OXFORD

Foams

Structure and Dynamics

Isabelle Cantat, Sylvie Cohen-Addad, Florence Elias, François Graner, Reinhard Höhler, Olivier Pitois, Florence Rouyer, Arnaud Saint-Jalmes

Foams

Structure and Dynamics

I. Cantat, S. Cohen-Addad, F. Elias, F. Graner, R. Höhler,
O. Pitois, F. Rouyer, and A. Saint-Jalmes

Translated by R. Flatman

Scientific editor (English edition) S.J. Cox

OXFORD
UNIVERSITY PRESS

OXFORD
UNIVERSITY PRESS

Great Clarendon Street, Oxford, OX2 6DP,
United Kingdom

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide. Oxford is a registered trade mark of
Oxford University Press in the UK and in certain other countries

Ouvrage publié avec le concours du Ministère français chargé de la culture – Centre national du livre

First Edition published in 2013
Impression: 1

Published in the United States of America by Oxford University Press
198 Madison Avenue, New York, NY 10016, United States of America

British Library Cataloguing in Publication Data
Data available

Library of Congress Control Number: 2013938927

ISBN 978–0–19–966289–0

Printed and bound by
CPI Group (UK) Ltd, Croydon, CR0 4YY

Foams

Preface

The bubbly world of foams

A foam consists of a large number of bubbles packed together (FIG. 0.1), which gives this state of matter its remarkable properties. We describe here liquid foams, which consist of a gas and a liquid (often soapy water). They are in general opaque, remarkably stable, and even elastic, as is evident in whipped cream, shaving foam, and sea foam.

A great deal of excellent work has been conducted on these mixtures of soapy water and air: Boys' captivating book (published in 1890), for example, which arose from public lectures in which the author entertained the audience with his soap bubble demonstrations, or the book of Mysels, Frankel, and Shinoda that elucidates some of the many secrets of soap films, Bikerman's book on industrial applications of foams, and more recently the book of Weaire and Hutzler on the physics of foams, with its focus on structural problems.

In this book we set out the fundamentals of current knowledge on liquid foams and discuss some recent advances in our understanding of their structure, generation, ageing, and rheology. We have sought to provide information at several different levels: from simple, concrete explanations, perhaps for industrialists who find themselves interested in foams, to an in-depth discussion of scaling laws and detailed mathematical models, suitable for academics and students; all should, in addition, find the exercises and suggested experiments straightforward to implement.

This is certainly not an exhaustive volume: we consider solid foams only briefly and we avoid discussion of a number of unresolved questions. It is also the product of team-work, so that in places we find ourselves explaining and comparing different points of view, fundamental or applied, which is in itself a stimulating exercise. Such polyphonic writing requires extensive proofreading and polishing: we thank in particular Christian Counillon, Agnès Haasser, and Michel Laguës for having done this and for their excellent advice. We also thank with great pleasure all those colleagues and students who have helped us make progress thanks to their remarks and suggestions. Finally, we would like to acknowledge the CNRS-funded GDR "Mousses et Emulsions" and its directors M. Adler and C. Gay for their encouragement.

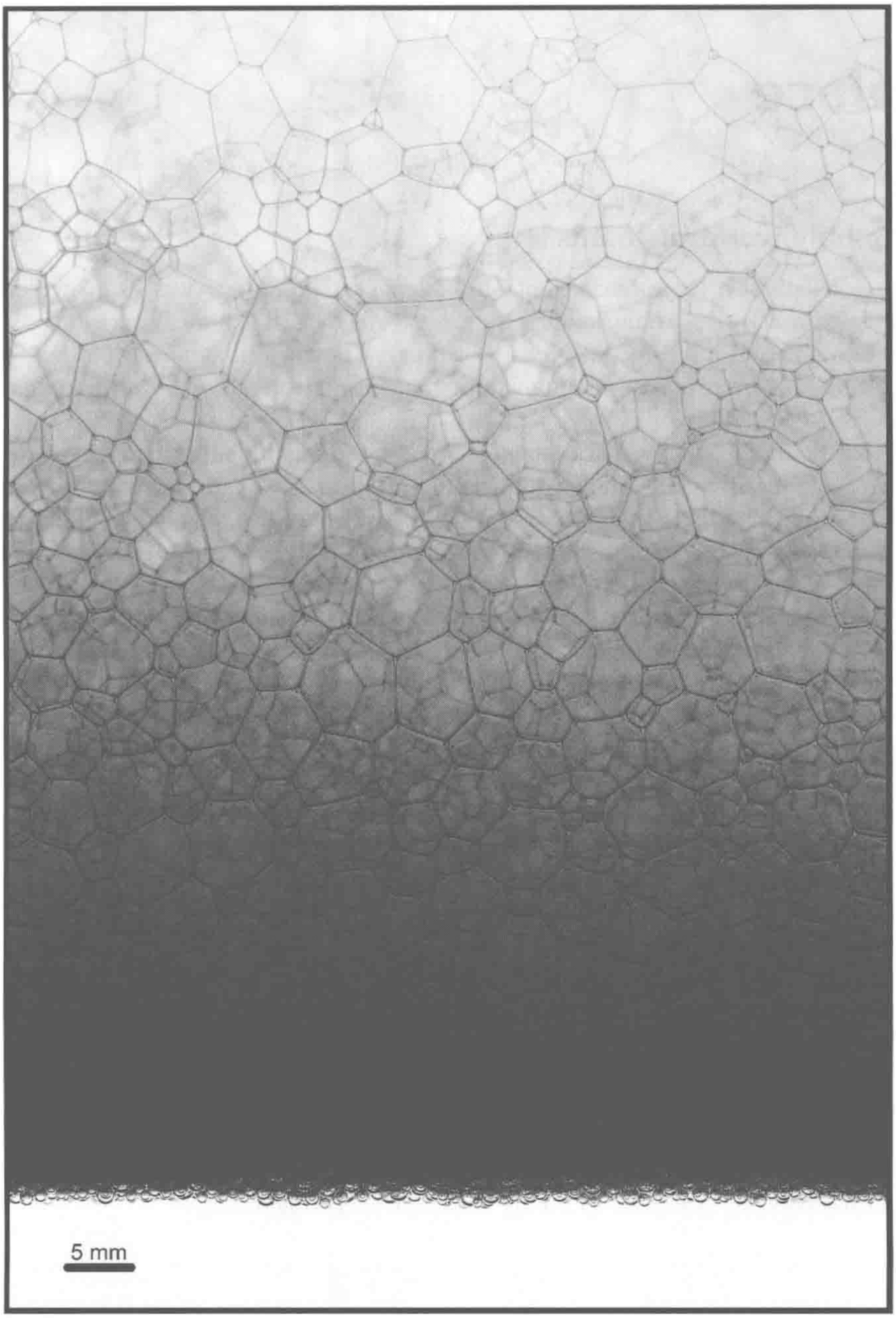

FIG. 0.1: A liquid foam some time after its creation. It is dry at the top, with large polyhedral bubbles, and wet at the bottom, with a smaller average bubble size. The bubbles become spherical when they come into contact with the liquid on which the foam floats. Photograph courtesy of S. Cohen-Addad, R.M. Guillermic, and A. Saint-Jalmes. See PLATE 1.

Experiments

The experiments presented at the end of each chapter aim to illustrate a number of points within that chapter. Some experiments can be carried out in minutes in a kitchen or bathroom, others require laboratory materials, but none are dangerous. Nonetheless, it is necessary to take the usual safety precautions and use common sense. At the beginning of each experiment, the theoretical prerequisites are indicated in the form of references to the pertinent paragraphs in the chapter. The level of difficulty and the time required for each experiment are classified according to four criteria:

Difficulty level: three levels of difficulty are identified for the experiment depending on the required materials:

: Materials generally found in a kitchen or bathroom

: Materials that can be bought or made at home

: Laboratory materials

Cost: the cost of the experiment is divided into three levels of expense:

($) : cheap, less than about 5 dollars, euros, or pounds

($)($) : moderate

($)($)($) : expensive, more than about 30 dollars, euros, or pounds

Preparation time: this refers to the time required to set up the experiment once the materials are assembled. Depending on the experiment this could take between five minutes and half a day.

Experimental time: once the experiment is set up, this is the actual experimental time, including the analysis, required to give a complete description of the phenomenon.

Contents

1
Uses of foams

Are foams really useful? We smile when scientists announce that they study foams, because bubbles are considered child's play, but in this first chapter we will show that the converse is true: liquid foams exhibit a range of complex and unique properties, and are well-adapted to diverse applications in our daily lives and to numerous industrial processes.

1 The foams around us

1.1 Foams in mythology

In the *Mahabharata*, Indra, having been captured by the demon Namuchi, is only freed in exchange for the promise that he will not kill his kidnapper by day or night, with something neither wet nor dry. Indra keeps his word: when he returns to slay the demon (FIG. 1.1), it is twilight and he uses foam! Neither wet nor dry, foam meets Namuchi's contradictory demands.

In Greek mythology, Cronos castrates his father Uranus and throws his genitals into the sea. Hesiod recounts that "a white foam surrounded the immortal flesh, and in it grew a girl. At first it touched on holy Cythera, from where it came to Cyprus, circled by the waves. And there the goddess came forth . . . " [6]. This goddess is named Aphrodite, which translates literally as "born of the foam". *Aphron* means foam in Greek, so the subject of this book can be described as aphrology!

A Chinese myth describes how in order to thwart two dragons who claimed his throne, the emperor collects the foam from their drooling jaws and locks it in a casket. Although foams are not usually so stable, this foam remained in the casket for 2,000 years; when the casket is opened, the foam escapes and takes the form of a small dragon. The dragon touches a young girl who, several years later, gives birth to Pao Sze, the dragon princess renowned for her great beauty and sadness.

Although short of a full anthology, these examples show that foams, whether for their unique properties or their (supposedly) superficial nature, appear frequently in literature. A final example is Joyce's *Ulysses*, where foam appears in diverse forms: from the first sentence, in Buck Mulligan's shaving bowl, to its association with the barrels of beer flowing into the street.

1.2 On your plate and in your glass

Foam is, of course, associated with certain beverages. Beer foam, stabilized amongst other things by proteins, appeals both to the eyes and to the palate. Champagne foam, which is more fragile, is so distinctive that a discerning drinker is able to predict the

FIG. 1.1: The properties of foam inspired Ganesh, the mythical author of the *Mahabharata*, in the scene in which Indra attacks Namuchi. © Amar Chitra Katha Pvt. Ltd.

quality of the wine from the foam alone. In champagne and certain beers, carbon dioxide, which is a product of fermentation in the bottle, is concentrated by an overpressure (6 bars for champagne). The liquid is supersaturated at ordinary pressure but degasses when the bottle is opened; bubbles appear, rise, and form a foam. Some draught beers are dispensed with air or nitrogen in order to slow the ageing of the foam. Fizzy drinks and carbonated water are produced by adding carbon dioxide, but the resulting foams are not very stable due to the lack of proteins. The long-lived froth on a cappucino is stabilized by milk proteins. This leads us naturally to questions about foaming, drainage, and ageing which are dealt with later in this book (chap. 3).

Not only are foams highly drinkable, but their consistency and lightness make them a pleasure to eat as well. Chocolate or fruit mousses (FIG. 1.2) immediately spring to

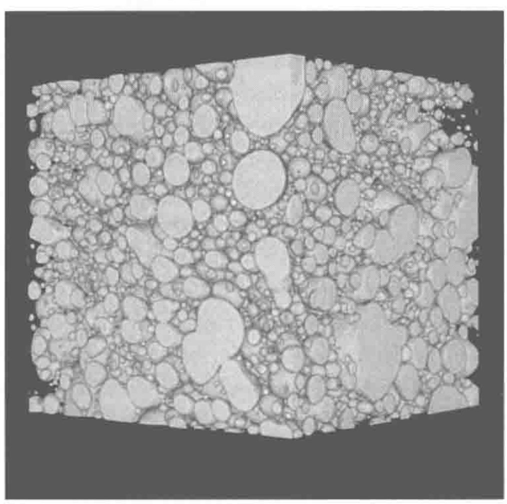

FIG. 1.2: Three-dimensional imaging experiment of the air bubbles in a chocolate mousse. The technique used is X-ray tomography, which is described in chap. 5. Image courtesy of P. Cloetens, ESRF.

mind, but air is also incorporated into ice cream, altering its texture and making it easier to serve, but without causing it to melt too quickly in the mouth. Air, of course, is a raw material which doesn't cost anything... whilst making a large contribution to the volume of the final product.

Edible foams are usually solid, obtained by solidifying a liquid foam either by refrigeration (chocolate mousse) or cooking (bread). The foaming or stabilizing agents for edible foams are natural, for example sugar (for meringue) or gelatine (for marshmallows, where it also serves as a gelling agent). Industrially produced edible foams tend to be stabilized by lecithin (from egg or soya) or xanthan gum, which makes them very viscous. Some foams, like bread and cake, have no need of a stabilizing agent because they are solidified before they collapse.

Baked alaska is an unusual combination of foams: ice cream is thermally stabilized by two other foams: the ice cream is placed on a solid foam, the sponge cake, and then covered by a liquid foam, an uncooked meringue, and placed in the oven. The ice cream is sufficiently well-insulated that it doesn't melt while the meringue is gently cooked!

There are also situations where foams appear without being sought, as a consequence of either boiling or simply agitation, as in the froth that is generated when cooking pasta or potatoes in water, where the proteins present enable the bubbles to persist. Stable milk foam can be seen when a baby is feeding from a bottle or when a glass of milk is shaken, while that which floats on coffee or tea is very short-lived.

1.3 Detergents and cosmetics

The presence of soap in a cleaning product has a consequence beyond the required property (removal of fat and solid particles): the appearance of a foam. It is widely believed that the presence of foam is a measure of cleaning efficacy but in fact the opposite is true: manufacturers try to suppress foams in mechanical cleaning (in washing machines and dishwashers). The addition of only a few drops of washing-up liquid to a dishwasher results in the machine overflowing due to a large quantity of stable foam. In order to avoid these problems, antifoam agents are added (cf. §5.3, chap. 3).

There are, however, advantages of using foams in some cases. For example, while tests show that the cleaning performances of non-foaming and foaming oven cleaners are hardly distinguishable, the latter will be desirable as the cleaner will cling to the vertical walls of the oven for longer. The ability of a foam to stick to a vertical surface, owing to its elasticity, also makes it useful for shaving; a small quantity of product covers the cheeks and stays there until the motion of the razor blade renders it sufficiently fluid to wash off. This leads to questions of rheology which will be discussed later in the book (chap. 4).

Generally speaking, foam products are very common in cosmetics: their ability to cover and cling to surfaces explains their use in hair gels or conditioners. When you wash your hair, the shampoo generates more foam in the second wash, indicating that the first application has succeeded in its role. But the shampoo foam is also there for your enjoyment. Similarly, it is in their role of providing comfort and pleasure that foaming bath products are successful.

1.4 Spontaneous or undesirable foams

As we have seen, foams arise from the presence of a gas in a liquid, for example the carbon dioxide in a fizzy drink or the alkanes in a shaving foam. A magma which degasses causes bubbles to accumulate, and therefore a foam forms in the magma chamber of a volcano. Depending on the conditions (gas flow rate, bubble size, cavity shape), the foam may collapse gradually or, as in Strombolian volcanoes, suddenly and spectacularly!

More common in nature is a foam that forms in a liquid that is agitated in such a way to allow air to be incorporated, as in a waterfall or a breaking wave. These foams are weak and transient if nothing stabilizes them, but in the presence of surfactants from pollutants or plankton, they become the long-lasting "white horses" seen along the coast where spectacular foam mountains can reach several metres high, as can be found for example in Australia. So the presence of a foam is a good indicator of contamination (industrial or natural) by surfactants.

In the same way, pouring washing-up liquid into a public fountain produces a splendid display of foam, which can be made more spectacular still if a few drops of food colouring are added. At the cinema, foams have a role in special effects, for example representing snow. In the final scene of *The Party* by Blake Edwards, a house, the scene of a lavish party, is overrun with soap bubbles and chaos ensues.

Undesirable foams are also encountered in the industrial world, where the focus is on developing products to get rid of them, a subject to which we will return later (§5.3, chap. 3). Such foams appear for example in settling tanks or during the manufacturing of steel, glass, pulp, sugar, watercolour paints, or products obtained by fermentation (like wine or penicillin). An over-acidic stomach secretes foam, and the recommended medicines contain an antifoam that allows them to reach the stomach wall before reacting.

2 Foam identification

As we have seen, liquid foams are commonly encountered all around us. We now describe the properties which make these materials unique and potentially useful in various industrial applications (see §3). Furthermore, a foam, under carefully controlled conditions, often serves as a model system for a cellular material or a biological tissue.

2.1 Physico-chemical constituents

A foam is a dispersion of gas in a liquid. The tightly packed gas bubbles occupy most of the volume (FIG. 0.1). The liquid phase, which consists of the soap films and their junctions, is continuous, unlike the gas phase. It contains special molecules, known as surfactants, which stabilize the bubbles by arranging themselves at the liquid/gas interfaces (see §2, chap. 3).

Different properties can be obtained by changing each constituent of a foam. Consider the gas: air, for example, which is easily available in large quantities and is non-flammable, is used to inflate the aqueous foams in fire extinguishers, enabling