, foam flows (e.g. Prud'homme and Khan 1996).

5.2. Concluding remarks

The impact of interfacial rheology on flows in foam films and during drainage are recognized and are now better characterized, though further research elaborating the role of interfacial mobility on the network flow may yet prove helpful. The influence of interfacial rheology on the dynamical aspects of macroscopic rheology remains incompletely understood. Many interesting research topics in the foams area remain, which make direct connections to other areas of complex fluids, rheology, etc.

Acknowledgments

References

Ashby M F, Evans A G, Fleck N A, Gibson L J, Hutchinson J W and Wadley H N G 2000 *Metal Foams: a Design Guide* (Boston: Society of Automotive Engineers)
Brooks C F, Fuller G G, Frank C W and Robertson C R 1999 *Langmuir* **15** 2450
Buzza D M A, Lu C-Y D and Cates M E 1995 *J. Physique* II **5** 37
Carrier V, Destouesse and Colin A 2002 *Phys. Rev.* E **65** 061404
Cates M E and Sollich P 2000 *Foams and Emulsions* ed J F Sadoc and N Rivier (Dordrecht: Kluwer)
Chomaz J M 2001 *J. Fluid Mech.* **442** 387
Cohen-Addad S, Hoballah H and Höhler R 1998 *Phys. Rev. Lett.* **57** 6897
Cox S J, Weaire D, Hutzler S, Murphy J, Phelan R and Verbist G 2000 *Proc. R. Soc.* A **456** 2441

Durand M and Langevin D 2002 *Eur. Phys. J.* E **7** 35

Durand M, Martinoty G and Langevin D 1999 *Phys. Rev.* E **60** R6307

Edwards D A, Brenner H and Wasan D T 1991 *Interfacial Transport Processes and Rheology* (Boston, MA: Butterworth–Heinemann)

Edwards D A and Wasan D T 1996 *Foams: Theory, Measurements and Applications* ed R K Prud'homme and S A Khan (New York: Dekker)

Gibson L J and Ashby M F 1999 *Cellular Solids: Structure and Properties* (Cambridge: Cambridge University Press)

Grassia P, Cilliers J J, Neethling S J and Ventura-Medina E 2001 *Eur. Phys. J.* E **6** 325

Hemar Y, Hocquart R and Lequeux F 1995 *J. Physique* II **5** 1567

Hemar Y and Horne D S 2000 *Langmuir* **16** 3050

Hilgenfeldt S, Koehler S A and Stone H A 2001 *Phys. Rev. Lett.* **86** 4704

Hutzler S and Weaire D 2000 *Phil. Mag. Lett.* **80** 419

Hutzler S, Weaire D and Crawford R 1998 *Europhys. Lett.* **41** 461

Koehler S A, Hilgenfeldt S and Stone H A 1999 *Phys. Rev. Lett.* **82** 4232

Koehler S A, Hilgenfeldt S and Stone H A 2000 *Langmuir* **16** 6327

Koehler S A, Hilgenfeldt S and Stone H A 2001 *Europhys. Lett.* **54** 335

Koehler S A, Hilgenfeldt S, Weeks E R and Stone H A 2002 *Phys. Rev.* E **66** 040601

Koehler S A, Stone H A, Brenner M P and Eggers J 1998 *Phys. Rev.* E **58** 2097

Kraynik A M 1988 *Annu. Rev. Fluid Mech.* **20** 325

Langevin D 2000 *Foams and Emulsions* ed J F Sadoc and N Rivier (Dordrecht: Kluwer)

Leonard R A and Lemlich R 1965 *AIChE J.* **11** 18

Loewenberg M 2002 personal communication

Mysels K J, Shinoda K and Frankel S 1959 *Soap Films: Studies of their Thinning and a Bibliography* (New York: Pergamon)

Neethling S J, Lee H T and Cilliers J J 2002 *J. Phys.: Condens. Matter* **14** 331

Nguyen A V 2002 *J. Colloid Interface Sci.* **249** 194

Prins A 1999 *Colloids Surf.* A **149** 467

Prud'homme R K and Khan S A (ed) 1996 *Foams: Theory, Measurements and Applications* (New York: Dekker)

Safouane M, Durand M, Saint-Jalmes A, Langevin D and Bergeron V 2001 *J. Physique* IV **11** Pr6–275

Saint-Jalmes A, Durand M, Maurdev G, Safouane M and Langevin D 2002 *Phys. Rev. Lett.* submitted

Saint-Jalmes A, Vera M U and Durian D J 2000 *Europhys. Lett.* **50** 695

Vera M U, Saint-Jalmes A and Durian D J 2000 *Phys. Rev. Lett.* **84** 3001

Verbist G, Weaire D and Kraynik A 1996 *J. Phys.: Condens. Matter* **8** 3715

Weaire D L and Hutzler S 2000 *The Physics of Foams* (Oxford: Oxford University Press)