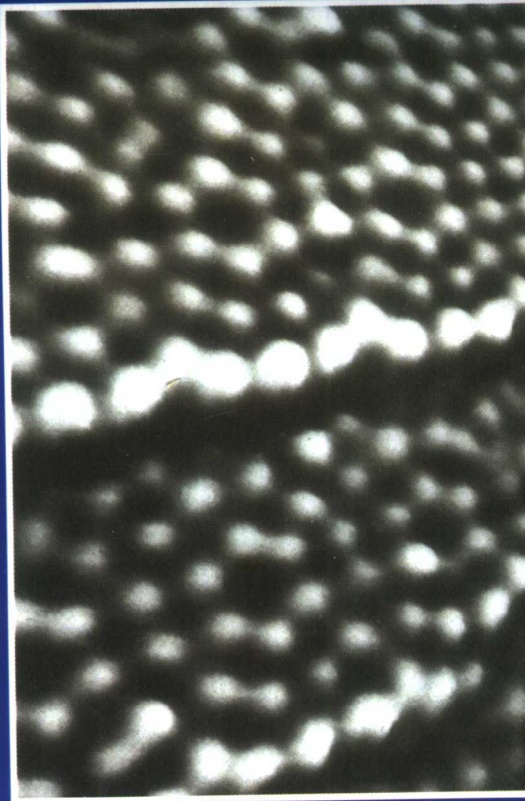


物理学经典英文教材系列

PHYSICS AT SURFACES

表面物理学

Andrew Zangwill



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内容简介

该书是一本优秀的关于固体表面物理的研究生教材。作者Zangwill教授一直从事表面物理、统计力学和纳米结构的理论研究，在Nature, PRL等专业杂志上著述不断。作者认为本书不是一般意义上的教科书，而更像是旅游指南——意在引领读者走入表面物理这一未臻完善，因而也就问题重重、机会与挑战并存的领域。全书共454页，内容广泛，文笔流畅，基础知识与前沿问题分析并重，具有很高的参考价值。该书自1988年第1版面市以来，深受广大读者的欢迎，目前已5次重印。本书适用于表面物理、表面化学、薄膜生长、材料科学等领域的专业研究人员、高年级本科生和研究生。本书由曹则贤先生推荐。

推荐人简介

曹则贤，男，1966年生，中国科技大学物理学学士、硕士，德国Kaiserslautern大学物理学博士、博士后。1998年入选中国科学院“百人计划”，现任职于中国科学院物理所表面物理国家重点实验室，研究员、博士生导师。研究领域包括薄膜技术与生长机理、表面分析、纳米结构发光等。曾为Science, APL等国际重要刊物撰写论文40篇。

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Andrew Zangwill, 1954年生，1981年于美国宾夕法尼亚大学获物理学博士学位。现为乔治亚理工学院物理学教授，目前研究重点为纳米半导体结构和纳米磁学。Zangwill教授一直致力于研究表面动力学过程，是此领域的杰出科学家。

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To the memory of Ronald D. Parks

PREFACE

The surfaces of bodies are the field of very powerful forces of whose action we know but little. *Lord Rayleigh*

The surface was invented by the devil. *Wolfgang Pauli*

The present volume is a graduate-level introduction to the physics of solid surfaces. It is designed for students of physics, physical chemistry and materials science who are comfortable with modern condensed matter science at the level of, say, *Solid State Physics* by Ashcroft & Mermin (1976) or *Principles of the Theory of Solids* by Ziman (1972). In the latter, Ziman points out that scientific knowledge passes from the laboratory to the classroom by a sequence of literary vehicles: original research papers, review articles, monographs and finally textbooks. I believe this book fits well into none of these categories. It is not a textbook – at least not in the traditional sense. The field of surface physics is simply not mature enough to support such an enterprise; too many results are untidy and too many loose ends remain. On the other hand, it is not a review or monograph either. My purpose is neither to set down an established wisdom nor to establish priority among claimants. Indeed, I steadfastly ignore who did what when – except when it is a matter of historical interest. Rather, my interest from the beginning has been to construct a coherent synthesis of an enormous range of material and to present the result in as heuristic and pedagogical a manner as possible. Consequently, I think it is useful to regard the account before you as a travelling companion – a tour guide if you will – through the world of surface physics. It possesses both the virtues and the faults of flesh-and-blood tour guides.

This book exists because Ron Parks wanted to learn something about surface physics. To that end, he asked me to prepare a graduate seminar course on the subject for the 1983–4 academic year at the Polytechnic Institute of New York. *Physics at Surfaces* is an expanded and refined version of lecture notes distributed to the attendees of that course. The notes were intended to fill what I perceived to be a yawning gap in the literature. At the undergraduate level, the slim volumes *Surface Physics*

by Prutton (1983) and *Principles of Surface Chemistry* by Somorjai (1972) very ably meet the needs of their intended audiences. At the graduate level, *Chemistry in Two Dimensions: Surfaces* by Somorjai (1981) and *Introduction to the Theory of Solid Surfaces* by Garcia-Moliner & Flores (1979) provide unique perspectives from the point of view of very active researchers in the field. Remarkably, the subject matter presented in these books form two almost disjoint sets!

Physics at Surfaces is an attempt to bridge the gap between textbook treatments of condensed matter physics and the primary research literature of surface science. It was necessary, as usual, to choose between depth and breadth of presentation. In opting for the latter, one is challenged to provide unity to a subject which attracts scientists from sub-specialties as diverse as semiconductor device physics, critical phenomena, catalytic chemistry, electron spectroscopy and many-body physics. The choice of topics and logical organization reflect the concerns and prejudices of a condensed matter physicist with a healthy interest in chemical physics. Experiment and theory are intertwined whenever possible although there is little detailed discussion of technique. Explicit references are cited whenever theoretical formulae are quoted without derivation. For experimental detail, the reader should consult *Modern Techniques of Surface Science* by Woodruff & Delchar (1986) or *Solid State Physics: Surfaces* edited by Park & Lagally (1985).

A word about usage. The book is meant to be read as an organic whole. It is heavily self-referential in the sense that I continually revisit concepts and examples introduced in early chapters. It is not a reference work; one cannot look up the work function of Ge(111) or the sticking coefficient of $N_2/Cu(100)$. In fact, the text contains no data tables (although I do provide an acronym table!). Instead, I stress trends which are presented visually in the figures. I wish to emphasize that careful study of the figures is of especial importance. This is so because the sheer volume of material covered and a desire to limit the cost of the book conspired to produce a rather terse prose style.

I owe a considerable debt to the Surface Physics Group at the University of Pennsylvania, circa 1976–80 (T. Gustafsson, E.W. Plummer, J.R. Schrieffer and P. Soven) for my initial introduction to this subject and to many members of the international surface science community for discussion and correspondence about their work since then. I am grateful to M. denBoer (CUNY), R. Bruinsma (UCLA), L. Roelofs (Haverford) and J. Tully (AT & T) who read and commented on selected chapters. Of course, any vagaries, misconceptions, or outright errors are entirely my responsi-

bility. Special thanks go to Norton Lang (IBM) and Bill Gadzuk (NBS) for moral support and encouragement at all stages and to my wife Sonia for these and, equally importantly, for patience.

Atlanta
January 1987

A. Zangwill

ACRONYMS

AES	Auger electron spectroscopy
ATR	attenuated total reflection
CS	commensurate solid
DOS	density of states
EDC	energy distribution curve
EELS	electron energy loss spectroscopy
ESCA	electron spectroscopy for chemical analysis
ESD	electron stimulated desorption
ESDIAD	electron stimulated desorption ion angular distribution
FIM	field ion microscope
FWHM	full-width at half-maximum
FVM	Frank-Van der Merwe
HEIS	high energy ion scattering
IRAS	infrared absorption spectroscopy
IS	incommensurate solid
KT	Kosterlitz-Thouless
LDA	local density approximation
LDOS	local density of states
LEED	low energy electron diffraction
LEF	laser-excited fluorescence
LEIS	low energy ion scattering
LGW	Landau-Ginzburg-Wilson
MBE	molecular beam epitaxy
MBRS	molecular beam relaxation spectroscopy
MD	misfit dislocation
MEIS	medium energy ion scattering
MIGS	metal-induced gap states
MOCVD	metalorganic chemical vapor deposition

MPI	multi-photon ionization
NEXAFS	near-edge x-ray absorption fine structure
NFE	nearly-free electron
PSD	photon stimulated desorption
RHEED	reflection high energy electron diffraction
SBZ	surface Brillouin zone
SCLS	surface core level shift
SERS	surface-enhanced Raman scattering
SEXAFS	surface-extended x-ray absorption fine structure
SIMS	secondary ion mass spectroscopy
SK	Stranski-Krastanov
SOS	solid-on-solid
SP	surface polariton
STM	scanning tunnelling microscopy
TPD	temperature programmed desorption
UHV	ultra-high vacuum
UPS	ultraviolet photoelectron spectroscopy
VW	Volmer-Weber
XPD	x-ray photoelectron diffraction
XPS	x-ray photoelectron spectroscopy

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HISTORICAL SKETCH

Physical phenomena explicitly associated with condensed matter surfaces have been studied since antiquity. Perhaps the oldest written record of experience in this area appears in Babylonian cuneiform dating from the time of Hammurabi (Tabor, 1980). A form of divination, known today as *lecanomancy*, involved an examination of the properties of oil poured into a bowl of water. The detailed behavior of the spreading oil film led the diviner, or *haru*, to prophesy the outcome of military campaigns and the course of illness.

In later years, many observers commented on the fact that choppy waves can be calmed by pouring oil into the sea. In particular, Pliny's account was known to Benjamin Franklin when he began his controlled experiments during one of his frequent visits to England. Franklin's apparatus consisted of a bamboo cane with a hollow upper joint for storage of the oil.

At length being at Clapham, where there is, on the common, a large pond, which I observed one day to be very rough with the wind. I fetched out a cruet of oil, and dropped a little of it on the water. I saw it spread itself with surprising swiftness upon the surface... the oil, though not more than a tea spoonful, produced an instant calm over a space several yards square, which spread amazingly and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass. (Seeger, 1973.)

Remarkably, Franklin did not perform the simple calculation which would have led him to conclude that the film thickness was only about one nanometer!

The firm establishment of modern methods of scientific analysis that occurred in the nineteenth century produced three notable results of

importance to the future of surface science. First, in 1833, Michael Faraday directed his attention to a mysterious phenomenon observed ten years earlier by Dobereiner: the presence of platinum could induce the reaction of hydrogen and oxygen well below their nominal combustion temperature (Williams, 1965). In characteristic fashion, he designed a sequence of experiments which led him to propose a qualitative theory of catalytic action (a term coined in 1836 by Berzelius) which remains valid to this day.

A second critical discovery was made in 1874 by the future Nobel laureate Karl Ferdinand Braun (Susskind, 1980). During the course of electrical measurements of metallic sulfides, Braun noticed deviations from Ohm's law in the conduction of current through a sandwich of Cu and FeS. Only a few years later, he speculated that the cause of the unusual asymmetrical resistance (today called rectification) must reside in a thin surface layer at the interface.

Finally, in 1877, J. Willard Gibbs published (by subscription) the second part of his monumental memoir, 'The Equilibrium of Heterogeneous Substances' in the *Transactions of the Connecticut Academy*. This work, rightly considered one of the crowning achievements of nineteenth century science, established the mathematical foundations of thermodynamics and statistical mechanics (Rice, 1936). As part of this program, Gibbs completely described the thermodynamics of surface phases. Essentially all subsequent work in the field consists of elucidation of his rather difficult exposition.

Despite the impetus provided by these investigations, it was primarily Irving Langmuir's efforts in the early years of this century that led to the recognition of surface science as a significant research discipline (Rosenfeld, 1962). Langmuir received his doctorate under Nernst at Gottingen in 1906 for a problem involving the dissociation of various gases produced by a hot platinum wire. Three years later he joined the fledgling General Electric Research Laboratory and began a remarkable career of scientific achievement. Langmuir's early interest in gases at very low pressures near very hot metal surfaces soon bore fruit with his invention of the nitrogen-filled tungsten incandescent lamp.

At General Electric, Langmuir was free to pursue his broad scientific interests. Consequently, in addition to pioneering the experimental methods necessary for high vacuum studies, he introduced the concepts of the adsorption chemical bond, the surface adsorption lattice, the accommodation coefficient and adsorption precursors. He performed fundamental studies on the work function of metals, heterogeneous catalysis and adsorption kinetics, and provided a detailed model of thermionic emission. Most notably, of course, he and Katherine Blodgett

explored the two-dimensional world of monomolecular films. In 1932, the Swedish Academy of Science rewarded Langmuir with its Nobel prize for 'outstanding discoveries and inventions within the field of surface chemistry'.

Two other Nobel prizes of the early twentieth century also have a direct bearing on the development of surface science, and surface physics in particular. The 1921 prize was awarded to Einstein for his explanation of the photoelectric effect and Clinton Davisson was co-recipient of the 1937 prize for his electron diffraction work with Lester Germer that confirmed the wave nature of quantum mechanical particles. Although Davisson and Germer were aware that they were probing the surface layer of their crystals, more than thirty years elapsed before photoemission spectroscopy and low energy electron diffraction became standard laboratory probes of surface electronic and geometrical structure, respectively.

The 1930s can be characterized as a period when a spurt of theoretical research defined a number of important directions for future work on the fundamentals of surface physics. The existence and properties of electron states localized at a crystal surface was explored by Tamm (1932), Maue (1935), Goodwin (1939) and Shockley (1939). In 1932, Lennard-Jones studied the nature of the physisorption precursor to dissociative chemisorption and soon thereafter, Gurney (1935) introduced the resonant level model of adsorbate electronic structure. The basic theory of a free metallic surface (which was to stand unchanged for over thirty years) was introduced at this same time (Bardeen, 1936). Fundamental studies of semiconductor surfaces quite naturally focused on the semiconductor/metal interface. Almost simultaneously, Mott (1938), Schottky (1939) and Davydov (1939) proposed theories of the rectifying junction.

Renewed interest in surfaces had to await the return of scientists from war-related research. In 1949, three papers appeared, each of which stimulated tremendous experimental activity. A sophisticated theory of crystal growth (Burton & Cabrera, 1949) motivated endeavors in that field while Cyril Stanley Smith's influential paper on 'Grains, Phases and Interfaces' (Smith, 1948) alerted much of the metallurgical community to the problems of surfaces. However, the most dramatic event by far was a discovery reported in *The New York Times* as 'a device called a transistor, which has several applications in radio where a vacuum tube ordinarily is employed' (Hoddeson, 1981). The invention of the point-contact transistor (Bardeen & Brattain, 1949) generated an unprecedented interest in the fundamental physics of surfaces, most particularly semiconductor surfaces. Fifteen years of intense research on surfaces and interfaces followed.

In the introduction to their classic monograph, *Semiconductor Surfaces*,

Many, Goldstein & Grover (1965) make an interesting distinction between a 'real' surface and a 'clean' surface. The former is obtained under ordinary laboratory procedures while the latter is prepared under 'carefully controlled conditions so as to ensure the absence of foreign matter'. Unfortunately, at the time, there did not exist any reliable experimental technique for the determination of the chemical composition of a 'clean' surface (Duke, 1984). This is not to say that a great deal of useful information was not obtained about practical rectifying junctions during this period. However, almost nothing was learned about atomically clean surfaces.

The true emergence of surface physics occurred in the late 1960s as a result of the coincidence of several events. The first of these was the realization that electron spectroscopy (Brundle, 1974) and Auger spectroscopy in particular (Harris, 1974) allows one to determine the chemical species present on a solid surface down to minute fractions of a monolayer. Second, technology associated with the space program permitted the commercial development of ultra-high vacuum chambers so that a sample could be *kept* clean for a substantial period of time. At last, controlled experiments could be performed on well-characterized solid surfaces and sensibly compared to theoretical expectations. Indeed, as a final ingredient, the development and availability of high-speed digital computers allowed sophisticated theoretical work to proceed far beyond the simple models of previous years.

The past decade bears witness to the evolution of surface physics out of its infancy. Experimental and theoretical progress has been truly striking. Nevertheless, in many cases, we lack the fundamental principles and unifying themes needed to guide a truly mature science. We are still in a groping phase. Accordingly, the chapters that follow should be regarded as a snapshot of this burgeoning field at a stage of development we might call adolescence.*

* I am indebted to Yves Chabal for this remark.

PART 1

CLEAN SURFACES