Small solid particles adsorbed at liquid interfaces arise in many industrial products and processes, such as anti-foam formulations, crude oil emulsions and flotation. They act in many ways like traditional surfactant molecules, but offer distinct advantages. However, the understanding of how these particles operate in such systems is minimal. This book brings together the diverse topics actively being investigated with contributions from leading experts in the field.

After an introduction to the basic concepts and principles, this book is divided into two sections. The first deals with particles at planar liquid interfaces, with chapters of an experimental and theoretical nature. The second concentrates on the behaviour of particles at curved liquid interfaces, including particle-stabilised foams and emulsions, and new materials derived from such systems.

This unique collection will be of interest to academic researchers and graduate students in chemistry, physics, chemical engineering, pharmacy, food science and materials science.

BERNARD P. BINKS is Professor of Physical Chemistry at the University of Hull.

TOMMY S. HOROZOV is a Research Fellow in the Department of Chemistry at the University Hull.

Back cover illustrations (from left to right): Spontaneously formed ordered horizontal monolayer of 3 µm diameter very hydrophobic silica particles after their spreading at the silicone oil – water interface. The particle contact angle through water is 170°. Inter-particle distances are 15.4 ± 0.6 µm. Taken from Horozov and Binks, Colloids Surf. A, 267 (2005), 64; with permission from Elsevier.

Spontaneous formation of a crystalline disk of 3 µm very hydrophobic silica particles bridging the surfaces of a free-standing octane film in water during its thinning. The particle contact angle through water is 152°. The disk diameter is 117 µm. Taken from Horozov et al., Langmuir, 21 (2005), 2330; with permission from the American Chemical Society.

Image of a Janus bubble, diameter ≈430 µm, covered with fluorescent polystyrene particles of diameters 4.9 µm (upper yellow half) and 4.0 µm (lower green half) using a microfluidic focusing device. Taken from Subramaniam et al., Nat. Mater. 4 (2005), 553; with permission from the Nature Publishing Group.

Image of a silicone oil droplet of diameter ≈30 µm in water covered with simultaneously self-assembled hydrophobic (green) and hydrophilic (red) fluorescent particles of diameter 1 µm. Taken from Tarimala and Dai, Langmuir, 20 (2004), 3492; with permission from the American Chemical Society.

Doughnut-like toroidal assemblies of diameter ≈0.9 µm obtained by drying of aqueous droplets of a 320 nm latex particle suspension placed on the surface of perfluoromethylene-calin in the presence of fluorinated surfactant. Taken from Velev et al., Science, 287 (2000), 2240; with permission from the American Institute for the Advancement of Science.
This book is dedicated to the memory of

PROFESSOR JOHN C. EARNSHAW (1944–1999)

John Earnshaw, Professor in the Department of Pure & Applied Physics at Queen’s University, Belfast died in a tragic climbing accident in Ireland on 17th January 1999. He was born in Edinburgh and obtained both his B.Sc. and Ph.D. degrees from the University of Durham. His thesis was on the muon content of cosmic ray air showers and he continued this work first as a Research Fellow at Durham and later as a Research Associate at Cornell University. In 1971, he went to Belfast where he spent exactly half of his life. John was extremely energetic and talented and was quickly promoted, becoming a Professor in 1990.

Following his appointment at Queen’s, John changed his research field – something he was to do several times in his career. He formed a highly successful group to study the application of laser light scattering to biological systems including human sperm motility. He later became interested in the dynamics of fluid interfaces, phase transitions in surface films and two-dimensional colloid systems. His first paper on the latter (with D.J. Robinson) reported an experimental study of particles spread at air-water surfaces and appeared in 1989. It has been widely quoted since. In later years, he studied the transition to chaos in interfacial systems and also extended his studies on soft condensed matter to encompass the physics of foams. At the time of his death, he was President of the European Colloid and Interface Society, and he was a great supporter of conferences both in the UK and abroad. His contribution to Irish science was acknowledged when he was elected a Member of the Royal Irish Academy. He published over one hundred papers in scientific journals, gave many invited talks and supervised 25 research students.

Outside the scientific world, John had many interests which, apart from his great love of the mountains, lay mainly in the arts. He was widely read and his interest in the works of Beckett was insatiable. John Earnshaw’s broad knowledge, his enthusiasm and flair for physics and his great curiosity provided intellectual stimulation to all around him. His enjoyment of life as an academic and physicist was contagious. It was of course much too soon but John died, as he would have liked to die, in the mountains.

I thank Professor C.J. Latimer of Queen’s University, Belfast for his help in this.

Bernard P. Binks – Hull, March 2006
COLLOIDAL PARTICLES
AT LIQUID INTERFACES

Edited by
BERNARD P. BINKS
and
TOMMY S. HOROZOV
University of Hull
Contents

Preface vii
List of Contributors ix

1 Colloidal Particles at Liquid Interfaces: An Introduction 1
B.P. Binks and T.S. Horozov

Section 1 Particles at Planar Liquid Interfaces

2 Structure and Formation of Particle Monolayers at Liquid Interfaces 77
L. Bergström

3 Theory for Interactions between Particles in Monolayers 108
J.C. Fernández-Toledano, A. Moncho-Jordá,
F. Martínez-López and R. Hidalgo-Álvarez

4 Particle-Assisted Wetting 152
W.A. Goedel

Section 2 Particles at Curved Liquid Interfaces

5 Particle-Laden Interfaces: Rheology, Coalescence, Adhesion and Buckling 169
G.G. Fuller, E.J. Stancik and S. Melle

6 Solids-Stabilized Emulsions: A Review 186
R.J.G. Lopetinsky, J.H. Masliyah and Z. Xu

7 Novel Materials Derived from Particles Assembled on Liquid Surfaces 225
K.P. Velikov and O.D. Velev
<table>
<thead>
<tr>
<th>Contents</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>8  Interfacial Particles in Food Emulsions and Foams</td>
<td>298</td>
</tr>
<tr>
<td>E. Dickinson</td>
<td></td>
</tr>
<tr>
<td>9  Collection and Attachment of Particles by Air Bubbles in</td>
<td>328</td>
</tr>
<tr>
<td>Froth Flotation</td>
<td></td>
</tr>
<tr>
<td>A.V. Nguyen, R.J. Pugh and G.J. Jameson</td>
<td></td>
</tr>
<tr>
<td>10 Antifoam Effects of Solid Particles, Oil Drops and Oil–Solid</td>
<td>383</td>
</tr>
<tr>
<td>Compounds in Aqueous Foams</td>
<td></td>
</tr>
<tr>
<td>N.D. Denkov and K.G. Marinova</td>
<td></td>
</tr>
<tr>
<td>11 Metal Foams: Towards High-Temperature Colloid Chemistry</td>
<td>445</td>
</tr>
<tr>
<td>N. Babcsán and J. Banhart</td>
<td></td>
</tr>
<tr>
<td>Index</td>
<td>501</td>
</tr>
</tbody>
</table>

© Cambridge University Press  
www.cambridge.org
Preface

Solid particles of colloidal dimensions (nm–μm) adsorb at fluid interfaces, either liquid–vapour or liquid–liquid, in many products and processes. Examples include fat crystals around air bubbles in certain foods, particles of sand or clay partially coating water drops in crude oil and the selective attachment of mineral particles to bubbles in froth flotation. The properties of these systems are due in part to the irreversible nature of particle adsorption, and such particles behave in many ways like surfactant molecules. The pioneering work in the area of particle-stabilised foams and emulsions was conducted by Ramsden and Pickering, respectively, early in the 20th century. During the last 10 years or so, there has been a revival of interest in this field, and in the behaviour of particles at planar liquid interfaces, and we felt that it was time to prepare the first book encompassing most of this activity. It is anticipated that this will be the start of a new series in this rapidly evolving field.

Following an introductory chapter to the whole area by the editors, the book is divided into two parts. The first part, dealing with particles at planar interfaces, contains chapters describing simulation and theoretical approaches to the structure, and dynamics of particle monolayers and how particles can assist with the wetting of oils on water. The second part, concerned with particles at curved liquid interfaces, contains chapters on emulsions stabilised solely by particles including mechanisms of stabilisation, various kinds of particle-stabilised foams (aqueous and metal), particle-containing antifoams, and novel materials derived from a range of systems with interfacial particles. The collection will be of interest to chemists, physicists, engineers and materials scientists. It should serve as a reference guide for graduate students and the novice, providing detailed accounts of the current state of research in the various fields.
Preface

We would like to thank all of the contributors to the chapters for their patience with us and the various staff members at Cambridge University Press for guiding us through the production stages.

Bernard P. Binks
Tommy S. Horozov
Hull, January 2006
List of Contributors

Norbert Babcsán
Department of Materials Science
Hahn-Meitner-Institut Berlin
Glienicker Straße 100, D-14109
Berlin
Germany

John Banhart
Institute of Materials Science and Technology
Technical University Berlin
Hardenbergstraße 36, D-10632
Berlin
Germany

Lennart Bergström
Department of Physical, Inorganic and Structural Chemistry
University of Stockholm
SE-106 91 Stockholm
Sweden

Bernard P. Binks
Surfactant and Colloid Group
Department of Chemistry
University of Hull
Hull
HU6 7RX
UK

Nikolai D. Denkov
Laboratory of Chemical Physics and Engineering
List of Contributors

Faculty of Chemistry
Sofia University
1 J. Bourchier Avenue, 1164 Sofia
Bulgaria

Eric Dickinson
Procter Department of Food Science
University of Leeds
Leeds LS2 9JT
UK

Juan C. Fernández-Toledano
Grupo de Fisica de Fluidos y Biocoloides
Departamento de Fisica Aplicada
Universidad de Granada
Campus de Fuente Nueva, 18071
Granada
Spain

Gerald G. Fuller
Department of Chemical Engineering
Stanford University
Stanford
CA 94305-5025
USA

Werner A. Goedel
Department of Physical Chemistry
Chemnitz University of Technology
Straße der Nationen 6209111
Chemnitz
Germany

Roque Hidalgo-Álvarez
Grupo de Fisica de Fluidos y Biocoloides
Departamento de Fisica Aplicada
Universidad de Granada
Campus de Fuente Nueva, 18071
Granada
Spain
List of Contributors

Tommy S. Horozov
Surfactant and Colloid Group
Department of Chemistry
University of Hull
Hull
HU6 7RX
UK

Graeme J. Jameson
Discipline of Chemical Engineering and Centre
for Multiphase Processes
School of Engineering
The University of Newcastle
Callaghan
New South Wales 2308
Australia

Robert J.G. Lopetinsky
Department of Chemical and Materials Engineering
University of Alberta
Edmonton
Alberta T6G 2C7
Canada

Krastanka G. Marinova
Laboratory of Chemical Physics and Engineering
Faculty of Chemistry
Sofia University
1 J. Bourchier Avenue, 1164 Sofia
Bulgaria

Francisco Martínez-López
Grupo de Fisica deFluidos y Biocoloides
Departamento de Fisica Aplicada
Universidad de Granada
Campus de Fuente Nueva, 18071
Granada
Spain

Jacob H. Masliyah
Department of Chemical and Materials Engineering
University of Alberta
xii    

List of Contributors

Edmonton  
Alberta T6G 2C7  
Canada

Sonia Melle  
Departamento de Óptica  
Facultad de Ciencias Físicas  
Universidad Complutense de Madrid  
Ciudad Universitaria, 28040  
Madrid  
Spain

Arturo Moncho-Jordá  
Grupo de Fisica de Fluidos y Biocoloides  
Departamento de Fisica Aplicada  
Universidad de Granada  
Campus de Fuente Nueva, 18071  
Granada  
Spain

Anh V. Nguyen  
Discipline of Chemical Engineering and Centre for Multiphase Processes  
School of Engineering  
The University of Newcastle  
Callaghan  
New South Wales 2308  
Australia

Robert J. Pugh  
Institute for Surface Chemistry  
Stockholm, S 11486  
Sweden

Edward J. Stancik  
Department of Chemical Engineering  
Stanford University  
Stanford  
CA 94305-5025  
USA
List of Contributors  xiii

Orlin D. Velev
Department of Chemical and Biomolecular Engineering
North Carolina State University
Raleigh
NC 27695-7905
USA

Krassimir P. Velikov
FSD, UFHRI
Unilever Research and Development Vlaardingen
Olivier van Noortlaan 120
3133 AT Vlaardingen
The Netherlands

Zhenghe Xu
Department of Chemical and Materials Engineering
University of Alberta
Edmonton
Alberta T6G 2C7
Canada