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# Foams and Emulsions

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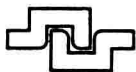
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## FOREWORD

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

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# **SURFACE ENERGY AND SURFACE RHEOLOGY RELATION TO FOAM PROPERTIES**

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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 substantial : for instance if one  $\text{cm}^3$  of solution with a surface of about one  $\text{cm}^2$  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



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  $\rho_1$  is located in the region  $z < 0$ , medium 2 of density  $\rho_2$  in the region  $z > 0$ , if  $F(\rho_i)$  is the total energy of medium  $i$  and  $f(z)$  the energy density at height  $z$ , the excess energy due to the presence of the interface in the region  $z \sim 0$  is given by, according to Gibbs :

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

Because the density  $\rho$  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  $\Delta F$  which is currently referred to as the "surface" energy. The surface tension  $\gamma$  is simply :

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

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"  $\Pi$ .

$$\gamma = \gamma_w - \Pi \quad (3)$$

where  $\gamma_w$  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,  $\mu_i$  the chemical potential of species  $i$ .