PROGRESS IN ADHESION AND ADHESIVES

Edited by K.L. Mittal

Scrivener Publishing
WILEY
Progress in Adhesion and Adhesives
Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Publishers at Scrivener
Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)
Progress in Adhesion and Adhesives

Edited by

K.L. Mittal
## Contents

<table>
<thead>
<tr>
<th>Preface</th>
<th>xv</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 Adhesion of Condensed Bodies at Microscale: Variation with</strong></td>
<td></td>
</tr>
<tr>
<td>Movable Boundary Conditions</td>
<td>1</td>
</tr>
<tr>
<td><em>Jian-Lin Liu, Jing Sun, Runni Wu and Re Xia</em></td>
<td></td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Kinematics: Energy Variation with Movable Boundary Conditions</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Microbeam/plate Adhesion</td>
<td>9</td>
</tr>
<tr>
<td>1.4 Droplet Adhesion to a Solid</td>
<td>13</td>
</tr>
<tr>
<td>1.5 Elastica Model of CNT Adhesion</td>
<td>17</td>
</tr>
<tr>
<td>1.6 Cell Adhesion</td>
<td>20</td>
</tr>
<tr>
<td>1.7 Summary and Prospects</td>
<td>23</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>24</td>
</tr>
<tr>
<td>References</td>
<td>24</td>
</tr>
</tbody>
</table>

| **2 Imparting Adhesion Property to Silicone Materials: Challenges and Solutions** | 31 |
| *R. Kalinova, R. Mincheva and Ph. Dubois*                              |    |
| 2.1 Introduction                                                       | 32 |
| 2.2 Cured PDMS                                                         | 32 |
| 2.2.1 Curing Reactions                                                 | 32 |
| 2.2.1.1 Free-Radical Curing                                            | 33 |
| 2.2.1.2 Condensation Curing                                            | 33 |
| 2.2.1.3 Hydrosilylation (Addition) Curing                              | 35 |
| 2.2.2 Surface Properties                                               | 36 |
| 2.2.3 Adhesion Property                                                | 37 |
| 2.3 Methods for Cross-Linked PDMS Surface Modification                 | 37 |
| 2.3.1 Physical Techniques                                              | 37 |
| 2.3.1.1 Plasma Treatment                                               | 37 |
| 2.3.1.2 Corona Treatment                                               | 39 |
| 2.3.1.3 UV/O$_3$ Treatment                                             | 40 |
## 2.3 Laser Treatment

- 2.3.1.4 Laser Treatment ........................................ 41
- 2.3.1.5 Physical Adsorption .................................... 41

## 2.3.2 Wet Chemical Techniques

- 2.3.2.1 LbL Deposition ........................................... 42
- 2.3.2.2 Sol-Gel Method .......................................... 43
- 2.3.2.3 Other Wet Chemical Treatments ....................... 43

## 2.3.3 Combination of Physical and Chemical Techniques

- 2.3.3.1 Covalent Surface Grafting .............................. 44
- 2.3.3.2 Modification by Amphiphilic Block Copolymers ... 46
- 2.3.3.3 Other Combination of Physical and Chemical Techniques ................................. 48

## 2.4 Summary and Prospects

Acknowledgements ................................................. 48
References .......................................................... 50

## 3 Functionally Graded Adhesively Bonded Joints

**M. Kemal Apalak**

- 3.1 Introduction .................................................. 57
- 3.2 Functionally Graded Materials .............................. 61
- 3.3 Constitutive Relations ....................................... 63
- 3.4 Joints with Functionally Graded Adherends ............... 67
- 3.5 Functionally Graded Adhesives ............................. 73
- 3.6 Conclusions .................................................. 77

References .......................................................... 78

## 4 Synthetic Adhesives for Wood Panels: Chemistry and Technology

**A. Pizzi**

- 4.1 Introduction .................................................. 85
- 4.2 Urea-formaldehyde (UF) Adhesives ......................... 87
- 4.3 Melamine-formaldehyde (MF) and Melamine-urea-formaldehyde (MUF) Adhesives .......... 93
- 4.4 Phenolic Resins .............................................. 99
  - 4.4.1 Reactivity and Hardening Reactions of PF Adhesive Resins .................................. 103
  - 4.4.2 Modification of Phenolic Resins ........................................................................... 104
    - 4.4.2.1 Post-addition of Urea .................................................................................. 104
    - 4.4.2.2 Co-condensation Between Phenol and Urea ................................................. 105
    - 4.4.2.3 Addition of Tannins, Lignins and Isocyanates ............................................. 105

References .......................................................... 108
4.5 Isocyanate Wood Adhesives
   4.5.1 Chemistry of Isocyanate Wood Adhesives 107
   4.5.2 Technology of Isocyanate as Adhesives 109
   4.5.3 Emulsified/emulsifiable Water-dispersed PMDI 112
   4.5.4 PF/pMDI and UF/pMDI Hybrid Adhesives 112
   4.5.5 Conditions for Application of Isocyanate Adhesives for Wood 114

4.6 Summary 116
References 116

5 Adhesion Theories in Wood Adhesive Bonding 125
   Douglas J. Gardner, Melanie Blumentritt, Lu Wang and Nadir Yildirim
   5.1 Introduction 125
      5.1.1 Wood Material Properties Relevant to Adhesion 126
      5.1.2 Objectives 129
   5.2 Mechanical Interlocking and Mechanics of Adhesive-Wood Interactions 129
      5.2.1 Atomic Force Microscopy (AFM) & Nanoindentation 132
   5.3 Electrostatic Adhesion 135
   5.4 Wettability, Surface Energy, Thermodynamic Adhesion 137
      5.4.1 Wood Anatomy Impact on Wetting 140
      5.4.2 Extractives 141
      5.4.3 Adhesive Wettability 141
      5.4.4 Wood Modification 141
         5.4.4.1 Acetylation 142
         5.4.4.2 Grafting 142
         5.4.4.3 Fire Retardants, Preservatives and Adhesion Promotion 142
      5.4.5 Test Methods 143
   5.5 Diffusion Theory of Adhesion 145
   5.6 Covalent Bonding 148
   5.7 Acid-base Theory 149
   5.8 Weak Boundary Layer 150
      5.8.1 Extractives 151
      5.8.2 Heat Treatment 152
      5.8.3 Wood Impregnation and Densification 153
      5.8.4 Machining Processes 153
      5.8.5 Surface Degradation 154
      5.8.6 Surface Activation 154
5.9 Discussion and Future Research Prospects 155
5.10 Summary 157
References 158

6 Adhesion and Surface Issues in Biocomposites and Bionanocomposites 169
Cintil Jose, Merin Sara Thomas, B. Deepa, Laly A. Pothan and Sabu Thomas
6.1 Introduction 170
6.2 Biopolymers 170
  6.2.1 Cellulose 170
  6.2.2 Chitin 171
  6.2.3 Starch 173
6.3 Chemical Modification of Cellulose, Chitin and Starch 174
6.4 Bio-based Matrices 177
  6.4.1 Poly(lactic acid) (PLA) 177
  6.4.2 Polyhydroxybutyrate (PHB) 178
  6.4.3 Cellulose 179
  6.4.4 Chitosan 180
  6.4.5 Starch 181
  6.4.6 Natural Rubber 182
6.5 Processing Techniques 184
6.6 Interfacial Adhesion Issues 185
  6.6.1 Challenges of Interfacial Adhesion of Natural Fibres in Polymer Matrix 185
    6.6.1.1 Challenges of Dispersion of Cellulose Nanofibres 186
  6.6.2 Strategies for Improving Interfacial Adhesion 186
  6.6.3 New Challenges and Future Trends in Fibre/Matrix Interfacial Adhesion 188
6.7 Interface Characterization Techniques 189
  6.7.1 Morphological Characterization 189
    6.7.1.1 Scanning Electron Microscopy (SEM) 190
    6.7.1.2 Atomic Force Microscopy (AFM) 194
  6.7.2 Thermal Analysis 196
    6.7.2.1 Thermogravimetric Analysis (TGA) 196
    6.7.2.2 Differential Scanning Calorimetry (DSC) 199
    6.7.2.3 Dynamic Mechanical Thermal Analysis (DMTA) 199
<table>
<thead>
<tr>
<th>6.7.3</th>
<th>Spectroscopic Techniques</th>
<th>203</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7.3.1</td>
<td>Fourier Transform Infrared (FTIR) and Raman Spectroscopies</td>
<td>203</td>
</tr>
<tr>
<td>6.7.3.2</td>
<td>Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)</td>
<td>205</td>
</tr>
<tr>
<td>6.7.3.3</td>
<td>Nuclear Magnetic Resonance (NMR) Spectroscopy</td>
<td>206</td>
</tr>
<tr>
<td>6.8</td>
<td>Summary and Conclusions</td>
<td>207</td>
</tr>
</tbody>
</table>

**References**

<table>
<thead>
<tr>
<th>7</th>
<th>Adhesion Phenomena in Pharmaceutical Products and Applications of AFM</th>
<th>219</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Emily Callard Preedy, Stefano Perni and Polina Prokopovich</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>220</td>
</tr>
<tr>
<td>7.2</td>
<td>Adhesion in Pharmaceuticals</td>
<td>222</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Adhesion Interactions</td>
<td>223</td>
</tr>
<tr>
<td>7.2.1.1</td>
<td>Drug-Drug/Carrier Interactions</td>
<td>223</td>
</tr>
<tr>
<td>7.2.1.2</td>
<td>Drug-Device/Packaging Interactions</td>
<td>224</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Factors Influencing Adhesion</td>
<td>225</td>
</tr>
<tr>
<td>7.2.2.1</td>
<td>Monitoring and Controlling Influential Factors</td>
<td>229</td>
</tr>
<tr>
<td>7.3</td>
<td>Atomic Force Microscopy</td>
<td>232</td>
</tr>
<tr>
<td>7.3.1</td>
<td>AFM and Pharmaceutical Formulations</td>
<td>233</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Advantages of AFM</td>
<td>234</td>
</tr>
<tr>
<td>7.4</td>
<td>Prospects</td>
<td>236</td>
</tr>
<tr>
<td>7.5</td>
<td>Summary</td>
<td>237</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td></td>
<td>237</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>237</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8</th>
<th>Cyanoacrylate Adhesives in Surgical Applications</th>
<th>245</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Edward M. Petrie</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>245</td>
</tr>
<tr>
<td>8.1.1</td>
<td>Basic Requirements of Surgical Adhesives</td>
<td>246</td>
</tr>
<tr>
<td>8.1.2</td>
<td>Surgical Substrates</td>
<td>248</td>
</tr>
<tr>
<td>8.1.3</td>
<td>Scope and Objectives of this Review</td>
<td>249</td>
</tr>
<tr>
<td>8.2</td>
<td>Types of Surgical Adhesives</td>
<td>249</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Full Scope of Surgical Adhesives</td>
<td>249</td>
</tr>
<tr>
<td>8.2.2</td>
<td>The Surgeon's Toolbox</td>
<td>252</td>
</tr>
<tr>
<td>8.2.2.1</td>
<td>Fibrin Sealants</td>
<td>252</td>
</tr>
<tr>
<td>8.2.2.2</td>
<td>Cyanoacrylates</td>
<td>254</td>
</tr>
</tbody>
</table>
8.2.2.3 Collagen-Based Adhesives 255
8.2.2.4 Poly(ethylene glycol) Polymers 255
8.2.2.5 Albumin and Glutaraldehyde Products 256
8.2.2.6 Others 256
8.2.3 Comparison of Adhesive Types 257
8.3 History of Cyanoacrylate Surgical Adhesives 257
  8.3.1 Development of Cyanoacrylates as Industrial Adhesives 257
  8.3.2 Development of Cyanoacrylate Tissue Adhesives 263
    8.3.2.1 n-Butyl-2-Cyanoacrylate 264
    8.3.2.2 2-Octyl-Cyanoacrylate 267
    8.3.2.3 Newer Cyanoacrylate Surgical Adhesives 269
8.4 Formulation Development 269
  8.4.1 Monomeric Derivatives 270
  8.4.2 Optimal Formulation Development 272
    8.4.2.1 Inhibitors 273
    8.4.2.2 Stabilizers Added Depending on the Surgical Procedure 274
    8.4.2.3 Accelerators 276
    8.4.2.4 Thickeners 277
    8.4.2.5 Plasticizers 277
8.5 Properties 278
  8.5.1 Curing Mechanism 278
    8.5.1.1 Comparative Shelf-Life 279
    8.5.1.2 Container Materials for Packaging 279
  8.5.2 Bond Strength 282
  8.5.3 Toxicity 283
  8.5.4 Biocompatibility 284
8.6 Clinical History 285
  8.6.1 Closure of Skin Wounds and Superficial Incision Closure 288
  8.6.2 Other Surgical Procedures and Future Uses 289
  8.6.3 Graft Fixation 289
8.7 Future Potential 290
  8.7.1 Development Path 290
    8.7.1.1 Light Curing Cyanoacrylates 291
    8.7.1.2 Solid Cyanoacrylate 291
  8.7.2 Drivers for Increased Demand 292
8.8 Summary 292
References 293
9 Ways to Generate Monosort Functionalized Polyolefin Surfaces 299

J. Friedrich, R. Mix and G. Hidde

9.1 Introduction 300
9.1.1 General Principles 300
9.1.2 Formation of Functional Groups at Polyolefin Surfaces by Plasma Exposure 304
9.1.3 Polymer Degradation Caused by Plasma Exposure 310
9.1.4 Possible Strategies to Produce Monosort Functional Groups on Polyolefin Surfaces 311

9.2 Production of Monotype Functional Groups 312
9.2.1 OH Group Formation by Exposure to Oxygen Plasma 312
9.2.2 Formation of COOH Groups by Exposure to Carbon Dioxide Plasma 315
9.2.3 Formation of Amino Groups by Exposure to Ammonia or Nitrogen Plasmas 318
9.2.3.1 Significance of Primary Amino Groups in Life Sciences 318
9.2.3.2 Ammonia Plasma Treatment of Polymers and Graphitic Materials 319
9.2.3.3 Undesired Oxygen Introduction on Exposure to Ammonia Plasma 320
9.2.3.4 Additional Side Reactions on Exposure to Ammonia Plasma 322
9.2.4 Surface Bromination 325
9.2.4.1 Kinetics, Thermodynamics and Mechanism 325
9.2.4.2 Parameter Dependence 327
9.2.4.3 Conversion of C-Br into Other Monotype Functional Groups 327

9.3 Other Methods for Introduction of Monotype Functional Groups onto the Polyolefin Surface (Plasma Polymerization, Underwater Plasma, ElectroSpray Ionization Deposition, Atmospheric-Pressure Chemical Ionization, Chemical Pretreatment) 329
9.3.1 Plasma Polymerization 329
9.3.2 Underwater Plasma 331
9.3.3 ElectroSpray Ionization (ESI) Deposition 332
9.3.4 Chemical Pretreatment 333
9.4 Hydrophobic Recovery 335
9.5 Grafting onto Functionalized Polyolefin Surfaces 336
  9.5.1 Direct Grafting onto Radical Sites 336
  9.5.2 Grafting onto Peroxy Radicals/Hydroperoxides 337
  9.5.3 Grafting onto Monosort Functional Groups by
  Nucleophilic Substitution 339
    9.5.3.1 Wet-Chemical Chain Extension at Amino
      Groups 339
    9.5.3.2 Spacer Grafting onto OH-Groups at
      Polymer Surface 340
    9.5.3.3 Spacer Anchoring onto C-Br Groups 340
    9.5.3.4 Silane Attachment 341
9.6 Summary and Conclusions 342
References 344

10 Nano-Enhanced Adhesives 357
  Shahin Shadlou, Babak Ahmadi-Moghadam and
  Farid Taheri
10.1 Introduction 357
10.2 Why Nanostructured Reinforcements? 358
  10.2.1 Carbon-based NPs 359
  10.2.2 Metal-based NPs 359
  10.2.3 POSS 360
  10.2.4 Other Nanomaterials 360
    10.2.4.1 Nanoclays 360
    10.2.4.2 Nanosilicas (SiO₂) 360
10.3 Development of Polymer-based Nanocomposites 360
  10.3.1 Sonication 361
  10.3.2 Three-roll Milling (Calendering) 363
  10.3.3 High-Shear Mixing 364
10.4 Mechanical Properties of Nano-reinforced Adhesives 364
  10.4.1 Effect of Adhesive Stiffness 365
  10.4.2 Effect of Fracture Toughness 374
  10.4.3 Effect of Surface Wettability 377
  10.4.4 Effects of Residual Stresses 380
  10.4.5 Effect of Durability of Adhesives 382
10.5 Other Advantages of Nano-Reinforced Adhesives 383
  10.5.1 Electrical Properties 384
  10.5.2 Thermal Properties 385
  10.5.3 Gas Permeation Barrier Properties 386
  10.5.4 Bio-Adhesives 387
11 Bonding Dissimilar Materials in Dentistry

Muhammad Zakir, James Kit-Hon Tsoi, Chun Hung Chu, Christie Ying Kei Lung and Jukka Pekka Matinlinna

11.1 Introduction
11.2 Silane Coupling Agents
11.3 Zirconate Coupling Agents
11.4 Phosphate Coupling Agents
11.5 Thione/thiol Coupling Agents
11.6 Titanate Coupling Agents
11.7 Zircoaluminate Coupling Agents
11.8 Other Coupling Agents
11.9 Conclusion

References

12 Flame Treatment of Polymeric Materials: Relevance to Adhesion

L. Mazzola and A. Cusma

12.1 Introduction
12.2 Flame Treatment Equipment
   12.2.1 Process Parameters
      12.2.1.1 Combustion Conditions – Air/Gas Ratio
      12.2.1.2 Flame Energy
      12.2.1.3 Burner to Substrate Gap
      12.2.1.4 System Layout
      12.2.1.5 Valve Train
      12.2.1.6 Control Instrumentation
      12.2.1.7 Gas Saving
   12.2.2 Flame Chemistry
      12.2.2.1 Pre-reaction Zone
      12.2.2.2 Main Reaction Zone
      12.2.2.3 Post-combustion Zone
12.3 Effects of Flame Treatment on Plastics
   12.3.1 Flame Treatment of Polypropylene
   12.3.2 Flame Treatment on Polyethylene
12.4 Conclusion

References
13 Mucoadhesive Polymers for Enhancing Retention in Ocular Drug Delivery

Anubha Khare, Kanchan Grover, Pravin Pawar and Inderbir Singh

13.1 Introduction

13.2 Composition of Mucus Layer

13.2.1 Expression of Human Mucin Genes

13.3 Natural Mucoadhesive Polymers

13.3.1 Chitosan

13.3.1.1 Chitosan-based Formulations

13.3.2 Human Serum Albumin (HSA)

13.3.3 Alginate

13.3.4 Gellan gum

13.3.5 Xanthan gum

13.3.6 Guar gum

13.3.7 Sodium Hyaluronate

13.3.8 Carrageenan

13.3.9 Tamarind Gum Polysaccharide (TGP)

13.3.10 Arabinogalactan

13.4 Synthetic Polymers

13.4.1 Poly (acrylic acid) PAA or Carbomer

13.4.2 Eudragit

13.4.3 Cellulose Derivatives

13.4.4 Poly (D, L-Lactic acid) and poly (D, L-Lactide-co-glycolide)

13.4.5 Poloxamers

13.5 Gene Delivery

13.6 Patented Formulations

13.7 Future Prospects

13.8 Conclusion

Acknowledgement

References

Index
Preface

This book is based on the 13 (a lucky number) review articles published in 2014 in the journal *Reviews of Adhesion and Adhesives* (RAA). The sole purpose of RAA is to publish concise, critical, illuminating and thought-provoking review articles on any topic within the broad purview of adhesion science and adhesive technology.

With the voluminous research being published, it is difficult, if not impossible, to stay abreast of current developments in a given area. So the review articles consolidating the information provide an alternative way to follow the latest research activity and developments in a particular subject area. It should be recorded that all these review articles were rigorously reviewed to maintain the highest standards of publication.

The rationale for publication of this book is that currently the RAA has limited circulation, so this book was conceived to provide broad exposure and dissemination of information published in RAA. Apropos, the authors of the articles published in RAA were consulted and they all enthusiastically endorsed the idea of this book.

Although the book is not formally divided into different sections, it essentially addresses the following four areas in the wide domain of adhesion and adhesives.

1. General adhesion aspects
2. Polymer surface modification and relevance to adhesion
3. Adhesion and adhesives in biomedical, pharmaceutical and dental fields
4. Adhesives and adhesive joints

The topics covered include: Adhesion of condensed bodies at microscale; imparting adhesion property to silicone materials; functionally graded adhesively bonded joints; synthetic adhesives for wood panels; adhesion theories in wood adhesive bonding; adhesion and surface issues in bio-composites and bionanocomposites; adhesion phenomena in pharmaceutical products and applications of AFM; cyanoacrylate adhesives in surgical
applications; ways to generate monosort functionalized polyolefin surfaces; nano-enhanced adhesives; bonding dissimilar materials in dentistry; flame treatment of polymeric materials with relevance to adhesion; and mucoadhesive polymers for enhancing retention in ocular drug delivery.

This book containing bountiful information on certain topics of contemporary interest should be valuable and useful to researchers and technologists in academia, industry, various research institutes and other organizations. Yours truly sincerely hopes that this book will be warmly received by the materials science community in general and the adhesion and adhesives community in particular.

Kash Mittal  
P.O. Box 1280  
Hopewell Jct., NY 12533  
E-mail: usharmittal@gmail.com  
June 3, 2015
Adhesion of Condensed Bodies at Microscale: Variation with Movable Boundary Conditions

Jian-Lin Liu1,*, Jing Sun1, Runni Wu2 and Re Xia2

1Department of Engineering Mechanics, China University of Petroleum, Qingdao, China
2School of Power and Mechanical Engineering, Wuhan University, Wuhan, China

Abstract
We review here the recent developments on the adhesion of condensed bodies at microscale, spanning from droplets, microbeams, CNTs (carbon nanotubes) to cells. We first introduce a general method to completely tackle the adhesion problem with movable boundary conditions, from the viewpoint of energy variation. Based on this theoretical framework, we then use the developed line of reasoning to investigate the adhesion behaviors of several condensed systems. According to the variation with movable boundary conditions, the governing equations and transversality conditions of these systems are derived, leading to closed-form problems. The presented method is verified via the concept of energy release rate or $J$-integral in fracture mechanics. This analysis provides a new approach to explore the mechanism of different systems with similarities as well as to better understand the unification of nature. The analysis results may be beneficial to the design of micro-machined MEMS (micro-electro-mechanical systems) structures, super-hydrophobic materials, nano-structured materials, and hold potential for predicting the adhesion behavior of cells or vesicles.

Keywords: Variational theory, transversality condition, beam adhesion, droplet adhesion, CNT adhesion, cell adhesion

1.1 Introduction
A plethora of adhesion phenomena exist widely at micro/nanoscale in nature, which are caused by van der Waals force, Casimir force, capillary force, or some other interaction forces. In these low-dimensional systems with considerable surface-to-volume ratio, the surface

*Corresponding author: liujianlin@upc.edu.cn
interaction dominates over the volume force as the scale reduces to micro/nano-meters, and this feature leads to many novel behaviors distinct from those of macroscopic systems [1]. An interesting example is the striking adhesion ability of geckos, which is primarily attributed to the van der Waals force between their feet and the contact surfaces [2, 3]. Besides, the adhesion of liquid drops plays a critical role in the famous “lotus effect” [4–6], water-walking capability of aquatic creatures like water strider, water spider [7–9], mosquito [10] and ant [11], and the ability of collecting dew by Namibia desert beetle Stenocara [12]. These magical phenomena inspired the spirit of “learning from nature”, and one of the challenging subjects is to mimic the microstructures of biological materials to achieve ultrahydrophobic properties of materials with microstructured surfaces [13]. Therefore, the core issue dealing with droplet adhesion is how to predict the macroscopic contact angle appropriately, which has spurred great interest in both fundamental science and engineering applications [14–18]. It has been further shown that the contact angle of a liquid drop can be derived from the energy variation on its energy functional [19–21], and this conclusion provides a new perspective on considering the adhesion of a droplet on a substrate.

Adhesion can also cause the failure of such slender structures as beams, fibers and plates in micro/nano systems. For instance, in micro-contact printing technology, adhesion associated with van der Waals force often produces stamp deformation because of small spacings [22], and the micro-machined MEMS structures will spontaneously come into contact with the substrate under the influence of solid surface energy or capillary force of liquid [23–27]. Similar problem has become a crucial bottleneck in the bottom-up approach, in which nanowires and nanobelts are widely used as building blocks of micro/nano-devices, typically, the micro-sensors, resonators, probes, transistors and actuators in micro/nano-electro-mechanical systems (M/NEMS) [27, 28]. This sort of failure mode has proved to be a major limitation to push further application of these novel engineering devices, and it has been highlighted as a hot research topic in the past decades.

Another topic is the deformation of CNT (carbon nanotube) induced by adhesion, holding great potential in a number of applications such as flexible and stretchable load-bearing structural components in nanoscale systems [29]. There are mainly two aspects of the CNT deformation, i.e. the adhesion and cross section collapse, which are due to the fact that CNTs are one of the strongest and most flexible materials with the C-C covalent bonding and the seamless hexagonal network architecture. In the pursuit of engineering applications, it is imperative to exploit this elastic behavior and mechanism of CNT adhesion. Among others, for a CNT ring adhered to a flat substrate, Zheng and Ke [30] established an elastica model for numerical simulation, and then experimentally characterized the CNT deformation under both compressive and tensile loadings. Like a microtubule inside a vesicle buckling into a racket-like shape [31], CNTs with a similar shape were also observed in a sample of HiPco single-walled nanotubes after 30-minute of sonication in dichloroethane [32]. This behavior is termed as “self-folding”, and its occurrence in such small-scale materials such as nanowires, microtubules and nanotubes is mainly attributed to the high aspect ratio. In this situation, the maximal size (e.g., the length of nanowire) is much larger than its persistence length [33, 34]. As a consequence, a CNT can be easily bent into an arc shape with significant curvature [35]. This form of adhesion or self-folding
Adhesion of Condensed Bodies at Microscale

of CNT is actually an energetically favorable state, with the interplay of elastic deformation and van der Waals attraction between different parts of CNT. The second aspect of the CNT deformation is cross section collapse, in which its initially circular cross section will jump to a flat ribbon-like shape. The reason lies in that CNTs capture the characteristic of hollow cylindrical structures, which renders them susceptible to lateral deformation. In reality, this morphology was first observed and explored by TEM (Transmission Electron Microscopy) [36, 37] and then by AFM (Atomic Force Microscopy) [38–40]. From the viewpoint of elastic stability, the collapse of CNTs is essentially a buckling process, which has been one of the recent topics of considerable interest. A number of shell, tube and elastica models have been developed to investigate the buckling of CNTs, with the adoption of continuum mechanics, finite element, and molecular simulations [41–45].

The last related problem is cell or vesicle adhesion, which has profound implications in the forming of biological tissues and organs [46]. It also involves many physiological activities, which contribute to cellular organization and structure, proliferation and survival, phagocytosis and exocytosis, metabolism, and gene expression [47]. Appropriate cell adhesion can induce such diseases as thrombosis, inflammation, and cancer. Excessive adhesion can even cause monocytes to bond to the aorta wall and eventually leads to atherosclerotic plaques [48], and conversely the lack of adhesion can result in the loss of synaptic contact and induce Alzheimer disease [49]. Especially, the adhesion of a vesicle or a cell to a solid substrate is of great significance in many application fields, such as the adhesion between the target tumor cells and drug membrane in drug delivery [50, 51], the surface-sensitive technique based on lipid-protein bilayers [52, 53], and stem cell division modulated by the substrate rigidity [54]. Much effort in the areas of molecular and cellular biomechanics, both theoretically and experimentally, has been devoted to exploring this adhesion behavior [55].

This review article is organized as follows. In Section 2, we introduce a general framework to deal with adhesion problem with movable boundary conditions, i.e., the transversality condition method, which can be verified with the energy release rate method. In Sections 3, 4, 5 and 6, we apply the developed approach to study the adhesion of a microbeam, droplet, CNT and cell, respectively. Through the transversality conditions and governing equations originating from the energy variation, we can completely solve the critical adhesion length and deflection of a microbeam, the morphology of a droplet, and the configuration of a CNT or cell. Then the conclusion and discussion follow in the last section.

1.2 Kinematics: Energy Variation with Movable Boundary Conditions

We start from a generalized condensed system represented as a continuous and smooth curve, where only a portion of the curve is adhered by interfacial forces. As schematized by the anti-clockwise arc length \( s \) in Figure 1.1, the total length of the curve is \( L \). We assume that the “generalized elastic deformation” only happens on the segment from \( s = 0 \) to \( s = a \). The “elastic deformation” is a more general terminology, referring to the strain energy or some other energies (such as the liquid/vapor interfacial energy which appears in Section 4) related with this segment. It is noticeable that this model is similar to the famous JKR model in contact mechanics [56]. The total potential energy of the system originates from three
sources, namely, elastic strain energy, interfacial energy, and potential energy of gravity. If the typical length of the structure is denoted as $L_c$, the scaling laws for a planar system are set forth as follows: the interfacial or surface energy $U_S \propto L_c$, the elastic strain energy $U_E \propto L_c^2$, and the potential energy of gravity $U_G \propto L_c^3$ [57]. Consequently, as the dimension of a macroscopic structure reduces to micro/nanometers, the effect of surface energy becomes significant and that of the gravitational energy becomes negligible. Hence, the interplay between the surface energy and elasticity is predominant in the current micro/nano-systems.

Point $s = a$ is a key point, as its value is an unknown and should be determined by calculation, so the total potential energy of the system $\Pi$ is viewed as a function of the parameter $a$: 

$$\Pi[a] = U(a) + \Gamma(a),$$  

(1.1)

where $\Gamma(a)$ is the interfacial energy, $U(a)$ is the strain energy stored in the system which is often expressed as $U = \int_0^a F[s, y(s,a), y'(s,a), y''(s,a)] ds$, and $y$ is a function with two variables, i.e. $y = y(s,a)$.

If the segment from $s = 0$ to $s = a$ is regarded as a crack, then according to the extreme condition of $\frac{d\Pi[a]}{da} = 0$, one can arrive at the definition of the energy release rate $G$ in classical fracture mechanics:

$$G = - \frac{\partial U(a)}{\partial a} \bigg|_{\Delta} = \frac{\partial \Gamma(a)}{\partial a} = W. \quad (1.2)$$

For elastic materials under displacement loading, the energy release rate is equal to the $J$-integral named after James Rice [58].
The parameter $W$ in Eq. (1.2) is the interfacial energy per unit area or the work of adhesion at the interface. The work of adhesion between two surfaces is normally expressed as

$$W = \gamma_1 + \gamma_2 - \gamma_{12},$$

(1.3)

where $\gamma_1$ and $\gamma_2$ are the surface energies per unit area of the two different phases, and $\gamma_{12}$ is the interfacial energy per unit area. In the conventional definition, the work of adhesion is actually the work per unit area which is necessary to create two new surfaces from a unit area of an adhered interface, which is a positive constant for any two homogeneous materials binding at an interface at a fixed temperature [59]. If the two materials are the same, the work of adhesion reduces to the work of cohesion:

$$W = 2\gamma_1.$$  

(1.4)

At micro and nanoscales, the work is normally termed as the binding energy $E_b$ [60]. For a droplet on a substrate, the work of adhesion becomes

$$W = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV} \left(1 + \cos \theta_Y\right),$$

(1.5)

where $\gamma_{SV}, \gamma_{SL}$ and $\gamma_{LV}$ are the interfacial tensions of the solid/vapor, solid/liquid and liquid/vapor interfaces, respectively, with $\theta_Y$ being the Young’s contact angle of the liquid. In the above derivation, the Young’s equation $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_Y$ has been used.

Considering the movable boundary of the integrand and using Eqs. (1.1) and (1.2), the energy release rate $G$ can be expressed as:

$$G = - \frac{\partial U(a)}{\partial a} \bigg|_\Delta = F(a) + \int_0^a \left(F_y \frac{\partial y}{\partial a} + F_{y'} \frac{\partial y'}{\partial a} + F_{y''} \frac{\partial y''}{\partial a}\right) ds = W,$$

(1.6)

where the partial derivative symbols are designated as $(\ )' = \frac{\partial (\ )}{\partial s}$, $(\ )'' = \frac{\partial^2 (\ )}{\partial s^2}$, $F(a) = \frac{\partial F}{\partial a}$. Equation (1.6) indicates that the energy release rate is compensated by a gain in the interfacial energy in the process of interface enlargement. Applying this line of reasoning to the current problem, it is straightforward to solve the unknown parameter $a$ in use of this energy balance relation. However, in many situations, the analytical expressions for the energy release rate and the function $F$ are not available, because they are dependent on the governing equation. Thus, we have to seek another route to obtain the governing differential equation and then tackle this problem. Since the value of $a$ needs to be determined when the system achieves an equilibrium state, the point $s = a$ can be considered as a moving boundary from the viewpoint of mathematics [61].
The functional of the total potential energy about the system schematized in Figure 1.1 is normally written as:

$$
\Pi[y(s,a)] = \int_0^L F[s,y(s,a),y'(s,a),y''(s,a)] ds - \int_a^L W ds.
$$

(1.7)

In fact, the energy functional of Eq. (1.7) is unique in that it deals with two variables, i.e. the function $y$ and the length $a$. This fact results in an intractable problem, because the undetermined variable $a$ causes the boundary movement of the system, which will create an additional term during the variational process.

Generally, the forced or fixed boundary conditions are prescribed as:

$$
y(0) = y_0, \quad y'(0) = y'_0; \quad y(a) = y_a, \quad y'(a) = y'_a.
$$

(1.8)

The governing equation and additional boundary conditions can then be derived according to the definition of variation with movable boundary condition. Let

$$
y(s) = y_0(s) + \varepsilon Y(s),
$$

(1.9)

where $y_0(s)$ denotes the extreme solution to be found [62]. According to the prescribed boundary condition of Eq. (1.8), the extreme and varied solutions must fulfill

$$
y_0(a_0) = ya, \quad y'_0(a_0) = y'_a; \quad y(a) = ya, \quad y'(a) = y'_a; \quad Y(0) = Y'(0) = 0.
$$

(1.10)

The unknown $a$ can be expanded as

$$
a(\varepsilon) = a_0 + \varepsilon \frac{da}{d\varepsilon} |_{\varepsilon=0} + O(\varepsilon^2).
$$

(1.11)

The boundary value in Eq. (1.9) can also be expanded as

$$
y(a) = y_0(a_0) + \varepsilon y'(a_0) \frac{da}{d\varepsilon} |_{\varepsilon=0} + \varepsilon Y(a_0) + O(\varepsilon^2),
$$

(1.12)

$$
y'(a) = y'_0(a_0) + \varepsilon y''(a_0) \frac{da}{d\varepsilon} |_{\varepsilon=0} + \varepsilon Y'(a_0) + O(\varepsilon^2).
$$

(1.13)

Comparing Eqs. (1.9), (1.12) and (1.13), one arrives at

$$
Y(a_0) = -y'(a_0) \frac{da}{d\varepsilon} |_{\varepsilon=0},
$$

(1.14)
Eqs. (1.14) and (1.15) give the variation of the “new” end-point $a(\varepsilon)$ as a function of the variation in $y$ and the derivatives $y'$ and $y''$ at the “old” end-point $a_0$.

Before proceeding further, we first revisit the definition of derivative about an integration including a parameter $a$. Let

$$
\phi(a) = \int_{a(a)}^{b(a)} F(x,a) \, dx ,
$$

and then we have its derivative

$$
\phi'(a) = \int_{a(a)}^{b(a)} F'(x,a) \, dx + F[b(a),a]b'(a) - F[a(a),a]a'(a) .
$$

Now let us return to the variation of the energy functional in Eq. (1.7). Substituting Eqs. (1.8), (1.9), (1.10), (1.12) and (1.14) into Eq. (1.15), and using Eq. (1.17), one can obtain the derivative of the functional

$$
\frac{d\Pi}{d\varepsilon} \bigg|_{\varepsilon=0} = [W+F]_{s=a_0} \frac{da}{d\varepsilon} \bigg|_{\varepsilon=0} + \int_{0}^{a_0} \left[ F_y Y + F_y Y' + F_y Y'' \right] ds
$$

$$
= [W+F]_{s=a_0} \frac{da}{d\varepsilon} \bigg|_{\varepsilon=0} + \left[ F_y Y + F_y Y' \right]_{0}^{a_0} + \int_{0}^{a_0} \left[ F_y Y - \frac{dF_y}{ds} Y - \frac{dF_y''}{ds} Y' \right] ds
$$

$$
= \left[ W + F - y F_y' - y'' F_y'' + y' \frac{dF_y''}{ds} \right]_{s=a_0} \frac{da}{d\varepsilon} \bigg|_{\varepsilon=0} + \left[ F_y Y + F_y Y' - \frac{dF_y''}{ds} Y \right]_{0}^{a_0}
$$

$$
+ \int_{0}^{a_0} \left[ F_y - \frac{dF_y'}{ds} + \frac{d^2 F_y''}{ds^2} \right] Y ds = 0 .
$$

The fact that the above integral equals zero leads to the governing differential equation, i.e. the Euler-Poisson equation:
\[ F_y - \frac{\partial}{\partial s} F_{ys} + \frac{\partial^2}{\partial s^2} F_{ysy} = 0 \, . \tag{1.19} \]

The remainder of Eq. (1.18) takes the following form
\[
\left[ W + F - y'F_{ys} - y''F_{ysy} + y'y'' \frac{dF_{ysy}}{ds} \right] \left. \frac{da}{de} \right|_{\varepsilon=0} = 0 \, . \tag{1.20}
\]

This expression vanishes for arbitrary \( \left. \frac{da}{de} \right|_{\varepsilon=0} \), which corresponds to arbitrary \( Y(a_0) \) if the bracket is zero. Then we can obtain the additional boundary condition, which is defined as transversality boundary condition for this variation problem:
\[
W = \left[ y'F_{ys} + y''F_{ysy} - y'y'' \frac{dF_{ysy}}{ds} - F \right]_{s=a} \, . \tag{1.21}
\]

In fact, the transversality condition dealing with movable boundaries has already been deciphered in the book titled as “Methods of Mathematical Physics”, authored by Courant and Hilbert in 1953 [63]. In essence, this additional condition indicates the equilibrium state originating from the competition between surface energy and elastic energy at the critical point.

Therefore, based on the above fundamental deductions, utilizing the principle of least potential energy and considering the movable boundary, one can obtain the following variation result
\[
\delta \Pi[ y(s,a) ] = \delta \Pi_1 + \delta \Pi_2 = 0 \, , \tag{1.22}
\]

where
\[
\delta \Pi_1 = \int_0^a \left( F_y \delta y + F_{ys} \delta y' + F_{yys} \delta y'' \right) ds
\]
\[
= \left[ F_y \delta y + F_{yys} \delta y' - \frac{\partial}{\partial x} F_{yys} \delta y \right]_0^a + \int_0^a \left( F_y - \frac{\partial}{\partial x} F_{yys} + \frac{\partial^2}{\partial x^2} F_{yys} \right) \delta y ds \, , \tag{1.23}
\]

and
\[
\delta \Pi_2 = \left[ F - y'F_{ys} - y''F_{ysy} + y'y'' \frac{dF_{ysy}}{ds} + W \right]_{s=a} \delta a \, . \tag{1.24}
\]
Inserting Eq. (1.23) and (1.24) into (1.22), and because of the arbitrariness of the variation, one can obtain the Euler-Poisson equation shown in Eq. (1.19), and the arbitrariness of variation about the point \(a\) leads to the transversality condition in Eq. (1.21).

The combination of Eqs. (1.6) and (1.21) yields

\[
\left[ y'F_y + y''F_y - y'y'\frac{dF_y}{ds} - F \right]_{s=0} = W = G(a) + \int_0^a \left( F_y \frac{\partial y}{\partial a} + F_{yy} \frac{\partial y'}{\partial a} + F_{yy} \frac{\partial y''}{\partial a} \right) ds. \tag{1.25}
\]

It is indicated from Eq. (1.25) that there are two approaches to determine the variable \(a\), namely the energy release rate method, and the movable boundary condition method. However, in most cases when adopting the first method, the explicit expression for the integral on the right side of Eq. (1.25) is impossible to obtain, and therefore the second one is the only choice. This idea sheds a new light on solving the problem with movable boundaries.

Next, we will review some case studies, where the governing equations and transversality conditions can be easily derived from the variation viewpoint in light of energy minimization. These issues include microbeam adhesion, CNT deformation, droplet wetting, and cell adhesion. From these examples, we can see that the novel idea of movable boundary condition proves to be more challenging and fruitful.

### 1.3 Microbeam/plate Adhesion

Within the above framework, the first typical example is a microbeam stuck to the substrate with strong work of adhesion \(W\), with the Young’s modulus \(E\), and the moment of inertia on the cross section \(I\), which is schematized in a Cartesian coordinate system \((o-xy)\). As shown in Figure 1.2, the gap height is \(h\), the detached segment length is \(a\), and the total length of the beam is \(L\). The potential energy of the system can be expressed as

\[
\Pi = \frac{1}{2} \int_0^a EIw''^2 dx - W(L - a). \tag{1.26}
\]

According to the variation method of Section 2, one can arrive at the governing equation

\[
w^{(4)} = 0 \tag{1.27}
\]

and the transversality condition at the moving boundary

\[
W = \frac{1}{2} EIw''(a)^2 = \frac{18EIh^2}{a^4}. \tag{1.28}
\]

This expression is in good agreement with the former results [24, 27]. According to the above equations, one can naturally determine the detachment length and the deflection of the beam.
To validate the aforementioned results, we revisit this problem from the viewpoint of fracture mechanics. The detached segment of the beam is modeled as a crack, and the energy release rate $G$ is then deduced as

$$G = -\left. \frac{\partial U}{\partial a} \right|_\Delta = \frac{18EIh^2}{a^4} = W,$$

which bears the same form as Eq. (1.28). This re-emphasizes the equivalence of the methods of movable boundary condition and the energy release rate.

However, for the nanobeam adhesion to a solid substrate, we must take the surface effects into account. Using the Gurtin’s theory, the potential energy of the beam-substrate system is given as [64]

$$\Pi = \frac{1}{2} (EI)^* \int_0^a (w'')^2 \, dx - \int_0^a qwdx - W (L - a),$$

where $(EI)^*$ is the modified bending stiffness due to surface elasticity, and $q$ is the transversely distributed load along the longitudinal direction of the beam due to the residual surface stress. Based on the presented variation method, the nanobeam deflection with surface effects can be presented, indicating that it is not in symmetric configuration.

However, these analyses are only applicable to the case of stiff substrate, and the boundary condition at the adhesion point is assumed to be a clamped end. Following the model in Figure 1.2, Zhang and Zhao [65, 66] considered the elastic deformation of the substrate, and mentioned that the slope angle at the movable point is not zero. They derived the boundary conditions through energy variation, where they named these transversality conditions as “matching conditions”. In essence, their approach offers a more accurate model for the stuck cantilever without prescribing its deflection shape.

Besides the system consisting of a single beam adhered to a substrate, considerable attention has been paid to the capillary adhesion of multiple beams with liquid bridges. For
illustration, the adhesion of two initially parallel microbeams with a rectangular cross section is shown in Figure 1.3, where $d$ is the initial distance between the two beams. Adopting the energy minimization method, Bico et al. [67] obtained the equilibrium sizes of two beams and two bundles of beams in capillary adhesion. Kim and Mahadevan [68] derived the rising height of the meniscus between two thin sheets dipped vertically in a liquid bath. In their model, the liquid bridge was first modeled as a thin liquid film and the equilibrium configuration of the static beams was determined. These theories have been verified by their experimental results respectively, but the meniscus height is found to be different from that predicted by Jurin’s law. By using the energy variation with movable boundary condition, Liu et al. [69] presented the total potential energy of the system, where the values of the strain energy and interfacial energy are twice those of Eq. (1.26). Based on these investigations and the minimum total potential energy principle, Liu et al. [69] derived the analytical expressions for the critical adhesion lengths of two beams, three beams, and two bundles of beams under capillary forces. Their solutions were also validated by experiments using polyester and silicone oil.

It is worth mentioning that the aforementioned studies are mainly based on the infinitesimal deformation theory of elastic structures. However, a slender structure under the action of capillary forces may undergo large deformation, especially when its characteristic sizes are in the range of micrometers or nanometers. For instance, Journet et al. [70] observed that when a volatile droplet is placed on an array of aligned CNTs, it will experience large deformation and will be adhered to bundles. In light of this experiment, Liu and Feng [71] studied the finite deformation of two originally parallel CNTs stuck with each other by a thin liquid film as schematized in Figure 1.3. With the variation of the energy functional of the system, the governing equation of an elastica beam was derived as

$$EI \frac{d^2 \theta}{ds^2} e_z + t \times R = 0,$$  

where $\theta$ denotes the angle between the horizontal and the tangential directions, $e_z$ the unit vector normal to the plane of the deformed beam, $t$ the tangential unit vector of

![Figure 1.3](image-url) Two microbeams adhered by a thin liquid film, where left is the side view, and right is the cross section.
the beam, and \( \mathbf{R} \) the constant vectorial tension acting on the beam. The critical point of the adhesion segment is unknown and can be viewed as a movable boundary condition during the variation process. By solving the elastica equation [72] and the corresponding transversality condition, Liu and Feng [71] obtained the solutions of key parameters and deflection curve of the adhered beams. In comparison with the solution of infinitesimal deformation, the finite deformation theory shows a better agreement with relevant experimental results.

Furthermore, Liu [73] generalized the existing models of microbeams to microplates with the effects of capillary adhesion. Assume that the plate is usually adhered to the rigid substrate due to the capillary force induced by the liquid film between the stiction zone of the plate and the substrate. Therefore, the plate includes a non-adhered portion and an adhered one, denoted as \( D_1 \) and \( D_2 \), respectively. The boundary of the adhesion zone is also assumed as a plane curve \( \Gamma_2 \). The initial distance of the substrate from the plate is \( H \), and the deflection of the plate is \( w \). As schematized in Figure 1.4, the potential energy functional of the plate-substrate system is expressed as

\[
\Pi = \int_{D_1} \left[ \frac{\kappa}{2} \left( \nabla^2 w \right)^2 + 2\gamma_{LV} \cos \theta \right] dxdy - 2 \int_{D_1+D_2} \gamma_{LV} \cos \theta x dxdy. \tag{1.32}
\]

From the variation of the energy functional of the solid/liquid system, Liu [73] derived the governing equation of a plate adhered to a substrate and the supplementary boundary condition, i.e. the transversality condition. The latter is written as

\[
\left\{ \kappa \left[ l \frac{\partial}{\partial x} \left( \nabla^2 w \right) + m \frac{\partial}{\partial y} \left( \nabla^2 w \right) \right] \frac{\partial w}{\partial n_2} - \kappa \nabla^2 w \left[ l \frac{\partial}{\partial x} \left( \frac{\partial w}{\partial n_2} \right) + m \frac{\partial}{\partial y} \left( \frac{\partial w}{\partial n_2} \right) \right] \right\}
\]

Figure 1.4 Adhesion of a microplate to the substrate by surface energy, where left is the top view, and right is the side view.