Foams & Emulsions

Foams and Emulsions

edited by

J. F. Sadoc
Université de Paris-Sud,
Laboratoire de Physique des Solides,
Orsay, France

and

N. Rivier
Université Louis Pasteur,
Institut de Physique,
Strasbourg, France

Kluwer Academic Publishers

Dordrecht / Boston / London

Published in cooperation with NATO Scientific Affairs Division

Proceedings of the NATO Advanced Study Institute on
Foams and Emulsions, Emulsions and Cellular Materials
Cargèse, Corsica
12–24 May, 1997

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 0-7923-5616-0

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

Printed in the Netherlands

Foams and Emulsions

NATO ASI Series

Advanced Science Institute Series

A Series presenting the results of activities sponsored by the NATO Science Committee, which aims at the dissemination of advanced scientific and technological knowledge, with a view to strengthening links between scientific communities.

The Series is published by an international board of publishers in conjunction with the NATO Scientific Affairs Division

A Life Sciences	Plenum Publishing Corporation
B Physics	London and New York
C Mathematical and Physical Sciences	Kluwer Academic Publishers
D Behavioural and Social Sciences	Dordrecht, Boston and London
E Applied Sciences	
F Computer and Systems Sciences	Springer-Verlag
G Ecological Sciences	Berlin, Heidelberg, New York, London,
H Cell Biology	Paris and Tokyo
I Global Environment Change	

PARTNERSHIP SUB-SERIES

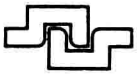
1. Disarmament Technologies	Kluwer Academic Publishers
2. Environment	Springer-Verlag / Kluwer Academic Publishers
3. High Technology	Kluwer Academic Publishers
4. Science and Technology Policy	Kluwer Academic Publishers
5. Computer Networking	Kluwer Academic Publishers

The Partnership Sub-Series incorporates activities undertaken in collaboration with NATO's Cooperation Partners, the countries of the CIS and Central and Eastern Europe, in Priority Areas of concern to those countries.

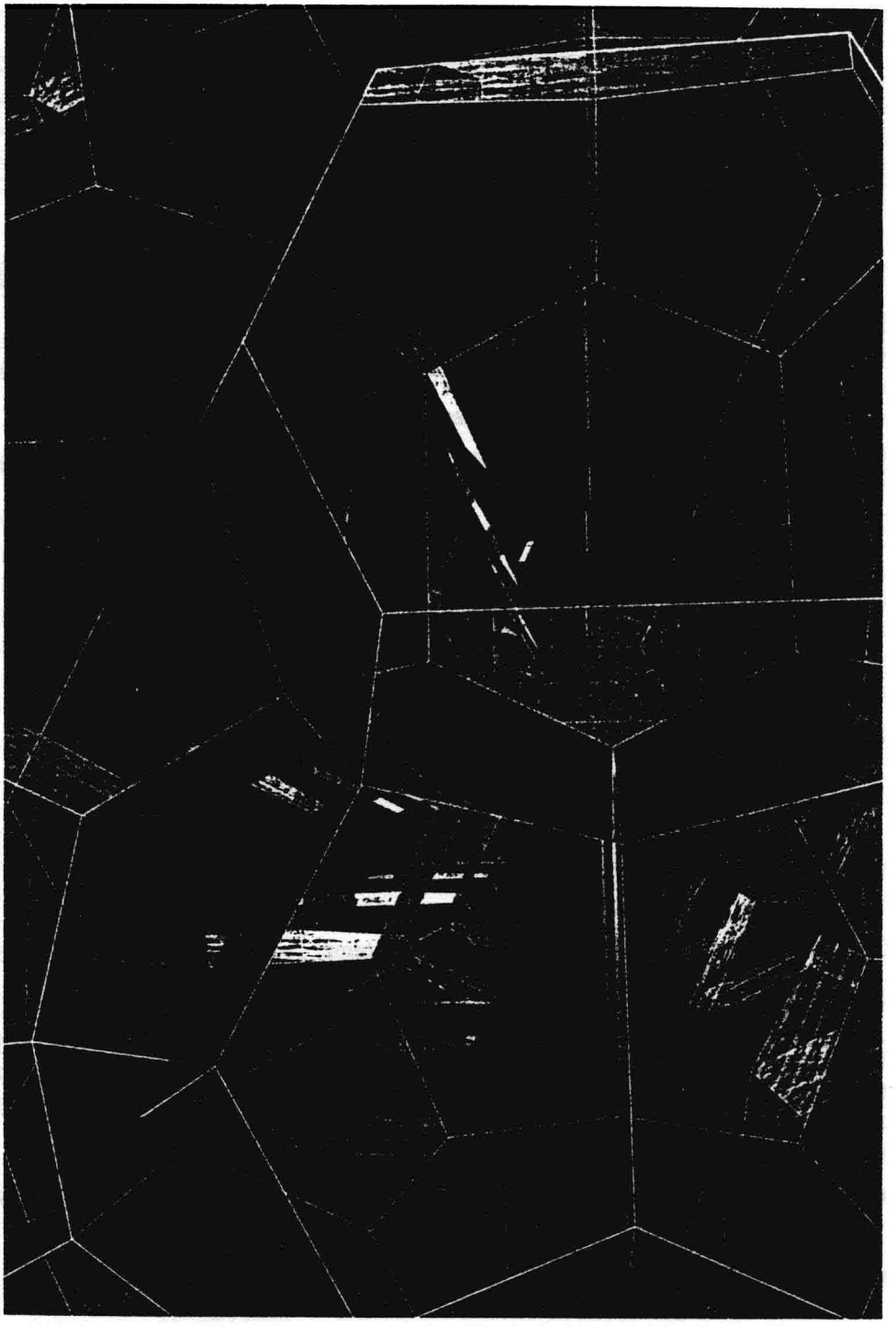
NATO-PCO-DATA BASE

The electronic index to the NATO ASI Series provides full bibliographical references (with keywords and/or abstracts) to about 50,000 contributions from international scientists published in all sections of the NATO ASI Series. Access to the NATO-PCO-DATA BASE is possible via a CD-ROM "NATO Science and Technology Disk" with user-friendly retrieval software in English, French, and German (©WTV GmbH and DATAWARE Technologies, Inc. 1989). The CD-ROM contains the AGARD Aerospace Database.

The CD-ROM can be ordered through any member of the Board of Publishers or through NATO-PCO, Overijse, Belgium.



Series E: Applied Sciences – Vol. 355



FOREWORD

This volume is the proceedings of the School on Foams, Emulsions and Cellular Materials, held in Cargèse (Corsica), May 12-24, 1997. The school gathered a wide spectrum of participants and lecturers, coming from various communities and countries, from university to industry (nuclear, petroleum, chemical, mechanical and thermal).

The volume is intended as a general and introductory survey of the field. The authors have tried to be clear and didactic. Because the field spans several scientific disciplines and is relatively new, there are no textbooks with all the basic tools necessary for research students. We trust that the present book will serve this purpose.

The chapters are grouped in sections, but with fairly loose boundaries. While cross-referencing has been encouraged, each chapter is intelligible on its own, and if a few concepts are not familiar to the reader, their explanation can be found in an earlier chapter, as referred to in the index.

The book contains all the lecture courses, and several contributions selected because they were new and promising developments, not yet available in print elsewhere, or because they covered aspects of the subject not discussed in the lectures. It was not possible to include the lecture course by Yann Barrandon on the renewal of the epidermis. It contained medical and biomedical applications, a very wide domain, which cannot be reduced to a single chapter in a general treatise on foams. For an introduction on the subject, see chapter 7 of the monograph by Dover and Wright [1]. The close connection between epidermis and foams is shown by the fact that Lewis's law was discovered on the epidermis of the cucumber, and by this photograph of the basement membrane of human epidermis (B. Dubertret [2]).

We are grateful to Michael Leunig for permission to reprint his cartoon, to J. Sullivan, G. Boissonnet and B. Dubertret for photographs of computer-generated or real foams. Other photographs are by T. Aste, B. Gardiner, D. Weaire, K. Stebe, U. Thiele and N. Rivier. C. Oguey has helped with the edition and the index.

We would like to thank the Centre of Cargèse and its Director, Elizabeth Dubois-Violette for their hospitality and for their help in the running of the school. The school has been sponsored and supported by NATO, by the Institut Français du Pétrole, by Rhone-Poulenc, and the French granting agencies: CNRS (Formation Permanente) and DGA. This volume has been published with the help of a special grant from NATO.

Jean-François Sadoc
Nicolas Rivier

1. Dover, R. and Wright, N.A. (1991) *Physiology Biochemistry and Molecular Biology of the Skin*, 2nd. edition, Oxford University Press.
2. Dubertret, B. and Rivier, N. (1977) The renewal of the epidermis: A topological mechanism, Biophys. J. **73**, 38-44

TABLE OF CONTENTS

(Introduction and conclusion of each chapter are not listed)

SURFACE ENERGY AND SURFACE RHEOLOGY RELATION TO FOAM PROPERTIES

D.LANGEVIN
Centre de Recherche Paul Pascal
Av. A.Schweitzer
33600, Pessac, France

Foams made from pure fluids are generally very unstable : bubbles obtained by shaking pure water last only for a few seconds. When a surface active substance is added to water, bubbles lifetime can become much longer. The increase in surface energy due to the increase in surface area after the creation of the bubbles is substancial : for instance if one cm^3 of solution with a surface of about one cm^2 is shaken to produce a foam with bubbles of millimetric size, the air-solution area increases by a factor of ten and the surface energy, which is proportional to the area, increases by the same factor. Of course, the surface tension of the solution is decreased by the presence of the substance, but the state of equilibrium is the state of minimal energy and is in any case the state of minimal area : the foam can never be stable. The difference between water and surfactant solutions lies therefore in the time scales involved in bubbles lifetime. Surface tension is not the main surface characteristic property there, and other properties such as surface elasticity, surface viscosity, dynamic surface tension, become extremely important. In this chapter, we will first define all these surface properties, indicate how they can be determined and discuss how they influence the foam properties.

I. Definition of surface properties

1. SURFACE ENERGY

1.1 Surface excess properties

The definition of properties such as viscosity for a purely two-dimensional system poses some difficulties. Real interfaces between two media are never perfect mathematical surfaces, all the physical properties change from those

J. F. Sadoc and N. Rivier (eds.), Foams and Emulsions, 1–20.

of the lower medium to those of the upper medium in a thin interfacial region, with a thickness comparable to molecular dimensions. This led Gibbs to define surface properties as excess properties [1]. For instance if z is the vertical coordinate, A the surface area, if medium 1 of density ρ_1 is located in the region $z<0$, medium 2 of density ρ_2 in the region $z>0$, if $F(\rho_i)$ is the total energy of medium i and f(z) the energy density at heigth z, the excess energy due to the presence of the interface in the region $z \sim 0$ is given by, according to Gibbs :

$$\Delta F = A \int_{-\infty}^{+\infty} f \, dz \quad - F(\rho_1) - F(\rho_2) \qquad (1)$$

Because the density ρ varies in a thin region around z=0, the integral is not equal the sum $F(\rho_1) + F(\rho_2)$: there is an excess energy ΔF which is currently referred to as the "surface" energy. The surface tension γ is simply :

$$\gamma = \Delta F / A \qquad (2)$$

When a surface active substance is added, it spontaneously adsorbs at the surface, and decreases the surface energy (otherwise, there would be no spontaneous adsorption). A monolayer is formed, with the polar parts of the surfactant molecule in contact with water, and the hydrophobic parts in contact with air. The surface tension decrease can be identified by dimensional arguments with a "surface pressure" Π.

$$\gamma = \gamma_w - P \qquad (3)$$

where γ_w is the surface tension of pure water. Extensive work done with water-insoluble substances showed that this identification is helpful to understand the monolayer properties and the transitions between the different surface phases that can be found with these systems[2]. For water-soluble substances, it becomes difficult to know the amount of surface material, because most of the molecules are dissolved in bulk water. Information about the surface concentration can be however obtained from thermodynamic arguments.

1.2 Surface Thermodynamics

The free energy F of the system is the sum of the internal energy U, the entropy term -TS and the chemical potential term $\sum \mu_i N_i$, where T is the absolute temperature, S, the entropy, μ_i the chemical potential of species i