

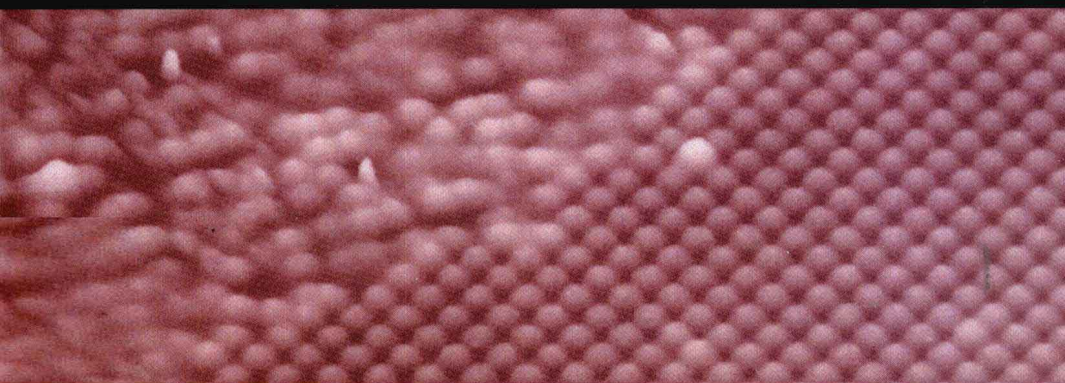
M. C. Desjonquères D. Spanjaard

# Concepts in Surface Physics

Second Edition

表面物理学概念

第2版



Springer

世界图书出版公司  
[www.wpcbj.com.cn](http://www.wpcbj.com.cn)

M. C. Deshpande, D. Sanyal

# Concepts in Surface Physics

Second Edition

表面物理學概念

第二版



Springer

9789819619575  
www.springer.com/9789819619575

M.-C. Desjonquères D. Spanjaard

# Concepts in Surface Physics

Second Edition

With 257 Figures



Springer

图书在版编目 (CIP) 数据

表面物理学概念: 第2版 = Concepts in Surface  
Physics 2nd ed. : 英文/ (法) 德容凯尔著. —影印  
本. 北京: 世界图书出版公司北京公司, 2011. 5  
ISBN 978 - 7 - 5100 - 3514 - 2

I. ①表… II. ①德… III. ①表面物理学—英文  
IV. ①0485

中国版本图书馆 CIP 数据核字 (2011) 第 074622 号

---

书 名: Concepts in Surface Physics 2nd ed.

作 者: M. C. Desjonquères, D. Spanjaard

---

中 译 名: 表面物理学概念 第2版

责任编辑: 高蓉 刘慧

---

出 版 者: 世界图书出版公司北京公司

印 刷 者: 三河市国英印务有限公司

发 行: 世界图书出版公司北京公司 (北京朝内大街 137 号 100010)

联系电话: 010 - 64021602, 010 - 64015659

电子信箱: kjb@wpcbj.com.cn

---

开 本: 24 开

印 张: 26

版 次: 2011 年 06 月

版权登记: 图字: 01 - 2011 - 1094

---

书 号: 978 - 7 - 5100 - 3514 - 2/0 · 873

定 价: 75.00 元

---

Dr. M.-C. Desjonquères  
Directeur de Recherche au Centre National de la Recherche Scientifique  
Service de Recherche sur les Surfaces et l'Irradiation de la Matière  
Centre d'Etudes de Saclay  
F-91191 Gif-sur-Yvette, France

Dr. D. Spanjaard  
Directeur de Recherche au Centre National de la Recherche Scientifique  
Laboratoire de Physique des Solides  
Université Paris-Sud  
Centre d'Orsay  
F-91405 Orsay, France

*Front cover:* STM picture of the (100) face of a copper crystal showing the border between the ordered and disordered phases appearing when phosphorous atoms segregate from the bulk to the surface (Courtesy of J. Cousty, C. E. de Saclay, Gif-sur-Yvette, France).

---

The 1st Edition appeared in 1993 as Vol. 30 of Springer-Series in Surface Sciences

---

Second Edition 1996 – Corrected Printing 1998

ISBN 3-540-58622-9 2nd Edition Springer-Verlag Berlin Heidelberg New York

ISBN 3-540-56506-X 1st Edition Springer-Verlag Heidelberg Berlin New York

ISBN 0-387-56506-X 1st Edition Springer-Verlag New York Berlin Heidelberg

Cataloging-in-Publication Data applied for

Die Deutsche Bibliothek – CIP-Einheitsaufnahme

Desjonquères, Marie-Catharine:

Concepts in surface physics/M.C. Desjonquères; D. Spanjaard. – 2nd ed. –

Berlin; Heidelberg; New York; Barcelona; Budapest; Hong Kong; London; Milan; Paris; Santa Clara; Singapore; Tokyo:  
Springer, 1996

ISBN 3-540-58622-9

NE: Spanjaard, Daniel:

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable for prosecution under the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1993, 1996

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

This reprint has been authorized by Springer-Verlag (Berlin/Heidelberg/New York) for sale in the Mainland China only and not for export therefrom

## Preface

The reprinting of this book has given us the opportunity of correcting some printing errors which appeared in the first edition.

Aside from this, we have added problems at the end of the various chapters in order to illustrate or supplement treatments. They have a rather broad range of difficulty. Some of them have even been inspired by research papers but the reader is guided in the derivation of the solution. This is the reason why the statements of these problems are sometimes quite lengthy. Solutions are not given. However if the reader is interested in the solution of a problem, we will be happy to send a photocopy of our notes which are rather detailed. Thus we suggest the reader should get in contact with us directly.

Finally we are grateful to J. Cousty who has provided us with the beautiful picture which illustrates the front cover.

Saclay, France  
Orsay, France  
April 1995

*M.-C. Desjonquères*  
*D. Spanjaard*

## Preface to the First Edition

This textbook is intended as an introduction to surface science for graduate students. It began as a course of lectures that we gave at the University of Paris (Orsay). Its main objectives are twofold: to provide the reader with a comprehensive presentation of the basic principles and concepts of surface physics and to show the usefulness of these concepts in the real world by referring to experiments. It starts at a rather elementary level since it only requires a knowledge of solid state physics, quantum mechanics, thermodynamics and statistical physics which does not exceed the background usually taught to students early in their university courses. However, since it finally reaches an advanced level, we have tried to render it as self-contained as possible so that it remains accessible even to an unexperienced reader. Furthermore, the emphasis has been put on a pedagogical level rather than on a technical level. In this spirit, whenever possible, models which are simplified, but which contain the features that are essential to the appearance of the phenomena, have been set up and solved in a completely analytical way. The logic should be transparent enough for the reader although, most often, a more rigorous solution would need the use of a computer. To conclude, we have tried to give an account of surface physics which should be of use to the theoretician as well as to the experimentalist.

The following comments can be made on the contents of this book. The field of surface physics is too vast to present a complete treatment of all its major aspects. For example, we have omitted surface magnetism, dynamical interactions between an incoming atom or molecule and a surface . . . , which merit a book of their own. We have limited ourselves to fundamental concepts concerning, on the one hand, the macroscopic properties and, on the other hand, the microscopic properties such as atomic, vibrational and electronic structures. These topics will be discussed both for clean and adsorbate covered surfaces. Finally, we have precluded any technical description of experimental methods, focussing ourselves on the presentation of their theoretical background. Two reasons have led to this choice: firstly, the lack of competence of the authors and, secondly, the existence of excellent monographs dealing with this subject.

This book includes many references. However, it should be perfectly clear that we do not necessarily consider these references as the most original or the most important contributions in the field. They have been simply chosen as a convenient source of information to supplement or illustrate those given in the book.

We are greatly indebted to J. Friedel and B. Piveteau for a very careful reading of a large part of the manuscript and for suggesting many improvements. We are very grateful to G. Allan, D. Chandesris, J. Cousty, F. Fabre, J. Joffrin, W. Kohn, Y. Lahrer, J. P. Landesman, J. Lapujoulade, C. Noguera, B. Salanon, M. Sauvage-Simkin, P. Trebbia, J. Villain, D.E. Wolf and all our colleagues for illuminating discussions and criticisms. It is also a pleasant duty to thank J.C. Boulliard and M. Sotto, R.M. Feenstra, J.C. Heyraud and J.J. Métois, A. Menand, S. Rousset who kindly took the trouble of sending us original photographs. The typing of the manuscript was done with competence and infinite patience by F. Kakou whose help is greatly acknowledged. Finally, the book would not have been written without the material facilities which were offered to us by the Service de Recherche sur les Surfaces et l'Irradiation de la Matière at the "Centre d'Etudes de Saclay".

Saclay, France  
Orsay, France  
July 1993

*M.-C. Desjonquères*  
*D. Spanjaard*



# Contents

<b>1. Introduction</b> . . . . .	<b>1</b>
<b>2. Thermodynamical and Statistical Properties of Clean Surfaces.</b> . . .	<b>4</b>
2.1 Thermodynamics of a Surface at Equilibrium . . . . .	4
2.2 Equilibrium Shape of a Crystal . . . . .	7
2.3 Facetting. . . . .	13
2.4 The Roughening Transition. . . . .	15
2.4.1 Generalities . . . . .	15
2.4.2 Macroscopic Approach: The Continuum Limit . . . . .	16
a) One Dimensional Case: Statistics of a Step . . . . .	16
b) The Two Dimensional Case: Statistics of a Surface . . . . .	25
2.4.3 Microscopic Approach . . . . .	29
a) Equilibrium Shape of a Step Edge . . . . .	29
b) Equilibrium Shape of a Surface: The Roughening Transition . . . . .	34
2.4.4 Consequences of the Roughening Transition for the Equilibrium Shape of Crystals and for Crystal Growth. . . . .	41
2.4.5 Experimental Evidences of the Roughening Transition. . . . .	41
2.4.6 Special Cases of Vicinal Surfaces . . . . .	43
Problems . . . . .	43
<b>3. Atomic Structure of Surfaces</b> . . . . .	<b>48</b>
3.1 Surface Crystallography. . . . .	48
3.1.1 Two-Dimensional Lattices . . . . .	48
3.1.2 Semi-Infinite Crystals. Relaxation. Reconstruction . . . . .	49
3.1.3 Notations for Surface Structures . . . . .	51
3.1.4 Vicinal Surfaces. . . . .	53
3.1.5 Reciprocal Lattice and Brillouin Zones. . . . .	53
3.2 Experimental Techniques . . . . .	57
3.2.1 Observation of the Real Lattice . . . . .	57
a) Field-ion Microscopy (FIM) . . . . .	57
b) Scanning Tunneling Microscopy (STM) . . . . .	60
3.2.2 Observation of the Reciprocal Lattice . . . . .	63
a) Principles of Diffraction. . . . .	63
b) Low Energy Electron Diffraction (LEED) . . . . .	71

c) Atom Scattering . . . . .	74
d) X-ray Scattering at Grazing Incidence . . . . .	78
3.2.3 Indirect Methods. . . . .	86
a) Photoelectron Diffraction (PhD). . . . .	86
b) Surface Extended X-ray Absorption Fine Structure (SEXAFS). . . . .	93
c) Other Methods. . . . .	99
Problems . . . . .	101
<b>4. Vibrations at Surfaces . . . . .</b>	<b>106</b>
4.1 Elastic Forces in Crystals. . . . .	106
4.1.1 Dynamical Matrix. . . . .	106
4.1.2 Interatomic Forces. . . . .	108
a) Central Forces . . . . .	108
b) Angular Forces. . . . .	111
4.2 Bulk Modes. . . . .	112
4.3 Surface Modes . . . . .	114
4.3.1 Semi-Infinite Linear Chain . . . . .	115
a) $M_0 \neq M$ . . . . .	115
b) $\beta_0 \neq \beta$ . . . . .	117
4.3.2 Semi-Infinite Crystals . . . . .	118
a) The Slab Method . . . . .	119
b) Exact Method for the Calculation of Surface Modes	120
c) Relaxation and Reconstruction of Surfaces from Phonon Calculations . . . . .	124
d) Experimental Determination of Surface Modes. . .	128
4.3.3 Brief Remarks on Adsorbed Layers. . . . .	131
4.4 Spectral Densities of Modes . . . . .	133
4.5 Vibrational Thermodynamical Functions. . . . .	137
4.5.1 Surface Vibrational Entropy . . . . .	138
4.5.2 Surface Internal Energy. . . . .	139
4.5.3 Surface Specific Heat at Constant Volume. . . . .	139
4.6 Mean Square Displacements . . . . .	140
4.6.1 Theory. . . . .	140
4.6.2 Experimental Techniques. . . . .	143
a) Diffraction Experiments. . . . .	143
b) PhD and SEXAFS Experiments. . . . .	147
c) Conclusion . . . . .	152
Problems . . . . .	153
<b>5. Electronic Structure of Surfaces. . . . .</b>	<b>162</b>
5.1 Jellium Model. . . . .	163
5.1.1 The Free Electron Gas Bounded by Infinite Barriers .	164
a) One-dimensional Electron Gas . . . . .	164
b) Three-dimensional Electron Gas . . . . .	167

5.1.2	The Free Electron Gas Bounded by Finite Barriers . .	170
5.1.3	The Jellium Model in the Local Density Functional Formalism. . . . .	177
	a) Homogeneous Jellium. . . . .	178
	b) General Case. . . . .	180
5.2	Nearly Free Electron Model-Surface States . . . . .	188
5.2.1	Nearly Free Electron Model for Bulk States . . . . .	188
5.2.2	Surface States in Simple Gaps (Gaps of Type A) . . . .	197
5.2.3	Surface States in Gaps of Type B . . . . .	204
5.2.4	An Example: Al(001). . . . .	210
	a) Band Structure along the $\bar{\Gamma}-\bar{X}$ Direction . . . . .	210
	b) Band Structure along the $\bar{\Gamma}-\bar{M}$ Direction . . . . .	211
5.2.5	Semiconductors . . . . .	215
5.3	Tight-Binding Approximation . . . . .	217
5.3.1	General Principles . . . . .	218
5.3.2	Computation Techniques for Semi-Infinite Crystals . .	219
	a) The Slab Method . . . . .	220
	b) The Continued Fraction Technique. . . . .	220
	c) Illustrative Examples . . . . .	224
5.4	Application of the Tight-Binding Approximation to Transition Metal Surfaces. . . . .	235
5.4.1	Brief Survey of Bulk Electronic Structure . . . . .	235
	a) Band Structure . . . . .	235
	b) Cohesive Energy . . . . .	238
5.4.2	Surface Densities of States and Potential. . . . .	242
5.4.3	Surface Energies . . . . .	247
5.4.4	Relaxation and Reconstruction from Energy Calculations. . . . .	251
5.5	Application of the Tight-Binding Approximation to Semiconductor Surfaces. . . . .	254
5.5.1	Brief Survey of Bulk Electronic Structure . . . . .	254
	a) Band Structure . . . . .	254
	b) Cohesive Energy . . . . .	265
5.5.2	Determination of the Surface Tight-Binding Parameters . . . . .	267
5.5.3	Qualitative Discussion of Surface States in Semiconductors . . . . .	268
5.5.4	Examples . . . . .	271
	a) The (111) Surface of Si . . . . .	271
	b) The (001) Surface of Si . . . . .	275
	c) Brief Remarks on Heteropolar Semiconductor Surfaces . . . . .	283
5.6	Other Methods . . . . .	284
5.6.1	The Propagation Matrix Method . . . . .	284
	a) Formulation of the Method . . . . .	284

	b) The Layer KKR Method. . . . .	294
	c) The Method of Appelbaum and Hamann . . . . .	303
5.6.2	Methods Using the Slab Geometry . . . . .	308
	a) The Single Slab Geometry . . . . .	309
	b) The Periodic Slab Geometry. . . . .	310
5.7	Surface Plasmons in Metals . . . . .	310
5.7.1	Summary of Bulk Plasmons in a Jellium. . . . .	311
	a) Elementary Classical Theory: the Plasma Frequency . . . . .	311
	b) Relation with the Dielectric Function:	
	Dispersion of Plasmons. . . . .	312
5.7.2	Surface Plasmons in a Jellium . . . . .	320
	a) The Simple Case of Charge Oscillations	
	Strictly Localized in the Surface Plane . . . . .	320
	b) The Surface Plasmon Dispersion . . . . .	323
5.7.3	Brief Remarks on the Effects of the Crystal	
	Potential. . . . .	335
	a) Bulk Plasmons . . . . .	335
	b) Surface Plasmons . . . . .	338
5.8	Image Potential. . . . .	338
5.8.1	Response of a Semi-Infinite Jellium to a Uniform	
	External Electric Field . . . . .	339
5.8.2	Interaction of an External Point Charge with a	
	Semi-Infinite Jellium: the Image Potential . . . . .	342
5.8.3	Image Potential in a Dielectric Medium . . . . .	346
5.8.4	Image Surface States . . . . .	348
	a) Basics of Image Surface States. . . . .	348
	b) A New Formulation of the Criterion for	
	the Existence of Surface States. . . . .	349
	c) Determination of the Electron Reflectivity of	
	the Surface Barrier. . . . .	351
	d) Determination of the Reflectivity of the Crystal	
	in the Nearly Free Electron Approximation. . . . .	352
	e) "An Example: Surface States in the L Gap of Cu(111)" . . . . .	353
	f) Conclusion . . . . .	355
5.9	Some Further Remarks on Exchange and Correlation Energies . . . . .	355
5.9.1	Exchange and Correlations in a Semi-Infinite Jellium:	
	Validity of the Local Density Functional Approximation . . . . .	356
5.9.2	Correlations in the Tight-Binding Formalism:	
	The Hubbard Hamiltonian. . . . .	361
	a) Electronic Correlations in a s Band . . . . .	362
	b) Electronic Correlations in Degenerate Bands . . . . .	367
	c) Influence on the Band Structure and Conclusions . . . . .	369
5.10	Experimental Techniques for Investigating the	
	Electronic Structure . . . . .	370
5.10.1	Surface Core Level Spectroscopy . . . . .	371

a) Microscopic Approach . . . . .	372
b) Thermodynamical Model. . . . .	373
c) An Example: Surface Core Level Binding Energy Shifts in Ta and W . . . . .	375
5.10.2 Photoemission of Valence Electronic States . . . . .	377
a) Principle of the Determination of Dispersion Curves from Photoemission Spectra . . . . .	378
b) An Example of Bulk Dispersion Curves: Cu(110). . . . .	381
c) An Example of a Surface State Dispersion Curve: Al(100). . . . .	384
d) Brief Outline of the Principles of the Intensity Calculations in Photoemission. . . . .	385
5.10.3 Inverse Photoemission . . . . .	387
5.10.4 Spatially-Resolved Tunneling Spectroscopy . . . . .	389
5.10.5 Measurement of Surface Plasmons . . . . .	392
5.10.6 Measurement of the Work Function . . . . .	393
a) Vibrating Capacitor Method or Kelvin Method . . . . .	393
b) Field Emission . . . . .	394
c) Thermionic Emission Method . . . . .	394
d) Secondary Electron Method . . . . .	394
5.10.7 Measurement of Surface Energies . . . . .	395
a) Measurements Based on the Study of the Equilibrium Shape of Crystals . . . . .	395
b) Thermal Creep Under Tension . . . . .	395
c) Surface Energy of Liquid Metals . . . . .	396
Problems . . . . .	397
<b>6. Adsorption Phenomena . . . . .</b>	<b>411</b>
6.1 Thermodynamical Approach . . . . .	412
6.2 Statistical Methods. . . . .	416
6.2.1 Adsorption Isotherms in the Absence of Lateral Interactions Between Adatoms. . . . .	417
a) Monolayer Adsorption: Langmuir Isotherms . . . . .	417
b) Multilayer Adsorption: Brunauer, Emmett and Teller (BET) Isotherms . . . . .	420
6.2.2 The Two-Dimensional Lattice Gas . . . . .	423
a) Study of Isotherms: Condensation Phase Transition. . . . .	423
b) Order-disorder Transition in Adsorbed Layers . . . . .	432
6.3 Physisorption . . . . .	438
6.3.1 The Classical Electrostatic Interaction Between a Polar Particle and a Dielectric Surface . . . . .	438
a) Interaction between Two Dipoles . . . . .	438
b) Interaction between a Dipole and a Dielectric Surface . . . . .	439
6.3.2 Interaction Between a Neutral Atom and a Dielectric Surface . . . . .	440

a)	Van der Waals Interaction between Two Neutral Atoms in S-States . . . . .	440
b)	Van der Waals Interaction between a Neutral Atom and a Dielectric Surface. . . . .	443
6.4	Chemisorption . . . . .	452
6.4.1	Generalities on Charge Transfer in Chemisorption. . . . .	455
a)	Variation of the Ionization Energy . . . . .	456
b)	Variation of the Affinity Energy. . . . .	457
6.4.2	Anderson–Grimley–Newns Hamiltonian. . . . .	458
a)	Hartree–Fock Treatment . . . . .	458
b)	Beyond the Hartree–Fock Treatment . . . . .	467
6.4.3	Chemisorption in the Local Density Functional Formalism . . . . .	469
a)	Atomic Chemisorption on a Jellium Surface. . . . .	469
b)	The Effective Medium Theory. . . . .	475
6.4.4	Chemisorption on Transition Metals in the Tight-Binding Approximation . . . . .	491
a)	General Characteristics of the Models . . . . .	491
b)	Analytical Models . . . . .	493
c)	Improved Models . . . . .	498
d)	An Example: Adsorption of Simple Elements on BCC Transition Metal Surfaces . . . . .	500
6.4.5	Vibrations of an Adsorbate. . . . .	505
a)	Rigid Substrate Approximation: $M_s \ll M$ . . . . .	505
b)	General Case . . . . .	512
c)	Experiments. . . . .	512
6.4.6	Conclusions. . . . .	514
6.5	Interactions Between Adsorbates . . . . .	515
6.5.1	Experimental Data. . . . .	515
6.5.2	Theory of Adatom–Adatom Interactions. . . . .	517
a)	Electronic Interactions . . . . .	517
b)	Dipolar Interactions. . . . .	523
c)	Elastic Interactions. . . . .	524
6.5.3	Consequences of Adatom–Adatom Interactions and Conclusions . . . . .	525
6.6	Electronic Structure of Ordered Overlayers. An Example: O on Ni(100) . . . . .	525
	Problems . . . . .	528
	<b>Appendices. . . . .</b>	<b>539</b>
A.	Theory of Scattering by a Spherical Potential: Brief Summary . . . . .	539
A.1	Solution of the Schrödinger Equation for a Particle in a Spherical Potential . . . . .	539
A.2	Scattering of a Free Particle by a Spherical Potential. . . . .	541
A.3	Friedel's Sum Rule . . . . .	543

B. The Continued Fraction Technique . . . . .	545
B.1 Principle of the Recursion Method . . . . .	545
B.2 Principle of the Moment Method . . . . .	547
B.3 Practical Calculations . . . . .	549
C. Electromagnetic Waves in Matter . . . . .	552
C.1 Brief Summary of Maxwell Equations in Vacuum . . . . .	552
C.2 Maxwell Equations and Dielectric Properties in a Homogeneous and Isotropic Medium . . . . .	553
C.3 An Equivalent Description of the Dielectric Properties of a Homogeneous and Isotropic Medium: Longitudinal and Transverse Dielectric Functions . . . . .	554
D. Calculation of the Variation of the Total Energy Due to a Perturbing External Charge Distribution Within the Density Functional Formalism . . . . .	556
E. Useful Relations for the Study of Many Body Interactions . . .	558
E.1 Relation Between the Expectation Value of the Interaction Energy and the Total Energy for a System of Interacting Particles . . . . .	558
E.2 Derivation of the Fredholm Formula . . . . .	558
F. Interaction of an Electron With an Electromagnetic Field and Theory of Angle-Resolved Ultra-Violet Photoemission (UPS) . . . . .	559
F.1 The Optical Matrix Element . . . . .	560
F.2 Expression of the Photoemitted Current in UPS . . . . .	562
F.2.1 Some Useful Relations . . . . .	562
F.2.2 Calculation of the Photoemitted Current in UPS . . .	564
F.3 Conservation of the Wave Vector in Photoemission . . . . .	567
G. Calculation of the Current in a Scanning Tunneling Microscope	571
H. Calculation of the Atomic Dynamic Polarizability . . . . .	578
I. Variation of the Density of States Due to a Perturbing Potential	579
J. Energy of Chemisorption in the Anderson-Grimley-Newns Model Using Contour Integrals . . . . .	580
K. Elastic Constants and Elastic Waves in Cubic Crystals . . . . .	581
K.1 Elastic Strain . . . . .	581
K.2 Elastic Stress . . . . .	582
K.3 Elastic Constants . . . . .	583
K.4 Propagation of Elastic Waves in Cubic Crystals . . . . .	583
K.5 Elastic Energy . . . . .	584
References . . . . .	585
Subject Index . . . . .	599

# 1. Introduction

The study of solid surface phenomena is of great importance in physics since a solid sample is always in contact with other media (vapour, liquid . . .) via its surface. The existence of such an interface modifies, at least locally, the properties of the sample and it is through it that the interactions with the outside world occur. Therefore, surface physics finds applications in many technologies, for example, in heterogeneous catalysis (oil industry, ammonia synthesis . . .), microelectronics, electrochemistry, corrosion, photography, lubrication, adhesion, biology. . . .

Although some physical properties of surfaces were known empirically as early as in Antiquity, it is only within the last century that surface physics has become a science of its own. Let us mention, for example, the works of T. Young (1805) and P.S. de Laplace (1806) on surface tension. The concept of surface energy was introduced by C.F. Gauss in 1830, followed by the fundamentals of classical thermodynamic theory of surface phenomena which were described in detail by W. Gibbs in 1877. A few years later Lord Rayleigh (originally named J.W. Strutt) proved the existence of waves localized at the surface of continuous elastic media. At the beginning of the twentieth century, the problem of minimizing the surface energy of a finite anisotropic solid in order to find its equilibrium shape was solved by G. Wulff (1901).

The first decades of the present century have seen the development of surface chemistry due largely to I. Langmuir. Inspired by the discovery of the crystalline nature of various surfaces by W.L. Bragg (1913), I. Langmuir advanced a theory of heterogeneous catalysis and adsorption kinetics. In addition, he provided a model of thermionic emission. In the same period, A. Einstein (1905) proposed an explanation of the photoelectric effect discovered by H. Hertz (1887). This interpretation relied on completely new ideas concerning the interaction between light and matter in which the energy transfer occurred by quanta, a concept which was already introduced by M. Planck (1900) in the theory of black body radiation. These ideas led to the advent of quantum mechanics, which took place in the 1920s and produced a turning point in the history of surface physics.

In 1927, C.J. Davisson and L. Germer performed the first low energy electron diffraction experiment which proved the wave nature of quantum mechanical particles. Very rapidly, quantum mechanics was applied to investigate the electronic structure of solids and the role played by the boundary conditions, due to the existence of surfaces, was raised. This led to new concepts



such as surface states (I. Tamm, 1932, W. Shockley, 1939), surface double layer (J. Bardeen, 1936) . . . and provided a means to calculate, on a microscopic basis, other quantities of physical interest.

Simultaneously the statistical approach to the study of crystal surfaces was developed by I.N. Stranski (1928), M. Volmer (1939) and the break through on the subject of crystal growth appeared with the works of W.K. Burton, N. Cabrera and F.C. Franck at the beginning of the 1950s. In this period, most of the physical phenomena (Auger effect, diffraction of particles, Kronig oscillations, field emission and field ionization) on which the modern experimental techniques of surface observation are based were also discovered. However, progress in the understanding of surface physics had been hampered by severe problems of experimental reproducibility, which were due to the difficulty in obtaining structurally and chemically well characterized surfaces.

This problem was only solved in the 1960s thanks to the appearance of ultra high vacuum technology which has led to the development of many experimental techniques as well as of chemical analysis on an atomic scale. At the same time, high speed digital computers became available allowing theoretical works to reach a degree of sophistication going far beyond the simple models developed in the previous period. As a consequence, the number of publications on surface physics grew rapidly and entire journals, as well as many conferences, devoted to this subject appeared. The description of most of the advances performed in these last decades is the subject of this book.

This book only deals with crystal surfaces and we have restricted ourselves to pure metal and semiconductor surfaces, clean or possibly in the presence of adsorbates, excluding from our study alloys or insulator surfaces, although some of the presented methods could also be applied to these materials. Let us first define what region we are referring to as the "surface". By this, we mean a region extending about 20 Å around the last atomic plane, i.e., it includes the first three or four atomic layers. Indeed, beyond this region the electronic density almost vanishes on the vacuum side and has attained its bulk behaviour on the solid side, as we will see in the following chapters. Note, however, that when the surface is significantly charged, as can be the case in some semiconductors or insulators, long range effects due to the Coulomb potential exist and can be analyzed by mean of bulk concepts, the surface playing a subsidiary boundary-value role. However, they will not be studied here since the materials that we will consider have quasi-neutral surfaces.

Let us end this introduction with a brief description of the content of each chapter.

In Chap. 2, we treat the classical and statistical thermodynamics of clean surfaces. We first define the relevant macroscopic thermodynamical quantities and discuss their implications on the equilibrium properties of crystals. As the temperature increases, defects appear on the surface and the corresponding increase of the internal energy may be counterbalanced by entropy effects. If this occurs below the melting point, the surface becomes rough and this "roughening transition" is also studied in this chapter by means of statistical methods.