Purpose of the Workshop
The aim of the workshop is to bring together all scientists, technology developers and technology users who are investigating or exploiting optically and electromagnetically excited acoustical and thermal phenomena for the investigation of a large variety of material properties and applications. The wealth of photoacoustic and photothermal (PA/PT) topics indicate that this field has developed a broad range of tools for fundamental and applied research. PA/PT research has reached a mature state, with an established position in measurement technology and materials characterisation and future progresses are guaranteed by the close synergy with advances in laser and measurement technology. This second workshop acknowledges the explosive growth of biomedical photoacoustics and tissue imaging, and the presence of an ever growing biomedical photoacoustics research community around the world and in Europe, in particular. It also acknowledges the significant and growing contributions of photoacoustic and photothermal non-destructive evaluation / characterization to nanoscale and other advanced materials (with connections to biomedical imaging by use of nanoparticles). Participants are encouraged to present their own results in the field.

Location & History
The conference site is the «Ettore Majorana» Foundation and Centre for Scientific Culture (EMFSCC) in Erice – Italy (see http://www.ccsem.infn.it/) EMFSCC has a long tradition in the organization of Schools, Workshops and International Conferences, covering all branches of Science. EMFSCC is situated in the old pre-mediaeval city of Erice where 3 monasteries (one of which was the residence of the Viceroy of Sicily during the XIV and XV Centuries) provide an appropriate setting for high intellectual endeavor.

Erice is a historic town in Sicily, Italy. It is located on top of Mount Erice, at around 750m above sea level, overlooking the city of Trapani, the low western coast towards Marsala the dramatic Punta del Saraceno and Capo san Vito to the north-east, and the Aegadian Islands on Sicily’s north-western coast. In Erice you can admire the Castle of Venus, the Cyclopean Walls (~800 B.C.) and the Gothic Cathedral (~1300 A.D.). Erice is at present a mixture of ancient and medieval architecture. Other masterpieces of ancient civilization are to be found in the neighborhood: at Motya (Phoenician), Segesta (Elyman), and Selinunte (Greek). On the Aegadian Islands — theatre of the decisive naval battle of the first Punic War (264-241 B.C.) — suggestive neolithic and paleolithic vestiges are still visible: the grottoes of Favignana, the carvings and murals of Levanzo. Splendid beaches are to be found at San Vito Lo Capo, Scopello, and Cornino, and a wild and rocky coast around Monte Cofano.

Session A: Biomedical and Biological PA & PT (Chair: A. Mandelis)
1. Instrumentation design, software and signal generation techniques for biomedical photoacoustics and imaging.
2. Clinical applications of biomedical photoacoustics
3. Microscopy, spectroscopy and endoscopy
4. Animal imaging
5. Dyes, nanoparticles and other contrast agents
6. Biothermophotonics and biomedical photothermal methodologies
7. Biological photoacoustics and photothermics

Session B: Nanoscale Heat Transfer and Imaging (Chairs: S. Volz and G. Tessier)
8. Ultrafast thermoelastic phenomena
9. Thermal and elastic properties on nanoscale
10. Picosecond photoacoustics
11. Phonon Transport

Session C: Non Destructive Evaluation & Testing (Chairs: R. Li Voti and A. Mandelis)
12. Infrared Thermography and Thermophotonic Imaging
13. Non-destructive testing and industrial applications
14. Depth profiling of materials and inverse problems
15. Semiconductors, Photovoltaics, MEMS, NEMS, and phononic bandgap materials
16. Environmental sensors, biosensors, new instrumentation, and methodology

Session D: Thermophysical Properties (Chair: C. Glorioce)
17. Complex fluids, phase transitions and glass transitions
18. Spectroscopy, analytical chemistry, nonlinear optics and photochemistry
19. Thermophysical and thermodynamic properties using PA and PT

Conference Fee
The Conference fee is 1000 Euro for each participant.

Application deadline: January 26th, 2012.

Further Details and Application
All information about the Workshop can be found on the website http://www.uniroma1.it/photoacoustic-photothermal/. In order to submit the application to attend the Workshop you are kindly asked to send a short email to the conference Secretariat at Roberto Li Voti Sapienza Università di Roma - Dipartimento SB/AI e-mail: WorkshopErice@uniroma1.it Application deadline: January 26th, 2012

In the email you are kindly asked to write the following info:
1) Name and affiliation of the participant
2) Option: poster presentation, oral presentation, none of them.

Directors of the Workshop: R. Li Voti - A. Mandelis
Director of the School: S. Martellucci - A.N. Chester
EMFSC President and Director of the Centre: A. Zichichi
Timetable of the Workshop

Thursday 19th April:

noon onwards: **Arrivals & Registration**
Lunch & Dinner: **Local Restaurants**
After Dinner: **Welcome Party** – **Piano Room San Rocco**

Friday 20th April:

*Morning Session: Foundations and Techniques*  
*San Rocco Lecture Hall*

Chairperson: A.N. Chester

- 9.00 – 9.15 Opening by A. Mandelis and R. Li Voti
- 9.15 – 10.15 Osamu Matsuda - Hokkaido University, Japan  
  *Picosecond laser ultrasonics in materials physics*
- 10.15 – 11.15 Roberto Li Voti – Sapienza Università di Roma -Italy  
  *Photothermal techniques for nondestructive testing (NDT) and evaluation (NDE) of materials*

11.15 – 11.30 **Coffee Break – San Rocco Cloister**

Chairperson: G. Diebold

- 11.30 – 12.30 Andreas Mandelis - University of Toronto - Canada  
  *Lock-in and heterodyne carrierographic imaging:  
  Dynamic optoelectronic diffusion-wave NDT methods with applications to quality control of industrial solar cells*
- 12.30 – 3.00 **Lunch: Local Restaurants**
Friday 20th April:

Afternoon Session - Foundations and Techniques
San Rocco Lecture Hall

Chairperson: A. Mandelis

3.30 – 4.30 Christ Glorieux - KUL Leuven, Belgium
Depth profiling and other inverse problems in PA&PT

4.30 – 5.30 Sebastian Volz - CNRS – France
Nanoscale Engineering Networks and Challenges

5.30 – 5.45 Coffee Break – San Rocco Cloister

Chairperson: S. Volz

5:45 – 6.45 Andrea Bettucci – Sapienza Università di Roma -Italy
Acoustic Microscopy: Introduction, Overview and Applications

7.00 – 9.00 Dinner: Local Restaurants

9.00 – 11.30 Poster Discussion & Marsala Room

Saturday 21st April:

Morning Session B: Nanoscale Heat Transfer and Imaging
San Rocco Lecture Hall

Chairperson: S. Volz

9.15 – 10.15 Ariane Deniset - Université Paris-Sud, France
When AFM met IR: Nanospectroscopy AFMIR for subcellular imaging

10.15 – 11.15 Olivier Chapuis - CNRS - INSA Lyon, France
Heat Conduction in Nanostructures Investigated with Electrical Means. An Comparison with Optical Techniques

11.15 – 11.30 Coffee Break – San Rocco Cloister

11.30 - 12.00 Andrea Bragas - CONICET Universidad de Buenos Aires - Argentina
Metal Nanoparticle Ensembles: Tunable Laser Pulses Distinguish Monomer from Dimer Vibrations

12.00 – 12.30 Colby Jensen - Utah State University, Logan, UT, USA
Thermal Conductivity of Proton-Irradiated ZrC using Scanning Thermal Microscopy and Photothermal Radiometry

12.30 – 3.00 Lunch: Local Restaurants
Saturday 21st April:

Afternoon Session B - Nanoscale Heat Transfer and Imaging
San Rocco Lecture Hall

Chairperson: G. Tessier

3.30 – 4.30  Christ Glorieux - KUL Leuven, Belgium
Thin film characterization by transient grating techniques:
on the way from micron to nanometer scales

4.30 – 5.00  Roberto Li Voti - Sapienza Università di Roma -Italy
Nanostructure characterization by PA&PT

5.00 – 5.30  Mario Bertolotti - Sapienza Università di Roma -Italy
Nanostructures for infrared management

5.30 – 5.45  Coffee Break – San Rocco Cloister

Chairperson: O. Chapuis

5.45 – 6.45  Gilles Tessier – Institut Langevin, ESPCI, Paris, France
Digital heterodyne holography images heating in nanostructures

6.45 – 7.10  Kyle Horne - Utah State University, Old Main Hill, Logan UT
Monte Carlo Uncertainty Analysis of Thermal Property
Measurements by Photothermal Methods

7.10 – 9.00  Dinner: Local Restaurants

9.00 – 11.30 Poster Discussion and more

Sunday 22nd April: 9.00 a.m. – 7.00 p.m.

Excursion to Selinunte and Segesta archeological sites.
Lunch at “Lido Azzurro”
Bus leaving Erice Parking area at 9.00 a.m.

7.00 – 9.00  Dinner: Local Restaurants

9.00 – 11.30 Poster Discussion and Marsala Room
Monday 23rd April:

Morning Session A: Biomedical and Biological PA&PT
San Rocco Lecture Hall

Chairperson: A. Mandelis

9.00 – 10.00 Vladimir Zharov - University of Arkansas for Medical Sciences, USA
Photoacoustic flow cytometry for early diagnosis of cancer, infections and cardiovascular diseases

10.00 – 11.00 Rinat Esenaliev - University of Texas Medical Branch, TX, USA
Optoacoustic Platform for Noninvasive, Continuous Monitoring of Multiple Physiologic Parameters

11.00 – 11.10 Coffee Break – San Rocco Cloister

Chairpersons: Rinat Esenaliev

11.10 – 12.10 Srirang Manohar - University of Twente, The Netherlands
Photoacoustic Breast Imaging: the Twente experience

12.10 – 1.10 Ekaterina Galanzha University of Arkansas for Medical Sciences
Negative contrast photoacoustic and photothermal imaging, spectroscopy and cytometry

1.10 – 3.00 Lunch: Local Restaurants

Afternoon Session A: Biomedical and Biological PA&PT
San Rocco Lecture Hall

Chairperson: V. Zharov

3.30 - 4.30 Guenther Paltauf - Karl-Franzens Univ. Graz, Austria
Focusing acoustic elements for photoacoustic imaging

4.30 - 5.30 Andreas Mandelis – University of Toronto, Canada
Thermophotonic and Photoacoustic Radar Imaging Methods for Biomedical and Dental Imaging

5.30 – 5.45 Coffee Break – San Rocco Cloister
Chairperson: **G. Paltauf**

5.45 – 6.45 **Amir Rosenthal** - Helmholtz Zentrum, Munich, Germany
Advances in multispectral optoacoustic tomography

7.00 – 9.00 **Dinner: Local Restaurants**

9.00 – 11.30 **Poster Discussion and Marsala Room**

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**Tuesday 24th April:**

Morning Session C: Non Destructive Evaluation & Testing
San Rocco Lecture Hall

Chairperson: **R. Li Voti**

9.15 - 10.15 **Osamu Matsuda** - Hokkaido University, Japan
Time-resolved two-dimensional imaging of GHz surface acoustic waves in phononic crystals and structures based on them

10.15 – 11.15 **Arantza Mendioroz** - University of the Basque Country UPV/EHU
Internal heat source reconstruction: an approach to defect characterization from vibrothermography data

11.15 – 11.30 **Coffee Break – San Rocco Cloister**

Chairperson: **A. Mandelis**

11.30 – 12.00 **Peter Burgholzer** - Research Center for Non Destructive Testing - Linz
Limits of spatial resolution for thermography and other non-destructive imaging methods based on diffusion waves

12.00 – 12.30 **Dmitriy Ksenofontov** - M.V.Lomonosov Moscow State University - Russia
Contact Laser Ultrasonic Evaluation of Graphite-Epoxy Composite Structure

12.30 – 3.00 **Lunch: Local Restaurants**
Tuesday 24th April:

Afternoon Session C: Non Destructive Evaluation & Testing
San Rocco Lecture Hall

Chairperson: A. Mendioroz

3.30 – 4.30 Gerald J. Diebold - Brown University, Providence - USA
Heat Conduction Effects, CW Photoacoustics, and Phononic Structures

Post Session B: Nanoscale Heat Transfer and Imaging
San Rocco Lecture Hall

Chairperson: O. Matsuda

4.30 – 5.30 Michel Orrit - Leiden University, The Netherlands
Photothermal Spectroscopy of Single Gold Nanoparticles

5.30 – 5.45 Coffee Break – San Rocco Cloister

Event of FLIR
San Rocco Lecture Hall

Chairperson: A. Mandelis

5.45 – 6.15 Francesco Messa – Antoine Billardello – FLIR
FLIR exhibition

6.15 - 7.00 FLIR Best Presentation Award
Celebration of the winner and brief talk

7.30 – 9.00 Social Dinner

9.00 – 11.30 Poster Discussion and Marsala Room

Wednesday 25th April:

Morning Session D: Thermophysical Properties
San Rocco Lecture Hall

Chairperson: A. Mandelis

9.15 – 10.15 Dorin Dadarlat - Institute for Isotopic and Molecular Technology, Romania
Recent Developments in the Photopyroelectric Calorimetry of Condensed Matter

10.15 – 11.15 Fulvio Mercuri - Università di Roma “Tor Vergata”, Italy
Active infrared thermography applied to the study of Cultural Heritage
11.15 – 11.30  
**Coffee Break – San Rocco Cloister**

Chairperson: **D. Dadarlat**

11.30 - 12.00  
**Viviane Pilla** – Universidade Federal de Uberlândia - Brasil  
*Thermo-Optical Characterization of CdSe/ZnS Quantum Dots Embedded in Biocompatible Materials*

12.00 - 12.30  
**Jose Ordonez Miranda** – Cinvestav-Mérida, México  
*Thermal Conductivity of Particulate Nanocomposites and Porous Media: Comparison between Experiment and Theory*

12.30 – 3.00  
**Lunch: Local Restaurants**

**Afternoon Session D: Thermophysical Properties**  
**San Rocco Lecture Hall**

Chairperson: **M. Bertolotti**

3.30 – 4.00  
**Esteban Alejo Domené** - Universidad de Buenos Aires - Argentina  
*Focus Shift Thermal Expansion Microscopy for Mapping Thermal Diffusivity*

4.00 – 4.25  
**Dmitriy Ksenofontov** - M.V.Lomonosov Moscow State University - Russia  
*High Energy States of Thermally Thin Metal Foils Induced by Nanosecond Laser Pulse Impact*

**Afternoon Session: Conclusions**  
**San Rocco Lecture Hall**

Chairperson: **A. Mandelis and R. Li Voti**

4.30 – 5.00  
**Presentation of the next International Conferences:**  
*ICPPP China*  
*18th Symposium on Thermophysical Properties at Boulder Colorado*  
*Third Mediterranean International Workshop on PA&PT*

5.00 – 5.30  
**Concluding Remark and Round Table**

7.00 – 9.00  
**Dinner: Local Restaurants**

9.00 – 11.30  
**Farewell Party – Marsala Room**

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**Thursday 26th April:**

noon onwards: **Departures**

Lunch & Dinner: **Local Restaurants**
Poster Presentations

P_1: Transition from Rayleigh waves to capillary waves at the free surface of a visco-elastic material
   J. Sermeus, O. Matsuda, J. Fivez, R. Salenbien, B. Verstraeten, C. Glorieux

P_2: Photothermal Depth Profiling in Hardened Steels: a new inverse approach based on Singular Value Decomposition
   Roberto Li Voti, Grigore Leahu, and Concita Sibili

P_3: NANOSCALE HEAT TRANSFER IN SYNTHETIC METALLIC OPALS
   Roberto Li Voti, Grigore Leahu, Luca Di Dio, Concita Sibili, and Mario Bertolotti

P_4: Fabrication at the nanoscale of Ultrasonic transducers
   LeonelMarques, Richard Smith, Jon Aylott, Matt Clark

P_5: Thermal conductivity and diffusivity measurements of glass coated magnetic microwires using lock-in thermography
   R. Fuente, A. Salazar, A. Mendioroz, A. Zhukov and V. Zhukova

P_6: Large depth of field scanning acoustic and photoacoustic microscopy

P_7: New pharmaceutical solid forms: a photothermal and structural approach
   Carmen Tripon, Irina Kacso, Marieta Muresan-Pop, Gh. Borodi, I. Bratu and D. Dadarlat

P_8: DEVELOPMENT OF A FOCUS ERROR PHOTOTHERMAL DETECTOR FOR THE CHARACTERIZATION OF OPTICAL AND THERMAL PROPERTIES IN MATERIALS
   Esteban A. Domené and Oscar E. Martínez

P_9: Prediction of the Maximal Safe Laser Radiant Exposure on an Individual Patient Basis Based on Photothermal Temperature Profiling
   Luka Vidovič, Matija Milanič, and Boris Majaron

P_10: Metal Nanoparticle Ensembles: Tunable Laser Pulses Distinguish Monomer from Dimer Vibrations
   Pablo M. Jais, Daniel B. Murray, Roberto Merlin and Andrea V. Bragas
Friday 20\textsuperscript{th} April

\textit{Foundations and Techniques}
Picosecond laser ultrasonics in materials physics

Osamu Matsuda

Division of Applied Physics, Faculty of Engineering, Hokkaido University

Abstract: Absorption of subpicosecond laser pulses in a medium may generate picosecond acoustic pulses therein. The propagation of generated acoustic pulses can be monitored with delayed laser pulses through the transient optical reflectance change. The technique is called picosecond laser ultrasonics and is used for the evaluation of multilayer structures in nano- or micrometer thicknesses as well as for the evaluation of physical properties of materials.

In this talk, some of our recent works to extend the applicability of laser picosecond acoustics are introduced; the generation and detection of sub-THz acoustic waves in semiconductor quantum wells[1], and the generation and detection of shear acoustic waves[2].

Semiconductor quantum wells have a fascinating nature which allows one to tailor the electronic structure. First part of the talk will be about the investigation of the GaAs/AlGaAs quantum well system with picosecond laser acoustics. When the electrons in the quantum well is excited by the infrared light pulses (pump pulses), the stress field corresponding to the confined electronic wave function is set up instantaneously and launches an acoustic pulse up to or beyond 1 THz band width. The frequency doubled blue laser pulses (probe pulses) are used to monitor the arrival of acoustic pulses to the sample surface with varying the delay time between the pump and probe pulses. A Sagnac interferometer is used to detect both real and imaginary part of the reflectance change caused by the photoelastic effect and the surface displacement. The sample containing several quantum wells with different well widths shows an optical wavelength selective acoustic pulse generation. Theoretical model of the light scattering by inhomogeneous modulation of the optical constants is developed and gives good agreement between the experimental result and calculation.

The second part of the talk will be about the shear acoustic waves generation and detection in picosecond laser acoustics. Because of the symmetry of samples and measurement configuration, longitudinal acoustic waves have been mostly concerned in laser picoseconds ultrasonics. However, an inclusion of transverse acoustic waves in the measurement would be desirable for the complete understandings of the materials properties, or for the practical application where the shear waves are essentially important. We have investigated the generation of shear acoustic waves exploiting an anisotropic crystal and the detection of shear waves in a transparent isotropic material with a special optical configuration. The light scattering theory is extended to handle the induced optical birefringence and obliquely incident probe light. The good agreement between the experiment result and calculation is obtained.

These achievements should form a basis for the divergent application of picosecond laser ultrasonics.

Photothermal techniques for nondestructive testing (NDT) and evaluation (NDE) of materials

Roberto Li Voti

Dipartimento di Scienze di Base ed Applicate all’Ingegneria, Sapienza Università di Roma, via A.Scarpa 16 – 00161 Roma - Italy

This tutorial wish to introduce the basis of the Thermal Wave Physics and recall the PA& PT techniques. It is divided into two parts:

We first recall the basic theory and discuss some fundamental phenomena as the thermal wave reflection and refraction, the thermal wave interferometry, the thermal wave resonance, and the thermal wave scattering, together with the main relative applications.

Then we recall the principle of the different PA&PT techniques, showing the main applications in the non-destructive testing NDT and evaluation of materials NDE.

The challenges for the future research are also presented.
Lock-in and heterodyne carrierographic imaging: Dynamic optoelectronic diffusion-wave NDT methods with applications to quality control of industrial solar cells

Andreas Mandelis\textsuperscript{1}, Yu Zhang\textsuperscript{1,2}, and Alexander Melnikov\textsuperscript{1}

\textsuperscript{1} Center for Advanced Diffusion-Wave Technologies (CADIFT), Mechanical and Industrial Engineering, University of Toronto, Toronto M5S 3G8, Canada
\textsuperscript{2} Department of Automation Measurement and Control, Harbin Institute of Technology, Harbin, 150001, China

Abstract

A solar cell lock-in carrierographic image generation theory based on the concept of non-equilibrium radiation chemical potential was developed. An optoelectronic diode expression was derived linking the emitted radiative recombination photon flux (current density), the solar conversion efficiency, and the external load resistance via the closed- and/or open-circuit photovoltage. The expression was shown to be of a structure similar to the conventional photovoltaic I-V equation, thereby allowing the carrierographic image to be used in a quantitative statistical pixel brightness distribution analysis with outcome being the non-contacting measurement of mean values of these important parameters averaged over the entire illuminated solar cell surface. This is the optoelectronic equivalent of the electrical (contacting) measurement method using an external resistor circuit and the outputs of the solar cell electrode grid, the latter acting as an averaging distribution network over the surface. The statistical theory was confirmed using multi-crystalline Si solar cells.
As in most fields experimental physics, the analysis of experimental data in photoacoustic and photothermal research requires the extraction of material parameters from a set of acquired experimental values. In most of the cases a theoretical model, calculating the observed signals given the material parameters is available. However, very often, there is no analytical equation available that explicitly expresses the material parameters as a function of the experimental data. Here we shed a light on a series of such non-trivial inverse problems related to photoacoustic and photothermal techniques, summarize typical approaches to deal with them, and propose some new approaches. We focus on the mildly ill-posed problem of photothermal depth profiling. Also examples of photopyroelectric signal analysis and related problems of fitting degeneracy are discussed. The limits of the inverse problem of photoacoustic depth profiling, i.e. the extraction of the depth profile of the elastic parameters from the frequency/wave number dependence of the surface acoustic wave velocity is revisited, and links are made to the extraction of elastic parameters from isotropic and anisotropic multilayers, with special attention on how to cope with fitting degeneracy via most-squares analysis and the introduction of non-degenerated parameters.
This presentation will first emphasize a link existing between nanoscale heat transfer, nanoelectronics, radiation and acoustics and mention the corresponding communities involved in Europe.

This network approach will be then illustrated by a specific challenge which is to consider heat as possible information carrier. This idea will be further supported by recent measurements of nanojunction thermal conductances proving ballistic thermal phonon transport at ambient temperature.

This measurement was performed based on a MEMS-in-TEM (MicroElectroMechanical System in Transmission Electron Microscope), which consists in generating a static temperature difference at the ends of a nanojunction. The nanojunction itself is formed by contacting microscale silicon surfaces and retract them to draw small wires of a few tens of nanometers. The conductance data clearly reveal the presence of ballistic phonon transport.
Acoustic Microscopy: Introduction, Overview and Applications

A. Bettucci

Department of Basic and Applied Sciences for Engineering,
SAPIENZA Università di Roma, Rome, Italy

Abstract: Nowadays there are a great number of available microscopy techniques to observe and characterize micro- or nano-structures: optical microscopy, electron microscopy, the large family of the scanning probe microscopy which includes, for example, the scanning tunneling and the atomic force microscopy, etc. Each of these techniques relies on a different contrast mechanism to reveal the structures and each technique has its own range of applications for which is particularly suitable. The acoustic microscope it is not a new entry in the field of microscopic imaging; its current configuration as a scanning instrument, in which a sample is placed in the focal region of a converging ultrasonic beam generated by an acoustic lens with a large numerical aperture, was introduced by C. Quate and R. Lemons at Stanford University in 1974 [1]. It is a miniature sonar system (e.g. an instrument based on the pulse-echo effect of the elastic waves) in which electroacoustical transducers and acoustic lenses work at Megahertz (or Gigahertz) frequencies to form high resolution images showing material properties not usually seen with other kinds of microscopy techniques. Actually, the nature of the acoustic contrast is based on the propagation of Surface Acoustic Waves (SAW), also known as Rayleigh waves, that are elastic waves traveling along the surface of the sample and whose energy is confined within few wavelengths below the surface itself: the SAW are responsible for highlighting the changes in elastic properties in acoustic images [2].

In normal operating condition the lateral resolution of an acoustic microscope is in the submicron range, consequently, for some applications, it has been superseded by instruments with higher resolving power i.e. Atomic Force Microscope (AFM) and, for subsurface imaging in solid samples, by acoustic AFM-based techniques such as Ultrasonic Force Microscope (UFM). Anyway, just for the very particular mechanism of contrast generation, the acoustic microscope remains unsurpassed in some applications; for example, the presence of a liquid as a coupling medium between the acoustic lens and the sample surface makes it a unique tool for probing mechanical properties of living cells and soft tissues that can be analyzed without the need of staining or some other kind of preparation.

In this talk the physics of the acoustic microscope will be analyzed with emphasis to the mechanism of contrast generation highlighting the role played by Rayleigh waves; examples of application will be reported in the field of non destructive evaluation and of imaging of living cells and biological tissue.

Saturday 21\textsuperscript{th} April

\textit{Nanoscale Heat Transfer and Imaging}
When AFM met IR: Nanospectroscopy AFMIR for subcellular imaging.

A Deniset-Besseau, a C. Martel b, J.M. Ortega a, R. Prazeres a, M.J. Virolle b, C. Policar c, and A. Dazzi a

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(b) Institut of genetic and microbiology, Université Paris-Sud-CNRS UMR 8621, Orsay, France
(c) Laboratoire of biomolecules - UMR 7203- École Normale Supérieure, Department of chemistry, Paris, France
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Abstract: Recently near-field techniques play a fundamental role in Nanoscience microscopy. Two different ways exist to make infrared studies with near-field techniques: optical techniques measuring the transmitted signal coming from the nano-object and photothermal approaches using thermometer to link temperature to absorption measurements. Considering these previous methods limitations, we have developed an innovative infrared nanospectromicroscopy, AFMIR. AFMIR is a cutting-edge near-field technique using a setup in which an atomic force microscope (AFM) is coupled with a tunable pulsed infrared laser to record spatially resolved absorption measurements. The AFM tip is in contact with the sample that is illuminated by a pulsed laser beam passed through a ZnSe prism. The laser wavelength is tuned to an IR absorption band of a molecule and, when the laser pulse occurs, the temperature increases locally with local temporary deformations. The AFM tip detects these local deformations and starts to oscillate. The maximum amplitude of the oscillations, corresponding to the AFMIR signal, is proportional to the local absorbance. AFMIR resolution is the same as the AFM (ca. 20–50 nm). It thus allows subcellular IR mapping of biological samples. The relevance of the technique was proved by following the growth of PolyHydroxyButyrate vesicules in Rhodobacter capsulatus.

To illustrate, two studies will be detailed on bacteria and eucarotic cells. First, we have recently shown that P89, a hydroxy-tamoxifene hormone conjugated to a Re-tris-carbonyl7 (a IR marker) is providing, after cellular incubation (1h, 1µM, cells MDA-MB231, non-hormono-dependent breast-cancer), an intense signal (at 1925 cm⁻¹) in classical FTIR and allows an efficient AFMIR mapping inside cells. Using the intrinsic IR-signal of phosphate (1240 cm⁻¹) and amide I (1650 cm⁻¹) the nucleus was localised without any probe. The colocalisation with P89 and the nucleus was evidenced due to the comparison of the high resolved mapping of AFMIR.

Then a study on Streptomyces, soil filamentous bacteria, will be presented. These bacteria produces many secondary metabolites with various chemical structures and useful. Recently, an inverse correlation between the presence of lipid vesicles and the production of secondary metabolites was highlighted in Streptomyces. Consequently, considering the size of the vesicles (≈ 100 nm) and their IR properties (C=O stretching of the esters at 1738 cm⁻¹), we have proposed to monitore the constitution and/or degradation of storage lipids in Streptomyces in relation with the production of secondary metabolism.

Heat Conduction in Nanostructures Investigated with Electrical Means – A Comparison with Optical Techniques

P-Olivier CHAPUIS\(^{(a,b)}\) *, Andrey Shchepetov\(^{(c)}\), Mika Prunnila\(^{(c)}\), Joumi Ahopelto\(^{(c)}\), Sebastian Volz\(^{(d)}\), Lars Schneider\(^{(b)}\), Clivia M. Sotomayor Torres\(^{(b,e)}\)

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\(^{(d)}\) Laboratoire EM2C, CNRS and Ecole Centrale Paris, 92295 Châtenay-Malabry, France \\
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Acoustic phonons – collective and extended modes of the atomic motions - are the dominant heat carriers in nonmetallic materials. At low frequencies (GHz range), a number of optical experiments (Brillouin scattering spectroscopy, ultrafast spectroscopy) are able to probe their behavior at a single frequency – coherent wave propagation, attenuation - whereas at higher frequencies (> 2 THz), being the ones responsible for the thermal transport at room temperature, a monochromatic investigation is more difficult due to the strong attenuation. In addition to the optical methods, Joule-heating thermal excitation is a solution to generate high-frequency phonons, but the full spectrum is excited and an averaged analysis has to be performed. The particle-picture appears particularly appropriate to describe the heat transfer.

We have probed the ridge-substrate geometry to analyze the confinement of the acoustic phonons, which, in our experiment, are generated through Joule effect in a deposited metallic resistor wire that lies on top of the ridge. We discuss the results as a function of the temperature, here used as a convenient way to tune the averaged phonon mean free path [1].

We discuss the fact than in nano-objects proper heat baths (and their associated temperatures) are difficult to define and show how the particle-picture helps then defining the heat flux flowing from one nano-object to a macroscopic one [2]. We also analyze the rarefied phonon regime, when the phonons are generated from sub-mean free path sources [3].


We acknowledge the support of EU FP7 projects NANOPOWER and NANOFUNCTION and French ANR grant “nanoHEAT”.
Metal Nanoparticle Ensembles: Tunable Laser Pulses Distinguish Monomer from Dimer Vibrations

Pablo M. Jais\(^{(a)}\), Daniel B. Murray\(^{(b)}\), Roberto Merlin\(^{(c)}\) and Andrea V. Bragas\(^{(a),(d)}\)*

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Abstract: Tunable optical pulses are used to excite selectively coherent mechanical oscillations in the 5-150 GHz range, assigned to vibrations of isolated spheres or pairs of contacting spheres, in an ensemble of gold nanoparticles. The amplitudes of the oscillations exhibit a strong enhancement when the laser central wavelength is tuned to resonate with the corresponding plasmon. Our approach distinguishes itself in that we are able to discriminate between modes of individual spheres and pairs of connecting spheres without recurring to single-particle detection. Because of the resonant selection in the excitation process, the widths of the acoustic modes are significantly smaller than broadening caused by the spread in radii in the ensemble.

There are various mechanisms by which light couples to nanoparticle (NP) vibrations [1]. For instance, absorption of an incident optical pulse at or near a plasmon resonance leads to an increase in temperature with the concomitant thermal expansion of the NP. If the temperature rise is sufficiently fast, this results in the coherent excitation of vibrational modes [2]. In the case of spherical NPs, light couples primarily to the radial breathing mode of monomers [2] and, as recently shown by Tchebotareva et al. [3], to the stretching mode of dimers. These authors could identify the respective modes by performing measurements on isolated spheres and dimers. Here [4], we work with an ensemble prepared by wet chemistry methods, which allow for fine control of the concentration and aggregation of the NPs [5,6]. Selectivity in excitation and detection of one or the other mode is attained by tuning the laser wavelength to match that of the corresponding monomer or dimer plasmon. We find that, due to resonant excitation and, thereby, parameter selectivity, the vibrational modes exhibit a higher quality factor than what is expected for the size dispersion in the ensemble.

![Fig. 1. Coherent phonons generated in an ensemble of 10 nm radius nanoparticles. Data obtained for laser central wavelengths corresponding to the plasmon resonance of (a) single particles (\(\lambda_C = 520\) nm) and (b) dimers (\(\lambda_C = 620\) nm). The top traces show the measured differential transmission, \(\Delta T/T\). Red curves are fits to the data. The lower panels show the individual phonon contributions obtained from the fit after subtraction of the electronic background. The cartoon in the middle shows schematically the stretching dimer mode and the breathing single-particle mode, which amplitude is strongly enhanced when the pulse wavelength resonates with the corresponding plasmon frequency.](attachment:figure1.png)
Thermal Conductivity of Proton-Irradiated ZrC using Scanning Thermal Microscopy and Photothermal Radiometry

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Understanding the change of thermophysical properties of materials under irradiation conditions is extremely important for the development of new technologies and materials to be used in next generation nuclear reactors. Using ion-irradiation in lieu of in-pile measurement provides an easier, quicker, and cheaper method of studying irradiation damage effects \cite{1}. As may be predicted by numerical simulation, the ion irradiation penetrates a thin zone (0.1-100 \(\mu\)m deep for laboratory accelerators) on the irradiated surface creating what at times may be approximated as a layered structure. Few studies of ion-irradiation-induced thermal property changes have been performed, mostly using photothermal methods \cite{2-4}.

Using an approach combining scanning thermal microscopy (SThM) and photothermal radiometry (PTR), the thermal conductivity change of a proton-irradiated zirconium carbide (ZrC) sample has been characterized. The cross section of the sample has been mapped using SThM to provide a thermal conductivity profile as a function of depth through the irradiation damaged layer into the bulk, undamaged material as shown in Fig. 1. Frequency scans performed using front-detection PTR on the irradiated face also demonstrate the capability to identify the thermophysical parameters of the damaged zone approximated as 2 layers on the bulk.

The measured SThM conductance profile evidences a quite uniform degradation of thermal conductivity in the damaged region with evidence of a thin transitory layer to the bulk, raw ZrC (Fig. 1) and provides valuable input in the parameter fitting process for the PTR data. DC calibration of the SThM conductance signal has been performed indicating ~50\% reduction of thermal conductivity in the irradiation-damaged layer. Best fits for the measured PTR spectra validates this result showing 53\% degradation. The SThM and PTR methods are shown to complement each other to characterize the strong degradation of thermal conductivity in the ZrC sample and may provide a useful methodology for future studies.

Fig. 1: Thermal conductance profiles for proton-irradiated ZrC cross section. Left: SThM probe power (\(\propto\) conductance) in constant temperature mode vs. penetration depth (Distance = 0 is ~10 \(\mu\)m from surface). Right: Conductance image showing clear thermal distinction between damaged zone (dark) and virgin material (light).

Thin film characterization by transient grating techniques: on the way from micron to nanometer scales

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Transient grating techniques exploit the large intrinsic bandwidth offered by laser excitation and detection via photothermal and photoacoustic effects, while channeling the signal energy into a narrow band wave number of choice. The wave number selection is controlled via the crossing angle between merged laser beams, with wavelengths down to the one of the used laser light. Due to the high precision on the frequency of the narrow band signals, thin film induced dispersive effects surface acoustic wave velocities can be determined very accurately, so that transient grating techniques allow to characterize films with thicknesses in the sub-100 nm range.

In this presentation we probe the current and expected ultimate limits of elastic thin film characterization by transient gratings. Also a theoretical model for and preliminary results on the use of a transient grating techniques for the thermal characterization of thin films are presented, and future perspectives on this approach are discussed.

Also some alternatives to the classical detection of transient grating signals by diffraction are proposed.
Heat transport at nanoscale is of importance for many nanotechnology applications [1]. There are typically two current problems related to this subject in nanophotonics: the first problem, of fundamental interest for semiconductor lasers [2], is the removal of the heat generated to maintain the functionality and reliability of these devices. The efficient evacuation of heat in the nanostructures is of crucial importance in order to avoid large thermal stresses devastating for the lifetime of the whole device. The second problem is to utilize nanostructures to manipulate the heat flow for thermoelectric energy conversion and thermophotovoltaic power generation. Here one has the inverse requirement, i.e. to limit thermal diffusion in order to guarantee a high energy conversion efficiency. Considerable efforts are nowadays to discover new geometries with a huge number of internal interfaces and thermal barriers in order to increase the thermal resistance. The study of the heat transport in such nanostructures is here performed by applying photothermal techniques. Photothermal radiometry is here applied to localize the internal heat sources where the light is absorbed and to measure the sample effective thermal diffusivity. In this work we discuss the results obtained on opals [3-5] and carbon nanotubes.

References

The term infrared signature generically describes how objects appear to infrared sensors. In most cases, infrared (IR) emissions from vehicles are used to detect, track, and lock-on to the target. The infrared signature of a given object depends on several factors, including the shape and size of the object, its temperature and its emissivity, as well as external conditions (illumination, background, to name some). One of the most challenging tasks regarding the IR vision is to reduce the infrared signature of objects.

Although the IR spectrum extends from the red light to microwave radiation, i.e. 0.77 to 1000 μm, there are only two wavelength ranges showing high IR transmittance in the atmosphere, i.e. 3-5 and 8-12 μm, known as mid (MWIR) and long (LWIR) IR windows, respectively. Outside these windows, CO₂ and H₂O vapour give rise to both absorption and scattering phenomena, determining strong attenuation of IR radiation.

Thermochromic materials, changing their spectral properties as a function of the temperature, are extensively studied in the seek of active control of thermal emission. Among the different thermochromic materials, the most known and widely diffused is vanadium dioxide, VO₂ that is also the object of the present study [1]. Its crystalline lattice exhibits an abrupt semiconductor-to-metal phase transition at a temperature T_C ≈ 341 K (68°C) characterized by an increase of reflectivity as well as a decrease of emissivity in the IR range. At a microscopic scale, through the phase transition VO₂ undergoes a physical change of its crystalline cell from monoclinic to tetragonal.

As well as other oxides showing this peculiar characteristic, as Nb dioxide (NbO₂) and V₂O₅, VO₂ has an insulating behavior under T_C, while above this temperature it exploits a metallic nature, dramatically changing its optical, electrical and magnetic properties. In particular, optical properties are sharply changed during the phase semiconductor-to-metal transition, thus the dispersion law of the complex refractive index n+iκ is strongly modified. [2,3]. As a consequence, the phase transition, occurring in a very short temporal range of the order of few picoseconds, can be exploited for the realization of an optical component switching from transparent (in the semiconductor state) to reflective (in the metallic state), as well as an efficient thermal switch. [4,5]

In general, the performance effectiveness of either optical or thermal switches can be quantified and estimated through the so-called dynamic range, which is the difference between the largest and smallest possible values of a changeable quantity. Within the present work we define this figure of merit as the difference between the emissivity values, averaged in the IR range 3-5 μm and calculated for the two different regimes, i.e. below and above T_C, respectively. Given this assumption, it’s worth to note that the sign of the dynamic range, i.e. if positive or negative, completely changes the filter behavior and thus determines the type of application. A thermochromic filter displaying positive dynamic range, i.e. its IR emissivity decreases with increasing temperature, is suitable for IR signature reduction as well as for smart windows for thermal control [6]. On the other side, a negative dynamic range is required for space applications and emissivity control of spacecraft [7].

Recent works have shown, both theoretically and experimentally, that the thermal emissivity behaviour with temperature (i.e. dynamic range) of VO₂ thin films is strongly influenced by the substrate used for the deposition.

In what follows we consider simulations of the optical response of VO₂ thin films first deposited on different substrates (section 2), and then in multilayer structures (section 3), below and above the T_C. We discuss the effect that different substrates as well as VO₂ layer thicknesses have on the sign of the dynamic range. Finally, we introduce some metallo-dielectric multilayer structures, composed by copper or silver and VO₂ alternating layers, where the layer thickness is systematically varied in order to further increase and optimize the dynamic range value.

Acknowledgments
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References
Digital heterodyne holography images heating in nanostructures

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Abstract: Heterodyne digital holography associates the advantages of full-field phase-sensitive imaging to the ability to probe modulated phenomena, such as photothermal phenomena. It is therefore very adapted to the 3D study of plasmonic phenomena, which direct or confine light, but also induce strongly localised heating. The possibilities of this method, which delivers signals directly proportional to the local temperature increase induced by dissipative phenomena, will be illustrated on nanodisc chains and rod pairs.

In metals displaying ohmic losses, the electron oscillation which is characteristic of plasmonic phenomena induces heating. Although detrimental to some applications, this heating can be considered a fingerprint of plasmonic phenomena, and has recently been used as ways to detect nanoparticles \[1, 2\], or to characterize plasmonic resonances in nanostructured systems \[3\]. Here, we propose a non contact, full field imaging method based on digital heterodyne holography \[4\], which measures variations in the light scattered by the structures as a result of refractive index changes related to local heating. A variety of nanodisc chains with different disc numbers, spacings and diameters were fabricated on glass substrates by e-beam lithography.

A heterodyne phase modulation of a low power probe beam (\(\lambda = 785\) nm, \(P = 50\) mW) allows the retrieval of high frequency changes induced by the modulation of an excitation beam (\(F_{\text{Heat}} = 1\) kHz, \(\lambda = 532\) nm, \(P < 1\)W) at a low frequency compatible with a slow CCD camera (\(F_{\text{CCD}} = 16\) Hz). A Green function - based analytical approach allowed us to show that the recorded signals are directly proportional to the temperature increase.

In the example shown in figure 1, on a 17 discs chain (\(d=150\)nm, gap=10nm), a clear photothermal signal is observed when the excitation beam is polarized parallel to the axis of the structure. The photothermal signal is 3.5 lower for a perpendicular polarization at identical laser fluence. This is a clear indication that a plasmonic resonance involving the whole disc chain, efficiently excited by an electric field along its axis, is the dominant dissipative source in this case, while the perpendicular polarization mostly excites individual disc modes.

We will present a systematic study of the dependence of photothermal signals on disc number, size and gap, as well as photothermal measurements on other types of plasmonic structures.

![Figure 1](image)

**Figure 1** : left: setup. Acousto Optical Modulators (AOM 1 and 2) modulate the optical phase of the probe beam (at 80 MHz and 80 MHz-\(F_{\text{Heat}}\)\(F_{\text{CCD}}/4\) respectively. Right : Thermally induced changes in the scattering by nanostructures, induced by a green laser modulated by AOM3 in amplitude at a frequency \(F_{\text{Heat}}\) (typ. 1 kHz), on a chain of 17 discs of 150 nm diameters, separated by 10 nm gaps.

Monte Carlo Uncertainty Analysis of Thermoproperty Measurement by Photothermal Methods

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Photothermal methods are used to measure thermal properties of layered samples with great with encouraging results[1-3]. Among these efforts is a method which computes the sample's properties from measured surface temperature phase lag at various frequencies using a multi-stage curve fit process. The curve fit process combines a brute force approach with more traditional curve fitting methods helps to remove the dependence of the fit parameters initial guess [4, 5]. Due to the complexity of curve fit process traditional Taylor’s series method cannot be used to estimate the uncertainty; therefore this work focuses on uncertainty estimation for different Photothermal methods through Monte Carlo simulations.

The Taylor series method of uncertainty propagation requires the development of a data reduction equation which relates input variables to the desired result. When general algorithms, such as curve fitting, are used to relate inputs to results it is often undesirable to define a data reduction equation due to the number of terms involved and complex correlated relationships. For such algorithms the Monte Carlo method is used, which simulates the process with random inputs and returns statistical data pertaining to the expected results [6]. This feature allows the Monte Carlo method to be more versatile than the Taylor Series method by accounting for correlated effects, and large numbers of terms but sacrifices generality; in general Monte Carlo results are only valid for the specific system simulated.

Initial investigations into the uncertainty of diffusivity and effusivity of a thin film on a known substrate have been completed. Using the method described, various measurements normally made during a material property calculation were given variations to simulate uncertainty in that value. The diffusivity and effusivity of the thin film were then calculated by an algorithm which is given only the believed values, not the true values. The statistics of the deviations from the true value in the simulated results quantify the uncertainty due to the variable inputs, seen in the figure. The asymmetrical diffusivity distribution indicates a measurement bias or dependent input variables in the calculation. The width of the distributions is used as the confidence interval for the measurement.

Monday 23rd April:

Biomedical and Biological PA&PT
PHOTOACOUSTIC FLOW CYTOMETRY FOR EARLY DIAGNOSIS OF CANCER, INFECTIONS, AND CARDIOVASCULAR DISEASES

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Recently we introduced a new platform of in vivo photoacoustic (PA) flow cytometry for real-time detection of circulating normal and abnormal cells, biomolecules, contrast agents, micro- and nanoparticles in various bioflows [1-4]. This report summarizes recent advances of this platform which include: multispectral laser array, multimodal photoacoustic-Raman detection schematics, ultrasharp rainbow nanoparticles, molecular targeting of multiple circulating biomarkers, in vivo magnetic enrichment, and combination of PA diagnosis with photothermal (PT) nanotherapy. The capacity of this technology was demonstrated by the real-time detection of circulating individual normal cells (e.g., erythrocytes and leukocytes) in different functional states (e.g., normal, apoptotic, or necrotic), circulating tumor cells (CTCs: melanoma, breast, squamous), bacteria (e.g., E. coli and S. aureus), nanoparticles (e.g., gold nanorods, carbon nanotubes, magnetic, and golden carbon nanotubes), and dyes (e.g., Lymphazurin, Evans blue, and Indocyanine Green) in blood, lymphatics, bone, and plants. The assessment of large blood volume in vivo, potentially the patient’s entire blood volume (in adults ∼5 L) significantly (10^3-fold) may enhance the sensitivity of CTC detection including rare cancer stem cells compared to the existing CTC assay ex vivo. If oncoming pilot clinical trials using the portable PA flow cytometry device are successful, this technology can provide breakthroughs for the early detection of CTCs when metastasis has not yet developed and, hence well-timed therapy is more effective.

REFERENCES
Optoacoustic Platform for Noninvasive, Continuous Monitoring of Multiple Physiologic Parameters

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Our laboratory has pioneered novel optical and ultrasound techniques can be used for noninvasive, high-resolution imaging and monitoring as well as for noninvasive therapy. We will present an overview of our results obtained using the following diagnostic and therapeutic techniques:

1. Optoacoustic imaging and monitoring;
2. Optical Coherence Tomography (OCT);
3. High-resolution ultrasound imaging;

The optoacoustic technique can be used for imaging (2-D and 3-D) and for monitoring of cerebral venous and central venous blood oxygenation, total hemoglobin concentration, and other physiological parameters. This technique is based on detection of thermoelastic ultrasound waves induced in tissues by optical pulses and yields a noninvasive diagnostic modality with high optical contrast and ultrasound spatial resolution. For more than 2 decades we have been developing biomedical optoacoustic monitoring, imaging, and sensing techniques and systems. At present, optoacoustics is the fastest growing area in biomedical optics.

One of our long-term objectives in this field is to improve the care of large populations of patients by developing the noninvasive, optoacoustic diagnostic platform that will accurately and continuously measure multiple important physiologic parameters including venous oxygenation (both cerebral and central) and total hemoglobin concentration. Currently, invasive measurements of these parameters are routinely used in patients with traumatic brain injury, patients with circulatory shock, critically ill, surgical, anemic and neonatal patients. We built optoacoustic systems for monitoring of these parameters by probing specific blood vessels including the radial artery, superior sagittal sinus, and central and peripheral veins. In these studies we used multi-wavelength, OPO-based optoacoustic systems tunable in the 700-1064 nm spectral range and highly-portable, light-weight, inexpensive, laser diode-based systems. We developed highly-sensitive, wide-band probes for detection of optoacoustic waves induced in the blood vessels. By using these probes and reconstruction algorithms developed for real-time, continuous signal acquisition and processing, we obtained high correlation between the optoacoustically predicted and reference blood parameters. High-resolution (30 microns) ultrasound imaging Vevo system and standard clinical GE ultrasound imaging systems were used in some studies for ultrasound-guided optoacoustic monitoring. Our results on noninvasive cancer therapy and drug delivery that are based on interaction of nanoparticles with laser or ultrasound radiation will be presented as well.
One of the relatively new methods being investigated for application in imaging the breast is photoacoustic imaging. The technique measures ultrasound excited by pulsed light illumination of optically absorbing structures in tissue. This allows the development of images of pathologies such as cancer that are endowed with higher absorption due to enhanced vascularization.

Early studies have demonstrated photoacoustic breast imaging in various configurations. We developed the Twente Photoacoustic Mammoscope (PAM I) to image the breast in the cranio-caudal transmission mode. After a successful pilot study in 2007, a new clinical study was started in December 2010 to investigate the clinical feasibility of photoacoustic mammography in a larger group of patients with different types of breast lesions. Here we present the results of the first phase of our study where 10 patient measurements on highly suspect lesions and 2 on benign lesions were performed.

Further, we present some developments in the field of photoacoustics in a computed tomography geometry which relies on acquiring several projections around the object under investigation. We show in phantoms and biological specimens that the presence of acoustic heterogeneities can produce artefacts when using a single speed-of-sound in acoustic backprojection reconstruction. We address the problem, by ascertaining a distribution of acoustic velocity through the object simultaneous to the acquisition of conventional photoacoustic images. This is achieved with the help of a passive element generating ultrasound, which is a high absorber of light and thus a photoacoustic source, placed in the path of the incident light outside the object. By choosing a passive element with a small cross-section, we show that simultaneous imaging of light absorption and acoustic velocity is possible. The distribution of the acoustic velocity can be used to compensate for acoustic heterogeneities in the acoustic backprojection procedure to obtain improved resolutions and contrast.

References
Negative contrast photoacoustic and photothermal imaging, spectroscopy and cytometry

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We introduced a new principle of negative dynamic contrasts for photoacoustic, photothermal and fluorescent flow cytometry in biomedical research. The advanced capabilities of this method has been demonstrated for ultrasensitive and noninvasive detection of circulating clots as early diagnostic and prognostic biomarkers of cardiovascular diseases. Using preclinical in vivo studies on mouse models of myocardial infarction and human blood samples, we found that low-absorbing circulating clots can be detected by photoacoustic negative contrast (i.e., signals from clots below background signal from blood) with the size down to 20 µm. Combination of this phenomenon with positive contrast expanded the capability of flow cytometry to distinguish white, red, and mixed clots. Taking into account the safe nature of the proposed biotechnology, we anticipate its quick translation for use in humans.

Selected publications:
Focusing Acoustic Elements for Photoacoustic Imaging

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Photoacoustic imaging (PAI) uses similar instrumentation as classical pulse echo ultrasound imaging, but differs from this established technique in several ways. First of all, the contrast in PAI is due to the optical properties of the object, which is hit by short laser pulses in order to emit thermoacoustically excited ultrasound transients. The second difference is the frequency content of the generated ultrasound waves. In PAI, the acoustic frequencies are largely determined by the size and shape of absorbing structures within the object, whereas in conventional ultrasound imaging they are given by the characteristics of the employed ultrasound transducer.

Focusing elements are widely used in PAI to improve the signal to noise ratio and to focus the sensitivity of the detector to a defined area. This enables efficient data acquisition, for example in photoacoustic microscopy, where two- or three-dimensional images are formed by collecting amplitude (A-) scans, without further reconstruction algorithm. But also in photoacoustic tomography, where sensors with wide acceptance angle are used and where images are formed by back projecting the received signals, sometimes cylindrical lenses are used to focus the sensitivity to a defined section within the object. In this case a reconstruction algorithm is used to obtain a two-dimensional image.

In this work, the design and implementation of special, broad bandwidth focusing elements is demonstrated. These elements have in common that they do not use classical acoustic lenses, but rather lens less focusing detectors or reflectors. Even more importantly, we attempt to optimize the image quality by using special line focusing elements.

The first approach is an axial line focus that enables large depth of field (DOF) PA microscopy using A-scans. This type of element focuses onto a line in direction of its symmetry axis. By contrast, a classical spherical lens focuses to a point. If the time of flight of an acoustic wave is used to form a depth resolved image the line focus has the advantage that lateral resolution stays constant along a large DOF. A single element that allows such an axial focus is a concave conical sensor. It is related to the convex conical axicon lens in optics that is used to generate Bessel beams. Simulations and experiments are shown to demonstrate the imaging properties of such an element, which was made from a piezoelectric polymer. Although it exhibits the desired large DOF, the detector suffers from strong artifacts due to incomplete filling of the frequency space of the object. Owing to the spatially constant point spread function some improvement can be achieved by deconvolution, but the lack of frequency components makes this processing quite ineffective. An improved but more complex solution is an array of concentric rings (up to 8). The signal formation for such a device is shown and the formation of A-scans by dynamic focusing, together with experimental results.

Another line focus is that of a long, cylindrically shaped lens (or lens less detector). Now the orientation of the line focus is in lateral direction, meaning that waves emitted from sources lying on the focal line arrive at the same time at the detector. Again for this device the signal generation and processing is shown. Image reconstruction from signals that are acquired while the sample rotates about an axis perpendicular to the focal line involves the inverse Radon transform. An implementation using a piezoelectric polymer film is shown and some experimental results on phantoms and biological objects. Finally, the line focus concept is combined with optical detection, using an elliptical reflector. Waves coming from the object around one focal line of the ellipse are collected in the other focal line, where the acoustically induced optical phase change is detected with an interferometer. Advantages of this approach compared piezoelectric sensor are that the optical detection is very accurate and has high bandwidth. The figure shows images of a zebra fish taken with this device.
In the first part of this presentation I will introduce thermophotonic radar imaging principles and techniques using chirped or binary-phase-coded modulation, methods which can break through the maximum detection depth/depth resolution limitations of conventional photothermal waves. Using matched-filter principles, a methodology enabling parabolic diffusion-wave energy fields to exhibit energy localization akin to propagating hyperbolic wave-fields has been developed. It allows for deconvolution of individual responses of superposed axially discrete sources, opening a new field: depth-resolved thermal coherence tomography. Several examples from dental enamel caries diagnostic imaging to metal subsurface defect thermographic imaging will be discussed. The second part will introduce the field of photoacoustic radar (or sonar) biomedical imaging. I will report the development of a novel biomedical imaging system that utilizes a continuous-wave laser source with a custom intensity modulation pattern, ultrasonic phased array for signal detection and processing coupled with a beamforming algorithm for reconstruction of photoacoustic correlation images. Utilization of specific chirped modulation waveforms (“waveform engineering”) achieves dramatic signal-to-noise-ratio increase and improved axial resolution over pulsed laser photoacoustics. The talk will conclude with aspects of instrumental sensitivity of the PA Radar to optical contrast using cancerous breast tissue-mimicking phantoms, super paramagnetic iron oxide nanoparticles as contrast enhancement agents and in-vivo tissue samples.

(*) With N. Tabatabaei, S. Telenkov and R. Alwi
Tuesday 24\textsuperscript{th} April :

\textit{Non Destructive Evaluation & Testing}
Time-resolved two-dimensional imaging of GHz surface acoustic waves in phononic crystals and structures based on them

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Abstract: Ultrashort light pulses of temporal width in the sub-picosecond regime can generate and detect high frequency acoustic waves up to and beyond 1 THz in solids[1]. The propagation of generated acoustic waves can be monitored as transient optical reflectivity changes which are detected with the delayed light pulses. The method is an optical pump-probe technique and is called picosecond laser acoustics. It has been widely used to study elastic properties and sample structure using the excitation of longitudinal or shear acoustic waves propagating towards the interior of the sample.

The combination of the picosecond laser ultrasonics technique, two-dimensional scanning of the probe light spot position over the sample surface, and optical interferometry allows one to follow the spatiotemporal evolution of GHz surface acoustic wave (SAW) fields with a lateral spatial resolution of 1 µm[2,3]. This time-resolved two-dimensional imaging of SAW is also very useful for investigating elastic and structural properties.

We have applied this SAW imaging method to the study of the acoustic properties of 1D and 2D phononic crystals[4,5] and devices based on them, such as phononic crystal waveguides. By taking temporal and spatial Fourier transforms of the spatio-temporal acoustic field data, the acoustic dispersion relations and, in particular, phononic band gaps are revealed. In the phononic crystal waveguides and cavities, the frequency dependence of the wave field confinement is clarified. These results are compared with numerical simulations based on the finite-element method[6,7]. This research forms a basis for the efficient evaluation of phononic structures based on the phononic crystals. The talk will, in particular, review our recent results in this field.

Internal heat sources reconstruction: an approach to defect characterization from vibrothermography data

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Infrared thermography using ultrasound (US) excitation was first introduced in the late seventies [1]. In this technique the sample is excited by ultrasonic vibrations, either modulated in amplitude (vibrothermography) or of short duration (sonic infrared). Ultrasonic waves generated at the contact travel along the continuous material without significant losses, but in the presence of discontinuities, like cracks or delaminations, friction between the two faces of the defect can generate heat that propagates inside the sample. These thermal waves eventually reach the sample surface and the corresponding temperature field can be detected using an infrared camera. In this configuration, defects behave like heat sources on a dark field, which makes this technique very suitable for the detection of defects elusive to other nondestructive evaluation tests [2,3].

In this work we develop an inversion technique to characterize the position, size and shape of internal flat heat sources from vibrothermography data: surface temperature amplitude and phase data at different US amplitude modulation frequencies. First we solve the direct problem, i. e., calculation of the surface temperature generated by an internal flat heat source of arbitrary shape. Then, we generate synthetic data by adding white noise to the direct problem solution and use these data for the inversion. The inversion is performed by defining a 2D mesh in the plane containing the heat source and applying the total variation regularization to determine the presence or absence of a heat source at each point of the mesh.

Finally, we have prepared samples containing calibrated artificial heat sources by attaching two pieces of AISI 304 stainless steel against each other through a flat surface. In order to localize the heat sources in an easy way, we have introduced between these two pieces a thin sheet of copper, whose shape and size is varied in different experiments. We have taken vibrothermography data on these samples that have been inverted according to the procedure previously developed. We have analyzed the accuracy of the reconstruction of different contours as a function of the depth of the heat source.

Acknowledgments

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24.3

Limits of spatial resolution for thermography and other non-destructive imaging methods based on diffusion waves

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In this work the measured variable, like temperature, is a random variable showing fluctuations. The loss of information caused by diffusion waves in non-destructive testing can be described by stochastic processes. In non-destructive imaging the information about the spatial pattern of a sample's interior has to be transferred to the sample surface by certain waves, e.g. thermal waves. At the sample surface these waves can be detected and the interior structure is reconstructed from the measured signals (Fig. 1). The amount of information about the interior of the sample, which can be gained from the detected waves on the sample surface, is essentially influenced by the propagation from its excitation to the surface. Diffusion causes an entropy production which results in a loss of information for the propagating waves. Mandelis has developed a unifying framework for treating diverse diffusion-related periodic phenomena under the global mathematical label of diffusion-wave fields [1], like thermal waves.

![Diagram](image)

**Fig. 1.** (a) The same structure is contained twice in the sample: just beneath the surface and at a higher depth. (b) Measured signal at the sample surface as a function of time: due to diffusion waves the signal from the deeper structure is not only smaller but it is also broadened compared to the signal from the structure just beneath the surface.

Thermography uses the time dependent diffusion of heat (either pulsed or modulated periodically) which goes along with entropy production and therefore a loss of information. The amplitude of a thermal wave decreases more than 500 times at a distance of just one wavelength [e.g. 2]. There have been made several attempts to compensate this diffusive effect to get a higher resolution for the reconstructed images of the sample's interior. In this work it is shown that fluctuations limit this compensation. Therefore also the spatial resolution for non-destructive imaging at a certain depth is limited by theory. Comparison of experimental results to theory shows the maximal potential to improve the resolution for a thermography setup.

Contact Laser Ultrasonic Evaluation of Graphite-Epoxy Composite Structure.

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A laser ultrasonic method for contact nondestructive evaluation of the structure of composite materials is proposed. Specimens of graphite-epoxy composites with both compact (i.e. cracks, cavities) and distributed (i.e. areas of increased porosity) defects are investigated. Two- and three-dimensional images of composite structure are obtained.

The method is based on backward-mode opto-acoustic investigation[1]. Wide-band acoustic probe pulse is generated thermooptically by laser pulse absorption in special generator on the front surface of the studied object. Then, probe pulse propagates in the specimen and being scattered on structural inhomogeneities. The backscattered acoustic pulses are registered by a wide-band piezotransducer, which makes it possible to detect acoustic pulses in the frequency range from 0.1 to 15 MHz[2, 3]. Since the generation and detection of acoustic pulses takes place on the front surface of the specimen, this method allows us to carry out nondestructive evaluation with one-sided access to the object under study. The spectral and time-domain analyses of backscattered OA signals are used for mathematical processing of the experimental data. The method developed makes it possible to determine the type of defects and the depth of their location.

Heat Conduction Effects, CW Photoacoustics, and Phononic Structures

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Abstract: The wave equation commonly used to describe the photoacoustic effect is derived under the condition of no heat conduction. Experiments show that sharp transients are found on the leading edges of photoacoustic waves from layers excited by short pulse lasers. The effect can be shown to arise from the effects of heat conduction where the enormous thermal gradients produced by absorption of pulsed laser beams at flat surfaces takes place. A wave equation for pressure with an additional term is derived, the solutions to which describe delta function pulses that travel in time at the front of the photoacoustic wave.

Experiments and theory are presented for the generation of photoacoustic waves by irradiation of an absorbing gas with a continuous, unmodulated laser. The effect arises from the fact that wherever there is a pressure maximum there will be a density maximum, an increase in the concentration of absorbing molecules, and hence enhanced heat deposition. This heat deposition increase tends to reinforce any acoustic wave. The opposite effect takes place where there are pressure minima—a smaller amount of heat is deposited at these points. An amplification effect is predicted to be present in a photoacoustic cell that is irradiated at one window. If a longitudinal acoustic wave is present in the absorbing gas, its amplitude will be enhanced by the addition of laser energy at the entrance window to the cell, so that oscillation of a standing wave in the cell should be sustained.

The theory of photoacoustic and photothermal wave generation in a modulated structure is described. We consider perhaps the simplest case of a phononic structure, namely, a one-dimensional structure with sinusoidal density or compressibility variations. The wave equation for pressure in a fluid or a one-dimensional solid is given by

$$\frac{d^2}{dz^2}p + \kappa \cdot 2 \frac{\partial}{\partial z} \cos \Omega z \cdot f(z) = 0$$

where \(a=\omega^2\), \(\gamma\) is a modulation depth, the dimensionless coordinate \(z = x / a\), where \(x\) is the coordinate, \(\omega\) is the modulation frequency, and \(\Omega\) is the cell dimension. The function \(f(z)\) is proportional to the optical absorption coefficient, the thermal expansion coefficient, and the distribution of optical radiation in space. The wave equation thus is found to reduce to the form of an inhomogeneous Mathieu equation. Solutions are found for an infinite structure, a finite length structure, a two dimensional structure with variations in only one direction, and a spherical structure. If Floquet theory is used, the dispersion relation, the position of the band gaps, the damping inside the band gaps, and the form of the solutions for the pressure inside and outside of the band gaps can be determined. It is now possible to use Mathematica to give all three types of Mathieu functions, the characteristic values, and the characteristic exponent. The computation of all results thus becomes straightforward.

If a structure is engineered so that the thermal diffusivity varies sinusoidally in space, the heat diffusion equation can be shown to reduce to a Mathieu equation, but with a complex value for the parameter \(a\). We show that Mathieu theory is still valid, and that solutions for the temperature can be obtained. Solutions do not show confinement, and the dispersion relation varies only slightly from that of an unmodulated structure.

![Fig. 1](image.png) (Left) Positions of the band gaps for a structure with \(\gamma = 0.25\). The height of the curve gives the magnitude of the damping constant for waves inside of the gaps. (Right) Dispersion relation for a structure with the same value of \(\gamma\). Both plots were found from the Mathieu characteristic exponent.
Photothermal Spectroscopy of Single Gold Nanoparticles

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Compared to electron microscopy or to scanning probe microscopy, the optical selection of individual nanoparticles in a far-field microscope has specific advantages. Laser excitation is non-invasive, can reach much beyond surface layers, and commands a wide range of time-resolved and frequency-resolved spectroscopic techniques. Optical signals provide unique insights into the dynamics of nano-objects [1]. I shall illustrate some applications of single-nanoparticle optics to dynamics with recent topics from our group.

i) We study single gold nanoparticles by photothermal and pump-probe microscopy. We detect their acoustic oscillations launched by a pump pulse [2]. This opens up uses of individual gold nanoparticles for local plasmonic, mechanical and chemical probing.

ii) Photothermal microscopy opens the study of non-fluorescent absorbers, down to single-molecule sensitivity [3]. Combining photothermal contrast with photoluminescence [4], we can measure the luminescence quantum yield on a single-particle basis and gain insight into the complex relaxation phenomena leading to emission by metal particles.

iii) We have built a near-infrared optical trap for gold nanoparticles [5]. Single nanorods orient along the polarization of the trapping laser. By means of polarized detection, we observe their translational and rotational Brownian motion in the trap. We use this dynamics to evaluate the optical restoring torque and the temperature of the particle.

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Thermophysical Properties
Recent Developments in the Photopyroelectric Calorimetry of Condensed Matter

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Abstract: In this review the possibilities offered by the two main used photopyroelectric (PPE) detection configurations, “back” and “front”, are analyzed, and the information contained in the amplitude and phase of the PPE signal are compared. A study of the accuracy of the investigations when using the frequency or thickness scan method is also made. The applications of the technique refer both to liquid and solid samples. Concerning liquids, high-resolution measurements of thermal diffusivity and effusivity of some “special liquid samples” (associative and non-associative binary liquids, isotopic liquid mixtures, nanofluids, vegetable oils) are described. Several particular PPE detection cases, used for thermal inspection (measurement of thermal parameters, detection of phase transitions, etc) of thin and/or bulk solids were also presented.

The photopyroelectric (PPE) calorimetry, together with other photothermal techniques, overtook the stages of development of theoretical aspects and qualitative applications [1]. People working in the field are now exploring the limits of the method for accurate investigations of thermal properties of condensed matter. In the PPE calorimetry, practically, one can combine different detection configurations (usually two - “back” or “front”), sources of information (PPE amplitude or phase) and scanning parameters (chopping frequency or sample’s thickness), in order to obtain the dynamic thermal parameters of a condensed matter material [2].

Concerning the investigated materials, during the last decades, the area of interest was dedicated mainly to liquids because, due to the perfect sample-sensor thermal contact, accurate quantitative results can be obtained. Consequently, intimate processes occurring in liquids (molecular associations, isotopic effects, structural changes in nanofluids, adulteration and spoilage of liquid foodstuffs, etc.) can be studied. The main PPE procedures applied for liquids’ calorimetry were the front and back configurations, coupled with the thermal-wave resonator cavity (TWRC) method [2, 3]. This procedures lead to highly accurate measurements of thermal diffusivity in the back configuration and thermal effusivity in the front one [2, 4-5]. In some cases the front configuration coupled with the TWRC method showed to be self-consistent, being able to allow the direct measurement of both dynamic thermal parameters mentioned above, provided a proper alternation of the investigated liquid with a known one in coupling fluid’s and backing’s position respectively, is performed [6].

If we refer to solid materials, the back PPE configuration, together with the frequency scanning procedure, showed to be suitable for investigation of both thermal diffusivity and effusivity, by using the information contained both in the phase and amplitude of the signal [7]. Using the same configuration, phase transitions investigations can be performed with the special feature of an intrinsic amplification of the discontinuity of the temperature behaviour of the thermal parameters in the critical region [8]. Recently, the front detection configuration, performed for a detection cell with 3 and/or 4 layers respectively, together with the TWRC procedure was applied to investigate thermal properties of bulk solids situated in a backing position in the detection cell, or thin solid layers, inserted as separators between the coupling fluid and a liquid backing [5, 9].

Active infrared thermography applied to the study of Cultural Heritage

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Several kind of art and historic artifacts like books and documents, archaeological findings, and artworks, as well as their component material, have been successfully investigated by the infrared thermography (IRT) which allowed to reveal structural features and inhomogeneities in the material and to characterize some of their thermal properties [1,2]. An overview of the applications of the active infrared thermography to the analysis of the cultural heritage is presented, describing the specific adopted configurations. Results are reported that have been obtained for different kind of artifacts: bronze sculptures made by lost wax casting where the workings performed after the casting on the bronze surface (repairs, fillings, surface cold working, etc,) are generally concealed under the final polishing and patination; historical bookbindings and its parchment components; texts hidden under the endleaf of ancient book or accessible only from on the back side of page; concretions on Roman terracottas (Fig.1), coins, etc.

**Fig. 1:** (a) Image (left) of the end paper of XVIII century book and corresponding thermogram showing the writing of an earlier manuscript leaf used for the binding beneath the end paper. (b) Concretions on the neck of a Roman amphora. The thermograms captured at different delay from the light pulse show the different state of adhesion the two shells indicated by the arrows to the earthenware.

In addition to the qualitative investigation of the various structures thermal diffusivity measurements of the artifact constituent material have been performed by means of the IRT. Such measurements, like the ones of other thermal properties [3], can be used, for instance, to characterize the preservation state of the parchment [4] or to reveal specific thermal and mechanical treatments operated by the artists on the bronze of the statues during the manufacturing process.

The application of active IRT to the investigation of the cultural heritage also stimulated its integration with methods such as other non-destructive digital imaging techniques. In this regard, a new system for 3D-termography based on the integration of 3D laser scanning and active IRT, has been developed and successfully tested on some of the studied cultural heritage artifacts.


Thermo-Optical Characterization of CdSe/ZnS Quantum Dots Embedded in Biocompatible Materials

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Abstract: Nanostructured semiconductors or Quantum Dots (QDs) are materials in continuous development that hold potential for a variety of new applications, including uses in fluorescent labels for biomedical science, photonic devices and sensor materials [1,2]. In biomedical applications, several nanodiagnostic assays have been developed that use QDs. They have been applied to diagnostics, the treatment of diseases, bioimaging, drug delivery, engineered tissues and biomarkers [2]. For example, CdSe/ZnS core-shell nanocrystals have been shown to be useful for tailoring the fluorescence of dental resin composites [3].

The solvent or matrix used to suspend the solute samples can exert important influence on such properties as the radiative quantum efficiency ($\eta$), absorption and emission spectra, stabilization and thermal parameters (including thermal diffusivity (D) and the thermal coefficient of the refractive index)\cite{4} of the investigated materials. For a nanoparticle to be a candidate for practical applications, it is important to characterize their thermo-optical properties. The present work reports the thermo-optical properties of \textit{cadmium selenide/zinc sulfide} (CdSe/ZnS) core-shell colloidal solutions measured with Thermal Lens technique [4]. Thermo-optical characterizations were performed on samples of CdSe/ZnS QDs suspended in aqueous solutions functionalized (with amine and carboxyl groups) and non-functionalized for biomedical applications. For non-functionalized QDs the studies were performed in samples of QDs embedded in biocompatible materials: dental resins composites and saliva. The thermo-optical properties, such D, fraction thermal load ($\phi$) and $\eta$ of the QDs samples were determined.

Thermal Conductivity of Particulate Nanocomposites and Porous Media: Comparison between Experiment and Theory

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Abstract
Over the past few decades, significant research efforts have been devoted to the study of the thermal properties of particulate composites and porous media, due to their many technological applications ranging from mechanical structures to electronics[1]. Despite their importance, the thermal performance of these smart materials is not well-understood to date, especially at high volume fractions of micro/nano-sized particles or pores.

In this work, the thermal conductivity $k$ of composites made up of nanoparticles or porous embedded in a solid matrix is investigated from the experimental and theoretical point of view. The model developed for the composites with nanoparticles is written as

$$
\frac{k}{k_m} = \exp \left( \frac{(A + B)f}{1 - B\psi f} \right)
$$

(1)

where $k_m$ is the thermal conductivity of the matrix, $f$ is the volume fractions of the nanoparticles and all other parameters depend on the thermal, geometrical and interfacial properties of the components materials, as well as on the mean free mean free paths of the heat carriers (electrons and/or phonons). When the size of the particles is of the order of the mean free path of the energy carriers, it is shown that the thermal conductivity of nanocomposites depends on: 1) the collision cross-section per unit volume of the particles and 2) the mean distance that the energy carriers can travel inside the particles.[2] On the other hand, for concentrations of particles up to their maximum packing volume fraction, the proposed approach exhibits a strong dependence on the crowding factor of the particles. Equation (1) generalizes various models reported in literature[3, 4]. For porous media with randomly oriented spheroidal pores, on the other hand, the following model is proposed

$$
k = k_m (1 - f)^m
$$

(2)

where the exponent $m$ depends strongly on the shapes of the pores. Similar results are also found for the thermal conductivities along the principal axes of spheroidal aligned pores. The obtained results can be applied for porous media with low as well as high porosities, and they show that: 1) the effect of the pores shape becomes stronger as the porosity increases. 2) The thermal conductivity for randomly oriented pores takes its maximum value for spherical pores and is a geometric average of the thermal conductivities along the three principal axes of the pores, when they are aligned. 3) In the case of aligned pores, the thermal conductivity increases with the size of the pores, such that it is larger along the side with longer dimension.

The predictions of Eqs.(1) and (2) are in good agreement with the measured thermal conductivity of various composites and porous media [5-7]. It is expected that the obtained results can provide useful insights on the thermal design of particulate nano and micro composites as well as porous media.

Focus Shift Thermal Expansion Microscopy for Mapping Thermal Diffusivity

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Abstract: A photothermal method based on the measurement of the surface curvature due to thermal expansion is presented. The technique allows the retrieval of the thermal diffusivity at microscopic levels and hence mapping such magnitude over a sample surface. Two ways to measure the surface curvature are presented and shown in figure 1a. Both techniques detect the shift in the focus of the probe beam due to the surface curvature. An optical fiber carries two laser beams of different wavelengths avoiding the problems arising from pointing instabilities [1]: one is modulated and acts as a pump; a second probes the surface deformation due to the thermal expansion at the modulating frequency [2]. The first detection scheme is through the same optical fiber that acts as a pinhole and thus is sensitive to the defocusing originated from the thermal expansion of the surface (δ) at the pump modulation frequency. The other technique consists of a beamsplitter (BS), a filter to block the pump laser (F1), an astigmatic lens (L3) and a 4 quadrant detector that generates a focus error signal proportional to the defocusing [3].

The induced thermal expansion defocuses the probe beam due to the surface deformation (curvature). The modulated surface curvature is proportional to the complex function \( g(f/f_0) \) where \( f \) is the modulating frequency (see Fig. 1b), and \( f_0=D_\tau/(\pi \sigma^2) \) is a cutoff frequency that only depends on the thermal diffusivity \( D_\tau \) and the pump beam size \( \sigma \), allowing a straightforward retrieval of the thermal diffusivity of the sample.

This non-destructive and non-contact technique allows the retrieval of crystalline phase maps as well as the study of thermal diffusivity and other thermal properties. Results in solids, such as metals, ceramics and glasses, will be shown.

\[ g(f/f_0) = \int_{-\infty}^{\infty} e^{-u^2/u} du \]

Fig. 1: a. Experimental setup. b. Frequency dependence of thermal expansion (amplitude and phase).

In current paper we propose an experimental approach for the achievement of thermodynamic states of metals with temperature ~ 10 kK and pressure ~ 10 kbar (near- and supercritical region of phase diagram) under impact of nanosecond laser pulse of moderate intensity – up to 1 GW/cm² (fluence – up to 7 J/cm²) – on confined surface.

In current research target was made of thin metal foil front and rear surfaces of which were confined by transparent dielectrics with rather low thermal conductivity (quartz glass K-8). The usage of confined geometry leads to significant effectiveness of pressure and temperature generation and prevents plasma plume formation so that temperature of heated surface can be measured by its thermal radiation.

Thickness of sample metal was chosen to be smaller than thermal diffusion length within laser pulse duration, which means that metal foil will be almost spatially isothermic when laser pulse ends. This approach allows estimating sample destiny dynamics by measuring pressure in it. Confining dielectrics also reduce heat dissipation from metal foil prolonging lifetime of high energy thermodynamic state of metal under study.

A table – top experimental setup for investigation of near- and supercritical states of metals, achievable under moderate intensities of incident laser radiation was created. Assembled setup allowed to measure pressure, temperature and reflectivity of the surfaces simultaneously with nanosecond temporal resolution.

Proposed approach was applied to study pulsed laser heating of ultrathin aluminum foils (thickness – 200nm) confined by quartz glass K-8. Thermodynamic states with pressure ~4kbar and 10 kK were obtained (supercritical area for aluminum). Temporal dynamic of thermodynamic state was studied both in near- and supercritical area of phase diagram.

Posters
Transition from Rayleigh waves to capillary waves at the free surface of a visco-elastic material

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Till now, the Impulsive Stimulated Scattering technique has been used to investigate, int. al., thin films [1], multi-layered structures [2], bulk fluids [3] and fluids at an interface with a solid [4]. In this report an extension of the technique is proposed to study the optically induced thermoelastic response at free liquid surfaces. The technique presented allows to determine both the viscosity and surface tension of viscoelastic liquids in the MHz region. At very low temperatures, when the material is in a solid-like state, Rayleigh waves carry information about the elastic moduli. When the material is viscoelastic, at intermediate temperatures, the acoustic surface wave propagation is governed by the shear modulus and thus previous wideband information about the viscosity can be recovered. At high temperatures, when the material has reached a liquid state, the surface tension is the dominating force, and can be extracted from the propagation features of the capillary wave.

In this paper, the theoretical background for thermoelastic signal generation in the free liquid surface configuration is given, in particular for the low frequency limit. The presented model forms an extension of an earlier report by Käding and Maznev in 1995 for bulk solids [5] and is complementary to models presented in Ref. [6,7,8]. The methodology is illustrated numerically for glycerol at different wave numbers and temperatures, and experimentally validated for water at room temperature.

Photothermal Depth Profiling in Hardened Steels: a new inverse approach based on Singular Value Decomposition

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Quality control of the performance of mechanical components subjected to hardness processing is a topic of fundamental importance, both in the field of automotive and aerospace systems both for civil and military applications. The lack of cementation, the burns in the steels, and the decarburisations of the power gears, and the statoric and rotoric equipments may cause catastrophic failures with serious repercussions. The industry and the companies responsible for the hardening processes as well as for the quality control of the mechanical components are continuously seeking for improvements in the standard destructive tests performed by Vicker or Brinell durometer where one mechanical component is chosen for random testing.

Since 1996 the use of IR systems based on photothermal radiometry for the non-destructive determination of the hardness profiles in steels has been deeply studied and discussed by several groups both in Europe in the framework of European Thematic Networks (BRRT-CT97-5032) [1], in North America [2], and more recently in Asia [3] as shown by the huge numbers of papers presented in the past ICPPP editions.

In this paper we introduce a new PTR compact system, integrable with mechanized and robotic arms for industrial needs, which use a simple Ge lens for collecting the IR radiation from the sample to the detector. The inverse problem to reconstruct the diffusivity profile $D(z)$ from the PTR signal in the frequency domain $S(f)$ has been linearized and solved by the Singular Value Decomposition by using a new approach. The hardness depth profile $HV(z)$ is eventually calculated thanks to the calibration curve hardness/diffusivity. Preliminary results on AISI9310 hardened steel gears show accurate hardness profile reconstructions in comparison with the hardness measurements by standard Vicker test.

References

NANOSCALE HEAT TRANSFER IN SYNTHETIC METALLIC OPALS

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Heat transport at nanoscale is of importance for many nanotechnology applications [1]. Considerable efforts are nowadays to discover new geometries with a huge number of internal interfaces and thermal barriers in order to increase the thermal resistance and/or manipulate the heat flow. A common material used to achieve these requirements is the synthetic opal, a special 3D Photonic Crystal (PhC) widely used in nanophotonics [2,3,4]. One of the most intriguing and relevant open question is how can heat be diffused in these nanostructures. In principle the heat flow should be reduced due to the huge numbers of internal interfaces and thermal barriers, but an exact answer is not trivial because the heat transport at nanoscale may differ substantially from that at macroscale [5].

This reason motivates our research on Nickel and Palladium inverse opals. The internal structure of the inverted opal is made of close-packed submicron air spheres (200nm÷500nm) regularly placed in the metal. Each metallic nanostructure has been thermally characterized by using photothermal radiometry [6] by a Ar laser @ 488 nm modulated by an acousto-optical modulator at a frequency ranging from 1 Hz up to 100 kHz so to change the penetration (i.e. the spatial resolution) of the induced thermal waves from 100nm to 1mm. The modulated infrared emission from the surface is collected by a Germanium lens and focused onto an infrared detector HgCdTe. The signal allows to measure the effective thermal diffusivity and the porosity of the whole structure.

The calculated porosity via photothermal radiometry is about 50-60% for opals with spheres of 320nm, while reaches 60-70% for larger spheres of 450nm. These values of thermal porosity (obtained via photothermal measurements) well fit with the expected geometrical porosity of the opaline structure [7].

This research demonstrates how photothermal radiometry may be particularly suitable to detect the thermal porosity and the effective thermal diffusivity in these nanostructures. This work has been done in the framework of the PhOREMOST Network of Excellence.

REFERENCES

Fabrication at the nanoscale of Ultrasonic transducers

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The importance of ultrasonic transducers in both biological and industrial applications is being growing with much interest in the recent years [1]. In our research group, we are researching into the production of smaller and high frequency transducers with the aim of performing ultrasonics at the cellular level. To date we have produced devices on the micron scale operating at up to 50 GHz. These are excited and probed using fs lasers [2]. The generation of nanoscale ultrasonic transducers can lead to new applications in biomedical sensing and imaging, especially when the target aimed is small structures such as cells. In this work, we discuss the design and fabrication of nanometre sized ultrasonic sensors (nanochots) using self-assembly process of hybrid nanostructures. The design leads to the formation of a core/shell structured nanoparticles [3], using a silica nanoparticle as the core (radius ~ 100 nm) and a shell made of gold nanoparticles (with ~ 10 nm coating). The nanochots are designed to be absorbing light at one optical wavelength to excite the vibrations and to be efficient resonant scatterers at a second optical wavelength to enhance the detection of the ultrasound. The optical and mechanical properties of these devices have been modeled using finite element modeling (FEM) and analytical techniques. The dimensions of the nanochots are tuned to operate at optimal wavelength and to generate acoustic waves in the GHz frequencies. Modifying the surface of the nanochot with different chemical receptors promotes the creation of a sensing device. The nanochot's surface functionalization is initially made with model proteins like streptavidin and biotin, aiming for at a later stage the conjugation of specific receptors to target cancer cells.

Thermal conductivity and diffusivity measurements of glass coated magnetic microwires using lock-in thermography

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Abstract. Magnetic microwires (with diameter of a few tens of micrometers) have been introduced in the last years following the tendency in miniaturization of magnetic sensor devices. The aim of this work is to measure the thermal diffusivity ($D$) and conductivity ($K$) of coated magnetic microwires made of a metallic core with glass coating. Lock-in thermograph is specially suited to study lateral heat propagation. Moreover, by annealing the magnetic wires at temperatures higher than 300ºC the amorphous wires become crystallized. The effect of this crystallization is to enhance the transport thermal properties by a factor of about 1.8.
Large depth of field scanning acoustic and photoacoustic microscopy

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Combining several imaging methods providing images with complementary information is an ongoing field of research [1-3]. In ultrasound, the classical ultrasonic pulse echo method uses the same device for ultrasound excitation and for detection. The contrast is based on acoustic impedance inhomogeneities. In photoacoustic imaging ultrasound waves are excited by the absorption of short laser pulses. The imaging contrast is purely optically. In microscopy both techniques use spherical ultrasonic lenses for focusing. Depth of field is limited by the Rayleigh criteria. Due to the limitation of the focal length scanning in depth is essential.

In this work we combine ultrasound pulse echo imaging and photoacoustic imaging in one single device. The same laser pulse is used for ultrasound excitation for the pulse echo mode and for illuminating the observed target directly for the photoacoustic mode.

The proposed dual mode scanning acoustic and photoacoustic microscope (DSAM) uses a special transducer, a so called axicon transducer for the pulse echo mode and an annular ring array for signal detection to allow large depth of field imaging [4,5]. Within one single scan the DSAM provides two images which show the specific contrast of the two imaging modalities. The advantage of an annular array in comparison to a single ring detector (a point source appears as an X) is the suppression of imaging artifacts [6,7]. Dynamic focusing, coherence weighting and Hilbert transformation are applied to enhance image quality.

Various phantom experiments are presented to demonstrate the capability of the DSAM for simultaneous acoustic and photoacoustic imaging.

![Fig. 1. cross section images of a sphere obtained from each ring – acoustic and photoacoustic](image)

New pharmaceutical solid forms: 
a photothermal and structural approach

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Abstract: The front photopyroelectric (FPPE) configuration was applied in order to measure the thermal effusivity of some ambazone-based new solid forms, inserted as backing layers in the detection cell. The technique is based on the scanning procedure of the coupling fluid’s thickness (TWRC method) [1]. Concerning the investigated compounds, their thermal effusivity was found to be different from the pure starting materials. The investigated solid samples were pressed powders and such a result can be ascribed to a different confinement of the powders or to the formation of a new compound. The second alternative is more probable being also supported by X-ray analysis, solid-state NMR, DSC calorimetry and FTIR spectroscopy.

The study of solid forms (polymorphs, salts, hydrates, solvates or co-crystals) of the pharmaceutical compounds is on the critical path of the drug development process because the different solid forms tend to have different physical and chemical properties, such as solubility and bio-availability which are essential for the drug development. The solid forms discovery and characterization may lead to understanding the overall crystallization behavior of the studied pharmaceutical compounds, such as their tendency to form hydrate and solvate forms, the crystal packing modes and the types of intra- and inter-molecular interactions. Systematic solid-state studies of the pharmaceutical compounds could contribute to defining rational elements that might be generally applied in the search of solid forms [2].

The present work is focused on the structural characterization of new ambazone-based compounds, with potential pharmaceutical applications. Thus, the practical innovative approach proposed here is the combination of complementarily structure-elucidation techniques, i.e. powder X-ray diffraction (PXRD), solid-state NMR, DSC calorimetry and FTIR spectroscopy. The PPE calorimetry, applied to pressed powders is a new approach, but if reaching high enough accuracy, this technique can establish connections between the value and behavior of thermal parameters and new solid forms composition, being also a very useful tool, together with the methods mentioned above, for the study of the potential pharmaceutical compounds [3].

The PPE investigations performed on the ambazone-based new solid forms shown that the value of the thermal effusivity of the investigated compounds is different from the values of the starting materials. Having in mind that the solid samples were in fact pressed powders, this result can be ascribed to two reasons: (i) a different confinement of the powders or (ii) the formation of the compound. Due to the fact that the pressure used for samples’ preparation was the same, the second alternative is more probable. In fact the formation of the compound was also supported by X-ray analysis, solid-state NMR, DSC calorimetry and FTIR spectroscopy [3,4].

In this work we show how a photothermal technique based on a DVD pickup head [1] can be used to characterize the thermal expansion of a tightly focused pump beam. In this situation the expansion not only defocuses the probe beam due to the surface displacement, but also due to the surface deformation (curvature). It is shown that the curvature has a stronger impact in the defocusing signal. The basic model regarding the surface shape and modulation phase is well known [2,3] and has been used before for thermal diffusivity measurements using slightly displaced pump and probe beams.

The experiment consists of an optical pump-probe setup where the thermal expansion caused by the amplitude modulated pump laser is detected indirectly as a focusing error of the probe laser. The focus error signal is obtained by impinging with the astigmatic probe beam on a four-quadrant detector after reflecting on the surface of the sample [1]. The frequency dependence of the signal depends only on the thermal diffusivity and the beam sizes, and hence allows a straightforward retrieval of the thermal diffusivity of the sample at the impinging location. The proposed method is both non-destructive and non-contact, has a high axial resolution (~10 pm) and a displacement sensitivity of 1 pm/µV.

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Simultaneous Laser Ultrasound and Photoacoustic Imaging

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In photoacoustics (PA) the ultrasonic wave pulses to be detected are generated directly inside the sample due to thermal expansion after the absorption of a short laser pulse. Therefore a photoacoustic image depicts the different absorbing properties of an object. On the other hand, in conventional pulse echo ultrasound imaging back scattering of ultrasound waves at interfaces between different acoustic impedances is the main source of contrast.

The laser ultrasound (US) method uses the photoacoustic effect for the generation of the incoming ultrasound waves. Acoustic waves are launched by an appropriate absorber that has been illuminated by light pulses of a certain wavelength. The geometry of the absorber has an influence on the shape of the produced acoustic field. In this work for example a plane absorber was illuminated by imaging the end face of an optical fiber onto its surface. This way plane ultrasound waves can be produced.

When combining both methods images based on two different contrast mechanisms can be obtained simultaneously when the absorber is illuminated by the same laser pulse as the target.

Here the detection of the pulses that have been generated, reflected and back scattered by the object is done optically. A Mach-Zehnder interferometer as described in [1] is used for detection thus providing a purely optical setup for simultaneous photoacoustic and ultrasound imaging.

With this successfully installed setup two different approaches for gaining images are tested on two- and three-dimensional objects, namely tomography and section imaging which differ in the kind of illumination and in the applied reconstruction algorithms [2-5]. Due to the simultaneous measurements the PA and US images completely overlap.

Metal Nanoparticle Ensembles: Tunable Laser Pulses Distinguish Monomer from Dimer Vibrations

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Abstract: Tunable optical pulses are used to excite selectively coherent mechanical oscillations in the 5-150 GHz range, assigned to vibrations of isolated spheres or pairs of contacting spheres, in an ensemble of gold nanoparticles. The amplitudes of the oscillations exhibit a strong enhancement when the laser central wavelength is tuned to resonate with the corresponding plasmon. Our approach distinguishes itself in that we are able to discriminate between modes of individual spheres and pairs of connecting spheres without recurring to single-particle detection. Because of the resonant selection in the excitation process, the widths of the acoustic modes are significantly smaller than broadening caused by the spread in radii in the ensemble.

Using self-assembly techniques with polyelectrolytes and nanoparticles, different architectures for the sample can be built, controlling up to some extent the coverage and aggregation of the nanoparticles. By adding new layers of polymer in between the nanoparticles, the mechanical coupling between nanoparticles could in principle be modified as well. We present preliminary results of the excitation of acoustic modes in those kinds of systems, observing that the oscillator quality factor is somehow degraded, although not due to spread in size of the nanoparticles but to the spread in the mechanical coupling nature.