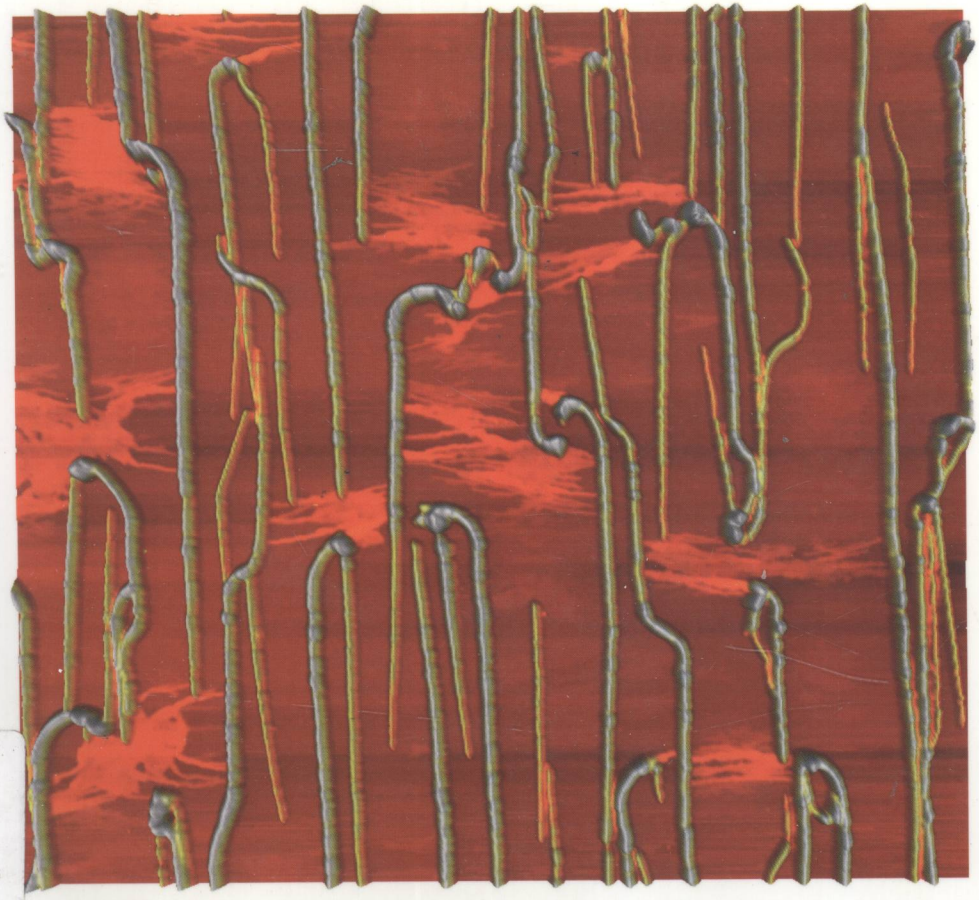
PHYSICS TEXTBOOK

Horst-Günter Rubahn

WILEY-VCH

Basics of Nanotechnology

Third, Revised and Enlarged Edition



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E2009001025

WILEY-VCH Verlag GmbH & Co. KGaA

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Cover

Atomic force microscopy image of walking stick like, light emitting nanostructures made via self-assembled growth of functionalised organic oligomers on a muscovite mica substrate. Image size: 42 x 42 micrometer squared. Height scale 200 nm.

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Original Title:

H.-G. Rubahn
Nanophysik und Nanotechnologie
2. Auflage, ISBN 3-519-10331-1
Teubner-Verlag, 2004

Translation:
H.-G. Rubahn

Library of Congress Card No.:
applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Composition Da-TeX, Gerd Blumenstein, Leipzig

Printing Betz-Druck GmbH, Darmstadt

Bookbinding Litges & Dopf GmbH, Heppenheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-40800-9

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Preface

'Nanotechnology is one of the most important technologies of the twenty-first century'. Such a statement would undoubtedly find support amongst an ever expanding number of scientists, engineers and laymen. The basis of all nanotechnology is 'nanoscience' or somewhat more specifically 'nanophysics', which describes the physics of nanoscaled systems, that is, the transition from atomic physics to continuum and solid state physics.

On such mesoscopic levels between microscopic and macroscopic physics many peculiarities of biology, chemistry and physics vanish. Thus nanotechnology might serve as a very efficient mediator between these disciplines of the natural sciences. The present book tries to take account of this fact – admittedly in a very selective way, biased by the research topics and interests of the author. The book begins with a *physical* approach, describing some of the laws that dictate the possibilities and limits of the new nano-based developments. Technological aspects become important once the processes are described that result in nanostructures, that allow one to characterize them and the ways that make manipulation on a nanoscale possible. *Selforganization* is one of the critical new concepts, a concept which has entered physical thinking on this size range from the chemistry and biology side. The multitude of possible applications in optics, electronics, information theory and biology is illustrated with the help of one-, two- and three-dimensionally nanostructured materials, biological templates and more complex nanomachinery.

This book is an update of a German edition, dating back to the years 2002 and 2004. Since the millenium shift the speed with which nanotechnology has introduced itself into the everyday world of scientists and the rest of the world is simply astonishing. This applies both the use of scientific instruments that base on nanotechnology as well as the appearance of products that are labeled 'nano'. An inofficial survey from 2008 produced over 600 'nano' products, more than 200 of them indeed contain-

Basics of Nanotechnology: 3rd Edition. Horst-Günter Rubahn

ISBN: 978-3-527-40800-9

ing nanoscaled particles or structures. In all research-oriented developed countries the amount of funding for nano-related research is increasing, and also high technology enterprises have discovered the promise of nanotechnology.

In spite of all the technological developments, all the research funding and all the publications in highly ranked journals, basic research breakthroughs that could be termed 'nanotechnology' are still rather scarce – partly because of the extensive optimism with which application writers have been sketching development prognoses within the last ten years. Finally, let us note that the 'Technology Roadmap for Nanoelectronics' (www.cordis.lu) distributed by the European Commission November 2000 is still relevant.

I am deeply grateful to my wife Katharina Rubahn and to my sons Alexander and Markus for the possibility to spend peaceful siesta times on this book. Thanks also to my colleagues Frank Balzer and Jakob Kjelstrup-Hansen for numerous discussions and hints.

Sonderborg, August 2008 *Hoerst-Günther Rubahn*

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Mesoscopic and Microscopic Physics

According to a generally accepted definition 'nanotechnology' is a technology concerned with objects that have at least in one dimension a size of less than 100 nm. This means that the underlying 'nanophysics' can be placed inbetween mesoscopic physics (the physics of objects between a few microns and one hundred nanometer) and microscopic physics (the physics of interactions between individual atoms and molecules).

Nanotechnology is currently one of the motors driving the introduction of new materials and technologies into all aspects of daily life: from communication and energy generation via health and leisure to traffic and environment. This development can be considered parallel to the present revolution in molecular biology, especially in the molecular biophysics of the post-genomic age. The European Union as well as the large American and Japanese (and to a certain degree also Chinese, Brazilian, Indian etc.) research societies currently invest substantial resources in research geared towards applied nanotechnologies[1]. The main goal for the immediate future is to generate new nano-electronic and nanomechanic elements, to integrate them and to produce the resulting devices in a cheap manner. One of the big expectations is that nanotechnology will eventually fulfill the dreams of scientists from all disciplines; from physicists waiting to see quantum mechanical concepts come to life; via chemists, longing to fabricate large molecules atom for atom; to biologists, seeking to control atom transport into and out of membranes and understand which functions the macromolecules composing the genome perform. *There's plenty of room at the bottom*, as Richard Feynman stated as early as 1959 in his famous lecture [1].

Since the early-1960s the potential of integrated circuits that are used in the computer industry has grown exponentially, fulfilling a prediction

1) Dedicated nanotechnology support through the European Community has been provided since 2000, initially via the 'Nanotechnology information devices'-initiative within framework five (FP5).

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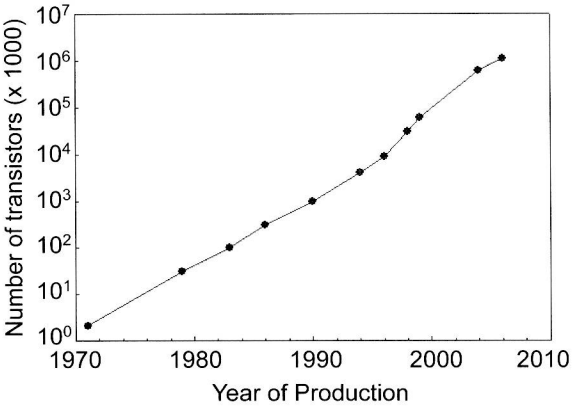

Figure 1.1 Moore's law, confirmed by a plot of number of transistors vs. production year.

by Gordon E. Moore, called 'Moore's law' [2] (Figure 1.1)[2]. Although this 'law' was initially proposed to hold only until the mid-1970s it has since been shown that the physical limit will not be reached until around 2017 [3]. Following a prediction of the SIA ('Semiconductor Industry Association') characteristic structure sizes of 40 nm will be standard in the year 2011 [4]. In fact, Intel currently routinely breaks the 30 nm or even 20 nm size limit. This rapid nano-miniaturization will eventually result in the integration of several tens of million logic elements on a single chip. The bandwidth of information that can be transmitted through an optical fiber doubles even every six months – this made the exponential distribution of the Internet and hence the information technology (IT) revolution possible. New concepts for the preparation of nanostructures, such as neuronal networks, are becoming increasingly important for the traditional, silicon based electronics industry.

Primarily the development has been driven by the microminiaturization of electronic components. This process is mainly limited by technological problems, which can normally be solved by clever engineering. However, approaching atom dimensions, new limits are set by those physical laws which gain increasing importance with decreasing size. This 'physics at small sizes' has the advantage that radically new concepts of information storage and processing can be used, all the way down to the use of quantum mechanical phenomena. In this context new developments such as 'quantum computing' or 'quantum cryptography' gain increasing importance [5].

2) The doubling rate of the number of elements on a chip has decreased from 12 months in the early seventies to roughly 30 months for the first decade of the 21^{st} century.

Although the prefix 'nano' serves in many cases a purely decorative purpose, it has become a synonym for the opening of a new dimension populated with objects that incorporate (or seem to incorporate) new structural, electronic, optical and magnetic properties. The hope is that we will eventually be able to create new materials and processing schemes for our daily 'macroscopic' life: partially via a fundamental understanding (and manipulation) of the microscopic properties and partially via empirical research. The availability of new technological concepts (scanning microscopies, submicron-lithography, laser, super computer) gives hope that these attempts may eventually become successful. Note, however, that the mere reduction in size of participating objects increases tremendously the complexity of the systems to be mastered on a nano-level (Figure 1.2). Present science and technology are still far away from such mastership.

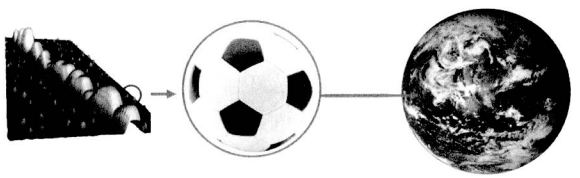

Figure 1.2 A football filled with nanoscaled objects resembles the complexity of the whole earth.

Taking into account all the above mentioned developments, it is nearly unavoidable to fall into a state of technological hybris. Let us, therefore, remember that many of the 'newly developed' nano effects have historical roots. Glasses, for example, which show extreme brilliance by the inclusion of colloidal quantum dots, have been know since ancient Greek times: from the famous Lycurgus cup to church windows. In these cases the colloidal solutions were generated in 400 B.C. via 'alchimia' and the quantum dots fabricated by the mechanical formation of gold and silver dust particles.

The most common method for the fabrication of structures in the submicrometer size regime is the 'top-down' technology ('from large to small'), where using lithographic techniques nanoscaled elements are cut from larger entities (Figure 1.3). However, as one approaches sizes below 100 nm the resolution and replication speed limit the efficiency, consequently in this size regime the 'bottom-up' technology ('from small to large') becomes important. Here nanosized objects are formed from their atomic or molecular compounds using appropriate building recipes. Two different approaches are available. In the first one non-biological molecular mechanisms are used on a surface or in a liq-

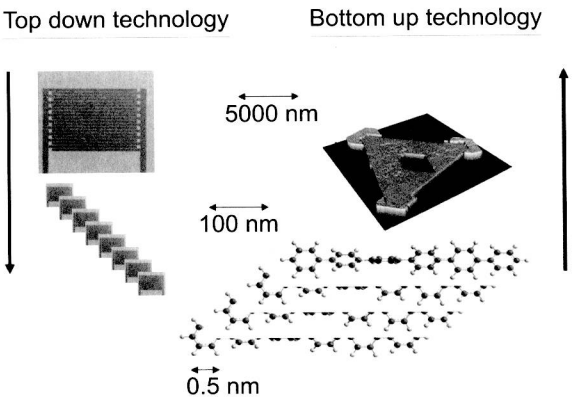

Figure 1.3 Top-down vs. bottom-up technology.

uid to run controlled chemical (surface) reactions that produce complex structures that are specified down to the atom scale. The results of such mechanistic engineering science on the atom level is a non-biological[3] 'molecular manufacturing' or 'molecular nanotechnology' [7, 8], which contains as its most important elements mechanical driven chemical synthesis (e.g. direct positioning of reactive molecules on a surface), energetically driven surface structure formation and/or molecular transformation of chemical into kinetic energy (e.g. via synthetic molecular actuators and motors).

It is worthwhile to compare top-down fabrication, such as conventional macroscopic or microstructure fabrication, with molecular manufacturing [7]. While the feature scale decreases from 1 mm (macroscopic fabrication) over 1 μm (microscopic fabrication) to 0.3 nm (molecular manufacturing), the product scale decreases from 1 m over 10 mm to about 100 nm, but at the same time the defect rate per component also decreases drastically from 10^{-4} over 10^{-7} to 10^{-15}. This is accompanied by an increase in cycle times from 1 s to 100 s. However, cycle times for molecular manufacturing are only of the order of 1 μs.

It is also possible to direct a self-consistent system development in a mimicry of biological development on an atomic or molecular level. This principle of 'self organization', driven by conversion of free energy [9], is not limited to biological systems[4] but can be applied to a large va-

3) Molecular nanotechnology has a rather wide range of implications, for example for a new kind of medical diagnosis and therapy[6].

4) Biology is limited to the aqueous phase and is concerned with 'soft' materials with characteristic energies of phase change of $k_B T$. Even small temperature changes result in huge struc-

riety of atomic and molecular architectures. Another advantage of the 'bottom-up' approach as compared to the 'top-down' approach is that it is a massive parallel approach. Every product mol unit contains some 10^{23} individual yet identically built nano systems.

A basic question to every approach on nanotechnology is: in how far do nanoscaled objects behave in the same way as objects in the macroscopic world, just on a smaller size scale. In other words: how reliably can one apply physical or chemical laws of the macroscopic world on objects that consist of a countable number of atoms and have distances from each other of the order of countable multitudes of atom diameters? It is found, for example, that in the nano world the equilibrium of forces is different from that in the macroscopic world: owing of the small mass of the objects, gravitational forces are less important while electrostatic attraction and van der Waals forces are of huge importance. The electrostatic force is about 11 orders of magnitude larger compared to the magnetic force between two parallel, 1 nm long conductor segments through which a current of 10 nA flows. This latter force is only $2 \cdot 10^{-23}$ N and thus much smaller than the covalent bond strength which is of the order of 10^{-9} N[5]. The small dimensions of the nano-objects and their low masses make fast frequency motion possible (100 ms^{-1} velocity mean that 1 nm is traversed in 10 ps). Pressure values are large for small forces due to the small areas involved – this is also true for light pressure. Photons can redirect easily non-bound nano objects.

If one aims to move nanoscaled objects to a defined location with a defined speed, then in additon to the quantum mechanical uncertainty limit the statistical movement of the nanoobjects has to be taken into account. This statistical movement is induced by the temperature of the environment ('Brownian movement'). The thermal velocity is proportional to the square root of the ratio between thermal energy and mass. For one cubic nanometer diamond (density $3.5 \cdot 10^3$ kgm^{-3}) one obtains at room temperature an average thermal velocity of 60 ms^{-1}, that is, 60×10^9 nms^{-1}.

In general, the ratio between thermal energy kT and quantum mechanical energy quantum $\hbar\omega$ determines whether statistical uncertainties due to thermal fluctuations or quantum mechanical uncertainties due to the quantum mechanical uncertainty principle are the dominant factors that limit the ability to localize position and velocity of a nanoscaled object with high precision.

tural changes. Self organization, however, can be found also in physical or chemical much stronger bound systems,e.g., within supramolecular chemistry.

5) Note, however, that these values result from classical continuum scaling laws, which might not represent accurately the nano world.

During the interplay of two objects on the nanoscale one has to take into account that classical lubricants no longer work as expected since fluids loose their viscosity close to surfaces and in many cases no longer behave as fluids; consequently, friction might lead to strong wear and thus to a short lifetime of nanoscaled mechanical machinery. However, if one looks closer at the problem in terms of attractive and repulsive molecule-surface forces instead of the macroscopic description via friction one finds that the resulting equilibrium of forces can significantly decrease wear and thus increase characteristic lifetimes. The lesson being that true nanophysical effects make simple estimates obsolete – both in the positive and in the negative directions.

Finally, it is noted that the 'nano revolution' is not limited to the structural dimension – the interaction *dynamics* on the atom level are just as important. Movement and movability of atomic, molecular and nanoscaled objects have to be investigated and understood before one can confidently manipulate them on a nanoscale. An important tool for such are ultrashort pulse lasers ('femtosecond' lasers) which allow one to image and manipulate elemental dynamics with atom resolution.

The uncertainty relation tells us that a light pulse with a duration of some ten femtoseconds (10^{-15} s) has a huge energy uncertainty of some electron volts (eV) (Figure 1.4a). Since the energetical distance between vibrational Eigenstates of a molecule is far below one eV, the excitation of the molecule with the femtosecond pulse results in a coherent superposition of excited Eigenstates. Further, this uncertainty in the energetic excitation means that the Eigenstates of the molecule are transformed from their original spatial distribution along the space coordinate to become localized within the femtosecond excited state into a wave packet with small spatial extension (Figure 1.4b). The movement of this wave packet along a potential curve can thus be registered with sub-Ångstrom resolution.

In the recent past this technology has also been applied to problems of biological relevance ('femtobiology'). One investigates, for example, conformational changes in proteins on a realtime scale or monitors temporally resolved electron transport via DNA. From the latter measurements it has been deduced, among others, that DNA possesses only a small conductance, similar to a semiconductor. This implies that the direct use of DNA as a 'molecular wire' in future quantum computers is not possible.

In summary, modern technology allows one to explore the nano-world with extremely high spatial and temporal resolution. However, there is still a long way to go from a detailed exploration to a complete understanding or directed manipulation.

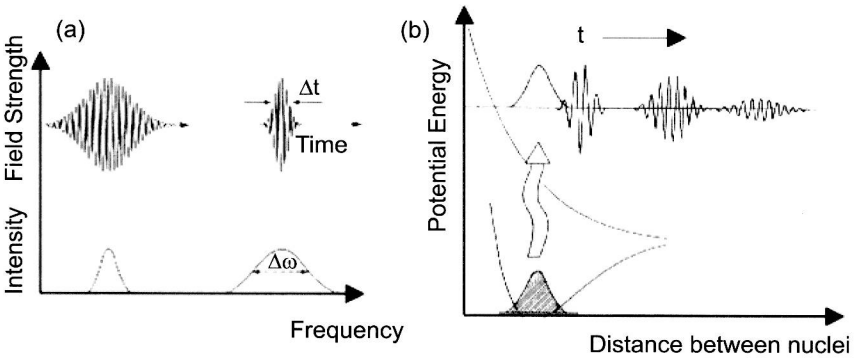

Figure 1.4 (a) The relationship between temporal and energetical uncertainty. (b) Generation of a localized wave packet via excitation with a femtosecond pulse. Printed with permission from [10]. Copyright 1993 Cambridge University Press.

Problems

Problem 1.1 Compare gravitational, electrostatic and van der Waals forces between two 100 nm diameter polystyrole spheres which are separated by a) one micrometer, b) one millimeter and c) one centimeter.

Problem 1.2 The momentum of a photon is $\hbar k$, where k is the wave vector. Assume an object moving at a speed of $10\,\mathrm{ms}^{-1}$. Objects of which mass can be stopped by elastic reflection of photon?

Problem 1.3 Ultrashort pulsed lasers allow one to investigate dynamics in the nano world with unprecedented temporal resolution. What is the minimum temporal length of a laser pulse of wavelength 800 nm?

Problem 1.4 A typical femtosecond laser pulse has a duration of 80 fs and a central wavelength of 800 nm. Calculate the corresponding spectral line width, that is, the uncertainty in energy of the photons. The temporal resolution allows one to study very precisely dynamics in nanoscaled systems, but is the corresponding energy definition sufficient to resolve optical transitions between a) electronic states, b) vibrational states, c) rotational states of molecules? Use as an example the lithium dimer and the electronically excited B-state. Term energy is $21926\,\mathrm{cm}^{-1}$, vibrational constant $351\,\mathrm{cm}^{-1}$ and rotational constant $0.67\,\mathrm{cm}^{-1}$.