

# **Electrowetting**

Fundamental Principles and Practical Applications

*Frieder Mugele and Jason Heikenfeld*

**WILEY-VCH**

## Contents

Preface *xi*

<b>1</b>	<b>Introduction to Capillarity and Wetting Phenomena</b>	<b>1</b>
1.1	Surface Tension and Surface Free Energy	2
1.1.1	The Microscopic Origin of Surface Energies	2
1.1.2	Macroscopic Definition of Surface Energy and Surface Tension	5
1.2	Young–Laplace Equation: The Basic Law of Capillarity	7
1.2.1	Laplace’s Equation and the Pressure Jump Across Liquid Surfaces	7
1.2.2	Applications of the Young–Laplace Equation: The Rayleigh–Plateau Instability	11
1.3	Young–Dupré Equation: The Basic Law of Wetting	13
1.3.1	To Spread or Not to Spread: From Solid Surface Tension to Liquid Spreading	13
1.3.2	Partial Wetting: The Young Equation	16
1.4	Wetting in the Presence of Gravity	19
1.4.1	Bond Number and Capillary Length	21
1.4.2	Case Studies	22
1.4.2.1	The Shape of a Liquid Puddle	22
1.4.2.2	The Pendant Drop Method: Measuring Surface Tension by Balancing Capillary and Gravity Forces	24
1.4.2.3	Capillary Rise	25
1.5	Variational Derivation of the Young–Laplace and the Young–Dupré Equation	26
1.6	Wetting at the Nanoscale	29
1.6.1	The Effective Interface Potential	30
1.6.2	Case Studies	32
1.6.2.1	The Effective Interface Potential for van der Waals Interaction	32
1.6.2.2	Equilibrium Surface Profile Near the Three-Phase Contact Line	34
1.7	Wetting of Heterogeneous Surfaces	35
1.7.1	Young–Laplace and Young–Dupré Equation for Heterogeneous Surfaces	35
1.7.2	Gibbs Criterion for Contact Line Pinning at Domain Boundaries	37
1.7.3	From Discrete Morphology Transitions to Contact Angle Hysteresis	38

- 1.7.4 Optimum Contact Angle on Heterogeneous Surfaces: The Laws of Wenzel and Cassie 43
- 1.7.5 Superhydrophobic Surfaces 45
- 1.7.6 Wetting of Heterogeneous Surfaces in Three Dimensions 48
- 1.7.7 Wetting of Complex Surfaces in Three Dimensions: Morphology Transitions, Instabilities, and Symmetry Breaking 50
- 1.A Mechanical Equilibrium and Stress Tensor 55
  - Problems 56
  - References 58
  
- 2 Electrostatics 61**
  - 2.1 Fundamental Laws of Electrostatics 61
    - 2.1.1 Electric Fields and the Electrostatic Potential 61
    - 2.1.2 Specific Examples 64
  - 2.2 Materials in Electric Fields 66
    - 2.2.1 Conductors 66
    - 2.2.2 Dielectrics 68
    - 2.2.3 Dielectric Liquids and Leaky Dielectrics 73
  - 2.3 Electrostatic Energy 76
    - 2.3.1 Energy of Charges, Conductors, and Electric Fields 76
    - 2.3.2 Capacitance Coefficients and Capacitance 78
    - 2.3.3 Thermodynamic Energy of Charged Systems: Constant Charge Versus Constant Potential 80
  - 2.4 Electrostatic Stresses and Forces 82
    - 2.4.1 Global Forces Acting on Rigid Bodies 82
    - 2.4.2 Local Forces: The Maxwell Stress Tensor 83
    - 2.4.3 Stress Boundary Condition at Interfaces 85
  - 2.5 Two Generic Case Studies 87
    - 2.5.1 Parallel Plate Capacitor 87
    - 2.5.2 Charge and Energy Distribution for Two Capacitors in Series 90
  - Problems 92
  - References 93
  
- 3 Adsorption at Interfaces 95**
  - 3.1 Adsorption Equilibrium 96
    - 3.1.1 General Principles 96
    - 3.1.2 Langmuir Adsorption 96
    - 3.1.3 Reduction of Surface Tension 99
  - 3.2 Adsorption Kinetics 101
  - 3.3 Surface-Active Solutes: From Surfactants to Polymers, Proteins, and Particles 105
  - 3.A A Statistical Mechanics Model of Interfacial Adsorption 107
    - Problems 110
    - References 110
  
- 4 From Electric Double Layer Theory to Lippmann's Electrocapillary Equation 113**
  - 4.1 Electrocapillarity: the Historic Origins 113

- 4.2 The Electric Double Layer at Solid–Electrolyte Interfaces 115
- 4.2.1 Poisson–Boltzmann Theory and Gouy–Chapman Model of the EDL 116
- 4.2.2 Total Charge and Capacitance of the Diffuse Layer 120
- 4.2.3 Voltage Dependence of the Free Energy: Electrowetting 122
- 4.3 Shortcomings of Poisson–Boltzmann Theory and the Gouy–Chapman Model 124
- 4.4 Teflon–Water Interfaces: a Case Study 125
- 4.A Statistical Mechanics Derivation of the Governing Equations 127
- Problems 130
- References 130
  
- 5 Principles of Modern Electrowetting 133**
- 5.1 The Standard Model of Electrowetting (on Dielectric) 133
- 5.1.1 Electrowetting Phenomenology 133
- 5.1.2 Macroscopic EW Response 136
- 5.1.3 Microscopic Structure of the Contact Line Region 138
- 5.2 Interpretation of the Standard Model of EW 145
- 5.2.1 The Electromechanical Interpretation 145
- 5.2.2 Standard Model of EW Versus Lippmann’s Electrocapillarity 145
- 5.2.3 Limitations of the Standard Model: Nonlinearities and Contact Angle Saturation 149
- 5.3 DC Versus AC Electrowetting 151
- 5.3.1 General Principles 151
- 5.3.2 Application Example: Parallel Plate Geometry 153
- Problems 156
- References 157
  
- 6 Elements of Fluid Dynamics 159**
- 6.1 Navier–Stokes Equations 159
- 6.1.1 General Principles: from Newton to Navier–Stokes 160
- 6.1.2 Boundary Conditions 163
- 6.1.3 Nondimensional Navier–Stokes Equation: The Reynolds Number 166
- 6.1.4 Example: Pressure-Driven Flow Between Two Parallel Plates 167
- 6.2 Lubrication Flows 170
- 6.2.1 General Lubrication Flows 170
- 6.2.2 Lubrication Flows with a Free Liquid Surface 173
- 6.2.3 Application I: Linear Stability Analysis of a Thin Liquid Film 174
- 6.2.4 Application II: Entrainment of Liquid Films 176
- 6.3 Contact Line Dynamics 179
- 6.3.1 Tanner’s Law and the Spreading of Drops on Macroscopic Scales 179
- 6.3.2 Surface Profiles on the Mesoscopic Scale: The Cox–Voinov Law 181
- 6.3.3 Dynamics of the Microscopic Contact Angle: The Molecular Kinetic Picture 182
- 6.3.4 Comparison to Experimental Results 183
- 6.4 Surface Waves and Drop Oscillations 185
- 6.4.1 Surface Waves 187

- 6.4.2 Oscillating Drops 188
- 6.4.3 Example: Electrowetting-Driven Excitation of Eigenmodes of a Sessile Drop 192
- 6.4.4 General Consequences 193
  - Problems 194
  - References 196
- 7 Electrowetting Materials and Fabrication 197**
  - 7.1 Practical Requirements 197
  - 7.2 Electrowetting Deviation: Caused by Non-obvious Materials Behavior 198
    - 7.2.1 Commonly Observed Temporal Deviations 199
      - 7.2.1.1 Dielectric Failure (Leakage Current) 199
      - 7.2.1.2 Dielectric Charging 201
      - 7.2.1.3 Charges into the Oil 202
      - 7.2.1.4 Oil Relaxation 202
      - 7.2.1.5 Surfactant Diffusion (Interface Absorption) 203
      - 7.2.1.6 Oil Film Trapping 203
    - 7.2.2 Commonly Observed Nontemporal Deviation 204
      - 7.2.2.1 Unexpected Young's Angles: Gravity Effects 204
      - 7.2.2.2 Unexpected Young's Angles: Surface and Interface Fouling 204
      - 7.2.2.3 Unexpected Young's Angles: Dielectric Charging 205
      - 7.2.2.4 Wetting Hysteresis 205
    - 7.2.3 Deviation That Is Often Both Highly Temporal and Nontemporal 206
      - 7.2.3.1 Chemical/Surface Potentials 206
  - 7.3 Electrowetting Saturation 207
  - 7.4 The Invariant Onset of Deviation or Saturation and Lack of a Universal Theory for This Invariance 208
    - 7.4.1 The Invariance of Saturation for Aqueous Conducting Fluids 208
    - 7.4.2 The Invariance of the Onset of Deviation or Saturation for All Types of Conducting Fluids with  $\gamma_{ci} > 5 \text{ mN m}^{-1}$  209
    - 7.4.3 Summary 209
  - 7.5 Choosing Materials: Large Young's Angle and Low Wetting Hysteresis 210
    - 7.5.1 Conventional Ultralow Surface Energy Coatings (Fluoropolymers) 211
    - 7.5.2 Hydrophilic Coatings Made Hydrophobic Through Proper Choice of Insulating Fluid 213
    - 7.5.3 Superhydrophobic Coatings: Larger Young's Angle in Air but Small Modulation Range 213
  - 7.6 Choosing Materials: the Electrowetting Dielectric (Capacitor) 215
    - 7.6.1 Current State of the Art for Low Potential Electrowetting: Multilayer Dielectrics 218
      - 7.6.2 A Note of Critical Importance for the Topcoat in a Multilayer System 219
      - 7.6.3 Carefully Choosing the Best Materials for Each Individual Layer of the Dielectric Stack 219

7.6.3.1	First Layer: Inorganic Dielectrics	219
7.6.3.2	Second Layer: Organic Dielectrics	220
7.6.3.3	Third Layer: Fluoropolymer	220
7.6.3.4	The Simplest Approaches Available to Electrowetting Practitioners	220
7.7	Choosing Materials: Insulating and Conducting Fluids	221
7.7.1	The Insulating Fluid	221
7.7.2	The Conducting Fluid	221
7.7.2.1	Ionic Content	222
7.7.2.2	Don't Use Water!	223
7.8	Summary of General Best Practices	224
7.9	Mitigating Surface Fouling in Biological Applications	224
7.10	Additional Issues for Complex or Integrated Devices	226
	Acknowledgement	227
7.A	Trapped Charge Derivation	227
	Problems	229
	References	231
<b>8</b>	<b>Fundamentals of Applied Electrowetting</b>	<b>235</b>
8.1	Introduction and Scope	235
8.2	Droplet Transport	235
8.2.1	Basic Force Balance Interpretation of Droplet Transport	235
8.2.2	Advanced Droplet Transport Physics: Threshold and Velocity	237
8.2.2.1	Advanced Droplet Transport Physics: Flow Field	239
8.2.3	Additional Practical Notes on Implementation of Basic Droplet Transport	240
8.3	Droplet Transport for Splitting, Dosing, Merging, and Mixing	240
8.3.1	Simple Experimental Examples	241
8.3.2	Fundamentals of Droplet Splitting	241
8.3.2.1	Influence of Vertical Radii of Curvature	242
8.3.2.2	Influence of Horizontal Radii of Curvature	242
8.3.3	Fundamentals of Droplet Dosing (Dispensing)	243
8.3.4	Fundamentals of Droplet Mixing	244
8.4	Stationary Droplet Oscillation, Jumping, and Mixing	244
8.4.1	Droplet Oscillation	244
8.4.2	Droplet Oscillation and Jumping	245
8.4.3	Droplet Oscillation and Hysteresis	245
8.4.4	Droplet Oscillation and Mixing	246
8.5	Gating, Valving, and Pumping	247
8.5.1	Fundamentals	247
8.6	Generating Droplets and Channels	249
8.6.1	Fundamentals for Droplet Generation	249
8.6.2	Fundamentals for Channel Generation	250
8.7	Shape Change in a Channel	251
8.7.1	Fundamentals	251
8.8	Control of Meniscus Curvature	252
8.8.1	Fundamentals	252

8.8.2	Additional Notes on Implementation	253
8.9	Control of Meniscus Surface Area/Coverage	253
8.9.1	Fundamentals	253
8.9.2	Additional Notes on Implementation	254
8.10	Control of Film Breakup and Oil Entrapment	255
8.10.1	Fundamentals	255
8.11	1D, 2D, and 3D Control of Rigid Objects	257
8.11.1	Fundamentals	257
8.12	Reverse Electrowetting and Energy Harvesting	258
	Problems	260
	References	261

**9 Related and Emerging Topics 265**

9.1	Introduction and Scope	265
9.2	Dielectrophoresis and Dielectrowetting	265
9.2.1	Basic Dielectrophoresis	265
9.2.2	Dielectrowetting	267
9.3	Innovations in Liquid Metal Electrowetting and Electrocapillarity	269
9.3.1	Electrowetting of GaInSn Liquid Metal Alloys	269
9.3.2	Giant Electrochemical Changes in Liquid Metal Interfacial Surface Tensions	270
9.4	Nonequilibrium Electrical Control Without Contact Angle Modulation	271
9.4.1	Some Limitations of Conventional Electrowetting	271
9.4.2	Electrowetting Without Wetting	272
	Problems	273
	References	274

**Appendix Historical Perspective of Modern Electrowetting:**

<b>Individual Testimonials</b>	277
Introduction and Scope	277
“CJ” Kim	277
Authors Note from Heikenfeld	278
Johan Feenstra	278
Tom Jones	279
Frieder Mugele	280
Richard Fair	281
Author’s Note from Heikenfeld	282
Bruno Berge	282
Glen McHale	285
Stein Kuiper	286
Jason Heikenfeld	288
Kwan Hyung Kang: An Appreciation by T. B. Jones	289
Author’s Note from Mugele	290
References	290