Active Plasmonic Nanomaterials

edited by Luciano De Sio

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The editor and those among the authors who had the fortune to meet her, want to dedicate this book to Daniela Pucci, a dear friend and a clever scientist. She was a pioneer member of the Metallomesogens Group at the University of Calabria and, recently, she started to be enthusiastically involved in researches on metal-containing chromonic systems, of interest for plasmonics.

Ciao Daniela!

Contents

Pr	Preface					
1	Plasmonics: A Theoretical Background					
	1 1	Introd	duction	a rulerino, una cesare officion	1	
	1.1	Electr	romagnet	ism of Metals	7	
	1.3	Surfa	re Plasmo	on Polariton	15	
	1.4	Local	ized Surfa	ace Plasmon	22	
2	Synt	thesis a	nd Surfac	e Engineering of Plasmonic		
	Nanoparticles					
	Roberto Comparelli, Tiziana Placido, Nicoletta Depalo,					
	Elisc	abetta F	- anizza, M	larinella Striccoli,		
	and	M. Luc	ia Curri			
	2.1	Intro	duction			
	2.2	Experimental Parameter Affecting Plasmon				
	Absorption					
		2.2.1	Size Dep	endence of Plasmon Absorption:		
			Mie's Th	leory	37	
		2.2.2	Shape-D	ependence of Plasmon Absorption:		
			Gans Th	eory and Discrete Dipole		
			Approxi	mation	38	
		2.2.3	Other Pa	arameters Affecting Plasmon		
			Absorpt	ion	40	
			2.2.3.1	Effect of surrounding medium: the		
				Drude model	40	
			2.2.3.2	Effect of interparticle coupling	41	
			2.2.3.3	Effect of temperature	41	
	2.3	Nano	particle C	haracterization	42	

	2.4	Synthesis of Hydrophilic Plasmonic Nanoparticles			44	
		2.4.1	Synthesis of S	Spherical Nanoparticles	44	
			2.4.1.1 Turk	evich method and its		
			mod	ifications	45	
			2.4.1.2 Seed	-mediated method	46	
			2.4.1.3 Phot	ochemical synthesis of spherical		
			meta	l nanoparticles	47	
		2.4.2	Shape Contro	l of Metal Nanoparticles	49	
			2.4.2.1 Gold	nanorods	49	
			2.4.2.2 Silve	r nanorods/wires	58	
		2.4.3	Other Shapes		59	
	2.5	Synth	esis of Hydrop	hobic Plasmonic Nanoparticles	60	
		2.5.1	Hydrophobic	Spherical Metal Nanoparticles	61	
		2.5.2	Shape Contro	l in Organic Media	62	
	2.6	Nano	eparation and	Purification Techniques: Size		
		and/o	r Shape Sortir	g of Plasmonic Nanoparticles	63	
		2.6.1	Gel Electroph	oresis	63	
		2.6.2	Centrifugatio	n	64	
		2.6.3	Size-Selective	Precipitation	65	
		2.6.4	Chromatogra	phic Separations	67	
		2.6.5	Filtration		67	
	2.7	Surfa	e Modification	n of Plasmonic Nanoparticles	68	
		2.7.1	Post-Synthes	s Functionalization	68	
		2.7.2	Post-Synthes	s Functionalization for Phase		
			Transfer		70	
		2.7.3	Growth of a S	ilica Shell	73	
			2.7.3.1 Grov	th of silica shell onto hydrophilic		
			nanc	particles	75	
			2.7.3.2 Grov	th of silica shell onto		
			hydr	ophobic nanoparticles	80	
	2.8	Concl	ision		82	
3	Amo	orphou	Nanoparticle	Assemblies by Bottom-Up		
	Prin	inciples				
	Alas	tair Cu	ningham, Mał	nshid Chekini, and Thomas Bürgi		
	3.1	Introduction				
	3.2	Electr	ostatic Forces		104	
	3.3	3 Assembly of Nanoparticles on Flat Surfaces 105				

	3.4	Build	ing Up the Third Dimension	109			
	3.5	Core-Shell Structures					
	3.6	.6 Conclusion					
4	Opt	imizing	Surfactant on Nanoparticles	123			
	Hari	M. Atk	uri, Ke Zhang, and John L. West				
	4.1	Intro	luction	123			
	4.2	Role o	of Surfactant	124			
		4.2.1	States of Surfactant	125			
		4.2.2	Surfactant IR Absorption Band	126			
	4.3	Exper	riment	128			
	4.4	Resul	ts and Discussion	130			
	4.5	Sumn	nary	140			
5	A Br	ief Ove	erview on Synthesis and Characterization of				
	Nan	omate	rials	143			
	Ariel Meneses-Franco, Eduardo Soto-Bustamante,						
	and Marcelo Kogan-Bocian						
	5.1	144					
	5.2	5.2 Major Methods of Chemical Synthesis of					
		Nano	145				
		5.2.1	Precipitation	145			
		5.2.2	Solvothermolysis and Recrystallization	146			
		5.2.3	Sol-Gel Nanoparticles Synthesis	148			
	5.3	Biosy	nthetic Methods: The Use of Microorganisms				
		and P	lants	150			
		5.3.1	Bacteria	151			
		5.3.2	Yeast and Fungus	152			
		5.3.3	Plants	153			
	5.4	Chara	cterization of Nanomaterials	153			
		5.4.1	Transmission Electron Microscopy	154			
		5.4.2	Scanning Electron Microscopy	155			
		5.4.3	Scanning Probe Microscopy	157			
		5.4.4	X-Ray Diffraction	158			
		5.4.5	X-Ray Photoelectron Spectroscopy	160			
		5.4.6	Dynamic Light Scattering	161			
		5.4.7	Zeta Potential	162			

6	Plasmon–Gain Interplay in Metastructures					
	Antonio De Luca, Melissa Infusino, Alessandro Veltri,					
	Kan	damma	the V. Sreekanth, Roberto Bartolino,			
	and	Giusep	pe Strangi			
		6.1 Introduction: Background and Significance				
	6.2	Plasm	on–Gain Interplay: Theory and Modeling	174		
		6.2.1	Single Spherical Nanoparticle	175		
		6.2.2	Core-Shell Spherical Nanoparticles	179		
		6.2.3	Plasmonic Mesocapsules	181		
		6.2.4	Effective Medium Theory	184		
	6.3	Syster	ms and Approaches Across Scales	186		
		6.3.1	Nanoscale Approach	187		
		6.3.2	Mesoscale Approach	197		
		6.3.3	Macroscale Approach	201		
	6.4	Sumn	nary	207		
7	Loca	lized S	urface Plasmons: A Powerful Tool for Sensing	215		
	Francesco Todescato					
	7.1 What Are Plasmons?					
		7.1.1	Dielectric Functions of Metals: The Drude			
			Model	217		
		7.1.2	Localized Surface Plasmon: Mie Model	218		
		7.1.3	Plasmon Platforms for Sensing	222		
	7.2 Surface Enhanced Raman Spectroscopy for Sensin		223			
		7.2.1	Raman Spectroscopy	223		
		7.2.2	Surface Enhanced Raman Spectroscopy	227		
		7.2.3	SERS Sensing Applications	229		
		7.2.4	Surface Enhanced Coherent Anti-Stokes Raman			
			Scattering	232		
	7.3	Metal	Enhanced Fluorescence for Sensing	233		
		7.3.1	Metal Enhanced Fluorescence Mechanism	233		
		7.3.2	Sensing Examples	236		
8	Self	Organi	zed Plasmonic Nanomaterials Based on Liquid			
	Crys	tals an	d Metal Nanoparticles	245		
	Toralf Scharf					
	8.1	Optica	al Properties of Metallic Plasmonic Entities	246		

		8.1.1	Plasmon Resonance of Nanoparticles and				
			Assemblies	247			
		8.1.2	Properties of Localized Plasmonic Resonance				
			of Small Nanoparticles	248			
		8.1.3	Density, Arrangements, and Optical Efficiency	252			
	8.2	Liquio	d Crystal Self-Organization and Nanoparticles	254			
		8.2.1	Sizes of Components	256			
		8.2.2	Alignment, Texture, and Characteristic Scales	259			
	8.3	Mater	ial Design Parameters and Concepts	261			
		8.3.1	Design of Building Blocks	262			
		8.3.2	Liquid-Crystalline Materials Incorporating				
			Metal Nanoparticles	266			
	8.4	Concl	usion and Outlook	270			
9	Tuna	able Pla	asmonics Based on Liquid Crystals	281			
	Yan	Jun Liu,	Guangyuan Si, Yanhui Zhao,				
	and	Eunice	Sok Ping Leong				
	9.1	Intro	luction	281			
	9.2	Different Tuning Schemes					
		9.2.1	Electric Tuning	284			
		9.2.2	Optical Tuning	288			
		9.2.3	Magnetic Tuning	292			
		9.2.4	Acoustic Tuning	293			
		9.2.5	Thermal Tuning	297			
	9.3	Outlo	ok	301			
		9.3.1	Current Challenges	301			
		9.3.2	Future Demands	302			
			9.3.2.1 Fast response liquid crystals	302			
			9.3.2.2 Large birefringence liquid crystals	302			
			9.3.2.3 Multi-function or multi-control				
			integration	303			
10	No	nlinear	Optical Enhancement with Plasmonic Core–Shell				
	Na	nowire	S	315			
	Ra	Rachel Grange					
	10.1 Introduction 3						
	10	.2 Sta	te of the Art	317			
	10	.3 Fab	prication	319			

		10.3.1	Bottom-I	Up Fabrication of the KNbO ₃ Core	319		
		10.3.2	Synthesis	s of the Gold Shell	320		
	10.4	0.4 Single Nanowire Spectrosocopy Measurements					
	10.5	Nonlinear Optical Measurements					
	10.6	Conclus	sion		329		
11	Nano	technolo	gy for Rer	newable Solar Energy	335		
	Xianh	e Wei an	d Ji Ma				
	11.1	Introdu	ction		336		
	11.2	Nanom	nomaterials for Photovoltaics				
		11.2.1	Basics of	Photovoltaics	337		
		11.2.2	Nanoma	terials for PVs	338		
			11.2.2.1	Nanoparticles	338		
			11.2.2.2	Nanowires	339		
			11.2.2.3	Nanocrystal quantum dots	341		
		11.2.3	Fabricati	on of Nanomaterials for PVs	342		
	11.3	Nanost	ructures f	or Thermoelectrics	345		
		11.3.1	Basics of	Thermoelectrics	346		
		11.3.2	Nanotecl	nnologies for TEs	348		
		11.3.3	Fabricati	on of Nanostructure for TEs	352		
			11.3.3.1	Template formation for			
				nanostructure	352		
			11.3.3.2	Nanostructure formation for TEs	353		
			11.3.3.3	Fabrication of bulk			
				nanocomposite materials for TEs	354		
	11.4	Conclus	sion		355		
12	Plasm	nonic Cou	upling bet	ween Nanostructures: From			
	Perio	dic and R	ligid to Ra	ndom and Flexible Systems	363		
	Ugo (Cataldi, R	oberto Ca	puto, Yuriy Kurylyak,			
	Gérard Klein, Mahshid Chekini. Cesare Umeton.						
	and T	homas B	ürgi				
	12.1	Introdu	iction		364		
	12.2	Couplin	ng betwee	n Near-Fields	366		
	12.3	Polariza	ation and	Inter-Distance Dependence of the			
	Plasmon Coupling						

	12.3.1	Enhancement of Coupling Due to			
		Polarization Effects of the Exciting			
		Electromagnetic Field	368		
12.4	Expone	ential Decay of Coupling for Well-Ordered			
	System	Systems			
	12.4.1	Two Interacting Gold Nanoparticles	370		
	12.4.2	Pair of Ordered Nanodisc Array:			
		Inter-Particle Plasmon Coupling and			
		Universal Scaling Behavior	372		
	12.4.3	Plasmon Ruler Equation	377		
12.5	Exponential Decay of Coupling for a Random				
	Self-Assembled System of Gold Nanoparticles				
	12.5.1	Introduction	378		
	12.5.2	Mechanically Induced Plasmonic Coupling	379		
12.6	12.6 Conclusion				
Index			387		

Preface

Science and technology seldom progress separately; more often they go hand in hand, in a combination that yields to a number of intellectual and practical paths. Nanotechnology is part of one of such vibrant paths, leading to a number of new findings that are maturing and thriving fast in both academia and industry, while nanophotonics gathers together all that can be utilized to manipulate light at the nanoscale, for a number of photonic applications. As a matter of fact, nanophotonic devices are of great interest for integrated optics, plasmonic circuits, biosensing and quantum information processing. Plasmonics is a subfield of nanophotonics, which involves exploitation of surface plasmons to realize the control of light at the nanoscale. Indeed, one promising way to localize the optical radiation into a nanometer-sized volume has been realized by using the unique properties of plasmonic metallic nanoparticles (NPs), which, represent an effective bridge between bulk materials and atomic or molecular structures. NPs can exhibit a highly vibrant color, which is absent both in the bulk material and in individual atoms; the physics behind this phenomenon can be understood by considering the collective oscillation of the conducting free electrons of the metallic NP, an effect that is referred as the "localized plasmonic resonance (LPR)". Such a resonance is strongly dependent on particle size and shape, and on the dielectric function of the medium surrounding the NPs; as an example, these parameters enable a "static" design of the resonance frequency throughout the visible and into the near-infrared spectra when keeping the particle size below 100 nm. A more effective method to influence the LPR is to vary the refractive index of the medium surrounding the NPs; the use of reconfigurable matter as the surrounding medium could hence provide an "active way" for controlling the plasmonic resonance.

This book is aimed at reviewing some recent efforts committed to utilize NPs in a number of research fields that include, but are not particularly limited to, photonics, optics, chemistry, material science, or metamaterials. In this framework, a particular interest is devoted to "active plasmonics", a concept related to NPs that play an 'active' role, and includes realization of gain-assisted means, utilization of NPs embedded in liquid crystalline materials, and exploitation of NPs for solar energy or even flexible plasmonics. Moreover, the book is designed to provide a powerful tool to people that are enthusiastic of technology, but have no, or minimal, scientific background. The book, indeed, begins with a theoretical background on the physical interaction between light and plasmonic materials. Further on, the most important techniques enabling size and or shape-controlled growth of NPs are highlighted, with an additional focus on their surface functionalization.

In editing and organizing the book, I have made all possible attempts to cover the growing field of plasmonic nanomaterials and related technologies. With this aim, the publication gathers various contributions of outstanding research groups all over the world, which are related to the field of plasmonic nanomaterials and provide both the basics and the necessary advanced knowledge in the field of plasmonics, photonics, and optics. I express my deep and sincere thanks to all the authors, who contributed their expertise and research findings for the success of this publication. Special thanks to Antonio De Luca for providing the cover image of the book and to Roberto Bartolino, Timothy Bunning Nelson Tabiryan, and Cesare Umeton for their nurturing and long-standing support. I thank Stanford Chong for his never-ending help in organizing and completing the book and to Hari M. Atkuri for talking over its content while participating with me in official and unofficial 10 km runs. I would like to express my gratitude to my family without whose support I would not have been able to published this work. I owe thanks to Francesca Petronella for encouraging me to materialize and finalize the book.

> Luciano De Sio Summer 2015

Chapter 1

Plasmonics: A Theoretical Background

Luigia Pezzi, Giovanna Palermo, and Cesare Umeton

Department of Physics and Centre of Excellence for the Study of Innovative Functional Materials, University of Calabria, 87036 Arcavacata di Rende, Italy luigia.pezzi@fis.unical.it

1.1 Introduction

The paper that best embodies the genesis of processes involved in plasmonics of nanostructured materials is the one by the Russian physicist Veselago (1968). In his visionary work, he lays the foundation of many topics that have been clarified in recent years. Plasmonics is a branch of optics that investigates the behavior of electromagnetic (EM) waves in the visible range in nanostructured materials. In order to study the propagation of EM waves in matter, the dispersion equation represents the starting point:

$$\left|\frac{\omega^2}{c^2}\varepsilon_{il}\mu_{lj} - k^2\delta_{ij} + k_ik_j\right| = 0$$
(1.1)

In this equation, the only involved parameters of the medium are ε_{il} and μ_{lj} , which are the components of the tensors dielectric permittivity ε and magnetic permeability μ , respectively; δ_{ij} is the

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Kronecker delta; ω is the frequency of a monochromatic impinging wave and k its wave vector. If we consider an isotropic material, Eq. (1.1) takes the simpler form:

$$k^2 = \frac{\omega^2}{c^2} n^2 \tag{1.2}$$

where n^2 is the square of the refractive index of the material and is given by

$$n^2 = \varepsilon \mu. \tag{1.3}$$

Veselago's analysis starts by assuming that a material with negative values of both dielectric permittivity ε and magnetic permeability μ might exist. This hypothesis does not change Eq. (1.3), but by considering the case $\varepsilon < 0$ and $\mu < 0$ from a purely formal point of view in Maxwell's equation, Veselago comes to rewrite some important laws of physics and to presume that new and interesting phenomena could occur.

The first case that he presents is the so called "left-handed" medium. For a monochromatic plane wave, in which all fields contain the phase factor $e^{i(kz-\omega t)}$, Maxwell's equations that involve the curl of the EM field become

$$\mathbf{k} \times \mathbf{E} = \omega \mu \mathbf{H}$$

$$\mathbf{k} \times \mathbf{H} = -\omega \varepsilon \mathbf{E}.$$
(1.4)

It is evident that if $\varepsilon > 0$ and $\mu > 0$, then **E**, **H**, and **k** form a righthanded triplet of vectors, but if $\varepsilon < 0$ and $\mu < 0$, then the vectors form a left-handed set. This means that the energy flux carried by the wave, which is determined by the Poynting vector **S**:

$$\mathbf{S} = \mathbf{E} \times \mathbf{H} \tag{1.5}$$

always forms a right-handed set with **E** and **H**. Now for righthanded substances, **k** (related to phase velocity) and **S** (related to energy flux and group velocity) are in the same direction, while for left-handed materials, **k** and **S** have opposite directions, with the consequence that left-handed materials exhibit a negative group velocity. Introducing the direction cosines for vectors **E**, **H**, and **k**, the determinant of the resulting matrix *p* is always +1 for righthanded set and -1 for left-handed set; thus, *p* characterizes the "right-ness" of the given medium, and with this difference in mind,



Figure 1.1 Passage of a light beam through the boundary between two media: from a right-handed medium to a left-handed one.

Veselago rewrites the laws of a lot of physical effects, like Doppler shift, Vavilov-Cerenkov effect, and Snell's law. In particular, for the refraction of a light beam from one medium into another, boundary conditions must be satisfied independently of the rightness of the media:

$$E_{t_1} = E_{t_2} H_{t_1} = H_{t_2} (1.6)$$

$$\varepsilon_1 E_{n_1} = \varepsilon_2 E_{n_2} \qquad \mu_1 H_{n_1} = \mu_2 H_{n_2} \qquad (1.7)$$

where subscripts 1,2 indicate the two media, while n and t stay for "normal" and "tangential" to the separation surface, respectively. It follows that the path of the resulting refracted beam (Fig. 1.1) lies on the opposite side with respect to the normal axis to the separation surface only in case of a right-handed second medium. Indeed, according to the above considerations, with notations of

Fig. 1.1, Snell's law is now written as

$$\frac{\sin\alpha}{\sin\beta} = n_{1,2} = \frac{p_2}{p_1} \left| \sqrt{\frac{\varepsilon_2 \mu_2}{\varepsilon_1 \mu_1}} \right|$$
(1.8)

where p_1 and p_2 are the "right-ness" of the two media and $\varepsilon_{1,2}$ and $\mu_{1,2}$ are their dielectric permittivity and magnetic permeability, respectively. Therefore, by going from a right-handed medium to a left-handed one, the angle of refraction turns out to be negative (the β angle in Fig. 1.1).

This law allowed scientists to experimentally verify the existence of the first "metamaterial" [Shelby et al. (2001)] operating in the microwave region, that is, a material that exhibits a frequency range where the effective index of refraction (n) is negative. The material consists of a two-dimensional array of repeated unit cells of copper strips and split ring resonators on interlocking strips of standard circuit board material. By measuring the scattering angle of the transmitted beam through a prism fabricated with this material. Shelby et al. determined the effective *n* value that satisfies Snell's law. These experiments directly confirmed the prediction of Maxwell's equations that *n* is given by the negative square root of $\varepsilon \mu$ for the frequencies where both the permittivity and the permeability are negative. An interesting case, pointed out by Veselago, is that of a beam going from a medium with $\varepsilon_1 > 0$, $\mu_1 > 0$ into another one with $\varepsilon_2 = -\varepsilon_1$, $\mu_2 = -\mu_1$. In this case, the beam undergoes refraction at the interface between the two media, but there is no reflected beam, since in Fresnel's formulas [see Born and Wolf (1999)] only the absolute values of quantities ε , μ , n, α , β have to be used; then the reflection coefficient turns out to be zero. The use of left-handed media would allow the design of very unusual refracting systems. An example (Fig. 1.2) is a simple plate of thickness d made of a left-handed medium with n = -1 and put in the vacuum (where n = 1). Such a plate can focus in a given point the radiation from a point source located at a distance l < d from the plate, but it is not a lens in the usual sense of the word since it will not focus in a given point a bundle of rays coming from infinity. Above considerations have been exposed by Pendry (2000) in his letter in which he assumed also the possibility to build a perfect lens. In addition, Pendry envisaged that the left-handed medium can prevent the decay of evanescent waves. Indeed, such waves decay in



Figure 1.2 Passage of rays of light through a plate of thickness d made of left-handed substance. A is a source of radiation. B is the detector of radiation.

amplitude, but not in phase, as they propagate away from the object plane; therefore, in order to be focused, they need to be amplified rather than corrected in their phase. Pendry showed that in above materials, evanescent waves emerge from the far side of the sample enhanced in amplitude by the transmission process. This does not violate the energy conservation, since evanescent waves do not transport energy, but by using this new lens, a distinctive feature can be exploited, represented by the circumstance that both propagating and evanescent waves contribute to the resolution of the image. As a consequence, there is no physical obstacle to realize a perfect reconstruction of the image beyond those practical limitations that are, in general, introduced by the numerical aperture value and by defects in the lens surface.

As a matter of fact, in order to get all the fantastic properties listed so far (and much more), it is, however, necessary to exploit a material that simultaneously exhibits negative values of both ε and μ . As this feature is not found in natural substances known to date, it is necessary to obtain it artificially. Today, it seems that the best way to obtain both $\varepsilon < 0$ and $\mu < 0$ is the fabrication of nanostructured (nonmagnetic) metallic materials which would naturally exhibit this characteristic. In the microwave region, this is

already a reality [Pendry et al. (1999); Smith et al. (2000); Shelby et al. (2001)], while, for the optical frequency range, there is still much to do.

As a starting point, in order to study these nanostructured materials, it is necessary to know in details the electromagnetism of metals and associated phenomena, which involve the volume plasmon (VP), the surface plasmon polaritons (SPP), and localized surface plasmon (LSP).

As well known from everyday experience, for frequencies up to the infrared part of the spectrum, metals are highly reflective and do not allow EM waves to propagate through them. At higher frequencies, toward the near-infrared and visible part of the spectrum, the EM field penetration increases significantly, leading to an increased dissipation. Finally, at ultraviolet frequencies, metals acquire dielectric character and allow the propagation of EM waves, albeit with varying degrees of attenuation, depending on the details of the electronic band structure of the medium. These dispersive properties can be described by a complex dielectric function $\varepsilon(\omega)$, which provides the basis of all previously listed phenomena (PV, SPP, LSP) associated with EM of metals.

The interaction of metals with EM fields can be investigated in a classical framework based on Maxwell's equations. Even metallic nanostructures down to sizes of the order of a few nanometres can be described without a need to resort to quantum physics. Indeed, this has been introduced as a solution to the failure of the classical model for physical systems at the atomic and molecular scale. The "unit" that is necessary to take into account for a particular physical system to be assigned a macroscopic or microscopic character is represented by Planck's constant \hbar : In the limit where $\hbar \rightarrow 0$, the formalism must reduce to the classical one. In fact, in a black body, assuming that the energy is discretely packed in energy packets called "quanta" with energy $h\nu = \hbar\omega$, by making use of the kinetic theory, Plank's Formula for the average energy gives $\overline{E} = h\nu/(e^{\frac{h\nu}{k_BT}} -$ 1); in the limit where Plank's constant tends to zero (i.e., when $k_BT \gg h\nu$), the classical result is obtained:

$$\lim_{\frac{h\nu}{k_BT}\to 0}\overline{E}\simeq \frac{h\nu}{1+\frac{h\nu}{k_BT}+\cdots-1}\simeq k_BT$$
(1.9)

Optics of metals was developed in the framework of Drude's theory, which considers (as we will see in the next section) only the effects of the electrons that are in the conduction band. Since the high density of free carriers results in a quite minute spacing between the electron energy levels if compared to the thermal energy $k_B T$ at room temperature, the argument falls within the realms of the classical theory.

1.2 Electromagnetism of Metals

For a long time the most known property of metals was the high electrical conductivity. After three years from Thompson's discovery of the electron, scientists became more interested in studying mechanisms of interaction between metals and electromagnetic fields. Around 1900, Paul Drude, a German physicist, used new concepts to postulate a classical model that well explained several phenomena related to the interaction between radiation and metals. This model links optical and electric properties of a metal through the behavior of electrons. The assumptions of Drude's model are as follows:

- Metals are made of heavy, static, positively charged ions immersed in a cloud of light, negatively charged, easily mobile electrons, which form an *electron gas* that follows the Maxwell–Boltzmann statistics.
- The electron-electron interactions can be neglected.
- The only considered interaction are the electron-ion collisions.

By following the kinetic theory of gases, electrons in the gas move in straight lines and make collisions only with the ion cores. The probability for an electron to make a collision in a short time *dt* is *dt*/ τ , where τ is the mean time between collisions, called *relaxation time*. This quantity, which is typically of the order of 10^{-14} s at room temperature, is related to another important quantity $\gamma = \frac{1}{\tau}$, which represents the collision frequency and thus has values of the order of 100 THz. Drude's model successfully determined the form of Ohm's law in terms of free electrons and the relation between electrical and thermal conduction [Drude (1900)], but it failed to explain electron heat capacity and the magnetic susceptibility of conduction electrons. Failures of the model are the result of the limitations of the classical model (and Maxwell–Boltzmann statistics in particular) [Ashcroft and Mermin (1976)].

In microscopic physics, it is common to express Ohm's law in terms of a dimension-independent conductivity, which is intrinsic to the substance that the wire is made of. In this framework, Ohm's law writes as:

$$\mathbf{J} = \sigma \mathbf{E} \tag{1.10}$$

where **E** represents the electric field, **J** the current density, and σ the conductivity of the material. We consider a wire of crosssectional area *A*, where an electrical current flows, which consists of *N* electrons per volume unit, all moving in the same direction with velocity *v*. The number of electrons flowing through the area *A* in time *dt* is given by dN=NAvdt, while the charge crossing *A* in *dt* is dQ= -edN= -NevAdt, so that **J** = -*Nev*. In the absence of electric fields, electrons move randomly inside the conductor due to their thermal energy, but when an electric field is applied, electrons are affected by the force **F** = $-e\mathbf{E}$ that pushes them to move all in the same direction, with an average speed given by:

$$\mathbf{v} = -\frac{e\tau}{m}\mathbf{E} \tag{1.11}$$

Thus, substituting in $\mathbf{J} = -Ne\mathbf{v}$, Eq. (1.11) yields

$$\mathbf{J} = -\frac{Ne^2\tau}{m}\mathbf{E}$$
(1.12)

Comparison with Eq. (1.10) gives the DC-Drude conductivity:

$$\sigma_0 = -\frac{Ne^2\tau}{m} \tag{1.13}$$

Drude's model can also predict a current as a response to an oscillating electric field with angular frequency ω . This can be achieved by considering that the equation of motion for an electron of the electron gas subjected to an external electric field **E**, is:

$$m\ddot{\mathbf{x}} + m\gamma\,\dot{\mathbf{x}} = -e\mathbf{E}\tag{1.14}$$

where *m* is the effective mass and γ is the already mentioned collision frequency that produces the damping. This expression can be rewritten as:

$$\dot{\mathbf{p}} = -\frac{\mathbf{p}}{\tau} - e\mathbf{E} \tag{1.15}$$

where $\mathbf{p} = m\dot{\mathbf{x}}$ is the momentum of an individual free electron. If **E** assumes the form $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$, we consider as a solution to Eq. (1.15) the expression $\mathbf{p}(t) = \mathbf{p}_0 e^{-i\omega t}$, by substituting we obtain:

$$-i\omega\mathbf{p}_0 = -\frac{\mathbf{p}_0}{\tau} - e\mathbf{E_0} \tag{1.16}$$

$$\mathbf{J} = -\frac{Ne\mathbf{p}}{m} = \frac{\sigma_0}{1 - i\omega\tau} \mathbf{E} = \sigma(\omega)\mathbf{E}$$
(1.17)

Thus, the AC-Drude conductivity is given by:

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \tag{1.18}$$

A useful application of the Drude model is the description of the propagation of electromagnetic waves in metals by considering a complex dielectric function $\varepsilon(\omega)$, which shows the dispersive properties of the substance. In order to derive the expression of $\varepsilon(\omega)$, we consider again Eq. (1.14), which takes into account the oscillations of the free electron gas induced by the electric field $\mathbf{E}(t)$. A solution to Eq. (1.14) is given by $\mathbf{x}(t) = \mathbf{x}_0 e^{-i\omega t}$, which, when replaced in Eq. (1.14), yields:

$$\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t).$$
(1.19)

Since the electric displacement **D** and the macroscopic polarization **P** are given by:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \varepsilon \mathbf{E} \tag{1.20}$$

$$\mathbf{P} = -Ne\mathbf{x} \tag{1.21}$$

respectively, where N is the number of electrons per unit volume. Thus,

$$\mathbf{D} = \varepsilon_0 \mathbf{E} - \frac{N e^2}{m(\omega^2 + i\gamma\omega)} \mathbf{E}$$
(1.22)

and

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$
(1.23)

that represents the dielectric function in the Drude model, where ω_p is the plasma frequency of the free electron gas, is defined by:

$$\omega_p = \left(\frac{Ne^2}{\varepsilon_0 m}\right)^{1/2} \tag{1.24}$$

From Eq. (1.23) it can be easily derived that the real and imaginary components of this complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ are given by:

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \tag{1.25}$$

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau}{\omega(1+\omega^2 \tau^2)} \tag{1.26}$$

The complex dielectric function $\varepsilon(\omega)$ is related to the complex refractive index of the medium $\tilde{n} = n(\omega) + i\kappa(\omega)$ through the relation $\tilde{n} = \sqrt{\varepsilon_r}$. Explicitly, this yields:

$$\varepsilon_1 = n^2 - \kappa^2 \tag{1.27}$$

$$\varepsilon_2 = 2n\kappa \tag{1.28}$$

$$n^{2} = \frac{\varepsilon_{1}}{2} + \frac{1}{2}\sqrt{\varepsilon_{1}^{2} + \varepsilon_{2}^{2}}$$
(1.29)

$$\kappa = \frac{\varepsilon_2}{2n} \tag{1.30}$$

Here, κ is called *extinction coefficient* and determines the absorption of optical EM waves propagating through the medium; it is linked to the absorption coefficient α of Beer's law, which describes the exponential attenuation of a beam intensity I(x) propagating through the medium via $I(x) = I_0 e^{-\alpha x}$. Indeed, since $E \propto \exp(i\frac{\omega}{c}\tilde{n}x)$ and then $I \propto E^2 \propto \exp(2i\frac{\omega}{c}(n+i\kappa)x)$, we have:

$$\alpha(\omega) = \frac{2\kappa(\omega)\omega}{c} \tag{1.31}$$

Equations (1.25) and (1.26) allow as to study the EM response of metals (related to the plasma frequency ω_p) distinguishing the three cases $\omega > \omega_p$, $\omega < \omega_p$, and $\omega = \omega_p$).

In the case $\omega > \omega_p$, \tilde{n} is positive because $\varepsilon(\omega)$ is real and positive, and $\varepsilon(\omega) \rightarrow 1$, which implies that the electromagnetic wave propagates through the metal that appears transparent. For noble metals, it is necessary to take into account that the response of the

material in this region is dominated by free s-electrons, since the filled d-band close to the Fermi surface causes a highly polarized environment [Maier (2007)]. This contribution to the polarization related to the ion cores can be considered by adding the term $\mathbf{P}_{\infty} = \varepsilon_0(\varepsilon_{\infty} - 1)\mathbf{E}$ to Eq. (1.20). This effect is, therefore, described by a dielectric constant ε_{∞} (usually $1 \le \varepsilon_{\infty} \le 10$), and we can write:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$$
(1.32)

The validity limits of the free-electron description (1.32) are illustrated for the case of gold in Fig. (1.3). It shows the real and imaginary components ε_1 and ε_2 of the dielectric function of a free electron gas, fitted with experimental data of the dielectric function of gold [Johnson and Christy (1972)]. In the visible frequency range, the applicability of the free-electron model clearly breaks down due to the occurrence of interband transitions, leading to an increase in ε_2 .

For frequencies $\omega < \omega_p$, we distinguish two subcases: $\omega \tau \gg 1$ and $\omega \tau \ll 1$.

In the case $\omega \tau \gg 1$, we are in the condition of frequency very close to ω_p and, as we have seen at the beginning of this discussion, metals totally reflect the EM waves; in this range the real and imaginary parts of the dielectric function become:

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \tag{1.33}$$

$$\varepsilon_2(\omega) \approx 0$$
 (1.34)

respectively. As we can see from these equations, the permittivity is real, which implies that there is no absorption; metals retain their metallic character of *perfect conductor*. This behavior is common among different metals but not for noble metals, in which the response is again affected by the interband transitions.

In the case $\omega \tau \ll 1$, we are in the condition of frequency very far from ω_p and the real and imaginary parts of the dielectric function become:

$$\varepsilon_1(\omega) = 1 - \omega_p^2 \tau^2 \tag{1.35}$$

$$\varepsilon_2(\omega) \approx \frac{\omega_p^2}{\omega}$$
 (1.36)



Figure 1.3 Real and imaginary components of the dielectric function for a free electron gas (dash) fitted to experimental data of the dielectric function of gold (dot).

respectively. In this case, $\varepsilon_2 \gg \varepsilon_1$, and the real and imaginary parts of the refractive index have a comparable magnitude:

$$n \approx \kappa = \sqrt{\frac{\varepsilon_2}{2}} = \sqrt{\frac{\tau \omega_p^2}{2\omega}}$$
 (1.37)

In this region, metals are mainly absorbing, with an absorption coefficient given by

$$\alpha(\omega) = \frac{2\kappa(\omega)\omega}{c} = \left(\frac{2\omega_p^2 \tau \omega}{c^2}\right)^{1/2}.$$
 (1.38)

Remembering the DC-Drude conductivity (1.13) and the expression for the plasma frequency ω_p , the expression of σ becomes $\sigma_0 = \omega_p^2 \tau \varepsilon_0$ and then

$$\alpha = \sqrt{2\sigma_0 \omega \mu_0} \tag{1.39}$$

. . . .

This coefficient is closely related to the skin depth, which represents the depth of penetration of the wave in the metal:

$$\delta = \frac{2}{\alpha} = \frac{c}{\kappa\omega} = \sqrt{\frac{2}{\sigma_0 \omega \mu_0}}$$
(1.40)

In order to complete the study of the response of metals to an EM field, it is necessary to consider the particular case $\omega = \omega_p$. To understand what happens in this case, it is necessary to introduce the fundamental relation that links conductivity and dielectric function in the Fourier domain. The relation can be derived by starting from Maxwell's equations [details of calculations in Maier (2007)] and can be written as

$$\varepsilon(\mathbf{K},\omega) = 1 + \frac{i\sigma(\mathbf{K},\omega)}{\varepsilon_0\omega}$$
(1.41)

We consider the traveling-wave solution to Maxwell's equations in the absence of external stimuli. Combining the curl equations:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{1.42}$$

$$\nabla \times \mathbf{H} = \mathbf{J}_{\text{ext}} + \frac{\partial \mathbf{D}}{\partial t}$$
(1.43)

leads to the wave equation, which in the Fourier domain becomes:

$$\mathbf{K}(\mathbf{K} \cdot \mathbf{E}) - K^{2}\mathbf{E} = -\varepsilon(\mathbf{K}, \omega)\frac{\omega^{2}}{c^{2}}\mathbf{E}$$
(1.44)

where $c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$ is the speed of light in vacuum. Looking at this equation, two cases have to be distinguished: the case of transverse waves, $\mathbf{K} \cdot \mathbf{E} = 0$, yielding the generic dispersion relation:

$$K^{2} = \varepsilon(\mathbf{K}, \omega) \frac{\omega^{2}}{c^{2}}$$
(1.45)



Figure 1.4 Dispersion relation of free electron gas.

where $\varepsilon(\mathbf{K}, \omega)$ is given by Eq. (1.41), and the case of longitudinal waves, for which Eq. (1.44) implies:

$$\varepsilon(\mathbf{K},\omega) = 0 \tag{1.46}$$

indicating that longitudinal collective oscillations can only occur at frequencies corresponding to zeros of $\varepsilon(\omega)$. The meaning of this oscillation can be elucidated by considering the dispersion relation of the traveling wave obtained by using Eq. (1.33) in Eq. (1.45):

$$\omega^2 = \omega_p^2 + K^2 c^2 \tag{1.47}$$

Figure 1.4 shows the plot of the dispersion relation for the traveling wave given by Eq. (1.47): there is clearly no propagation of EM waves below the plasmon frequency ($\omega < \omega_p$), while for $\omega > \omega_p$ waves propagate with a group velocity $v_g = \frac{d\omega}{dK} < c$; the special case $\omega = \omega_p$ can be interpreted in the following way. In the small damping limit, $\mathbf{K} = 0$ and $\varepsilon(\omega_p) = 0$; this implies that $\mathbf{D} = 0$ and that the electric field becomes a pure depolarization field ($\mathbf{E} = \frac{-\mathbf{P}}{\varepsilon_0}$). This leads to a collective longitudinal oscillation of the conduction electron gas with respect to the fixed background of positive ion cores in a plasma slab (Fig. 1.5). A collective displacement *u* of the slab boundaries and yields a homogeneous electric field $\mathbf{E} = \frac{Neu}{\varepsilon_0}$



Figure 1.5 Longitudinal collective oscillations of the conduction electrons of a metal:volume plasmons.

inside the slab. Thus, the displaced electrons experience a restoring force, and their movement can be described by the equation of motion $Nm\ddot{u} = -Ne\mathbf{E}$. Inserting the expression for the electric field leads to

$$Nm\ddot{u} = -\frac{N^2 e^2 u}{\varepsilon_0} \tag{1.48}$$

$$\ddot{u} + \omega_p^2 u = 0 \tag{1.49}$$

Thus, the plasma frequency ω_p represents the natural frequency of a free oscillation of the electron sea and the quanta of these charge oscillations are called *plasmons or volume plasmons* (VPs). Due to the longitudinal nature of the excitation, VPs do not couple to transverse EM waves and can only be excited by particle impacts.

1.3 Surface Plasmon Polariton

In the framework of a classical approach, not only the VP, but also the other two fundamental excitations of plasmonics can be described: surface plasmon polariton (SPP) and localized surface plasmon (LSP). In this section, the SPP will be treated. It occurs when an EM radiation enters sliding at the interface of separation between a dielectric and a conductor and represents an EM excitation propagating at the interface, evanescently confined in the perpendicular direction. In order to investigate the physical properties of SPPs, it is convenient to start from the *Helmholtz*



Figure 1.6 Sketch of the geometry of the system.

equation [Riley and Bence (2002)]:

$$\nabla^2 \mathbf{E} + k_0^2 \varepsilon \mathbf{E} = 0 \tag{1.50}$$

where $k_0 = \omega/c$ is the wave vector of the EM wave propagating in vacuum. This equation is obtained from Maxwell's equations under the conditions and assumptions:

- Absence of external stimuli: $\nabla \cdot \mathbf{D} = 0$
- Negligible variation of the profile of the dielectric susceptivity ε(r) over distances of the order of one optical wavelength: ∇ε/ε ≃ 0
- Harmonic time dependence of the EM field: $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0(\mathbf{r})e^{-i\omega t}$

The propagation geometry is defined as follows (Fig. 1.6):

- Assumption of a one-dimensional problem, that is, ε depends on one spatial coordinate only: $\varepsilon = \varepsilon(z)$.
- Waves propagate along the *x*-direction of the Cartesian coordinate system.
- Waves show no spatial variation along the *y*-direction.
- The plane z = 0 coincides with the interface.

With the hypothesis that the wave propagates in the *x*-direction, while slow variations of the electric field amplitude can occur only

in the *z*-direction, we look for a solution that can be written as $\mathbf{E}(x, y, z) = \mathbf{E}(z)e^{i\beta x}$; thus, Eq. (1.50) assumes the form

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) \mathbf{E}(z) = 0$$
(1.51)

Of course, the same relation exists for the magnetic field **H**. As a matter of fact, Eq. (1.51) has to be solved separately in regions of different, constant ε values, and the obtained solutions have to be matched by exploiting suitable boundary conditions.

In order to use Eq. (1.51) for determining the spatial field profile and the dispersion of propagating waves, we need to find explicit expressions for the different field components of **E** and **H**. This can be achieved by using the curl of Maxwell's equations (1.42) and (1.43) in the specific case of harmonic time dependence $(\frac{\partial}{\partial t} = -i\omega)$, propagation along the *x*-direction $(\frac{\partial}{\partial x} = i\beta)$ and homogeneity in the *y*-direction $(\frac{\partial}{\partial y} = 0)$. The obtained system of equations is

$$\frac{\partial E_y}{\partial z} = -i\omega\mu_0 H_x \tag{1.52a}$$

$$\frac{\partial E_x}{\partial z} - i\beta E_z = i\omega\mu_0 H_y \tag{1.52b}$$

$$i\beta E_y = i\omega\mu_0 H_z \tag{1.52c}$$

$$\frac{\partial H_y}{\partial z} = i\omega\varepsilon_0\varepsilon E_x \tag{1.52d}$$

$$\frac{\partial H_x}{\partial z} - i\beta H_z = -i\omega\varepsilon_0\varepsilon E_y \tag{1.52e}$$

$$i\beta H_y = -i\omega\varepsilon_0\varepsilon E_z \tag{1.52f}$$

which provides two sets of self-consistent solutions with different polarization characteristics of the propagating waves: the transverse magnetic (TM) mode, where only the field components E_x , E_z , and H_y are nonzero, and the transverse electric (TE) mode, with only H_x , H_z , and E_y being nonzero. For TM modes, by starting from Eq. (1.52d) and Eq. (1.52f), we obtain the expression of E_x and E_z as functions of H_y :

$$E_x = -i \frac{1}{\omega \varepsilon_0 \varepsilon} \frac{\partial H_y}{\partial z}$$
(1.53a)

$$E_z = -\frac{\beta}{\omega\varepsilon_0\varepsilon} H_y \tag{1.53b}$$

Here, ${\cal H}_y$ has to be obtained from the solution to the TM wave equation

$$\frac{\partial^2 H_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) H_y = 0$$
 (1.53c)

For TE modes, the analogous set is

$$H_x = i \frac{1}{\omega \mu_0} \frac{\partial E_y}{\partial z}$$
(1.54a)

$$H_z = -\frac{\beta}{\omega\mu_0} E_y \tag{1.54b}$$

where E_y has to be obtained from the TE wave equation

$$\frac{\partial^2 E_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) E_y = 0$$
 (1.54c)

By utilizing the above equations, we are able to describe SPPs. The simplest geometry sustaining SPPs is the one of a single, flat interface (Fig. 1.6) between a dielectric, nonabsorbing half space (z > 0) characterized by a positive real dielectric constant ε_{diel} , and a conducting half space (z < 0) characterized by a dielectric function $\varepsilon(\omega)$, where the requirement of a metallic character implies that $\Re[\varepsilon(\omega)] < 0$. As shown in the previous section, in metals this condition is fulfilled at frequencies that are below the bulk plasmon frequency ω_p . We look for propagating waves confined at the interface, that is, with evanescent decay in the perpendicular *z*-direction (separately for the two cases TM and TE).

Let us first look at TM solutions. Using the equation set (1.53) in both half spaces and searching for solutions to (1.53c), which are propagating in the *x*-direction and exponentially decreasing along the *z*-direction, we obtain

$$H_{y}(z) = A_{2}e^{i\beta x}e^{-k_{2}z}$$
(1.55a)

$$E_x(z) = iA_2 \frac{1}{\omega\varepsilon_0\varepsilon_2} k_2 e^{i\beta x} e^{-k_2 z}$$
(1.55b)

$$E_z(z) = -iA_2 \frac{\beta}{\omega\varepsilon_0\varepsilon_2} e^{i\beta x} e^{-k_2 z}$$
(1.55c)

for z > 0 and

$$H_{y}(z) = A_{1}e^{i\beta x}e^{k_{1}z}$$
(1.56a)

$$E_x(z) = -iA_1 \frac{1}{\omega \varepsilon_0 \varepsilon_1} k_1 e^{i\beta x} e^{k_1 z}$$
(1.56b)

$$E_z(z) = -A_1 \frac{\beta}{\omega \varepsilon_0 \varepsilon_1} e^{i\beta x} e^{k_1 z}$$
(1.56c)

for z < 0.

Here A_1 , A_2 are magnetic field amplitudes, $k_{z,i}$ (i = 1, 2) is the component of the wave vector perpendicular to the interface in the two media; its reciprocal value, $\hat{z} = \frac{1}{|k_z|}$, defines the *evanescent decay length* of fields perpendicular to the interface, which quantifies the confinement of the wave. Continuity of H_y , E_x , and $\varepsilon_i E_z$ at the interface (z = 0) requires that $A_1 = A_2$ and

$$\frac{k_2}{k_1} = -\frac{\varepsilon_{diel}}{\varepsilon(\omega)} \tag{1.57}$$

According to the convention assumed for signs in the exponents in Eqs. (1.55, 1.56), confinement to the surface demands that $\Re[\varepsilon(\omega)] < 0$ if $\varepsilon_{diel} > 0$, thus surface waves can exist only at interfaces between materials with opposite signs of the real part of their dielectric permittivity, that is, between a conductor and an insulator. In addition, the expression for H_y has to fulfill the wave equation (1.53c), yielding

$$k_1^2 = \beta^2 - k_0^2 \varepsilon(\omega)$$
 (1.58a)

$$k_2^2 = \beta^2 - k_0^2 \varepsilon_{diel}$$
 (1.58b)

By combining Eqs. (1.57) and (1.58), we obtain the main result concerning the argument of this section, that is, the dispersion relation of SPPs propagating at the interface between a conductor half space and an insulator one:

$$\beta = k_0 \sqrt{\frac{\varepsilon(\omega)\varepsilon_{diel}}{\varepsilon(\omega) + \varepsilon_{diel}}}$$
(1.59)

This expression is valid both for real and complex ε , that is, for conductors without and with attenuation.

Where TE solutions are concerned, expressions for the field components can be obtained by using Eq. (1.54) and are

$$E_{y}(z) = A_{2}e^{i\beta x}e^{-k_{2}z}$$
(1.60a)

$$H_{x}(z) = -iA_{2}\frac{1}{\omega\mu_{0}}k_{2}e^{i\beta x}e^{-k_{2}z}$$
(1.60b)

$$H_{z}(z) = A_{2} \frac{\beta}{\omega \mu_{0}} e^{i\beta x} e^{-k_{2}z}$$
(1.60c)



Figure 1.7 Dispersion relation of SPPs real part (red curve) and imaginary part (green curve), at the interface between a metal with negligible collision frequency and silica.

for z > 0, and

$$E_{y}(z) = A_{1}e^{i\beta x}e^{k_{1}z}$$
(1.61a)

$$H_{x}(z) = i A_{1} \frac{1}{\omega \mu_{0}} k_{1} e^{i\beta x} e^{k_{1} z}$$
(1.61b)

$$H_z(z) = A_1 \frac{\beta}{\omega\mu_0} e^{i\beta x} e^{k_1 z}$$
(1.61c)

for z < 0.

Here, A_1 , A_2 are now electric field amplitudes. Continuity of E_y and H_x at the interface leads to the condition $A_1 = A_2$ and

$$A_1(k_1 + k_2) = 0. (1.62)$$

Since confinement at the surface requires $\Re[k_1] > 0$ and $\Re[k_2] > 0$, condition (1.62) is only fulfilled if $A_1 = 0$, that means also $A_2 = 0$; thus, no surface modes can exist with TE polarization.

Figure 1.7 shows its plots for a metal, with negligible damping described by the real (Drude) dielectric function (1.33) interfaced with fused silica ($\varepsilon_{diel} = 2.25$). In the plot, both the real (red curves) and the imaginary parts (green curves) of the wave vector β are shown (frequency ω and wave vector β are normalized to the plasma frequency ω_p). The light line represents plane wave propagation in the dielectric, while ω_{sp} is the characteristic *surface plasmon frequency*, whose physical meaning will be discussed later on.

- For ω > ω_p, we are in the transparency regime of metals: the propagation constant is only real and radiation propagates through the metal.
- For $\omega < \omega_p$, different behaviors occur:
 - For very low frequencies, the SPP propagation constant is close to k_0 at the light line: waves extend over many wavelengths into the dielectric space because the metal does not allow to be crossed.
 - For higher frequencies, the SPPs approach the characteristic surface plasmon frequency ω_{sp} , which is the frequency value that makes the denominator in Eq. (1.59) (with $\varepsilon = 1 \omega_p^2 / \omega^2$) vanishing:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon_{diel}}} \tag{1.63}$$

In the limit of negligible damping of the conduction electron oscillation $(\Im[\varepsilon(\omega)] = 0)$, the wave vector β goes to infinity as the frequency approaches ω_{sp} , and the group velocity $v_g = d\omega/dk \rightarrow 0$. The mode thus acquires an electrostatic character and is known as the *surface plasmon*. The electrostatic character is confirmed by the circumstance that the condition $\varepsilon(\omega) + \varepsilon_{diel} = 0$ is obtained also via straightforward solution to the Laplace equation $\nabla^2 \Phi = 0$ (imposing the continuity of Φ and $\varepsilon \partial \Phi/\partial z$ in order to ensure the continuity of tangential and normal field components).

- In the region between ω_{sp} and ω_{p} , the propagation constant is only imaginary and no SPP propagation occurs.

So far we have assumed an ideal conductor that presents $\Im[\beta] = 0$; however, real metals present a complex $\varepsilon(\omega)$ and also an SPP propagation constant β . Since SPPs travel according to the term $e^{i\beta x}$ ($e^{2i\beta x}$ for the intensity), if β is complex, its imaginary part $\Im[\beta] \neq 0$ establishes an *energy attenuation length* $L = (2\Im[\beta])^{-1}$, which has a maximum finite value in correspondence of the plasmon frequency ω_{sp} . In Fig. 1.8, the actual behavior of silver obtained from data by Johnson and Christy (1972) is shown.



Figure 1.8 Dispersion relation of SPPs real part (red curve) and imaginary part (green curve), at the interface between silver and air.

If we turn our attention to SPPs in multilayers consisting of alternating conducting and dielectric thin films, we can say that each single interface can sustain bound SPPs. When the separation between adjacent interfaces is comparable to or smaller than the decay length \hat{z} of the interface mode, interactions between SPPs give rise to coupled modes. The general properties of coupled SPPs are elucidated in [Maier (2007)].

1.4 Localized Surface Plasmon

When a light beam impinges on a particle, the optical electric field puts into oscillation the electrical charges of matter (conduction electrons and protons). As a consequence, there is an absorption of part of the impinging radiation and an emission of a secondary radiation, a phenomenon known as scattering. In order to describe both effects, it is necessary to write down the expressions of EM fields **E**, **H** starting from Maxwell's equations. The most famous exact solution to Maxwell's equations, for the case of small particles with arbitrary radius and refractive index, has been obtained in the framework of the Mie theory [Bohren and Huffman (1983); Mie (1908)], developed by Gustav Mie in 1908 with the aim of explaining the different colors exhibited, in absorption and scattering processes, by small colloidal particles of gold suspended in water.

In a linear, isotropic, homogeneous medium, a time-harmonic EM field (**E**, **H**) must satisfy the wave equation:

$$\nabla^2 \mathbf{E} + k^2 \mathbf{E} = 0 \tag{1.64}$$

$$\nabla^2 \mathbf{H} + k^2 \mathbf{H} = 0 \tag{1.65}$$

where $k^2 = \omega^2 \varepsilon \mu$. Fields (**E**, **H**), which have a null divergence:

$$\nabla \cdot \mathbf{E} = 0 \qquad \nabla \cdot \mathbf{H} = 0 \tag{1.66}$$

are not independent, since they are related by the following relations:

$$\nabla \times \mathbf{E} = i\omega\mu\mathbf{H} \qquad \nabla \times \mathbf{H} = -i\omega\varepsilon\mathbf{E} \tag{1.67}$$

Equations (1.64) and (1.65) are complicated because of their vectorial character. Mie's theory simplifies the problem by reducing their solution to the solution of a single scalar wave equation:

$$\nabla^2 \psi + k^2 \psi = 0 \tag{1.68}$$

whose solution enables to obtain the expressions of fields (E, H).

The detailed procedure is exhaustively reported in [Bohren and Huffman (1983)], and the main steps can be shortly resumed as follows.

Suppose that the scalar function ψ and an arbitrary constant vector **c** define a vectorial field **M**:

$$\mathbf{M} = \nabla \times (\mathbf{c}\psi) \tag{1.69}$$

By keeping in mind that the divergence of the curl of any vectorial field vanishes $(\nabla \cdot \mathbf{M} = 0)$, and using the vectorial identities $\nabla \times (\mathbf{A} \times \mathbf{B}) = \mathbf{A}(\nabla \cdot \mathbf{B}) - \mathbf{B}(\nabla \cdot \mathbf{A}) + (\mathbf{B} \cdot \nabla)\mathbf{A} - (\mathbf{A} \cdot \nabla)\mathbf{B}$ and $\nabla(\mathbf{A} \cdot \mathbf{B}) = \mathbf{A} \times (\nabla \times \mathbf{B}) + \mathbf{B} \times (\nabla \times \mathbf{A}) + (\mathbf{B} \cdot \nabla)\mathbf{A} + (\mathbf{A} \cdot \nabla)\mathbf{B}$, we find that **M** satisfies the vector wave equations (1.64) and (1.65) if ψ is a solution to the scalar wave equation (1.68). We may also write $\mathbf{M} = -\mathbf{c} \times \nabla \psi$, which shows that **M** is perpendicular to **c**. Now, we derive from **M** a second vectorial field:

$$\mathbf{N} = \frac{\nabla \times \mathbf{M}}{k} \tag{1.70}$$

which has a null divergence and also satisfies the vector wave equation. Since $\nabla \times \mathbf{N} = k\mathbf{M}$, we can state that both **M** and **N** exhibit all the properties required to be an EM field: they satisfy the vector wave equation, they are divergence-free, the curl of **M** is proportional to N, and the curl of N is proportional to M. Thus, the problem of finding solutions to the wave equations (1.64), (1.65) reduces to the simpler problem of finding solutions to the scalar wave equation (1.68). The scalar function ψ is named generating *function* for the vector harmonics **M** and **N**, while the vector **c** is sometimes called the *guiding or pilot vector*. In general, the choice of *generating functions* is suggested by whatever symmetry may exist in the problem; thus, being interested in scattering by a sphere, we choose functions ψ that satisfy the wave equation written in spherical coordinates r, θ , φ (Fig. 1.9). The choice of the pilot vector is somewhat less obvious. We could choose some arbitrary vector **c**; however. if we write:

$$\mathbf{M} = \nabla \times (\mathbf{r}\psi) \tag{1.71}$$

where **r** is the radius vector, then **M** is a solution to the vector wave equation in spherical coordinates. In problems involving spherical symmetry, therefore, we assume **M** as given in Eq. (1.71) and the associated **N** as the fundamental solutions to the field equations. Note that **M** is everywhere tangential to any sphere $|\mathbf{r}| = constant$ (i.e., $\mathbf{r} \cdot \mathbf{M} = 0$).

The scalar wave equation in spherical coordinates is

$$\frac{1}{r^{2}}\frac{\partial}{\partial r}\left(r^{2}\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^{2}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^{2}\sin^{2}\theta}\left(\frac{\partial^{2}\psi}{\partial\varphi^{2}}\right) + k^{2}\psi = 0 \quad (1.72)$$

We seek particular solutions to Eq. (1.72) in the form:

$$\psi(r,\,\theta,\,\phi) = R(r)\Theta(\theta)\Phi(\varphi) \tag{1.73}$$

which, when substituted into Eq. (1.72), yields three separated equations linked by two separation constants (*m* and *n*), to be determined by subsidiary conditions that have to be satisfied by ψ . The request of single-valued functions and linearly independent