Thermoplasmonics

Heating Metal Nanoparticles Using Light

Plasmonics is an important branch of optics concerned with the interaction of metals with light. Under appropriate illumination, metal nanoparticles can exhibit enhanced light absorption, becoming nanosources of heat that can be precisely controlled. This book provides an overview of the exciting new field of thermoplasmonics and a detailed discussion of its theoretical underpinnings in nanophotonics. This topic has developed rapidly in the last decade, and is now a highly active area of research due to countless applications in nanoengineering and nanomedicine. These important applications include photothermal cancer therapy, drug and gene delivery, nanochemistry and photothermal imaging. This timely and self-contained text is suited to all researchers and graduate students working in plasmonics, nano-optics and thermal-induced processes at the nano scale.

Guillaume Baffou is a CNRS Research Scientist at the Institut Fresnel in Marseille. His research is focused on the interface between nano-optics and small-scale thermal effects. Specifically, he has been investigating the interaction between light and plasmonic metal nanoparticles, and the resulting applications in physics, chemistry, and biology. In 2015 he was awarded the bronze medal of the CNRS in recognition of his important contributions to the field.

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Foreword

In the spring of 1999 I was working at my desk at C. P. M. O. H. (Centre de physique moléculaire optique et hertzienne) in Bordeaux when I received an unexpected phone call from Claude Boccara from E. S. P. C. I. (École supérieure de physique et de chimie industrielles de la ville de Paris) in Paris. Claude had been particularly interested in photoacoustic and photothermal spectroscopies, as he had used them to optimize the mirrors of the VIRGO gravitational wave detector.[1] He asked me about work by a Japanese colleague – it turned out to be Tsuguo Sawada from Tokyo University – who used a thermal-lens microscope to detect very weak concentrations of molecules, potentially even down to single molecules.[2,3] I did not know the work, but as we were thinking of detecting single molecules at room temperature through their absorption instead of their fluorescence, I was immediately thrilled to learn about this new possibility. Some weeks later, I attended a talk by David A. Schultz from San Diego about applications of gold nanoparticles in bioimaging.[4] Putting these two pieces of information together, I proposed that my young colleagues Philippe Tamarat and Abdelhamid Maali should start with the photothermal detection of gold nanoparticles instead of trying the absorption of single molecules at room temperature. Indeed, these gold nanoparticles neither bleach nor blink, and they exist in different sizes. This makes it much easier to optimize a technique on large nanoparticles before attempting to detect smaller ones. Contrary to the work of Tsuguo Sawada and Takehiko Kitamori, who investigated fluid suspensions in which diffusing molecules could enter and leave the detection volume during the detection period, we decided to work on immobilized gold nanoparticles, with which we had previous experience. A further advantage of

[1] Optical and Thermal Characterization of Coatings
J. P. Roger, P. Gleyzes, H. Elrhaleb, D. Fournier, A.C. Boccara,
Thin Solid Films 261 (1995) 132–138
DOI: 10.1016/S0040-6090(95)06533-4

[2] Single- and Countable-Molecule Detection of Non-Fluorescent Molecules in Liquid Phase
M. Tokeshi, M. Uchida, K. Uchiyama, T. Sawada, T. Kitamori,
J. Lumin. 83–84 (1999) 261–264.
DOI: 10.1016/S0022-2313(99)00109-X

[3] Determination of Subyoctomole Amounts of Nonfluorescent Molecules Using a Thermal Lens Microscope: Subsingle Molecule Determination
M. Tokeshi, M. Uchida, A. Hibara, T. Sawada, T. Kitamori,
Anal. Chem. 73 (2001) 2112–2116
DOI: 10.1021/ac001479g

[4] Single-Target Molecule Detection with Nonbleaching Multicolor Optical Immunolabels
S. Schultz, D. R. Smith, J. J. Mock, D. A. Schultz
Proc. Natl. Acad. Sci. 97 (2000) 996–1001
DOI: 10.1073/pnas.97.3.996

photothermal detection was the high-frequency modulation of the heating beam, leading to very efficient rejection of background scattering by the sample and of low-frequency noise, both appreciable features in the complex and heterogeneous environment of biological cells. This project eventually led to our group's first work on photothermal detection, published in 2002.[5] Later work by Brahim Lounis' group[6] and by others has established the thermal-lens microscope as a unique tool for the detection of single absorbing objects down to individual molecules.[7] Thermal lens experiments can be seen as the first application of the coupling of optics to thermal gradients in a material; indeed, of the new field of thermoplasmonics. However, the effects of light on absorbing structures include many effects beyond thermal ones, notably acoustic wave generation, chemical reactions, mechanical transport phenomena through thermophoresis and photophoresis, and many more, which are described and explored in the present volume.

Thanks to improved fabrication techniques such as ion milling and nanolithography from the electronics industry, plasmonics and nanophotonics emerged as unique methods to control light at the nanoscale in the late 1990s. They have steadily developed since then. The collective motion of conduction electrons in metals gives rise to surface plasmon polariton (SPP) excitations, which enable the concentration, manipulation and control of light at subdiffraction scales, sometimes down to less than a nanometer in size. Several new techniques using SPPs were designed in the past 20 years, starting with near-field optics (SNOM), surface-enhanced or, more recently, tip-enhanced Raman scattering (SERS or TERS), and related spectroscopies in the near-infrared or far-infrared, collectively designed as nanophotonics. Nanophotonics find applications in many scientific and applied fields, from lighting and solar energy harvesting to biomedical tracking and sensing. However, unavoidable ohmic losses lead to significant dissipation of optical power in metal structures, and therefore to significant heating of plasmonic assemblies and of their environment. The associated temperature changes and gradients can produce a wide range of physical and chemical phenomena with potential impact in a growing range of research areas, from solid-state physics to chemical physics, catalysis, life sciences and medicine.

The heat released upon optical excitation of plasmonic structures may have disrupting effects, particularly in biological systems. Whereas those effects are sometimes desirable, as in photothermal therapy where apoptosis of sick cells is selectively triggered by heating, temperature rises are mostly damaging to proteins and most other biomolecules. Therefore, unless temperature is carefully measured and controlled, heat release may be a serious limitation to biomedical applications. Metal structures themselves are sensitive to temperature elevations. The temperature-assisted diffusion of surface metal atoms leads to reshaping of

[5] Photothermal Imaging of Nanometer-Sized Metal Particles Among Scatterers
D. Boyer, P. Tamarat, A. Maali, B. Lounis, M. Orrit
Science 297 (2002) 1160–1163
DOI: 10.1126/science.1073765

[6] Photothermal Heterodyne Imaging of Individual Nonfluorescent Nanoclusters and Nanocrystals
S. Berciaud, L. Cognet, G. A. Blab, B. Lounis
Phys. Rev. Lett. 93 (2004) 257402
DOI: 10.1103/PhysRevLett.93.257402

[7] Room-Temperature Detection of a Single Molecule's Absorption by Photothermal Contrast
A. Gaiduk, M. Yorulmaz, P. V. Ruijgrok, M. Orrit
Science 330 (2010) 353–356
DOI: 10.1126/science.1195475

the structures, *e.g.,* to blunting of sharp edges, tips or gaps, and to shape changes leading to irreversible alterations of the desired plasmonic properties. Here again, accurate temperature measurements are required to limit the structural changes and thereby to mitigate long-term loss of desired plasmonic functions.

Thermal effects can also be harnessed for useful goals, as started to be realized in the past ten years. The heat released can give rise to nearly background-free signals to detect the presence of absorbing objects, or to provide the quantum efficiency of heat dissipation (and therefore the luminescence quantum yield) of small nanoparticles or single molecules. Temperature gradients lead to thermophoretic effects, which can be applied to the manipulation and guiding of nanoparticles. An exciting application of those effects is photon nudging,[8] where an asymmetric particle – called a *swimmer* – is directed towards a desired target through absorption of a heating beam at well-chosen times. Other applications involve the assembly of particles, or the laser-printing of nanostructures,[9] through optically controlled heating and chemistry. Besides these potential applications, the field of nanoscale heat transfer, heat generation and thermal fields poses a number of fundamental questions about heat and molecule dynamics in thermal non-equilibrium, the existence of effective temperatures, the applicability of Fourier's law at small enough scales, the characteristics of nanoscale phase transitions, and more, which themselves contain the germs of new perspectives and applications. Guillaume Baffou, who has been a prominent actor in the recent development of thermoplasmonics, gathers his experience and insights in this monography. He follows heat from its production in the metal structure to its transport towards the environment, describes qualitatively and quantitatively the various effects it may generate, and details the applications which have already emerged or can be expected in the near future. The present book establishes a conceptual basis encompassing optical, thermal and material properties and their interdependence, providing the reader with the necessary keys to enter the field of thermoplasmonics. The conceptual basis and the many illustrations of the book will prove equally useful to experimentalists, simulators and theorists working with nano-optics, colloidal systems, thermophoresis and photophoresis, labels and sensing for biomedical applications. By providing an accessible framework for this broad range of systems, phenomena and observations, the book will favor the design and interpretation of new experiments and eventually spawn new applications combining focused laser beams with metal nanostructures. Compiling this rich volume and the variety of complex physics and chemistry it describes made me keenly aware of how much progress has been achieved since the early experiments of the late 1990s.

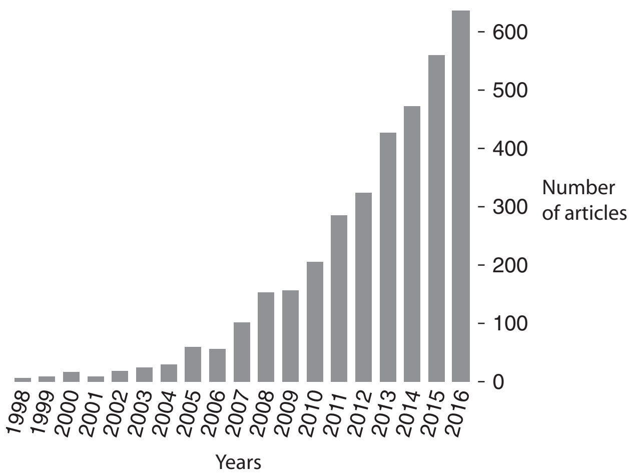
Michel Orrit
MoNOS, Leiden Institute of Physics, Huygens-Kamerlingh Onnes Laboratory

[8] Harnessing Thermal Fluctuations for Purposeful Activities: The Manipulation of Single Micro-Swimmers by Adaptive Photon Nudging
B. Qian, D. Montiel, A. Bregulla, F. Cichos, H. Yang,
Chem. Science 4 (2013) 1420–1429
DOI: 10.1039/c2sc21263c

[9] Nanolithography by Plasmonic Heating and Optical Manipulation of Gold Nanoparticles
M. Fedoruk, M. Meixner, S. Carretero-Palacios, T. Lohmüller, J. Feldmann,
ACS Nano 7 (2013) 7648–7653.
DOI: 10.1021/nn402124p

Preface

Heating metal nanoparticles with light. This is what the field of *thermoplasmonics* deals with, and this is what this book is all about. The chart below displays statistics collected from `webofknowledge.com` in March 2017.[1] It is intended to give an idea of the evolution of the field of thermoplasmonics.



These data show that the field is recent (established around 2002–2003), important and still rapidly growing.

At first glance, it may be surprising that heating metal nanoparticles with light could occupy so many researchers for more than a decade. I can see two main reasons for this. First, gold nanoparticles under illumination are nothing but nanosources of heat, and this is one of the most basic concept in science one can think of. Second, many or all fields of science exhibit some thermal-induced effects (just think about chemistry, fluid dynamics, magnetism, cell biology, phase transitions, polymer science, etc.). Consequently, many applications from a wide variety of backgrounds can be tackled on the nano and micro scales as soon as one uses nanosources of heat, with only one limitation: the imagination. In agreement with this idea, since the early 2000s, heating gold nanoparticles using light has found applications in physics, chemistry, cell biology and biomedicine. Before 2002, the plasmonics community was already active, but it was considering photothermal effects of nanoparticles as side effects that had to be minimized. In 2002–2003, thanks to a couple of

[1] The Webofknowledge search criterion was "TOPIC: (plasmon* and nanoparticle* and (thermal or photothermal or heat*))."

pioneering works in photothermal cancer therapy and photothermal microscopy, the plasmonics community realized that the heat generation arising from plasmonic nanoparticles under illumination could also be beneficial, with some imagination.

The most exciting aspect of thermoplasmonics to me is that it enables one to carry out research in many fields of science. Upon reading these pages or just by looking at the table of Contents, you will see that a general understanding of the world of thermoplasmonics involves knowledge in (take a deep breath!) nano-optics, plasmonics, thermodynamics, molecular fluorescence, Raman spectroscopy, X-ray spectroscopy, NV centers and nanodiamonds, cell biology, organic and inorganic chemistry, fluid dynamics, phase transition, magnetism and magnetic recording, biomedicine, cancer therapy, graphene, lanthanides, acoustics, SERS, thermophoresis, fluid superheating, bubble dynamics, black body radiation, . . . and I am certainly missing some fields.

This diversity of concepts, along with the fact that thermoplasmonics couples optics and thermodynamics, makes a general understanding of thermoplasmonics difficult. This book was born from this observation. At the time of writing these lines, there are no textbooks devoted to thermoplasmonics. A couple of review articles exist, but they are under 20 pages long, and they only represent introductions to this field of research. Once read, much work remains to be done before one can become experienced in the field of thermoplasmonics, and it is far from easy to acquire all the necessary information. Moreover, even when gathering all that information, one still has to learn a lot of new concepts due to the multidisciplinary nature of thermoplasmonics. Thus, I have done my best to tackle all the facets of the fields in order to draw a comprehensive overview. I have also done my best to explain many concepts from scratch because I expect the potential readers of this book to have very different scientific backgrounds, from physics to chemistry and biology. For instance, I have taken the time to detail the basic principles of Raman spectroscopy, X-ray spectroscopy, NV-center fluorescence, fluid superheating, thermophoresis in liquids, etc. This way, not only first-year Ph. D. students but also experienced researchers from various scientific origins can benefit from this book.

The success of thermoplasmonics not only stems from its multidisciplinarity, it also benefits from the success of the even larger field of *plasmonics*. Of course, researchers working plasmonics are not all working in thermoplasmonics but my experience is that researchers in plasmonics are bound to be concerned at some point with photothermal effects: even when photothermal effects are not desirable but detrimental, they have to be quantified in order to avoid misinterpretation of the results, to discard possible artifacts or to avoid damage to the samples. Heating up is what metal nanoparticles do best under illumination.

So please do not hesitate to contact me if you think you can help improve the quality of this book. Furthermore, thermoplasmonics is a fast-growing field of research with several exciting new applications on the verge of being developed. A second edition of this book will certainly make sense in the future.

Investigating thermoplasmonics for a decade has been a rich endeavor for me. I would have enjoyed owning this book when I started working in this field of research a decade ago. It would have saved me a lot of time. I wrote it with that in mind, and I hope you will enjoy reading this book as much as I have enjoyed writing it.

Acknowledgments

I wish to express my thanks to colleagues and students for their careful reading of these pages and their valuable input. I am grateful to Romain Quidant, who aroused my interest in this whole area of research. I want also to express especial thanks to Michel Orrit for accepting to write the Foreword, for his careful reading of the whole book and for his wise comments. I also received helpful feedback from Xavier Audier, Johann Berthelot, Mauricio Garcia-Vergara, Karl Joulain, Adrien Lalisse, Serge Monneret, Hervé Rigneault, Hadrien Robert, Julien Savatier and Siddharth Sivankutty. This book definitely benefited also from the initiative of Alexandra Elbakyan.