Capillarity and Wetting Phenomena

Pierre-Gilles de Gennes
Françoise Brochard-Wyart
David Quéré

Capillarity and Wetting Phenomena

Drops, Bubbles, Pearls, Waves

Translated by Axel Reisinger

With 177 Figures

Springer

Pierre-Gilles de Gennes
Collège de France & Institute Curie
F-75005 Paris
France

Françoise Brochard-Wyart
Institute Curie
F-75005 Paris
France

David Quéré
Collège de France
F-75005 Paris
France

Cover Illustration: Pete Turner/Getty Images, 2002.

Library of Congress Cataloging-in-Publication Data

Pierre-Gilles de Gennes.
Capillarity and wetting phenomena: drops, bubbles, pearls, waves/Pierre-Gilles de Gennes, Françoise Brochard-Wyart, David Quéré.
p. cm.
Includes bibliographical references and index.

1. Capillarity. I. Quéré, David. II. Gennes, Pierre-Gilles de. III. Title.

QC183.B874 2003
541.3'3—dc21 2003042431

This book is a translation of the French edition.

ISBN 978-1-4419-1833-8 ISBN 978-0-387-21656-0 (eBook)
DOI 10.1007/978-0-387-21656-0

9 8 7 6 5 4 3 2

springeronline.com

Preface

As I glance out my window in the early morning, I can see beads of droplets gracing a spider web. The film of dew that has settled on the threads is unstable and breaks up spontaneously into droplets. This phenomenon has implications for the treatment of textile fibers (the process known as "oiling"), glass, and carbon. It is no less important when applying mascara!

I take my morning shower. The moment I step out, I dry off by way of evaporation (which makes me feel cold) and by dewetting (the process by which dry areas form spontaneously and expand on my skin).

As I rush into my car under a pelting rain, my attention is caught by small drops stuck on my windshield. I also notice larger drops rolling down and others larger still that, like snails, leave behind them a trail of water. I ask myself what the difference is between these rolling drops and grains of sand tumbling down an incline. I wonder why the smallest drops remain stuck. The answers to such questions do help car manufacturers treat the surface of glass and adjust the tilt of windshields.

The traffic light suddenly turns red. I slam on the brakes and the car skids before finally coming to a halt. A firm grip on the road hinges on eliminating the film of water between tires and pavement. The car will stop only if direct contact can be established between the rubber and the asphalt, all in a matter of a few milliseconds.

The rain finally stops and I hear the squeaking sound of the windshield wipers rubbing against the glass. Friction between the rubber and the dry glass now opposes the movement of the wipers. Clever treatments of the glass can minimize that friction.

The sun is now shining and I hurry back to my garden to spray a fungicide onto a cluster of leaves covered with mildew. Unfortunately, drops fall off like so many beads, and only a small fraction of the product remains in place to perform its intended function. Is there a way to prevent the fungicide film from dewetting? Conversely, can one treat concrete (or the stones of historic monuments) to prevent them from soaking up water every time it rains?

These few examples illustrate the need to understand and tame the phenomenon of wetting. How can one turn a hydrophilic surface into one that is hydrophobic, and vice versa? We will describe a few solutions. Some rely on chemical treatments, such as coating a surface with a molecular layer of the right material. Others are rooted in physics, for instance, altering the surface roughness. We will also examine the dynamics of the wetting process. Drops spread spontaneously at a rate that slows with time. It may take years for a small drop to form a thin film covering a large surface area. In practice, films can be tricked by forcing them to spread suddenly. We will describe a few of their many-faceted dynamical properties.

When the word *bubble* is mentioned, most of us think of soap bubbles. Special additives are required for water to foam. The reason that a soap film can be made to stretch is just now beginning to be understood. Foams are desirable in a shampoo but can be a nuisance in a dishwasher detergent. Antifoam agents have been developed and have become commonplace, but how do they work? It is also possible to generate bubbles and foams without the help of surfactants, for example, in very viscous liquids such as glycerin, molten glass, and polymers. As we will see, the laws governing draining and bursting then turn out to be quite different from the conventional ones.

A child tosses a stone into a lake. He delights in watching capillary waves propagate by forming circular ripples on the water's surface. All of us have heard the sonic boom produced by an aircraft crossing the sound barrier. But how many of us are aware that we can also observe shock waves of capillary origin every day when we turn our kitchen faucet on: on the bottom of the sink water flows outward as a thin film. But a few centimeters away from the center, we see a hydraulic jump—very similar to a shock!

Our hope is that this book will enable the reader to understand in simple terms such mundane questions affecting our daily lives—questions that have often come to the fore during our many interactions with industry. Our methodology will consist in simplifying systems that often prove quite complex so as to isolate and study a particular physical phenomenon. In the course of developing models, detailed descriptions requiring advanced numerical techniques will often be replaced by an "impressionistic" approach based on more qualitative arguments. This strategy may at times sacrifice scientific rigor, but it makes it possible to grasp things more clearly and to dream up novel situations. Such is the spirit in which we wrote this book.

Paris, France

Pierre-Gilles de Gennes
Françoise Brochard-Wyart
David Quéré

Contents

Preface v

Introduction xiii
References xiv

1 Capillarity: Deformable Interfaces 1
1.1 Surface Tension 1
1.1.1 Physical Origin 2
1.1.2 Mechanical Definition: Surface Energy and Capillary Force 3
1.1.3 Measurements of Surface (or Interfacial) Tensions 6
1.1.4 Laplace Pressure 6
1.1.5 Minimal Surfaces 9
1.1.5.1 Jet 10
1.1.5.2 Drop on a Fiber 11
1.1.6 Minimal Surfaces With Zero Curvature 13
1.2 Contact Between Three Phases: Wetting 15
1.2.1 Two Types of Wetting: The Spreading Parameter S 16
1.2.2 Wetting Criteria: Zisman's Rule 18
1.2.3 Choice of Solid/Liquid Pairs 21
1.2.3.1 Ideal Liquids 21
1.2.3.2 Solid Substrates 23
1.2.4 Liquid Substrates: Neumann's Construction 27

Appendix: Minimal Surfaces – Euler-Lagrange Equations 29
References 30

2 Capillarity and Gravity **33**
2.1 The Capillary Length κ^{-1} 33
2.2 Drops and Puddles in the Partial Wetting Regime 35
2.2.1 The Shape of Drops 35
2.2.2 Droplets ($R \ll \kappa^{-1}$) 36
2.2.3 Heavy Drops ($R \gg \kappa^{-1}$) 36
2.2.4 Experimental Techniques for Characterizing Drops 38
2.3 Menisci 43
2.3.1 Characteristic Size 43
2.3.2 Shape of a Meniscus Facing a Vertical Plate 45
2.3.3 Meniscus on a Vertical Fiber 47
2.4 Capillary Rise in Tubes: Jurin's Law 49
2.4.1 Historical Background 49
2.4.2 The Law of Capillary Rise 51
2.4.3 Pressure Argument for the Capillary Rise 52
2.5 Floating Lenses 54
2.5.1 The Spreading Parameter 54
2.5.2 The Shape of Floating Lenses ($S < 0$) 54
2.6 Supplement on Techniques for Measuring Surface Tensions 56
2.6.1 The Shape of Drops 57
2.6.1.1 The Pendant Drop Method 57
2.6.1.2 Spinning Drops 60
2.6.2 Pressure Measurements 61
2.6.3 Force Measurements 62
2.6.4 Soft Solid Interfaces 63
References 67

3 Hysteresis and Elasticity of Triple Lines **69**
3.1 Description of Phenomena 69
3.1.1 Advancing and Receding Angle 69
3.1.2 Pinning of the Triple Line 71
3.2 Elasticity of the Triple Line 72
3.2.1 The Myth of the Line Tension 72
3.2.2 The Fringe Elasticity of the Line of Contact 73
3.3 Hysteresis Due to Strong, Sparse Defects 76
3.4 Surfaces With Dense Defects 78
3.4.1 A Realistic Example 78
3.4.2 Small, Uncorrelated Defects 79
3.5 Two Cases Consistent With the Elasticity of Vibrating Strings 80

3.5.1 Hele-Shaw Cells 80
3.5.2 Puddle Edges 81
3.5.3 Puddle Distortions 83
3.6 The Role of Thermal Fluctuations 84
References 84

4 Wetting and Long-Range Forces **87**
4.1 Energy and Properties of Films 87
4.1.1 Transition From Macroscopic to Microscopic 87
4.1.2 Thickness Change and Disjoining Pressure 88
4.1.3 Overall Stress in a Film 90
4.1.4 Three Types of Wetting 91
4.1.4.1 Stability Condition 91
4.1.4.2 Total Wetting 93
4.1.4.3 Partial Wetting 93
4.1.4.4 Pseudo-Partial Wetting 93
4.2 The Nature of Long-Range Forces 94
4.2.1 van der Waals Forces 94
4.2.2 Case of Temperature-Dependent
van der Waals Forces 96
4.2.3 Van der Waals Interactions in Layered Solids:
Surface Treatments 97
4.2.4 Other Long-Range Forces 98
4.3 Some Manifestations of Long-Range Forces 99
4.3.1 Films on Slightly Rough Substrates:
The Healing Length 99
4.3.2 Fine Structure of the Triple Line 101
4.4 Stratified Film 103
References 104

5 Hydrodynamics of Interfaces **107**
5.1 Mechanics of Films: The Lubrication Approximation 107
5.2 Dynamics of Thin Films 111
5.2.1 Thinning of a Vertical Film 111
5.2.2 Levelling of a Horizontal Film 112
5.2.3 Rayleigh-Taylor Instability 115
5.2.4 Plateau-Rayleigh Instability 118
5.3 Forced Wetting 122
5.3.1 The Landau-Levich-Derjaguin Model
(and Variant Thereof) 122
5.3.2 Soapy Liquids 126
5.3.3 Other Geometries 127
5.4 Dynamics of Impregnation 129
5.4.1 Description of the Phenomenon 129
5.4.2 Washburn's Law 130

5.4.3 Inertial Regime 131
5.5 Waves and Ripples 133
5.5.1 Deep Water Condition 133
5.5.2 Dispersion Relation in the Inertial Regime 134
5.5.3 Attenuation 135
References 136

6 Dynamics of the Triple Line 139
6.1 Basic Experiment 139
6.2 Relation Between Force and Velocity 141
6.2.1 Mechanical Model (Viscous Dissipation) 142
6.2.2 Chemical Model 144
6.3 Oscillations Modes of a Triple Line 146
6.4 Dynamics of Total Wetting 148
References 150

7 Dewetting 153
7.1 Critical Thickness for Dewetting 155
7.1.1 Film on a Solid Substrate 155
7.1.2 Film on a Liquid Substrate 158
7.1.3 Sandwiched Liquid Films 159
7.2 Viscous Dewetting 160
7.2.1 Ideal Solid Substrates 161
7.2.2 Imperfect Solid Substrates 166
7.2.2.1 Surfaces With Hysteresis 166
7.2.2.2 "Slippery" Substrates 168
7.2.3 Liquid Substrates 169
7.2.4 Spinodal Dewetting 170
7.3 Inertial Dewetting 174
7.3.1 The Reynolds Number 175
7.3.2 The Froude Number
(Condition for Shock Waves) 177
7.3.3 Liquid/Liquid Inertial Dewetting 180
7.4 Visco-Elastic Dewetting 181
7.4.1 Rupture of Ultra-Viscous Films 182
7.4.2 Life and Death of Viscous Bubbles 185
References 187

8 Surfactants 191
8.1 Frustrated Pairs 191
8.1.1 Principle 191
8.1.2 The Notion of Hydrophilic/Lipophilic
Balance (HLB) 192
8.2 Aggregation of Surfactants 194
8.2.1 Aggregation in Volume: Micelles 194

8.2.2 Water/Air Interfaces 196
8.2.2.1 Insoluble Monolayers 197
8.2.2.2 Soluble Monolayers 197
8.2.2.3 Dynamical Surface Tensions 199
8.3 Some Applications of Surfactants 200
8.3.1 Flotation 200
8.3.2 Detergents 202
8.3.3 Emulsification 203
8.3.4 Surfactants as Wetting and Dewetting Agents 204
8.4 Soap Films and Bubbles 206
8.4.1 Fabrication of Films 206
8.4.2 The Role of Surfactants 207
8.4.3 Draining Mechanisms 208
8.4.4 Aging and Death of Films 209
8.4.5 The Case of Bubbles 211
References 212

9 Special Interfaces **215**
9.1 Outline 215
9.2 Wetting of Textured Surfaces 216
9.2.1 Basic Model 216
9.2.1.1 Experiment of Johnson and Dettre 216
9.2.1.2 Wenzel's Model 217
9.2.1.3 The Cassie-Baxter Model 218
9.2.2 Composite Rough Surfaces 219
9.2.2.1 Hydrophilic Surfaces 219
9.2.2.2 Hydrophobic Surfaces 221
9.2.2.3 Summary 225
9.2.3 Liquid Pearls and Marbles 226
9.2.3.1 Implementation 226
9.2.3.2 Static States 229
9.2.3.3 Dynamical States 230
9.3 Wetting and Porous Media 235
9.3.1 Capillary Rise in a Porous Medium 235
9.3.2 Equilibrium Angle at the Surface
of a Porous Medium 237
9.3.3 Suction Experiments on Drops 238
9.3.4 Suction Experiments on Films 239
9.4 Wetting at Soft Interfaces 240
9.4.1 Principles of "Elastic" Wetting 241
9.4.1.1 The Spreading Parameter S 242
9.4.1.2 Young's Relation No Longer Holds! 242
9.4.1.3 Penny-Shaped Trapped Drops 242
9.4.2 Experimental Observation of Elastic Wetting 243

9.4.2.1 The Three Partners: Soft Solid, Liquid, and Elastomer 243
9.4.2.2 Observation of the Contact: Reflection Interference Contrast Microscopy 244
9.4.2.3 Drop Profile and Measurement of S 245
9.4.3 "Elastic" Dewetting of Wedged-in Films 246
9.4.3.1 Drainage 247
9.4.3.2 Controlled Dewetting: Nucleators 248
9.4.4 Wetting Transitions Under Shear: The Principle of Hydroplaning 252
9.4.5 Role of Nucleators in Forced Wetting: Cerenkov Wake 255
9.4.6 Conclusion 256
References 258

10 Transport Phenomena **261**
10.1 Chemical Gradients 261
10.1.1 Experiments With Vapors 261
10.1.2 Transport Toward Wettable Regions 263
10.2 Thermal Gradients 268
10.2.1 Drops Favoring the Cold 268
10.2.2 Finger Formation 271
10.3 Reactive Wetting 275
10.3.1 Examples 275
10.3.2 Liquid Column in a Capillary 276
10.3.3 Bidrops 278
10.3.4 "Running Drops" on a Solid Planar Surface 280
10.4 Transport by Electric Field 281
10.4.1 Relevance of Microsystems 281
10.4.2 Electrocapillarity 282
10.4.3 Principle of Electro-Osmosis 283
10.4.4 Examples 283
10.4.4.1 Electrostatic Lenses 283
10.4.4.2 Transfer of Bubbles 285
10.4.4.3 Limitations 285
10.4.4.4 Comparison with Capacitive Effects 286
References 286

Index **289**

Introduction

Years ago, Henri Bouasse wrote a classic French text on the topic of capillarity.[1] Bouasse has long been something of a celebrity in his field, not just on the strength of his technical writings but also because of his biting prefaces, in which he excoriated some of his colleagues. He was particularly intolerant of the professors at the Collège de France, who were not burdened by heavy teaching loads and devoted much of their time to such esoteric topics as the then nascent quantum physics. Bouasse failed to understand the physics revolution of the 20th century; yet he contributed with his legendary flair a number of enduring advances in classical physics, notably in his book on surface phenomena.

Eighty years later, capillarity continues to be a science in development. The Russian school led by Derjaguin worked on capillarity problems for 50 years.[2] In 1959, Mysels, Shinoda, and Frankel published their famous text on soap films.[3] Zisman, motivated by applied research on the lubrication of the clockwork of timepieces, elucidated the criteria for wetting.[4] Tanner, an aeronautics engineer, and Hoffman, a chemist, determined the experimental laws governing the spreading of liquids.[5] Many new concepts have emerged. Hence our incentive to write a new book.

We wanted to do it in the Bouasse tradition, that is to say, by aiming at an audience of students. What we offer here is not a comprehensive account of the latest research but rather a compendium of principles. Also following in Bouasse's footsteps, we do not claim to provide a detailed, up-to-date bibliography. All through these chapters, we suggest but a few major references with little regard for historical chronology.

We have endeavored to maintain as simple a presentation as possible. Our treatment is even less mathematical than was Bouasse's with its cycloids and other analytical tricks. Our goal is to illustrate concepts rather than to delve into detailed quantitative derivations. Even within this framework, we had to exercise restraint and be selective. For instance, we do not treat Cahn's problem of wetting transitions, fascinating as the subject may be.[6] We rely on physical chemistry more than on statistical physics. In the same vein, we have elected not to cover the following topics:

- Superfluids, which are systems of exquisite elegance, but require of students the kind of technical maturity that only comes with experience
- Certain recent developments of a purely hydrodynamic nature, such as the inertial behavior of drops hitting a surface
- Wetting by volatile fluids
- The dynamic behavior of wetting in the presence of surfactants

Our task was not easy. Fortunately, we operated in marvelously stimulating environments, both at the Collège de France and at the Institut Curie, where several generations of experimenters and theorists had already done pioneering research on wetting. To mention but some of the founding members, we owe much to A. M. Cazabat, J. M. di Meglio, H. Hervet, F. Heslot, J. F. Joanny, L. Léger, T. Ondarçuhu, E. Raphaël, and F. Rondelez. We are also grateful to our outside friends, notably P. Pincus, Y. Pomeau, T. Witten, and M. Shanahan. They did not always embrace our views, but they did force us to think. We realize this book is far from perfect. But we did try to convey the sense of curiosity and joy that infused the members of our various research teams as they grappled for the past 20 years with drops large and small.

Acknowledgments: We owe a special debt of gratitude to our capable proofreaders, Christian Counillon, Annick Lesne, and Emilie Echalier, and to our "electronic editors," Florence Bonamy, Yvette Heffer, and Pierre-Henri Puech, assisted by Nicole Blandeau. Their willingness to invest so much of their time and energy in this project is enormously appreciated. Without the discipline they wisely imposed on us, this book would never have seen the light of day.

References

[1] H. Bouasse, *Capillarité et phénomènes superficiels* (Capillarity and Surface Phenomena) (Paris: Delagrave, 1924).

[2] B. Derjaguin, *Kolloid Zh* **17**, 191 (1955).

[3] K. Mysels, K. Shinoda, and S. Frankel, *Soap Films* (London: Pergamon, 1959).

[4] W. Zisman, Contact angles, wettability and adhesion, *Adv. in Chem. Series*, No. 43, Amer. Chem. Soc., Washington, D.C., ed. by F. M. Fowkes, p. 1.

[5] P. G. de Gennes, Wetting: Statics and dynamics, *Rev. Modern Physics* **57**, 827 (1985).

[6] D. Bonn and D. Ross, Wetting transitions, *Rep. Prog. Phys.* **64**, 1085 (2001).