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Introduction

About 40 years ago, research on nanoparticles and nanoparticle matter restarted. The development of new techniques (laser, ESCA, STM, AFM, SNOM, etc.) and the continuous improvement of existing techniques (vacuum technology, electron microscopy, etc.) has allowed new insights into an old subject – the transition from the atom or molecule to the bulk solid matter.

The results obtained at the beginning of this period showed that the *size* of the object plays the key role: almost all physical properties show a significant size dependence on going to sizes less than 100 nm. This is, however, not new at all. For more than 150 years chemists and physicists have been concerned with the colloidal state of matter, being called by Ostwald *Welt der vernachlässigten Dimensionen* (world of the disregarded dimensions) [1]. Well known are, for example, the colloidal gold dispersions of Faraday in the nineteenth century. Colloidal systems can even be traced back to the Romans, who empirically developed methods to stain glass with small inclusions of gold or silver. One famous example is the Lycurgus cup (fourth century AD; see book cover), which can be viewed at the British Museum. First descriptions of how to obtain ruby gold glass can be found as early as in the bibliography of Ashurbanipal in Nineve (seventh century BC). Industrial manufacturing of stained glass with colloidal particles was established in the seventeenth century, for example by Kunckel [2]. In the nineteenth and twentieth centuries, colloidal nanoparticles found applications mainly in photography based on silver halide nanocrystals, as color pigments, and in catalysis, with their size often exceeding the magic threshold of 100 nm used in nanotechnology. The basic structures in nanotechnology are one-dimensional structures which are less than 100 nm in size in all three dimensions (nanoparticles, nanopores), line-shaped structures with two dimensions less than 100 nm (nanowires, nanocages, nanogrooves), and layers which are nanoscaled in only one dimension. To avoid further semantic problems, I will use the term *nanoparticle* for all particles that are at least in one dimension less than *999 nm*. Hence I include a larger range of particles relevant for applications beyond the nanotechnology horizon, such as organic and inorganic color pigments.

The newly recognized size and quantum size effects of the last 40 years not only led to a better insight into the transitions from molecule to bulk matter, but also to a new, rapidly growing market of possible applications. Although we usually do

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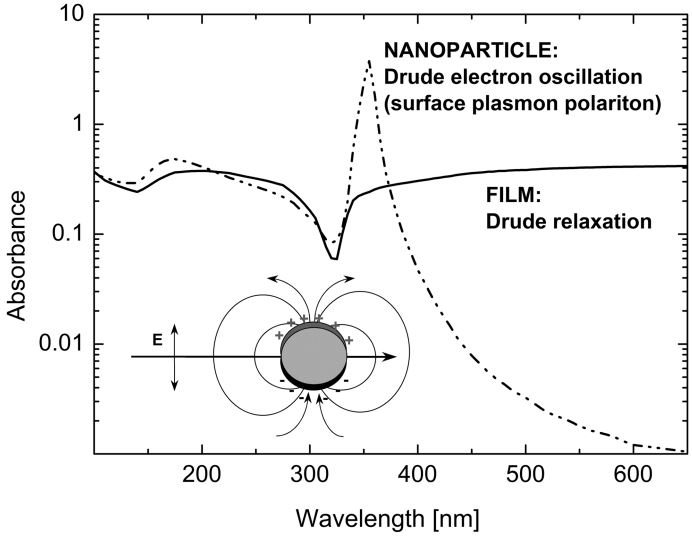

Figure 1.1 The conduction electron oscillator in a silver nanoparticle compared with the conduction electron relaxator in a silver film.

not realize it, nanoparticles belong to our everyday life: cosmetics, medicines, alternative energy, communication, and displays are examples which benefit from the basic science of nanotechnology. As in various applications the magic threshold of 100 nm is exceeded, this book also treats nanoparticles up to 999 nm in size so as to include these cases.

A reduction in size down to a few nanometers often leads to size- or material-specific peculiarities which can be used in new applications of the materials. These peculiarities cannot be observed with macroscopic pieces of the same material. For example, nanoparticulate matter exhibits increased hardness, fracture strength, additional electronic states, increased chemical selectivity, and increased surface energy. One of the most interesting peculiarities is the resonant absorption of light by nanometer-sized gold or silver particles. Unlike in bulk gold and silver, the collective excitation of the conduction electrons by an external electromagnetic field does not result in a relaxator but is transformed into an oscillator type of behavior with a distinct resonance, called surface plasmon polariton. Figure 1.1 illustrates this behavior for a silver nanoparticle (oscillator) compared with a bulk silver film (relaxator).

Hence metal nanoparticles play a particularly pronounced role in nanomaterial science. Nature even seems to have a preference for metals. More than two-thirds of all elements are metals. When looking at the optical properties of nanoparticles, not all metals exhibit such striking properties as gold and silver, nor do most of the metal particles remain unchanged under ambient conditions. Rather, oxides, sulfides, nitrides, and so on are formed with their own specific peculiarities. Therefore, this book considers also the optical properties of nonmetallic nanopar-

ticles and provides many examples of various nanoparticle systems of metallic, semiconducting, carbonaceous, and dielectric particles.

During the last 40 years, a huge number of papers, reviews, and books have appeared which are concerned with nanotechnology, nanoelectronics, nanooptoelectronics, information technology with nanomaterials, self-assembly, nanostructured magnetic materials, nanocomposites, nanowires, and nanobelts. They mainly cover mechanical, electronic, quantum mechanical, and medical aspects, with little attention to optical properties. The most perceptible to humans, however, are the optical properties, for example, the color of paintings and the colors due to interference.

Optical properties of nanomaterials include elastic light scattering, absorption, reflectance and transmittance, second harmonic generation, third-order nonlinear optical properties, surface-enhanced Raman scattering, and others. This book concentrates on the *linear* optical properties: elastic light scattering and absorption of single nanoparticles and on reflectance and transmittance of nanoparticle matter.

Elastic light scattering has turned out to be a powerful tool for examination of the properties of small particles. Scientists and engineers from a large variety of disciplines – physics, electrical engineering, meteorology, chemistry, biophysics, and astronomy – are concerned with this field.

Hence light scattering and absorption by small particles has already been treated in numerous textbooks [3–5] and monographs [6–16], so it would appear almost unnecessary to write a further book on this topic. However, these monographs either deal mainly with particles larger than 1000 nm that are important in geophysics, planetary science, and astrophysics; nanoparticles appear here almost only for species that are relevant for the Earth's radiation budget and in astrophysics, for example, carbon or silicates; or, they mainly consider in detail the spatial (angular) distribution of scattered light. Only Kreibig and Vollmer [11] have given a comprehensive overview of the optical properties of metallic nanoparticles, clusters, and cluster matter, including a discussion of size and quantum size effects. Their book is restricted to particle sizes less than approximately 100 nm and to metals for which nanoparticles exhibit characteristic resonances in absorption and scattering. It gives a good overview of the developments in nanoparticle science from the beginning in the 1970s until 1995 and includes also an overview of preparation techniques. The present book is intended to fill the gap in the description of the optical properties of small particles with sizes less than 1000 nm and to provide a comprehensive overview of the *spectral behavior* of nanoparticulate matter of metallic, semiconducting, carbonaceous, and dielectric particles.

From the physical point of view, the spectral behavior must be a function of the photon energy $\hbar\omega$. On the other hand, the optical properties of small particles strongly depend on the size compared with the size of the electromagnetic radiation, that is, the wavelength λ. Moreover, in commonly used spectrometers for the ultraviolet, visible, and near-infrared spectral ranges, the output is usually given versus the wavelength. In this respect, the wavelength seems to be the appropriate quantity which permits direct comparison with experimental results, for which I

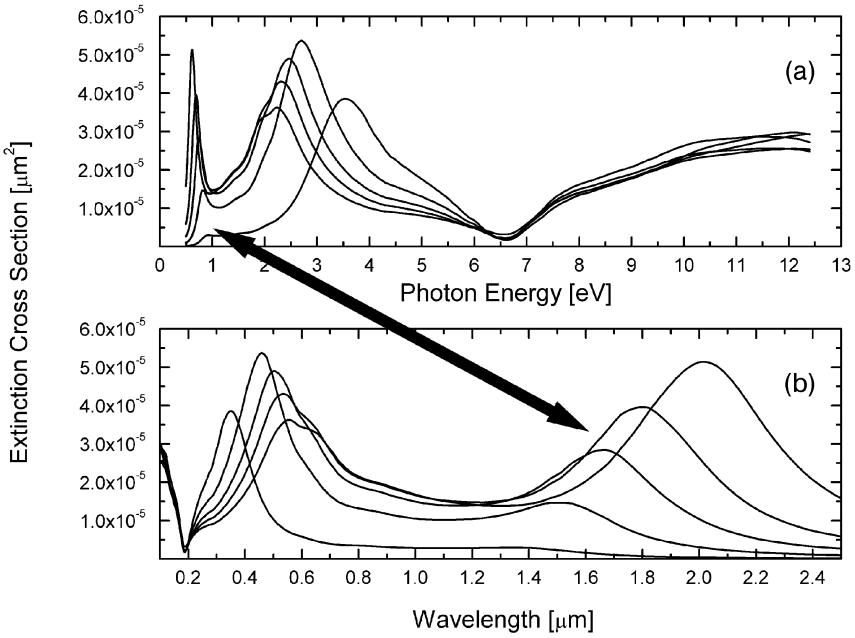

Figure 1.2 The influence of abscissa scaling on the appearance of optical data: extinction cross-section spectra of yttrium nanoparticles (a) versus photon energy and (b) versus wavelength.

preferably use the wavelength as abscissa to allow comparison with measured optical properties. Note that in the mid- and far-infrared regions the wavenumber in cm^{-1} is often used. This quantity is proportional to the energy $\hbar\omega$, but has the advantage of being measured in simple natural numbers instead of floating point numbers. Figure 1.2 demonstrates the difference between wavelength and photon energy as abscissa in the optical absorption spectra of nanoparticles. Using the photon energy, the UV region becomes spread and the IR region squeezed, and vice versa when using the (vacuum) wavelength.

In general, there are two steps on the way to the optical properties of a nanoparticle system. The first step (Figure 1.3) considers the geometry of a single isolated nanoparticle and its intrinsic optical properties, that is, its dielectric function. This information enters a suitable classical electrodynamic model, derived either rigorously or approximately, or formulated as a numerical method. The enormous practical advantage of any electrodynamic scattering model is that it enables one to compute *numerically* the optical response for arbitrary *realistic* particle materials. However, the classical electrodynamics used, being a phenomenological theory to describe light propagation, does not yield information about optical material properties. They enter via the dielectric functions inserted into the Maxwell boundary conditions, which must be taken from elsewhere, for example, from experiments or from quantum solid-state theory model calculations. The results of the first step are the optical properties of a single particle.

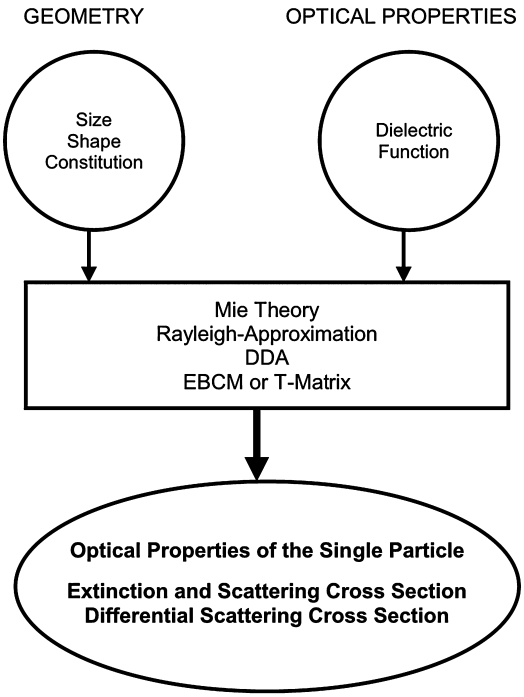

Figure 1.3 Step 1 on the way to the optical properties of a nanoparticle system: optical properties of the single particle.

The second step (Figure 1.4) considers the optical properties of the single particle from the first step and combines it with statistical information on size, shape, and the spatial distribution of many particles. New models that take into consideration all this information allow the calculation of, finally, the macroscopic optical properties of the nanomaterial, such as reflectance, transmittance, absorbance, and color.

The present book continues in Chapter 2 with an attempt to classify nanoparticle systems according to different properties and parameters. Then, it is emphasized how the main parameters of nanoparticle matter – size, shape, and constitution of the individual particle, optical constants of the particle material, concentration and spatial distribution of the particles – influence in principle the optical properties of a nanoparticle system.

One of the most important parameters – the dielectric function of the individual particle material – is discussed in Chapter 3 before any electromagnetic scattering model, because the understanding of intrinsic material-dependent interaction of light with matter is essential for the understanding of light scattering processes by an arbitrary obstacle. Once having established optical constants for the particle material, either from a table in a published work or by well-known and well-defined models, they can be used in an electromagnetic scattering model. Each of these

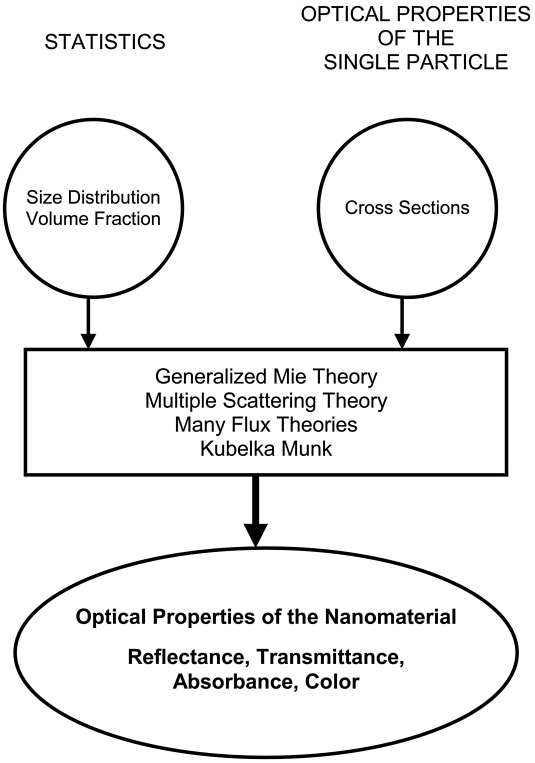

Figure 1.4 Step 2 on the way to the optical properties of a nanoparticle system: optical properties of the nanomaterial.

scattering models, rigorously established as numerical method for solving Maxwell's equations, has the same basis, described in Chapter 4.

In the subsequent chapters, various electrodynamic models are introduced which consider either the shape of the particle or the concentration of the particles in the nanoparticle matter. The models are supplemented by a considerable number of calculations of the spectral dependence of scattering and absorption, and by selected experimental results.

The most evolved model on light scattering and absorption by small particles stems from Gustav Mie [17] and describes the scattering by a spherical particle. Mie's theory, presented in Chapter 5, is fundamental and has found many applications in physics, astrophysics, chemistry, and engineering whenever light scattering by particles is important. Resonances in scattering and absorption play an important role for the spectrally resolved optical response of the nanoparticles and are discussed in detail in this chapter.

The importance of Mie's theory is emphasized in Chapter 6, where it is applied to calculate the size-dependent spectra of various nanoparticles. Metallic nanoparticles of different metals play a pronounced role also in these calculations. Further

relevant material groups are semiconductors and oxides, with corresponding calculations presented here. The calculations are supplemented by many experimental examples.

Mie's theory has often been extended to permit calculations on particles taking into account certain boundary conditions. Chapter 7 considers the most important extensions on coated spheres, spheres on substrates, and inhomogeneous incident waves and other extensions. Again, appropriate experimental examples are given.

So far, Mie's theory and its extensions appear to be almost the ideal model to describe the optical properties of nanoparticles. However, particularly for metal particles where electrons form a quasi-free carrier gas with generic properties, the limitations of Mie's theory become obvious on going to sizes less than about 30 nm. They are discussed in Chapter 8.

The strongest limitation of Mie's theory, however, follows from its applicability to only spherical particles. Beyond Mie's theory, further electrodynamic models have been developed for particles of nonspherical shape. They are summarized and discussed in Chapter 9. Models for light scattering by ellipsoids, spheroids, cylinders, and cubes are available, partly as a rigorous solution of Maxwell's equations, and partly in the approximation of particles that are small compared with the wavelength of light. All these models are again supplemented by representative calculations and experimental results. Finally, numerical models for arbitrarily shaped particles have been developed. Among them, the *discrete dipole approximation* and the *T-matrix method* are the mostly commonly used and best known models.

Beyond Mie's theory, not only models for light scattering by nonspherical particles are available, but also models that take into account electromagnetic interactions among neighboring particles in nanoparticulate matter. With the *generalized Mie theory* (GMT) we present in Chapter 10 a rigorous solution for interacting spherical particles. Interaction introduces new parameters on which the optical properties now depend, in addition to the parameters of the isolated particle. The main new parameters are the size and shape of so-called aggregates – more or less densely lumped particles – and the interparticle distance. Their influence on the optical properties are discussed in detail in this chapter.

Similarly to single isolated particles, Chapter 11 gives an overview of the optical properties of aggregates and on nanoparticulate matter where the concentration of particles is high as the electromagnetic interaction among the nanoparticles can never be neglected. This is done with numerous calculations for various particle materials and certain aggregate topologies, and also with calculations on higher concentration nanoparticle systems. The calculations are supplemented by some experimental data.

So far, the GMT seems to be almost the most comprehensive model to describe the linear optical properties of clustered nanoparticles, similar to the Mie-theory for isolated particles. However, the computational burden increases rapidly with increasing number of particles and requires more and more computer capabilities with correspondingly longer computation times. Therefore, for densely packed

nanoparticle systems such as paintings and lacquers the GMT must be replaced by faster models.

Faster and even much simpler models for dense nanoparticle matter are introduced and discussed in Chapter 12. They are based on the calculation of energy fluxes through the samples from left to right and vice versa. Individual particle properties enter these calculations by absorption and scattering rates. The results of such calculations are the reflectance and transmittance of the nanoparticulate matter. For the simplest flux model by Kubelka and Munk [18] improvements are discussed using the GMT for the calculation of the absorption and scattering rates of individual blocks of nanoparticle matter.

Special emphasis is given to the electromagnetic near-field in Chapter 13. This plays a certain role in applications such as surface-enhanced Raman spectroscopy (SERS) and also for near-field microscopy techniques and for waveguides with sizes below the wavelength.

Chapter 14, finally, is dedicated to the optical properties of bulk inhomogeneous matter which consists of a matrix material with nanoparticles as inclusions. The optical response of the inhomogeneous matter is described here as the response of homogeneous matter with modified dielectric function. Various *effective medium theories* are available in which the size of the inclusions is meaningless and scattering by the particles is neglected. The result of all these models is a so-called effective dielectric function that enters the macroscopic optical response of the bulk inhomogeneous matter, that is, the reflectance, transmittance, and intrinsic absorption. We discuss in this final chapter both the strengths and weaknesses of these models.