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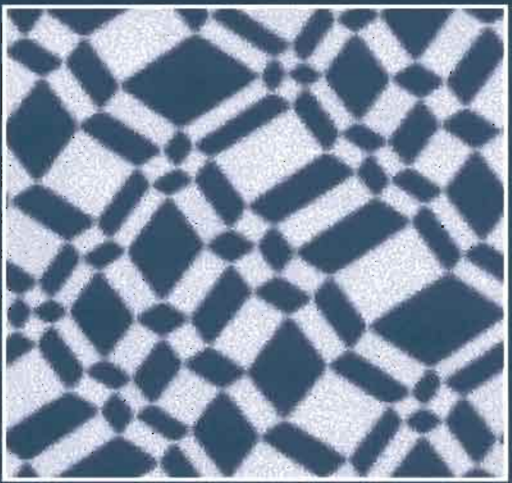
THE COMING OF MATERIALS SCIENCE

R.W. CAHN



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VOLUME 5

The Coming of Materials Science

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The Coming of Materials Science

by

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Cambridge, UK

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This book is dedicated to the memory of
Professor DANIEL HANSON (1892–1953)
of Birmingham University
who played a major role in modernising the teaching of Metallurgy
and thereby helped clear the ground for the emergence of Materials Science

Preface

My objective in writing this book, which has been many years in preparation, has been twofold. The discipline of materials science and engineering emerged from small beginnings during my professional life, and I became closely involved with its development; accordingly, I wanted to place on record the historical stages of that development, as well as premonitory things that happened long ago. My second objective, inseparable from the first, was to draw an impressionistic map of the present state of the subject, for readers coming new to it as well as for those well ensconced in research on materials. My subject-matter is the science, not the craft that preceded it, which has been well treated in a number of major texts. My book is meant primarily for working scientists and engineers, and also for students with an interest in the origins of their subject; but if some professional historians of science also find the contents to be of interest, I shall be particularly pleased.

The first chapter examines the emergence of the materials science concept, in both academe and industry, while the second and third chapters delve back into the prehistory of materials science (examining the growth of such concepts as atoms, crystals and thermodynamics) and also examine the evolution of a number of neighbouring disciplines, to see what helpful parallels might emerge. Thereafter, I pursue different aspects of the subject in varying depth. The book is in no sense a textbook of materials science; it should rather be regarded as a pointilliste portrait of the discipline, to be viewed from a slight distance. The space devoted to a particular topic is not to be regarded as a measure of the importance I attach to it, neither is the omission of a theme meant to express any kind of value judgment. I sought merely to achieve a reasonable balance between many kinds of themes within an acceptable overall length, and to focus on a few of the multitude of men and women who together have constructed materials science and engineering.

The numerous literature references are directed to two distinct ends: many refer to the earliest key papers and books, while others are to sources, often books, that paint a picture of the present state of a topic. In the early parts of the book, most references are to the distant past, but later on, as I treat the more modern parts of my subject, I refer to more recent sources.

There has been some dispute among professional historians of science as to who should be entitled to write a history such as this. Those trained as historians are understandably apt to resent the presumption of working scientists, in the evening of their days, in trying to take the bread from the historians' mouths. We, the superannuated scientists, are decried by some historians as 'whigs', mere uncritical celebrants of a perpetually advancing and improving insight into and control over nature. (A.R. Hall has called Whiggism "the writing of history as the story of an ascent to a splendid and virtuous climax"). There is some justice in this criticism, although not as much as its proponents are apt to claim. Another dispute, which has erupted recently into the so-called 'science wars', is between externalists who perceive science as an approach conditioned largely by social pressures (generally not recognized by the scientific practitioners themselves) and those, like myself, who take a mostly internalist stance and see scientific research as being primarily conditioned by the questions which flow directly from developing knowledge and from technological imperatives. The internalist/externalist dispute will never be finally resolved but the reader should at least be aware of its existence. At any rate, I have striven to be critical about the history of my own discipline, and to draw general conclusions about scientific practice from what I have discovered about the evolution of materials science.

One other set of issues runs through the book like a leitmotif: What *is* a scientific discipline? How do disciplines emerge and differentiate? Can a discipline also be interdisciplinary? Is materials science a real discipline? These questions are not just an exercise in lexicography and, looking back, it is perhaps the last of these questions which gave me the impetus to embark on the book.

A huge range of themes is presented here and I am bound to have got some matters wrong. Any reader who spots an error will be doing me a favor by kindly writing in and telling me about it at: rwc12@cam.ac.uk. Then, if by any chance there is a further edition, I can include corrections.

ROBERT CAHN
Cambridge, August 2000

Preface to Second Printing

The first printing being disposed of, the time has come to prepare a second printing. I am taking this opportunity to correct a substantial number of typographic mistakes and other small errors, which had escaped repeated critical read-throughs before the first printing. In addition, a small number of more substantial matters, such as inaccurate claims for priority of discovery, need to be put right, and these matters are dealt with in a *Corrigenda* at the very end of the book.

I am grateful to several reviewers and commentators for uncovering misprints, omissions and factual errors which I have been able to correct in this printing. My thanks go especially to Masahiro Koiwa in Japan, Jean-Paul Poirier and Jean Philibert in France, Jack Westbrook and Arne Hessenbruch in the United States.

ROBERT CAHN
Cambridge, October 2002

Acknowledgments

My thanks go first of all to Professor Sir Alan Cottrell, metallurgist, my friend and mentor for more than half a century, who has given me sage advice almost since I emerged from swaddling clothes. He has also very kindly read this book in typescript and offered his comments, helpful as always.

Next, I want to acknowledge my deep debt to the late Professor Cyril Stanley Smith, metallurgist and historian, who taught me much of what I know about the proper approach to the history of a technological discipline and gave me copies of many of his incomparable books, which are repeatedly cited in mine.

Professor Sir Brian Pippard gave me the opportunity, in 1993, to prepare a book chapter on the history of the physics of materials for a book, *Twentieth Century Physics*, that he was editing and which appeared in 1995; this chapter was a useful 'dry run' for the present work. I have also found his own contributions to that book a valuable source.

A book published in 1992, *Out of the Crystal Maze*, edited by Lillian Hoddeson and others, was also a particularly valuable source of information about the physics of materials, shading into materials science.

Dr. Frederick Seitz, doyen of solid-state physicists, has given me much helpful information, about the history of semiconductors in particular, and has provided an invaluable exemplar (as has Sir Alan Cottrell) of what a scientist can achieve in retirement.

Professor Colin Russell, historian of science and emeritus professor at the Open University, gave me helpful counsel on the history of chemistry and showed me how to take a philosophical attitude to the disagreements that beset the relation between practising scientists and historians of science. I am grateful to him.

The facilities of the Science Periodicals Library of Cambridge University, an unequalled source of information recent and ancient, and its helpful staff, together with those of the Whipple Library of the History and Philosophy of Science and the Library of the Department of Materials Science and Metallurgy, have been an indispensable resource.

Professors Derek Hull, Colin Humphreys and Alan Windle of my Department in Cambridge have successively provided ideal facilities that have enabled me to devote myself to the preparation of this book. My thanks go to them.

Hundreds of friends and colleagues all over the world, far too many to name, have sent me preprints and reprints, often spontaneously. The following have provided specific information, comments or illustrations, or given me interviews:

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ROBERT CAHN

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Chapter 1
Introduction

1.1. GENESIS OF A CONCEPT

Materials science emerged in USA, some time in the early 1950s. That phrase denoted a new scientific concept, born out of metallurgy, and this book is devoted to the emergence, development and consequences of that concept, in the US and elsewhere. Just who first coined the phrase is not known, but it is clear that by 1956 a number of senior research scientists had acquired the habit of using it. In 1958 and 1959 the new concept began to stimulate two developments in America: the beginnings of a change in the nature of undergraduate and graduate teaching in universities, and a radically new way of organising academic research on materials. The concept also changed the way industrial research was conceived, in a few important laboratories at least.

In this introductory chapter, I shall focus on the institutional beginnings of materials science, and materials engineering as well; indeed, "MSE" became an accepted abbreviation at quite an early stage. Following an examination, in Chapter 2, of the earlier emergence of some related disciplines, the intellectual antecedents to and development of materials science in its early stages are treated in Chapter 3. The field made its first appearance in USA, and for a number of years developed only in that country. Its development elsewhere was delayed by at least a decade.

1.1.1 Materials science and engineering in universities

Northwestern University, in Illinois not far from Chicago, was the first university to adopt materials science as part of a department title. That grew out of a department of metallurgy. Morris Fine, who was head of the department at the time, has documented the stages of the change (Fine 1990, 1994, 1996). He was a metallurgist, doing research at Bell Laboratories, when in early 1954 he was invited to visit Northwestern University to discuss plans to create a new graduate department of metallurgy there. (It is common at the leading American universities to organise departments primarily for work at graduate level, and in contrast to many other countries, the graduate students are exposed to extensive compulsory lecture courses.) In the autumn of 1954 Fine started at the University as a member of the new metallurgy department. In his letter of acceptance he had already mooted his wish to start a materials science programme in cooperation with other departments.

In spite of its graduate status, the new department did offer some undergraduate courses, initially for students in other departments. One of the members of faculty was Jack Frankel, who "was a disciple of Daniel Rosenthal at the University of California, Los Angeles... who had developed such a course there". Frankel worked out some of the implications of this precursor by developing a broadly based undergraduate lecture course at Northwestern and, on the basis of this, writing a book entitled *Principles of the Properties of Materials* (Frankel 1957). Fine remarks that "this course and Jack's thinking were key elements in developing materials science at Northwestern". Various other departments accepted this as a service course. According to the minutes of a faculty meeting in May 1956, it was resolved to publish in the next University Bulletin a paragraph which included the statement: "A student who has satisfactorily completed a programme of study which includes most of these (undergraduate) courses will be adequately prepared for professional work or graduate study in metallurgy and *materials science*". So, from 1957, undergraduates could undertake a broad study of materials in a course provided by what was still a metallurgy department. In February of 1958, a memorandum was submitted to the responsible academic dean, with the title *The Importance of Materials Science and Engineering*. One sentence in this document, which was received with favour by the dean, reads: "Traditionally the field of material science (even at this early stage, the final 's' in the adjective, 'materials', was toggled on and off) has developed along somewhat separate channels – solid state physics, metallurgy, polymer chemistry, inorganic chemistry, mineralogy, glass and ceramic technology. Advance in materials science and technology is hampered by this artificial division of the whole science into separate parts." The document went on to emphasise "the advantages of bringing together a group of specialists in the various types of materials and allowing and *encouraging* their cooperation and free interchange of ideas". Clearly this proposal was approved at a high level, for at a meeting a few months later, in December 1958, the metallurgy faculty meeting resolved, nemine contradicente, to change the name of the Graduate Department of Metallurgy to Graduate Department of Materials Science, and in January 1959 the university trustees approved this change.

At almost the same time as the 1958 faculty meeting, the US President's Science Advisory Committee referred to universities' attempts to "establish a new materials science and engineering" and claimed that they needed government help (Psaras and Langford 1987, p. 23).

The dean told the head of the department that various senior metallurgists around America had warned that the new department might "lose out in attracting students" by not having 'metallurgy' as part of its title. That issue was left open, but the department clearly did not allow itself to be intimidated and *Materials Science* became its unqualified name (although '*and Engineering*' was soon afterwards added to that name, to "better recognise the character of the department that had been formed"). The department did not lose out. Other departments in the English-speaking world have been more cautious: thus, my own department in Cambridge University began as "Metallurgy", eventually became "Metallurgy and Materials Science" and finally, greatly daring, changed to "Materials Science and Metallurgy". The final step cannot be more than a few decades off. The administrators of Oxford University, true to their reputation for pernicketiness, raised their collective eyebrows at the use of a plural noun, 'materials', in adjectival function. The department of materials science there, incensed, changed its name simply to 'Department of Materials', and some other universities followed suit.

Fine, who as we have seen played a major part in willing the new structure into existence, had (Fine 1996) "studied solid-state quantum mechanics and statistical mechanics as a graduate student in metallurgy (at the University of Minnesota)". It is striking that, as long ago as the 1940s, it was possible for an American student of metallurgy to work on such topics in his graduate years: it must have been this early breadth of outlook that caused materials science education, which is centred on the pursuit of breadth, to begin in that part of the world.

From 1959, then, the department of materials science at Northwestern University taught graduates the new, broad discipline, and an undergraduate course for materials science and engineering majors followed in due course. The idea of that discipline spread fast through American universities, though some eminent metallurgists such as Robert F. Mehl fiercely defended the orthodox approach to physical metallurgy. Nevertheless, by 1969 (Harwood 1970) some 30% of America's many university departments of metallurgy carried a title involving combinations of the words 'materials science' and 'metallurgy'. We are not told how quickly the 'materials engineering' part of the nomenclature was brought in. By 1974, the COSMAT Report (COSMAT 1974), on the status of MSE, remarked that America had some 90 "materials-designated" baccalaureate degree courses, $\approx$60 of them accredited, and that $\approx$50 institutions in America by then offered graduate degrees in materials. Today, not many departments of metallurgy remain in America; they have almost all changed to MSE. Different observers give somewhat inconsistent figures; thus, Table 1.1 gives statistics assembled by Lyle Schwartz in 1987, from American Society of Metals sources.

Henceforth, 'materials science' will normally be used as the name of the field with which this book is concerned; when the context makes it particularly appropiate to include 'and engineering' in the name, I shall use the abbreviation "MSE", and occasionally I shall be discussing materials engineering by itself.

There were also universities which did not set up departments of materials science but instead developed graduate programmes as an interdepartmental venture, usually but not always within a 'College of Engineering'. An early

Table 1.1. Trends in titles of materials departments at US universities, 1964–1985, after Lyle, in Psaras and Langford 1987.

Department title	Number of departments, by year		
	1964	1970	1985
Minerals and mining	9	7	5
Metallurgy	31	21	17
Materials	11	29	51
Other	18	21	17
Total	69	78	90

example of this approach was in the University of Texas at Austin, and this is described in some detail by Fine (1994). At the time he wrote his overview, 38 fulltime faculty members and 90 students were involved in this graduate programme: the students gain higher degrees in MSE even though there is no department of that name. "Faculty expertise and graduate student research efforts are concentrated in the areas of materials processing, solid-state chemistry, polymer engineering and science, X-ray crystallography, biomaterials, structural materials, theory of materials (whatever that means!) and solid-state (electronic?) materials and devices". Fine discusses the pros and cons of the two distinct ways of running graduate programmes in MSE. It may well be that the Texas way is a more effective way of forcing polymers into the curriculum; that has always proved to be a difficult undertaking. I return to this issue in Chapter 14. The philosophy underlying such interdepartmental programmes is closely akin to that which led in 1960 to the interdisciplinary materials research laboratories in the USA (Section 1.1.3).

To give a little more balance to this story, it is desirable to outline events at another American university, the Massachusetts Institute of Technology. A good account of the very gradual conversion from metallurgy to MSE has been provided in a book (Bever 1988) written to celebrate the centenary of the first course in which metallurgy was taught there (in combination with mining); this has been usefully supplemented by an unpublished text supplied by David Kingery (1927–2000), an eminent ceramist (Kingery 1999). As is common in American universities, a number of specialities first featured at graduate level and by stages filtered through to undergraduate teaching. One of these specialities was ceramics, introduced at MIT by Frederick H. Norton who joined the faculty in 1933 and taught there for 29 years. Norton, a physicist by training, wrote the definitive text on refractory materials. His field expanded as mineral engineering declined and was in due course sloughed off to another department. Kingery, a chemist by background, did his doctoral research with Norton and joined the faculty himself in 1950. He says: "Materials science, ceramic science and most of what we think of as advanced technology did not exist in 1950, but the seeds had been sown in previous decades and were ready to sprout. The Metallurgy Department had interests in process metallurgy, physical metallurgy, chemical metallurgy and corrosion, but, in truth, *the properties and uses of metals are not very exciting* (my italics). The ceramics activity was one division of the Metallurgy Department, and from 1949 onwards, higher degrees in ceramic engineering could be earned. During the 1950s, we developed a ceramics program as a fully interdisciplinary activity." He goes on to list the topics of courses taken by (presumably graduate) students at that time, in colloid science, spectroscopy, thermodynamics and surface chemistry, crystal structure and X-ray diffraction, dielectric and ferroelectric materials and quantum physics. The words in italics, above, show what we all know, that to succeed in a new endeavour it is necessary to focus one's enthusiasm intensely. For Kingery, who has been extremely influential in the evolution of ceramics as a constituent of MSE, ceramics constitute the heart and soul of MSE. With two colleagues, he wrote a standard undergraduate text on ceramics (Kingery 1976). By stages, he refocused on the truly modern aspects of ceramics, such as the role of chemically modified grain boundaries in determining the behaviour of electronic devices (Kingery 1981).

In 1967, the department's name (after much discussion) was changed to 'Metallurgy and Materials Science' and not long after that, a greatly broadened undergraduate syllabus was introduced. By that time, 9 years after the Northwestern initiative, MIT took the view that the change of name would actually enhance the department's attractiveness to prospective students. In 1974, after further somewhat acrimonious debates, the department's name changed again to 'Materials Science and Engineering'. It is to be noted, however, that the reality changed well before the name did. Shakespeare's Juliet had, perhaps, the essence of the matter:

> "What's in a name? That which we call a rose By any other name would smell as sweet".

All the foregoing has been about American universities. Materials science was not introduced in European universities until well into the 1960s. I was in fact the first professor to teach and organise research in MSE in Britain – first as professor of materials technology at the University College of North Wales, 1962–1964, and then as professor of materials science at the University of Sussex, 1965–1981. But before any of this came about, the Department of Physical Metallurgy at the University of Birmingham, in central England, under the visionary leadership of Professor Daniel Hanson and starting in 1946, transformed the teaching of that hitherto rather qualitative subject into a quantitative and rigorous approach. With the essential cooperation of Alan Cottrell and Geoffrey Raynor, John Eshelby and Frank Nabarro, that Department laid the foundation of what was to come later in

America and then the world. This book is dedicated to the memory of Daniel Hanson.

1.1.2 MSE in industry

A few industrial research and development laboratories were already applying the ideas of MSE before those ideas had acquired a name. This was true in particular of William Shockley's group at the Bell Telephone Laboratories in New Jersey and also of General Electric's Corporate Laboratory in Schenectady, New York State. At Bell, physicists, chemists and metallurgists all worked together on the processing of the semiconductors, germanium and silicon, required for the manufacture of transistors and diodes: William Pfann, the man who invented zone-refining, without which it would have been impossible in the 1950s to make semiconductors pure enough for devices to operate at all (Riordan and Hoddeson 1997), was trained as a chemical engineer and inspired by his contact with a famous academic metallurgist. Later, Bell's interdisciplinary scientists led the way in developing hard metallic superconductors. Such a broad approach was not restricted to inorganic materials; the DuPont Research Station in Delaware, as early as the 1930s, had enabled an organic chemist, Carothers, and a physical chemist, Flory, both scientists of genius, to create the scientific backing that eventually brought nylon to market (Morawetz 1985, Hounshell and Smith 1988, Furukawa 1998); the two of them, though both chemists, made quite distinct contributions.

The General Electric Laboratory has a special place in the history of industrial research in America: initially directed by the chemist Willis Whitney from 1900, it was the first American industrial laboratory to advance beyond the status of a troubleshooting addendum to a factory (Wise 1985). The renowned GE scientists, William Coolidge and Irving Langmuir (the latter a Nobel prizewinner for the work he did at GE) first made themselves indispensable by perfecting the techniques of manufacturing ductile tungsten for incandescent light bulbs, turning it into coiled filaments to reduce heat loss and using inert gases to inhibit blackening of the light bulb (Cox 1979). Langmuir's painstaking research on the interaction of gases and metal surfaces not only turned the incandescent light bulb into a practical reality but also provided a vital contribution to the understanding of heterogeneous catalysis (Gaines and Wise 1983). A steady stream of scientifically intriguing and commercially valuable discoveries and inventions continued to come from the Schenectady laboratory, many of them relating to materials: as to the tungsten episode, a book published for Coolidge's 100th birthday and presenting the stages of the tungsten story in chronological detail (including a succession of happy accidents that were promptly exploited) claims that an investment of just $116,000 produced astronomical profits for GE (Liebhafsky 1974).

In 1946, a metallurgist of great vision joined this laboratory in order to form a new metallurgy research group. He was J.H. (Herbert) Hollomon (1919–1985). One of the first researchers he recruited was David Turnbull, a physical chemist by background. I quote some comments by Turnbull about his remarkable boss, taken from an unpublished autobiography (Turnbull 1986): "Holloman, then a trim young man aged 26, was a most unusual person with quite an overpowering personality. He was brash, intense, completely self-assured and overflowing with enthusiasm about prospects for the new group. He described the fascinating, but poorly understood, responses of metals to mechanical and thermal treatments and his plans to form an interdisciplinary team, with representation from metallurgy, applied mechanics, chemistry and physics, to attack the problems posed by this behaviour. He was certain that these researches would lead to greatly improved ability to design and synthesise new materials that would find important technological uses and expressed the view that equipment performance was becoming more materials- than design-limited... Hollomon was like no other manager. He was rarely neutral about anything and had very strong likes and dislikes of people and ideas. These were expressed openly and vehemently and often changed dramatically from time to time. Those closely associated with him usually were welcomed to his inner sanctum or consigned to his outer doghouse. Most of us made, I think, several circuits between the sanctum and the doghouse. Hollomon would advocate an idea or model vociferously and stubbornly but, if confronted with contrary evidence of a convincing nature, would quickly and completely reverse his position without the slightest show of embarrassment and then uphold the contrary view with as much vigour as he did the former one..." In an internal GE obituary, Charles Bean comments: "Once here, he quickly assembled an interdisciplinary team that led the transformation of metallurgy from an empirical art to a field of study based on principles of physics and chemistry". This transformation is the subject-matter of Chapter 5 in this book.

Hollomon's ethos, combined with his ferocious energy and determination, and his sustained determination to recruit only the best researchers to join his group, over the next 15 years led to a sequence of remarkable innovations related to materials, including man-made diamond, high-quality thermal insulation, a vacuum circuit-breaker, products based on etched particle tracks in irradiated solids, polycarbonate plastic and, particularly, the "Lucalox" alumina envelope for a metal–vapour lamp. (Of course many managers besides Hollomon were involved.) A brilliant, detailed account of these innovations and the arrangements that made them possible was later written by Guy Suits and his successor as director, Arthur Bueche (Suits and Bueche 1967). Some of these specific episodes will feature later in this book, but it helps to reinforce the points made here about Hollomon's conception of broad research on materials if I point out that the invention of translucent alumina tubes for lamps was a direct result of untrammelled research by R.L. Coble on the mechanism of densification during the sintering of a ceramic powder. There have been too few such published case-histories of industrial innovation in materials; many years ago, I put the case for pursuing this approach to gaining insight (Cahn 1970).

The projects outlined by Suits and Bueche involved collaborations between many distinct disciplines (names and scientific backgrounds are punctiliously listed), and it was around this time that some of the protagonists began to think of themselves as materials scientists. Hollomon outlined his own conception of "Materials Science and Engineering"; this indeed was the title of an essay he brought out some years after he had joined GE (Hollomon 1958), and here he explains what kind of creatures he conceived materials scientists and materials engineers to be. John Howe, who worked in the neighbouring Knolls Atomic Power Laboratory at that time, has told me that in the 1950s, he and Hollomon frequently discussed "the need for a broader term as more fundamental concepts were developed" (Howe 1987), and it is quite possible that the new terminology in fact evolved from these discussions at GE. Hollomon concluded his essay: "The professional societies must recognise this new alignment and arrange for its stimulation and for the association of those who practice both the science and engineering of materials. We might even need an American Materials Society with divisions of science and engineering. Metallurgical engineering will become materials engineering. OUT OF METALLURGY, BY PHYSICS, COMES *MATERIALS SCIENCE* (my capitals)." It was to be many years before this prescient advice was heeded; I return to this issue in Chapter 14. Westbrook and Fleischer, two luminaries of the GE Laboratory's golden days, recently dedicated a major book to Hollomon, with the words: "Wise, vigorous, effective advocate of the relevance and value of scientific research in industry" (Westbrook and Fleischer 1995); but a little later still, Fleischer in another book (Fleischer 1998) remarked drily that when Hollomon left the Research Center to take up the directorship of GE's General Engineering Laboratory, he suddenly began saying in public: "Well, we know as much about science as we need. Now is the time to go out and use it". Circumstances alter cases. It is not surprising that as he grew older, Hollomon polarised observers into fierce devotees and implacable opponents, just as though he had been a politician.

Suits and Bueche conclude their case-histories with a superb analysis of the sources, tactics and uses of applied research, and make the comment: "The case histories just summarised show, first of all, the futility of trying to label various elements of the research and development process as 'basic', 'applied' or 'development'. Given almost any definition of these terms, one can find variations or exceptions among the examples."

Hollomon's standing in the national industrial community was recognised in 1955 when the US National Chamber of Commerce chose him as one of the ten outstanding young men in the country. Seven years later, President Kennedy brought Hollomon to Washington as the first Assistant Secretary of Commerce for Science and Technology, where he did such notable things as setting up a President's Commission on the Patent System in order to provide better incentives for overcoming problems in innovation. He showed his scientific background in his habit of answering the question: "What is the problem?" with "90% of the problem is in understanding the problem" (Christenson 1985).

1.1.3 The materials research laboratories

As we have seen, the concept of MSE emerged early in the 1950s and by 1960, it had become firmly established, as the result of a number of decisions in academe and in industry. In that year, as the result of a sustained period of intense discussion and political lobbying in Washington, another major decision was taken, this time by agencies of the US Government. The Interdisciplinary Laboratories were born.

According to recent memoirs by Frederick Seitz (1994) and Sproull (1987), the tortuous negotiations that led to this outcome began in 1954, when the great mathematician and computer theorist, John von Neumann, became '*the* scientist commissioner' of the five-member Atomic Energy Commission (AEC). (This remark presumably means that the other four commissioners were not scientists.) He thereupon invited Seitz to visit him (he had witnessed Seitz's researches in materials science – indeed, Seitz is one of the most eminent progenitors of materials science – during his frequent visits to the University of Illinois) and explained that he "was especially upset that time and time again what he wanted to do was prevented by an inadequate science of materials. When he asked what limited the growth of that science, he was told 'Lack of people'." According to Seitz, von Neumann worried that MSE was being treated as a side issue by the Government, and he proposed that federal agencies, starting with the AEC, join in funding a number of interdisciplinary materials research laboratories at universities. He then asked Seitz to join him in specifically developing a proposal for the protoype laboratory to be set up at the University of Illinois, to be funded at that stage just by the AEC. Clearly in view of his complaint, what von Neumann had in mind was *both* a place where interdisciplinary research on materials would be fostered *and* one where large numbers of new experts would be nurtured.

A formal proposal was developed and submitted, early in 1957, but before this could result in a contract, von Neumann was taken ill and died. Things were then held in abeyance until the launch of the Soviet Sputnik satellite in October 1957 changed everything. Two things then happened: a proposal to fund 12 laboratories emerged in Washington and Charles Yost of the Air Force's Office of Air Research was put in charge of making this happen. Thereupon Donald Stevens, head of the

Metallurgy and Materials Branch of the AEC, who remembered von Neumann's visionary plan for the University of Illinois specifically, set about putting this into effect. Seitz (1994) recounts the almost surrealistic difficulties put in the way of this project by a succession of pork-barrelling Senators; Illinois failed to become one of the three (not twelve, as initially proposed) initial Materials Research Laboratories chosen out of numerous applicants (the first ones were set up at Cornell, Pennsylvania and Northwestern), but in 1962 Illinois did finally acquire an MRL. Sproull (1987) goes into considerable detail concerning the many Government agencies that, under a steady push from Dr. Stevens and Commissioner Willard Libby of the AEC, collaborated in getting the project under way. Amusingly, a formal proposal from Hollomon, in early 1958, that a National Materials Laboratory should be created instead, quickly united everyone behind the original proposal; they all recognised that Hollomon's proposed laboratory would do nothing to enhance the supply of trained materials scientists and engineers.

Some 20 years after the pressure for the creation of the new interdisciplinary laboratories was first felt, one of the academics who became involved very early on, Prof. Rustum Roy of Pennsylvania State University, wrote eloquently about the underlying ideal of interdisciplinarity (Roy 1977). He also emphasised the supportive role played by some influential industrial scientists in that creation, notably Dr. Guy Suits of GE, whom we have already encountered, and Dr. William Baker of Bell Laboratories who was a major force in pushing for interdisciplinary materials research in industry and academe alike. A magisterial survey by Baker (1967), under the title *Solid State Science and Materials Development*, indicates the breadth and scope of his scientific interests.

Administratively, the genesis of these Laboratories, which initially were called Interdisciplinary Research Laboratories and later, Materials Research Laboratories, involved many complications, most of them in Washington, not least when in 1972 responsibility for them was successfully transferred to the National Science Foundation (NSF). As Sproull cynically remarks: "To those unfamiliar with the workings of federal government (and especially Capitol Hill), transfer of a program sounds simple, but it is simple only if the purpose of transfer is to kill the program".

Lyle, in a multiauthor book published by the two National Academies to celebrate the 25th birthday of the MRLs (Psaras and Langford, 1987), gives a great deal of information about their achievements and modus operandi. By then, 17 MRLs had been created, and 7 had either been closed down or were in process of termination. The essential feature of the laboratories was, and is, the close proximity and consequent cooperation between members of many different academic departments, by constructing dedicated buildings in which the participating faculty members had offices as well as laboratories. This did not impede the faculty members' continuing close involvement with their own departments' activities. At the time of the transfer to the NSF, according to Lyle, in 12 MRLs, some 35% were physicists, 25% were chemists, 19% were metallurgists *or members of MSE departments*, 16% were from other engineering disciplines (mainly electrical), and 5% from other departments such as mathematics or earth sciences. In my view, the most significant feature of these statistics is the large percentage of physicists who in this way became intimately involved in the study of materials. This is to be viewed in relation to Sproull's remark (Sproull 1987) that in 1910, "chemistry and metallurgy had already hailed many centuries of contributions to the understanding of materials... but physics' contribution had been nearly zero".

The COSMAT Report of 1974 (a major examination of every aspect of MSE, national and international, organised by the National Academy of Sciences, itself reviewed in 1976 in some depth by Cahn (reprinted 1992), was somewhat critical of the MRLs in that the rate of increase of higher degrees in the traditional metallurgy/materials department was no faster than that of engineering degrees overall. Lyle counters this criticism by concluding that "much of the interdisciplinarity sought in the original... concept was realised through evolutionary changes in the traditional materials departments rather than by dramatic changes in interactions across university departmental lines. This cross-departmental interaction would come only with the group research concept introduced by NSF." The point here is that teaching in the 'traditional' departments, even at undergraduate levels, was deeply influenced by the research done in the MRLs. From the perspective of today, the 37 years, to date, of MRLs can be considered an undiluted good.

1.1.4 Precursors, definitions and terminology

This book is primarily directed at professional materials scientists and engineers, and they have no urgent need to see themselves defined. Indeed, it would be perfectly reasonable to say about materials science what Aaron Katchalsky used to say about his new discipline, biophysics: "Biophysics is like my wife. I know her, but I cannot define her" (Markl 1998). Nevertheless, in this preliminary canter through the early history of MSE, it is instructive to examine briefly how various eminent practitioners have perceived their changing domain.

David Turnbull, in his illuminating *Commentary on the Emergence and Evolution of "Materials Science"* (Turnbull 1983), defined materials science "broadly" as "the characterisation, understanding, and control of the structure of matter at the ultramolecular level and the relating of this structure to properties (mechanical, magnetic, electrical, etc.). That is, it is 'Ultramolecular Science'." In professional and educational practice, however, he says that materials science focuses on the more complex features of behaviour, and especially those aspects controlled by crystal defects. His definition at once betrays Turnbull's origin as a physical chemist. Only a chemist, or possibly a polymer physicist, would focus on molecules when so many important materials have no molecules, as distinct from atoms or ions. Nomenclature in our field is sometimes highly confusing: thus in 1995 a journal began publication under the name *Supramolecular Science*, by which the editor-in-chief means "supramolecular aggregates, assemblies and nanoscopic materials"; that last adjective seems to be a neologism.

The COSMAT Report of 1974, with all its unique group authority, defines MSE as being "concerned with the generation and application of knowledge relating the composition, structure, and processing of materials to their properties and uses". It is probably a fair comment on this simple definition that in the early days of MSE the chief emphasis was on structure and especially structural defects (as evidenced by a famous early symposium proceedings entitled *Imperfections in Nearly Perfect Crystals* (Shockley et al. 1952), while in recent years more and more attention has been paid to the influence of processing variables.

As mentioned above, Sproull (1987) claimed that physics had contributed almost nothing to the understanding of materials before 1910, but went on to say that in the 1930s, books such as Hume-Rothery's *The Structure of Metals and Alloys*, Mott and Jones's *Properties of Metals and Alloys*, and especially Seitz's extremely influential *The Modern Theory of Solids* of 1940, rapidly advanced the science of the solid state and gave investigators a common language and common concepts. Sproull's emphasis was a strongly physical one. Indeed, the statistics given above of disciplinary affiliations in the MRLs show that physicists, after a long period of disdain, eventually leapt into the study of materials with great enthusiasm. Solid-state physics itself had a hard birth in the face of much scepticism from the rest of the physics profession (Mott 1980, Hoddeson et al. 1992). But now, physics has become so closely linked with MSE that at times there have been academic takeover bids from physicists for the entire MSE enterprise... unsuccessful up to now.

Names of disciplines, one might think, are not particularly important: it is the reality that matters. I have already quoted Shakespeare to that effect. But it is not really as simple as that, as the following story from China (Kuo 1996) illustrates. In 1956, my correspondent, an electron microscopist, returned to China after a period in the West and was asked to help in formulating a Twelve-Year Plan of Scientific and Technological Development. At that time, China was overrun by thousands of Soviet experts who were not backward in making suggestions. They advised the"Chinese authorities to educate a large number of scientists in *metallovedenie*, a Russian term which means 'metal-knowledge', close to metallography, itself an antiquated German concept (*Metallographie*) which later converted into *Metallkunde* (what we today call *physical metallurgy* in English). The Russians translated *metallovedenie* into the Chinese term for *metal physics*, since Chinese does not have a word for physical metallurgy. The end-result of this misunderstanding was that in the mid-1960s, the Chinese found that they had far too many metal physicists, all educated in metal physics divisions of physics departments in 17 universities, and a bad lack of "engineers who understand alloys and their heat-treatment", yet it was this last which the Soviet experts had really meant. By that time, Mao had become hostile to the Soviet Union and the Soviet experts were gone. By 1980, only 3 of the original 17 metal physics divisions remained in the universities. An attempt was later made to train students in materials science. In the days when all graduates were still directed to their places of work in China, the "gentleman in the State Planning Department" did not really understand what materials science meant, and was inclined to give materials science graduates "a post in the materials depot".

Although almost the whole of this introductory chapter has been focused on the American experience, because this is where MSE began, later the 'superdiscipline' spread to many countries. In the later chapters of this book, I have been careful to avoid any kind of exclusive focus on the US. The Chinese anecdote shows, albeit in an extreme form, that other countries also were forced to learn from experience and change their modes of education and research. In fact, in most of the rest of this book, the emphasis is on topics and approaches in research, and not on particular places. One thing which is entirely clear is that the pessimists, always among us, who assert that all the really important discoveries in MSE have been made, are wrong: in Turnbull's words at a symposium (Turnbull 1980), "10 or 15 years from now there will be a conference similar to this one where many young enthusiasts, too naive to realize that all the important discoveries have been made, will be describing materials and processes that we, at present, have no inkling of". Indeed, there was and they did.

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Chapter 2

The Emergence of Disciplines

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Chapter 2

The Emergence of Disciplines

2.1. DRAWING PARALLELS

This entire book is about the emergence, nature and cultivation of a new discipline, materials science and engineering. To draw together the strings of this story, it helps to be clear about what a scientific discipline actually is; that, in turn, becomes clearer if one looks at the emergence of some earlier disciplines which have had more time to reach a condition of maturity. Comparisons can help in definition; we can narrow a vague concept by examining what apparently diverse examples have in common.

John Ziman is a renowned theoretical solid-state physicist who has turned himself into a distinguished metascientist (one who examines the nature and institutions of scientific research in general). In fact, he has successfully switched disciplines. In a lecture delivered in 1995 to the Royal Society of London (Ziman 1996), he has this to say: "Academic science could not function without some sort of internal social structure. This structure is provided by subject specialisation. Academic science is divided into disciplines, each of which is a recognised domain of organised teaching and research. It is practically impossible to be an academic scientist without locating oneself initially in an established discipline. *The fact that disciplines are usually very loosely organised* (my italics) does not make them ineffective. An academic discipline is much more than a conglomerate of university departments, learned societies and scientific journals. It is an 'invisible college', *whose members share a particular research tradition* (my italics). This is where academic scientists acquire the various theoretical paradigms, codes of practice and technical methods that are considered 'good science' in their particular disciplines... A recognised discipline or sub-discipline provides an academic scientist with a home base, a tribal identity, a social stage on which to perform as a researcher." Another attempt to define the concept of a scientific discipline, by the science historian Servos (1990, Preface), is fairly similar, but focuses more on intellectual concerns: "By a discipline, I mean a family-like grouping of individuals sharing intellectual ancestry and united at any given time by an interest in common or overlapping problems, techniques and institutions". These two wordings are probably as close as we can get to the definition of a scientific discipline in general.

The concept of an 'invisible college', mentioned by Ziman, is the creation of Derek de Solla Price, an influential historian of science and "herald of scientometrics" (Yagi et al. 1996), who wrote at length about such colleges and their role in the scientific enterprise (Price 1963, 1986). Price was one of the first to apply quantitative methods to the analysis of publication, reading, citation, preprint distribution and other forms of personal communication among scientists, including 'conference-crawling'. These activities define groups, the members of which, he explains, "seem to have mastered the art of attracting invitations from centres where they can work along with several members of the group for a short time. This done, they move to the next centre and other members. Then they return to home base, but always their allegiance is to the group rather than to the institution which supports them, unless it happens to be a station on such a circuit. For each group there exists a sort of commuting circuit of institutions, research centres, and summer schools giving them an opportunity to meet piecemeal, so that over an interval of a few years everybody who is anybody has worked with everybody else in the same category. Such groups constitute an *invisible college*, in the same sense as did those first unofficial pioneers who later banded together to found the Royal Society in 1660." An invisible college, as Price paints it, is apt to define, not a mature discipline but rather an emergent grouping which may or may not later ripen into a fully blown discipline, and this may happen at breakneck speed, as it did for molecular biology after the nature of DNA had been discovered in 1953, or slowly and deliberately, as has happened with materials science.

There are two particularly difficult problems associated with attempts to map the nature of a new discipline and the timing of its emergence. One is the fierce reluctance of many traditional scientists to accept that a new scientific grouping has any validity, just as within a discipline, a revolutionary new scientific paradigm (Kuhn 1970) meets hostility from the adherents of the established model. The other difficulty is more specific: a new discipline may either be a highly specific breakaway from an established broad field, or it may on the contrary represent a broad synthesis from a number of older, narrower fields: the splitting of physical chemistry away from synthetic organic chemistry in the nineteenth century is an instance of the former, the emergence of materials science as a kind of synthesis from metallurgy, solid-state physics and physical chemistry exemplifies the latter. For brevity, we might name these two alternatives *emergence by splitting* and *emergence by integration*. The objections that are raised against these two kinds of disciplinary creation are apt to be different: emergence by splitting is criticised for breaking up a hard-won intellectual unity, while emergence by integration is criticised as a woolly bridging of hitherto clearcut intellectual distinctions.

Materials science has in its time suffered a great deal of the second type of criticism. Thus Calvert (1997) asserts that "metallurgy remains a proper discipline, with fundamental theories, methods and boundaries. Things fell apart when the subject extended to become materials science, with the growing use of polymers, ceramics, glasses and composites in engineering. The problem is that all materials are different and we no longer have a discipline."

Materials science was, however, not alone in its integrationist ambitions. Thus, Montgomery (1996) recently described his own science, geology, in these terms: "Geology is a magnificent science; a great many phenomenologies of the world fall under its purview. It is unique in defining a realm all its own yet drawing within its borders the knowledge and discourse of so many other fields – physics, chemistry, botany, zoology, astronomy, various types of engineering and more (geologists are at once true 'experts' and hopeless 'generalists')." Just one of these assertions is erroneous: geology is not unique in this respect... materials scientists are both true experts and hopeless generalists in much the same way.

However a new discipline may arrive at its identity, once it has become properly established the corresponding scientific community becomes "extraordinarily tight", in the words of Passmore (1978). He goes on to cite the philosopher Feyerabend, who compared science to a church, closing its ranks against heretics, and substituting for the traditional "outside the church there is no salvation" the new motto "outside my particular science there is no knowledge". The most famous specific example of this is Rutherford's arrogant assertion early in this century: "There's physics... and there's stamp-collecting". This intense pressure towards exclusivity among the devotees of an established discipline has led to a counter-pressure for the emergence of broad, inclusive disciplines by the process of integration, and this has played a major part in the coming of materials science.

In this chapter, I shall try to set the stage for the story of the emergence of materials science by looking at case-histories of some related disciplines. They were all formed by splitting but in due course matured by a process of integration. So, perhaps, the distinction between the two kinds of emergence will prove not to be absolute. My examples are: physical chemistry, chemical engineering and polymer science, with brief asides about colloid science, solid-state physics and chemistry, and mechanics in its various forms.

2.1.1 The emergence of physical chemistry

In the middle of the nineteenth century, there was no such concept as *physical chemistry*. There had long been a discipline of inorganic chemistry (the French call it 'mineral chemistry'), concerned with the formation and properties of a great variety of acids, bases and salts. Concepts such as equivalent weights and, in due course, valency very slowly developed. In distinction to (and increasingly in opposition to) inorganic chemistry was the burgeoning discipline of organic chemistry. The very name implied the early belief that compounds of interest to organic chemists, made up of carbon, hydrogen and oxygen primarily, were the exclusive domain of living matter, in the sense that such compounds could only be synthesised by living organisms. This notion was eventually disproved by the celebrated synthesis of urea, but by this time the name, organic chemistry, was firmly established. In fact, the term has been in use for nearly two centuries.

Organic and inorganic chemists came into ever increasing conflict throughout the nineteenth century, and indeed as recently as 1969 an eminent British chemist was quoted as asserting that "inorganic chemistry is a ridiculous field". This quotation comes from an admirably clear historical treatment, by Colin Russell, of the progress of the conflict, in the form of a teaching unit of the Open University in England (Russell 1976). The organic chemists became ever more firmly focused on the synthesis of new compounds and their compositional analysis. Understanding of what was going on was bedevilled by a number of confusions, for instance, between gaseous atoms and molecules, the absence of such concepts as stereochemistry and isomerism, and a lack of understanding of the nature of chemical affinity. More important, there was no agreed atomic theory, and even more serious, there was uncertainty surrounding atomic weights, especially those of 'inorganic' elements. In 1860, what may have been the first international scientific conference was organised in Karlsruhe by the German chemist August Kekulé (1829–1896 – he who later, in 1865, conceived the benzene ring); some 140 chemists came, and spent most of their time quarrelling. One participant was an Italian chemist, Stanislao Cannizzaro (1826–1910) who had rediscovered his countryman Avogadro's Hypothesis (originally proposed in 1811 and promptly forgotten); that Hypothesis (it deserves its capital letter!) cleared the way for a clear distinction between, for instance, H and H_2. Cannizzaro eloquently pleaded Avogadro's cause at the Karlsruhe conference and distributed a pamphlet he had brought with him (the first scattering of reprints at a scientific conference, perhaps); this pamphlet finally convinced the numerous waverers of the rightness of Avogadro's ideas, ideas which we all learn in school nowadays.

This thumbnail sketch of where chemistry had got to by 1860 is offered here to indicate that chemists were mostly incurious about such matters as the nature and strength of the chemical bond or how quickly reactions happened; all their efforts went into methods of synthesis and the tricky attempts to determine the numbers of different atoms in a newly synthesised compound. The standoff between organic and inorganic chemistry did not help the development of the subject, although by the time of the Karlsruhe Conference in 1860, in Germany at least, the organic synthetic chemists ruled the roost.

Early in the 19th century, there were giants of natural philosophy, such as Dalton, Davy and most especially Faraday, who would have defied attempts to categorise them as physicists or chemists, but by the late century, the sheer mass of accumulated information was such that chemists felt they could not afford to dabble in physics, or vice versa, for fear of being thought dilettantes.

In 1877, a man graduated in chemistry who was not afraid of being thought a dilettante. This was the German Wilhelm Ostwald (1853–1932). He graduated with a master's degree in chemistry in Dorpat, a "remote outpost of German scholarship in Russia's Baltic provinces", to quote a superb historical survey by Servos (1990); Dorpat, now called Tartu, is in what has become Latvia, and its disproportionate role in 19th-century science has recently been surveyed (Siilivask 1998). Ostwald was a man of broad interests, and as a student of chemistry, he devoted much time to literature, music and painting – an ideal student, many would say today. During his master's examination, Ostwald asserted that "modern chemistry is in need of reform". Again, in Servos's words, "Ostwald's blunt assertion... appears as an early sign of the urgent and driving desire to reshape his environment, intellectual and institutional, that ran as an extended motif through his career... He sought to redirect chemists' attention from the substances participating in chemical reactions to the reactions themselves. Ostwald thought that chemists had long overemphasised the taxonomic aspects of their science by focusing too narrowly upon the composition, structure and properties of the species involved in chemical processes... For all its success, the taxonomic approach to chemistry left questions relating to the rate, direction and yield of chemical reactions unanswered. To resolve these questions and to promote chemistry from the ranks of the descriptive to the company of the analytical sciences, Ostwald believed chemists would have to study the conditions under which compounds formed and decomposed and pay attention to the problems of chemical affinity and equilibrium, mass action and reaction velocity. The arrow or equal sign in chemical equations must, he thought, become chemists' principal object of investigation."

For some years he remained in his remote outpost, tinkering with ideas of chemical affinity, and with only a single research student to assist him. Then, in 1887, at the young age of 34, he was offered a chair in chemistry at the University of Leipzig, one of the powerhouses of German research, and his life changed utterly. He called his institute (as the Germans call academic departments) by the name of 'general chemistry' initially; the name 'physical chemistry' came a little later, and by the late 1890s was in very widespread use. Ostwald's was however only the Second Institute of Chemistry in Leipzig; the First Institute was devoted to organic chemistry, Ostwald's bête noire. Physics was required for the realisation of his objectives because, as Ostwald perceived matters, physics had developed beyond the descriptive stage to the stage of determining the general laws to which phenomena were subject; chemistry, he thought, had not yet attained this crucial stage. Ostwald would have sympathised with Rutherford's gibe about physics and stamp-collecting. It is ironic that Rutherford received a Nobel Prize in *Chemistry* for his researches on radioactivity. Ostwald himself also received the Nobel Prize for Chemistry, in 1909, nominally at least for his work in catalysis, although his founding work in physical chemistry was on the law of mass action. (It would be a while before the Swedish

Academy of Sciences felt confident enough to award a chemistry prize overtly for prowess in physical chemistry, upstart that it was.)

Servos gives a beautifully clear explanation of the subject-matter of physical chemistry, as Ostwald pursued it. Another excellent recent book on the evolution of physical chemistry, by Laidler (1993) is more guarded in its attempts at definition. He says that "it can be defined as that part of chemistry that is done using the methods of physics, or that part of physics that is concerned with chemistry, i.e., with specific chemical substances", and goes on to say that it cannot be precisely defined, but that he can recognise it when he sees it! Laidler's attempt at a definition is not entirely satisfactory, since Ostwald's objective was to get away from insights which were specific to individual substances and to attempt to establish laws which were general.

About the time that Ostwald moved to Leipzig, he established contact with two scientists who are regarded today as the other founding fathers of physical chemistry: a Dutchman, Jacobus van 't Hoff (1852–1911) and a Swede, Svante Arrhenius (1859–1927). Some historians would include Robert Bunsen (1811–1899) among the founding fathers, but he was really concerned with experimental techniques, not with chemical theory.

Van't Hoff began as an organic chemist. By the time he had obtained his doctorate, in 1874, he had already published what became a very famous pamphlet on the 'tetrahedral carbon atom' which gave rise to modern organic stereochemistry. After this he moved, first to Utrecht, then to Amsterdam and later to Berlin; from 1878, he embarked on researches in physical chemistry, specifically on reaction dynamics, on osmotic pressure in solutions and on polymorphism (van't Hoff 1901), and in 1901 he was awarded the first Nobel Prize in chemistry. The fact that he was the first of the trio to receive the Nobel Prize accords with the general judgment today that he was the most distinguished and original scientist of the three.

Arrhenius, insofar as his profession could be defined at all, began as a physicist. He worked with a physics professor in Stockholm and presented a thesis on the electrical conductivities of aqueous solutions of salts. A recent biography (Crawford 1996) presents in detail the humiliating treatment of Arrhenius by his sceptical examiners in 1884, which nearly put an end to his scientific career; he was not adjudged fit for a university career. He was not the last innovator to have trouble with examiners. Yet, a bare 19 years later, in 1903, he received the Nobel Prize for Chemistry. It shows the unusual attitude of this founder of physical chemistry that he was distinctly surprised not to receive the Physics Prize, because he thought of himself as a physicist.

Arrhenius's great achievement in his youth was the recognition and proof of the notion that the constituent atoms of salts, when dissolved in water, dissociated into charged forms which duly came to be called *ions*. This insight emerged from laborious and systematic work on the electrical conductivity of such solutions as they were progressively diluted: it was a measure of the 'physical' approach of this research that although the absolute conductivity decreases on dilution, the molecular conductivity goes up... i.e., each dissolved atom or ion becomes more efficient on average in conducting electricity. Arrhenius also recognised that no current was needed to promote ionic dissociation. These insights, obvious as they seem to us now, required enormous originality at the time.

It was Arrhenius's work on ionic dissociation that brought him into close association with Ostwald, and made his name; Ostwald at once accepted his ideas and fostered his career. Arrhenius and Ostwald together founded what an amused German chemist called "the wild army of ionists"; they were so named because (Crawford 1996) "they believed that chemical reactions in solution involve only ions and not dissociated molecules", and thereby the ionists became "the Cossacks of the movement to reform German chemistry, making it more analytical and scientific". The ionists generated extensive hostility among some – but by no means all – chemists, both in Europe and later in America, when Ostwald's ideas migrated there in the brains of his many American research students (many of whom had been attracted to him in the first place by his influential textbook, *Lehrbuch der Allgemeinen Chemie*).

Later, in the 1890s, Arrhenius moved to quite different concerns, but it is intriguing that materials scientists today do not think of him in terms of the concept of ions (which are so familiar that few are concerned about who first thought up the concept), but rather venerate him for the *Arrhenius equation* for the rate of a chemical reaction (Arrhenius 1889), with its universally familiar exponential temperature dependence. That equation was in fact first proposed by van 't Hoff, but Arrhenius claimed that van 't Hoff's derivation was not watertight and so it is now called after Arrhenius rather than van 't Hoff (who was in any case an almost pathologically modest and retiring man).

Another notable scientist who embraced the study of ions in solution – he oscillated so much between physics and chemistry that it is hard to say where his prime loyalty belonged – was Walther Nernst, who in the way typical of German students in the 19th century wandered from university to university (Zürich, Berlin, Graz, Würzburg), picking up Boltzmann's ideas about statistical mechanics and chemical thermodynamics on the way, until he fell, in 1887, under Ostwald's spell and was invited to join him in Leipzig. Nernst fastened on the theory of electrochemistry as the key theme for his research and in due course he brought out a precocious book entitled *Theoretische Chemie*. His world is painted, together with acute sketch-portraits of Ostwald, Arrhenius, Boltzmann and other key figures of physical chemistry, by Mendelssohn (1973). We shall meet Nernst again in Section 9.3.2.

During the early years of physical chemistry, Ostwald did not believe in the existence of atoms... and yet he was somehow included in the wild army of ionists. He was resolute in his scepticism and in the 1890s he sustained an obscure theory of 'energetics' to take the place of the atomic hypothesis. How ions could be formed in a solution containing no atoms was not altogether clear. Finally, in 1905, when Einstein had shown in rigorous detail how the Brownian motion studied by Perrin could be interpreted in terms of the collision of dust motes with moving molecules (Chapter 3, Section 3.1.1), Ostwald relented and publicly embraced the existence of atoms.

In Britain, the teaching of the ionists was met with furious opposition among both chemists and physicists, as recounted by Dolby (1976a) in an article entitled "Debate on the Theory of Solutions – A Study of Dissent" and also in a book chapter (Dolby 1976b). A rearguard action continued for a long time. Thus, Dolby (1976a) cites an eminent British chemist, Henry Armstrong (1848–1937) as declaring, as late as 4 years after Ostwald's death (Armstrong 1936), that "the fact is, there has been a split of chemists into two schools since the intrusion of the Arrhenian faith... a new class of workers into our profession – people without knowledge of the laboratory and with sufficient mathematics at their command to be led astray by curvilinear agreements." It had been nearly 50 years before, in 1888–1898, that Armstrong first tangled with the ionists' ideas and, as Dolby comments, he was "an extreme individualist, who would never yield to the social pressures of a scientific community or follow scientific trends". The British physicist F.G. Fitzgerald, according to Servos, "suspected the ionists of practising physics without a licence". Every new discipline encounters resolute foes like Armstrong and Fitzgerald; materials science was no exception.

In the United States, physical chemistry grew directly through the influence of Ostwald's 44 American students, such as Willis Whitney who founded America's first industrial research laboratory for General Electric (Wise 1985) and, in the same laboratory, the Nobel prizewinner Irving Langmuir (who began his education as a metallurgist and went on to undertake research in the physical chemistry of gases and surfaces which was to have a profound effect on industrial innovation, especially of incandescent lamps). The influence of these two and others at GE was also outlined by the industrial historian Wise (1983) in an essay entitled "Ionists in Industry: Physical Chemistry at General Electric, 1900–1915". In passing, Wise here remarks: "Ionists could accept the atomic hypothesis, and some did; but they did not have to". According to Wise, "to these pioneers, an ion was not a mere incomplete atom, as it later became for scientists". The path to understanding is usually long and tortuous. The stages of American acceptance of the new discipline is also a main theme of Servos's (1990) historical study.

Two marks of the acceptance of the new discipline, physical chemistry, in the early 20th century were the Nobel prizes for its three founders and enthusiastic industrial approval in America. A third test is of course the recognition of a discipline in universities. Ostwald's institute carried the name of physical chemistry well before the end of the 19th century. In America, the great chemist William Noyes (1866–1936), yet another of Ostwald's students, battled hard for many years to establish physical chemistry at MIT which at the turn of the century was not greatly noted for its interest in fundamental research. As Servos recounts in considerable detail, Noyes had to inject his own money into MIT to get a graduate school of physical chemistry established. In the end, exhausted by his struggle, in 1919 he left MIT and moved west to California to establish physical chemistry there, jointly with such giants as Gilbert Lewis (1875–1946). When Noyes moved to Pasadena, as Servos puts it, California was as well known for its science as New England was for growing oranges; this did not take long to change. In America, the name of an academic department is secondary; it is the creation of a research (graduate) school that defines the acceptance of a discipline. In Europe, departmental names are more important, and physical chemistry departments were created in a number of major universities such as for instance Cambridge and Bristol; in others, chemistry departments were divided into a number of subdepartments, physical chemistry included. By the interwar period, physical chemistry was firmly established in European as well as American universities.

Another test of the acceptance of a new discipline is the successful establishment of new journals devoted to it, following the gradual incursion of that discipline into existing journals. The leading American chemical journal has long been the *Journal of the American Chemical Society*. According to Servos, in the key year 1896 only 5% of the articles in *JACS* were devoted to physical chemistry; 10 years later this had increased to 15% and by the mid 1920s, to more than 25%. The first journal devoted to physical chemistry was founded in Germany by Ostwald in 1887, the year he moved to his power base in Leipzig. The journal's initial title was *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre* (the last word means 'lore of relationships'), and a portrait of Bunsen decorated its first title page.

Nine years later, the *Zeitschrift für physikalische Chemie* was followed by the *Journal of Physical Chemistry*, founded in the USA by Wilder Bancroft (1867–1953), one of Ostwald's American students. The 'chequered career' of this journal is instructively analysed by both Laidler (1993) and Servos (1990). Bancroft (who spent more than half a century at Cornell University) seems to have been a difficult man, with an eccentric sense of humour; thus at a Ph.D. oral examination he asked the candidate "What in water puts out fires?", and after rejecting some of the answers the student gave with increasing desperation, Bancroft revealed that the right answer was 'a fireboat'. Any scientific author will recognize that this is not the ideal way for a journal editor to behave, let alone an examiner. There is no space here to go into the vagaries of Bancroft's personality (Laidler can be consulted about this), but many American physical chemists, Noyes among them, were so incensed by him and his editorial judgment that they boycotted his journal. It ran into financial problems; for a while it was supported from Bancroft's own ample means, but the end of the financial road was reached in 1932 when he had to resign as editor and the journal was taken over by the American Chemical Society. In Laidler's words, "the various negotiations and discussions that led to the wresting of the editorship from Bancroft also led to the founding of an important new journal, the *Journal of Chemical Physics*, which appeared in 1933". It was initially edited by Harold Urey (1893–1981) who promptly received the Nobel Prize for Chemistry in 1934 for his isolation of deuterium (it might just as well have been the physics prize). Urey remarked at the time that publication in the *Journal of Physical Chemistry* was "burial without a tombstone" since so few *physicists* read it. The new journal also received strong support from the ACS, in spite of (or because of?) the fact that it was aimed at physicists.

These two journals, devoted to *physical chemistry* and *chemical physics*, have continued to flourish peaceably side by side until the present day. I have asked expert colleagues to define for me the difference in the reach of these two fields, but most of them asked to be excused. One believes that chemical physics was introduced when quantum theory first began to influence the understanding of the chemical bond and of chemical processes, as a means of ensuring proper attention to quantum mechanics among chemists. It is clear that many eminent practitioners read and publish impartially in both journals. The evidence suggests that *JCP* was founded in 1933 because of despair about the declining standards of *JPC*. Those standards soon recovered after the change of editor, but a new journal launched with hope and fanfare does not readily disappear and so *JCP* sailed on. The inside front page of *JCP* carries this message: "The purpose of the *JCP* is to bridge a gap between the journals of physics and journals of chemistry. The artificial boundaries between physics and chemistry have now been in actual fact completely eliminated, and a large and active group is engaged in research which is as much the one as the other. It is to this group that the journal is rendering its principal service...".

One of the papers published in the first issue of *JCP*, by F.G. Foote and E.R. Jette, was devoted to the defect structure of FeO and is widely regarded as a classic. Frank Foote (1906–1998), a metallurgist, later became renowned for his contribution to the Manhattan Project and to nuclear metallurgy generally; so chemical physics certainly did not exclude metallurgy.

It is to be noted that 'chemical physics', its own journal apart, does not carry most of the other trappings of a recognised discipline, such as university departments bearing that name. It is probably enough to suggest that those who want to be thought of as chemists publish in *JPC* and those who prefer to be regarded as physicists, in *JCP* (together with a few who are neither physicists nor chemists).

But I am informed that theoretical *chemists* tend to prefer *JCP*. The path of the generaliser is a difficult one.

The final stage in the strange history of physical chemistry and chemical physics is the emergence of a new journal in 1999. This is called *PCCP*, and its subtitle is: *Physical Chemistry Chemical Physics: A Journal of the European Chemical Societies*. *PCCP*, we are told "represents the fusion of two long-established journals, *Faraday Transactions* and *Berichte der Bunsen-Gesellschaft* – the respective physical chemistry journals of the Royal Society of Chemistry (UK) and the Deutsche Bunsen-Gesellschaft für Physikalische Chemie...". Several other European chemical societies are also involved in the new journal. There is a 'college' of 12 editors. This development appears to herald the re-uniting of two sisterly disciplines after 66 years of separation.

One other journal which has played a key part in the recognition and development of physical chemistry needs to be mentioned; in fact, it is one of the precursors of the new *PCCP*. In 1903, the Faraday Society was founded in London. Its stated object was to "promote the study of electrochemistry, electrometallurgy, chemical physics, metallography and kindred subjects". In 1905, the *Transactions of the Faraday Society* began publication. Although 'physical chemistry' was not mentioned in the quoted objective, yet the Transactions have always carried a hefty dose of physical chemistry. The journal included the occasional reports of 'Faraday Discussions', special occasions for which all the papers are published in advance so that the meeting can concentrate wholly on intensive debate. From 1947, these *Faraday Discussions* have been published as a separate series; some have become famous in their own right, such as the 1949 and 1993 *Discussions on Crystal Growth*. Recently, the 100th volume (Faraday Division 1995) was devoted to a *Celebration of Physical Chemistry*, including a riveting account by John Polanyi of "How discoveries are made, and why it matters".

Servos had this to say about the emergence of physical chemistry: "Born out of revolt against the disciplinary structure of the physical sciences in the late 19th century, it (physical chemistry) soon acquired all the trappings of a discipline itself. Taking form in the 1880s, it grew explosively until, by 1930, it had given rise to a half-dozen or more specialities..." – the perfect illustration of *emergence by splitting*, twice over. Yet none of these subsidiary specialities have achieved the status of fullblown disciplines, and physical chemistry – with chemical physics, its alter ego – has become an umbrella field taking under its shelter a great variety of scientific activities.

There is yet another test of the acceptance of a would-be new discipline, and that is the publication of textbooks devoted to the subject. By this test, physical chemistry took a long time to 'arrive'. One distinguished physical chemist has written an autobiography (Johnson 1996) in which he says of his final year's study for a chemistry degree in Cambridge in 1937: "Unfortunately at this time, there was no textbook (in English) in general physical chemistry available so that to a large extent it was necessary to look up the original scientific papers referred to in the lectures. In many ways this was good practice though it was time-consuming." In 1940 this lack was at last rectified; it took more than half a century after the founding of the first journal in physical chemistry before the new discipline was codified in a comprehensive English-language text (Glasstone 1940).

So, physical chemistry has developed far beyond the vision of its three famous founders. But then, the great mathematician A.N. Whitehead once remarked that "a science which hesitates to forget its founders is lost"; he meant that it is dangerous to refuse to venture in new directions. Neither physical chemistry nor materials science has ever been guilty of such a refusal.

2.1.2 The origins of chemical engineering

Chemical engineering, as a tentative discipline, began at about the same time as did physical chemistry, in the 1880s, but it took rather longer to become properly established. In fact, the earliest systematic attempt to develop a branch of engineering focused on the large-scale manufacture of industrial chemicals took place at Boston Tech, the precursor of the Massachusetts Institute of Technology, MIT. According to a recent account of the early history of chemical engineering (Cohen 1996), the earliest course in the United States to be given the title 'chemical engineering' was organized and offered by Lewis Norton at Boston Tech in 1888. Norton, like so many other Americans, had taken a doctorate in chemistry in Germany. It is noteworthy that the first hints of the new discipline came in the form of a university teaching course and not, as with physical chemistry, in the form of a research programme. In that difference lay the source of an increasingly bitter quarrel between the chemical engineers and the physical chemists at Boston Tech, just about the time it became MIT.

Norton's course combined a "rather thorough curriculum in mechanical engineering with a fair background in general, theoretical and applied chemistry". Norton died young and the struggling chemical engineering course, which was under the tutelage of the chemistry department until 1921, came in due course under the aegis of William Walker, yet another German-trained American chemist who had established a lucrative sideline as a consulting chemist to industry. From the beginning of the 1900s, an irreconcilable difference in objectives built up in the Chemistry Department, between two factions headed by Arthur Noyes (see Section 2.1.1) and William Walker. Their quarrels are memorably described in Servos's book (1990). The issue was put by Servos in these words: "Should MIT broaden its goals by becoming a science-based university (which it scarcely was in 1900) with a graduate school oriented towards basic research and an undergraduate curriculum rooted in the fundamental sciences? Or should it reaffirm its heritage by focusing on the training of engineers and cultivating work in the applied sciences? Was basic science to be a means towards an end, or should it become an end in itself?" This neatly encapsulates an undying dispute in the academic world; it is one that cannot be ultimately resolved because right is on both sides, but the passage of time gradually attenuates the disagreement.

Noyes struggled to build up research in physical chemistry, even, as we have seen, putting his own personal funds into the endeavour, and Walker's insistence on focusing on industrial case-histories, cost analyses and, more generally, enabling students to master production by the ton rather than by the test tube, was wormwood and gall to Noyes. Nevertheless, Walker's resolute industry-centred approach brought ever-increasing student numbers to the chemical engineering programme (there was a sevenfold increase over 20 years), and so Noyes's influence waned and Walker's grew, until in desperation, as we have seen, Noyes went off to the California Institute of Technology. That was another academic institution which had begun as an obscure local 'Tech' and under the leadership of a succession of pure scientists it forged ahead in the art of merging the fundamental with the practical. The founders of MSE had to cope with the same kinds of forceful disagreements as did Noyes and Walker.

The peculiar innovation which characterised university courses from an early stage was the concept of *unit operations*, coined by Arthur Little at MIT in 1916. In Cohen's (1996) words, these are "specific processes (usually involving physical, rather than chemical change) which were common throughout the chemical industry. Examples are heating and cooling of fluids, distillation, crystallisation, filtration, pulverisation and so forth." Walker introduced unit operations into his course at MIT in 1905 (though not yet under that name), and later he, with coauthors, presented them in an influential textbook. Of the several advantages of this concept listed by Cohen, the most intriguing is the idea that, because unit operations were so general, they constituted a system which a consultant could use throughout the chemical industry without breaking his clients' confidences. Walker, and other chemical engineers in universities, introduced unit operations because of their practical orientation, but as Cohen explains, over the years a largely empirical treatment of processes was replaced by an ever more analytical and science-based approach. The force of circumstance and the advance in insight set at naught the vicious quarrel between the practical men and the worshippers of fundamental science.

Chemical engineering, like every other new discipline, also encountered discord as to its name: terms like 'industrial chemistry' or 'chemical technology' were widely used and this in turn led to serious objections from existing bodies when the need arose to establish new professional organisations. For instance, in Britain the Society for Chemical Industry powerfully opposed the creation of a specialised institution for chemical engineers. There is no space to detail here the involved minuets which took place in connection with the British and American Institutes of Chemical Engineering; Cohen's essay should be consulted for particulars.

The science/engineering standoff in connection with chemical engineering education was moderated in Britain because of a remarkable initiative that took place in Cambridge, England. Just after the War, in 1945, Shell, the oil and petrochemicals giant, gave a generous benefaction to Cambridge University to create a department of chemical engineering. The department was headed by a perfectionist mechanical engineer, Terence Fox (1912–1962)[1], who brought in many chemists, physical chemists in particular. One physical chemist, Peter Danckwerts (1916–1984), was sent away to MIT to learn some chemical engineering and later, in 1959, became a famous department head in his turn. (This was an echo of an early Cambridge professor of chemistry in the unregenerate days of the university in the 18th century, a priest who was sent off to the Continent to learn a little chemistry.) The unusual feature in Cambridge chemical engineering was that students could enter the department either after 2 years' initial study in engineering or alternatively after 2 years study in the natural sciences, including chemistry. Either way, they received the same specialist tuition once they started chemical engineering. This has worked well; according to an early staff member (Harrison 1996), 80–90% of chemical engineering students have always come by the 'science route'. This experience shows that science and engineering outlooks can coexist in fruitful harmony.

It is significant that the Cambridge benefaction came from the petroleum industry. In the early days of chemical engineering education, pioneered in Britain in Imperial College and University College in London, graduates had great difficulty in finding acceptance in the heavy chemicals industry, especially Imperial Chemical Industries, which reckoned that chemists could do everything needful. Chemical engineering graduates were however readily accepted by the oil industry, especially when refineries began at last to be built in Britain from 1953 onwards (Warner 1996). Indeed, one British university (Birmingham) created a department of oil engineering and later converted it to chemical engineering. Warner (1996) believes that chemists held in contempt the forcible breakdown of petroleum constituents before they were put together again into larger molecules, because this was so different from the classical methods of synthesis of complex organic molecules. So the standoff between organic and physical chemists finds an echo in the early hostility between organic chemists and petroleum technologists. Other early chemical engineers went into the explosives industry and, especially, into atomic energy.

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[1] Fox's perfectionism is illustrated by an anecdote: At a meeting held at ICI (his previous employer), Fox presented his final design for a two-mile cable transporter. Suddenly he clapped his hand to his head and exclaimed: "How *could* I have made such an error!" Then he explained to his alarmed colleagues: "I forgot to allow for the curvature of the Earth".

It took much longer for chemical engineering, as a technological profession, to find general acceptance, than it took for physical chemistry to become accepted as a valid field of research. Finally it was achieved. The second edition of the great Oxford English Dictionary, which is constructed on historical principles, cites an article in a technical journal published in 1957: "Chemical engineering is now recognized as one of the four primary technologies, alongside civil, mechanical and electrical engineering".

2.1.3 Polymer science

In 1980, Alexander Todd, at that time President of the Royal Society of Chemistry in London, was asked what had been chemistry's biggest contribution to society. He thought that despite all the marvellous medical advances, chemistry's biggest contribution was the development of polymerisation, according to the preface of a recent book devoted to the history of high-technology polymers (Seymour and Kirshenbaum 1986). I turn now to the stages of that development and the scientific insights that accompanied it.

During the 19th century chemists concentrated hard on the global composition of compounds and slowly felt their way towards the concepts of stereochemistry and one of its consequences, optical isomerism. It was van 't Hoff in 1874, at the age of 22, who proposed that a carbon atom carries its 4 valencies (the existence of which had been recognized by August Kekulé (1829–1896) in a famous 1858 paper) directed towards the vertices of a regular tetrahedron, and it was that recognition which really stimulated chemists to propose *structural* formulae for organic compounds. But well before this very major step had been taken, the great Swedish chemist Jöns Jacob Berzelius (1779–1848), stimulated by some comparative compositional analyses of butene and ethylene published by Michael Faraday, had proposed in 1832 that "substances of equal composition but different properties be called *isomers*". The following year he suggested that when two compounds had the same relative composition but different absolute numbers of atoms in each molecule, the larger one be called *polymeric*. These two terms are constructed from the Greek roots *mer* (a part), *iso* (same) and *poly* (many).

The term 'polymer' was slow in finding acceptance, and the concept it represented, even slower. The French chemist Marcellin Berthelot (1827–1907) used it in the 1860s for what we would now call an *oligomer* (*oligo* = few), a molecule made by assembling just 2 or 3 monomers into a slightly larger molecule; the use of the term to denote long-chain (macro-) molecules was delayed by many years. In a lecture he delivered in 1863, Berthelot was the first to discuss polymerisation (actually, oligomerisation) in some chemical detail.

Van 't Hoff's genial insight showed that a carbon atom bonded to chemically distinct groups would be asymmetric and, depending on how the groups were disposed in space, the consequent compound should show optical activity – that is, when dissolved in a liquid it would rotate the plane of polarisation of plane-polarised light. Louis Pasteur (1822–1895), in a famously precocious study, had discovered such optical activity in tartrates as early as 1850, but it took another 24 years before van 't Hoff recognized the causal linkage between optical rotation and molecular structure, and showed that laevorotary and dextrorotary tartrates were *stereoisomers*: they had structures related by reflection. Three-dimensional molecular structure interested very few chemists in this period, and indeed van 't Hoff had to put up with some virulent attacks from sceptical colleagues, notably from Berthelot who, as well as being a scientist of great energy and ingenuity, was also something of an intellectual tyrant who could never admit to being wrong (Jacques 1987). It was thus natural that he spent some years in politics as foreign minister and minister of education.

These early studies opened the path to the later recognition of steroisomerism in polymers, which proved to be an absolutely central concept in the science of polymers.

These historical stages are derived from a brilliant historical study of polymer science, by Morawetz (1985, 1995). This is focused strongly on the organic and physical chemistry of macromolecules. The corresponding technology, and its close linkage to the chemistry and stereochemistry of polymerisation, is treated in other books, for instance those by McMillan (1979), Liebhafsky et al. (1978), and Mossman and Morris (1994), as well as the previously mentioned book by Seymour and Kirshenbaum (1986).

Once stereochemistry had become orthodox, the chemistry of monomers, oligomers and polymers could at length move ahead. This happened very slowly in the remainder of the 19th century, although the first industrial plastics (based on natural products which were already polymerised), like celluloid and viscose rayon, were produced in the closing years of the century without benefit of detailed chemical understanding (Mossman and Morris 1994). Much effort went into attempts to understand the structure of natural rubber, especially after the discovery of vulcanisation by Charles Goodyear in 1855: rubber was broken down into constituents (devulcanised, in effect) and then many attempted to re-polymerise the monomer isoprene, with very indifferent success until O. Wallach, in 1887, succeeded in doing so with the aid of illumination – photopolymerisation. It was not till 1897 that a German chemist, C. Engler, recognised that "one need not assume that only similar molecules assemble" – the first hint that copolymers (like future synthetic rubbers) were a possibility in principle.

Rubber was only one of the many natural macromolecules which were first studied in the nineteenth century. This study was accompanied by a growing revolt among organic chemists against the notion that polymerised products really consisted of long chains with (inevitably) varying molecular weights. For the organic chemists, the holy grail was a well defined molecule of known and constant composition, molecular weight, melting-point, etc., usually purified by distillation or crystallisation, and those processes could not usually be applied to polymers. Since there were at that time no *reliable* methods for determining large molecular weights, it was hard to counter this resolute scepticism. One chemist, O. Zinoffsky, in 1886 found a highly ingenious way of proving that molecular weights of several thousands did after all exist. He determined an empirical formula of $C_{712}H_{1130}N_{214}S_2Fe_1O_{245}$ for haemoglobin. Since a molecule could not very well contain only a fraction of one iron atom, this empirical formula also represented the smallest possible size of the haemoglobin molecule, of weight 16,700. A molecule like haemoglobin was one thing, and just about acceptable to sceptical organic chemists: after all, it had a constant molecular weight, unlike the situation that the new chemists were suggesting for synthetic long-chain molecules.

At the end of the nineteenth century, there was one active branch of chemistry, the study of colloids, which stood in the way of the development of polymer chemistry. Colloid science will feature in Section 2.1.4; suffice it to say here that students of colloids, a family of materials like the glues which gave colloids their name, perceived them as small particles or micelles each consisting of several molecules. Such particles were supposed to be held together internally by weak, "secondary valences" (today we would call these van der Waals forces), and it became an article of orthodoxy that supposed macromolecules were actually micelles held together by weak forces and were called 'association colloids'. (Another view was that some polymers consisted of short closed-ring structures.) As Morawetz puts it, "there was almost universal conviction that large particles must be considered aggregates"; even the great physical chemist Arthur Noyes publicly endorsed this view in 1904. Wolfgang Ostwald (1886–1943), the son of Wilhelm Ostwald, was the leading exponent of colloid science and the ringleader of the many who scoffed at the idea that any long-chain molecules existed. Much of the early work on polymers was published in the *Kolloid-Zeitschrift*.

There was one German chemist, Hermann Staudinger (1881–1965), at one time a colleague of the above-mentioned Engler who had predicted copolymerisation, who was the central and obstinate proponent of the reality of long-chain molecules held together by covalent bonds. He first announced this conviction in a lecture in 1917 to the Swiss Chemical Society. He referred to "high-molecular compounds" from which later the term "high polymers" was coined to denote very long chains. Until he was 39, Staudinger practised conventional organic chemistry. Then he switched universities, returning from Switzerland to Freiburg in Germany, and resolved to devote the rest of his long active scientific life to macromolecules, especially to synthetic ones. As Flory puts it in the historical introduction to his celebrated polymer textbook of 1953, Staudinger showed that "in contrast to association colloids, high polymers exhibit colloidal properties in all solvents in which they dissolve" – in other words, they had *stable* molecules of large size.

At the end of the 1920s, Staudinger also joined a group of other scientists in Germany who began to apply the new technique of X-ray diffraction to polymers, notably Herman Mark (1895–1992) who was to achieve great fame as one of the fathers of modern polymer science (he was an Austrian who made his greatest contributions in America and anglicised his first name). One of the great achievements of this group was to show that natural rubber (which was amorphous or glasslike) could be crystallised by stretching; so polymers were after all not incapable of crystallising, which made rubber slightly more respectable in the eyes of the opponents of long chains. Staudinger devoted much time to the study of poly(oxymethylenes), and showed that it was possible to crystallise some of them (one of the organic chemists' criteria for 'real' chemical compounds). He showed that his crystalline poly(oxymethylene) chains, and other polymers too, were far too long to fit into one unit cell of the crystal structures revealed by X-ray diffraction, and concluded that the chains could terminate anywhere in a crystal after meandering through several unit cells. This, once again, was a red rag to the organic bulls, but finally in 1930, a meeting of the Kolloid-Gesellschaft, in Morawetz's words, "clearly signified the victory of the concept of long-chain molecules". *The consensus is that this fruitless battle, between the proponents of long-chain molecules and those who insisted that polymers were simply colloidal aggregates, delayed the arrival of large-scale synthetic polymers by a decade or more.*

Just how long-chain molecules can in fact be incorporated in regular crystal lattices, when the molecules are bound to extend through many unit cells, took a long time to explain. Finally, in 1957, three experimental teams found the answer; this episode is presented in Chapter 8.

The story of Staudinger's researches and struggles against opposition, and also of the contributions of Carothers who is introduced in the next paragraph, is brilliantly told in a very recent historical study (Furukawa 1998).

There are two great families of synthetic polymers, those made by addition methods (notably, polyethylene and other polyolefines), in which successive monomers simply become attached to a long chain, and those made by condensation reactions (polyesters, polyamides, etc.) in which a monomer becomes attached to the end of a chain with the generation of a small by-product molecule, such as water. The first sustained programme of research directed specifically to finding new synthetic macromolecules involved mostly condensation reactions and was masterminded by Wallace Carothers (1896–1937) an organic chemist of genius who in 1928 was recruited by the Du Pont company in America and the next year (just before the colloid scientists threw in the towel) started his brilliant series of investigations that resulted notably in the discovery and commercialisation, just before the War, of nylon. In Flory's words, Carothers's investigations "were singularly successful in establishing the molecular viewpoint and in dispelling the attitude of mysticism then prevailing in the field". Another major distinction which needs to be made is between polymers made from bifunctional monomers (i.e., those with just two reactive sites) and monomers with three or more reactive sites. The former can form unbranched chains, the latter form branched, three-dimensional macromolecules. What follows refers to the first kind.

The first big step in making addition polymers came in 1933 when ICI, in England, decided to apply high-pressure methods to the search, inspired by the great American physicist Percy Bridgman (1882 1961) who devoted his life as an experimentalist to determining the changes in materials wrought by large hydrostatic pressures (see Section 4.2.3). ICI found that in the presence of traces of oxygen, ethylene gas under high pressure and at somewhat raised temperature would polymerise (Mossman and Morris 1994). Finally, after many problems had been overcome, on the day in 1939 that Germany invaded Poland, the process was successfully scaled up to a production level. Nothing was announced, because it turned out that this high-pressure polyethylene was ideal as an insulator in radar circuits, with excellent dielectric properties. The Germans did not have this product, because Staudinger did not believe that ethylene could be polymerised. Correspondingly, nylon was not made publicly available during the War, being used to make parachutes instead.

The ICI process, though it played a key part in winning the Battle of Britain, was difficult and expensive and it was hard to find markets after the War for such a costly product. It was therefore profoundly exciting to the world of polymers when, in 1953, it became known that a 'stereoactive' polymerisation catalyst (aluminium triethyl plus titanium tetrachloride) had been discovered by the German chemist Karl Ziegler (1898–1973) that was able to polymerise ethylene to yield crystallisable ('high-density') polyethylene. This consisted of unbranched chains with a regular (trans) spatial arrangement of the CH_2 groups. It was 'high-density' because the regularly constructed chains can pack more densely than the partly amorphous ('semicrystalline') low-density material made by ICI's process.

Ziegler's success was followed shortly afterwards by the corresponding achievement by the Italian chemist Giulio Natta (1903–1979), who used a similar catalyst to produce stereoregular (isotactic) polypropylene in crystalline form. That in turn was followed in short order by the use of a similar catalyst in America to produce stereoregular polyisoprene, what came to be called by the oxymoron synthetic natural rubber'. These three products, polyethylene, polypropylene and polyisoprene and their many derivatives, were instantly taken up by industry around the world and transformed the markets for polymers, because (for instance) high-density polyethylene was very much cheaper to make than the low-density form and moreover its properties and physical form could be tailor-made for particular end-uses. Through the canny drafting of contracts, Ziegler was one of the few innovators who has actually made a good deal of money from his discovery.

This entire huge development was dependent on two scientific insights and one improvement in technique. The insights were the recognition of the chain nature of high polymers and of the role of the stereotactic nature of those chains. These insights were not generally accepted until after 1930. The technique (or better, battery of techniques) was the collection of gradually improved methods to determine average molecular weight and of molecular weight distribution. These methods included osmometry and viscometry (early methods) and moved on to use of the ultracentrifuge, light-scattering and finally, gel-permeation chromatography. A lively eyewitness account of some of these developments is provided by two of the pioneers, Stockmayer and Zimm (1984), under the title "When polymer science looked easy".

Up to about 1930, polymer science was the exclusive province of experimental chemists. Thereafter, there was an ever-growing input from theoretical chemists and also physicists, who applied the methods of statistical mechanics to understanding the thermodynamics of assemblies of long-chain molecules, and in particular to the elucidation of rubber elasticity, which was perhaps *the* characteristic topic in polymer science. The most distinguished contributor to the statistical mechanics was Paul Flory (1910–1985), who learnt his polymer science while working with Carothers at Du Pont. His textbook of polymer chemistry (Flory 1953) is perhaps the most distinguished overview of the entire field and is still much cited, 48 years after publication.

The input of physicists has become ever greater: two of the most active have been Samuel Edwards in Cambridge and Pierre-Gilles de Gennes in Paris; the latter introduced the method of the renormalisation group (invented by particle physicists) to the statistics of polymer chains (de Gennes 1979) and also, jointly with Edwards, came to an understanding of diffusion in polymers. The physics of polymers (chain statistics, rubber elasticity, crystallisation mechanisms, viscoelasticity and plasticity, dielectric behaviour) has gradually become an identifiable subfield and has been systematised in a recent textbook (Strobl 1996).

Physical chemistry, as we have seen, after its founding quickly acquired dedicated scientific journals, but was very slow in acquiring textbooks. Polymer science was slow on both counts. Flory's text of 1953 was the first major book devoted to the field, though Staudinger made an early first attempt (Staudinger 1932). Many of the early papers appeared in the *Kolloid-Zeitschrift*; this was founded in 1906 and continued under that name until 1973, when it was converted into *Colloid and Polymer Science*. In spite of the uneasy coexistence of colloid science and polymer science in the 1920s, the journal still today mixes papers in the two disciplines, though polymer papers predominate. As late as 1960, only four journals were devoted exclusively to polymers – two in English, one in German and one in Russian. Now, however, the field is saturated: a survey in 1994 came up with 57 journal titles devoted to polymers that could be found in the Science Citation Index, and this does not include minor journals that were not cited. One major publisher, alone, publishes 9 polymer journals! *Macromolecules*, *Polymer* and *Journal of Applied Polymer Science* are the most extensively cited titles. One journal (*Journal of Polymer Science: Polymer Physics*) has 'physics' in its title. Many of the 57 journals have an engineering or applied science flavour, and the field of polymer science is by no means now coterminous with polymer chemistry, as it was half a century ago.

So, although the discipline had a very slow and hesitant emergence, there is no doubt that polymer science is now an autonomous and thoroughly recognised field. It has had its share of Nobel Prizes – Staudinger, Ziegler, Natta, Flory and de Gennes spring to mind. The 1994 *Metallurgy/Materials Education Yearbook* published by ASM International lists 15 university departments in North America specialising in polymer science, with names like Polymer Science and Engineering, Macromolecular Science and Plastics Engineering. Many observers of the MSE field judge that polymers are on their way to becoming, before long, the most widespread and important of all classes of materials.

More about polymers will be found in Chapter 8.

2.1.4 Colloids

The concept of a colloid goes back to an Englishman, Thomas Graham (1805–1869) (Graham 1848). He made a comprehensive study of the diffusion kinetics of a number of liquids, including notably solutions of a variety of substances. Some substances, he found, are characterised by ultraslow diffusion (solutions of starch or dextrin, and albumin, for instance) and are moreover unable to crystallise out of solution: he called these *colloids* (i.e., glue-like). The term, apparently, could apply either to the solution or just to the solute. Ordinary solutions (of salts, for instance), in which diffusion was rapid, were named *crystalloids*. Graham also proposed the nomenclature of *sols* (highly fluid solutions of colloids) and *gels* (gelatinous solutions). What Graham did not realise (he did not have the techniques needed to arrive at such a conclusion) was that what his colloids had in common was a large particle size – large, that is, compared to the size of atoms or molecules, but generally too small to be seen in optical microscopes. That recognition came a little later.

What was recognised from the beginning was that colloidal solutions are two-phase materials.

The study of colloids accelerated rapidly after Graham's initial researches, and much attention was focused on the properties of interfaces, adsorption behaviour in particular. Because of this, 'colloid chemistry' expanded to cover emulsions and foams, as well as aerosols. It took quite a long time to reach the recognition that though a sol (like the gold sol earlier studied by Faraday, for instance) had to be regarded as a suspension of tiny particles of one phase (solid gold) in another phase, water, yet such a two-phase solution behaved identically, in regard to such properties as osmotic pressure, to a true (crystalloid) solution. This was established by Perrin's elegant experiments in 1908 which showed that the equilibrium distribution in a gravitational field of suspended colloid particles large enough to be observed in a microscope follows the same law as the distribution of gas molecules in the atmosphere, and thereby, a century after John Dalton, at last convinced residual sceptics of the reality of atoms and molecules (Nye 1972) (see also Chapter 3, Section 3.1.1).

As Morawetz puts the matter, "an acceptance of the validity of the laws governing colligative properties (i.e., properties such as osmotic pressure) for polymer solutions had no bearing on the question whether the osmotically active particle is a molecule or a molecular aggregate". The colloid chemists, as we have seen, in regard to polymer solutions came to favour the second alternative, and hence created the standoff with the proponents of macromolecular status outlined above.

What concerns us here is the attempt by the champions of colloid chemistry to establish it as a distinct discipline. There was something of an argument about its name; for a while, the term 'capillarity' favoured by Herbert Freundlich (1881–1941), a former assistant of Wilhelm Ostwald, held pride of place. The field has long had its own journals (e.g., the *Kolloid-Zeitschrift* already referred to) and a number of substantial texts have been published. An introduction to colloid chemistry by Wolfgang Ostwald, which originally appeared in 1914, went through numerous editions (Ostwald 1914). Its title, in translation, means "the world of neglected dimensions", and as this suggests, his book has a messianic air about it. Other important texts were those by the American chemist Weiser (1939) and especially a major overview by the Cambridge physical chemists Alexander and Johnson (1949). The last of these was entitled *Colloid Science* (not colloid chemistry) and the authors indicate in their preface that the main reason for this choice of title was that this was the name of an academic department in Cambridge in which they had worked for some years.

That department, the Department of Colloid Science in Cambridge University, was the creation and brainchild of Eric Rideal (1890–1974). In his own words, writing in 1947, "some twenty years ago it was my duty to attempt to build up a laboratory for teaching and research which would serve as a bridge between the biological sciences and physics and chemistry". As a physical chemistry lecturer in Cambridge in 1920, he was intensely interested in surfaces and interfaces and he collaborated with an extraordinary range of Cambridge scientists, with interests in photochemistry, electrochemistry, corrosion (metallurgy) and the statistical mechanics of gases. A wellwisher secured an endowment from the International Education Board, a charity, and a chair in Colloidal Physics was created in 1930. Rideal was appointed to it and moved into exiguous quarters to build up the department. Soon, a further charitable donation materialised, specifically intended for the setting up of chairs in 'bridging subjects', and so the chair in Colloidal Physics was allowed to lapse and Rideal became Professor of Colloid Science instead. As Rideal remarked much later (Rideal 1970), "Not having the remotest idea what colloidal physics were, I naturally accepted it (the chair).... (Later) I was asked whether I would resign my chair and be appointed the first Plummer Professor of Colloid Science, a name which I coined because I thought it was much more suitable than Colloidal Physics. It sounded better and meant just as little." On such accidents do the names of disciplines, or would-be disciplines, depend. At first, the new department was actually a subdepartment of the Chemistry department, but in 1943 Rideal was able to force independence for his fief, on the grounds that in this way collaboration with biologists would be easier. Rideal's interest in interfaces was both literal and metaphorical.

Much of this outline history comes from Johnson's unpublished autobiography (1996). This, and Rideal's obituary for the Royal Society (Eley 1976) show that in research terms the department was a great success, with excellent staff and a horde of research students. Rideal was one of those research supervisors who throw out an endless stream of bright ideas and indications of relevant literature, and then leaves the student to work out all the details; this worked. It did not always work, however; the young Charles Snow was one of his collaborators; Snow and another young man thought that they had discovered a new vitamin and celebrated the discovery with Rideal in a local pub. As Rideal remarked later (Rideal 1970): "It was all wrong unfortunately... C.P. Snow... went off to Sicily, or maybe Sardinia, and thought he was going to die and started to write. He came back with a book; and this book, 'The Search', he presented to me, and that started him on his literary career." One never knows what an unsuccessful piece of research will lead to. Unfortunately, Snow disliked his mentor and is reputed to have used him as raw material for one of his less sympathetic fictional characters.

The department's input to undergraduate teaching was slight, and moreover it was geographically separated from the rest of Cambridge chemistry. In 1946, Rideal accepted an invitation to become director of the Royal Institution in London, taking some of his staff with him, and another professor of colloid science (Francis

Roughton) was appointed to succeed him in Cambridge. In due course the university set up a highly secret committee to consider the future of the department, and it was only years later that its decision to wind up the department leaked out, to the fury of many in the university (Johnson 1996). Nevertheless, the committee members were more effective politicians than were the friends of colloid science, and when the second professor retired in 1966, the department vanished from the scene. (An organisation that is cataloguing Roughton's personal archives has recently commented (NCUACS 2000) that Roughton "presided over a rather disparate group in the Department whose interests ranged from physical chemistry of proteins to ore flotation. During the latter part of his tenure he attempted to redirect the work of the Department towards the study of membranes and biological surface effects. *However, such were the doubts about the existence of a definable subject called Colloid Science* (my emphasis) that on his retirement in 1966 the title of the department was extinguished in favour of Biophysics.")

One of the Department's luminaries, Ronald Ottewill, went off to Bristol University, where he became first professor of colloid science and then professor of physical chemistry, both in the Department of Physical Chemistry. The Bristol department has been one of the most distinguished exponents of colloid science in recent years, but Ottewill considers that it is best practised under the umbrella of physical chemistry.

It is perhaps appropriate that the old premises of the Department of Colloid Science are now occupied by the Department of the History and Philosophy of Science. To the best of my knowledge, there has never been another department of colloid science anywhere in the academic world.

This episode has been displayed in some detail because colloid science is a clear instance of a major field of research which has never quite succeeded in gaining recognition as a distinct discipline, in spite of determined attempts by a number of its practitioners. The one feature that most distinguishes colloid science from physical chemistry, polymer science and chemical engineering is that universities have not awarded degrees in colloid science. That is, perhaps, what counts most for fields with ambitions to become fullblown disciplines.

Lest I leave the erroneous impression here that colloid science, in spite of the impossibility of defining it, is not a vigorous branch of research, I shall conclude by explaining that in the last few years, an entire subspeciality has sprung up around the topic of *colloidal (pseudo-) crystals*. These are regular arrays that are formed when a suspension (sol) of polymeric (e.g., latex) spheres around half a micrometre in diameter is allowed to settle out under gravity. The suspension can include spheres of one size only, or there may be two populations of different sizes, and the radius ratio as well as the quantity proportions of the two sizes are both controllable variables. 'Crystals' such as AB_2, AB_4 and AB_{13} can form (Bartlett et al. 1992, Bartlett and van

Megen 1993, Grier 1998, Pusey 2001); there is an entire new crystallography in play. The field has in fact emerged from a study of natural opal, which consists of tiny silica spheres in the form of colloidal crystals. Such colloidal crystals are in fact stabilised by subtle entropic factors (Frankel 1993) combined with a weak repulsion provided by electrostatic charges at the particle surfaces. In fact, the kind of colloidal supension used in this work was designed some years ago by colloid chemists as a medium for paints, and now they are used by physicists to study (in slow motion, because of the weak interactions) phase transitions, 'melting' in particular (Larsen and Grier 1996). This growing body of research makes copious use of colloid ideas but is carried out in departments of physical chemistry and physics. An inchoate field of 'colloid engineering' is emerging; colloidal crystals can be used to confine and control light, analogously to bandgap engineering in semiconductors; photons with energies lying in the bandgap cannot propagate through the medium. Such 'photonic band gap' materials have recently been discussed by Joannopoulos et al. (1997) and by Berger (1999); a particularly clear explanation is by Pendry (1999).

The broader field of colloid science continues to attract overviews, the most recent being a book entitled *The Colloidal Domain, Where Physics, Chemistry and Biology Meet* (Evans and Wennerström 1999).

2.1.5 Solid-state physics and chemistry

Both of these crucial fields of research will surface repeatedly later in this book; here they are briefly discussed only as fields which by at least one of the criteria I have examined do not appear to qualify as fully blown disciplines. Both have emerged only in this century, because a knowledge of crystal structure is indispensable to both and that only emerged after 1912, when X-ray diffraction from crystals was discovered.

The beginnings of the enormous field of solid-state physics were concisely set out in a fascinating series of recollections by some of the pioneers at a Royal Society Symposium (Mott 1980), with the participation of a number of professional historians of science, and in much greater detail in a large, impressive book by a number of historians (Hoddeson et al. 1992), dealing in depth with such histories as the roots of solid-state physics in the years before quantum mechanics, the quantum theory of metals and band theory, point defects and colour centres, magnetism, mechanical behaviour of solids, semiconductor physics and critical statistical theory.

As for solid-state chemistry, that began in the form of 'crystal chemistry', the systematic study of the chemical (and physical) factors that govern the structures in which specific chemicals and chemical families crystallise, and many books on this topic were published from the 1930s onwards. The most important addition to straight crystal chemistry from the 1940s onwards was the examination of *crystal* *defects* – point, line and planar defects, including grain boundaries and interphase boundaries. In fact, crystal defects were first studied by the solid-state physicists; the first compilation of insights relating to crystal defects was a symposium proceedings organised by a group of (mostly) American physicists (Shockley et al. 1952). This was followed after some years by a classic book by the Dutch chemist Kroeger (1974), again focused entirely on crystal defects and their linkage to non-stoichiometry, and an excellent book on disorder in crystals (Parsonage and Staveley 1979). The current status is surveyed in an excellent overview (Rao and Gopalakrishnan 1986, 1997). It will clarify the present status of solid-state chemistry to list the chapter headings in this book: Structure of solids – old and new facets; new and improved methods of characterisation; preparative strategies; phase transitions; new light on an old problem – defects and non-stoichiometry; structure-property relations; fashioning solids for specific purposes – aspects of materials design; reactivity of solids. The linkage with materials science is clear enough.

The enormous amount of research at the interface between physical and structural chemistry has been expertly reviewed recently by Schmalzried in a book about chemical kinetics of solids (Schmalzried 1995), dealing with matters such as morphology and reactions at evolving interfaces, oxidation specifically, internal reactions (such as internal oxidation), reactions under irradiation, etc.

Both fields are very well supplied with journals, some even combining physics with chemistry (e.g., *Journal of Physics and Chemistry of Solids*). Some are venerable journals now focusing on solid-state physics without indicating this in the title, such as *Philosophical Magazine*. The *Journal of Solid-State Chemistry* has recently been complemented by several journals with 'materials chemistry' in the title, but I know of no journals devoted explicitly to the physics of materials: indeed that phrase has only just entered use, though it was the title of a historical piece I wrote recently (Cahn 1995), and the term has been used in the titles of multiauthor books (e.g., Fujita 1994, 1998). 'Applied physics', which overlaps extensively with the concept of physics of materials, appears in the title of numerous journals. (Some mathematicians eschew the term "applied mathematics" and prefer to use "applicable mathematics", as being more logical; "applicable physics" would be a good term, but it has never been used.) Many papers in both solid-state physics and solid-state chemistry are of course published in general physics and chemistry journals.

An eminent researcher at the boundaries between physics and chemistry, Howard Reiss, some years ago explained the difference between a solid-state chemist and a solid-state physicist. The first thinks in configuration space, the second in momentum space; so, one is the Fourier transform of the other.

It is striking that in the English-speaking world, where academic 'departments' are normal, no departments of either solid-state physics or of solid-state chemistry are to be found. These vast fields have been kept securely tethered to their respective parent disciplines, without any visible ill consequences for either; students are given a broad background in physics or in chemistry, and in the later parts of their courses they are given the chance to choose emphasis on solids if they so wish... but their degrees are simply in physics or in chemistry (or, indeed, in physical chemistry). In continental Europe, where specialised 'institutes' take the place of departments, there are many institutes devoted to subfields of solid-state physics and solid-state chemistry, and a few large ones, as in the University of Paris-Sud and in the University of Bordeaux, cover these respective fields in their entirety.

2.1.6 Continuum mechanics and atomistic mechanics of solids

My objective here is to exemplify the stability of some scientific fields in the face of developments which might have been expected to lead to mergers with newer fields which have developed alongside.

Most materials scientists at an early stage in their university courses learn some elementary aspects of what is still miscalled "strength of materials". This field incorporates elementary treatments of problems such as the elastic response of beams to continuous or localised loading, the distribution of torque across a shaft under torsion, or the elastic stresses in the components of a simple girder. 'Materials' come into it only insofar as the specific elastic properties of a particular metal or timber determine the numerical values for some of the symbols in the algebraic treatment. This kind of simple theory is an example of *continuum mechanics*, and its derivation does not require any knowledge of the crystal structure or crystal properties of simple materials or of the microstructure of more complex materials. The specific aim is to design simple structures that will not exceed their elastic limit under load.

From 'strength of materials' one can move two ways. On the one hand, mechanical and civil engineers and applied mathematicians shift towards more elaborate situations, such as "plastic shakedown" in elaborate roof trusses; here some transient plastic deformation is planned for. Other problems involve very complex elastic situations. This kind of continuum mechanics is a huge field with a large literature of its own (an example is the celebrated book by Timoshenko 1934), and it has essentially nothing to do with materials science or engineering because it is not specific to any material or even family of materials.

From this kind of continuum mechanics one can move further towards the domain of almost pure mathematics until one reaches the field of *rational mechanics*, which harks back to Joseph Lagrange's (1736–1813) mechanics of rigid bodies and to earlier mathematicians such as Leonhard Euler (1707–1783) and later ones such as Augustin Cauchy (1789–1857), who developed the mechanics of deformable bodies. The preeminent exponent of this kind of continuum mechanics was probably Clifford Truesdell in Baltimore. An example of his extensive writings is *A First Course in*

Rational Continuum Mechanics (1977, 1991); this is a volume in a series devoted to pure and applied mathematics, and the author makes it very clear that rational continuum mechanics is to be regarded as almost pure mathematics; at one point in his preface, he remarks that "physicists should be able to understand it, should they wish to". His initial quotations are, first, from a metaphysician and, second, from the pure mathematician David Hilbert on the subject of rigorous proofs. Truesdell's (1977, 1991) book contains no illustrations; in this he explicitly follows the model of Lagrange, who considered that a good algebraist had no need of that kind of support. I should perhaps add that Dr. Truesdell wrote many of his books in the study of his renaissance-style home, called *Il Palazzetto*, reportedly using a quill pen. I do not know why the adjective 'rational' is thought necessary to denote this branch of mathematics; one would have thought it tautological.

I cannot judge whether Truesdell's kind of continuum mechanics is of use to mechanical engineers who have to design structures to withstand specific demands, but the total absence of diagrams causes me to wonder. In any case, I understand (Walters 1998, Tanner and Walters 1998) that rational mechanics was effectively Truesdell's invention and is likely to end with him. The birth and death of would-be disciplines go on all the time.

At the other extreme from rational continuum mechanics we have the study of elastic and plastic behaviour of single crystals. Crystal elasticity is a specialised field of its own, going back to the mineralogists of the nineteenth century, and involving tensor mathematics and a detailed understanding of the effects of different crystal symmetries; the aforementioned Cauchy had a hand in this too. Crystal elasticity is of considerable practical use, for instance in connection with the oscillating slivers of quartz used in electronic watches; these slivers must be cut to precisely the right orientation to ensure that the relevant elastic modulus of the sliver is invariant with temperature over a limited temperature range. The plastic behaviour of metal crystals has been studied since the beginning of the present century, when Walter Rosenhain (see Chapter 3, Section 3.2.1) first saw slip lines on the surface of polished polycrystalline metal after bending and recognised that plasticity involved shear ('slip') along particular lattice planes and vectors. Crystal plasticity was studied intensely from the early 1920s onwards, and understanding was codified in two important experimental texts (Schmid and Boas 1935, Elam 1935); crucial laws such as the critical shear stress law for the start of plastic deformation were established. In the 1930s a start was also made with the study of plastic deformation in polycrystalline metals in terms of slip in the constituent grains. This required a combination of continuum mechanics and the physics of single-crystal plasticity. This branch of mechanics has developed fruitfully as a joint venture between mechanical engineers, applied (applicable) mathematicians, metallurgists and solid-state physicists. The leading spirit in this venture was Geoffrey (G.I.) Taylor

(1886–1975), a remarkable English fluid dynamics expert who became interested in plasticity of solids when in 1922 he heard a lecture at the Royal Society about the work of Dr. Constance Elam (the author of one of the above-mentioned books). Elam and Taylor worked together on single-crystal plasticity for some 10 years and this research led Taylor to the co-invention of the dislocation concept in 1934, and then on to a classic paper on polycrystal plasticity (Taylor 1938). This paper is still frequently cited: for instance, Taylor's theory concerning the minimum number (5) of distinct slip elements needed to ensure an arbitrary shape change of a grain embedded in a polycrystal has been enormously influential in the understanding of plastic deformability. Taylor's collected papers include no fewer than 41 papers on the solid state (Batchelor 1958). His profound influence on the field of plasticity is vividly analysed in a recent biography (Batchelor 1996).

A good picture of the present state of understanding of polycrystal plasticity can be gleaned from a textbook by Khan and Huang (1995). Criteria for plastic yield, for instance, are developed both for a purely continuum type of medium and for a polycrystal undergoing slip. This book contains numerous figures and represents a successful attempt to meet crystal plasticity experts at a halfway point. A corresponding treatment by metallurgists is entitled "deformation and texture of metals at large strains" and discusses the rotation of individual crystallites during plastic deformation, which is of industrial importance (Aernoudt et al. 1993).

In 1934, a new kind of crystal defect, the dislocation, was invented (independently by three scientists) and its existence was confirmed some years later. The dislocation can be briefly described as the normal (but not exclusive) vector of plastic deformation in crystals. This transformed the understanding of such deformation, especially once the elastic theory of dislocation interaction had been developed (Cottrell 1953). Cottrell went on to write a splendid student text in which he contrived to marry continuum mechanics and 'crystal mechanics' into an almost seamless whole (Cottrell 1964). From that point on, the understanding, in terms of the interaction of point, line and planar defects, of both fast and slow plastic deformation in single and polycrystals developed rapidly. A fine example of what modern theory can achieve is the creation of *deformation-mechanism maps* by Frost and Ashby (1982); such maps plot normalised stress and normalised temperature on a double-log plot, for particular metals or ceramics with a particular grain (crystal) size, and using theoretically derived *constitutive relations*, the domain of the graph is divided into areas corresponding to different deformation mechanisms (some further details are in Section 5.1.2.2). This kind of map has proved very useful both to materials engineers who develop new materials, and to mechanical engineers who use them.

The upshot of all this is that the mechanics of elastic and plastic types of deformation spans a spectrum from the uncompromising and highly general rational mechanics to the study of crystal slip in single crystals and its interpretation in terms of the elastic theory of interaction between defects, leading to insights that are specific to particular materials. There is some degree of a meeting of minds in the middle between the mathematicians and mechanical engineers on the one side and the metallurgists, physicists and materials scientists on the other, but it is also true to say that continuum mechanics and what might (for want of a better term) be called *atomistic mechanics* have remained substantially divergent approaches to the same set of problems. One is a part of mechanical engineering or more rarefied applied mathematics, the other has become an undisputed component of materials science and engineering, and the two kinds of specialists rarely meet and converse. This is not likely to change.

Another subsidiary domain of mechanics which has grown in stature and importance in parallel with the evolution of polymer science is *rheology*, the science of flow, which applies to fluids, gels and soft solids. It is an engaging mix of advanced mathematics and experimental ingenuity and provides a good deal of insight specific to particular materials, polymers in particular. A historical outline of rheology, with concise biographical sketches of many of its pioneers, has been published by Tanner and Walters (1998).

Very recently, people who engage in computer simulation of crystals that contain dislocations have begun attempts to bridge the continuum/atomistic divide, now that extremely powerful computers have become available. It is now possible to model a variety of aspects of dislocation mechanics in terms of the atomic structure of the lattice around dislocations, instead of simply treating them as lines with 'macroscopic' properties (Schiøtz et al. 1998, Gumbsch 1998). What this amounts to is 'linking computational methods across different length scales' (Bulatov et al. 1996). We will return to this briefly in Chapter 12.

2.2. THE NATURAL HISTORY OF DISCIPLINES

At this stage of my enquiry I can draw only a few tentative conclusions from the case-histories presented above. I shall return at the end of the book to the issue of how disciplines evolve and when, to adopt biological parlance, a new discipline becomes self-fertile.

We have seen that physical chemistry evolved from a deep dissatisfaction in the minds of a few pioneers with the current state of chemistry as a whole – one could say that its emergence was research-driven and spread across the world by hordes of new Ph.Ds. Chemical engineering was driven by industrial needs and the corresponding changes that were required in undergraduate education. Polymer science started from a wish to understand certain natural products and moved by slow stages, once the key concept had been admitted, to the design, production and understanding of synthetic materials. One could say that it was a synthesis-driven discipline. Colloid science (the one that 'got away' and never reached the full status of a discipline) emerged from a quasi-mystic beginning as a branch of very applied chemistry. Solid-state physics and chemistry are of crucial importance to the development of modern materials science but have remained fixed by firm anchors to their parent disciplines, of which they remain undisputed parts. Finally, the mechanics of elastic and plastic deformation is a field which has always been, and remains, split down the middle, and neither half is in any sense a recognisable discipline. The mechanics of flow, rheology, is closer to being an accepted discipline in its own right.

Different fields, we have seen, differ in the speed at which journals and textbooks have appeared; the development of professional associations is an aspect that I have not considered at this stage. What seems best to distinguish recognized disciplines from other fields is academic organisation. Disciplines have their own distinct university departments and, even more important perhaps, those departments have earned the right to award degrees in their disciplines. Perhaps it is through the harsh trial of academic infighting that disciplines win their spurs.

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Chapter 3

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Chapter 3

Precursors of Materials Science

3.1. THE LEGS OF THE TRIPOD

In Cambridge University, the final examination for a bachelor's degree, irrespective of subject, is called a 'tripos'. This word is the Latin for a three-legged stool, or tripod, because in the old days, when examinations were conducted orally, one of the participants sat on such a stool. Materials science is examined as one option in the Natural Sciences Tripos, which itself was not instituted until 1848; metallurgy was introduced as late as 1932, and this was progressively replaced by materials science in the 1960s. In earlier days, it was neither the nervous candidate, nor the severe examiner, who sat on the 'tripos'; this was occupied by a man sometimes called the 'prevaricator' who, from the 14th century, if not earlier, was present in order to inject some light relief into the proceedings: when things became too tense, he would crack a joke or two and then invite the examiner to proceed. I believe this system is still sometimes used for doctoral examinations in Sweden.

The tripod and its occupant, then, through the centuries helped students of classics, philosophy, mathematics and eventually natural science to maintain a sense of proportion. One might say that the three prerequisites for doing well in such an examination were (and remain) knowledge, judgment and good humour, three preconditions of a good life. By analogy, I suggest that there were three preconditions of the emergence of materials science, constituting another tripod: those preconditions were an understanding of (1) atoms and crystals, (2) phase equilibria, and (3) microstructure. These three forms of understanding were the crucial precursors of our modern understanding and control of materials. For a beginning, I shall outline how these forms of understanding developed.

3.1.1 Atoms and crystals

The very gradual recognition that matter consists of atoms stretched over more than two millennia, and that recognition was linked for several centuries with the struggles of successive generations of scientists to understand the nature of crystals. This is why I am here combining sketches of the history of atoms and of the history of crystals, two huge subjects.

The notion that matter had ultimate constituents which could not be further subdivided goes back to the Greeks (atom = Greek *a-tomos*, not capable of being cut). Democritus (circa 460 BC – circa 370 BC), probably leaning on the ideas of

Epicurus, was a very early proponent of this idea; from the beginning, the amount of empty space associated with atoms and the question whether neighbouring atoms could actually be in contact was a source of difficulty, and Democritus suggested that solids with more circumatomic void space were in consequence softer. A century later, Aristotle praised Democritus and continued speculating about atoms, in connection with the problem of explaining how materials can change by combining with each other... *mixtion*, as the process came to be called (Emerton 1984).

Even though Democritus and his contemporaries were only able to speculate about the nature of material reality, yet their role in the creation of modern science is more crucial than is generally recognised. That eminent physicist, Erwin Schrödinger, who in his little book on *Nature and the Greeks* (Schrödinger 1954, 1996) has an illuminating chapter about *The Atomists*, put the matter like this: "The grand idea that informed these men was that the world around them was something that *could be understood*, if only one took the trouble to observe it properly; that it was not the playground of gods and ghosts and spirits who acted on the spur of the moment and more or less arbitrarily, who were moved by passions, by wrath and love and desire for revenge, who vented their hatred, and could be propitiated by pious offerings. These men had freed themselves of superstition, they would have none of all this. They saw the world as a rather complicated mechanism, according to eternal innate laws, which they were curious to find out. This is of course the fundamental attitude of science to this day." In this sense, materials science and all other modern disciplines owe their origin to the great Greek philosophers.

The next major atomist was the Roman Lucretius (95 BC – circa 55 BC), who is best known for his great poem, *De rerum natura* (Of the Nature of Things), in which the author presents a comprehensive atomic hypothesis, involving such aspects as the ceaseless motion of atoms through the associated void (Furley 1973). Lucretius thought that atoms were characterised by their shape, size and weight, and he dealt with the problem of their mutual attraction by visualising them as bearing hooks and eyes... a kind of primordial 'Velcro'. He was probably the last to set forth a detailed scientific position in the form of verse.

After this there was a long pause until the time of the 'schoolmen' in the Middle Ages (roughly 1100–1500). People like Roger Bacon (1220–1292), Albertus Magnus (1200–1280) and also some Arab/Moorish scholars such as Averroes (1126–1198) took up the issue; some of them, notably Albertus, at this time already grappled with the problem of the nature of crystalline minerals. Averroes asserted that "the natural minimum...is that ultimate state in which the form is preserved in the division of a natural body". Thus, the smallest part of, say, alum would be a particle which in some sense had the form of alum. The alternative view, atomism proper, was that alum and all other substances are made up of a few basic building units none of which is specific to alum or to any other single chemical compound. This difference of opinion (in modern terms, the distinction between a molecule and an atom) ran through the centuries and the balance of dogma swung backwards and forwards. The notion of molecules as distinct from atoms was only revived seriously in the 17th century, by such scientists as the Dutchman Isaac Beeckman (1588–1637) (see Emerton 1984, p. 112). Another early atomist, who was inspired by Democritus and proposed a detailed model according to which atoms were in perpetual and intrinsic motion and because of this were able to collide and form molecules, was the French philosopher Pierre Gassendi (1592–1655). For the extremely involved history of these ideas in antiquity, the Middle Ages and the early scientific period, Emerton's excellent book should be consulted.

From an early stage, as already mentioned, scholars grappled with the nature of crystals, which mostly meant naturally occurring minerals. This aspect of the history of science can be looked at from two distinct perspectives – one involves a focus on the appearance, classification and explanation of the forms of crystals (i.e., crystallography), the other, the role of mineralogy in giving birth to a proper science of the earth (i.e., geology). The first approach was taken, for instance, by Burke (1966) in an outstanding short account of the origins of crystallography, the second, in a more recent study by Laudan (1987).

As the era of modern science approached and chemical analysis improved, some observers classified minerals in terms of their compositions, others in terms of their external appearance. The 'externalists' began by measuring angles between crystal faces; soon, crystal symmetry also began to be analysed. An influential early student of minerals – i.e., crystals – was the Dane Nicolaus Stenonius, generally known as Steno (1638–1686), who early recognised the constancy of interfacial angles and set out his observations in his book, *The Podromus, A Dissertation on Solids Naturally Contained within Solids* (see English translation in Scherz 1969). Here he also examines the juxtaposition of different minerals, hence the title. Steno accepted the possibility of the existence of atoms, as one of a number of rival hypotheses. The Swedish biologist Carolus Linnaeus (1707–1778) somewhat later attempted to extend his taxonomic system from plants and animals to minerals, basing himself on crystal shape; his classification also involved a theory of the genesis of minerals with a sexual component; his near-contemporaries, Romé de l'Isle and Haüy (see below) credited Linnaeus with being the true founder of crystallography, because of his many careful measurements of crystals; but his system did not last long, and he was not interested in speculations about atoms or molecules.

From quite an early stage, some scientists realised that the existence of flat crystal faces could be interpreted in terms of the regular piling together of spherical or ellipsoidal atoms. Figure 3.1 shows some 17th-century drawings of postulated crystal structures due to the Englishman Robert Hooke (1635–1703) and the Dutchman Christiaan Huygens (1629–1695). The great astronomer, Johannes

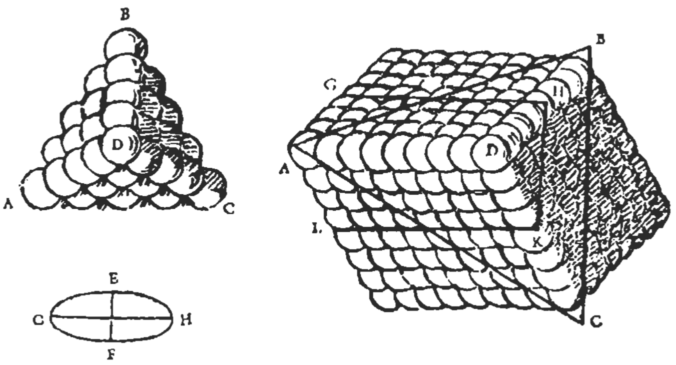


Figure 3.1. (from Emerson, p. 134) Possible arrangements of spherical particles, according to Hooke (left, from a republication in *Micrographia Restaurata*, London 1745) and Huygens (right, from *Traité de la Lumière*, Leiden 1690).

Kepler (1571–1630) had made similar suggestions some decades earlier. Both Kepler and Huygens were early analysts of crystal symmetries in terms of atomic packing. This use of undifferentiated atoms in regular arrays was very different from the influential corpuscular models of René Descartes (1596–1650), as outlined by Emerton (1984, p. 131 et seq.): Descartes proposed that crystals were built up of complicated units (star- or flower-shaped, for instance) in irregular packing; according to Emerton, this neglect of regularity was due to Descartes's emphasis on the motion of particles and partly because of his devotion to Lucretius's unsymmetrical hook-and-eye atoms.

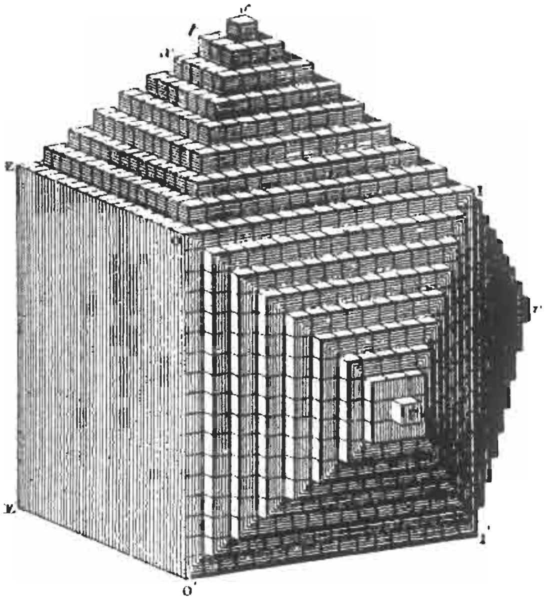
In the 18th century, the role of simple, spherical atoms was once more in retreat. An eminent historian of metallurgy, Cyril Stanley Smith, in his review of Emerton's book (Smith 1985) comments: "...corpuscular thinking disappeared in the 18th century under the impact of Newtonian anti-Cartesianism. The new math was so useful because its smoothed functions could use empirical constants without attention to substructure, while simple symmetry sufficed for externals. Even the models of Kepler, Hooke and Huygens showing how the polyhedral form of crystals could arise from the stacking of spherical or spheroidal parts were forgotten." The great French crystallographers of that century, Romé de l'Isle and Haüy, thought once again in terms of non-spherical 'molecules' shaped like diminutive crystals, and not in terms of atoms.

Jean-Baptiste Romé de l'Isle (1736–1790) and René Haüy (1743–1822), while they, as remarked, credited Linnaeus with the creation of quantitative crystallography, themselves really deserve this accolade. Romé de l'Isle was essentially a chemist and much concerned with the genesis of different sorts of crystal, but his real claim to fame is that he first clearly established the principle that the interfacial angles of a particular species of crystal were always the same, however different the shape of individual specimens might be, tabular, elongated or equiaxed – a principle foreshadowed a hundred years earlier by Steno. This insight was based on very exact measurements using contact goniometers; the even more exact optical goniometer was not invented until 1809 by William Wollaston (1766–1826). (Wollaston, incidentally, was yet another scientist who showed how the stacking of spherical atoms could generate crystal forms. He was also an early scientific metallurgist, who found out how to make malleable platinum and also discovered palladium and rhodium.)

Haüy, a cleric turned experimental mineralogist, built on Romé's findings: he was the first to analyse in quantitative detail the relationship between the arrangement of building-blocks (which he called 'integrant molecules') and the position of crystal faces: he formulated what is now known as the law of rational intercepts, which is the mathematical expression of the regular pattern of 'treads and steps' illustrated in Figure 3.2(a), reproduced from his *Traité de Cristallographie* of 1822. The tale is often told how he was led to the idea of a crystal made up of integrant molecules shaped like the crystal itself, by an accident when he dropped a crystal of iceland spar and found that the small cleavage fragments all had the same shape as the original large crystal. "Tout est trouvé!" he is reputed to have exclaimed in triumph.

From the 19th century onwards, chemists made much of the running in studying the relationship between atoms and crystals. The role of a German chemist, Eilhardt Mitscherlich (1794–1863, Figure 3.2(b)) was crucial (for a biography, see Schütt 1997). He was a man of unusual breadth who had studied oriental philology and history, became 'disillusioned with these disciplines' in the words of Burke (1966) and turned to medicine, and finally from that to chemistry. It was Mitscherlich who discovered, first, the phenomenon of isomorphism and, second, that of polymorphism. Many salts of related compositions, say, sodium carbonate and calcium carbonate, turned out to have similar crystal symmetries and axial ratios, and sometimes it was even possible to use the crystals of one species as nuclei for the growth of another species. It soon proved possible to use such *isomorphous* crystals for the determination of atomic weights: thus Mitscherlich used potassium selenite, isomorphous with potassium sulphate, to determine the atomic weight of selenium from the already known atomic weight of sulphur. Later, Mitscherlich established firmly that one and the same compound might have two or even more distinct crystal structures, stable (as was eventually recognised) in different ranges of temperature. (Calcite and aragonite, two quite different *polymorphs* of calcium carbonate, were for mineralogists the most important and puzzling example.) Finally, Wollaston and the French chemist François Beudant, at about the same time, established the existence of mixed crystals, what today we would in English call *solid solutions* (though *Mischkristall* is a term still used in German).

(a)



(b)

These three findings – isomorphism, polymorphism, mixed crystals – spelled the doom of Haüy's central idea that each compound had one – and one only – integrant molecule the shape of which determined the shape of the consequent crystal and, again according to Cyril Smith (Smith 1960, p. 190), it was the molecule as the combination of atoms in fixed proportions – rather than the atoms themselves, or any integrant molecules – which now became the centre of chemical interest. When John Dalton (1766–1844) enunciated his atomic hypothesis in 1808, he did touch on the role of regularly combined and arranged atoms in generating crystals, but he was too modest to speculate about the constitution of molecules; he thought that "it seems premature to form any theory on this subject till we have discovered *from other principles* (my italics) the number and order of the primary elements" (Dalton 1808).

The great Swedish chemist Jöns Berzelius (1779–1848) considered the findings of Mitscherlich, together with Dulong and Petit's discovery in 1819 that the specific heats of solids varied inversely as their atomic weights, to be the most important empirical proofs of the atomic hypothesis at that time. It is to be noted that one of these two cornerstones was based on crystallography, which thus became one of the foundations of modern atomic theory.

Another 19th century scientist is one we have met before, in Chapter 2, Section 2.1.4. Thomas Graham (1805–1869), the originator of the concept of colloids, made a reputation by studying the diffusion of fluids (both gases and liquids) in each other in a quantitative way. As one recent commentator (Barr 1997) has put it, "the crucial point about Graham's law (of diffusion) is its quantitative nature and that it could be understood, if not completely explained, by the kinetic theory of gases developed by Maxwell and Clausius shortly after the middle of the nineteenth century. In this way the ideas of diffusion being connected with the random motion of molecules over a characteristic distance, the mean free path, entered science." Jean Perrin, whose crucial researches we examine next, could be said to be the inheritor of Graham's insights. Many years later, in 1900, William Roberts-Austen (1843–1905), a disciple of Graham, remarked of him (Barr 1997): "I doubt whether he would have wished any other recognition than that so universally accorded to him of being the leading atomist of his age".

We move now to the late 19th century and the beginning of the 20th, a period during which a number of eminent chemists and some physicists were still resolutely sceptical concerning the existence of atoms, as late as hundred years after John Dalton's flowering. Ostwald's scepticism was briefly discussed in Section 2.1.1, as

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Figure 3.2. (a) Treads and risers forming crystal faces of various kinds, starting from a cubic primitive form (after Haüy 1822). (b) Eilhardt Mitscherlich (1794–1863) (courtesy Deutsches Museum, Munich).

was his final conversion by Einstein's successful quantitative interpretation of Brownian motion in 1905 in terms of the collisions between molecules and small suspended particles, taken together with Jean Perrin's painstaking measurements of the Brownian motion of suspended colloidal gamboge particles, which together actually produced a good estimate of Avogadro's number. Perrin's remarkable experimental tour de force is the subject of an excellent historical book (Nye 1972); it is not unreasonable to give Perrin the credit for finally establishing the atomic hypothesis beyond cavil, and Nye even makes a case for Perrin as having preceded Rutherford in his recognition of the necessity of a compound atom. Perrin published his results in detail, first in a long paper (Perrin 1909) and then in a book (Perrin 1913). The scientific essayist Morowitz (1993) laments that "one of the truly great scientific books of this century gathers dust on library shelves and is missing from all libraries established after 1930". Morowitz shows a table from Perrin's 1913 book, reproduced here in the earlier form presented by Nye (1972), which gives values of Avogadro's number from 15 distinct kinds of experiment; given the experimental difficulties involved, these values cluster impressively just above the value accepted today, 60.22×10^{22}. If no atoms...then no Avogadro's number. Perrin received the Nobel Prize for Physics in 1926.

Phenomena observed	N (Avogadro's Number)/10^{22}
Viscosity of gases (kinetic theory)	62
Vertical distribution in dilute emulsions	68
Vertical distribution in concentrated emulsions	60
Brownian movement (Perrin)	
Displacements	69
Rotations	65
Diffusion	69
Density fluctuation in concentrated emulsions	60
Critical opalescence	75
Blueness of the sky	65
Diffusion of light in argon	69
Blackbody spectrum	61
Charge on microscopic particles	62
Radioactivity	
Helium produced	64
Radium lost	71
Energy radiated	60

The detailed reasons for Ostwald's atomic scepticism when he gave a major lecture in Germany in 1895 are set out systematically in a book by Stehle (1994), who remarks: "The great obstacle faced by those trying to convince the sceptics of the reality of atoms and molecules was the lack of phenomena making apparent the graininess of matter. It was only by seeing individual constituents, either directly or indirectly through the observation of fluctuations about the mean behaviour predicted by kinetic theory, that the existence of these particles could be shown unambiguously. Nothing of the kind had been seen as yet, as Ostwald so forcefully pointed out...". In fact, Johann Loschmidt (1821–1895) in 1866 had used Maxwell's kinetic theory of gases (which of course presupposes the reality of atoms, or rather molecules) together with a reasonable estimate of an atomic cross-section, to calculate a good value for Avogadro's Number, that longterm criterion of atomic respectability. Ostwald's resolute negation of the existence of atoms distressed some eminent scientists; thus, Ludwig Boltzmann's statistical version of thermodynamics (see Section 3.3.2), which was rooted in the reality of molecules, was attacked by opponents of atomism such as Ostwald, and it has been asserted by some historians that this (together with Ernst Mach's similarly implacable hostility) drove Boltzmann into a depression which in turn led to his suicide in 1906. Even today, the essential link between the atomic hypothesis and statistical thermodynamics provokes elaborate historical analyses such as a recent book by Diu (1997).

Just after Ostwald made his sceptical speech in 1895, the avalanche of experiments that peaked a decade later made his doubts untenable. In the 4th (1908) edition of his textbook, *Grundriss der physikalischen Chemie*, he finally accepted, exactly a hundred years after Dalton enunciated his atomic theory and two years after Boltzmann's despairing suicide, that Thomson's discovery of the electron as well as Perrin's work on Brownian motion meant that "we arrived a short time ago at the possession of experimental proof for the discrete or particulate nature of matter – proof which the atomic hypothesis has vainly sought for a hundred years, even a thousand years" (Nye 1972, p. 151). Not only Einstein's 1905 paper and Perrin's 1909 overview of his researches (Perrin 1909), but the discovery of the electron by J.J. Thomson in 1897 and thereafter the photographs taken with Wilson's cloud-chamber (the 'grainiest' of experiments), Rutherford's long programme of experiments on radioactive atoms, scattering of subatomic projectiles and the consequent establishment of the planetary atom, followed by Moseley's measurement of atomic X-ray spectra in 1913 and the deductions that Bohr drew from these... all this established the atom to the satisfaction of most of the dyed-in-the-wool disbelievers. The early stages, centred around the electron, are beautifully set out in a very recent book (Dahl 1997). The physicist's modern atom in due course led to the chemist's modern atom, as perfected by Linus Pauling in his hugely influential book, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, first published in 1939. Both the physicist's and the chemist's atoms were necessary precursors of modern materials science.

Nevertheless, a very few eminent scientists held out to the end. Perhaps the most famous of these was the Austrian Ernst Mach (1838–1916), one of those who inspired Albert Einstein in his development of special relativity. As one brief biography puts it (Daintith *et al.* 1994), "he hoped to eliminate metaphysics – all those purely 'thought-things' which cannot be pointed to in experience – from science". Atoms, for him, were "economical ways of symbolising experience. But we have as little right to expect from them, as from the symbols of algebra, more than we have put into them". Not all, it is clear, accepted the legacy of the Greek philosophers, but it is appropriate to conclude with the words (Andrade 1923) of Edward Andrade (1887–1971): "The triumph of the atomic hypothesis is the epitome of modern physics".

3.1.1.1 X-ray diffraction. The most important episode of all in the history of crystallography was yet to come: the discovery that crystals can diffract X-rays and that this allows the investigator to establish just where the atoms are situated in the crystalline unit cell. But before that episode is outlined, it is necessary to mention the most remarkable episode in crystallographic theory – the working out of the 230 space groups. In the mid-19th century, and based on external appearances, the entire crystal kingdom was divided into 7 systems, 14 space lattices and 32 point-groups (the last being all the self-consistent ways of disposing a collection of symmetry elements passing through a single point), but none of these exhausted all the intrinsically different ways in which a motif (a repeated group of atoms) can in principle be distributed within a crystal's unit cell. This is far more complicated than the point-groups, because (1) new symmetry elements are possible which combine rotation or reflection with translation and (2) the various symmetry elements, including those just mentioned, can be situated in various positions within a unit cell and generally do not all pass through one point in the unit cell. This was recognised and analysed by three mathematically gifted theorists: E. Fedorov in Russia (in 1891), A. Schoenfliess in Germany (in 1891) and W. Barlow in England (in 1894). All the three independently established the existence of 230 distinct space groups (of symmetry elements in space), although there was some delay in settling the last three groups. Fedorov's work was not published in German until 1895 (Fedorov 1895), though it appeared in Russian in 1891, shortly before the other two published their versions. Fedorov found no comprehension in the Russia of his time, and so his priority is sometimes forgotten. Accounts of the circumstances as they affected Fedorov and Schoenfliess were published in 1962, in *Fifty Years of X-ray Diffraction* (Ewald 1962, pp. 341, 351), and a number of the earliest papers related to this theory are reprinted by Bijvoet *et al.* (1972). The remarkable feature of this piece of triplicated pure theory is that it was perfected 20 years before an experimental method was discovered for the analysis of actual crystal structures, and when such a method at length appeared, the theory of space groups turned out to be an indispensable aid to the process of interpreting the diffraction patterns, since it means that when one atom has been located in a unit cell, then many others are automatically located as well if the space group has been identified (which is not difficult to do from the diffraction pattern itself). The Swiss crystallographer P. Niggli asserted in 1928 that "every scientific structure analysis must begin with a determination of the space group", and indeed it had been Niggli (1917) who was the first to work out the systematics that would allow a space group to be identified from systematic absences in X-ray diffractograms.

In 1912 Max von Laue (1879–1960), in Munich, instructed two assistants, Paul Knipping and Walter Friedrich, to send a beam of (polychromatic) X-rays through a crystal of copper sulphate and on to a photographic plate, and immediately afterwards they did the same with a zincblende crystal: they observed the first diffraction spots from a crystal. Laue had been inspired to set up this experiment by a conversation with Paul Ewald, who pointed out to him that atoms in a crystal had to be not only periodically arranged but much more closely spaced than a light wavelength. (This followed simply from a knowledge of Avogadro's Number and the measured density of a crystal.) At the time, no one knew whether X-rays were waves or particles, and certainly no one suspected that they were both. As he says in his posthumous autobiography (Von Laue 1962), he was impressed by the calculations of Arnold Sommerfeld, also in Munich, which were based on some recent experiments on the diffraction of X-rays at a wedge-shaped slit; it was this set of calculations, published earlier in 1912, that led von Laue to the idea that X-rays had a short wavelength and that crystals might work better than slits. So the experiments with copper sulphate and zincblende showed to von Laue's (and most other people's) satisfaction that X-rays were indeed waves, with wavelengths of the order of 0.1 nm. The crucial experiment was almost aborted before it could begin because Sommerfeld forbade his assistants, Friedrich and Knipping, to get involved with von Laue; Sommerfeld's reason was that he estimated that thermal vibrations in crystals would be so large at room temperature that the essential periodicity would be completely destroyed. He proved to be wrong (the periodicity is not destroyed, only the intensity of diffraction is reduced by thermal motion). Friedrich and Knipping ignored their master (a hard thing to do in those days) and helped von Laue, who as a pure theorist could not do the experiment by himself. Sommerfeld was gracious: he at once perceived the importance of what had been discovered and forgave his errant assistants.

The crucial experiments that determined the structures of a number of very simple crystals, beginning with sodium chloride, were done, not by von Laue and his helpers, but by the Braggs, William (1862–1942) and Lawrence (1890–1971), father and son, over the following two years (Figure 3.3). The irony was that, as von Laue declares in his autobiographical essay, Bragg senior had only shortly before declared his conviction that X-rays were particles! It was his own son's work which led Bragg senior to declare at the end of 1912 that "the problem becomes...not to decide between two theories of X-rays, but to find...one theory which possesses the capabilities of both", a prescient conclusion indeed. At a meeting in London in 1952 to celebrate the 40th anniversary of his famous experiment, von Laue remarked in public how frustrated he had felt afterwards that he had left it to the Braggs to make these epoch-making determinations; he had not made them himself because he was focused, not on the nature of crystals but on the nature of X-rays. By the time he had shifted his focus, it was too late. It has repeatedly happened in the history of science that a fiercely focused discoverer of some major insight does not see the further consequences that stare him in the face. The Ewald volume already cited sets out the minutiae of the events of 1912 and includes a fascinating account of the sequence of events by Lawrence Bragg himself (pp. 59–63), while the subtle relations between Bragg père and Bragg fils are memorably described in Gwendolen Caroe's memoir of her father, William H. Bragg (Caroe 1978). Recent research by an Australian historian (Jenkin 1995), partly based on W.L. Bragg's unpublished autobiography,

Figure 3.3. Portraits of the two Braggs (courtesy Mr. Stephen Bragg).

has established that the six-year-old schoolboy Lawrence, in Adelaide, fell off his bicycle in 1896 and badly injured his elbow; his father, who had read about the discovery of X-rays by Wilhelm Röntgen at the end of 1895, had within a year of that discovery rigged up the first X-ray generator in Australia and so he was able to take a radiograph of his son's elbow – the first medical radiograph in Australia. This helped a surgeon to treat the boy's elbow properly over a period of time and thereby save its function. It is perhaps not so surprising that the thoughts of father and son turned to the use of X-rays in 1912.

Henry Lipson, a British crystallographer who knew both the Braggs has commented (Lipson 1990) that "W.H. and W.L. Bragg were quite different personalities. We can see how important the cooperation between people with different sorts of abilities is; W.H. was the good sound eminent physicist, whereas W.L. was the man with intuition. The idea of X-ray reflection came to him in the grounds of Trinity College, Cambridge, where he was a student of J.J. Thomson's and should not have been thinking of such things."

Lawrence Bragg continued for the next 59 years to make one innovation after another in the practice of crystal structure analysis; right at the end of his long and productive life he wrote a book about his lifetime's experiences, *The Development of X-ray Analysis* (Bragg 1975, 1992), published posthumously. In it he gives a striking insight into the beginnings of X-ray analysis. In 1912, he was still a very young researcher with J.J. Thomson in the Cavendish Laboratory in Cambridge, and he decided to use the Laue diffraction technique (using polychromatic X-rays) to study ZnS, NaCl and other ionic crystals. "When I achieved the first X-ray reflections, I worked the Rumkorff coil too hard in my excitement and burnt out the platinum contact. Lincoln, the mechanic, was very annoyed as a contact cost 10 shillings, and refused to provide me with another one for a month. In these days (i.e., ≈1970) a researcher who discovered an effect of such novelty and importance would have very different treatment. I could never have exploited my ideas about X-ray diffraction under such conditions... In my father's laboratory (in Leeds) the facilities were on quite a different scale." In 1913 he moved to Leeds and he and his father began to use a newly designed X-ray spectrometer with essentially monochromatic X-rays. A 1913 paper on the structure of diamond, in his own words "may be said to represent the start of X-ray crystallography". By the time he moved back to Cambridge as Cavendish professor in 1938, the facilities there had distinctly improved.

Though beaten in that race by the Braggs, von Laue received the Nobel Prize in 1914, one year before the Braggs did.

In spite of these prompt Nobel awards, it is striking how long it took for the new technique for determining atomic arrangements in crystals – crystal structures – to spread in the scientific community. This is demonstrated very clearly by an editorial written by the German mineralogist P. Groth in the *Zeitschrift für Kristallographie*, a journal which he had guided for many years. Groth, who also taught in Munich, was the most influential mineralogist of his generation and published a renowned textbook, *Chemische Kristallographie*. In his 1928 editorial he sets out the genesis and development of his journal and writes about many of the great crystallographers he had known. Though he refers to Federov, the creator of space groups (whom he hails as one of the two greatest geniuses of crystallography in the preceding 50 years), Groth has nothing whatever to say about X-ray diffraction and crystal structure analysis, 16 years after the original discovery. Indeed, in 1928, crystal structure analysis was only beginning to get into its stride, and mineralogists like Groth had as yet derived very few insights from it; in particular, the structure analysis of silicates was not to arrive till a few years later.[1]

Metallurgists, also, were slow to feel at ease with the new techniques, and did not begin to exploit X-ray diffraction in any significant way until 1923. Michael Polanyi (1891–1976), in an account of his early days in research (Polanyi 1962) describes how he and Herman Mark determined the crystal structure of white tin from a single crystal in 1923; just after they had done this, they received a visit from a Dutch colleague who had independently determined the same structure. The visitor vehemently maintained that Polanyi's structure was wrong; in Polanyi's words, "only after hours of discussion did it become apparent that his structure was actually the same as ours, but looked different because he represented it with axes turned by 45° relative to ours".

Even the originator was hesitant to blow his own trumpet. In 1917, the elder Bragg published an essay on "physical research and the way of its application", in a multiauthor book entitled "Science and the Nation" (Bragg 1917). Although he writes at some length on Röntgen and the discovery of X-rays, he includes not a word on X-ray diffraction, five years after the discoveries by his son and himself.

This slow diffusion of a crucial new technique can be compared with the invention of the scanning tunnelling microscope (STM) by Binnig and Rohrer, first made public in 1983, like X-ray diffraction rewarded with the Nobel Prize 3 years later, but unlike X-ray diffraction quickly adopted throughout the world. That invention, of comparable importance to the discoveries of 1912, now (2 decades later) has sprouted numerous variants and has virtually created a new branch of surface science. With it, investigators can not only see individual surface atoms but they can also manipulate atoms singly (Eigler and Schweitzer 1990). This rapid adoption of the STM is of course partly due to much better communications, but it is certainly in part to be attributed to the ability of so many scientists to recognise very rapidly what could be done with the new technique, in distinction to what happened in 1912.

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[1] Yet when Max von Laue, in 1943, commemorated the centenary of Groth's birth, he praised him for keeping alive the hypothesis of the space lattice which was languishing everywhere else in Germany, and added that without this hypothesis it would have been unlikely that X-ray diffraction would have been discovered and even if it had been, it would have been quite impossible to make sense of it.

In Sweden, a precocious school of crystallographic researchers developed who applied X-ray diffraction to the study of metallic phases. Their leaders were Arne Westgren and Gösta Phragmén. As early as 1922 (Westgren and Phragmén 1922) they performed a sophisticated analysis of the crystal structures of various phases in steels, and they were the first (from measurements of the changes of lattice parameter with solute concentration) to recognise that solutions of carbon in body-centred alpha-iron must be 'interstitial' – i.e., the carbon atoms take up positions between the regular lattice sites of iron. In a published discussion at the end of this paper, William Bragg pointed out that Sweden, having been spared the ravages of the War, was able to undertake these researches when the British could not, and appealed eloquently for investment in crystallography in Britain. The Swedish group also began to study intermetallic compounds, notably in alloy systems based on copper; Westgren found the unit cell dimensions of the compound Cu_5Zn_8 but could not work out the structure; that feat was left to one of Bragg's young research students, Albert Bradley, who was the first to determine such a complicated structure (with 52 atoms in the unit cell) from diffraction patterns made from a powder instead of a single crystal (Bradley and Thewlis 1926); this work was begun during a visit by Bradley to Sweden. This research was a direct precursor of the crucial researches of William Hume-Rothery in the 1920s and 1930s (see Section 3.3.1.1).

In spite of the slow development of crystal structure analysis, once it did 'take off' it involved a huge number of investigators: tens of thousands of crystal structures were determined, and as experimental and interpretational techniques became more sophisticated, the technique was extended to extremely complex biological molecules. The most notable early achievement was the structure analysis, in 1949, of crystalline penicillin by Dorothy Crowfoot-Hodgkin and Charles Bunn; this analysis achieved something that traditional chemical examination had not been able to do. By this time, the crystal structure, and crystal chemistry, of a huge variety of inorganic compounds had been established, and *that* was most certainly a prerequisite for the creation of modern materials science.

Crystallography is a very broad science, stretching from crystal-structure determination to crystal physics (especially the systematic study and mathematical analysis of anisotropy), crystal chemistry and the geometrical study of phase transitions in the solid state, and stretching to the prediction of crystal structures from first principles; this last is very active nowadays and is entirely dependent on recent advances in the electron theory of solids. There is also a flourishing field of applied crystallography, encompassing such skills as the determination of preferred orientations, alias textures, in polycrystalline assemblies. It would be fair to say that within this broad church, those who determine crystal structures regard themselves as being members of an aristocracy, and indeed they feature prominently among the recipients of the 26 Nobel Prizes that have gone to scientists best described as crystallographers; some of these double up as chemists, some as physicists, increasing numbers as biochemists, and the prizes were awarded in physics, chemistry or medicine. It is doubtful whether any of them would describe themselves as materials scientists![2]

Crystallography is one of those fields where physics and chemistry have become inextricably commingled; it is however also a field that has evinced more than its fair share of quarrelsomeness, since some physicists resolutely regard crystallography as a technique rather than as a science. (Thus an undergraduate specialisation in crystallography at Cambridge University was killed off some years ago, apparently at the instigation of physicists.) What all this shows is that scientists go on arguing about terminology as though this were an argument about the real world, and cannot it seems be cured of an urge to rank each other into categories of relative superiority and inferiority. Crystallography is further discussed below, in Section 4.2.4.

3.1.2 Phase equilibria and metastability

I come now to the second leg of our notional tripod – phase equilibria.

Until the 18th century, man-made materials such as bronze, steel and porcelain were not 'anatomised'; indeed, they were not usually perceived as having any 'anatomy', though a very few precocious natural philosophers did realise that such materials had structure at different scales. A notable exemplar was René de Réaumur (1683–1757) who deduced a good deal about the fine-scale structure of steels by closely examining fracture surfaces; in his splendid *History of Metallography*, Smith (1960) devotes an entire chapter to the study of fractures. This approach did not require the use of the microscope. The other macroscopic evidence for fine structure within an alloy came from the examination of metallic meteorites. An investigator of one collection of meteorites, the Austrian Aloys von Widmanstätten (1754–1849), had the happy inspiration to section and polish one meteorite and etch the polished section, and he observed the image shown in Figure 3.4, which was included in an atlas of illustrations of meteorites published by his assistant Carl von Schreibers in Vienna, in 1820 (see Smith 1960, p. 150). This 'micro'structure is very much coarser

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[2] In a letter of unspecified date to a biologist, Linus Pauling is reported as writing (Anon 1998): "You refer to me as a biochemist, which is hardly correct. I can properly be called a chemist, or a physical chemist, or a physicist, or an X-ray crystallographer, or a mineralogist, or a molecular biologist, but not, I think, a biochemist."

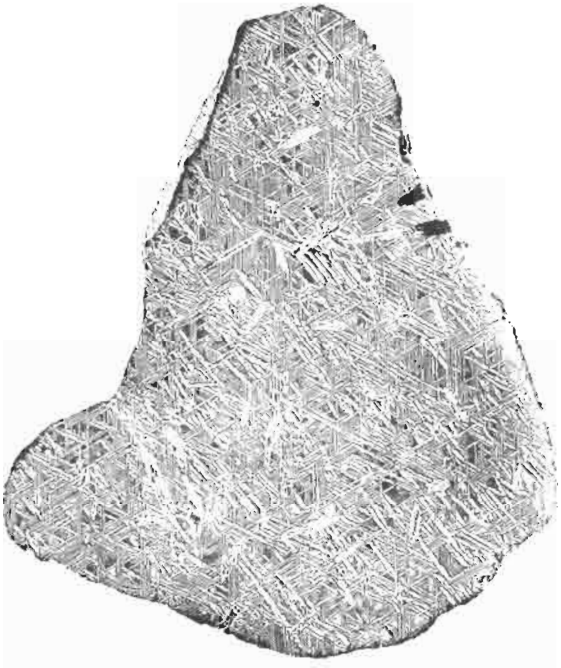

Figure 3.4. (from Smith 1960, p. 151). The Elbogen iron meteorite, sectioned, polished and etched. The picture was made by inking the etched surface and using it as a printing plate. The picture is enlarged about twofold. From a book by Carl von Schreibers published in 1820, based upon the original observation by von Widmanstätten in 1808. (Reproduced from Smith 1960.) This kind of microstructure has since then been known as a Widmanstätten structure.

than anything in terrestrial alloys, and it is now known that the coarseness results from extremely slow cooling ($\approx$ one degree Celsius per one million years) of huge meteorites hurtling through space, and at some stage breaking up into smaller meteorites; the slow cooling permits the phase transformations during cooling to proceed on this very coarse scale. (This estimate results both from measurements of nickel distribution in the metallic part of the meteorite, and from an ingenious technique that involves measurement of damage tracks from plutonium fission fragments that only left residual traces – in mineral inclusions within the metallic body – once the meteorite had cooled below a critical temperature (Fleischer *et al.* 1968); a further estimate is that the meteorite during this slow-cooling stage in its life had a radius of 150–250 km.)

In the penultimate sentence, I have used the word 'phase'. This concept was unknown to von Widmanstätten, and neither was it familiar to Henry Sorby (1826–1908), an English amateur scientist who was the prime pioneer in the microscopic study of metallic structure. He began by studying mineralogical and petrographic sections under the microscope in transmitted polarised light, and is generally regarded as the originator of that approach to studying the microstructure of rocks; he was initially rewarded with contempt by such geologists as the Swiss de Saussure who cast ridicule on the notion that one could "look at mountains through a microscope". Living as he did in his native city of Sheffield, England, Sorby naturally moved on for some years, beginning in 1864, to look at polished sections of steels, adapting his microscope to operate by reflected light, and he showed, as one commentator later put it, that "it made sense to look at railway lines through a microscope". Sorby might be described as an intellectual descendant of the great mediaeval German craftsman Georgius Agricola (1494–1555), who became known as the father of geology as well as the recorder of metallurgical practice. Sorby went on to publish a range of observations on steels as well as description of his observational techniques, mostly in rather obscure publications; moreover, at that time it was not possible to publish micrographic photographs except by expensive engraving and his 1864 findings were published as a brief unillustrated abstract. The result was that few became aware of Sorby's pioneering work, although he did have a vital influence on the next generation of metallographers, Heycock and Neville in particular, as well as the French school of investigators such as Floris Osmond. Sorby's influence on the early scientific study of materials is analysed in a full chapter in Smith's (1960) book, and also in the proceedings of a symposium devoted to him (Smith 1965) on the occasion of the centenary of his first observations on steel. One thing he was the first to suggest (later, in 1887, when he published an overview of his ferrous researches) was that his micrographs indicated that a piece of steel consists of an array of separate small crystal grains.

Our next subject is a man who, in the opinion of some well-qualified observers, was the greatest native-born American man of science to date: Josiah Willard Gibbs (1839–1903, Figure 3.5). This genius began his university studies as a mechanical engineer before becoming professor of mathematical physics at Yale University in 1871, before he had even published any scientific papers. It is not clear why his chair had the title it did, since at the time of his appointment he had not yet turned to the theory of thermodynamics. Yale secured a remarkable bargain, especially as the university paid him no salary for many years and he lived from his family fortune. In passing, at this point, it is worth pointing out that a number of major pure scientists began their careers as engineers: the most notable example was Paul Dirac (electrical), another was John Cockroft (also electrical); Ludwig Wittgenstein, though hardly a scientist, began as an aeronautical engineer. Unlike these others, Gibbs continued to undertake such tasks as the design of a brake for railway cars and of the teeth for gearwheels, even while he was quietly revolutionising physical chemistry and metallurgy. He stayed at Yale all his life, working quietly by himself,

J. Willard Gibbs.

Figure 3.5. Portrait of Josiah Willard Gibbs (courtesy F. Seitz).

with a minimum of intellectual contacts outside. He did not marry. It is not perhaps too fanciful to compare Gibbs with another self-sufficient bachelor, Isaac Newton, in his quasi-monastic cell in Cambridge.

In the early 1870s, Gibbs turned his attention to the foundations of thermodynamics (a reasonable thing for a mechanical engineer to do), when through the work of Clausius and Carnot "it had achieved a measure of maturity", in the words of one of Gibbs' biographers (Klein 1970–1980). Gibbs sought to put the first and second laws of thermodynamics on as rigorous a basis as he could, and he focused on the role of entropy and its maximisation, publishing the first of his terse, masterly papers in 1873. He began by analysing the thermodynamics of fluids, but a little later went on to study systems in which different states of matter were present together. This situation caught his imagination and he moved on to his major opus, "On the equilibrium of heterogeneous substances", published in 1876 in the *Transactions of the Connecticut Academy of Arts and Sciences* (Gibbs 1875–1978). In the words of Klein, in this memoir of some 300 pages Gibbs hugely extended the reach of thermodynamics, including chemical, elastic, surface, electromagnetic and electrochemical phenomena in a single system. When Gibbs (1878) published a short memoir about this paper, he wrote as follows:

> "It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has by no means escaped the attention of physicists, its importance does not seem to have been duly appreciated. *Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium* (my italics)."

Gibbs focused on the concept of a *phase*. This concept is not altogether easy to define. Here are three definitions from important modern textbooks: (1) Darken and Gurry, in *Physical Chemistry of Metals* (1953) say: "Any homogeneous portion of a system is known as a phase. Different homogeneous portions at the same temperature, pressure and composition – such as droplets – are regarded as the same phase". (2) Ruoff, *Materials Science* (1973) says: "A phase is the material in a region of space which in principle can be mechanically separated from other phases". (3) Porter and Easterling, in *Phase Transformations in Metals and Alloys* (1981) say: "A phase can be defined as a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system". A phase may contain one or more chemical *components*. The requirement for uniformity (homogeneity) of composition only applies so long as the system is required to be in equilibrium; metastable phases can have composition and property gradients; but then Gibbs was entirely concerned with the conditions for equilibrium to be attained.

In his 1878 abstract, Gibbs formulated two alternative but equivalent forms of the criterion for thermodynamic equilibrium: "For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy (entropy), the variation of its entropy (energy) shall either vanish or be negative (positive)". Gibbs moved on immediately to apply this criterion to the issue of chemical equilibrium between phases. According to Klein, "the result of this work was described by Wilhelm Ostwald as determining the form and content of chemistry for a century to come, and by Henri Le Chatelier as comparable in its importance for chemistry with that of Antoine Lavoisier" (the co-discoverer of oxygen). From his criterion, Gibbs derived a corollary of general validity, the *phase rule*, formulated as $\delta = n + 2 - r$. This specifies the number of independent variations δ (usually called 'degrees of freedom') in a system of r coexistent phases containing n independent chemical components. The phase rule, when at last it became widely known, had a definitive effect on the understanding and determination of *phase*, or *equilibrium*, *diagrams*.

There are those who say nowadays that Gibbs's papers, including his immortal paper on heterogeneous equilibria, present no particular difficulties to the reader.

This was emphatically not the opinion of his contemporaries, to some of whom Gibbs circulated reprints since the *Connecticut Transactions* were hardly widely available in libraries. One of his most distinguished admirers was James Clerk Maxwell, who made it his business to alert his fellow British scientists to the importance of Gibbs's work, but in fact few of them were able to follow his meaning. According to Klein's memoir, "(Gibbs) rejected all suggestions that he write a treatise that would make his ideas easier to grasp. Even Lord Rayleigh (in a letter he wrote to Gibbs) thought the original paper 'too condensed and difficult for most, I might say all, readers'. Gibbs responded by saying that in his own view the memoir was instead 'too *long*' and showed a lack of 'sense of the value of time, of (his) own or others, when (he) wrote it'." In Germany, it was not till Ostwald translated Gibbs's papers in 1892 that his ideas filtered through.

The man who finally forced Gibbs's ideas, and the phase rule in particular, on the consciousness of his contemporaries was the Dutchman H.W. Bakhuis Roozeboom (1856–1907), a chemist who in 1886 succeeded van 't Hoff as professor of chemistry in the University of Amsterdam. Roozeboom heard of Gibbs's work through his Dutch colleague Johannes van der Waals and "saw it as a major breakthrough in chemical understanding" (Daintith *et al.* 1994). Roozeboom demonstrated in his own research the usefulness of the phase rule, in particular, in showing what topological features are thermodynamically possible or necessary in alloy equilibria – e.g., that single-phase regions must be separated by two-phase regions in an equilibrium diagram. In Cyril Smith's words, "it was left to Roozeboom (1900) to discuss constitution (equilibrium) diagrams in general, and by slightly adjusting (William) Roberts-Austen's constitution diagram, to show the great power of the phase rule". By 1900, others, such as Henri Le Chatelier (1850–1936) were using Gibbs's principles to clarify alloy equilibria; Le Chatelier's name is also immortalised by his Principle, deduced from Gibbs, which simply states that any change made to a system in equilibrium results in a shift in the equilibrium that minimises the change (see overview by Bever and Rocca 1951).

Roozeboom engaged in a long correspondence (outlined by Stockdale 1946) with two British researchers in Cambridge who had embarked on joint alloy studies, Charles Thomas Heycock (1858–1931) and Francis Henry Neville (1847–1915) (Figure 3.6), and thereby inspired them to determine the first really accurate non-ferrous equilibrium diagram, for the copper–tin binary system. Figure 3.7 reproduces this diagram, which has the status of a classic. Apart from the fact that in their work they respected the phase rule, they made two other major innovations. One was that they were able to measure high temperatures with great accuracy, for the first time, by carefully calibrating and employing the new platinum resistance thermometer, developed by Ernest Griffiths and Henry Callendar, both working in Cambridge (the former with Heycock and Neville and the latter in the Cavendish Laboratory); (at about the same time, in France, Le Chatelier perfected the platinum/platinum-

Figure 3.6. Charles Heycock and Francis Neville.

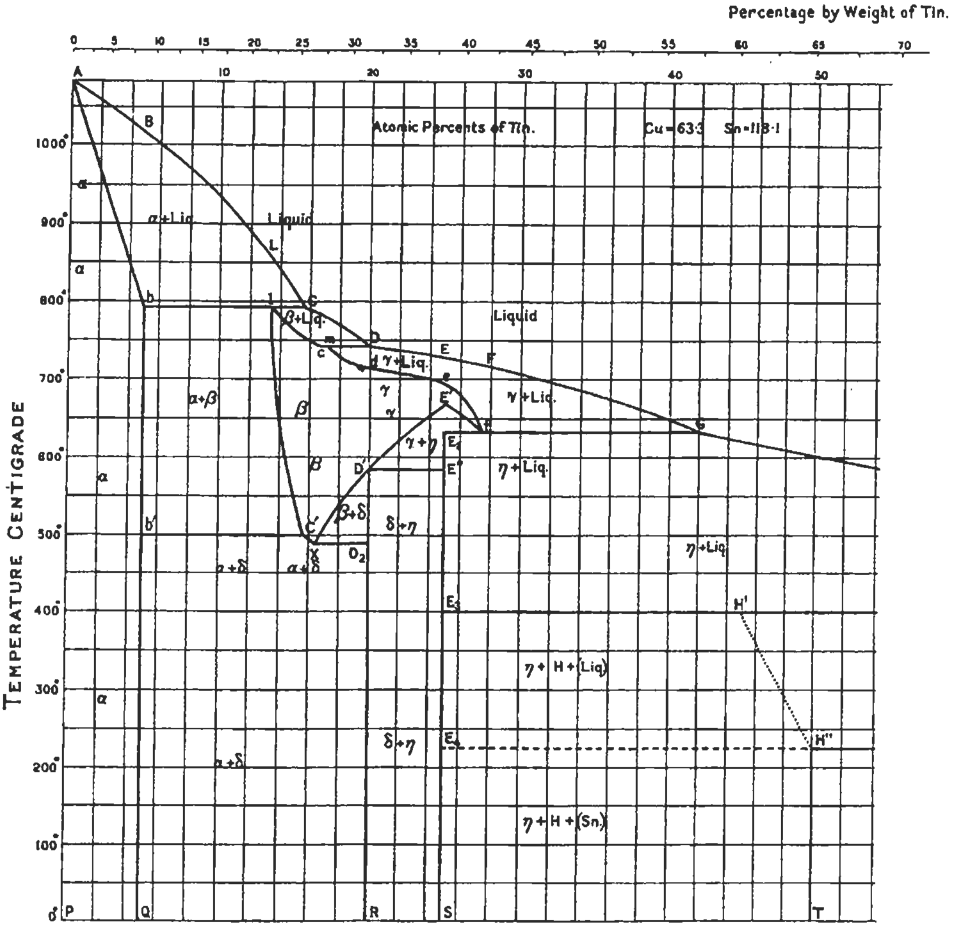

Figure 3.7. Part of Heycock and Neville's Cu–Sn phase diagram.

rhodium thermocouple). Heycock and Neville's other innovation was to use the microscope in the tradition of Sorby, but specifically to establish equilibria, notably those holding at high temperatures which involved quenching specimens from the relevant temperatures (see Section 3.1.3). Heycock and Neville set up their joint laboratory in the garden of one of the Cambridge colleges, Sidney Sussex, and there they studied alloy equilibria from 1884 until Neville's retirement in 1908. A full account of the circumstances leading to the operation of a research laboratory in a single college as distinct from a central university facility, and detailed information about the careers of Heycock and Neville, can be found in a book published in 1996 to mark the fourth centenary of Sidney Sussex College (Greer 1996).