OPTICAL PROPERTIES OF SURFACES

This invaluable book represents a substantial body of work describing the theory of the optical properties of thin island films and rough surfaces. In both cases the feature sizes are small compared to the wavelength of light. The approach is extremely rigorous and theoretically very thorough.

The reflection, transmission and absorption of light are described. Computer programs that provide exact solutions for theoretical properties of thin island films have recently become available, and this makes the book of great practical use.

The early chapters provide a comprehensive theoretical framework. The electromagnetic properties of a boundary layer are described in terms of excess of the electric current, charge density and electric and magnetic fields, in Chapters 2 and 3. The reflection, transmission and absorption of light are described in Chapter 4. Chapters 5 to 10 present a spectrum of specific island films. Spheres and spheroids with the axis of revolution normal to the substrate are treated. The region of contact is finite in both cases and the bottom of the island planar. Both the low coverage limit and finite coverage are discussed. In all cases the electromagnetic interaction with the image charge distribution in the substrate is taken into account rigorously. In Chapter 11 the theory is applied to stratified layers, reproducing well-known results in a simple and straightforward manner. The Green functions for the general solution of the wave equation are given in Chapter 12 and used in Chapter 13 in the derivation of the symmetry relations. The last chapter deals with rough surfaces.

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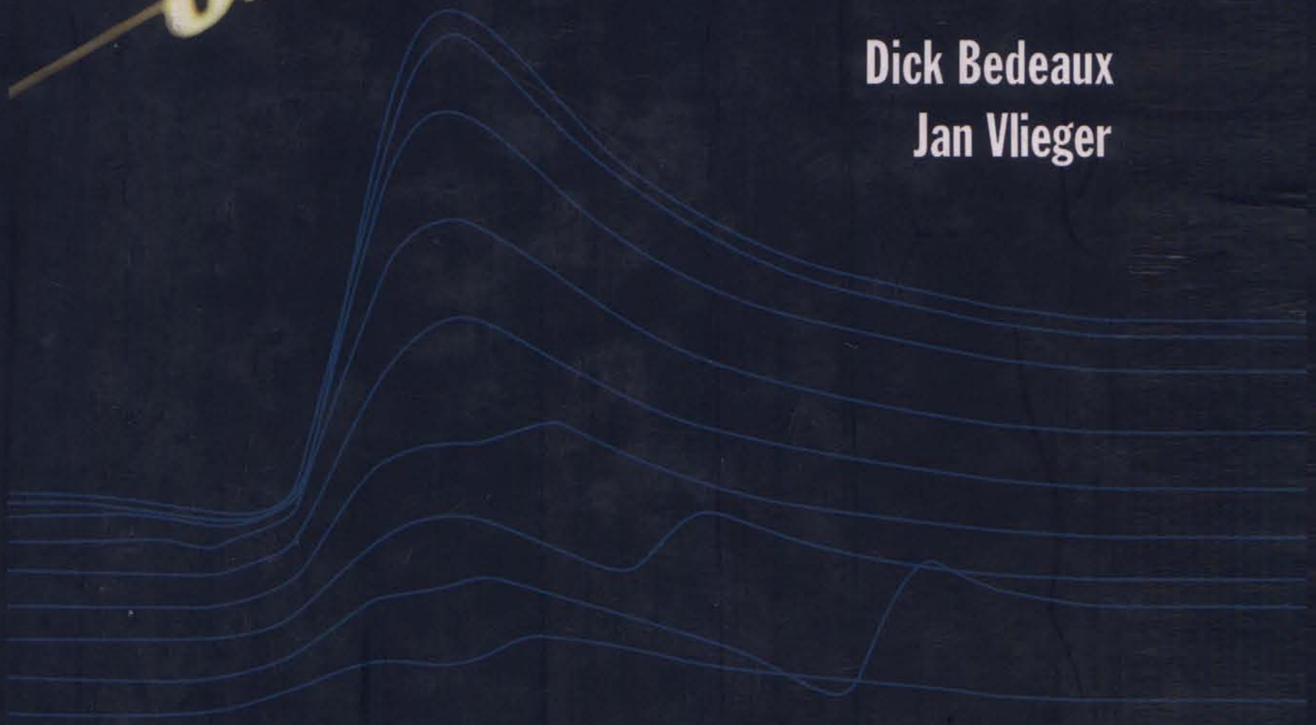

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PREFACE

The aim of the book is to present in a systematic manner the exact results the authors obtained over the years for the description of the optical properties of thin films and rough surfaces. This work found its origin 30 years ago in a discussion of one of us (J.V.), during a sabbatical, with the late Professor Dr. G.D. Scott of the University of Toronto, Canada, about the Maxwell Garnett theory. Many questions arose which resulted in a paper by Vlieger on the reflection and transmission of light by a two-dimensional square lattice of polarizable dipoles (Physica 64, page 63, 1973). When the other author (D.B.) read this paper he was surprised by the efforts to describe the results in terms of a layer of a finite thickness, using Maxwell Garnett, while the original model had a polarizability, which was so clearly restricted to the plane of the surface. A choice of the optical thickness in terms of the distance between the dipoles seemed to be constructed. It appeared much more reasonable to replace a thin layer, compared to the wavelength of the incident light, by an infinitesimally thin layer, than the other way around. Of course the formulation of a new theory in terms of an infinitesimally thin polarizable dipole layer, which was compatible with Maxwell's equations, is easier said than done. It turned out to be necessary to introduce singularities in the electric and magnetic field at the surface in addition to the occurrence of such singularities in the sources of these fields (Physica A 67, page 55, 1973). A general description was developed, using constitutive coefficients, to describe the electromagnetic response of the surface. Having thus convinced ourselves that this approach was feasible, we started to apply these ideas to thin island films and rough surfaces.

In the treatment of surfaces a confusing element is "where to choose the precise location of the surface". For instance, for an island film one has two possible choices, one through the average centre of the islands and the other on the surface of the usually flat substrate. The constitutive coefficients depend on this choice. As the choice of this dividing surface is only a matter of convenience in the mathematical description, it is clear that the relevant observable properties, like for instance the ellipsometric angles, are independent of this choice. To make this independence clear so-called "invariants" were introduced. These invariants are appropriately chosen combinations of the constitutive coefficients independent of the location of the dividing surface. The introduction of such invariants was first done by Lekner, for the special case of thin stratified layers, and described in 1987 in his monograph on the "Theory of Reflection". One of the chapters in this book considers the case of thin stratified layers in detail and compares with Lekner's work.

When one moves a dipole from one choice of the dividing surface to another the dipole moment remains the same. The displacement leads to a contribution to the quadrupole moment, however. In order to properly describe the equivalence of different choices of the dividing surface it is therefore necessary to describe the surface to quadrupolar order. The relative importance of these quadrupolar terms is very dependent on the nature of the surface. For highly absorbing metal island films they are not important. If the island material is dielectric or when the surface is rough, the quadrupolar terms are found to be very important. In the comparison with Lekner's results for thin stratified layers, these quadrupolar terms are found to be essential.

For island films, thin compared to the wavelength of the incident light, two aspects are found to be of importance. The first is the interaction of the islands with their image in the substrate. The second is the interaction with the other islands, and with their images. For the first problem the shape of the island is very important. Over the years we were able to construct explicit solutions for spheres, truncated spheres, spheroids and truncated spheroids. For different shapes, the same amount of island material is found to lead to very different optical properties. This was also the reason to construct these explicit solutions, as they give insight into which precise aspect of the shape might be responsible for certain observed behavior. For the interaction along the surface one would expect the correlations in the distribution to be important. This, however, turned out not to be the case. Only for coverages larger than 50% this starts to be an issue. A square and a triangular array lead to essentially the same properties as a random distribution for coverages below 50%. Nevertheless the interaction with the other islands, though not dependent on the details of the distribution, changes the polarizability of the islands considerably.

For rough surfaces the correlations along the surface play a more essential role. The quadrupolar contributions are crucial in this case. It was in fact in the study of the contribution of capillary waves on fluid surfaces to the ellipsometric coefficient, that we discovered the relevance of these quadrupolar contributions.

Over the years we had many stimulating contacts. Over a period of more than 25 years Professor Dr. O. Hunderi from the Norwegian University of Science and Technology, Trondheim, Norway, has been a source of inspiration. His knowledge of the properties of island films has been a great help. We are also indebted to Professors Dr. C.G. Grandqvist and Dr. G.A. Niklasson from the University of Uppsala, Sweden, for many discussions about island films. For the foundation of the use of singular fields, charge and current densities we are grateful to Professor Dr. A.M. Albano from Bryn Mawr College, Penn., USA. We had a very rewarding collaboration with Dr. R. Greef from the University of Southampton, UK, on the optical properties of films sparsely seeded with spherical islands with a size comparable to the wavelength. Though this subject is not covered in this book, it added much to our understanding of the subject.

In the past decade we had an active collaboration with the group of Professor Dr. P. Schaaf and Dr. E.K. Mann from the Institute Charles Sadron, Strasbourg, France, and with Dr. G.J.M. Koper of our own institution. Our insight in the use and the practical relevance of invariants gained immensely due to this work.

Over the years we had many graduate students who contributed to the contents of this book. In chronological order we have: Dr. B.J.A. Zielinska, Dr. M.M. Wind, Dr. P.A. Bobbert, Dr. E.M. Blokhuis, Dr. M. Haarmans, Dr. E.A. van der Zeeuw and R. van Duijvenbode. In particular the theoretical work of Wind and Bobbert led to significant progress for the foundation of the whole methodology.

Recently I. Simonsen from the Norwegian University of Science and Technology, Trondheim, Norway, (Ingve.Simonsen@phys.ntnu.no), wrote software to perform the calculations outlined in chapters 4-10. These programs have been put into operation together with R. Lazzari from the CEA Grenoble, France (Lazzari@drfmc.ceng.cea.fr) and it is now possible to make practical use of the analytical results in these chapters, see http://www.phys.ntnu.no/~ingves/Software/GranularFilm/. We are very grateful to both of them for this and for many clarifying discussions. About 60 % of the figures in this book were made by Lazzari who thereby contributed greatly to the usefulness and the clarity of the sections on island films with applications. The software is available for use. For this purpose one should consult the above mentioned web site and in case of difficulties contact either Simonsen or Lazzari. For the other figures we are grateful to J. van der Ploeg from our group and to L. Nummedal from the Norwegian University of Science and Technology, Trondheim, Norway. Nummedal was also, on many occasions, a great help solving the various software problems.

Leiden, February, 2001

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CONTENTS

Chapter 1
INTRODUCTION

It is the aim of this book to describe the optical properties of surfaces with a thickness small compared to the wavelength of the incident light. The emphasis will be on two kind of surfaces. The first kind consists of a film of discrete islands, small compared to the wavelength, attached to a flat substrate. An important example of such films are metallic films. The second kind is the rough surface. In that case the surface resembles a landscape with hills and valleys. The height is again small compared to the wavelength of the light.

Historically the first description of metallic films was given by Maxwell Garnett in 1904[1]. He developed a theory for metallic glasses, assuming the metal to be distributed in the form of small spherical islands. The polarizability of such an island may be shown to be equal to

$$\alpha = 4\pi\epsilon_a R^3 \frac{\epsilon - \epsilon_a}{\epsilon + 2\epsilon_a} \tag{1.1}$$

where ϵ_a is the dielectric constant of the glass, ϵ the complex frequency dependent dielectric "constant" of the metal, and R the radius of the sphere. Using the Lorentz–Lorenz formula one then finds for the effective complex frequency dependent dielectric constant of the metallic glass the following formula

$$\frac{\epsilon_{eff} - \epsilon_a}{\epsilon_{eff} + 2\epsilon_a} = \phi \frac{\epsilon - \epsilon_a}{\epsilon + 2\epsilon_a} \tag{1.2}$$

where ϕ is the volume fraction of the spheres. This formula is successful, in that it explains for instance the striking colors of the metallic glass and their dependence on the volume fraction. In the same paper Maxwell Garnett also applied his theory to metallic films. In that case the islands are on the surface of the glass and surrounded by the ambient with a dielectric constant ϵ_a. The volume fraction is a parameter which is not systematically defined. In practice one fits it to the experimental data, like for instance to the minimum in the transmission, and interprets it as the weight thickness divided by the so-called optical thickness. The experiment in this way measures the optical thickness of the film.

Even though the Maxwell Garnett theory is very useful to describe the qualitative behavior of thin metallic films, the quantitative agreement is not very satisfactory. One has tried to improve this along various lines. One observation is that Lorentz–Lorenz is not adequate. An alternative popular choice for the effective dielectric constant is given, for instance, by the symmetric Bruggeman formula[2], [3]

$$\phi\frac{\epsilon_{eff}-\epsilon}{\epsilon_{eff}+2\epsilon}+(1-\phi)\frac{\epsilon_{eff}-\epsilon_a}{\epsilon_{eff}+2\epsilon_a}=0 \tag{1.3}$$

One may show that this expression reduces to Maxwell Garnett for small volume fractions. For a history and a description of alternative effective medium theories one is referred to Landauer [4]. It is not our aim to discuss the various methods to make effective medium theories work. For this we refer to various reviews, [5], [6], [7], [8] and [9].

There are two major reasons, why effective medium theories are only qualitatively correct for surfaces. The first reason is, that the direct electromagnetic interaction between the islands along the surface is taken into account using some local field argument. The choice of this local field is appropriate for a three dimensional distribution of islands, as for instance in a metallic glass, but not for a two dimensional array. The second reason is, that all these theories neglect the electromagnetic interaction with the substrate. The electric field due to the images of the spheres is not taken into account. These images cause the polarizability of the spheres to be different in the directions along and normal to the surface. The surface breaks the symmetry. A dipolar model for this effect was first given by Yamaguchi, Yoshida and Kinbara [10].

In this book a theory for thin island films and rough surfaces is given, which describes both the direct electromagnetic interaction along the surface and the interaction with the substrate. The electromagnetic properties of the surface are described in terms of four susceptibilities, γ, β, τ and δ. The first coefficient γ gives the integrated surface polarization parallel to the surface in terms of the electric field along the surface. The second coefficient β gives the integrated surface polarization normal to the surface in terms of the electric displacement field normal to the surface. The third and the fourth coefficients τ and δ are of quadrupolar order. They are not very important for the description of metallic films, where γ and β dominate the behavior. For rough surfaces, but also for films of latex spheres on a glass substrate, these quadrupolar terms are found to be needed, however. The book discusses the general case for which also the integrated surface magnetization is taken along. For the details of this aspect, which requires the introduction of magnetic analogs of the above susceptibilities, we refer to the main text. The work described was done over many years in our group in Leiden and will be referred to when used in the text.

For thin island films the analysis in this book is based on the calculation of the polarizabilities of the islands. The surface is assumed to be isotropic for translation along the surface and rotation around a normal. All islands are therefore (statistically) equivalent. Effects due to electromagnetic interaction between islands are calculated assuming the islands to be identical. Both regular arrays and random arrays of islands are considered. The analysis to dipolar order gives the (average) polarizabilities parallel, $\alpha_\parallel$, and normal, $\alpha_\perp$, to the surface per island. The resulting dipolar susceptibilities are

$$\gamma=\rho\alpha_\parallel \quad\text{and}\quad \beta=\rho\alpha_\perp/\epsilon_a^2 \tag{1.4}$$

where ρ is the number of islands per unit of surface area. The (average) quadrupole polarizabilities parallel, $\alpha_{\parallel}^{10}$, and normal, $\alpha_{\perp}^{10}$, to the surface per island give the dipole moment of the island in the direction parallel to the surface in terms of the parallel derivative of the electric field along the surface, and the dipole moment of the island in the direction normal to the surface in terms of the normal derivative of the electric field normal to the surface, respectively. The resulting susceptibilities are

$$\tau = -\rho\alpha_{\parallel}^{10} \text{ and } \delta = -\rho[\alpha_{\perp}^{10} + \alpha_{\parallel}^{10}]/\epsilon_a \tag{1.5}$$

See chapter 5 for a discussion of the definition of the polarizabilities and their relation to the susceptibilities in the small ρ case. Chapters 5–10 give the explicit calculation of dipole and quadrupole polarizabilities for spheres, spheroids, truncated spheres and truncated spheroids on a substrate, both for small and finite ρ.

One may substitute the polarizabilities of the sphere surrounded by the ambient into eq.(1.4). This gives

$$\gamma = \epsilon_a^2\beta = \rho\alpha = 4\pi\epsilon_a R^3\rho\frac{\epsilon - \epsilon_a}{\epsilon + 2\epsilon_a} = 3t_w\epsilon_a\frac{\epsilon - \epsilon_a}{\epsilon + 2\epsilon_a} \tag{1.6}$$

where the weight thickness was identified with $t_w = 4\pi R^3\rho/3$. In the calculation of the integrated excess quadrupole moments one must specify the location of the surface, on which one locates this dipole moment. The natural choice for this dividing surface is the surface of the substrate. Shifting the dipoles from the center of the spheres to the surface of the substrate leads to quadrupole polarizabilities given by

$$\alpha_{\parallel}^{10} = \alpha_{\perp}^{10} = -R\alpha \tag{1.7}$$

Substituting this equation, together with eq.(1.1) for the polarizability, into eq.(1.5) then gives, with eq.(1.6),

$$\tau = \frac{\epsilon_a}{2}\delta = 3t_w R\epsilon_a\frac{\epsilon - \epsilon_a}{\epsilon + 2\epsilon_a} = R\gamma = R\epsilon_a^2\beta \tag{1.8}$$

It should be noted that the quadrupole moment, due to a constant field, can be identified with the dipole moment, due to a gradient field, on the basis of symmetry considerations, cf. chapter 5. All interactions between the spheres have been neglected. The above expressions are therefore only correct in the low coverage, i.e. low weight thickness regime. Also they assume, that the interaction with the image charges in the substrate is unimportant. This is only correct if the difference between the dielectric constants of the ambient and the substrate is negligible.

In order to compare with the Maxwell Garnett or the Bruggeman theory, one must calculate the susceptibilities for a thin layer with a dielectric constant ϵ_{eff} and a thickness t_{opt}. In chapter 11 the expressions for the susceptibilities of a stratified medium are derived. Applying these expressions to a thin layer one finds

$$\begin{aligned} \gamma &= t_{opt}(\epsilon_{eff} - \epsilon_a), \qquad \beta = t_{opt}(\epsilon_{eff} - \epsilon_a)/\epsilon_{eff}\epsilon_a \\ \tau &= \frac{1}{2}t_{opt}^2(\epsilon_{eff} - \epsilon_a), \quad \delta = \frac{1}{2}t_{opt}^2(\epsilon_{eff}^2 - \epsilon_a^2)/\epsilon_{eff}\epsilon_a \end{aligned} \tag{1.9}$$