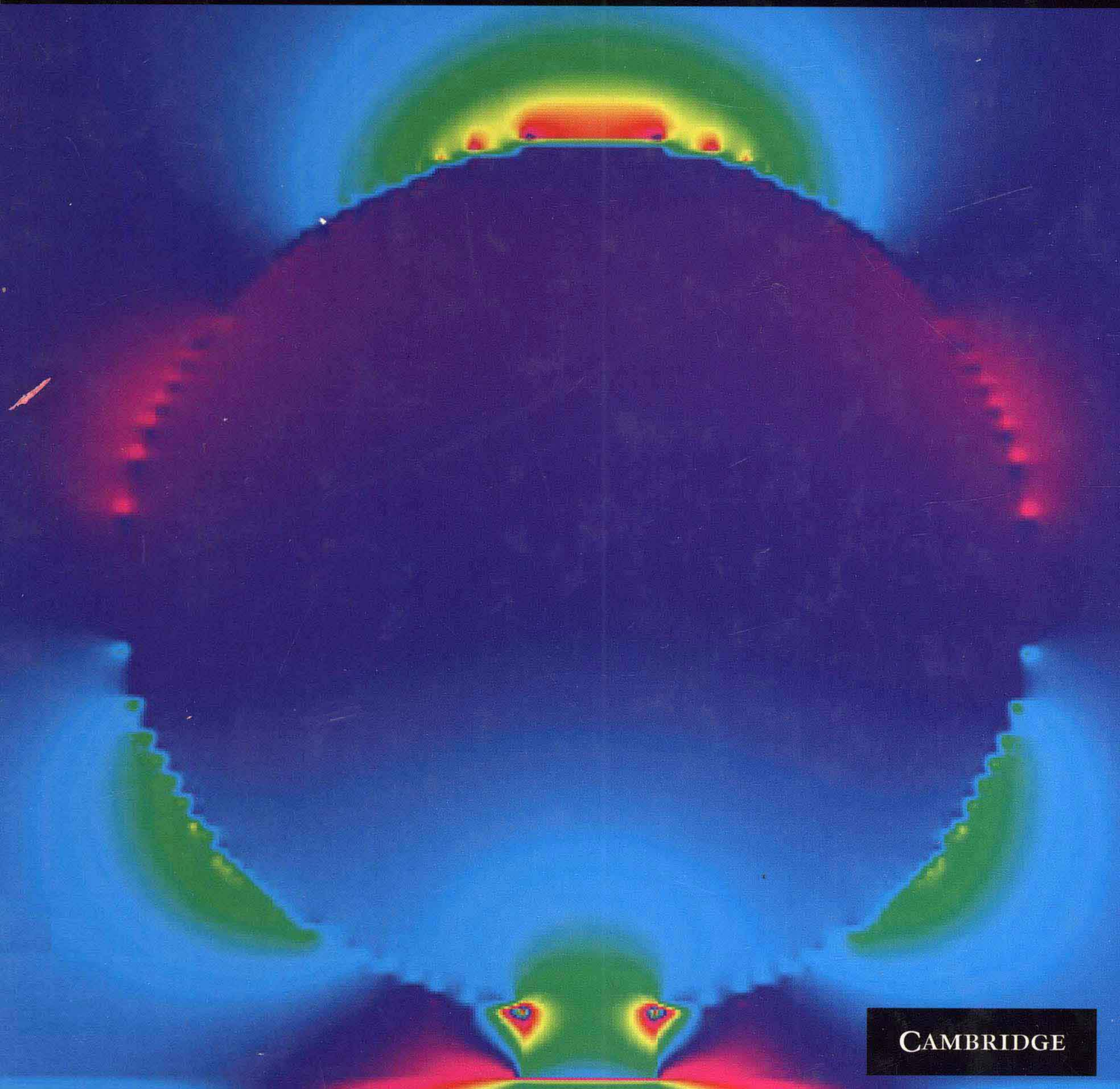
MODERN INTRODUCTION TO

Surface Plasmons

Theory, Mathematica Modeling, and Applications

Dror Sarid and William Challener



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MODERN INTRODUCTION TO SURFACE PLASMONS

Theory, *Mathematica* Modeling and Applications

Introducing graduate students in physics, optics, materials science and electrical engineering to surface plasmons, this book also covers guided modes at planar interfaces of metamaterials with negative refractive index.

The physics of localized and propagating surface plasmons on planar films, gratings, nanowires and nanoparticles is developed using both analytical and numerical techniques. Guided modes at the interfaces between materials with any combination of positive or negative permittivity and permeability are analyzed in a systematic manner. Applications of surface plasmon physics are described, including near-field transducers in heat-assisted magnetic recording and biosensors.

Resources at www.cambridge.org/9780521767170 include *Mathematica* code to generate figures from the book, color versions of many figures, and extended discussion of topics such as vector diffraction theory.

DROR SARID is Professor and former Director of the Optical Data Storage Center at the College of Optical Sciences, the University of Arizona. He participated in the development of the field of surface plasmons, identifying the long- and short-range surface plasmons and their important applications in science and technology.

WILLIAM CHALLENER is a Research Scientist at Seagate Technology. He has worked on optical and magnetic data storage materials and systems, and various chemical and biological sensors employing surface plasmons and other evanescent wave optics.

To Lea, Rami, Uri, Karen and Danieli, and to Helen, Douglas and Gregory

Preface

When deciding how to organize a book on surface plasmons, it seemed natural to consider the dimensionality of the surfaces on which they exist. On planar surfaces, which include both semi-infinite surfaces as well as multilayer thin films, there is a rich body of phenomena related to propagating surface plasmons. The same is true for surfaces of nanoparticles having a rich variety of phenomena for localized surface plasmons. Surfaces of nanowires and nanogrooves lie in between these two regimes, and these surfaces support both propagating and nonpropagating surface plasmons. In this book, therefore, we have initially categorized the chapters by surface dimensionality, trying to point out both the differences and similarities of the surface plasmon phenomena in these three regimes.

This book does not hesitate to include mathematical derivations of the equations that describe the basic surface-plasmon properties. After all, it was our desire to base the book on *Mathematica* precisely so that these equations could be explored in detail. Our derivations of the properties of surface plasmons are based on Maxwell's equations in SI units. In Chapter 2, Maxwell's equations are introduced for dense media, i.e., media which can be described by frequency dependent permittivity, permeability and conductivity. Because interfaces are essential to surface plasmons, the electromagnetic boundary conditions are required. Practically all of the results in this book are based on time-harmonic fields that can be most simply represented in complex notation. Unfortunately, in the literature there is no standard definition for the complex functional dependence on time of the electric and magnetic fields. We choose a time dependence of $\exp(-i\omega t)$, which has the advantage of making both real and imaginary parts of the complex optical refractive indices positive numbers as they are generally given in standard handbooks. Other properties of waves, including their group velocity, phase velocity, impedance and Poynting vectors are also derived in Chapter 2.

At optical frequencies (near IR and visible) it has been standard practice until recently to automatically set the permeability equal to unity. With the discovery of metamaterials and the predictions of potentially amazing properties like perfect lenses and invisibility cloaks, it is no longer adequate or safe to do so. In Chapters 2 to 7, the physics of surface waves propagating along single and double interfaces are carefully examined for all combinations of materials with both positive and negative permittivity and positive and negative permeability. As a result, unfamiliar modes such as surface magnons, which depend upon negative permeability, are analyzed in addition to those of surface plasmons. It transpires that it is important to define the refractive index of a medium, n, as the product of the square roots of the relative permittivity and permeability, $\sqrt{\epsilon_r}\sqrt{\mu_r}$, rather than the square root of their product. A new formalism is presented in which the media of single- and double-interface structures are characterized in terms of an ϵ_r'–μ_r' parameter space, represented as a vector in polar coordinates, where the prime denotes the real part. This formalism also uses a medium with a double positive set (ϵ_r', μ_r') to generate the other three sets of media, $(\epsilon_r', -\mu_r')$, $(-\epsilon_r', \mu_r')$ and $(-\epsilon_r', -\mu_r')$. The properties of guided modes propagating along single- and double-interface structures, obtained by using this formalism, are then discussed in detail in these chapters. With the single- and double-interface model, it is also straightforward to understand the manner in which prism coupling via attenuated total reflection is used to launch surface plasmons on metallic surfaces and what effect the prism has upon the properties of the surface plasmon, such as propagation distance and line width.

In the remaining chapters, the discussion is narrowed to surface plasmons alone (positive μ_r), both propagating and localized modes. Quasi-one-dimensional surfaces, nanowires and nanogrooves, are discussed in Chapter 8 and quasi-zero-dimensional surfaces, nanoparticles and nanovoids, are discussed in Chapter 9. Interactions among neighboring nanoparticles are also considered. Although the Otto and Kretschmann prism-coupling configurations were analyzed in Chapter 2, they are briefly reconsidered and compared to other techniques for launching surface plasmons in Chapter 10. In particular, the Chandezon technique for computing vector diffraction in a semi-analytical way is implemented to discuss the ability of gratings to couple optical energy into surface plasmons. A detailed analysis of this technique is described in the online supplemental materials for this book found at the web site www.cambridge.org/9780521767170. Newer techniques, that make use of near-field interactions to excite surface plasmons, are also described.

The text would not be complete without a discussion of plasmonic materials. There are relatively few metals that are plasmonic at optical frequencies and it is not surprising that both gold and silver are so frequently used in surface-plasmon calculations and devices. The relationship between the complex permittivity of a material and its ability to exhibit surface-plasmon phenomena is considered in Chapter 11. The Drude dielectric function, as a phenomenological model for metals, is also considered in this chapter. Chapter 12 is a survey of various actual and potential applications of surface plasmons. This marvelous effect has already proven itself in the form of label-free biosensing for pharmaceutical development and medical diagnostics. It may soon find even larger applications in nanophotonics and magnetic data storage.

The finite difference time domain (FDTD) technique – a numerical method for computing the response of materials to incident electromagnetic fields when the geometry is too complex for analytical techniques – is described in the Appendix. Although FDTD is not implemented within *Mathematica* (it would take forever to run even simple calculations), it has been used to model some of the examples that are considered within the text and it is shown to deliver highly accurate results. A short discussion of the connection between the Poynting vector and the local power flow is also included in the Appendix.

Most chapters conclude with several exercises that are meant to stimulate further thought about the properties of surface plasmons that could not be covered in detail in the text, and are well worth the time and effort to study. Generally, the *Mathematica* routines that are included with the online supplementary materials are employed to solve these exercises.

Every chapter also has a reference section. The field of surface plasmons has grown so much over the last two decades that no one text can do an adequate job of covering it. The aim of this book is to provide a sufficient level of understanding of surface-plasmon physics so that the reader can both begin to design his, or her, own research program and also be prepared to tackle the scientific literature on this subject. There are literally thousands of journal articles related to surface plasmons. We have tried to cite many of the more important articles, including some which at this point are several decades old or older, for a more historical context, and these should give the reader a good start in further investigations, but there are also many important articles that we did not include or, unfortunately, overlooked.

This book, which represents the product of many months of collaborative work, was on the whole a very enjoyable experience. Obviously, most of the results described in the text are not original to us. Nevertheless, we have striven to make sure of the accuracy of the equations, derivations, *Mathematica* implementations and descriptions of experimental results, and any errors that remain are solely our responsibility.

We would like to express our appreciation for the kind support and encouragement provided by Seagate Technology during the writing of the book. This book could not have been written without the many contributions of the students, postdocs, collaborators and granting agencies, cited in Dror Sarid's (one of the author's) papers related to short- and long-range surface plasmons. Many thanks are also due to Professor Richard W. Ziolkowski for helpful discussions involving metamaterials, and to Tammy Orr and Juliet A. Hughes for their able help in editing chapters of this book. Bill Challener (one of the authors) would also like to thank several of his colleagues who have shared their expertise with him in both the theory and applications of surface plasmons, including Dr. Edward Gage, Dr. Amit Itagi, Dr. Chubing Peng, Dr. Timothy Rausch and Dr. Zhongping Yang.

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Contents

1
Introduction

In 1952 Pines and Bohm discussed a quantized bulk plasma oscillation of electrons in a metallic solid to explain the energy losses of fast electrons passing through metal foils [1]. They called this excitation a "plasmon." Today these excitations are often called "bulk plasmons" or "volume plasmons" to distinguish them from the topic of this book, namely surface plasmons. Although surface electromagnetic waves were first discussed by Zenneck and Sommerfeld [2, 3], Ritchie was the first person to use the term "surface plasmon" (SP) when in 1957 he extended the work of Pines and Bohm to include the interaction of the plasma oscillations with the surfaces of metal foils [4].

SPs are elementary excitations of solids that go by a variety of names in the technical literature. For simplicity in this book we shall always refer to them as SPs. However, the reader should be aware that the terms "surface plasmon polariton" (SPP) or alternately "plasmon surface polariton" (PSP) are used nearly as frequently as "surface plasmon" and have the advantage of emphasizing the connection of the electronic excitation in the solid to its associated electromagnetic field. SPs are also called "surface plasma waves" (SPWs), "surface plasma oscillations" (SPOs) and "surface electromagnetic waves" (SEWs) in the literature, and as in most other technical fields, the acronyms are used ubiquitously. Other terms related to SPs which we will discuss in the course of this book include "surface plasmon resonance" (SPR), "localized surface plasmons" (LSPs), "long-range surface plasmons" (LRSPs) and of course "short-range surface plasmons" (SRSPs).

There are a variety of simple definitions in the literature for SPs. Many of these are inadequate or incomplete. The "on" suffix emphasizes the fact that SPs have particle-like properties including specific energies and (for propagating modes) momenta, and strictly speaking should be considered in the context of quantum mechanics. In this spirit, one might define a SP as a quantized excitation at the interface between a material with a negative permittivity and free charge carriers (usually a metal) and a material with a positive permittivity which involves a collective oscillation of surface charge and behaves like a particle with a discrete energy and, in the case of propagating SPs, momentum. We will find, however, that most of the important properties of SPs can be satisfactorily described in a classical electromagnetic model, which is all that we will employ in this book. A SP may be defined classically as a fundamental electromagnetic mode of an interface between a material with a negative permittivity and a material with a positive permittivity having a well-defined frequency and which involves electronic surface-charge oscillation. It is, of course, relevant to ask whether or not a classical description of SPs is acceptable. Bohren and Huffman address this question for nanoparticles directly [5]. They state,

> "Surface modes in small particles are adequately and economically described in their essentials by simple classical theories. Even, however, in the classical description, quantum mechanics is lurking unobtrusively in the background; but it has all been rolled up into a handy, ready-to-use form: the dielectric function, which contains all the required information about the collective as well as the individual particle excitations. The effect of a boundary, which is, after all, a macroscopic concept, is taken care of by classical electrodynamics."

This statement can be extended to all of the systems we are considering, not just small particles. If the objects supporting SPs are large enough that they can be described by a dielectric function (permittivity), then the classical approach should generally be adequate. This will be the case if the mean free path of the conduction electrons is shorter than the characteristic dimensions of the objects in the SP system. In practice it is found that the bulk dielectric constant accurately describes objects with dimensions down to ~10 nm, and that a size-dependent dielectric constant can be employed for objects with dimensions down to about 1–2 nm [6–8]. For a detailed discussion about size effects of the dielectric function for small metal clusters, see Refs. [9] and [10]. As discussed in the Preface, the equations in this text are derived from Maxwell's equations as expressed in the SI system of units.

This text is based on *Mathematica*. *Mathematica* was not simply used as a word processor for formatting mathematical equations, but was also used to generate numerous figures within the text. The *Mathematica* notebooks, which are included in the online supplementary materials at the web site www.cambridge.org/9780521767170, contain all of the *Mathematica* code, color figures and some additional text. The notebooks can be used to regenerate many of the figures. Moreover, the reader may easily modify parameters in the *Mathematica* notebook code and recompute the figure for perhaps a different wavelength range or different material, etc. In chapters that discuss material properties, the refractive indices for a wide variety of plasmonic, noble and transition metals are available for calculations in addition to those materials which are specifically used in the figures. Some examples of the algorithms that are included in the *Mathematica* notebooks are a simple theory of the interaction of light with cylindrical nanowires and nanotubes in Chapter 8, Mie theory for calculations with spherical nanoparticles and nanoshells in Chapter 9, and the theory of Chandezon for vector diffraction of light from gratings in Chapter 10. In general, the reader should open the *Mathematica* notebook for the chapter of interest (it is, of course, necessary to purchase and install *Mathematica* first) and at the very beginning of each notebook there is a section labelled "Code." The experienced *Mathematica* user knows to double click on the downward arrow of the rightmost bracket of this section in order to expand it. The first paragraph in the Code section describes the steps that the *Mathematica* user should employ to reproduce a figure in the text. The reader is strongly encouraged to take advantage of these *Mathematica* features to gain the full benefit of the text! The online supplementary materials also include a pdf version of the color figures and a description of the Chandezon vector diffraction theory.

References

[1] D. Pines and D. Bohm. A collective description of electron interactions: II. Collective vs individual particle aspects of the interactions. *Phys. Rev.* **85** (1952) 338.

[2] J. Zenneck. Über die fortpflanzung ebener elektromagnetisch Wellen längs einer ebenen Leiterfläche und ihre Beziehung zur drahtlosen telegraphie. *Ann. Phys.* **328** (1907) 846.

[3] A. Sommerfeld. Über die ausbreitung der Wellen in der drahtlosen telegraphie. *Ann. Phys.* **333** (1909) 665.

[4] R. H. Ritchie. Plasma losses by fast electrons in thin films. *Phys. Rev.* **106** (1957) 874.

[5] C. F. Bohren and D. R. Huffman. *Absorption and Scattering of Light by Small Particles*. (New York, John Wiley & Sons, 1983) p. 336.

[6] E. Coronado and G. Shatz. Surface plasmon broadening for arbitary shape nanoparticles: a geometric probability approach. *J. Chem. Phys.* **119** (2003) 3926.

[7] T. Okamoto, *Near-field Optics and Surface Plasmon Polaritons*, ed. S. Kawata. (New York, Springer-Verlag, 2001) pp. 99, 100.

[8] J. P. Kottmann, O. J. F. Martin, D. R. Smith and S. Schultz. Plasmon resonances of silver nanowires with a nonregular cross section. *Phys. Rev. B* **64** (2001) 235402.

[9] U. Kreibig and M. Vollmer. *Optical Properties of Metal Clusters* (Berlin, Springer-Verlag, 1995) Ch. 2.

[10] H. Hövel, S. Fritz, A. Hilger, U. Kreibig and M. Vollmer. Width of cluster plasmon resonances: bulk dielectric functions and chemical interface damping. *Phys. Rev. B* **48** (1993) 18178.

2

Electromagnetics of planar surface waves

2.1 Introduction

This chapter presents the electromagnetic theory that describes the main characteristics of surface electromagnetic modes in general and surface plasmons (SPs) in particular that propagate along single- and double-interface planar guiding structures. We begin with an introduction to electromagnetic theory that discusses Maxwell's equations, the constitutive equations and the boundary conditions. Next, Maxwell's equations in terms of time-harmonic fields, electric and magnetic fields in terms of each other, and the resultant wave equations are presented. Group velocity and phase velocity, surface charge at a metal/dielectric interface and the perfect electric conductor conclude this introduction. Following this introduction are sections that describe the properties of electromagnetic modes that single- and double-interface planar guiding structures can support in terms of the media they are composed of. These media will be presented in terms of their permittivity and permeability whose real part can be either positive or negative. A new formalism will be developed to treat such media in the context of natural materials such as metals and dielectrics and in terms of a collection of subwavelength nanostructures dubbed metamaterials. Finally, the power flow along and across the guiding structures is presented, and the reflectivity from the base of a coupling prism and the accompanied Goos–Hänchen shift are treated. The material covered in this chapter draws heavily from Refs. [1] to [3] for the theory of electromagnetic fields and from Refs. [4] and [5] for the theory of optical waveguides. The theory of metamaterials and their applications as guiding media makes use of Refs. [6] to [12] where citations to a vast body of literature can be found. The concept of Poynting vectors and energy flow in general and in metamaterials in particular is adapted from Refs. [13] to [15].