

# Introduction to Surface and Thin Film Processes

John A. Venables

This page intentionally left blank

## **Introduction to Surface and Thin Film Processes**

This book covers the experimental and theoretical understanding of surface and thin film processes. It presents a unique description of surface processes in adsorption and crystal growth, including bonding in metals and semiconductors. Emphasis is placed on the strong link between science and technology in the description of, and research for, new devices based on thin film and surface science. Practical experimental design, sample preparation and analytical techniques are covered, including detailed discussions of Auger electron spectroscopy and microscopy. Thermodynamic and kinetic models of electronic, atomic and vibrational structure are emphasized throughout. The book provides extensive leads into practical and research literature, as well as to resources on the World Wide Web. Each chapter contains problems which aim to develop awareness of the subject and the methods used.

Aimed as a graduate textbook, this book will also be useful as a sourcebook for graduate students, researchers and practitioners in physics, chemistry, materials science and engineering.

JOHN A. VENABLES obtained his undergraduate and graduate degrees in Physics from Cambridge. He spent much of his professional life at the University of Sussex, where he is currently an Honorary Professor, specialising in electron microscopy and the topics discussed in this book. He has taught and researched in laboratories around the world, and has been Professor of Physics at Arizona State University since 1986. He is currently involved in web-based (and web-assisted) graduate teaching, in Arizona, Sussex and elsewhere. He has served on several advisory and editorial boards, and has done his fair share of reviewing. He has published numerous journal articles and edited three books, contributing chapters to these and others; this is his first book as sole author.



# Introduction to **Surface and Thin Film Processes**

JOHN A. VENABLES

*Arizona State University  
and  
University of Sussex*



**CAMBRIDGE**  
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE  
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS

The Edinburgh Building, Cambridge CB2 2RU, UK

40 West 20th Street, New York, NY 10011-4211, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

Ruiz de Alarcón 13, 28014 Madrid, Spain

Dock House, The Waterfront, Cape Town 8001, South Africa

<http://www.cambridge.org>

© John A. Venables 2004

First published in printed format 2000

ISBN 0-511-03558-6 eBook (Adobe Reader)

ISBN 0-521-62460-6 hardback

ISBN 0-521-78500-6 paperback

# Contents

Preface	page xi
<b>Chapter 1</b> Introduction to surface processes	1
<b>1.1 Elementary thermodynamic ideas of surfaces</b>	1
1.1.1 <i>Thermodynamic potentials and the dividing surface</i>	1
1.1.2 <i>Surface tension and surface energy</i>	3
1.1.3 <i>Surface energy and surface stress</i>	4
<b>1.2 Surface energies and the Wulff theorem</b>	4
1.2.1 <i>General considerations</i>	5
1.2.2 <i>The terrace–ledge–kink model</i>	5
1.2.3 <i>Wulff construction and the forms of small crystals</i>	7
<b>1.3 Thermodynamics versus kinetics</b>	9
1.3.1 <i>Thermodynamics of the vapor pressure</i>	11
1.3.2 <i>The kinetics of crystal growth</i>	15
<b>1.4 Introduction to surface and adsorbate reconstructions</b>	19
1.4.1 <i>Overview</i>	19
1.4.2 <i>General comments and notation</i>	20
1.4.3 <i>Examples of (1×1) structures</i>	22
1.4.4 <i>Si(001) (2×1) and related semiconductor structures</i>	24
1.4.5 <i>The famous 7×7 structure of Si(111)</i>	27
1.4.6 <i>Various ‘root-three’ structures</i>	28
1.4.7 <i>Polar semiconductors, such as GaAs(111)</i>	28
1.4.8 <i>Ionic crystal structures, such as NaCl, CaF<sub>2</sub>, MgO or alumina</i>	30
<b>1.5 Introduction to surface electronics</b>	30
1.5.1 <i>Work function, <math>\phi</math></i>	30
1.5.2 <i>Electron affinity, <math>\chi</math>, and ionization potential <math>\Phi</math></i>	30
1.5.3 <i>Surface states and related ideas</i>	31
1.5.4 <i>Surface Brillouin zone</i>	32
1.5.5 <i>Band bending, due to surface states</i>	32
1.5.6 <i>The image force</i>	32
1.5.7 <i>Screening</i>	33
<b>Further reading for chapter 1</b>	33
<b>Problems for chapter 1</b>	33
<b>Chapter 2</b> Surfaces in vacuum: ultra-high vacuum techniques and processes	36
<b>2.1 Kinetic theory concepts</b>	36
2.1.1 <i>Arrival rate of atoms at a surface</i>	36
2.1.2 <i>The molecular density, <math>n</math></i>	37
2.1.3 <i>The mean free path, <math>\lambda</math></i>	37
2.1.4 <i>The monolayer arrival time, <math>\tau</math></i>	38

<b>2.2 Vacuum concepts</b>	39
2.2.1 <i>System volumes, leak rates and pumping speeds</i>	39
2.2.2 <i>The idea of conductance</i>	41
2.2.3 <i>Measurement of system pressure</i>	42
<b>2.3 UHV hardware: pumps, tubes, materials and pressure measurement</b>	42
2.3.1 <i>Introduction: sources of information</i>	42
2.3.2 <i>Types of pump</i>	43
2.3.3 <i>Chambers, tube and flange sizes</i>	44
2.3.4 <i>Choice of materials</i>	45
2.3.5 <i>Pressure measurement and gas composition</i>	46
<b>2.4 Surface preparation and cleaning procedures : <i>in situ</i> experiments</b>	47
2.4.1 <i>Cleaning and sample preparation</i>	47
2.4.2 <i>Procedures for in situ experiments</i>	50
2.4.3 <i>Sample transfer devices</i>	51
2.4.4 <i>From laboratory experiments to production processes</i>	52
<b>2.5 Thin film deposition procedures: sources of information</b>	54
2.5.1 <i>Historical descriptions and recent compilations</i>	54
2.5.2 <i>Thermal evaporation and the uniformity of deposits</i>	54
2.5.3 <i>Molecular beam epitaxy and related methods</i>	57
2.5.4 <i>Sputtering and ion beam assisted deposition</i>	57
2.5.5 <i>Chemical vapor deposition techniques</i>	59
<b>Further reading for chapter 2</b>	60
<b>Problems for chapter 2</b>	60
<b>Chapter 3 Electron-based techniques for examining surface and thin film processes</b>	63
<b>3.1 Classification of surface and microscopy techniques</b>	63
3.1.1 <i>Surface techniques as scattering experiments</i>	63
3.1.2 <i>Reasons for surface sensitivity</i>	64
3.1.3 <i>Microscopic examination of surfaces</i>	65
3.1.4 <i>Acronyms</i>	69
<b>3.2 Diffraction and quasi-elastic scattering techniques</b>	70
3.2.1 <i>LEED</i>	70
3.2.2 <i>RHEED and THEED</i>	72
3.2.3 <i>Elastic, quasi-elastic and inelastic scattering</i>	74
<b>3.3 Inelastic scattering techniques: chemical and electronic state information</b>	76
3.3.1 <i>Electron spectroscopic techniques</i>	76
3.3.2 <i>Photoelectron spectroscopies: XPS and UPS</i>	79
3.3.3 <i>Auger electron spectroscopy: energies and atomic physics</i>	81
3.3.4 <i>AES, XPS and UPS in solids and at surfaces</i>	84
<b>3.4 Quantification of Auger spectra</b>	88
3.4.1 <i>General equation describing quantification</i>	88
3.4.2 <i>Ratio techniques</i>	92
<b>3.5 Microscopy-spectroscopy: SEM, SAM, SPM, etc.</b>	95
3.5.1 <i>Scanning electron and Auger microscopy</i>	95

---

3.5.2 Auger and image analysis of ‘real world’ samples	98
3.5.3 Towards the highest spatial resolution: (a) SEM/STEM	100
3.5.4 Towards the highest spatial resolution: (b) scanned probe microscopy-spectroscopy	104
<b>Further reading for chapter 3</b>	105
<b>Problems, talks and projects for chapter 3</b>	105
<b>Chapter 4 Surface processes in adsorption</b>	108
<b>4.1 Chemi- and physisorption</b>	108
<b>4.2 Statistical physics of adsorption at low coverage</b>	109
4.2.1 General points	109
4.2.2 Localized adsorption: the Langmuir adsorption isotherm	109
4.2.3 The two-dimensional adsorbed gas: Henry law adsorption	110
4.2.4 Interactions and vibrations in higher density adsorbates	113
<b>4.3 Phase diagrams and phase transitions</b>	114
4.3.1 Adsorption in equilibrium with the gas phase	115
4.3.2 Adsorption out of equilibrium with the gas phase	118
<b>4.4 Physisorption: interatomic forces and lattice dynamical models</b>	119
4.4.1 Thermodynamic information from single surface techniques	119
4.4.2 The crystallography of monolayer solids	120
4.4.3 Melting in two dimensions	124
4.4.4 Construction and understanding of phase diagrams	125
<b>4.5 Chemisorption: quantum mechanical models and chemical practice</b>	128
4.5.1 Phases and phase transitions of the lattice gas	128
4.5.2 The Newns–Anderson model and beyond	130
4.5.3 Chemisorption: the first stages of oxidation	133
4.5.4 Chemisorption and catalysis: macroeconomics, macromolecules and microscopy	135
<b>Further reading for chapter 4</b>	141
<b>Problems and projects for chapter 4</b>	141
<b>Chapter 5 Surface processes in epitaxial growth</b>	144
<b>5.1 Introduction: growth modes and nucleation barriers</b>	144
5.1.1 Why are we studying epitaxial growth?	144
5.1.2 Simple models – how far can we go?	145
5.1.3 Growth modes and adsorption isotherms	145
5.1.4 Nucleation barriers in classical and atomistic models	145
<b>5.2 Atomistic models and rate equations</b>	149
5.2.1 Rate equations, controlling energies, and simulations	149
5.2.2 Elements of rate equation models	150
5.2.3 Regimes of condensation	152
5.2.4 General equations for the maximum cluster density	154
5.2.5 Comments on individual treatments	155
<b>5.3 Metal nucleation and growth on insulating substrates</b>	157
5.3.1 Microscopy of island growth: metals on alkali halides	157

5.3.2	<i>Metals on insulators: checks and complications</i>	159
5.3.3	<i>Defect-induced nucleation on oxides and fluorides</i>	161
<b>5.4</b>	<b>Metal deposition studied by UHV microscopies</b>	165
5.4.1	<i>In situ UHV SEM and LEEM of metals on metals</i>	165
5.4.2	<i>FIM studies of surface diffusion on metals</i>	167
5.4.3	<i>Energies from STM and other techniques</i>	169
<b>5.5</b>	<b>Steps, ripening and interdiffusion</b>	174
5.5.1	<i>Steps as one-dimensional sinks</i>	174
5.5.2	<i>Steps as sources: diffusion and Ostwald ripening</i>	176
5.5.3	<i>Interdiffusion in magnetic multilayers</i>	179
	<b>Further reading for chapter 5</b>	181
	<b>Problems and projects for chapter 5</b>	181
<b>Chapter 6</b>	<b>Electronic structure and emission processes at metallic surfaces</b>	184
<b>6.1</b>	<b>The electron gas: work function, surface structure and energy</b>	184
6.1.1	<i>Free electron models and density functionals</i>	184
6.1.2	<i>Beyond free electrons: work function, surface structure and energy</i>	190
6.1.3	<i>Values of the work function</i>	193
6.1.4	<i>Values of the surface energy</i>	196
<b>6.2</b>	<b>Electron emission processes</b>	200
6.2.1	<i>Thermionic emission</i>	201
6.2.2	<i>Cold field emission</i>	202
6.2.3	<i>Adsorption and diffusion: FES, FEM and thermal field emitters</i>	206
6.2.4	<i>Secondary electron emission</i>	207
<b>6.3</b>	<b>Magnetism at surfaces and in thin films</b>	210
6.3.1	<i>Symmetry, symmetry breaking and phase transitions</i>	210
6.3.2	<i>Anisotropic interactions in 3D and '2D' magnets</i>	211
6.3.3	<i>Magnetic surface techniques</i>	213
6.3.4	<i>Theories and applications of surface magnetism</i>	218
	<b>Further reading for chapter 6</b>	224
	<b>Problems and projects for chapter 6</b>	224
<b>Chapter 7</b>	<b>Semiconductor surfaces and interfaces</b>	227
<b>7.1</b>	<b>Structural and electronic effects at semiconductor surfaces</b>	227
7.1.1	<i>Bonding in diamond, graphite, Si, Ge, GaAs, etc.</i>	227
7.1.2	<i>Simple concepts versus detailed computations</i>	229
7.1.3	<i>Tight-binding pseudopotential and ab initio models</i>	230
<b>7.2</b>	<b>Case studies of reconstructed semiconductor surfaces</b>	232
7.2.1	<i>GaAs(110), a charge-neutral surface</i>	232
7.2.2	<i>GaAs(111), a polar surface</i>	234
7.2.3	<i>Si and Ge(111): why are they so different?</i>	235
7.2.4	<i>Si, Ge and GaAs(001), steps and growth</i>	239
<b>7.3</b>	<b>Stresses and strains in semiconductor film growth</b>	242
7.3.1	<i>Thermodynamic and elasticity studies of surfaces</i>	242
7.3.2	<i>Growth on Si(001)</i>	245

---

7.3.3 Strained layer epitaxy: <i>Ge/Si(001)</i> and <i>Si/Ge(001)</i>	249
7.3.4 Growth of compound semiconductors	252
<b>Further reading for chapter 7</b>	256
<b>Problems and projects for chapter 7</b>	257
<b>Chapter 8</b> Surface processes in thin film devices	260
<b>8.1 Metals and oxides in contact with semiconductors</b>	260
8.1.1 Band bending and rectifying contacts at semiconductor surfaces	260
8.1.2 Simple models of the depletion region	263
8.1.3 Techniques for analyzing semiconductor interfaces	265
<b>8.2 Semiconductor heterojunctions and devices</b>	270
8.2.1 Origins of Schottky barrier heights	270
8.2.2 Semiconductor heterostructures and band offsets	272
8.2.3 Opto-electronic devices and 'band-gap engineering'	274
8.2.4 Modulation and $\delta$ -doping, strained layers, quantum wires and dots	279
<b>8.3 Conduction processes in thin film devices</b>	280
8.3.1 Conductivity, resistivity and the relaxation time	281
8.3.2 Scattering at surfaces and interfaces in nanostructures	282
8.3.3 Spin dependent scattering and magnetic multilayer devices	284
<b>8.4 Chemical routes to manufacturing</b>	289
8.4.1 Synthetic chemistry and manufacturing: the case of <i>Si-Ge-C</i>	289
8.4.2 Chemical routes to opto-electronics and/or nano-magnetics	291
8.4.3 Nanotubes and the future of flat panel TV	293
8.4.4 Combinatorial materials development and analysis	294
<b>Further reading for chapter 8</b>	295
<b>Chapter 9</b> Postscript – where do we go from here?	297
9.1 Electromigration and other degradation effects in nanostructures	297
9.2 What do the various disciplines bring to the table?	299
9.3 What has been left out: future sources of information	301
<b>Appendix A</b> Bibliography	303
<b>Appendix B</b> List of acronyms	306
<b>Appendix C</b> Units and conversion factors	309
<b>Appendix D</b> Resources on the web or CD-ROM	312
<b>Appendix E</b> Useful thermodynamic relationships	314
<b>Appendix F</b> Conductances and pumping speeds, <i>C</i> and <i>S</i>	318
<b>Appendix G</b> Materials for use in ultra-high vacuum	320
<b>Appendix H</b> UHV component cleaning procedures	323
<b>Appendix J</b> An outline of local density methods	326
<b>Appendix K</b> An outline of tight binding models	328
<b>References</b>	331
<b>Index</b>	363



# Preface

This book is about processes that occur at surfaces and in thin films; it is based on teaching and research over a number of years. Many of the experimental techniques used to produce clean surfaces, and to study the structure and composition of solid surfaces, have been around for about a generation. Over the same period, we have also seen unprecedented advances in our ability to study materials in general, and on a microscopic scale in particular, largely due to the development and availability of many new types of powerful microscope.

The combination of these two fields, studying and manipulating clean surfaces on a microscopic scale, has become important more recently. This combination allows us to study what happens in the production and operation of an increasing number of technologically important devices and processes, at all length scales down to the atomic level. Device structures used in computers are now so small that they can be seen only with high resolution scanning and transmission electron microscopes. Device preparation techniques must be performed reproducibly, on clean surfaces under clean room conditions. Ever more elegant schemes are proposed for using catalytic chemical reactions at surfaces, to refine our raw products, for chemical sensors, to protect surfaces against the weather and to dispose of environmental waste. Spectacular advances in experimental technique now allow us to observe atoms, and the motion of individual atoms on surfaces, with amazing clarity. Under special circumstances, we can move them around to create artificial atomic-level assemblies, and study their properties. At the same time, enormous advances in computer power and in our understanding of materials have enabled theorists and computer specialists to model the behavior of these small structures and processes down to the level of individual atoms and (collections of) electrons.

The major industries which relate to surface and thin film science are the micro-electronics, opto-electronics and magnetics industries, and the chemistry-based industries, especially those involving catalysis and the emerging field of sensors. These industries form society's immediate need for investment and progress in this area, but longer term goals include basic understanding, and new techniques based on this understanding: there are few areas in which the interaction of science and technology is more clearly expressed.

Surfaces and thin films are two, interdependent, and now fairly mature disciplines. In his influential book, *Physics at Surfaces*, Zangwill (1988) referred to his subject as an interesting adolescent; so as the twenty-first century gets underway it is thirty-something. I make no judgment as to whether growing up is really a maturing process, or whether the most productive scientists remain adolescent all their lives. But the various stages of a subject's evolution have different character. Initially, a few academics and industrial researchers are in the field, and each new investigation or experiment opens many new possibilities. These people take on students, who find employment in closely

related areas. Surface and thin film science can trace its history back to Davisson and Germer, who in effect invented low energy electron diffraction (LEED) in 1927, setting the scene for the study of surface structure. Much of the science of electron emission dates from Irving Langmuir's pioneering work in the 1920s and 1930s, aimed largely at improving the performance of vacuum tubes; these scientists won the Nobel prize in 1937 and 1932 respectively.

The examination of surface chemistry by Auger and photoelectron spectroscopy can trace its roots back to cloud chambers in the 1920s and even to Einstein's 1905 paper on the photo-electric effect. But the real credit arguably belongs to the many scientists in the 1950s and 1960s who harnessed the new ultra-high vacuum (UHV) technologies for the study of clean surfaces and surface reactions with adsorbates, and the production of thin films under well-controlled conditions. In the past 30 years, the field has expanded, and the 'scientific generation' has been quite short; different sub-fields have developed, often based on the expertise of groups who started literally a generation ago. As an example, the compilation by Duke (1994) was entitled '*Surface Science: the First Thirty Years*'. The Surface Science in question is the journal, not the field itself, but the two are almost the same. That one can mount a retrospective exhibition indicates that the field has achieved a certain age.

Over the past ten years there has been a period of consolidation, where the main growth has been in employment in industry. Scientists in industry have pressing needs to solve surface and thin film processing problems as they arise, on a relatively short timescale. It must be difficult to keep abreast of new science and technology, and the tendency to react short term is very great. Despite all the progress in recent years, I feel it is important not to accept the latest technical development at the gee-whizz level, but to have a framework for understanding developments in terms of well-founded science. In this situation, we should not reinvent the wheel, and should maintain a reasonably reflective approach. There are so many forces in society encouraging us to communicate orally and visually, to have our industrial and international collaborations in place, to do our research primarily on contract, that it is tempting to conclude that science and frenetic activity are practically synonymous. Yet lifelong learning is also increasingly recognized as a necessity; for academics, this is itself a growth industry in which I am pleased to play my part.

This book is my attempt to distill, from the burgeoning field of *Surface and Thin Film Processes*, those elements which are scientifically interesting, which will stand the test of time, and which can be used by the reader to relate the latest advances back to his or her underlying knowledge. It builds on previous books and articles that perhaps emphasize the description of surfaces and thin films in a more static, less process-oriented sense. This previous material has not been duplicated more than is necessary; indeed, one of the aims is to provide a route into the literature of the past 30 years, and to relate current interests back to the underlying science. Problems and further textbook reading are given at the end of each chapter. These influential textbooks and monographs are collected in Appendix A, with a complete reference list at the end of the book, indicating in which section they are cited. The reader does not, of course, have to rush to do these problems or to read the references; but they

can be used for further study and detailed information. A list of acronyms used is given in Appendix B.

The book can be used as the primary book for a graduate course, but this is not an exclusive use. Many books have already been produced in this general area, and on specialized parts of it: on vacuum techniques, on surface science, and on various aspects of microscopy. This material is not all repeated here, but extensive leads are given into the existing literature, highlighting areas of strength in work stretching back over the last generation. The present book links all these fields and applies the results selectively to a range of materials. It also discusses science and technology and their inter-relationship, in a way that makes sense to those working in inter-disciplinary environments. It will be useful to graduate students, researchers and practitioners educated in physical, chemical, materials or engineering science.

The early chapters 1–3 underline the importance of thermodynamic and kinetic reasoning, provide an introduction to the terms used, and describe the use of ultra-high vacuum, surface science and microscopy techniques in studying surface processes. These chapters are supplemented with extensive references and problems, aimed at furthering the students' practical and analytical abilities across these fields. If used for a course, these problems can be employed to test students' analytical competence, and familiarity with practical aspects of laboratory designs and procedures. I have never required that students do problems unaided, but encouraged them to ask questions which help towards a solution, that they then write up when understanding has been achieved. This allows more time in class for discussion, and for everyone to explore the material at their own pace. A key point is that each student has a different background, and therefore finds different aspects unfamiliar or difficult.

The following chapters 4–8 are each self-contained, and can be read or worked through in any order, though the order presented has a certain logic. Chapter 4 treats adsorption on surfaces, and the role of adsorption in testing interatomic potentials and lattice dynamical models, and in following chemical reactions. Chapter 5 describes the modeling of epitaxial crystal growth, and the experiments performed to test these ideas; this chapter contains original material that has been featured in recent multi-author compilations. Further progress in understanding cannot be made without some understanding of bonding, and how it applies to specific materials systems. Chapter 6 treats bonding in metals and at metallic surfaces, electron emission and the operation of electron sources, and electrical and magnetic properties at surfaces and in thin films. Chapter 7 takes a similar approach to semiconductor surfaces, describing their reconstructions and the importance of growth processes in producing semiconductor-based thin film device structures. Chapter 8 concentrates on the science needed to understand electronic, magnetic and optical effects in devices. The short final chapter 9 describes briefly what has been left out of the book, and discusses the roles played by scientists and technologists from different educational backgrounds, and gives some pointers to further sources of information. Chapters 4–7 give suggestions for projects based on the material presented and cited. Appendices C–K give data and further explanations that have been found useful in practice.

In graduate courses, I have typically not given all this material each time, and

certainly not in this 4–8 order, but have tailored the choice of topics to the interests of the students who attended in a given term or semester. Recently, I have taught the material of chapters 1 and 2 first, and then interleaved chapter 3 with the most pressing topics in chapters 4–8, filling in to round out topics later. Towards the end of the course, several students have given talks about other surface and/or microscopic techniques to the class, and yet others did a ‘mini-project’ of 2000 words or so, based on references supplied and suggested leads into the literature.

With this case-study approach, one can take students to the forefront of current research, while also relating the underlying science back to the early chapters. I am personally very interested in models of electronic, atomic and vibrational structure, though I am not expert in all these areas. As a physicist by training, heavily influenced by materials science, and with some feeling for engineering and for physical/analytical chemistry, I am drawn towards nominally simple (elemental) systems, and I do not go far in the direction of complex chemistry, which is usually implicated in real-life processes such as chemical vapor deposition or catalytic schemes. With so much literature available one can easily be overwhelmed; yet if conflicts and discrepancies in the original literature are never mentioned, it is too easy for students, and indeed the general public, to believe that science is cut and dried, a scarcely human endeavor. In the workplace, employees with graduate degrees in physics, chemistry, materials science or engineering are treated as more or less interchangeable. Understanding obtained via the book is a contribution to this interdisciplinary background that we all need to function effectively in teams.

Having extolled the virtues of a scholarly approach to graduate education in book form, I also think that graduate courses should embrace the relevant possibilities opened up by recent technology. I have been using the World Wide Web to publish course notes, and to teach students off-campus, using e-mail primarily for interactions, in addition to taking other opportunities, such as meeting at conferences, to interact more personally. Writing notes for the web and interacting via e-mail is enjoyable and informal. Qualitative judgments trip off the fingers, which one would be hard put to justify in a book; if they are shown to be wrong or inappropriate they can easily be changed. Perhaps more importantly, one can access other sites for information which one lacks, or which colleagues elsewhere have put in a great deal of time perfecting; my [web-based resources](#) page can be accessed via Appendix D. One can be interested in a topic, and refer students to it, without having to reinvent the wheel in a futile attempt to become the world’s expert overnight. And, as I hope to show over the next few years, one may be able to reach students who do not have the advantages of working in large groups, and largely at times of their choosing.

It seems too early to say whether course notes on the web, or a book such as this will have the longer shelf life. In writing the book, after composing most but not all of the notes, I am to some extent hedging my bets. I have discovered that the work needed to produce them is rather different in kind, and I suspect that they will be used for rather different purposes. Most of the notes are on my home page <http://venables.asu.edu/> in the /grad directory, but I am also building up some related material for graduate

courses at Sussex. Let me know what you think of this material: an e-mail is just a few clicks away.

I would like to thank students who have attended courses and worked on problems, given talks and worked on projects, and co-workers who have undertaken research projects with me over the last several years. I owe an especial debt to several friends and close colleagues who have contributed to and discussed courses with me: Paul Calvert (now at University of Arizona), Roger Doherty (now at Drexel) and Michael Hardiman at Sussex; Ernst Bauer, Peter Bennett, Andrew Chizmeshya, David Ferry, Bill Glaunsinger, Gary Hembree, John Kouvetakis, Stuart Lindsay, Michael Scheinfein, David Smith, John Spence and others at ASU; Harald Brune, Robert Johnson and Per Stoltze in and around Europe. They and others have read through individual chapters and sections and made encouraging noises alongside practical suggestions for improvement. Any remaining mistakes are mine.

I am indebted, both professionally and personally, to the CRMC2-CNRS laboratory in Marseille, France. Directors of this laboratory (Raymond Kern, Michel Bienfait, and Jacques Derrien) and many laboratory members have been generous hosts and wonderful collaborators since my first visit in the early 1970s. I trust they will recognize their influence on this book, whether stated or not.

I am grateful to many colleagues for correspondence, for reprints, and for permission to use specific figures. In alphabetical order, I thank particularly C.R. Abernathy, A.P. Alivisatos, R.E. Allen, J.G. Amar, G.S. Bales, J.V. Barth, P.E. Batson, J. Bernholc, K. Besocke, M. Brack, R. Browning, L.W. Bruch, C.T. Campbell, D.J. Chadi, J.N. Chapman, G. Comsa, R.K. Crawford, H. Daimon, R. Del Sole, A.E. DePristo, P.W. Deutsch, R. Devonshire, F.W. DeWette, M.J. Drinkwine, J.S. Drucker, G. Duggan, C.B. Duke, G. Ehrlich, D.M. Eigler, T.L. Einstein, R.M. Feenstra, A.J. Freeman, E. Ganz, J.M. Gibson, R. Gomer, E.B. Graper, J.F. Gregg, J.D. Gunton, B. Heinrich, C.R. Henry, M. Henzler, K. Hermann, F.J. Himpel, S. Holloway, P.B. Howes, J.B. Hudson, K.A. Jackson, K.W. Jacobsen, J. Janata, D.E. Jesson, M.D. Johnson, B.A. Joyce, H. von Känel, K. Kern, M. Klaua, L. Kleinman, M. Krishnamurthy, M.G. Lagally, N.D. Lang, J. Liu, H.H. Madden, P.A. Maksym, J.A.D. Matthew, J.-J. Métois, T. Michely, V. Milman, K. Morgenstern, R. Monot, B. Müller, C.B. Murray, C.A. Norris, J.K. Nørskov, J.E. Northrup, A.D. Novaco, T. Ono, B.G. Orr, D.A. Papaconstantopoulos, J. Perdew, D.G. Pettifor, E.H. Poindexter, J. Pollmann, C.J. Powell, M. Prutton, C.F. Quate, C. Ratsch, R. Reifenburger, J. Robertson, J.L. Robins, L.D. Roelofs, C. Roland, H.H. Rotermund, J.R. Sambles, E.F. Schubert, M.P. Seah, D.A. Shirley, S.J. Sibener, H.L. Skriver, A. Sugawara, R.M. Suter, A.P. Sutton, J. Suzanne, B.S. Swartzentruber, S.M. Sze, K. Takayanagi, M. Terrones, J. Tersoff, A. Thomy, M.C. Tringides, R.L. Tromp, J. Unguris, D. Vanderbilt, C.G. Van de Walle, M.A. Van Hove, B. Voigtländer, D.D. Vvedensky, L. Vescan, M.B. Webb, J.D. Weeks, P. Weightman, D. Williams, E.D. Williams, D.P. Woodruff, R. Wu, M. Zinke-Allmann and A. Zunger.

Producing the figures has allowed me to get to know my nephew Joe Whelan in a new way. Joe produced many of the drawings in draft, and some in final form; we had some good times, both in Sussex and in Arizona. Mark Foster in Sussex helped

effectively with scanning original copies into the computer. Publishers responded quickly to my requests for permission to reproduce such figures. Finally I thank, but this is too weak a word, my wife Delia, whose opinion is both generously given and highly valued. In this case, once I had started, she encouraged me to finish as quickly as practicable: aim for a competent job done in a finite time. After all, that's what I tell my students.

John A. Venables (john.venables@asu.edu or john@venables.co.uk)  
Arizona/Sussex, November/December 1999

## References

- Duke, C.B. (Ed.) (1994) *Surface Science: the First Thirty Years* (*Surface Sci.* **299/300** 1–1054).  
Zangwill, A. (1988) *Physics at Surfaces* (Cambridge University Press, pp. 1–454).

# 1 Introduction to surface processes

---

In this opening chapter, section 1.1 introduces some of the thermodynamic ideas which are used to discuss small systems. In section 1.2 these ideas are developed in more detail for small crystals, both within the terrace–ledge–kink (TLK) model, and with examples taken from real materials. Section 1.3 explores important differences between thermodynamics and kinetics; the examples given are the vapor pressure (an equilibrium thermodynamic phenomenon) and ideas about crystal growth (a non-equilibrium phenomenon approachable via kinetic arguments); both discussions include the role of atomic vibrations.

Finally, in section 1.4 the ideas behind reconstruction of crystal surfaces are discussed, and section 1.5 introduces some concepts related to surface electronics. These sections provide groundwork for the chapters which follow. You may wish to come back to individual topics later; for example, although the thermodynamics of small crystals is studied here, we will not have covered many experimental examples, nor more than the simplest models. The reason is that not everyone will want to study this topic in detail. In addition to the material in the text, some topics which may be generally useful are covered in appendices.

## 1.1 Elementary thermodynamic ideas of surfaces

### 1.1.1 *Thermodynamic potentials and the dividing surface*

The idea that thermodynamic reasoning can be applied to surfaces was pioneered by the American scientist J.W. Gibbs in the 1870s and 1880s. This work has been assembled in his collected works (Gibbs 1928, 1961) and has been summarized in several books, listed in the further reading at the end of the chapter and in Appendix A. These references given are for further exploration, but I am not expecting you to charge off and look all of them up! However, if your thermodynamics is rusty you might read Appendix E.1 before proceeding.

Gibbs' central idea was that of the 'dividing surface'. At a boundary between phases 1 and 2, the concentration profile of any elemental or molecular species changes (continuously) from one level  $c_1$  to another  $c_2$ , as sketched in figure 1.1. Then the extensive thermodynamic potentials (e.g. the internal energy  $U$ , the Helmholtz free energy  $F$ , or the Gibbs free energy  $G$ ) can be written as a contribution from phases 1, 2 plus a surface

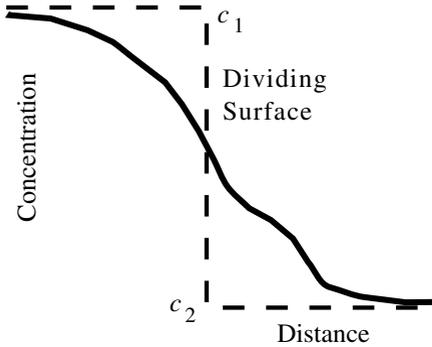


Figure 1.1. Schematic view of the ‘dividing surface’ in terms of macroscopic concentrations. See text for discussion.

term. In the thermodynamics of bulk matter, we have the bulk Helmholtz free energy  $F_b = F(N_1, N_2)$  and we know that

$$dF_b = -SdT - pdV + \mu dN = 0, \quad (1.1)$$

at constant temperature  $T$ , volume  $V$  and particle number  $N$ . In this equation,  $S$  is the (bulk) entropy,  $p$  is the pressure and  $\mu$  the chemical potential. Similar relationships exist for the other thermodynamic potentials; commonly used thermodynamic relations are given in Appendix E.1.

We are now interested in how the thermodynamic relations change when the system is characterized by a surface area  $A$  in addition to the volume. With the surface present the total free energy  $F_t = F(N_1, N_2, A)$  and

$$dF_t = dF_b(N_1, N_2) + f_s dA. \quad (1.2)$$

This  $f_s$  is the extra Helmholtz free energy per unit area due to the presence of the surface, where we have implicitly assumed that the total number of atomic/molecular entities in the two phases,  $N_1$  and  $N_2$  remain constant. Gibbs’ idea of the ‘dividing surface’ was the following. Although the concentrations may vary in the neighborhood of the surface, we consider the system as uniform up to this ideal interface:  $f_s$  is then the surface excess free energy.

To make matters concrete, we might think of a one-component solid–vapor interface, where  $c_1$  is high, and  $c_2$  is very low; the exact concentration profile in the vicinity of the interface is typically unknown. Indeed, as we shall discuss later, it depends on the forces between the constituent atoms or molecules, and the temperature, via the statistical mechanics of the system. But we can define an imaginary dividing surface, such that the system behaves as if it comprised a uniform solid and a uniform vapor up to this dividing surface, and that the surface itself has thermodynamic properties which scale with the surface area; this is the meaning of (1.2). In many cases described in this book, the concentration changes from one phase to another can be sharp at the atomic level. This does not invalidate thermodynamic reasoning, but it leads to an interesting

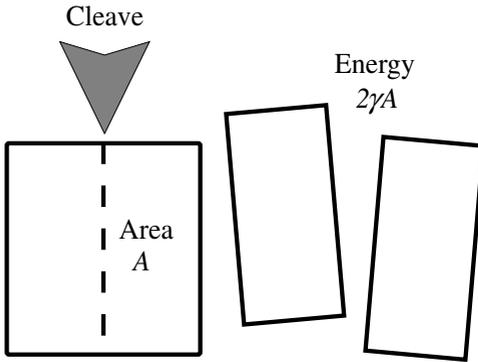


Figure 1.2. Schematic illustration of how to create new surface by cleavage. If this can be done reversibly, in the thermodynamic sense, then the work done is  $2\gamma A$ .

dialogue between macroscopic and atomistic views of surface processes, which will be discussed at many points in this book.

### 1.1.2 Surface tension and surface energy

The surface tension,  $\gamma$ , is defined as the reversible work done in creating unit area of new surface, i.e.

$$\gamma = \lim (dA \rightarrow 0) dW/dA = (dF_t/dA)_{T,V}. \quad (1.3)$$

In the simple illustration of figure 1.2,  $\Delta F = F_1 - F_0 = 2\gamma A$ ;  $dF_t = \gamma dA$ . At const  $T$  and  $V$ ,

$$dF_t = -SdT - p dV + \sum \mu_i dN_i + f_s dA = f_s dA + \sum \mu_i dN_i. \quad (1.4)$$

Therefore,

$$\gamma dA = f_s dA + \sum \mu_i dN_i. \quad (1.5)$$

In a one-component system, e.g. metal–vapor, we can choose the dividing surface such that  $dN_i = 0$ , and then  $\gamma$  and  $f_s$  are the same. This is the sense that most physics-oriented books and articles use the term. In more complex systems, the introduction of a surface can cause changes in  $N_i$ , i.e. we have  $N_1 + N_2$  in the bulk, and  $dN_i \rightarrow$  surface, so that  $dN_i$ , the change in the bulk number of atoms in phase  $i$ , is negative. We then write

$$dN = -\Gamma dA \text{ and } \gamma = f_s - \sum \Gamma_i \mu_i, \quad (1.6)$$

where the second term is the free energy contribution of atoms going from the bulk to the surface;  $\gamma$  is the surface density of  $(F - G)$  (Blakely 1973, p. 5). An equivalent view is that  $\gamma$  is the surface excess density of Kramers' grand potential  $\Omega = -p(V_1 + V_2) + \gamma A$ , which is minimized at constant  $T$ ,  $V$  and  $\mu$  (Desjonquères & Spanjaard 1996, p. 5). You might think about this – it is related to statistical mechanics of open systems using the grand canonical ensemble . . . ! Realistic models at  $T > 0$  K need to map onto the

relevant statistical distribution to make good predictions at the atomic or molecular level; such points will be explored as we proceed through the book.

The simple example leading to (1.6) shows that care is needed: if a surface is created, the atoms or molecules can migrate *to* (or sometimes *from*) the surface. The most common phenomena of this type are as follows.

- (1) A soap film lowers the surface tension of water. Why? Because the soap molecules come out of solution and form (mono-molecular) layers at the water surface (with their ‘hydrophobic’ ends pointing outwards). Soapy water (or beer) doesn’t mind being agitated into a foam with a large surface area; these are examples one can ponder every day!
- (2) A clean surface in ultra-high vacuum has a higher free energy than an oxidized (or contaminated) surface. Why? Because if it didn’t, there would be no ‘driving force’ for oxygen to adsorb, and the reaction wouldn’t occur. It is not so clear whether there are exceptions to this rather cavalier statement, but it is generally true that the surface energy of metal oxides are much lower than the surface energy of the corresponding metal.

If you need more details of multi-component thermodynamics, see Blakely (1973, section 2.3) Adamson (1990, section 3.5) or Hudson (1992, chapter 5). For now, we don’t, and thus  $\gamma = f_s$  for one-component systems. We can therefore go on to define surface excess internal energy,  $e_s$ ; entropy  $s_s$ , using the usual thermodynamic relationships:

$$e_s = f_s + Ts_s = \gamma - T(d\gamma/dT)_V; s_s = -(df_s/dT)_V. \quad (1.7)$$

The entropy  $s_s$  is typically positive, and has a value of a few Boltzmann’s constant ( $k$ ) per atom. One reason, not the only one, is that surface atoms are less strongly bound, and thus vibrate with lower frequency and larger amplitude than bulk atoms; another reason is that the positions of steps on the surface are not fixed. Hence  $e_s > f_s$  at  $T > 0$  K. The first reason is illustrated later in figure 1.17 and table 1.2.

### 1.1.3 Surface energy and surface stress

You may note that we have not taken the trouble to distinguish surface energy and surface stress at this stage, because of the complexity of the ideas behind surface stress. Both quantities have the same units, but surface stress is a second rank tensor, whereas surface energy is a scalar quantity. The two are the same for fluids, but can be substantially different for solids. We return to this topic in chapter 7; at this stage we should note that surface stresses, and stresses in thin films, are not identical, and may not have the same causes; thus it is reasonable to consider such effects later.

## 1.2 Surface energies and the Wulff theorem

In this section, the forms of small crystals are discussed in thermodynamic terms, and an over-simplified model of a crystal surface is worked through in some detail. When

this model is confronted with experimental data, it shows us that real crystal surfaces have richer structures which depend upon the details of atomic bonding and temperature; in special cases, true thermodynamic information about surfaces has been obtained by observing the shape of small crystals at high temperatures.

### 1.2.1 General considerations

At equilibrium, a small crystal has a specific shape at a particular temperature  $T$ . Since  $dF=0$  at constant  $T$  and volume  $V$ , we obtain from the previous section that

$$\gamma dA = 0, \text{ or } \int \gamma dA \text{ is a minimum,} \quad (1.8a)$$

where the integral is over the entire surface area  $A$ . A typical *non-equilibrium* situation is a thin film with a very flat shape, or a series of small crystallites, perhaps distributed on a substrate. The *equilibrium* situation corresponds to *one* crystal with  $\{hkl\}$  faces exposed such that

$$\int \gamma(hkl) dA(hkl) \text{ is minimal,} \quad (1.8b)$$

where the surface energies  $\gamma(hkl)$  depend on the crystal orientation. This statement, known as the Wulff theorem, was first enunciated in 1901 (Herring 1951, 1953). If  $\gamma$  is isotropic, the form is a sphere in the absence of gravity, as wonderful pictures of water droplets from space missions have shown us. The sphere is simply the unique geometrical form which minimizes the surface area for a given volume. With gravity, for larger and more massive drops, the shape is no longer spherical, and the ‘sessile drop’ method is one way of measuring the surface tension of a liquid (Adamson 1990, section 2.9, Hudson 1992, chapter 3); before we all respected the dangers of mercury poisoning, this was an instructive high school experiment. For a solid, there are also several methods of measuring surface tension, most obviously using the zero creep method, in which a ball of material, weight  $mg$ , is held up by a fine wire, radius  $r$ , in equilibrium via the surface tension force  $2\pi r\gamma$  (Martin & Doherty, 1976, chapter 4). But in fact, it isn’t easy to measure surface tension or surface energy accurately: we need to be aware of the likelihood of impurity segregation to the surface (think soap or oxidation again), and as we shall see in section 1.3, not all surfaces are in true equilibrium.

The net result is that one needs to know  $\gamma(hkl)$  to deduce the equilibrium shape of a small crystal; conversely, if you know the shape, you *might* be able to say something about  $\gamma(hkl)$ . We explore this in the next section within a simple model.

### 1.2.2 The terrace–ledge–kink model

Consider a simple cubic structure, lattice parameter  $a$ , with nearest neighbor (nn) bonds, where the surface is inclined at angle  $\theta$  to a low index (001) plane; a two-dimensional (2D) cut of this model is shown in figure 1.3, but you should imagine that the 3D crystal also contains bonds which come out of, and go into, the page.

In this model, bulk atoms have six bonds of strength  $\phi$ . The sublimation energy  $L$ , per unit volume, of the crystal is the  $(6\phi/2)(1/a^3)$ , where division by 2 is to avoid double

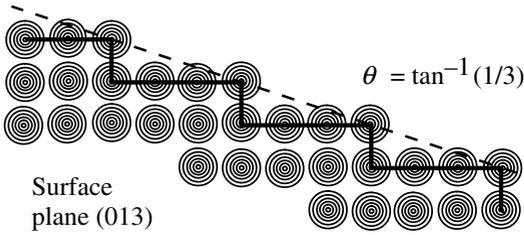


Figure 1.3. 2D cut of a simple cubic crystal, showing terrace and ledge atoms in profile. The tangent of the angle  $\theta$  which the (013) surface plane makes with (001) is  $1/3$ . The steps, or ledges, continue into and out of the paper on the same lattice.

counting: 1 bond involves 2 atoms. Units are (say)  $\text{eV}/\text{nm}^3$ , or many (chemical) equivalents, such as  $\text{kcal}/\text{mole}$ . Useful conversion factors are  $1 \text{ eV} \equiv 11\,604 \text{ K} \equiv 23.06 \text{ kcal}/\text{mole}$ ; these and other factors are listed in Appendix C.

Terrace atoms have an extra energy  $e_t$  per unit area with respect to the bulk atoms, which is due to having five bonds instead of six, so there is one bond missing every  $a^2$ . This means

$$e_t = (6 - 5) \phi / 2a^2 = \phi / 2a^2 = La/6 \text{ per unit area.} \quad (1.9a)$$

Ledge atoms have an extra energy  $e_l$  per unit length *over terrace atoms*: we have four bonds instead of five bonds, distributed every  $a$ . So

$$e_l = (5 - 4) \phi / 2a = La^2/6 \text{ per unit length.} \quad (1.9b)$$

Finally kink atoms have energy  $e_k$  *relative to the ledge atoms*, and the same argument gives

$$e_k = (4 - 3) \phi / 2 = La^3/6 \text{ per atom.} \quad (1.9c)$$

More interestingly a kink atom has  $3\phi$  *relative to bulk atoms*. This is the same as  $L/\text{atom}$ , so adding (or subtracting) an atom from a kink site is equivalent to condensing (or subliming) an atom from the bulk.

This last result may seem surprising, but it arises because moving a kink around on the surface leaves the number of T, L and K atoms, and the energy of the surface, unchanged. The kink site is thus a ‘repeatable step’ in the formation of the crystal. You can impress your friends by using the original German expression ‘wiederholbarer Schritt’. This schematic simple cubic crystal is referred to as a Kossel crystal, and the model as the TLK model, shown in perspective in figure 1.4. The original papers are by W. Kossel in 1927 and I.N. Stranski in 1928. Although these papers seem that they are from the distant past, my own memory of meeting Professor Stranski in the early 1970s, shortly after starting in this field, is alive and well. The scientific ‘school’ which he founded in Sofia, Bulgaria, also continues through social and political upheavals. This tradition is described in some detail by Markov (1995).

Within the TLK model, we can work out the surface energy as a function of (2D or 3D) orientation. For the 2D case shown in figure 1.3, we can show that

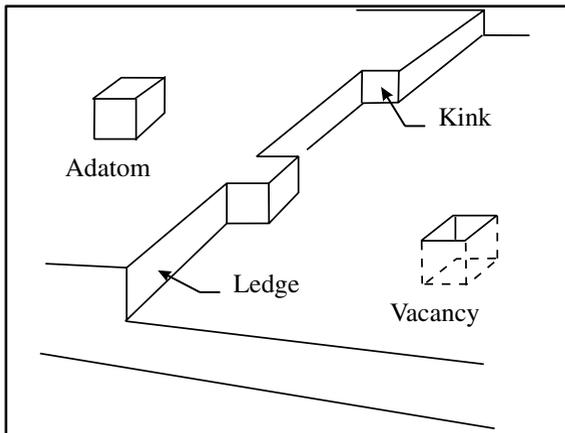


Figure 1.4. Perspective drawing of a Kossel crystal showing terraces, ledges (steps), kinks, adatoms and vacancies.

$$e_s = (e_t + e_1/na) \cos \theta. \quad (1.10a)$$

But  $1/n = \tan |\theta|$ . Therefore,  $e_s = e_t \cos |\theta| + e_1/a \sin |\theta|$ , or, within the model

$$e_s = (La/6)(\cos |\theta| + \sin |\theta|). \quad (1.10b)$$

We can draw this function as a polar diagram, noting that it is symmetric about  $\theta = 45^\circ$ , and repeats when  $\theta$  changes by  $\pm 90^\circ$ . This is sufficient to show that there are cusps in all the six  $\langle 100 \rangle$  directions, i.e. along the six  $\{100\}$  plane normals, four of them in, and two out, of the plane of the drawing. The  $|\theta|$  form arises from the fact that  $\theta$  changes sign as we go through the  $\{100\}$  plane orientations, but  $\tan |\theta|$  does not. In this model it does not matter whether the step train of figure 1.3 slopes to the right or to the left; if the surface had lower symmetry than the bulk, as we discuss in section 1.4, then the surface energy might depend on such details.

### 1.2.3 Wulff construction and the forms of small crystals

The Wulff construction is shown in figure 1.5. This is a polar diagram of  $\gamma(\theta)$ , the  $\gamma$ -plot, which is sometimes called the  $\sigma$ -plot. The Wulff theorem says that the minimum of  $\int \gamma dA$  results when one draws the perpendicular through  $\gamma(\theta)$  and takes the inner envelope: this is the equilibrium form. The simplest example is for the Kossel crystal of figure 1.3, for which the equilibrium form is a cube; a more realistic case is shown in figure 1.5.

The construction is easy to see qualitatively, but not so easy to prove mathematically. The deepest cusps (C in figure 1.5) in the  $\gamma$ -plot are always present in the equilibrium form: these are *singular* faces. Other higher energy faces, such as the cusps H in the figure, may or may not be present, depending in detail on  $\gamma(\theta)$ . Between the singular faces, there may be rounded regions R, where the faces are *rough*.

The mathematics of the Wulff construction is an example of the calculus of variations; the history, including the point that the original Wulff derivation was flawed, is

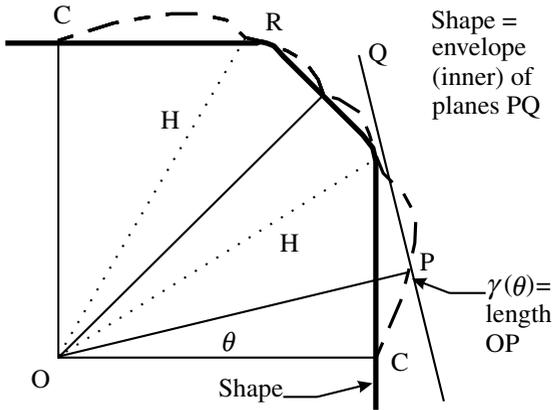


Figure 1.5. A 2D cut of a  $\gamma$ -plot, where the length  $OP$  is proportional to  $\gamma(\theta)$ , showing the cusps  $C$  and  $H$ , and the construction of the planes  $PQ$  perpendicular to  $OP$  through the points  $P$ . This particular plot leads to the existence of facets and rounded (rough) regions at  $R$ . See text for discussion

described by Herring (1953). There are various cases which can be worked out precisely, but somewhat laboriously, in order to decide by calculation whether a particular orientation is mechanically stable. Specific expressions exist for the case where  $\gamma$  is a function of one angular variable  $\theta$ , or of the lattice parameter,  $a$ . In the former case, a face is mechanically stable or unstable depending on whether the surface stiffness

$$\gamma(\theta) + d^2\gamma(\theta)/d\theta^2 \text{ is } > \text{ or } < 0. \quad (1.11)$$

The case of negative stiffness is an unstable condition which leads to *faceting* (Nozières 1992, Desjonquères & Spanjaard 1996). This can occur at 2D internal interfaces as well as at the surface, or it can occur in 1D along steps on the surface, or along dislocations in elastically anisotropic media, both of which can have unstable directions. In other words, these phenomena occur widely in materials science, and have been extensively documented, for example by Martin & Doherty (1976) and more recently by Sutton & Balluffi (1995). These references could be consulted for more detailed insights, but are not necessary for the following arguments.

A full set of 3D bond-counting calculations has been given in two papers by MacKenzie *et al.* (1962); these papers include general rules for nearest neighbor and next nearest neighbor interactions in face-centered (f.c.c.) and body-centered (b.c.c.) cubic crystals, based on the number of broken bond vectors  $\langle uvw \rangle$  which intersect the surface planes  $\{hkl\}$ . There is also an atlas of ‘ball and stick’ models by Nicholas (1965); an excellent introduction to crystallographic notation is given by Kelly & Groves (1970). More recently, models of the crystal faces can be visualized using CD-ROM or on the web, so there is little excuse for having to duplicate such pictures from scratch. A list of these resources, current as this book goes to press, is given in Appendix D.

The experimental study of small crystals (on substrates) is a specialist topic, aspects of which are described later in chapters 5, 7 and 8. For now, we note that close-packed

faces tend to be present in the equilibrium form. For f.c.c. (metal) crystals, these are  $\{111\}$ ,  $\{100\}$ ,  $\{110\}$  . . . and for b.c.c.  $\{110\}$ ,  $\{100\}$  . . .; this is shown in  $\gamma$ -plots and equilibrium forms, calculated for specific first and second nearest neighbor interactions in figure 1.6, where the relative surface energies are plotted on a stereogram (Sundquist 1964, Martin & Doherty 1976). For really small particles the discussion needs to take the discrete size of the faces into account. This extends up to particles containing  $\sim 10^6$  atoms, and favors  $\{111\}$  faces in f.c.c. crystals still further (Marks 1985, 1994). The properties of stereograms are given in a student project which can be found via Appendix D.

The effect of temperature is interesting. *Singular* faces have low energy and low entropy; *vicinal* (stepped) faces have higher energy and entropy. Thus for increasing temperature, we have lower free energy for non-singular faces, and the equilibrium form is more rounded. Realistic finite temperature calculations are relatively recent (Rottman & Wortis 1984), and there is still quite a lot of uncertainty in this field, because the results depend sensitively on models of interatomic forces and lattice vibrations. Some of these issues are discussed in later chapters.

Several studies have been done on the anisotropy of surface energy, and on its variation with temperature. These experiments require low vapor pressure materials, and have used Pb, Sn and In, which melt at a relatively low temperature, by observing the profile of a small crystal, typically 3–5  $\mu\text{m}$  diameter, in a specific orientation using scanning electron microscopy (SEM). An example is shown for Pb in figures 1.7 and 1.8, taken from the work of Heyraud and Métois; further examples, and a discussion of the role of roughening and melting transitions, are given by Pavlovska *et al.* (1989).

We notice that the anisotropy is quite small (much smaller than in the Kossel crystal calculation), and that it decreases, but not necessarily monotonically, as one approaches the melting point. This is due to three effects: (1) a nearest neighbor bond calculation with the realistic f.c.c. structure gives a smaller anisotropy than the Kossel crystal (see problem 1.1); (2) realistic interatomic forces may give still smaller effects; in particular, interatomic forces in many metals are less directional than implied by such bond-like models, as discussed in chapter 6; and (3) atomistic and layering effects at the monolayer level can affect the results in ways which are not intuitively obvious, such as the missing orientations close to (111) in the Pb crystals at 320°C, seen in figure 1.7(b). The main qualitative points about figure 1.8, however, are that the maximum surface energy is in an orientation close to  $\{210\}$ , as in the f.c.c. bond calculations of figure 1.6(b), and that entropy effects reduce the anisotropy as the melting point is approached. These data are still a challenge for models of metals, as discussed in chapter 6.

### 1.3 Thermodynamics versus kinetics

Equilibrium phenomena are described by thermodynamics, and on a microscopic scale by statistical mechanics. However, much of materials science is concerned with kinetics, where the rate of change of metastable structures (or their inability to change) is

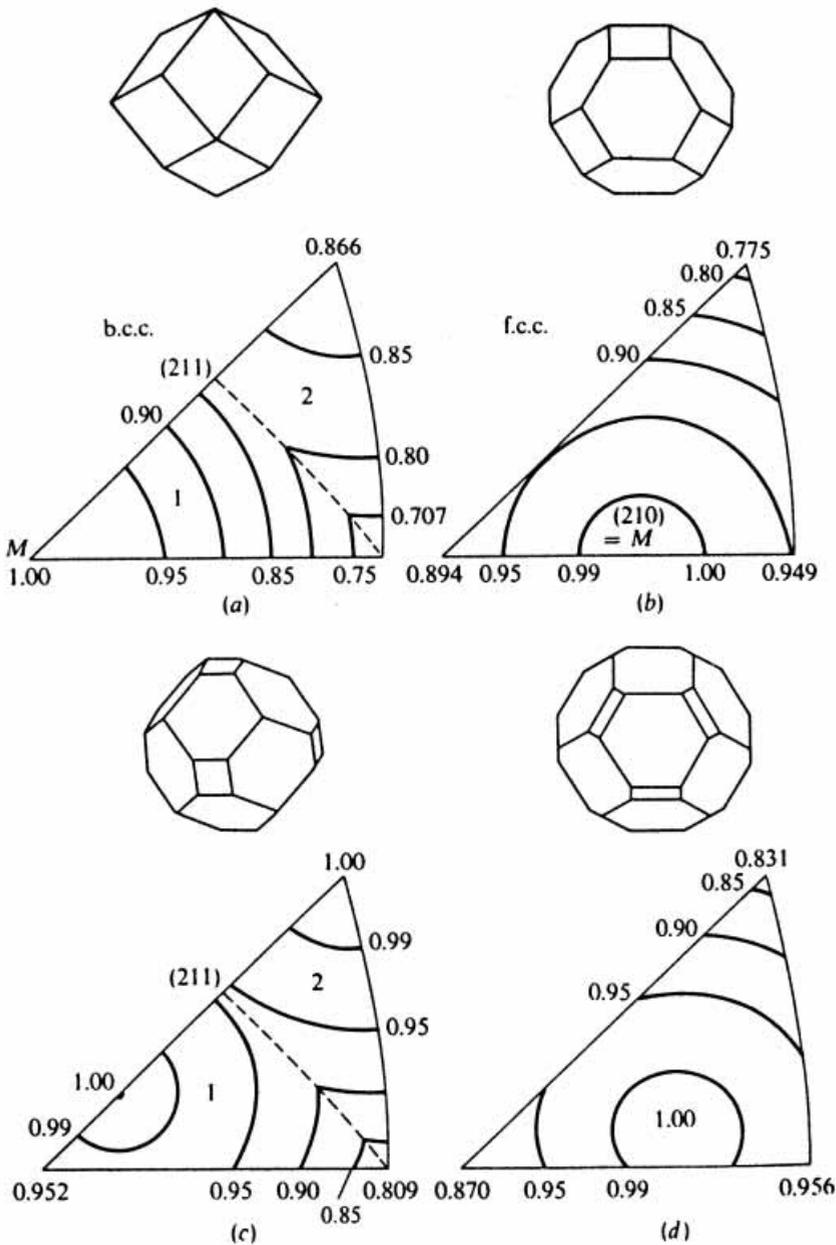


Figure 1.6.  $\gamma$ -Plots in a stereographic triangle (100, 110 and 111) and the corresponding equilibrium shapes for (a) b.c.c., (b) f.c.c., both with  $\rho=0$ ; (c) b.c.c. with  $\rho=0.5$ , and (d) f.c.c. with  $\rho=0.1$ ;  $\rho$  is the relative energy of the second nearest bond to that of the nearest neighbor bond (from Sundquist 1964, via Martin & Doherty 1976, reproduced with permission).

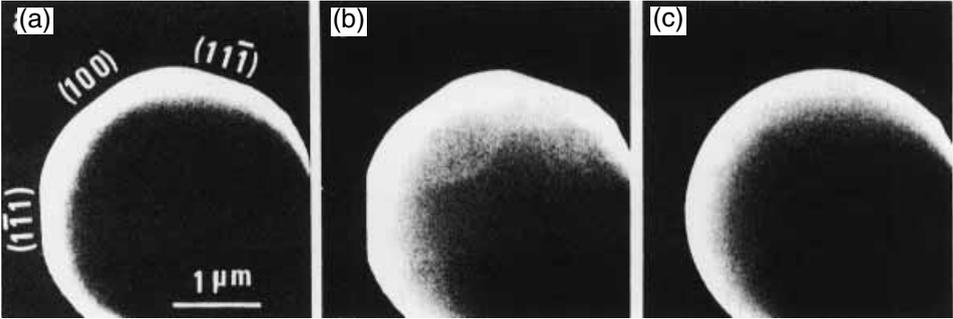


Figure 1.7. SEM photographs of the equilibrium shape of Pb crystals in the [011] azimuth, taken *in situ*: (a) at 300 °C, (b) at 320 °C, showing large rounded regions at 300 °C, and missing orientations at 320 °C; (c) at 327 °C where Pb is liquid and the drop is spherical (from Métois & Heyraud 1989, reproduced with permission).

dominant. Here this distinction is drawn sharply. An equilibrium effect is the vapor pressure of a crystal of a pure element; a typical kinetic effect is crystal growth from the vapor. These are compared and contrasted in this section.

### 1.3.1 Thermodynamics of the vapor pressure

The sublimation of a pure solid at equilibrium is given by the condition  $\mu_v = \mu_s$ . It is a standard result, from the theory of perfect gases, that the chemical potential of the vapor at low pressure  $p$  is

$$\mu_v = -kT \ln(kT/p\lambda^3), \quad (1.12)$$

where  $\lambda = h/(2\pi mkT)^{1/2}$  is the thermal de Broglie wavelength. This can be rearranged to give the equilibrium vapor pressure  $p_e$ , in terms of the chemical potential of the solid, as<sup>1</sup>

$$p_e = (2\pi m/h^2)^{3/2} (kT)^{5/2} \exp(\mu_s/kT). \quad (1.13)$$

Thus, to calculate the vapor pressure, we need a model of the chemical potential of the solid. A typical  $\mu_s$  at low pressure is the ‘quasi-harmonic’ model, which assumes harmonic vibrations of the solid, at its (given) lattice parameter (Klein & Venables 1976). This free energy per particle

$$F/N = \mu_s = U_0 + \langle 3h\nu/2 \rangle + 3kT \langle \ln(1 - \exp(-h\nu/kT)) \rangle, \quad (1.14)$$

where the  $\langle \rangle$  mean average values. The (positive) sublimation energy at zero temperature  $T$ ,  $L_0 = -(U_0 + \langle 3h\nu/2 \rangle)$ , where the first term is the (negative) energy per particle in the solid relative to vapor, and the second is the (positive) energy due to zero-point vibrations.

<sup>1</sup> This result is derived in most thermodynamics textbooks but not all. See e.g. Hill (1960) pp. 79–80, Mandl (1988) pp. 182–183, or Baierlein (1999) pp. 276–278.

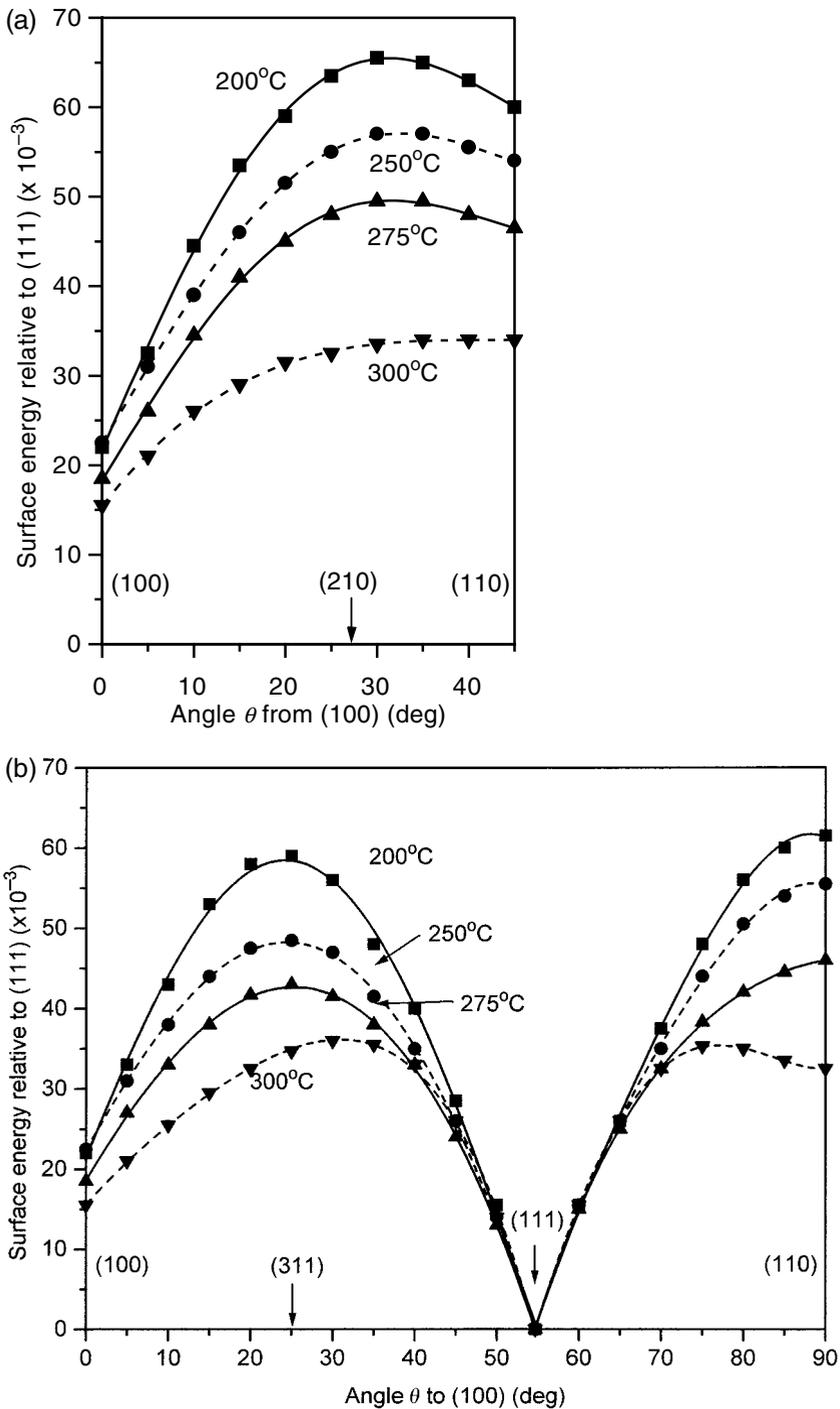


Figure 1.8. Anisotropy of  $\gamma(\theta)$  for Pb as a function of temperature, where the points are the original data, with errors  $\sim \pm 2$  on this scale, and the curves are fourth-order polynomial fits to these data: (a) in the  $\langle 100 \rangle$  zone; (b) in the  $\langle 110 \rangle$  zone. The relative surface energy scale is  $(\gamma(\theta)/\gamma(111) - 1) \times 10^{-3}$ , so 70 corresponds to  $\gamma(\theta) = 1.070 \times \gamma(111)$  (after Heyraud & Métois 1983, replotted with permission).

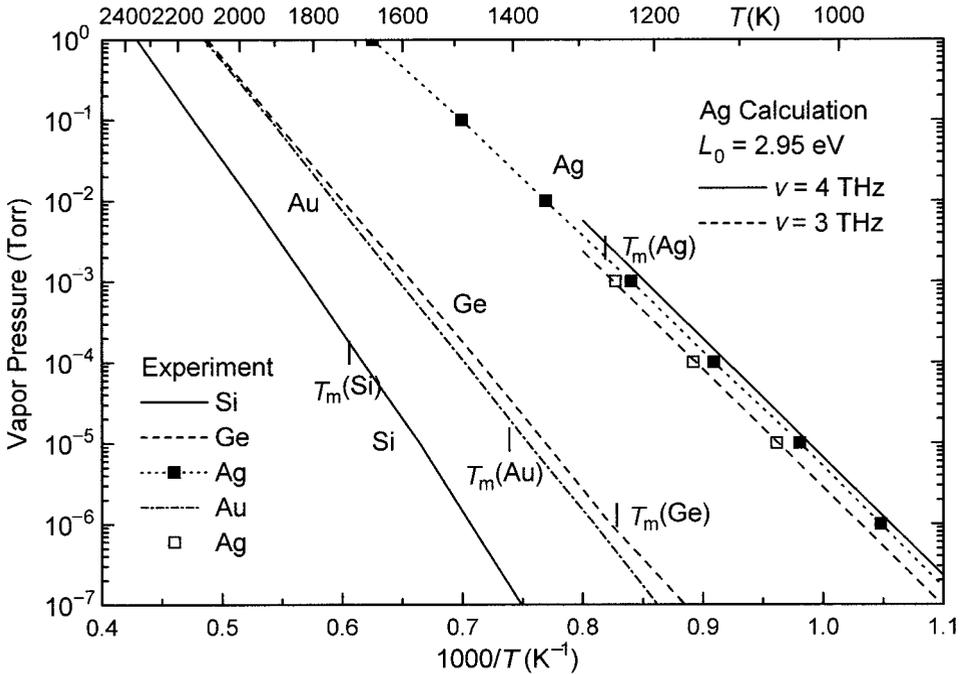


Figure 1.9. Arrhenius plot of the vapor pressure of Ge, Si, Ag and Au, using data from Honig & Kramer (1969). In the case of Ag, earlier handbook data for the solid are also given (open squares); the Einstein model with  $L_0 = 2.95$  eV and  $\nu = 3$  and 4 THz is shown for comparison with the Ag data.

The vapor pressure is significant typically at high temperatures, where the Einstein model of the solid is surprisingly realistic (provided thermal expansion is taken into account in  $U_0$ ). Within this model (all  $3N$   $\nu$ s are the same), in the high  $T$  limit, we have  $\langle \ln(1 - \exp(-h\nu/kT)) \rangle = \langle \ln(h\nu/kT) \rangle$ , so that  $\exp(\mu_s/kT) = (h\nu/kT)^3 \exp(-L_0/kT)$ . This gives

$$p_e = (2\pi m \nu^2)^{3/2} (kT)^{-1/2} \exp(-L_0/kT), \quad (1.15)$$

so that  $p_e T^{1/2}$  follows an Arrhenius law, and the pre-exponential depends on the lattice vibration frequency as  $\nu^3$ . The absence of Planck's constant  $h$  in the answer shows that this is a classical effect, where equipartition of energy applies.

The  $T^{1/2}$  term is slowly varying, and many tabulations of vapor pressure simply express  $\log_{10}(p_e) = A - B/T$ , and give the constants  $A$  and  $B$ . This equation is closely followed in practice over many decades of pressure; some examples are given in figures 1.9 and 1.10. Calculations along the above lines yield values for  $L_0$  and  $\nu$ , as indicated for Ag on figure 1.9. Values abstracted using the Einstein model equations in their general form are given in table 1.1. For the rare gas solids, vapor pressures have been measured over 13 decades, as shown in figure 1.10; yet this can still often be well fitted by the two-parameter formula (Crawford 1977). This large data span means that the sublimation energies are accurately known: the frequencies given here are good to

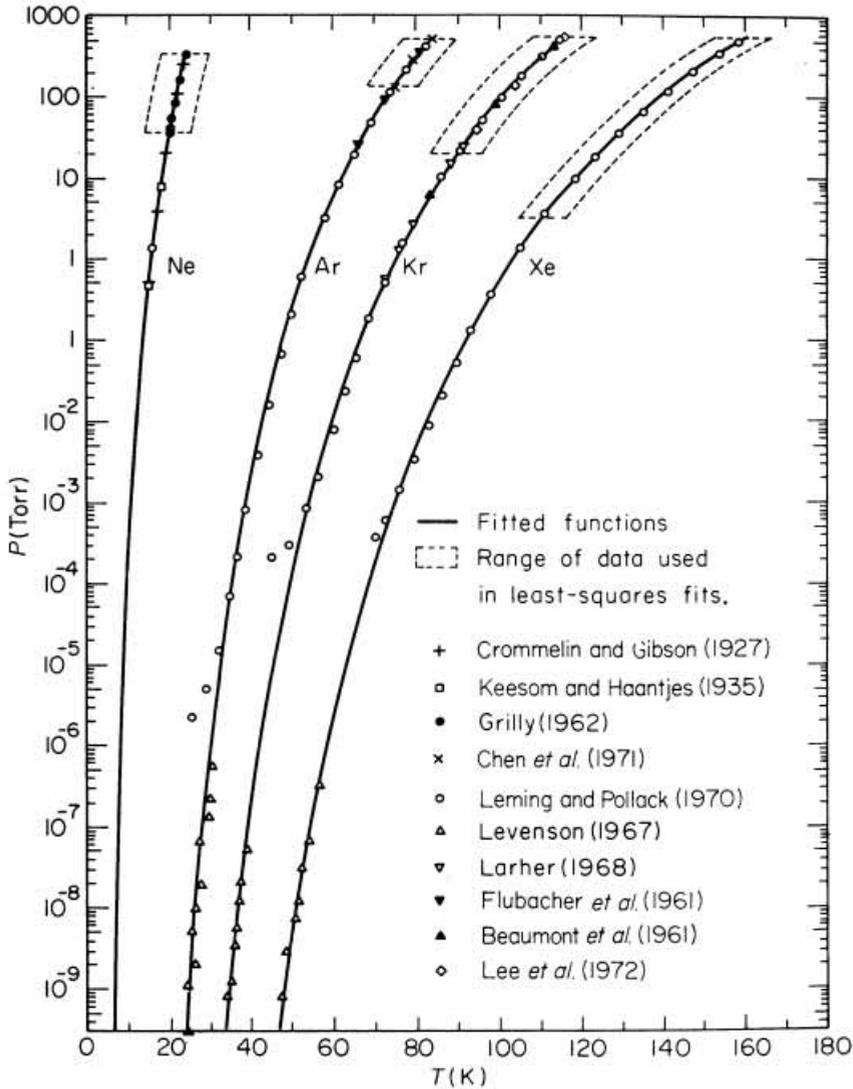


Figure 1.10. Vapor pressure of the rare gases Ne, Ar, Kr and Xe. The fits (except for Ne) are to the simplest two-parameter formula  $\log_{10}(p_v) = A - B/T$  (from Crawford 1977, and references therein; reproduced with permission).

maybe  $\pm 20\%$ , and depend on the use of the (approximate) Einstein model. These points can be explored further via problem 1.3.

The point to understand about the above calculation is that the vapor pressure does not depend on the structure of the surface, which acts simply as an intermediary: i.e., the surface is ‘doing its own thing’ in equilibrium with both the crystal and the vapor. What the surface of a Kossel crystal looks like can be visualized by Monte Carlo (MC) or other simulations, as indicated in figure 1.11. At low temperature, the terraces are

Table 1.1. *Lattice constants, sublimation energies and Einstein frequencies of some elements*

Element	Lattice constant ( $a_0$ ) nm	Sublimation energy ( $L_0$ ) eV or K	Einstein frequency $\nu$ (THz)
Metals			
Ag	0.4086 (f.c.c.) at RT	$2.95 \pm 0.01$ eV	4
Au	0.4078	$3.82 \pm 0.04$	3
Fe	0.2866 (b.c.c.)	$4.28 \pm 0.02$	11
W	0.3165	$8.81 \pm 0.07$	7
Semiconductors			
Si	0.5430 (diamond)	$4.63 \pm 0.04$	15
Ge	0.5658	$3.83 \pm 0.02$	6
Van der Waals			
Ar	0.5368 (f.c.c.) at 50 K	84.5 meV or 981 K	1.02
Kr	0.5692	120      1394	0.84
Xe	0.6166	167      1937	0.73

almost smooth, with few adatoms or vacancies (see figure 1.4 for these terms). As the temperature is raised, the surface becomes rougher, and eventually has a finite interface width. There are distinct roughening and melting transitions at surfaces, each of them specific to each  $\{hkl\}$  crystal face. The simplest MC calculations in the so-called SOS (solid on solid) model show the first but not the second transition. Calculations on the roughening transition were developed in review articles by Leamy *et al.* (1975) and Weeks & Gilmer (1979); we do not consider this phenomenon further here, but the topic is set out pedagogically by several authors, including Nozières (1992) and Desjonquères & Spanjaard (1996, section 2.4).

### 1.3.2 The kinetics of crystal growth

This picture of a fluctuating surface which doesn't influence the vapor pressure applies to the equilibrium case, but what happens if we are not at equilibrium? The classic paper is by Burton, Cabrera & Frank (1951), known as BCF, and much quoted in the crystal growth literature. We have to consider the presence of kinks and ledges, and also (extrinsic) defects, in particular screw dislocations. More recently, other defects have been found to terminate ledges, even of sub-atomic height, and these are also important in crystal growth. The BCF paper, and the developments from it, are quite mathematical, so we will only consider a few simple cases here, in order to introduce terms and establish some ways of looking at surface processes.

First, we need the ideas of supersaturation  $S = (p/p_e)$ , and thermodynamic driving force,  $\Delta\mu = kT \ln S$ .  $\Delta\mu$  is clearly zero in equilibrium, is positive during condensation, and negative during sublimation or evaporation. The variable which enters into exponents is therefore  $\Delta\mu/kT$ ; this is often written  $\beta\Delta\mu$ , with  $\beta \equiv 1/kT$  standard notation in

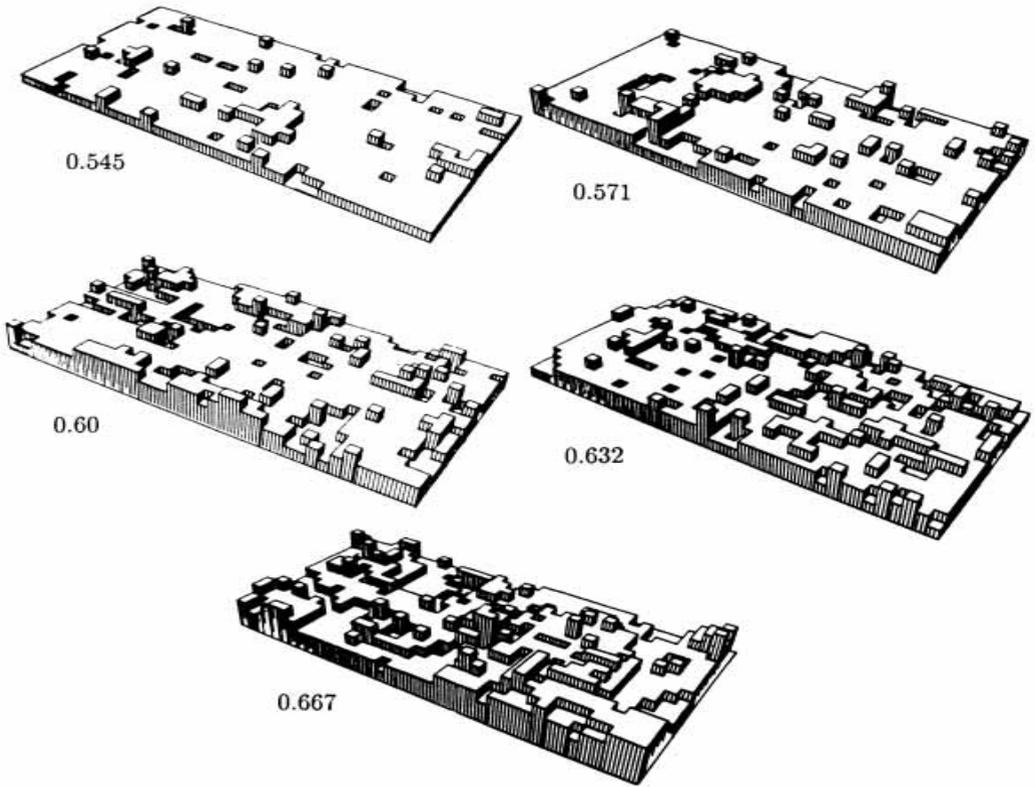


Figure 1.11. Monte Carlo simulations of the Kossel crystal developed within the solid on solid model for five reduced temperature values ( $kT/\phi$ ). The roughening transition occurs when this value is  $\sim 0.62$  (Weeks & Gilmer 1979, reproduced with permission).

statistical mechanics. The deposition rate or flux ( $R$  or  $F$  are used in the literature) is related, using kinetic theory, to  $p$  as  $R = p/(2\pi mkT)^{1/2}$ .

Second, an atom can adsorb on the surface, becoming an adatom, with a (positive) adsorption energy  $E_a$ , relative to zero in the vapor. (Sometimes this is called a desorption energy, and the symbols for all these terms vary wildly.) The rate at which the adatom desorbs is given, approximately, by  $\nu \exp(-E_a/kT)$ , where we might want to specify the pre-exponential frequency as  $\nu_a$  to distinguish it from other frequencies; it may vary relatively slowly (not exponentially) with  $T$ .

Third, the adatom can diffuse over the surface, with energy  $E_d$  and corresponding pre-exponential  $\nu_d$ . We expect  $E_d < E_a$ , maybe much less. Adatom diffusion is derived from considering a random walk in two dimensions, and the 2D diffusion coefficient is then given by

$$D = (\nu_d a^2 / 4) \exp(-E_d/kT), \quad (1.16)$$

and the adatom lifetime before desorption,

$$\tau_a = \nu_a^{-1} \exp(E_a/kT). \quad (1.17)$$

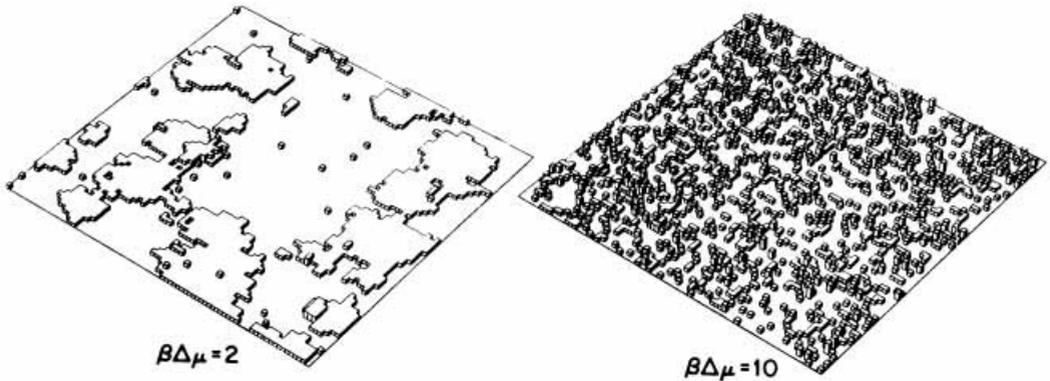


Figure 1.12. MC interface configurations after 0.25 monolayer deposition at the same temperature on terraces, under two different supersaturations  $\beta\Delta\mu = 2$  and 10; the bond strength is expressed as  $\phi = 4kT$  (Weeks & Gilmer 1979, reproduced with permission).

BCF then showed that  $x_s = (D\tau_a)^{1/2}$  is a characteristic length, which governs the fate of the adatom, and defines the role of ledges (steps) in evaporation or condensation. It is a useful exercise to familiarize oneself with the ideas of local equilibrium, and diffusion in one dimension. Local equilibrium can be described either in terms of differential equations or of chemical potentials as set out in problems 1.2 and 1.4; diffusion needs a differential equation formulation and/or a MC simulation.

The main points that result from the above considerations are as follows.

- (1) Crystal growth (or sublimation) is difficult on a perfect terrace, and substantial supersaturation (undersaturation) is required. When growth does occur, it proceeds through nucleation and growth stages, with monolayer thick islands (pits) having to be nucleated before growth (sublimation) can proceed; this is illustrated by early MC calculations in figure 1.12.
- (2) A ledge, or step on the surface captures arriving atoms within a zone of width  $x_s$  either side of the step, statistically speaking. If there are only individual steps running across the terrace, then these will eventually grow out, and the resulting terrace will grow much more slowly (as in point 1). In general, rough surfaces grow faster than smooth surfaces, so that the final ‘growth form’ consists entirely of slow growing faces;
- (3) The presence of a screw dislocation in the crystal provides a step (or multiple step), which spirals under the flux of adatoms. This provides a mechanism for continuing growth at modest supersaturation, as illustrated by MC calculations in figure 1.13 (Weeks & Gilmer 1979).

Detailed study shows that the growth velocity depends quadratically on the supersaturation for mechanism 3, and exponentially for mechanism 1, so that dislocations are dominant at low supersaturation, as shown in figure 1.14. Growth from the liquid and from solution has been similarly treated, emphasizing the internal energy change on melting  $L_m$ , and a single parameter  $\alpha$  proportional to  $L_m/kT$ , where  $\alpha < 2$  typical for melt growth of elemental solids corresponds to rough liquid–solid interfaces (Jackson

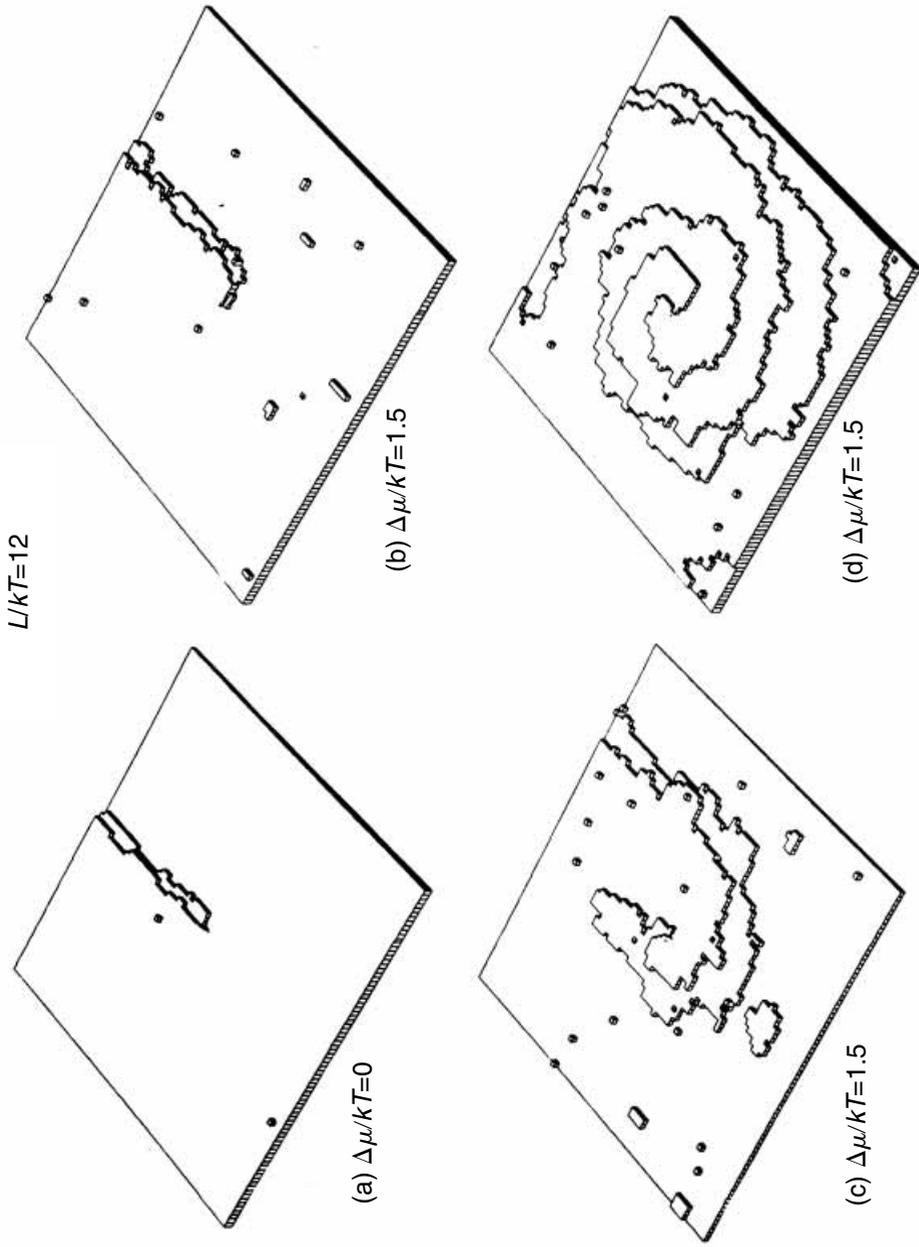


Figure 1.13. MC interface configurations during deposition in the presence of a screw dislocation which causes a double step (a) in equilibrium, and (b)–(d) as a function of time under supersaturation  $\beta\Delta\mu = 1.5$ , for bond strength expressed in terms of temperature as  $L/kT = 12$ , equivalent to  $\phi = 4kT$  (Weeks & Gilmer 1979, reproduced with permission).

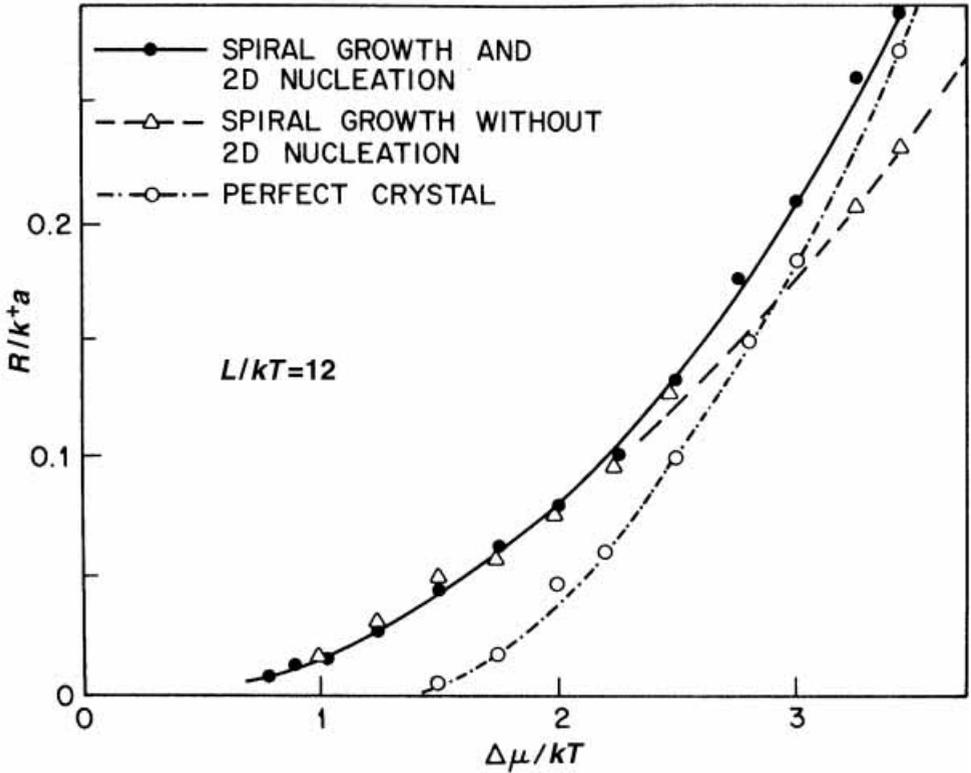


Figure 1.14. MC growth rates ( $R/k+a$ ) during deposition for spiral growth (in the presence of a screw dislocation) compared with nucleation on a perfect terrace as a function of supersaturation  $\beta\Delta\mu$ , for bond strength expressed in terms of temperature as  $L/kT=12$ , equivalent to  $\phi=4kT$  (Weeks & Gilmer 1979, reproduced with permission).

1958, Jackson *et al.* 1967, Woodruff 1973). Growth from the vapor via smooth interfaces are characterized by larger  $\alpha$  values, either because the sublimation energy  $L_0 \gg L_m$ , and/or the growth temperature is much lower than the melting temperature. Such an outline description is clearly only an introduction to a complex topic, and further information can be obtained from the books quoted, from several review articles (e.g. Leamy *et al.* 1975, Weeks & Gilmer 1979), or from more recent handbook articles (Hurle 1993, 1994). But the reader should be warned in advance that this is not a simple exercise; there are considerable notational difficulties, and the literature is widely dispersed. We return to some of these topics in chapters 5, 7 and 8.

## 1.4 Introduction to surface and adsorbate reconstructions

### 1.4.1 Overview

In this section, the ideas about surface structure which we will need for later chapters are introduced briefly. However, if you have never come across the idea of surface

reconstruction, it is advisable to supplement this description with one in another text-book from those given under further reading at the end of the chapter. This is also a good point to become familiar with low energy electron diffraction (LEED) and other widely used structural techniques, either from these books, or from a book especially devoted to the topic (e.g. Clarke 1985, chapters 1 and 2). A review by Van Hove & Somorjai (1994) contains details on where to find solved structures, most of which are available on disc, or in an atlas with pictures (Watson *et al.* 1996). We will not need this detail here, but it is useful to know that such material exists (see Appendix D).

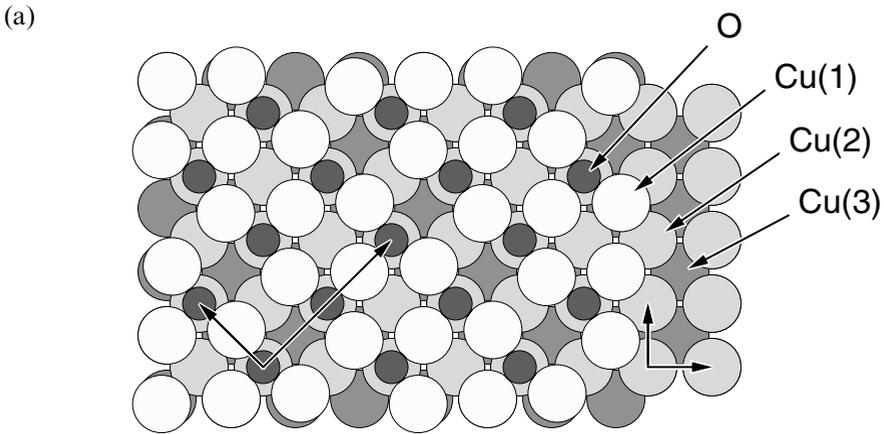
The rest of this section consists of general comments on structures (section 1.4.2), and, in sections 1.4.3–1.4.8, some examples of different reconstructions, their vibrations and phase transitions. There are many structures, and not all will be interesting to all readers: the structures described all have some connection to the rest of the book.

### 1.4.2 General comments and notation

Termination of the lattice at the surface leads to the destruction of periodicity, and a loss of symmetry. It is conventional to use the  $z$ -axis for the surface normal, leaving  $x$  and  $y$  for directions in the surface plane. Therefore there is no need for the lattice spacing  $c(z)$  to be constant, and in general it is not equal to the bulk value. One can think of this as  $c(z)$  or  $c(m)$  where  $m$  is the layer number, starting at  $m = 1$  at the surface. Then  $c(m)$  tends to the bulk value  $c_0$  or  $c$ , a few layers below the surface, in a way which reflects the bonding of the particular crystal and the specific crystal face.

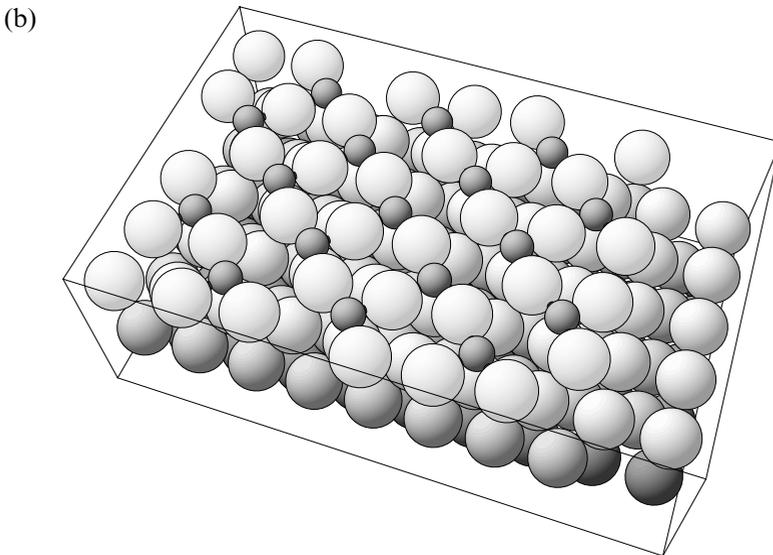
Equally, it is not necessary that the lateral periodicity in  $(x, y)$  is the same as the bulk periodicity  $(a, b)$ . On the other hand, because the surface layers are in close contact with the bulk, there is a strong tendency for the periodicity to be, if not the same, a simple multiple, sub-multiple or rational fraction of  $a$  and  $b$ , a commensurate structure. This leads to Wood's (1964) notation for surface and adsorbate layers. An example related to chemisorbed oxygen on Cu(001) is shown here in figure 1.15 (Watson *et al.* 1996). Note that we are using (001) here rather than the often used (100) notation to emphasize that the  $x$  and  $y$  directions are directions *in* the surface; however, these planes are equivalent in cubic crystals and can be written in general as  $\{100\}$ ; similarly, specific directions are written  $[100]$  and general directions  $\langle 100 \rangle$  in accord with standard crystallographic practice (see e.g. Kelly & Groves 1970).

But first let us get the basic notation straight, as this can be somewhat confusing. For example, here we have used  $(a, b, c)$  for the lattice constants; but these are not necessarily the normal lattice constants of the crystal, since they were defined with respect to a particular (hkl) surface. Also, several books use  $a_{1,2,3}$  for the real lattice and  $b_{1,2,3}$  for the reciprocal lattice, which is undoubtedly more compact. Wood's notation originates in a  $(2 \times 2)$  matrix  $M$  relating the surface parameters  $(a, b)$  or  $\mathbf{a}_s$  to the bulk  $(a_0, b_0)$  or  $\mathbf{a}_b$ . But the full notation, e.g. Ni(110)c(2 × 2)O, complete with the matrix  $M$ , is rather forbidding (Prutton 1994). If you were working on oxygen adsorption on nickel you would simply refer to this as a c(2 × 2), or 'centered 2 by 2' structure; that of adsorbed O on Cu(001)-(2√2 × √2)R45°-2O shown in figure 1.15 would, assuming the context were not confusing, be termed informally a 2√2 structure.



$\text{Cu}(100)-(2\sqrt{2}\times\sqrt{2})\text{R}45^\circ\text{-}2\text{O}$  (top view)

BALSAC plot



$\text{Cu}(100)-(2\sqrt{2}\times\sqrt{2})\text{R}45^\circ\text{-}2\text{O}$  (perspective)

BALSAC plot

Figure 1.15. Wood's notation, as illustrated for the chemisorbed structure  $\text{Cu}(001)-(2\sqrt{2}\times\sqrt{2})\text{R}45^\circ\text{-}2\text{O}$  in (a) top and (b) perspective view. The  $2\sqrt{2}$  and the  $\sqrt{2}$  represent the ratios of the lengths of the adsorbate unit cell to the substrate  $\text{Cu}(001)$  surface unit cell. The  $\text{R}45^\circ$  represents the angle through which the adsorbate cell is rotated to this substrate surface cell, and the  $2\text{O}$  indicates there are two oxygen atoms per unit cell. The different shading levels indicate Cu atoms in layers beneath the surface (after Watson *et al.* 1996, reproduced with permission).