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Friction, Superhydrophobicity, and Biomimetics

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——摩擦、超疏水性与仿生

（影印版）

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序　　言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础，同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天，物理学不仅囿于基础科学和技术应用研究的范畴，而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到，改革开放三十多年来，随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展，我国物理学取得了跨越式的进步，做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下，近年来物理学相关书籍也呈现百花齐放的良好态势，在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看，尽管国内各出版社相继推出了一些质量很高的物理教材和图书，但系统总结物理学各门类知识和发展，深入浅出地介绍其与现代科学技术之间的渊源，并针对不同层次的读者提供有价值的教材和研究参考，仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展，特别是展现近年来中国物理学者的研究水平和成果，北京大学出版社在国家出版基金的支持下推出了“中外物理学精品书系”，试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家，确保了整套丛书的权威性和前瞻性。

这套书系内容丰富，涵盖面广，可读性强，其中既有对我国传统物理学发展的梳理和总结，也有对正在蓬勃发展的物理学前沿的全面展示；既引进和介绍了世界物理学研究的发展动态，也面向国际主流领域传播中国物理的优秀专著。可以说，“中外物理学精品书系”力图完整呈现近现代世界和中国物理

科学发展的全貌，是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

“中外物理学精品书系”另一个突出特点是，在把西方物理的精华要义“请进来”的同时，也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻，引进和翻译世界物理的经典著作和前沿动态，可以满足当前国内物理教学和科研工作的迫切需求。另一方面，改革开放几十年来，我国的物理学研究取得了长足发展，一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域，使世界对中国物理学的过去和现状有更多的深入了解，不仅充分展示出中国物理学研究和积累的“硬实力”，也向世界主动传播我国科技文化领域不断创新的“软实力”，对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是，“中外物理学精品书系”还对中国近现代物理学科的经典著作进行了全面收录。20 世纪以来，中国物理界诞生了很多经典作品，但当时大都分散出版，如今很多代表性的作品已经淹没在浩瀚的图书海洋中，读者们对这些论著也都是“只闻其声，未见其真”。该书系的编者们在这方面下了很大工夫，对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值，不仅可以很好地保护和传承我国物理学的经典文献，充分发挥其应有的传世育人的作用，更能使广大物理学人和青年学子切身体会我国物理学研究的发展脉络和优良传统，真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在 2006 年中国科学技术大会上指出，“加强基础研究是提升国家创新能力、积累智力资本的重要途径，是我国跻身世界科技强国的必要条件”。中国的发展在于创新，而基础研究正是一切创新的根本和源泉。我相信，这套“中外物理学精品书系”的出版，不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣，也将进一步推动其他相关基础科学更好更快地发展，为我国今后的科技创新和社会进步做出应有的贡献。

“中外物理学精品书系”编委会　主任

中国科学院院士，北京大学教授

王恩哥

2010 年 5 月于燕园

Michael Nosonovsky
Bharat Bhushan

Multiscale Dissipative Mechanisms and Hierarchical Surfaces

Friction, Superhydrophobicity, and Biomimetics

With 112 Figures

Springer

Preface

This book is intended to serve as an introduction to a developing field of engineering biologically inspired surfaces with hierarchical structures. Recent advances in micro- and nanoscience reveal a growing number of surfaces with hierarchical structures, that is, with nanoscale details superimposed on the microscale details, sometimes superimposed on larger macroscale details. Such hierarchical structures are required for certain functions, such as achieving extremely low or extremely high friction and adhesion, and water-repellency. Friction, adhesion, and wetting are complicated processes, which involve effects at different scale levels with different characteristic scale lengths. Engineers are trying to mimic nature in order to design artificial surfaces with desirable properties, referred to as bioinspired or biomimetic surfaces. The field is referred to as biomimetics.

Our purpose is, first of all, to present the qualitative picture of physical phenomena, rather than to provide rigorous mathematical derivations or many technical details, which may be found in the references. We concentrate upon such issues as scale and dimension, linearity and nonlinearity, and the fundamental physical mechanisms and effects involved in the phenomena under consideration. This allows a reader who is not familiar with the field or not a specialist in surface science to grasp quickly the essence of the processes and the issues discussed. On the other hand, we felt it necessary to present a brief discussion of modern analytical and experimental methods and approaches used in mesoscale and multiscale science and recent trends in the development of the surface science and multiscale modeling.

The book is divided into three parts. The first part is devoted to the solid–solid dry friction, which is a traditional subject of study of tribology. In this part, we cover topics such as the statistical and fractal characterization of rough random surfaces and solid–solid contact, which have been developed over the past 30 years and are used widely in engineering. We discuss the measurement techniques and equipment that allows scientists to study surfaces at nanoscale resolution—including scanning probe microscopy, which emerged in the early 1980s. Our emphasis is on the multiscale, hierarchical nature of the dissipation mechanisms, which are becoming evident as more and more data about the nanoscale friction are obtained.

In the second part of the book, we study the solid–liquid friction and wetting of rough surfaces, as well as related capillary phenomena. Rough water-repellent or superhydrophobic surfaces, which are often found in biological systems, in many cases have a complicated hierarchical structure that is required for certain functionality, such as nonwetting, low solid–liquid friction, high friction and adhesion. Leaves of water-repellent plants, such as the lotus, constitute an example of these surfaces. Their surfaces are extremely hydrophobic, and a droplet can flow over them with low energy dissipation. However, the mechanisms involved in the process are complicated and have different characteristic length scales, so the surfaces should also be hierarchical. Roughness-induced superhydrophobicity and the "lotus-effect" have been studied extensively during the past decade with the number of articles in peer-reviewed journals growing exponentially since the early 2000s. This is because the technology that allows us to produce an artificial lotus leaf surface became available. However, there has been no single book that covers the theory of superhydrophobicity, the observation and characterization of natural superhydrophobic surfaces, and the methods of production and characterization of artificial superhydrophobic surfaces. This book's purpose is to cover this gap in the literature.

Another example of natural hierarchical surfaces is the gecko foot, which has an ability to achieve very high adhesion (so that it can climb upon a vertical wall) and detach from the surface at will. These abilities are known as smart adhesion. Smart adhesion, along with other functional hierarchical biological surfaces, such as the shark skin and the moth eye, are studied in the third part of the book. These functional biological surfaces inspired engineers to design artificial surfaces with similar properties. Biomimetic hierarchical surfaces are discussed in that part of the book along with other practical issues, such as techniques to experimentally study the wetting of rough surfaces.

The book is written with a broad multidisciplinary readership in mind. It can serve as a supplementary textbook for a graduate course in surface science, tribology, or nanotechnology. It can be used by engineers and scientists who want to familiarize themselves with the basic concepts of nanotribology and biologically inspired surfaces. The authors hope that the book will be useful to a broad audience of readers from various backgrounds.

We thank our colleagues, Dr. Stephen M. Hsu, Dr. Seung-Ho Yang and Dr. Huan Zhang from the National Institute of Standards and Technology (NIST) in Gaithersburg, MD; Mr. Yong-Chae Jung and Dr. Tae-Wan Kim at the Ohio State University (OSU) in Columbus, OH; and Ms. Caterina Runyon-Spears from the OSU and others who helped in preparation of this book. The book was written partially while one of the authors, Dr. Michael Nosonovsky, was a National Research Council postdoctoral research fellow at NIST. However, none of the equipment, results, or commercial products mentioned or presented in this book should be treated as endorsed or approved by NIST.

November 2007

Michael Nosonovsky
Bharat Bhushan

Nomenclature

a—contact radius; width
A_a, A_r—apparent and real areas of contact, respectively
A_{SL}, A_{SA}, A_{LA}, A_F—solid–liquid, solid–air, liquid–air, flat contact areas, respectively
b—distance
c, C—constants
Ca—capillary number
d—distance
D—diameter, fractal dimension
E—elastic modulus
E_b—energy barrier
E_{tot}—total energy
f_{SL}, f_{LA}—fractions of the solid–liquid and liquid–air interfaces under the droplet
f_0—adhesion stress
F—friction force
F_{cap}—capillary adhesive force
g—gravitational constant
h—height; position of the interface
H—height; hardness of a softer material; film thickness
H_p—component of friction due to surface roughness and plowing
H_r—component of contact angle hysteresis due to surface roughness
k—the Boltzmann constant
k_{nj}—stiffness
K—kurtosis
l—length
l_c—capillary length
l_N—scale lengths
L—sampling length
m—mass; mean
N—number of contacts
N_I—number of springs
p—probability
P—pitch; pressure
P_0 is the atmospheric pressure

P_{sat}—saturated vapor pressure and P is the actual liquid pressure
Q—heat
r—radius
R—radius
R_p—mean asperity peak radius
R_1, R_2—principal radii of curvature
R_f—roughness factors
R_k—Kelvin radius
R_p—peak radius
Re—Reynolds number
S—entropy; space between neighboring fibers
S_f—spacing factor
t—length of the triple line
T—temperature; total energy
T_c—critical temperature
V, $\vec{V}$—velocity
V—volume
W—normal load; work of cohesion; work of cohesion
W_E is the elastic energy
ΔW—energy barriers between the two states
We—Weber number
z—separation distance
z_0—equilibrium distance
α—slope
β—kinetic coefficient
β, β^*—correlation length
γ—surface free energy, surface tension
γ_{SL}, γ_{SA}, γ_{LA}—solid–liquid, solid–air, and liquid–air interface energies, respectively
δ—droop of the droplet; Tolman's length
$\nabla\varepsilon$—strain gradient
η—density of asperities per unit area; packing density; order-parameter
θ, θ_{adv}, θ_{rec}, θ_0, θ_{adv0}, θ_{rec0}—contact angle, advancing and receding contact angles for rough and flat surfaces, respectively
θ—state parameter in dynamic friction models
θ_0—normalization parameter
K—curvature
λ—gradient coefficient; periodicity of a surface profile
μ—coefficient of friction
μ_L, μ_G—liquid and gas viscosities
ρ—density of liquid
σ—surface tension; standard deviation
σ_Y—yield stress
τ—contact line tension; normalized temperature
τ_f—shear strength at the interface
ψ—plasticity index
ω—frequency

Glossary

Asperity is a roughness detail of a surface. Even nominally flat surfaces have some roughness, so asperities are present at virtually every surface. An asperity is characterized by height, width, tip radius of curvature, etc. For fractal surfaces, the concept of asperity is controversial, since the fractal topography implies that the surface consists of the same asperity repeatedly superimposed on itself at different magnification, so there is no way to determine where one asperity ends and another one begins. Asperity may be defined as a roughness detail that participates in the contact and forms a contact spot.

Barbs are a series of branches fused to the rachis of a feather. The barbs themselves are also branched and form the barbules.

Biomimetics (bionics, biognosis, etc.) is the application of methods and systems found in living nature to the study and design of engineering systems and modern technology.

Carbone nanotube (CNT), fullerene, and graphene are allotropes of carbon (other carbon allotropes are diamond and graphite) with unusual properties. They were discovered since 1980s and they are promising for nanotechnology applications. CNTs are cylindrical molecules with very high length to diameter ratios. Fullerenes (the most common example is the C_{60} molecule) are spherical carbon molecules. Graphene is single-sheet monolayer of carbon.

Cornea is the transparent front part of the eye that provides most of an eye's optical power.

Critical point specifies the temperature and pressure at which the liquid state of the matter ceases to exist. As a liquid is heated within a confined space, its density decreases while the pressure and density of the vapor being formed increases, so that their densities become equal at the critical temperature. Near-critical states have unusual properties, in particular, the correlation length in these states can become infinitely large and physical properties are related by power laws (the critical exponents).

Cuticle of a plant is a protective waxy covering produced by the epidermal cells of leaves, young shoots and other aerial plant organs.

Elytron (pl. elytra) is a modified, hardened forewing of certain insects.

Epidermis in plants, the outermost layer of cells covering the leaves and young parts of a plant.

Fractal is a rough or fragmented geometric object that can be subdivided in parts, each of which is at least approximately a reduced-size copy of the whole.

Frustule a unique cell wall made of silica (hydrated silicon dioxide) into which diatom cells are enclaved. Diatoms are one of the most common types of unicellular phytoplankton.

Lamella is a thin plate-like structure, often one amongst many lamellae very close to one another that appears, in particular, in the traction surfaces of geckos.

Lotus-effect is the ability of very rough surfaces for self-cleaning and extreme water-repellency (superhydrophobicity).

Micro/nanoelectromechanical systems (MEMS/NEMS) are small devices that involve mechanical elements, sensors, actuators and electronics on a common silicon substrate through microfabrication technology. Typical MEMS devices include actuators, switches, sensor systems, micromirrors, etc.

Microfluidics is a multidisciplinary discipline that deals with the behavior, precise control and manipulation of microliter and nanoliter volumes of fluids.

Microtrichia are very small protuberances on cornea of moth eye.

Moth-eye-effect is non-reflective ability of a surface with a certain submicron structure, imitating the moth eye.

Papilla (pl. papillae) (papillose epidermal cells) are microscopic bumps on the surface of many water-repellent plant leaves.

Placoid is a special type of scales covering the shark skin that form small V-shaped bumps.

Self-organized criticality (SOC) is a property of certain dynamical systems that have a critical point as an attractor. Their behavior thus displays characteristics of the critical point of a phase transition, but without the need to tune control parameters to precise values. A small perturbation in such system can have a long-lasting effect. It has been speculated that the complexity and hierarchy in nature arises from the SOC.

Seta (pl. setae) is a stiff hair or a hair-like structure. Setae on gecko's footpads are responsible for its ability to cling to vertical surfaces.

Shark-skin-effect is drag reduction can in turbulent flow due to microscopic ridges upon the skin of a shark.

Sol-gel is a wet-chemical technique for the fabrication of materials (typically a metal oxide) starting from a chemical solution containing colloidal precursors.

Spatula (pl. spatulae) are substructures of a seta in a gecko foot.

Spinodal limit is the limit at which the difference between gas and liquid ceases to exist. For water, the pressure corresponding to the spinodal limit at a given temperature can constitute the tensile strength of metastable liquid water.

Stick-slip is a spontaneous jerking motion that can occur while two objects are sliding over each other. The reason for the stick-slip is that the static coefficient of friction is usually greater than the kinetic coefficient of friction.

Stiction is sticking together of two solid bodies, especially components of microdevices, due to adhesion and static friction.

Trichomes are fine outgrowths on plants that have diverse structure and function.

Water-strider-effect is the ability of the water strider to walk upon a water surface without sinking using the surface tension force due to the hierarchical structure of its legs.

Abbreviations

AFM—atomic force microscope
AKD—alkylketene dimmer
BCH—brucite-type cobalt hydroxide
CBD—chemical bath deposition
CNT—carbon nanotube
CVD—chemical vapor deposition
DI—deionized
DMF—dimethylformamide
DMT—Derjagin–Muller–Toporov
DNA—deoxyribonucleic acid
ESEM—environmental scanning electron microscope
GL—Ginzburg–Landau
GSED
HAR—high aspect ratio
ITO—indium tin oxide
JKR—Johnson–Kendall–Roberts
LA—lauric acid
LAR—low aspect ratio
LBL—layer by layer
MD—molecular dynamics
MEMS—microelectromechanical systems
NEMS—nanoelectromechanical systems
NIST—National Institute of Standards and Technology
NLBB—Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics
OSU—Ohio State University
OTS—octadecyltricholorosilane
PAA—poly(acrylic acid)
PAA—porous anodic alumina
PAH—poly(allylamine hydrochloride)
PDF—probability distribution function
PDMS—polydimethylsiloxane
PE—polyethylene
PET—poly(ethylene terephthalate)

PF_3—tetrahydroperfluorodecyltrichlorosilane
PFDTES—perfluorodecyltriethoxysilane
PFOS—perfluorooctanesulfonate
PMMA—polymethylmethacrylate
PPy—polypyrrole
PS—polystyrene
P-V—peak-valley
PVD—physical vapor deposition
PVS—poly(vinylsiloxane)
RH—relative humidity
RMS—root-mean square
SAM—self-assembled monolayer
SEM—scanning electron microscope
SOC—self-organized criticality
STM—scanning tunneling microscope
SU8—thick photoresist for MEMS
TMS—tetramethylsilane
UV—ultraviolet

Contents