

Chapter 1

Introduction

Today, nanotechnology is still at the beginning, and only rudimentary nanostructures can be created with some control. The science of atoms and simple molecules, on one end, and the science of matter from microstructures to larger scales, on the other, are generally established. The remaining size-related challenge is at the nanometer scale — roughly between 1 and 100 molecular diameters — where the fundamental properties of materials are determined and can be engineered. A revolution has been occurring in science and technology, based on the developed ability to measure, manipulate and organize matter on this scale. Recently discovered organized structures of matter (such as carbon nano-tubes, molecular motors, DNA-based assemblies, quantum dots, and molecular switches) and new phenomena (such as giant magnetoresistance, coulomb blockade, and those caused by size confinement) are scientific breakthroughs that merely hint at possible future developments [Roco, Sims, 2001].

More and more, small structures with dimensions in the nanometer regime play an important role within molecular biology, chemistry, materials science and solid-state physics.

Of particular interest in biology there is, for example, the replication of proteins, the functionality of special molecular mechanisms like haemoglobin or even such seemingly simple structures like the flagella of certain bacteria. Chemistry, on the other hand, deals with the synthesis — and therefore also with an improvement — of these structures with which nature solves so many problems. For example, the design of catalysts is a considerable commercial factor within the chemical industry. Specific modifications of properties of well-known materials using small particles and the development of fabrication processes of nano-particles are topics of modern

material sciences. Self-cleaning surfaces as well as pigments are typical examples for applications of nanostructures where, interestingly, the latter already led to some success within the cosmetic industry [Siegel, 1997].

But nanotechnology comprises more than just producing small structures — the concept goes much further. Nanotechnology is an anticipated manufacturing technology giving thorough, inexpensive control of the structure of matter where other terms, such as *molecular manufacturing*, *nano-engineering*, etc. are also often applied. Researchers hope to design and program *nano-machines* that build large-scale objects atom by atom. With such self-replicating *assemblers* objects of any size and in any quantity could be manufactured using common materials like dirt, sand, and water. Computers 1000 times faster and cheaper than current devices; biological nano-robots that fix cancerous cells; towers, bridges, and roads made of unbreakable diamond strands; or buildings that can repair themselves or change shape on command might be future but likely implications of nanotechnology.

What makes nanostructures different? They show significantly different properties compared to the bulk material. As is known from quantum mechanics the electronic states of nano-particles are considerably changed compared to the bulk. This is due to quantization effects caused by the spatial restriction. The electronic structure, on the other hand, is responsible for all those material properties like electronic conductivity, optical absorption, chemical reactivity or even the mechanical properties. Therefore, these nanostructures appear as particles with new material properties [Jena *et. al*, 1987].

The investigation of nanostructures is a highly topical field of solid state physics and materials research. New, sophisticated characterization methods have been successfully developed during the last twenty years like the scanning tunnelling microscope (STM), for example, which has been established as standard instrument for scanning nanostructures on surfaces or the transmission electron microscope (TEM) combined with theoretical modeling for visualization of periodic structures. Even scattering methods (ions, electrons, X-rays, neutrons) have been improved to an extent which is hard to beat. Finally, spectroscopic information with high resolution has become available through the use of synchrotron radiation sources of the third generation [FZJ, 1998].

Beside all these experimental characterization techniques, which are applicable to existing structures only and which are most often time and cost intensive, computational methods for many-particle systems have

made their entrance into all branches of science for which the term nanotechnology has been established. Computer experiment, computer chemistry, molecular design, nano-machinery, nano-manufacturing and nano-computation are just a few subjects which have come up in connection with numerical calculations in the field of nanotechnology [Alig *et. al*, 2000].

Here, one tendency is clearly recognizable: nanotechnology makes *design* the most important part of any development process. With nanotechnology the amount of design work increases enormously due to its complexity. Planning for the widespread change, each nano-design could make design planning incredibly important [Milanski, 2000]. To summarize, design will change radically under nanotechnology and for nano-engineers or nano-designers, respectively, a broad knowledge will become even more important in the future.

Trying to categorize the numerical solution techniques for many-particle systems basically leads to four different topics: quantum theoretical calculations (*ab initio*), molecular mechanics, Monte Carlo, and molecular dynamics methods.

While the solution of *Schrödinger's* equation for many-particle systems is inherently impossible — the calculation time increases exponentially with the particle number — quantum theoretical calculation methods focus on approximation and separation approaches to simplify the calculation scheme. Some of the most common *ab initio* methods are self-consistent field methods, the linear combination of atomic orbitals or the density functional method [Sauer, 2000].

In contrast to *ab initio* methods, molecular mechanics and molecular dynamics are based on classical mechanics. The particles are treated as mass points interacting through force fields which in turn are derived from interacting potentials. The goal of molecular mechanics (as well as of *ab initio* calculations) is to find stable configurations for a set of particles, that is, to determine saddle points (local minima) on the potential energy surface. While quantum mechanical calculations lack an *a priori* concept of chemical bonds, molecular mechanic methods use the approach, known from traditional organic chemistry, where molecules are characterized by ball-and-stick models in which each ball represents an atom and each stick represents a bond. Depending on the kind of bond, appropriate interaction potentials have to be chosen and, therefore, energy functions and parameters have to be tailored to specific local arrangements of atoms. In this way molecular mechanics programs treat the potential energy as a sum of

terms accounting chiefly for bond stretching, bending, torsion and for *van-der Waals*, overlap and electrostatic interactions among non-bonded atoms. Molecular mechanics systems have, however, been successfully applied to just a narrow range of molecular structures in configurations not too far from equilibrium [Drexler, 1992].

Similar considerations are valid for molecular dynamics calculations. But in contrast to Monte Carlo methods where new particle configurations are created randomly step by step, molecular dynamics works through the solution of *Newton's equations of motion*. Therefore, the evolution of a many-particle system can be calculated in certain time steps where the total information (particle positions, velocities, kinetic and potential energies, etc.) of the system is available for each time step. All further properties — like for example the temperature — can be determined without any additional parameters.

This is not the case for Monte Carlo methods. Here one generally samples system configurations according to a given statistical ensemble, characterized by *Boltzmann* distributions which include the temperature as external parameter and, therefore, such calculations are only applicable for configurations near the equilibrium. Additional problems arise in the attempt to assign time steps to the different configurations [Ciccotti *et. al*, 1986]. *Ab initio* calculations also lack the subject temperature by nature, because there are no dynamic considerations involved.

Beside this, each of the four calculation techniques has its advantages as well as limitations. When performing computational methods the results should basically mirror reality as closely as possible. *Ab initio* calculations work without additional *a priori* input like interaction potentials and — depending on the degree of simplification used in the particular method — the results include explicitly several different quantum effects. On the other hand, the computational effort is enormous, i.e. usually the systems are restricted to less than a few hundred atoms. Nevertheless, these methods have revolutionized chemistry with the computer aided design of molecules among many other applications.

While both, molecular mechanics and molecular dynamics methods, are based on classical many-particle physics, there are no explicit results from quantum effects available. Furthermore, these methods need a detailed knowledge of the particle interactions before the numerical calculation can be started, that is, specific models have to be established differing from case to case and depending on the study. Here, quantum mechanics comes into play implicitly with the use of interaction potentials, gained, for example,

from *ab initio* calculations. Most often additional fits of such potentials to experimental data are necessary to obtain realistic results.

However, the precision and validity of the interaction potentials within molecular mechanics and molecular dynamics calculations restrict the field of application of these methods. On the other hand, both methods are able to handle large systems with about 10^5 to 10^7 atoms depending on the study.

Most modern commercial molecular mechanics programs use libraries of phenomenological potentials to describe all the different types of interactions occurring in the field of organic chemistry. With these it is possible to study minimum-energy configurations, stiffness, bearing and other properties of nanostructures (molecules), which are built largely of carbon atoms joint by strong, directional, covalent bonds (single, double, triple, hybrid) which in turn are often augmented with one or more different elements. Due to the simplified description of the atomic interactions — aside from the small inaccuracies found in all structures — standard molecular mechanic programs cannot realistically describe certain structures. For example, they can model many stable structures, even when strained, but they cannot describe chemical transformations or systems which are close to the transformation point. Therefore, computational results must be examined closely for such invalid conditions. However, studies for broad classes of organic structures including large biomolecules as well as polymers are possible with a computation cost favor by a factor of more than 10^3 compared to *ab initio* methods [Drexler, 1992].

Since molecular dynamics methods are more sensitive to inappropriate forces — with respect to the validity of the results — it is even more important to concentrate on the use of properly determined interaction potentials. It is absolutely necessary to consider the range of validity, the applicability as well as the accurateness of the underlying interaction potentials whenever molecular dynamics methods are applied [Gehlen *et. al.*, 1972].

While most works use either many-body forces (for the description of covalent bonds) or phenomenological inter-atomic potentials, in this book, in contrast, we focus mainly on mono-atomic nanosystems for which reliable, precise interaction forces are available within a wide range of applicability. To be more specific, we restrict ourselves — as far as possible — to studies using exclusively one of the two materials: a noble gas (krypton) and a simple metal (aluminium).

At first glance, however, this seems not to promise spectacular results, but — as will be shown later on — even seemingly simple nanostructures

most often do not behave like they are assumed to do. While this is typical for the whole field of nanotechnology, the focus within the present monograph is laid on such basic “nano-effects” which can only be detected by the use of realistic descriptions of the atomic interactions. On the other hand, more complicated scenarios like nano-machines with metallic parts will be outlined, too.

Finally, it should be emphasized that working within computational nano-physics by means of molecular dynamics implies a combination of several scientific fields like atomic interaction potential theory (which in turn is a combination of several different branches of theoretical and experimental physics), computer science and statistical mechanics.

Therefore, we start with a brief introduction into atomic potentials for noble gases and simple metals and then continue with an excursus through the field of molecular dynamics and nano-design which is followed by a review of several characterization functions known from statistical mechanics. Finally, these introducing chapters are succeeded by presentations and discussions of different application examples and studies which provide an insight into the world of computational nano-engineering.