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RELAZIONE
DEL
COORDINATORE
Research and Mobility Project in Physics

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Il programma Research & Mobility (R&M) si prefigge di finanziare progetti che per complessità e natura richiedono la collaborazione tra l’Università degli Studi di Messina ed almeno un’Università partner straniera. I principi guida del Programma R&M sono: Alta qualità scientifica del progetto; alta qualità formativa del progetto e alta qualità scientifica del partner straniero. Il finanziamento per un progetto prevede l'erogazione da un minimo di 50 kEuro ad un massimo di 75 kEuro per un anno. Il responsabile del progetto è il coordinatore scientifico (CS) costituito da un docente dell’Università di Messina.

Nel 2016 un tale progetto è stato assegnato dalla Università di Messina al Prof. Lorenzo Torrisi, Ordinario di Fisica Sperimentale presso il Dipartimento di Scienze Fisiche MIFT dell’Università di Messina e Coordinatore del Dottorato di Ricerca in Fisica del medesimo Ateneo. Il titolo del progetto presentato è “Physics of Nanoparticles and nanostructures: production, characterization, functionality and employment”. Oltre al Prof. Torrisi, partecipano al progetto i professori: Francesco Mallamace, Salvatore Magazù, Rosalba Saija e AnnaMaria Visco, tutti docenti del Ns. Ateneo. Le università ed i centri di ricerca stranieri che partecipano al progetto sono:

- L’Istituto di Tecnologia del Massachusetts (MIT, USA), che è una delle più importanti università di ricerca del mondo con sede a Cambridge, nel Massachusetts.
- La Loughborough University (UK), inglesi che vanta di un’alta reputazione internazionale per l’eccellenza dei suoi qualificati docenti e della sua ricerca, fortemente legata al mondo industriale.
- La Charles University of Prague (Czech Republic), la più antica ed importante università della Repubblica Ceca.
- L’Istituto di Fisica Nucleare CANAM di Řež (Czech Republic), una infrastruttura Europea di collaborazione, di analisi e di interscambio che ha un accordo scientifico col Nostro Dottorato di Ricerca in Fisica.
- La Fulbright Board Hungary University in Budapest, che collabora da anni con alcuni Docenti del Nostro Collegio di Dottorato di Ricerca.
- L’Università di Paris Sud, fondata nel 1971 e situata nei dipartimenti dell’Essonne, Hauts-de-Seine e Val-de-Marne francese.

Stato dell’Arte e descrizione della ricerca

Le nanoparticelle (NP) hanno una dimensione che generalmente misura più o meno 10–100 nanometri. Le proprietà di molti materiali convenzionali cambiano quando sono formate da nanoparticelle perché hanno un rapporto superficie per peso maggiore rispetto alle particelle più grandi che le rende più reattive ai processi fisici e chimici, quali
l’assorbimento, la dispersione della luce o la reattività chimica. Il progetto è suddiviso su più fronti che riguardano il NP, la loro preparazione e caratterizzazione, lo studio e l’interazione con specifiche molecole, nanostrutture e materiali e le loro possibili applicazioni.

Le proprietà fisiche e chimiche delle nanoparticelle (ottiche, elettriche, catalitiche, termiche, ...) dipendono non solo dalla loro composizione e dal mezzo in cui sono incorporate, ma anche da altre due caratteristiche: dimensione e forma, rapporto superficie/volume, funzionalizzazione chimica. Pertanto, al fine di caratterizzare correttamente il punto di vista teorico di questi sistemi, è necessario disporre di una tecnica di calcolo adatta che sia flessibile e che permetta di determinare il comportamento di questi sistemi complessi anche in presenza di aggregazione. Una delle fasi del progetto presentata dal team di ricerca, infatti, è quella di caratterizzare teoricamente i sistemi prodotti con le più recenti tecnologie sperimentali e di indicare la realizzazione sperimentale di nuovi sistemi ibridi con proprietà interessanti per specifiche possibili applicazioni.

Nanoparticelle (NP) e nanostrutture (NS) sono utilizzate, o in corso di valutazione per l’uso, in molti importanti settori scientifici e sociali. In Medicina NP possono essere utilizzate per somministrare farmaci a tumori o ad organi e tessuti malati, per migliorare l’imaging di contrasto nella diagnostica e per migliorare l’efficacia della radioterapia [1]. In Biologia possono essere impiegate per essere trasportate da specie biochimiche molecolari in cellule specifiche per il trattamento di infezioni batteriche croniche, per stimolare le risposte immunitarie, per rimuovere i radicali liberi dell’ossigeno o per aumentare la crescita ossea intorno agli impianti protesici. Nella Scienza dei Materiali possono essere impiegate per modificare molte proprietà fisiche e chimiche, come la durezza, la densità, la bagnabilità di superfici, l’assorbimento di luce visibile e delle radiazioni ionizzanti, la resistenza meccanica, la conducibilità elettrica e termica, il dрогaggio di materiali semiconduttori e di polimeri, i sensori di specifici gas [2].

Uno studio speciale di NP e NS è dedicato alla loro preparazione in soluzioni acquose [3] per raggiungere specifici obiettivi avanzati. Per esempio NP e NS possono essere adoperate per promuovere assorbimento risonante a specifiche lunghezze d’onda laser e per generare plasmi di non equilibrio nel vuoto in cui alti campi elettrici dovuti alla separazione di carica possono accelerare ioni ed elettroni e promuovere emissione di alte intensità di raggi X [4]. Adoperando laser di potenza al fs l’energia degli ioni può essere superiore a 10 MeV per nucleone, evidenziando tante possibili applicazioni che vanno dalla Fisica Nucleare alla Radioterapia, dai processi di impiantazione ionica alla fotolitografia in microelettronica. Importanti applicazioni che la tecnologia delle nano particelle è svolta nel campo della radioterapia convenzionale con fasci di raggi X e di elettroni e in quella innovativa che fa uso di fasci di ioni (protoni e ioni carbonio).

Lo studio del NP nelle soluzioni acquose rappresenta un importante argomento di ricerca poiché l’acqua svolge un ruolo chiave nel guidare tutti i processi biologici vitali. In questo quadro, studi sull’interazione tra molecole d’acqua e macromolecole biologiche (e non), come le proteine, hanno dimostrato che uno dei parametri di controllo è la temperatura che rappresenta una fondamentale funzionalità del sistema [5, 6].
Negli ultimi anni i sistemi molecolari come i polioli, i disaccaridi e i sistemi di formazione del vetro sono stati oggetto di crescente attenzione, sia in termini specificamente scientifici che inerenti specifici risultati applicativi [7, 8]. L’interesse è principalmente legato all’efficacia come bio-protettori e all’osservazione che alcune organizzazioni cellulari mostrano la capacità di sopravvivenza alla disidratazione e al congelamento. Ciò consente loro di passare a uno stato di vetro sospeso e di animazione in caso di reidratazione, per ripristinare le funzioni vitali. Inutile ribadire che lo spin-off interessa notevolmente molti spazi differenti: la conservazione, a temperatura ambiente, gli organi espiantati, l’integrità funzionale, il metabolismo degli organismi biologici, la conservazione del cibo, ecc ... Queste proprietà oggi richiedono un incapsulamento della molecola che costituisce il principio attivo nel seno delle particelle nanoscopiche che fungono da portatori molecolari.

Lo studio teorico dei processi di interazione tra il campo elettromagnetico e le nanoparticelle svolge un ruolo chiave nella scelta e selezione dei materiali che costituiscono le nanostrutture. La caratterizzazione teorica di NP e NS consiste nell’analisi della dispersione della radiazione elettromagnetica prodotta dalle nanoparticelle e nello studio di approccio alla matrice di transizione [9]. Attraverso questo approccio è possibile analizzare nel processo di scattering anche le interazioni meccaniche e la conversione di energia elettromagnetica in calore [10]. Utilizzando le procedure della termodinamica dei processi irreversibili è possibile sviluppare alcuni modelli per sistemi nanometrici con nanoparticelle interne, al fine di studiare il trasporto del calore, l’ottimizzazione termica, la dissipazione interna (una delle caratteristiche che limitano l’efficienza dei dispositivi miniaturizzati) e anche effetti tra i diversi campi presenti in questi nanosistemi (anche con dislocazioni o punti di difetto) aventi particelle di impurità che modificano la conduttività elettrica, conducibilità termica o altre proprietà [11, 12].

La possibilità di utilizzare solidi partnership con rinomati istituti di ricerca a livello internazionale rende possibile raggiungere questi obiettivi. Inoltre, la condivisione del know-how tra le diverse unità di ricerca coinvolte nel progetto è sinonimo di crescita per i dottorandi partecipanti al progetto che hanno l’opportunità di sviluppare competenze all’interno di una scienza che si pone alle massime punte di ricerca nei campi della fisica, chimica, biologia, medicina e tecnologia. Gli argomenti del progetto sono stati presentati al recente congresso internazionale PPLA2017 (Fisica dei Plasmi Laser e applicazioni) tenutosi presso l’Università di Messina il 5-7 Luglio 2017.

La radioterapia convenzionale (a sinistra) irradia il tessuto sano mentre la terapia protonica (destra) specifica di più sul tumore. La preenza di Au-NPs ne migliora l’efficienza.

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Reports
Ph.D. Students
Cycle XXX
Overview on applications based on Silicon Carbide

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Abstract

Silicon Carbide, is one of the most promising wide bandgap semiconductor material in the production of radiation hard detector as widely described in literature. But actually, thanks to its excellent chemical and physical properties, this material has already found a very huge range of applications in many fields. This work has the aim to give a wide overview of the main uses of this material starting from the first applications up to the new ones, and there will be show how SiC could change in the next future the sensors field and also our way of traveling, describing the most promising project and results for biomedical and electronic applications.

Keywords: Silicon Carbide technologies, Power devices.

Introduction

In recent years Silicon Carbide (SiC) material has gained an increasingly interest in numerous applications which require hardness, stiffness and high temperature operation. In fact SiC, belonging to the covalently bounded material, can offer excellent performance up to 1000 °C thanks to the high thermal conductivity, low coefficient of thermal expansion, good oxidation and corrosion resistance.

![Figure 1: Comparison of the main properties at room temperature of 4H-SiC, Si and GaAs.][3]

From the graph of Fig. 1 are evident the strong points of Silicon Carbide when compared with Silicon or other semiconductor material. The higher breakdown electric field of the 4H-SiC (3 MV/cm) versus Silicon (0.25 MV/cm) and the excellent thermal conductivity, 4 versus 1.5 W/cm°C for SiC and Si respectively, allow the realization of high power electronics and high thermal devices. The resistance of SiC power devices is orders of magnitude lower than that of Silicon devices at a given blocking voltage, leading to much higher efficiency in electric power conversion. The wide bandgap and high thermal stability make it possible to work for indefinite periods without any appreciable degradation at very high junction temperature. Another important aspect, related to the strong Si–C bonding, is the higher displacement energy in SiC (25eV) respect to Silicon (14eV). Consequently it is possible to realize innovative radiation detector with an improved radiation hardness [1]. These detectors present longer lifetimes, and can also operate in harsh environments characterized by high dose and high flux. Finally it should be observed that the effective atomic number of SiC is about 12.5 and this opens the way to new interesting applications as dosimeter[2].

Development of SiC-based technology

Since the1980s, sustained efforts have been directed toward developing SiC material and device technology. The wide-scale production is dated February 1945 when Achinson has patented the method for making silicon carbide powder. He also developed the electrical batch furnace by which SiC can still be made today. The first use of SiC was as abrasive medium. This was followed by electronic applications and, based on a number of breakthroughs in the 1980s and 1990s, SiC Schottky barrier diodes (SBDs) were released as commercial products in 2001. The market for SiC SBDs has grown rapidly over the last several years as can be seen in Fig. 2 and the previsions for the future are equally optimistic.
SBDs are employed in a variety of power systems, including switch mode power supplies, photovoltaic converters, air conditioners, and motor controls for elevators and subways. Commercial production of SiC power switching devices, primarily JFETs (junction field-effect transistors) and MOSFETs (metal-oxide-semiconductor field-effect transistors), began in 2006–2010. These devices are well accepted by the markets and many industries are now taking advantage of the benefits of SiC power switches. As an example, the volume and weight of a power supply or inverter can be reduced by a factor of 4–10, depending on the extent to which SiC components are employed. In addition to the size and weight reduction, there is also a substantial reduction in power dissipation, leading to improved efficiency in electric power conversion systems due to the use of SiC components. In recent years, the SiC professional community has grown rapidly in both academia and industry at testified by the Global forecast report on Silicon Carbide Market, [4]. The interest in such material is driven by the increasing demand of SiC based devices for radio frequency applications or innovative “green” technologies.

The major players in the market include Infineon Technologies AG (Germany), CREE Inc. (Wolf-speed) (US), ROHM Semiconductor (Japan), STMicroelectronics N.V. (Switzerland), ON Semiconductor (US), United Silicon Carbide, Inc. (US), General Electric (US), GeneSiC Semiconductor Inc. (US), Fuji Electric Co., Ltd. (Japan), and Renesas Electronics Corporation (Japan). Most of the leading companies have followed the organic strategy of product launches to boost the revenue of the company.

Early usage

With its voltage-dependent resistance, SiC pellet columns were connected between high-voltage power lines and the earth ground. If lightning strikes the power line, the line voltage rises over the VT of the SiC arrester causing the strike current to conduct to ground and pass harmlessly to the earth rather than along the power line.

However, these SiC arresters were determined to conduct significantly at normal operating power-line voltages. This required them to be placed in series with a spark gap. When a lightning strike raises the voltage of the power line conductor, the spark gap ionizes and conducts, effectively connecting the SiC arrester to the power conductor and earth ground. Later it was found that spark gaps used in lightning arresters were unreliable. They either failed to strike an arc when needed or the arc failed to quench when the lightning event ended due to material failure or dust or salt contamination. SiC lightning arresters were originally intended to eliminate the need for the spark gap, but due to their unreliability, the gapped SiC arrester has largely been replaced by no-gap varistors that use zinc oxide pellets. Silicon carbide is still used as an abrasive in many industrial applications. In the electronics industry, the main use is in lapping films which are used for polishing the ends of fiber-optic strands prior to splicing. These films produce the high surface finishes required for fiber-optic splices to function in the most efficient manner.

Biomedical applications

SiC is emerging for a variety of biomedical applications because it shows a good bio-compatibility in vitro and in vivo (higher than silicon), and is also chemically inert which means it will not corrode in bodily fluids, [10]. Examples of biomedical applications include bioeramic scaffolds for tissue engineering, biosensors, biomembranes, drug delivery, SiC-based quantum dots and so on. The newest development regards the production of innovative neural probes for electrocorticography and peripheral nerve recording. In vivo experiments have already been conducted in which electrocorticography recordings from the primary visual cortex of a rat were ob-
tained with similar quality to those of polymer based arrays representing the standard in such field, [11].

Moreover SiC devices have not a limited device lifetime of a few years. Through accelerated aging tests the outstanding long term stability of insulating silicon carbide films has been proved. These tests consist of heating up the system and read the leakage current through a 1 MΩ resistor in series with the sample when 3.2 V are applied to the overall system. Thicker SiC films (360 nm and 450 nm) were aged for several days and, unlike thermal oxide samples that soon reach the failure region, they maintain a leakage current below 300 nA/cm² for up to 140 h of aging.

**Automotive applications**

One of the primary uses of silicon carbide is high performance "ceramic" brake discs. The silicon combines with the graphite in the composite to become carbon-fiber-reinforced silicon carbide (C/SiC). These brake discs are used on some sports cars, supercars, and other performance vehicles.

Another use of SiC is as an oil additive. In this application, SiC reduces friction, emissions, and harmonics. An innovative application concerns its usage in Hybrid- and Electric Vehicles HEV and EV, respectively. It can be used as the Main Inverter that drives the electric motor, but it can be useful for regenerative braking and feeding energy back to the battery. It can be also used as high-power DC/AC or DC/DC. In the first case it replaces the belt-driven auxiliaries such as water pump, PTC Heater HVAC in electric power driven devices, while in the last case is need to charges the conventional 12 V power supply net from the high-voltage battery, replacing the former belt driven alternator. It can be also found in AC or DC electric accessory load On-board charger and battery where the adoption of SiC leads to a reduction of battery size and weight with an increase in efficiency and autonomy (+5% to 10%) as can be seen also in Fig. 5, [12].

**Fast Power MOSFETs and diodes**

Thanks to its electrical properties SiC can be use for the production of fast power MOSFET that found important applications for examples in "green" technologies. A 650 V SiC fast power MOSFET prototype has been realized by STMicroelectronics [14] with the aim to develop a new power inverter that is a mandatory elements in all grid-connected applications in order to amplify the low DC voltage generated by module array of which any photovoltaic system is made and the higher AC level required by the grid.

The adoption of these MOSFETs in each stage between the PV panels and the grid, leads to the reduction in the size of passive components, saving cost and board space and open the way to the development of new inverter topology. It should be noted that these fast power devices have to be used with very fast diode in order to avoid system failure. Again the best solution seems to be the use of SiC based technology as can be seen from Fig. 6. It compares the recovery response between a SiC diode (STPCS1006D) and a ultra-fast silicon diode (STTH8L06D) with the same forward parameters using a \( \frac{di}{dt} = 800 \, \text{A/µs} \). SiC has the advantage of having a very low recovery current if compared with silicon using the same forward and breakdown voltage. The higher value of silicon diode (about 3 times higher) would lead to the failure of the power MOSFET. Now these are commercial technologies, MDMesh Power MOSFET by STMicroelectronic, and represents the faster power MOSFET and diodes on the market.

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![Graph](image1.png)  
**Figure 4:** (a) Leakage current and photos of SiO₂ (b) and SiC (c) probes after accelerated aging test, [11].

**Figure 5:** Comparison of a Boost + Inverter + Generator with Si (a) and SiC (b), [13].

**Figure 6:** SiC and Silicon diode response using a \( \frac{di}{dt} = 800 \, \text{A/µs} \).
Conclusions

SiC seems to be the most promising material for applications including high frequency, high power, high voltages and high temperature operation creating many opportunities for chemists, physicists, engineers, health professional, industry and technologies. It should be noted that despite the large commercial development of silicon carbide, the growth processes, not yet fully optimized, do not allow a wider diffusion, especially in the academic and research fields where very strict quality standards are required. For example the cost of a single crystal n-type 4H-SiC wafer, 3” inches diameter with a thickness of 250 µm is about 225$ [5] that is very high if compared with that of a silicon wafer with similar characteristics, i.e. about 21$, [6]. Moreover if the concentration of defects in the silicon is practically negligible, in the case of SiC only lately a micropipe density less than 1/cm² has been achieved and this reduces the maximum wafer size achievable 150 mm, [7]. Despite this, in literature it is possible to find a wide production showing the usage of SiC for radiation detection [1–3]. In Fig. 7 is reported a typical configuration of a SiC Schottky barrier detector and some experimental prototypes through which it is possible not only the detection of low fluxes radiation source (monitoring of radioactive nuclides, RBS analysis) but also the diagnostic of plasma generated in the interaction between an intense laser pulse and a solid or gas target.

![SiC Schottky barrier detector](image)

Figure 7: (a) Typical SiC Schottky barrier detector and (b) photos of some prototypes.

The interest in this material is growing also for X-rays, UV and neutron detection and it is not difficult to imagine that in the next future there will be greater competitiveness of prices leading to a better diffusion of this technologies.

References


Ion beam from laser-generated plasma and applications

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Abstract

This paper resumes some applications in the field of laser generated plasma, in order to produce good quality beam, all possible range of available ions and big current, laser ion sources are employed for give ions at the accelerator system. The beam divergence can be by-passed using Direct Plasma Injection Schema (DPIS). This schema was successfully employed in conjunction with an Radio Frequency Quadrupole (RFQ) system. Obtaining Al ions with current of about 50 mA. Coupling Laser Ion source with classical source, creating in this way an hybrid source, during the ECLISSE project was possible to increase the charge state value of the produced ions from 10+ up to close 34+, was a very interesting result for the possibility to coupling with an accelerator. Other application is in the field of material modification where the plasma can be used in order to implanted ions at different depth using post acceleration system and the multi charge states that are present inside the plasma.

Keywords: Laser, plasma, ion source, implantation, accelerator.

Introduction

Laser ion sources (LIS) have the possibility to produce beams with high charge states ions from any kind of solid material using high intensity lasers. Coupling the Laser ion sources to the high energy accelerator complex including several acceleration steps shown that the results are very interesting. However the multiple charge-state beams from the laser ion source have wide energy spreads and it is quite difficult to suppress space-charge effects in a low energy transport line, which usually consists of an extraction system and focusing elements, such as magnetic lens, between the source and the first stage accelerator. In order to overcome the low energy beam transport, a new injection method called Direct Plasma Injection Scheme (DPIS) can be used [1]. One of the system that can be couled with this scheme is the Radio Frequency Quadrupole (RFQ) Linac, a linear accelerator that accelerate, and focalize the beam for possible subsequent acceleration stages. In this scheme, the target, from which the particles are produced, is located in a vacuum chamber placed in front the entrance of RFQ. The chamber is electrically isolated from ground so that a high voltage can be applied to adjust the initial beam velocity to the RFQ design. A high energy laser hit the target producing a plasma in which the ions have several charge states (energy, charge state and plasma temperature depends strongly from the laser parameters) and a large fraction of the plasma goes directly into the RFQ channel where the ions are extracted from the plasma, accelerated by the DC potential, trapped by the RFQ focusing force, and then accelerated up to the design energy. The characteristics of laser-generated plasma are useful for other types of applications such as the creation of hybrid sources for particle injection in accelerators other than RFQs, such as cyclotrones. Generally a source of particles for the cyclotron is a plasma obtained from evaporation in ovens, or thanks to microwaves in Electron cyclotron resonance ion source (ECRIS). The possibility to produce intense metal ion beams, pulsed or dc mode, by means of an hybrid source, consisting of a LIS as the 1st stage and of an ECRIS as the 2nd stage, was under study at the Laboratori Nazionali del Sud (LNS) with the project ECLISSE [2]. In this study the low charge state plasma produced in the interaction expands inside a plasma produced by microwaves (generally O₂, N₂ or Ar). The expansion inside this plasma allows laser generated plasma to increase its charge state several times and using an extraction voltage of tens of kV it is possible to extract the beam and inject in superconductive cyclotron. Also in this application the possibility to produce all kind of ions is very important in order to obtaine very high energy beam of , for example, the high melting point materials (Ta, W, Re). Other application can be found for the laser generate plasma is the ion implantation using post acceleration systems. Generally the implantation is performed using monoenergetic ion beam, having the fixed beam energy, the ions are implanted at the same depth. Here is the advantage of plasmas, that have several
charge states that using a post acceleration voltage can create a beam with several energies [3]. Each charge state will be implanted at different depth. Using lasers in repetition rate, generally in the order of tens Hz, permits to extract a near constant ion beam from the plasma. The post acceleration voltage that we use is 30 kV in order to produce beam with energy $30 \text{ keV}/z$, where $z$ is the charge state of the post accelerated ion.

**DPIS-Radio Frequency Quadrupole**

We took in consideration the RFQ of the Brookhaven National Laboratory where the DPIS scheme was studied by coupling a Nd: Yag laser with a RFQ that operates at a frequency of 100 MHz and from an input energy of 20 keV/u to 270 keV/u, where with $u$ indicate the atomic mass unit.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFQ Type</td>
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</tr>
<tr>
<td>Length [m]</td>
<td>2.0</td>
</tr>
<tr>
<td>Input Energy [keV/u]</td>
<td>20</td>
</tr>
<tr>
<td>Output Energy [keV/u]</td>
<td>270</td>
</tr>
<tr>
<td>RF Frequency [MHz]</td>
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</tr>
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</table>

The concept of DPIS is shown in Fig.1 [4]. The laser ion source is directly connected to the RFQ linac without low energy beam transport line. Kashiwagi et al (2008) shown that using DPIS with Nd:YAg laser with pulse duration of 6 ns and energy of 1.89 J irradiating an Al target it is possible to obtain a high current of ions up to 50 mA. Changing the position of extraction and voltage it is possible to observe the behavior of current, in particular were studied the results at 0, 5, and 10 mm from the cavity edge and voltage from 40 and 70 kV. Fig.2 shows the measured beam current dependence on the beam extraction voltage and the plasma electrode position. The beam current indicates the peak current.

**Hybrid Sources**

The electron cyclotron resonance coupled to a laser ion source for charge state enhancement (ECLISSE) is hybrid ion source where the first stage of the source is a LIS which gives intense beams of electrons and of multiply charged ions ($z/m = 1/10$ or lower) to the ECR-generated plasma, where its charge state is increased. In Fig.3 a cross section of the plasma chamber (called SERSE [5]) is shown with the laser beam that was injected into the beamline from the 0° port of the 90° analysis magnet, on-axis with the extracted beam (the interaction between the laser beam and the beam of highly charged ions extracted from the source is negligible). The Nd:YAG laser has been aligned along the normal to the target surface, by means of a He-Ne laser. A focusing lens (4 m focal distance) is placed in air at about 20 cm from the window placed on the 0° flange of the magnet, and a circular beam spot dimension variable from 1 to 3 mm$^2$ is obtained on the target. Generally, the employed laser repetition rate was 30 Hz or 1 Hz. The optical path of the laser beam was about 8 m and the free path after the lens about 4 m, passing through many beamline elements (slits and extractor electrodes) to hit the target, slightly off-centered, so that its rotation may permit to launch the laser beam over an annular shape.
By using a Nd:YAG laser, 9 ns impulse duration, 900 mJ maximum pulse energy, and 30 Hz repetition rate, it is possible to get on the target an intensity of the order of $10^{10}$ W/cm$^2$ on the target, with this laser parameters, Gammino et al. (2004) shows the possibility to obtained high charge state enhancement coupling the plasma generated by laser with the ECRIS system. The plasma generated by laser with a maximum charge state up to $Q = 10^+$ for heavy ions, such as Ta or Au, was produced in front to an argon plasma produced by ECRIS. The experiments performed with Ta plasma produced by laser, shown up to 8 charge states, after the transition through the argon plasma, it enhanced the number of charge states up to $34^+$. Like shows in Fig.4 we were able to get 40 $\mu$A $Ta^{25^+}$ and $Ta^{26^+}$, 12 $\mu$A of $Ta^{31^+}$, 1 $\mu$A of $Ta^{33^+}$ [2].

The production of Ta ion beams is particularly interesting, as they cannot be produced by evaporation, for this reason is very important the development of these hybrid sources for the cyclotron and other accelerators.

**Implantation using post-acceleration**

Ion implantation is a process by which ions of one element are accelerated into a solid target. Ion implantation equipment typically consists of an ion source, where ions of the desired element are produced, an accelerator, where the ions are electrostatically accelerated to a high energy, and a target chamber, where the ions are implanted on a target, which is the material to be implanted. Typically the accelerator produces a monoenergetic beam, in this case the implantation take place for all particles at the same depth. Using like source a laser-generated plasma, it is possible to obtain several charge states and coupling with a post accelerator system it is possible to produce beams with multi-energetic ions. A post acceleration system consist of mainly of a positive bias on target surface and a negative voltage (generally high voltage) in front to the plasma in order to accelerate the positive ion produced by laser-matter interaction. After extraction, ions are accelerated by the intense electric field between the electrodes. If the applied potential difference is $V$, one would expect that ions reach an energy roughly equal to $Z_i eV$. A Nd:YAg pulsed laser operating with 1064 nm wavelength, 9 ns pulse width and 200 mJ pulse energy, in single shot mode, was employed to irradiate Ge target in vacuum chamber. The ion energy distributions shown in Fig. 5, obtained by varying the IEA deflection bias, indicate that the ions follow a Boltzmann distribution but it is different for each charge state three charge states and it follows a Coulomb-Boltzmann-shifted distribution, as reported in the literature [7].
The mean ion energies were about 400 eV, 800 eV and 1200 eV for Ge$^{+1}$, Ge$^{+2}$ and Ge$^{+3}$, respectively, as reported in the energy distributions of Fig.5. By using the 30 kV acceleration voltage, the IEA ion energy distributions of the post-accelerated ions have been acquired by changing the E/z ratios around the mean energy of 30 keV, 60 keV and 90 keV for the three charge states of the two ion species. The multi energetic ion implantation in different materials can be followed by using the SRIM simulation program, which allows to determine the range and the straggling of ion implanted in a bulk. In this case three simulations with Ge ions like beam and SiO$_2$ like substrate were performed. The Ge ions were consireded emitted from a plasma with maximum charge state 3+, using a post acceleration of 30 kV, therefore the three simulated beams will have energy 30 keV, 60 keV and 90 keV respectively. The results of the three simulations are overlapped and shown in Fig.6 were are indicate the average implantation depths in an SiO$_2$ substrate.

Conclusions

How shown in this report the laser-generated plasma can be apply in many field and with several final applications. The possibility to change many parameter in laser parameters, pulse time, energy, focalization, angle of interaction, give the opportunity to obtain many kinds of ion sources from the single charge beam to full stripped, from low current to very high current etc. In addition there is the advantages to produce ions from all kind of solid target, this allow at this system to be employed in many facility for the described applications.

References


Coherent Resonant Coupling of States in Hybrid Quantum Systems

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Much of the interesting physics sees the use of cross-systems: artificial and natural atoms together with optomechanical systems are the blocks of construction of the newborn quantum engineering. There are many ongoing efforts to create hybrid quantum system (HQS), that combine the best characteristics of different systems while avoiding their shortcomings [12]. The fundamental requirement for the realization of a functional HQS is the ability to communicate, with high fidelity, quantum states and properties between its different components. To make this possible it is necessary that the subsystems interact each other. The interaction between subsystems is described by the perturbative part of the total Hamiltonian. The perturbation gives rise to coherent resonant coupling between states nearly degenerate including those which not conserve the number of excitations. In quantum systems whose Hamiltonian depends on a variable parameter, two energy levels can cross for some value of this parameter. If the Hamiltonian is perturbed by an interaction which couples the levels, the degeneracy at the crossing is broken and the levels repel. The perturbation, not only modifies the energy eigenvalues but also mix the old eigenstates (bare states) into the new ones (dressed states). The effective coupling rate between the subsystems must be large enough to allow quantum-state transfer between them within the shortest coherence time, giving rise to observable avoided-level crossings.

In the paper Multiphoton quantum Rabi oscillations in ultrastrong cavity QED (Physical Review A 92, 063830 (2015)), we show that this regime can strongly modify the concept of vacuum Rabi oscillations, enabling multiphoton exchanges between the atom and the resonator. We find that experimental state-of-the-art circuit-QED systems can undergo two- and three-photon vacuum Rabi oscillations. The process can be explained and understood in terms of avoided level crossings arising from interaction between subsystems.

Anomalous Rabi oscillations

When an atom is strongly coupled to a cavity, the two systems can exchange a single photon through a coherent Rabi oscillation [6]. Recently, a new regime of cavity QED was reached experimentally [8], where the strength of the interaction between light and artificial atoms (qubits) becomes comparable to the atomic transition frequency or the resonance frequency of the cavity mode. This light-matter regime presents a great variety of new exciting effects [2, 3, 8–10] that are not observed in the conventional weak- and strong-coupling regimes.

Avoided-level crossings play an important role in quantum mechanics. Here, I want to discuss some effects studied during my PhD course, which can be explained and understood in terms of avoided level crossings arising from interaction between subsystems.

In the paper Multiphoton quantum Rabi oscillations in ultrastrong cavity QED (Physical Review A 92, 063830 (2015)), we show that this regime can strongly modify the concept of vacuum Rabi oscillations, enabling multiphoton exchanges between the atom and the resonator. We find that experimental state-of-the-art circuit-QED systems can undergo two- and three-photon vacuum Rabi oscillations. The process can be explained and understood in terms of avoided level crossings, resulting from the coupling between the states $|e, 0\rangle$ and $|g, 2\rangle$, where $g(e)$ indicates the ground (excited) state of the qubit and the second entry in the kets represents the photon number. It is due to the presence of counterrotating terms in the system Hamiltonian. The anticrossing is not present in the Jaynes-Cummings model [7], since it arises from the coherent coupling between states with a different number of excitations.
Simultaneous excitation of atoms by a single photon

Two-photon absorption consists in the simultaneous absorption of two photons of identical or different frequencies by an atom or a molecule. Multiphoton excitation and emission processes were predicted in 1931 by Göppert-Mayer in her doctoral dissertation on the theory of two-photon quantum transitions, while multiphoton exchanges between the qubit and the resonator has been predicted as seen above. One may wonder if the reverse phenomenon, i.e., joint multiatom emission of one photon or multiatom excitation with a single photon, is ever possible.

In the paper A single photon can simultaneously excite two or more atoms (Physical Review Letters 117, 043601 (2016)), we show that these processes not only can be enabled by the strong correlation between the states of the atoms and those of the field occurring in cavity quantum electrodynamics (QED), but they can even take place with probability approaching one.

We consider two separate atoms interacting with a single-mode optical or microwave resonator. When the frequency of the resonator field is twice the atomic transition frequency, we show that there exists a resonant coupling between one photon and two atoms. The states \( |g,g,1\rangle \) and \(|e,e,0\rangle\), where \(g(e)\) indicates the ground (excited) state of the atoms and the second entry in the kets represents the photon number. The states are connected, via intermediate virtual states by counterrotating processes. If the resonator is prepared in its one-photon state, the photon can be jointly absorbed by the two atoms in their ground state which will both reach their excited state with a probability close to one. Like ordinary quantum Rabi oscillations, this process is coherent and reversible, so that two atoms in their excited state will undergo a downward transition jointly emitting a single cavity photon. This joint absorption and emission process can also occur with three atoms.

One can give a physical interpretation of this effect, in terms of physical virtual process. With P.Ball’s words (APS Physics Focus 9, 83 (2016)), we can say:

the system briefly “borrows” a second photon from chance fluctuations in the vacuum within the cavity. Such “virtual” photons pop in and out of existence all the time. The two atoms and the single real photon become entangled in a three-particle quantum state. Then, with the aid of a virtual photon, this three-particle system can attain a quantum state that is a combination of two situations: (1) both atoms in their ground states with a real photon in the cavity and (2) the two atoms in their excited states with no real photon present. The system can then emerge from this blend of states purely in the latter one.

Quantum nonlinear optics vs Virtual photons

The understanding of the mechanisms that explain the physical processes described above, has allowed us to show that analogs of a large number of well-known nonlinear-optics phenomena can be realized with one or more two-level atoms coupled to one or more resonator modes. Through higher-order processes, where virtual photons are created and annihilated, an effective deterministic coupling between two states of such a system can be created.

In the paper Deterministic quantum nonlinear optics with single atoms and virtual photons (Physical Review A 95, 063849 (2017)), we show how analogs of three-wave mixing, four-wave mixing, higher-harmonic and -subharmonic generation (i.e., up- and down-conversion), multiphoton absorption, parametric amplification, Raman and hyper-Raman scattering, the Kerr effect, and other nonlinear processes can be realized. In contrast to most conventional implementations of nonlinear optics, these analogs can reach unit efficiency, only use a minimal number of photons (they do not require any strong external drive), and do not require more than two atomic levels. Also in the paper Quantum Nonlinear Optics without Photons (Physical Review A 96, 023818 (2017)), we propose an analogous physical process where one excited atom directly transfers its excitation to a pair of spatially separated atoms with probability approaching 1. The interaction is mediated by the exchange of virtual rather than real photons. This nonlinear atomic process is coherent and reversible, so the pair of excited atoms can transfer the excitation back to the first one: the atomic analog of sum-frequency generation of light.

Dynamical Casimir effect in Cavity Optomechanics

The dynamical Casimir effect (DCE) describes the generation of photons from the quantum vacuum due to rapid changes of the geometry (in particular, the positions of some boundaries) or material properties of electrically neutral macroscopic or mesoscopic objects. The experimental detection of the DCE is challenging owing to the difficulty in changing the boundary conditions, e.g., by moving physical objects, such as massive mirrors, sufficiently fast for generation of a significant number of photons.

Recently, using superconducting circuits, the DCE has been demonstrated experimentally, implementing some all-optical proposals, [1, 2, 4, 5, 11]. In particular, it was observed in a superconducting circuit consisting of a coplanar transmission line terminated by a SQUID whose inductance was modulated at high frequency (> 10 GHz). Of course,
these all-optical experiments do not demonstrate the conversion of mechanical energy into photons, as predicted by the DCE. Such a direct observation is still lacking.

In the paper Nonperturbative Dynamical Casimir Effect in Optomechanical Systems: Vacuum Casimir-Rabi Splittings (arXiv:1706.04134; submitted to Physical Review X (2017)), we investigate the DCE in cavity optomechanical systems, treating both the cavity field and the moving mirror as quantum-mechanical systems. Calculations are made without performing any linearization of the dynamical equations. Multiple scattering between the two subsystems is taken into account nonperturbatively. A surprising feature of this approach is that the DCE can be described without the need for a time-dependent light-matter interaction. The only time-dependent Hamiltonian term considered here is the one describing the external drive of the vibrating mirror. Actually, within this approach, the DCE can be described, at least in principle, even without considering any time-dependent Hamiltonian. The interactions of the two subsystems with the environment is described by using a master equation. Specifically, we find that vacuum radiation can originate from the free evolution of an initial pure mechanical excited state, in analogy with the spontaneous emission from excited atoms. We find that the resonant generation of photons from the vacuum is determined by a ladder of mirror-field vacuum Rabi-like energy splittings. When the loss rates are lower than the corresponding frequency splittings, a reversible exchange of energy between the vibrating mirror and the cavity field, which we call vacuum Casimir-Rabi oscillations, can be observed. We also find that the dynamical Casimir effect can create steady state entanglement between the oscillating mirror and the radiation produced by its motion in the vacuum field. Moreover, we find that resonant production of photons out from the vacuum can be observed for mechanical frequencies lower than the cavity mode frequency. Hence, this coupling regime, which experiments are rapidly approaching, removes one of the major obstacles for the observation of this long sought effect.

Conclusions

In conclusion, looking at the recent scientific literature, there is a very fast increase in the interest in studying light-matter interactions in the ultrastrong coupling (USC) regime. I believe that quite soon this interest will spread towards many different hybrid quantum systems. This is a very hot and important area of research, perhaps the future works in this research field, will have a significant impact in the field of interacting quantum systems, and may contribute to the development of novel quantum technologies.

References


In situ high pressure study of $\alpha$-quartz by Raman spectroscopy

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Abstract

The use of diamond anvil cell (DAC) allows to perform in situ ultra-high pressure investigations in order to probe possible structural changes, phase transitions or explore new states of matter. In this study, the pressure dependence of the room-temperature Raman spectra of $\alpha$-quartz has been investigated in the range 0 - 26 GPa by using a screw diamond-anvil cell. Substantial pressure induced changes in frequency were observed for the vibrational modes 204, 263 and 463 cm$^{-1}$.

Keywords: Diamond Anvil Cell, Raman spectra, $\alpha$-quartz.

Introduction

The diamond anvil cell (DAC) is the most performing ultra-high-pressure device that makes possible the investigation of structural, chemical or biological transformations within a wide range of pressure (0–300 GPa) and temperature (4–000 K).

Thanks to these valuable prerogatives, the DAC is used to recreate the condition existing in the depth of planets and in the sea abysses, to synthesize materials and explore phases not observable under normal ambient conditions.

The samples under high pressure observed through the diamonds can be illuminated by X-rays or visible light, allowing to perform measurements of X-ray diffraction, fluorescence, optical absorption, photoluminescence, Mössbauer, Raman and Brillouin scattering, positron annihilation on the systems of interest [1].

High-temperature heating of the samples is also executable by attaching electrodes (2000 K) or with laser-induced heating (up to 7000 K) [2], as well as the cooling down to a few millikelvins [3].

In particular, the quartz has a considerable importance in crustal processes, due to its natural abundance. Thus, the variations of its physical and structural properties with temperature [4, 5] and pressure [6, 7] are extensively studied.

In this paper, in situ-Raman spectroscopic investigations of $\alpha$-quartz at different pressure are presented.

Experimental procedure

Diamond anvil cell

The basic principle of the DAC device consists in placing a metal gasket containing the sample, a pressure transmitting medium and a pressure sensor between the smallest parallel faces of two diamond anvils (culets): by pushing the opposed anvils together, the compression of the sample occurs.

High pressure experiments are aimed to be carried out under hydrostatic conditions, i.e. the transmitting media are supposed to support no shear. Nitrogen, helium, silicon oil, methanol and ethanol mixture, etc. are the typical transmitting systems [8].

Figure 1: a) The scheme of a DAC cell and b) the three-screw diamond anvil cell used for the experiment.
pressure. After the indenting, the gasket is drilled at the center of indentation by an Electric Discharge Machine or Spark Eroder.

The use of diamond for the anvils has two important advantages: it is the hardest known material and it is transparent in a wide frequency range including X-ray and IR-visible range. A scheme of the diamond Anvil cell is provided in (Figure 1).

The pressure monitoring by the ruby fluorescence method

The pressure inside DAC cell is generally monitored by using a reference material whose behaviour under pressure is known.

The most used pressure probe is the ruby. Indeed, the ruby fluorescence emission spectrum, at room temperature and ambient pressure, consists of two quite intense lines with wavelength 694.25 nm (R1) and 692.86 nm (R2), which shift at higher wavelengths by increasing the pressure. The R line trend is well described by the Mao-Bell equation [9]:

\[
P(GPa) = \frac{A}{B} \left[ \left( \frac{\lambda}{\lambda_o} \right)^B - 1 \right]
\]

where \( P \) is expressed in GPa, \( A \) is a parameter equal to 1904 GPa, \( \Delta \lambda \) is the wavelength displacement with respect to the ambient pressure, \( \lambda_o \) is the wavelength of the ruby fluorescence line R1 at room pressure and temperature, expressed in nm; the \( B \) parameter is related to the conditions of the measurements: it is equal to 5 under non-hydrostatic conditions, 7.665 for quasi-hydrostatic conditions (the condition of the current study) and 7.715 under hydrostatic conditions [10].

Experimental details

In the experiments, a three-screw diamond anvil cell has been used to apply pressure. The cell was equipped with type-IA diamond anvils (\( \sim 2 \times 10^3 \) ppm of nitrogen), characterized by 16-sided, Ultra Low Raman Fluorescence and (100)-orientation. Moreover, the anvils have 3.25 mm diameters, 0.50 mm culets and bevels up to 0.70 mm at 8°.

A 200 \( \mu \)m thick stainless steel disk that had been pre-indented to 100\( \pm \)10 \( \mu \)m has been used as a gasket material. Gasket drilling has been performed using the automatic Spark Eroder SEA 303 equipped with tungsten electrodes, which have generated a 200 \( \mu \)m diameter cavity acting as a sample chamber. The pressure transmitting medium was an extremely low fluorescence oil, Cargille type HF.

The wavelength changes of the R1 fluorescence line were evidenced from the Raman spectra of two different ruby grains with 15 and 20 \( \mu \)m diameters.

The pressure on the cell was produced by tightening three screws through a dynamometric key ranging between 0 and 120 N-cm with a 1 N-cm sensitivity. The uncertainty on pressure measurements increases with pressure because of the loss of liquid hydrostaticity and it is observable in the line R enlargement.

The B parameter used in Mao-Bell Equation for the pressure calculation is 7.665 (quasi-hydrostatic conditions). The investigated sample is a 20 \( \mu \)m chip of \( \alpha \)-quartz.

High pressure Raman measurements were carried out at room temperature by using a Jobin-Yvon Horiba LabRam-HR Evolution micro Raman Spectrometer, equipped with liquid nitrogen cooled charge coupled device (CCD) detector and an Olympus BX41 confocal microscope. The data were collected in back scattering configuration with a 1800 lines/mm grating.

The 532 nm laser excitation was used and kept with a power lower than 100 mW in order to avoid undue heating of the sample and a 50X objective (numerical aperture 0.100) was used to image the laser spot on the sample. The measurements on the ruby pressure markers were performed with a low power (0.01 mW) because of the extremely high intensity of their signal.

Results and discussions

In Figure 2, the ruby fluorescence spectra at some of the investigated pressure are shown. The R lines very clearly shift at higher frequencies by increasing the applied pressure.

![Figure 2: Emission spectra of the ruby grains inside the DAC cell at different pressures.](image)

The background-subtracted data are normalized to the R1 line intensity.
Figure 3: **Effect of pressure on low frequency Raman spectra of α-quartz.**

In Figure 3 the in situ Raman spectra of α-quartz at 0 GPa, 3.7 GPa, 7.5 GPa and 22 GPa are plotted.

Figure 4 shows the Raman shifts as a function of pressure of six low frequency-vibrational modes, which are consistent with the trends obtained by Jayaraman [11].

The frequency changes appear negligible for the modes 304, 393, 402 cm\(^{-1}\). Conversely, a strong pressure dependence is observed for the modes 204, 263 and 463 cm\(^{-1}\), that show a large initial increase of the frequency and rapidly flatten out at higher pressure.

Figure 4: **Frequency shifts of the Raman active modes in α-quartz as a function of pressure.**

The variations in vibrational spectra are inferable to pressure-induced changes in structure of α-quartz. In the investigated low frequency range, they are ascribed to complex translations and rotations of SiO\(_4\) tetrahedra [12].

Particularly, the strongest bands at 463 cm\(^{-1}\) is ascribed to the symmetric Si-O-Si stretching modes and it depends on the smallest ring size (and therefore smallest teta Θ\(_{Si-O-Si}\) angle) in the structure [13]. The compression generates the reduction of the Si-O-Si angle, which has been shown to decrease from 144° under ambient conditions to 134° at 6 GPa [14], involving a consistent increase of frequency.

**Conclusions**

The diamond anvil cell allows to perform in situ investigation of the high-pressure induced transformations of materials.

Raman spectroscopy is shown to be a useful method of studying the effects of compression on the structure and vibrational dynamics.

In this paper the crystalline silica α-phase of quartz has been studied. Noticeable shifts of Raman modes 204, 263 and 463 cm\(^{-1}\) have been observed. Particularly the increase of 463 cm\(^{-1}\) mode indicate that there is a decrease in the teta Θ\(_{Si-O-Si}\) angles.

**Acknowledgement**

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Spongy TiO$_2$ gig-lox scaffold for Dye Sensitized Solar Cells and Perovskite Solar Cells

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Abstract

Multi-Porous TiO$_2$ layers were prepared at low temperature by using pulsed DC magnetron reactive sputtering processes in grazing incidence configuration assisted by local oxidation to be used as scaffolds for Hybrid Solar Cells (Dye-Sensitized Solar Cells and Perovskite Solar Cells). Our material gains porosity, stability and infiltration capability superior if compared to conventionally sputtered TiO$_2$ layers. Its competition level with chemically synthesized reference counterparts is also doubly demonstrated: in Dye Sensitized Solar Cells, by the infiltration and chemisorption of N-719 dye ($\sim 1 \times 10^{20}$ molecules/cm$^3$); and in Perovskite Solar Cells, by the capillary infiltration of solution processed CH$_3$NH$_3$PbI$_3$ which allowed reaching efficiency of 11.7%.

Keywords: TiO$_2$, grazing incidence geometry, sputtering, DSSC, PSC, Scaffold, Porosity.

1. Introduction

Dye-sensitized solar cells (DSCs)$^{[1]}$ are attracting the scientific community due to the large versatility and the low production cost. They are especially attractive for integrated building photovoltaic applications for which a less severe effect of the photon incident angle on the light harvesting efficiency is expected. In the standard scheme of the photo-anode of a DSC, a meso-porous thin film of nano-sized TiO$_2$ crystals is deposited on a Transparent Conductive Oxide (TCO)$^{[2]}$, annealed for grains sintering and anatase crystallization (typically at 500$^\circ$C), and subsequently imbued with a photoactive dye. Meso-porous TiO$_2$ in the anatase polymorphism has emerged as the most appropriate choice for cell scaffold. The most diffused and versatile way to generate nano-TiO$_2$ architectures is by chemical approaches. They offer a large plethora of fascinating hierarchical and mesoporous structures with high infiltration capability. On the other hand, standard physical growth methods cannot straightforwardly compete with chemical approaches since they have an intrinsic tendency to form compact layers. The advent of modified sputtering methodologies to grow, instead, TiO$_2$ scaffolds with high porosity levels would open the field to high production throughput as linked to the reproducibility of the materials and to the up-scalability of the processes.

In this paper we propose a material with multi-scale porosity ranging from nano- to meso-dimensionalities grown by a modified (up-scalable) sputtering method, and we demonstrate its attitude to be functionalized with species of different nature. To this intent, two photoactive blends, namely TiO$_2$+dye and TiO$_2$+perovskite$^{[3]}$, are realised, characterised and tested in prototype DSCs and PSCs to provide a proofs-of-concept on the transversal empowering of the material.

2. Material and methods

TiO$_2$ deposition by grazing incidence geometry assisted by local oxidation (gig-lox). TiO$_2$ layers have been deposited a DC Magnetron Sputter equipment (Kensosistine S.r.l.). We used a customized grazing incidence source of Titanium (2-inch circular target); the Ar flow-rate was optimized at 69 sccm and the depositions were done in reactive ambient of O$_2$ pumped with a flow rate of 2 sccm. The process was calibrated on the basis of the semi-empirical Thornton’s model. Specifically, the deposition was carried out by applying a constant power of 140 W (475 mA, 295 V, power loading 6.9 W/cm$^2$) for 12000s at room temperature. The corresponding growth rate was of 4 nm/min, able to guarantee
the proper layer stoichiometry (as demonstrated by X-ray photoelectron spectroscopy analyses). A pressure of 10.5 mTorr and an anode–cathode distance of 1.2 cm were set. Each deposition process is preceded by a pre-sputtering step to clean up the surface of the Ti target and to remove residual thin oxide layer. During the deposition the substrate keeps rotating under the beam (20 rpm) in order to improve the uniformity over the sample surface.

**DSC architecture and I-V characterization.** Fluorine-doped tin oxide (FTO, 15 Ω/sq, provided by Solaronix S.A.) glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Compact TiO₂ layers were prepared as follows: FTO glasses were coated with 0.15 M titanium diisopropoxide bis(acetylacetonate) (75% Aldrich) in 1-butanol (Aldrich) solution by the spin-coating method, which was heated at 125°C for 5 min. After the coated film was cooled down to the room temperature, the same process was repeated and the two times coated FTO glasses were finally heated at 500°C for 30 min. The prepared dense TiO₂ blocking layer were thus covered by: 1) mesoporous TiO₂ gig-lox layers deposited by sputtering at RT; or 2) standard nanocrystalline TiO₂ pastes (reference) deposited by a doctor-blading technique using a commercial diluted colloidal titania paste (Dyesol 30NR-T). The reference samples were heated in air at 450°C for 1 h. The annealing is equivalent to 500°C 30s.

The perovskite films were deposited from a precursor solution containing 461 mg of PbI₂, 159 mg of CH₃NH₃I, and 78 mg of DMSO (molar ratio 1:1:1) in 600 mg of DMF. The completely dissolved solution was spin-coated on the TiO₂ layer at 4000 rpm for 25 sec and 100 μL of toluene were poured on the spinning substrate 15 s prior to the end of the program. The film were heated at 65°C for 1 min and 100°C for 2 min in order to obtain a dense CH₃NH₃Pbl₃ film. The hole transporting material solution, Spiro-MeOTAD, 50 mM in chlorobenzene containing 25 mM bis(trifluoromethylsulfonyl)-imide lithium salt (Li-TFSI) and 200 mM 4tert-butylpyrididine (TBP) was spun at 3000 rpm for 30 s. As a last step, 60 nm of gold top electrode were thermally evaporated under high vacuum. Photocurrent-voltage measurements were performed using a Keithley unit (Model 2400 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 1000 W Xenon arc lamp) serving as a light source.

**Photocurrent-voltage measurements.** Photocurrent-voltage measurements were performed using a Keithley unit (Model 2400 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 1000 W Xenon arc lamp) serving as a light source.

3. Results and discussion

**Grazing incidence-local oxidation (gig-lox) process description.** The idea to use a different deposition geometry to build the new material is based on the exploitation of a double strategy to provide the material with a double-range-porosity during growth (in-situ processes). In fact, we combined the nanoporosity (1-5 nm) offered by the application of the Thornton’s conditions with the meso-porosity (10-50 nm) arising from the use of a modified sputtering approach. We used a customized sputtering equipment empowered by a Ti off-axis source with an inclination angle θ (Figure 1) and an oxidizing zone confined at the sample surface, far from the cathode sheath.
The success in growing a layer with multi-porosity extending through thick layers (e.g. through 1 μm) mainly resides in the choice of the inclination angle θ. An optimum inclination angle of 12.7° was identified in our setup as a compromise between the shadowing effect by the starting TiO₂ seeds (this define the lower limit in θ and the verticalization of the Ti flux by increasing θ, that has a tendency to progressively close the pores by proceeding the deposition. Hereafter we refer to our refined methodology at inclination angle of 12.7° as gig-lox; the reference process, related to the use of a standard parallel plate geometry in Thornton’s conditions, will be indicated by ppg.

The result, although it does not outperform existing devices in the literature that apply higher sensitized volumes (10 times scaffolds thickness) and different dyes to get records, needs to be framed in relationship to the scaled thickness of the scaffold and to the low molar absorption coefficient of the N-719 dye.[1] In the panorama of the recent literature, viable solutions to increase the efficiency facing on the light harvesting capability of the dye (new molecular engineering) or on the electrolyte performances (new electrolytes or gel with carrier mobility, stability) have been explored to further increase the cell efficiency and durability.

**Figure 1:** Chamber section of our customized sputtering equipment used to develop the new method called gig-lox.

**Figure 2:** I–V curves of DSCs. Devices (~1μm-thick) based on gig-lox TiO₂ layers compared to a reference made by commercial TiO₂ pastes (Dyesol 18NR-T) under 1.0 sun illumination. The Cells parameters are listed in the table.

Besides them, our issue represents the first demonstration that a sputtered TiO₂ layer can aspire to compete with chemically prepared ones. Our approach affords the advantages of an easy integration of the material on large-area-technologies (upscaleability) and encourages further investigations towards new records in the field of hybrid flexible solar cells, comprised perovskites-based solutions wherein thinner scaffold (typically around 300 nm) are required.

**TiO₂ gig-lox integrated in a Perovskite Solar Cells architecture.** To tailor the device ar-
architecture, our findings definitely authorized to scale the gig-lox layer thickness to 150 nm and to use it in a blend with solution processed MAPbI$_3$ in a complete pore filling arrangement. The related cell performances are shown in Figure 3. The cell architecture was that used by Prof. T. Miyasaka and co-workers (meso-structure). The solar cell based on the gig-lox TiO$_2$ scaffold exhibited a photo conversion efficiency of 11.7%. Compared to a device fabricated using commercially available colloidal TiO$_2$ grains (commercialised by Dyesol), which reached 10.5% efficiency, it is even better. The I-V curves do not show hysteresis.

![Figure 3: I–V curves of Perovskite Solar Cells. Devices based on gig-lox TiO$_2$ layers (~150 nm-thick) under 1.0 sun illumination (both are reverse curves). The cell architecture is also schematically drawn.](image)

4. Conclusion

We grow multi-porosity (nano and meso) TiO$_2$ scaffolds developing a new method based on two different effects: the shadowing effect and the local oxidation effect. The material gains an average porosity of ~40% in volume which is maintained up to (at least) 500°C of post-deposition annealing; additionally, surface faceting represents an added-value for the TiO$_2$ surface to interact with functional materials. In all those respects, the gig-lox layer structure surpasses what achievable by sputtering in conventional ways. Its competition level with chemically synthesized reference counterparts is doubly demonstrated by integration of the gig-lox TiO$_2$ scaffold in DSC and PSC architectures. A high photo-active molecular infiltration was proved by chemisorption of N-719 (~1·10$^{20}$ molecules/cm$^3$) on the TiO$_2$ surfaces. In Perovskite Solar Cells, the capillary infiltration of CH$_3$NH$_3$PbI$_3$ into the differently sized pores of the TiO$_2$ architecture allowed reaching efficiency values of 11.7%, higher than in the reference cell made with commercial TiO$_2$ under the same conditions.

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References


Thermodynamical studies of aqueous systems

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Abstract

During my PhD course, the thermodynamical properties of several complex and biological systems have been investigated focusing, in particular, on experimental studies of water and its interaction with other biosystems. In fact, the study of how water regulates the properties of biological systems is a hot topic because it affects different fields from medicine to cultural heritage. By means of several techniques of Nuclear Magnetic Resonance (NMR) spectroscopy, that allows to investigate the dynamical characteristic of water systems, several experiments were performed in the temperature range between 200 K and 370 K to highlight the behavior of the investigated aqueous systems.

Keywords: complex systems, water, biomaterials, aqueous systems, thermodynamics, hydrogen bond, NMR.

Water is the most abundant inorganic molecule in the universe after hydrogen and it is essential to life and human activity [1]. In fact, all life on Earth needs water to survive (i.e., living organisms require, contain and maintain a balance of water) and/or to fulfill its functional activity. In the human body, water contributes to many biological and physiological functions such as the triggering of enzymatic activity (e.g., water-lysozyme interaction in the human saliva). In nature, it is possible to find water in gaseous, liquid and solid phases, and, in particular, water is the only inorganic substance that is liquid at atmospheric pressure and ambient temperature. Furthermore, liquid water is the most extraordinary substance even for its unusual and counterintuitive properties (e.g., its anomalies) when compared with normal liquids, especially in the supercooled regime [2]. In particular, water possesses many thermodynamic anomalies due to the clustering behavior in the development of the hydrogen bond (HB) network. From the point of view of biology, water plays a very essential role as a solvent and sustaining the biochemistry of life [1]. In fact, over the past three decades, water is no longer considered only as a simply "life's solvent", but indeed as a "matrix of life" that actively interacts with biomolecules. Water may be considered as a biomolecule in the sense that aggregates of H₂O molecules accomplish delicate biochemical tasks in their interaction with biosystems. Water is an extremely "good solvent" for ions allowing their dissociation in salts and greatly bond to other polar substances (e.g., alcohols). When a polar compound is inserted in aqueous solution, it is surrounded by small sized water molecules that constitute an interface called hydration shell. In particular, two different types of substances can be distinguished: (i) hydrophilic ("water-loving") polar substances that will mix well and dissolve in water, and (ii) hydrophobic ("water-fearing") non-polar substances, that do not mix well in H₂O. These non-polar molecules are called hydrophobes and usually have a long chain of carbons that do not interact with water. This tendency of water to exclude hydrophobes is named "hydrophobic effect" [3]. In fact, when a hydrophobe is dropped in water, highly dynamic HBs between liquid water molecules will be broken to make room for the hydrophobe. So, hydrophobic solutes in water experience a force that causes them to aggregate. In particular, it seems clear that this hydrophobic interaction is in some way responsible for several important biological processes, e.g., the folding of proteins. Particularly interesting is the case of the interaction of water and amphiphiles, such as methanol.

Indeed, aqueous solutions of small amphiphile that have both hydrophobic and hydrophilic domains can be used as model systems to test water HB interactions and the hydrophobic effect [4]. The simplest amphiphilic molecule is methanol, CH₃OH, which consists of a single hydrophilic (OH) and a single hydrophobic (CH₃) group. Whereas bulk liquid water is essentially a fragile glass-former, methanol is a strong glass-forming liquid and its transport parameters, such as viscosity η, exhibit an Arrhenius behavior (η = η₀ exp(E/k₆T) [5]). As shown in ref. [5], the behavior of the methanol-water solution is more complex than that one found in simple mixtures: in fact, the thermodynamic and transport properties are anomalous because the interaction between the two liquids is strong. In particular, for high T, the hydrophobicity in water-methanol solutions is
stronger than the water-glycerol ones [4]. Glycerol, C₃H₅O₃, an alcohol with three hydroxyl groups, unlike methanol, is a fragile glass-forming liquid. The interaction between glycerol and water are of special interest in the context of supercooled materials for the strong resistance to crystallization of this substance. Generally, adding an alcohol to water affects both the water network and the supercooling temperature. In fact, the alcohol concentration and the HB patterns formed in these alcohol-water solutions inhibit ice crystallization, e.g., moderate water concentrations in methanol allow supercooling at temperatures down to ≈100K, and for glycerol down to ≈180K [4]. Furthermore, water-glycerol system has been studied to demonstrate other thermodynamical aspects of water systems [6].

Water plays an important role even in hydrated proteins. Proteins are macromolecules with a wide variety of biologically important functions consisting of one or more long chains of 20 different types of amino acid. Hydrophobic amino acids usually lie in the native state of the body (that is not exposed to water) forming the "heart" of the protein. In contrast, hydrophilic amino acids are in contact with water and are usually found on the surface of the protein. Proteins are highly complex systems and they can "fold" in different ways (folding process) because of their characteristic structural disorder. In spite of their complexity, real proteins have a well-defined native status and "fold" in it through a fast and secure folding process. This is to say that for real proteins the folding process is generally reversible. In protein folding, water mediates the collapse of the chain and, in particular, it is believed that the conformational motion is coupled with the dynamics of the hydration water. The folding process of proteins depends on the incompatibility between low-density water and the hydrophobic surface that folds to form a hydrophobic core. This competition between hydrophobic groups that remove water (cluster) structures from the surface of the protein is controlled by the interactions among charged groups and polar ones and each of them with water molecules. The protein folding corresponds to that complex of phenomena through which the amino acid chain (peptide) comes to assume the native state of the protein. Another important process that characterizes protein is denaturation. The denaturing process occurs when the protein loses its native conformation to return to the state of a simple linear polypeptide chain. Denatured protein naturally also loses its physiological function.

In the frame of the dynamics of water-protein interaction, the HBs drive the structure and functioning of proteins, stabilizing the amide functional groups of the protein. Thus, the stable configuration for hydrated peptides corresponds to the formation of two HBs between water molecules and peptide moieties. For this reason, understanding the behavior of water and its interaction with biomolecules is key to comprehend the essential phenomena that occur in biological processes making life possible. In particular, the experiments were performed on aqueous solutions of lysozyme, a small protein of 14.4 kDa constituted by 129 amino acid residuals that in the native state has a globular shape [7–10]. To be precise, the protein functionality is activated when the hydrated biomolecule becomes flexible. For lysozyme this condition corresponds to an hydration level h = 0.3, for which the protein is surrounded by a certain quantity of water that forms a monolayer, the first hydration shell [7].

Another complex biosystem whose properties are strongly controlled by the presence of water is cellulose [11], the main component of a lot of artifacts since ancient times. Paper is probably the most common and widespread material made of cellulose and it has been used as a convenient vehicle for the acquisition, storage and dissemination of human knowledge. It is mainly composed of cellulose fiber, an almost equimolar amount of bound water and small amounts of organic or inorganic additives or impurities. At a molecular level, cellulose is a linear homopolymer composed of D-anhydroglucopyranose units (C₆H₁₀O₅)n, which are linked together by β-(1→4)-glycosidic bonds. The cellulose chains have a strong tendency to aggregate into highly ordered structural entities through an extended network of both intramolecular and intermolecular hydrogen bonds. In this frame, water allows the availability of free protons for hydrolysis of glycosidic bonds and the molecular oxygen to be a fairly good oxidizing agent through the production of active oxygen species (superoxide, hydrogen peroxide and hydroxyl radicals). Water molecules can be absorbed by cellulose wherever hydroxyl groups are available. Interaction between cellulose and water always occurs at the surface of cellulose polymer aggregates, therefore at the surface of crystallite or within amorphous regions. As a consequence the cellulose fiber, and paper as whole, absorb water into its structure. Indeed, water is essential for paper production starting from a dilute suspension of cellulose fiber drained through a screen, so that a network of randomly interwoven fiber is formed.

On the basis of these observations, by means of Nuclear Magnetic Resonance (NMR) measurements, from the stable water liquid phase to the deeply supercooled regime, it is possible to verify how water affects the thermodynamical properties of several complex systems [4–11]. Indeed, the dynamical and thermodynamical properties of the previously described systems have been studied as a function of different control parameters (such as temperature T) by means
of different experimental methods.

Nuclear Magnetic Resonance (NMR) spectroscopy is based on the physical phenomenon in which nuclei in a magnetic field, perturbed by a radiation pulse, relax re-emitting an electromagnetic radiation. The experiments were performed using a Bruker AVANCE NMR spectrometer operating at 700 MHz (Larmor frequency of hydrogen nuclei), located at the MIFT department of University of Messina in collaboration with the Italian CNR, and the techniques used are the Magic Angle Spinning (MAS) approach and the Pulsed Field Gradient Stimulated Echo (PFGSTE) technique.

In water-alcohol systems, as shown in refs. [4–6], all the data examined indicate that the temperature T* ≈ 320 K is directly related to the HB network and thus dominates water dynamics and strongly affects the properties of the investigated solutions. This "magic" temperature corresponds to the situation where water passes from the normal fluid state to that of complex and anomalous liquid. Another temperature noted as T_L ≈ 225 K is really important in aqueous systems marking impressive change in their dynamics. Precisely, T_L represents the crossover temperature of the fragile-to-strong transition below which HBs lifetime increases significantly. In particular, the properties of such systems are the result of methanol and glycerol interactions with water by means of their hydrophilic and hydrophobic groups. The difference in the number of the HB acceptors and donors of the two alcohol molecules is also relevant. Comparing the behaviors of the two alcohols reveals that the effect of the hydrophobic interaction on the transport properties of the solution is stronger in the methanol/water solution because there is a limited number of HBs involved, and the methyl groups dominate when the HBs become weak. The data confirm that for liquid solutions (or mixtures) there is a universality behavior evidenced by molecular fluids.

Fortunately, to demonstrate the importance of T*, in ref. [10] has been reported a study on the mean squared displacements as a function of diffusion time at high-temperature. In particular, the system undergoes from a condition of sub-diffusion dynamics to a super-diffusion limit and, in this frame, the onset of this change in the dynamics of the system can be identified exactly in the temperature T*.

As we have mentioned above, the hydrophilic interaction is an important driving force in the aggregation and folding processes in proteins. However, the process that maintains their stability and functionality is the hydrophilic interaction [7]. In fact, HBs formed between hydrophilic protein groups and water molecules are vital to protein activity. The diffusion coefficient data allow to identify three important temperatures that characterize the dynamics of lysozyme-water solution [8]. In addition to the temperatures T_L and T*, that we already seen in the case of alcohol-water mixtures, for T higher than T*, when HBs lifetime decreases increasing the protein flexibility, the temperature T_D identifies the irreversible protein denaturation. Above T_D there is a decoupling between water and protein [7, 8]: the strength of the interaction sharply decrease and the protein is no more "slave" of the solvent (but the biomolecule loses its functionality). In ref. [8], it has been confirmed that the hydration level of h = 0.3 is key for the activation of the functionality of lysozyme. Therefore, the data for h = 0.61, after T ≈ 260 K, have the same behavior as the hydration water monolayer (h = 0.3): excess water freezes at lower temperature, and the first hydration shell remains liquid.

Furthermore, the properties of lysozyme hydropophilic and hydrophobic parts have been investigated in different thermal cycles to obtain an experimental proof of the free-energy landscape model.

The two forms of protein water, hydration water and internal water, are essential in protein folding. In particular, internal water "drives" the protein structure from a globular configuration to an open, unfolded configuration. This mechanism involves HBs shared by water, carbonyl oxygen (C=O) and amidic proton (N–H). A comparison between the behavior of these three peptide groups confirms how HBs play a fundamental role in protein folding. The higher molecular mobility is caused by the burial effect of the HBs on the hydrophobic groups, which is particularly strong in the case of the methyl groups. In particular, clusters of hydrophobic residues are formed in the folded protein and the methine groups are more mobile than the methyl groups. Finally, the validity of the theoretical scenario (energy landscape) of a process dominated by different energetic routes has been confirmed, also explaining the water role in the protein configuration stability [9].

In ref. [11], the role of water in the hydration and degradation processes of cellulose in artificially and naturally aged paper has been investigated by means of the NMR technique known as High-Resolution Magic Angle Spinning (HR-MAS) to increase the spectral resolution. In such a way we were able to separate three different contributions to the overall relaxation with distinct trends. The measurements of the longitudinal component T_1 of the NMR magnetization as a function of hydration show different trends for the three identified contributions. The component associated to free water is the slowest one and shows a value at the smallest hydration even longer than that of bulk water due to the presence
of molecules in vapor-phase trapped within voids of cellulose fibers. This contribution decreases upon increasing hydration due to the swelling of cellulose fibers. The component with a constant trend corresponding to bound water constantly interacts with hydroxyl groups of cellulose. Finally, the fastest component that corresponds to cellulose protons slowly increases raising h because of there is an enhancement of mobility with h. Furthermore, the data furnish a clear evidence that the interactions between water and cellulose act over time to progressively break HBs between cellulose polymers causing the swelling of the fibers and as a powerful catalyst of hydrolytic and oxidative reactions with a consequent transformation of cellulose polymers into low molecular weight products. The $T_1$ data as a function of degradation time display a linear decreasing behavior after the first 12 days of degradation. This holds for all the three distinct components that cross each other at about 212 degradation days. This value may define the limit of artificial degradation corresponding to the levelling-off of the degree of depolymerization of cellulose polymers. It is well evident that $T_1$ evolution provides therefore a non-destructive method for estimating the degradation of cellulosic materials in terms of an equivalent time of artificial aging [11].

The knowledge of the hydration mechanisms is essential for the understanding and the control of the possible degradation pathways. Moreover, the dependence of the water dynamics on hydration and aging can suggest appropriate strategies for the preservation and restoration of cultural heritage materials based on cellulose.

To conclude, the results of the illustrated scientific activity were subjects of about 8 publications [4–11] in relevant international journals. The research activity involves national and even international collaborations with e.g. the “Center for Colloids and Surface Science” (CSGI) in Florence, the “Boston University” in Boston (USA), the “Massachusetts Institute of Technology” in Cambridge (USA).

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CYCLE XXXI
Acoustic Levitation by Standing Wave

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Abstract

In this work, one-dimensional acoustic levitation by standing wave, for enough small droplets (0.5 – 3.5 mm of diameter), is presented. Levitation is a process in which an upward force counteracts the gravitational force of an object so that there is no physical contact between the object and the ground. Different levitation techniques have been conceived, such as optical, electromagnetic, electrostatic, gas-film, aerodynamic and acoustic levitation. Among these techniques, acoustic levitation has the advantage of not requiring any specific physical properties of the sample. After the description of standing wave approach, the acoustic potential is reported and viscous corrections are described; finally, the description of acoustic levitation is extended to its applications.

Keywords: Acoustic Levitation, Standing Waves, Contactless Techniques, Microgravity.

Introduction

Acoustic waves are mechanical waves, which propagate through a physical medium and scatter on obstacles, transferring some of their momentum on some obstacles and creating a force. This force can be seen as consequence of a small radiation pressure, which over 20 kHz overcomes gravity force. To understand how acoustic levitation works, it is useful to provide a definition of gravity, air and sound. To understand how acoustic levitation works, it is useful to provide a definition of gravity, air and sound. Gravity is a force that causes objects to attract one another and the relative theory is the Isaac Newton’s law of universal gravitation that asserts that every particle in the universe attracts every other particle. Air is a fluid that behaves the same way liquids; it is made of microscopic particles that move in relation to one another. Air also moves like water and the particles in gasses, like the ones that make up air, are simply farther apart and move faster than the particles in liquids. Sound is a vibration that travels through a medium, like a gas, a liquid or a solid object and its source is an object that moves or changes shape very rapidly. The sound wave travels as the moving molecules push and pull the molecules around them; each molecule moves the one next to it and turn; without this movement of molecules, the sound could not travel. Acoustic levitation uses sound traveling through a fluid, such as a gas, to balance the force of gravity. In the present work one-dimensional acoustic levitation by standing wave, known as King’s approach, for enough small droplets of a diameter between 0.5 and 3.5 mm, was presented. After the description of standing wave approach, the acoustic potential was presented and viscous corrections were described; finally, the description of acoustic levitation was extended to its applications.

Acoustic levitation

An acoustic levitator [1-7] is a device constituted by two concave surfaces to help focus the sound: a transducer, a vibrating surface that makes sound and a reflector. A sound wave travels away from the transducer and bounces off the reflector. Three basic properties of this traveling, reflecting wave help it to suspend objects in midair: i) sound, is a longitudinal pressure wave, where the movement of the points is parallel to the direction the wave travels; ii) the wave can bounce off of surfaces and to follow the law of reflection, which states that the angle of incidence, i.e. the angle at which something strikes a surface, is equal to the angle of reflection, i.e. the angle at which it leaves the surface; iii) when a sound wave reflects off of a surface, the interaction between its compressions and rarefactions causes interference. The compressions that meet other compressions amplify one another, and compressions that meet rarefactions balance one another out and sometimes, the reflection and interference can combine to create a standing wave. Standing waves shift back and forth and vibrate in segments rather than travel from place to place. This illusion of stillness is what gives standing waves their name. Standing sound waves have defined nodes (areas of minimum pressure), and antinodes (areas of maximum pressure). Nodes are at the heart of acoustic levitation. By placing a reflector
the right distance away from a transducer, the acoustic levitator creates a standing wave. The distance between the transducer and the reflector must be a multiple of half of the wavelength of the sound the transducer produces. When the orientation of the wave is parallel to the pull of gravity, portions of the standing wave have a constant downward pressure and others have a constant upward pressure. Nonlinear acoustics is a complex field, and the physical phenomena that cause these effects can be difficult to understand. They can combine to make an intense sound far more powerful than a quieter one. It is because of these effects that a wave’s acoustic radiation pressure can become strong enough to balance the pull of gravity. Intense sound is central to acoustic levitation, in fact the transducers in many levitators produce sounds in excess of 160 dB. In a microgravity environment, the stable areas in the nodes must be large enough to support the floating sample. The object should measure between one third and half of the wavelength of the sound, higher the frequency of the sound, smaller the diameter of the objects it is possible to levitate. Droplets being levitated must have a suitable Bond number, which is a ratio that describes the liquid’s surface tension, density and size in the context of gravity and the surrounding fluid. If the Bond number is too low, the drop will burst. The intensity of the sound must not overwhelm the surface tension of liquid droplets being levitated. If the sound field is too intense, the drop will flatten into a donut and then burst.

Standing wave levitation approach

Standing wave levitation approach takes in account a model which assumes enough small, incompressible and rigid sphere levitating in presence of acoustic standing wave. For fluid it assume that effect of viscosity can be neglected and that barotropic relation \( p = f(\rho) \) holds. Because of our assumptions we can use Euler’s equation (1):

\[
\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla)\vec{v} = -\frac{\nabla p}{\rho}
\]

assuming that the flow of fluid is irrotational, it is possible to express vector of velocity with gradient of scalar function \( \Phi \) (velocity potential): \( \vec{v} = \nabla \Phi \). Continuity equation holds (2):

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0
\]

which can be written as (3):

\[
\frac{1}{\rho} \frac{\partial \rho}{\partial t} = \nabla^2 \Phi
\]

For a medium, such as air, in which from barotropic relation follows \( \frac{dp}{d\rho} = f(\rho) = \text{const} = \rho^2 \) differential equation for \( \Phi \) exact to first order leads to wave equation for \( \Phi \) (4):

\[
\nabla^2 \Phi = \frac{1}{\epsilon^2} \frac{\partial^2 \Phi}{\partial t^2}.
\]

Eq. (1) can be written as (5)

\[
\nabla \Phi = \nabla \left( f \frac{dp}{\rho} \right)
\]

from which follows non-stationary Bernoulli equation (6):

\[
\Phi - \int \frac{dp}{\rho} = \frac{v^2}{2}
\]

For further derivation of integral \( \int \frac{dp}{\rho} \) we expand barotropic relation into series in terms of factor \( s = \frac{\rho - \rho_0}{\rho_0} \) (7):

\[
p = f(\rho_0 - sp_0) \approx f(\rho_0) + sp_0 f'(\rho_0) + \frac{1}{2} s^2 \rho_0^2 f''(\rho_0) + \ldots
\]

From this expansion we can express \( dp \) and combine it with expression \( \rho^{-1} \approx \rho_0^{-1}(1 - s + s^2 - \ldots) \). Eliminating factor \( s \) and regarding \( f(\rho_0) = p_0 \) for pressure variation in the medium can be expressed (8):

\[
\delta p = p_0 - \rho_0 \frac{\partial p}{\partial t} + \frac{\rho_0}{2\epsilon^2} \left( \frac{\partial \Phi}{\partial t} \right)^2 - \frac{1}{2} \rho_0 \vec{v}^2.
\]

To get solutions for pressure variation it is need to calculate velocity potential from wave eq. (4). For that we need to take into consideration boundary conditions which of course sharply depend on geometry of the levitated object. Solution for \( \Phi \) from (4) will be oscillatory. For small spheres equality \( \Phi = |\Phi| \cos(\omega t) \) can be shown (h denotes position of levitated particle in z-direction). From definition of velocity potential and Bernoulli equation (6) it follows that pressure variation will also oscillate along distance between sound radiator and levitated object. It can be shown that force on enough small-levitated particle created in travelling waves is smaller for few orders of magnitude \( (F \propto \nu^4) \).
than force created in stationary waves. This is why effect of travelling waves can be neglected. Acoustic force on a small, rigid sphere (model described before) in a standing wave is derived to be (9):

\[ F = 8\pi r^2 (kr_0)\tilde{E}\sin(2\kappa h) f \left( \frac{\rho_s}{\rho_0} \right). \]

It is expressed with wave number \( k \), radius of sphere \( r_s \), mean total energy-density of sound in a medium \( \tilde{E} = \frac{1}{2}\rho_0 k^2 |\phi| \), density of sphere \( \rho_s \) and so called relative density factor \( f \) which in case for stationary wave is defined as (10):

\[ f \left( \frac{\rho_s}{\rho_0} \right) = \frac{1 + \frac{2}{3} \left( 1 - \frac{\rho_s}{\rho_0} \right)}{2 \left( \frac{\rho_s}{\rho_0} \right)}. \]

Another different approach to derive force on small particle in standing wave field is with acoustic potential. The acoustic force is obtained from (11)

\[ \vec{F} = -\nabla U \]

Expression for acoustic force, like (9), is of course the same, regardless which approach we use. Acoustic potential is often expressed in form (12)

\[ U = 2\pi r_s \left[ f_1 \left\langle \frac{v_0^2}{3\rho_0 v^2} \right\rangle - f_2 \frac{\rho_s}{2} \left\langle \frac{v_0^2}{v^2} \right\rangle \right] \]

with \( \left\langle v_0^2 \right\rangle \) and \( \left\langle \rho_0^2 \right\rangle \) being time-averaged square of velocity and pressure of the acoustic wave, both considered in the point where levitated object is found. \( f_1 \) (monopole coefficient) and \( f_2 \) (dipole coefficient) are numerical factors given by (13)

\[ f_1 = 1 - \frac{\rho_s}{\rho_0} \frac{r_0^2}{r_s^2} \]

and (14)

\[ f_2 = \frac{2(\rho_0 - \rho_s)}{3\rho_0 + \rho_s} \]

where again index 0 presents surroundings (medium) and index s particle (sphere). Eq. (12) can be presented with maybe more intuitive form (15):

\[ U = V_s \left[ f_1 \langle E_{pot} \rangle - \frac{3}{2} f_2 \langle E_{kin} \rangle \right] \]

with \( V_s \) as volume of a sphere \( \langle E_{pot} \rangle = 1/(2\rho_0 v^2) \langle \phi \rangle \) and \( \langle \langle E_{kin} \rangle \rangle = \frac{\rho_0}{2} \left\langle \frac{v_0^2}{v^2} \right\rangle \) being averaged potential (of compressed medium) and kinetic (due motion of medium) energy density of acoustic wave. Particle’s equilibrium points are at \( F_i = \frac{\partial F}{\partial x_i} = 0 \).

Acoustic force according to (11) depends on geometry of a chamber in which experiment is performed. With definition of acoustic potential (11) we can see that particle’s tendency to minimal force can be seen as tendency to potential minima. In presence of gravity, gravitational term has to be added to expression for acoustic potential (into (12) or (15)):

\[ U = U_{acoustic} + U_{grav} \]

where gravitational contribution is defined as

\[ U_{grav} = (m_s - m_0)gh \]

where \( m_s \) and \( m_0 \) are the mass of the sample and the mass of fluid, which is displaced because of presence of particle whereas \( h \) again denotes vertical position of particle.

By now viscosity of medium was neglected. This approximation is justified when there is no presence of rigid boundary in medium and wave attenuation is neglected. Otherwise viscous term \( \eta \nabla^2 \vec{v} \) has to be added to Euler’s eq. (1).

Because of viscosity acoustic attenuation is emerged, in other words, momentum of acoustic waves is transferred to the medium, resulting in net displacement of it (i.e. acoustic streaming) in space between boundaries. This net displacement creates gradient of streaming velocity and viscous force which acts as holding force. Hence, levitated object is considered stabilized. Experimentally it was noticed that this streaming velocity is proportional to amplitude of sound radiator, by increasing amplitude, streaming velocity (and viscous force) also increases. In standing waves levitation, system different corrections are considered. Thickness of viscous boundary layer is defined as (16):

\[ \delta = \sqrt{\frac{2\eta}{\rho_0 \omega}} \]

Expressed with \( \eta \) as coefficient of viscosity and \( \omega \) frequency of sound. In standing wave levitation effect of viscosity can be neglected as long distances within a few \( \delta \) are not reached.

It can also be neglected for particles for which characteristic dimension exceeds characteristic dimension of viscous boudary layer \( (r_s >> \delta) \). Since we consider model which assumes particles with \( rs << \delta \) we have to regard viscous corrections.

Viscous corrections can be presented with numerical factors \( f_1 \) and \( f_2 \). Since viscosity does not affect pressure in medium but only velocity of its flow, only factor \( f_2 \) has to be redefined into (17)

\[ f_2 = \left( \frac{\rho_s}{\rho_0} \right)^{\frac{1}{3}} r_s \]

with factor (18)
\[ \gamma(\delta) = \frac{3}{2} (1 + i(1 + \delta)) \delta \]

and taking only (19)

\[ \text{Ref}_\delta(\rho, \delta) \]


Acoustic levitation by standing wave has been employed for several different techniques. Main advantage of this approach is the fact that levitated object is isolated and it can not react with its surroundings any more. This is very desirable when studying or dealing with chemical reactions especially with the fact that levitated particle is easy reachable and available for handling. In physics isolating of sample is desirable when observing phase transitions, process of crystallization or to study the structure of proteins or nanoparticles. Similar use of standing wave levitation is in interesting experiment to isolate droplets of liquid and observe their evaporation process by illuminating droplet and determining its volume with help of shadows.

**Conclusions**

In this work, a new approach to study acoustic levitation by standing wave, was presented. After the description of standing wave approach, the acoustic potential was reported and viscous corrections were described; finally, the description of acoustic levitation was extended to its applications.

**References**


Methods to test the performance of a restricted area physical-mathematical model with variation of the physical parameterization of convective phenomena

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Abstract

In the restricted area physical-mathematical models, the physical parameterization of convective phenomena plays a key role. In this work, the extreme weather event of 25\textsuperscript{th} November 2016, occurring in Sicily, is considered as case of study. The heavy rainfalls recorded in this event were caused by cloudy systems of convective nature. For this reason, the performance of the restricted area physical-mathematical model, optimized for complex orography areas, has been tested varying the physical parameters of the convective phenomena. Performance were evaluated using appropriate verification methods.

Keywords: Weather Research and Forecasting model, Physical Parameterizations, Cumulus Parameterization.

Introduction

The central issue related to the condensation and evaporation processes is the convection phenomena. Convection influences the environment by diabatic heating and cooling due to the condensation, evaporation, formation and melting of ice through vertical flows of sensitive heat, humidity, and momentum and through horizontal pressure field disturbances.

Therefore, the parametrization of convective phenomena plays a fundamental role for a good simulation of the atmospheric dynamics. Physical processes associated with condensation of water vapor are essentially non-linear, so their overall effect can directly affect large-scale circulation. However, most of the convective clouds, where condensation processes take place, have horizontal dimensions ranging from 0.1 to 10 km, typically smaller than those the spatial grid usually account in restricted area models. Therefore, there is therefore a typical sub-grid phenomenon, which must be parameterized in terms of prognostic variables.

Physical parameterization of convective phenomena:

In order to parameterize convective phenomena it is necessary to consider the statistical behavior of convective cloudy systems which are influenced by different large-scale conditions. Before tackling this problem it is important to introduce the potential temperature equation $\theta$, defined as follows:

$$\theta = T \left( \frac{p_0}{p} \right) \frac{\theta}{\theta}$$

where $T$ is the temperature, $p$ is the pressure, $p_0$ is the ground pressure, $R$ is the gas constant for dry air and $c_p$ is the specific heat at constant pressure. In formulating the collective effect of convective cloud systems, one should consider a "closure problem" in which a limited number of equations that govern the statistics of a huge system are searched. The most important aspect is the choice of the appropriate system shutdown conditions. A first classification of these conditions can be provided starting from the equilibrium equations of the potential temperature $\theta$ and the specific humidity $q$, which represents the ratio between the water vapor mass and the fluid particle total mass on large scale of pressure coordinates [2]

$$c_p \left[ \frac{\partial \tilde{\theta}}{\partial t} + \bar{v} \cdot \nabla h \tilde{\theta} + \bar{\omega} \frac{\partial \tilde{\theta}}{\partial p} \right] = \left( \frac{p_0}{p} \right) \kappa_{\theta} Q_1$$

$$L \left[ \frac{\partial \tilde{q}}{\partial t} + \bar{v} \cdot \nabla h \tilde{q} + \bar{\omega} \frac{\partial \tilde{q}}{\partial p} \right] = - Q_2$$

where the marked variables indicate a large scale average and $Q_1$ and $Q_2$ are respectively the heat source and the moisture well. All the other symbols have the standard meaning.
that take in literature. To simplify, it is possible to express these two equations respectively as:

\[
\frac{\partial T}{\partial t} = \left( \frac{\partial T}{\partial t} \right) + \frac{1}{c_p} Q_1
\]

\[
\frac{\partial q}{\partial t} = \left( \frac{\partial q}{\partial t} \right) - \frac{1}{L} Q_2
\]

where:

\[
\left( \frac{\partial \bar{T}}{\partial t} \right) = - \left( \frac{\partial \bar{T}}{\partial t} \right) \frac{R}{c_p} \left( \bar{v} \cdot \nabla \bar{\theta} + \bar{\omega} \frac{\partial \bar{\theta}}{\partial p} \right)
\]

\[
\left( \frac{\partial \bar{q}}{\partial t} \right) = - \left( \frac{\partial \bar{q}}{\partial t} \right) \frac{R}{c_p} \left( \bar{v} \cdot \nabla \bar{q} + \bar{\omega} \frac{\partial \bar{q}}{\partial p} \right)
\]

To solve this system of two equations it is necessary to have at least two types of closing conditions among the three possible choices [3]

- Coupling of terms \( \frac{\partial T}{\partial t} \) and \( \frac{\partial q}{\partial t} \)
- Coupling of terms \( Q_1 \) and \( Q_2 \)
- Coupling of terms \( Q_1 \) and \( Q_2 \) with the two terms \( \frac{\partial \bar{T}}{\partial t} \) and \( \frac{\partial \bar{q}}{\partial t} \)

The first choice is equivalent to assume a condition on the variation time of the system state (on a large scale) and is usually achieved by imposing a balance state condition.

On the other hand, the coupling of source terms is a condition for the humid-convective processes and is usually present in the form of a cloud parameterization model. The combination of these two types of closure represents the methodological basis for those parameterization schemes known as 'adjustment schemes', like Arakawa and Schubert [4] and Betts and Miller [5] schemes. The third type of choice requires a direct coupling between large-scale circulation and humid-convective processes. It represents the starting point for many schemes, such as the Kuo [7] and Anthes [8] schemes and, starting from the Fritsch and Chappel [9] scheme, the Kain Fritsch [10] scheme.

### Case of study 25th November 2016

This case of study involves the extreme weather event recorded in Sicily on 25 November 2016. In that event, the heavy rainfall recorded by the network of weather stations of the Sicilian Civil Protection Department (DRPC) was caused by a purely convective systems cloudy. For this reason it was considered appropriate to perform a re-analysis test to analyze and understand which physical parameterization of the convective phenomena provided the best performance. In particular, the Weather Research and Forecasting (WRF) model has been optimized for complex orography territories [1]. Simulations with spatial domains of 5km and time resolution were performed. The following physical parameters for convective phenomena have been considered:

- **CU0**: Explicit convection
- **CU1**: New Kain Fritsch
- **CU2**: Betts – Miller - Janic
- **CU3**: Grell-Devenyi
- **CU5**: Grell 3D
- **CU6**: Tiedtke
- **CU14**: New Simplified Arakawa – Schubert

In the first analysis, the extrapolation of the rainfall accumulations recorded by the 13 weather stations examined was carried out. The choice of meteorological stations has been done accounting for the spatial localization of the extreme recorded meteorological event. In particular, the following stations have been chosen as reference: 5 stations in the north of Sicily (Castelbuono, Lascari, Pettineo, Polizzi and Cefalù), 4 in the northeast sector (Antillo, Fiumedinisi, Linguaglossa and San Pier Niceto) and 4 in the south-west (Bivona, Giuliana, Ribera and Sciacca).

Subsequently, using the restricted area model the rainfall data for each simulation in which only the physical parameterization of the convective phenomena were modified, have been calculated. These data were compared with the observed data, as shown in Figure 1:

![Figure 1: Observed rainfall data (24H Rain mm) and predicted by the WRF varying the physical parameterization of convective processes.](image)

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Performance Testing Method:
In order to establish which of the simulations provided the best performance, it is necessary to use statistical methods. The performance of a forecast model can be calculated using one or more scalar verification indices. A possible method to obtaining these indices is provided by the dicotomic predictions, yes/no. In order to calculate these indices it is necessary place the data in a table of I x J elements, called "contingency table", which contains the absolute frequencies of all possible combinations of the observed and predicted data pairs. Considering the case I = J = 2, as shown in Figure 2, a indicates the number of cases in which the event was expected to occur and its actually happening, b is the number of cases in which the event was expected to happens but it did not occur, c represents the number of cases in which the event occurred but was not expected and finally d represents the number of cases in which the absence of the event was properly scheduled.

Figure 2: Contingency Table Schedule

Dividing by \( N = a + b + c + d \), it is possible to obtain the combined distribution of prediction relative frequencies and the observed data; a perfect forecast have zero values only for the elements on the diagonal of the table. From the contingency table it is possible to define the categorical indexes used to quantify the yield of the simulations performed with this model, in particular:

- **Hit rate**: defined as the ratio between the number of cases in which the event was correctly predicted and the total number of cases considered, \( n \). The value 0 indicates a bad forecast, on, the value 1 indicates a perfect forecast.

- **Threat score**: is an alternative to the hit rate, useful when the event considered has a substantially lower occurrence frequency than non-occurrence. If the threat score assumes the value 0, the forecast will be bad, otherwise, if it assumes the value 1, the forecast will be perfect.

- **Bias**: It represents the ratio between the predicted and observed data average.

- **False Alarms Rate**: is designed to highlight the tendency to predict events that will not happen. It is especially useful to verify the prediction ability of extreme events. If it assumes the value 0, the forecast will be perfect, if it assumes value 1 there will be the prediction of events that will not happen.

- **Equitable Threat Score**: is based on TS. By definition ranging from -1/3 to 1 (perfect prediction)

- **Hanssen-Kuipers Discriminant**: is given by the ratio between the events correctly predicted and those actually occurred less the probability of having a false alarm. By definition ranging from -1 to 1 (perfect prediction)

Figure 3 shows the index values obtained for the case considered:

<table>
<thead>
<tr>
<th>Accuracy</th>
<th>CU0</th>
<th>CU1</th>
<th>CU2</th>
<th>CU3</th>
<th>CU5</th>
<th>CU6</th>
<th>CU14</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>0.53</td>
<td>0.45</td>
<td>0.54</td>
<td>0.53</td>
<td>0.51</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>0.49</td>
<td>0.43</td>
<td>0.12</td>
<td>0.38</td>
<td>0.35</td>
<td>0.30</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>1.47</td>
<td>0.49</td>
<td>1.13</td>
<td>1.07</td>
<td>0.91</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>0.22</td>
<td>0.04</td>
<td>-0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>0.64</td>
<td>0.74</td>
<td>0.16</td>
<td>0.58</td>
<td>0.54</td>
<td>0.44</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>0.50</td>
<td>0.67</td>
<td>0.48</td>
<td>0.50</td>
<td>0.51</td>
<td>0.51</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

The analysis shows that the explicit resolution of convective processes (\( CU = 0 \)) is the most reliable and accurate solution with the highest accuracy in term of Threat Score and Equitable Threat score. The Betts-Miller-Janic scheme (\( CU = 2 \)) is the worst and is the one that also generates the highest number of false alarms (FARs).

The New Simplified Arakawa-Schubert (\( CU = 2 \)) and Tiedtke (\( CU = 6 \)) schemes are only slightly better than the BMJ (\( CU = 2 \)).

New Kain Fritsch schemes (\( CU = 1 \)), Grell-Devenyi (\( CU = 3 \)) and Grell 3D (\( CU = 5 \)) show only small differences and they are the only ones that tend to
overestimate the rain.
The New Kain Fritsch scheme ($CU = 1$), excluding an excessive BIAS overlapping, has good overall behavior and is the one that shows the maximum POD (Probability Of Detection).

References


Numerical simulation of heavy precipitation event occurred in Sicily with WRF model: the role of the Planetary Boundary Layer in the development and evolution of convective storms.

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Abstract

In meso-scale meteorological models, such as the Weather Research and Forecasting (WRF), the choice of the planetary boundary layer (PBL) scheme can significantly affect spatial distribution and forecast precipitation quantities. In order to test the behavior of three different PBL schemes among the most commonly used, a study was conducted during a severe convective event that occurred on Sicily on 25 November 2016. The event was simulated using the WRF-ARW model, configured with three different PBL schemes: the Yonsei University (YSU) scheme, the Mellor-Yamada-Janjic (MYJ) scheme and the asymmetric convex model (ACM2) scheme version 2.

Keywords: Numerical weather prediction, precipitation forecast, heavy precipitations, Boundary layer parameterization, convective storm.

Introduction

One of the most important causes of meteorological forecast error in mesoscale models is the low troposphere kinematic and thermodynamic structures modeling [1]. The accurate representation of these structures is crucial in improving the prediction of extreme meteorological phenomena, as the model output can provide useful information to assess whether the conditions necessary for the development of such phenomena could either be or not satisfied [2]. In fact, the development of a thunderstorm requires minimum conditions which includes high values of moisture, upstream currents, moderate or strong atmospheric instability and a vertical wind shear. Furthermore, the intensity of a storm system depends strongly from the moisture present in the low layers and the heat provided by the soil. The moisture and heat vertical transport is determined by the PBL physical characteristics. The PBL is defined as the lowest portion of the troposphere that is directly affected by the Earth’s surface and that responds to the surface forcings with scale rates of one hour or less. These forcings include the wind friction, the evapotranspiration, the processes of momentum exchange as well as of heat and water vapour. During heavy storms, the vertical extension of convective motions affects the whole troposphere and therefore it is impossible to clearly distinguish the top of the PBL [3]. An important property of turbulent flows is that they can carry momentum, energy and mass quantities. In the boundary layer, the dominant direction of turbulent transport is the vertical one due to the strong vertical gradients that are near the surface. Therefore, the turbulent nature of the flows within the planetary boundary layer is responsible for the effective exchange of momentum, sensitive heat and water vapor. In detail, the transport of the latter means transporting energy, which is the latent heat released during the condensation. Consequently, the moisture transport is equivalent to latent heat transport. These turbulent flows evolve and act on space-time scales that cannot be explicitly represented on the scales and time intervals used in most of the middle-scale models. For this reason their effects are expressed by PBL parameterization schemes [4]. In this paper, three of the PBL schemes most commonly used in the meteorological centers that uses the WRF model have been tested. During the simulations, the only modified parameter is the PBL scheme, in order to conduct a comparative analysis of the 24 hours precipitations and the spatial distribution.
Preparation and description of the numeric simulation

High-resolution numerical models are needed to accurately simulate mesoscale processes or smaller scales such as storms. The spatial domain on which the tests were conducted covers the whole territory of Sicily with a grid of 120x90 cells and 4 km of grid-spacing obtained by one-way nest from a parent domain with 100x100 grid and 12 km of grid-spacing and 42 vertical levels (Fig.1).

Figure 1: Main domain and nest

For the initialization of the model and boundary conditions were used the 00:00 UTC GFS global model data on 24.11.2016 with 0.25 degree of resolution. The data forecast by WRF during the first 24 hours were not used in the experiment and were used as the model roll-out phase, while the data expected between 00:00 (T+24) and 24:00 UTC (T+48) on November 25 were used to analyze and calculate the variables subject of study. In this work, similarly to other studies conducted in other parts of the world are compared local, non-local, and hybrid PBL schemes with closure patterns of 1 and 1.5 turbulence order. Therefore, our choice took into account the first-order non-local scheme developed by Yonsei University (YSU), the local pattern with closure order 1.5 Mellor-Yamada-Janic (MYJ), and the hybrid scheme with first-order closure Pleim (ACM2).

Data analysis

In the spatial distribution of the precipitations produced by the event in examination, three relative maxima are present (Fig. 2): the first one located along a band of territory oriented from SW to NE, whose maximum values have been recorded in the more southern coastal area; the second one located along the north-eastern coastal band and finally a third, whose values result inferior to the above described, located along northern coast. In order to carry out comparisons, the data from 13 stations of the Sicilian Observatory Regional network were used (Fig.2). Four of these (Sciacca, Bivona, Ribera and Giuliana) fall into the center-west region where the first peak was reached, five stations fall along the northern coastline affected by medium intensity precipitations and the remaining four (Linguaglossa, Antillo, San Pietro Niceto and Fiumedinisi) fall into the eastern territory that was affected by the second peak.

The first type of verification carried out was about the total accumulation in 24 hours observed by the stations and compared with the forecast data obtained, using the 3 PBL schemes, in the closest grid point. For convenience, the data was divided between southern side (Fig.4), north side (Fig.5) and east side (Fig.6).
Discussions

Spatial distribution analysis

The compared analysis of the forecast precipitation fields obtained using the three PBL schemes, shows a general failure of all PBL schemes along the southern coast of Sicily (Fig. 7). The flood affected the area of Bivona and Sciacca has not been forecast at all by the numerical model. In this case, the bad performance could be due to the unforecast and rapid V-shaped storm development that produced so high quantity of precipitations and damages in the whole area. The performances are generally better for the north-eastern coast, where the maximum of rain occurred has been well forecast as well the secondary maximum of rain occurred along the northern coast. Each PBL scheme shows anyway difference both in quantity of rain and in spatial distribution.

24 hours accumulation verification

The verification of model predicted precipitation has been performed using the neighborhood-based verification. For all stations and for all PBL schemes it shows a big difference between observed and forecast 24 hours rain accumulation. In the southern area of Sicily (Fig. 4), the WRF has strongly underestimated the precipitations and the performance obtained by each PBL schemes are really poor. The same verification carried out for the north-eastern stations of Linguaglossa, Antillo, San Pier Niceto and Fiumedinisi (Fig. 6) shows better performance. Here, the forecast obtained using the ACM2 scheme results to be overestimated for all stations. Moreover, the rain forecast in San Pier Niceto, results to be overestimated by all the PBL schemes. This could be explained because the geographic position of the station, positioned on the Tyrrhenian coast slope, leeward the south-eastern main wind stream [5]. The compared forecast accumulations shows generally better performance for ACM2 scheme, followed by YSU and MYJ. Finally, the verification performed on the weather stations of the northern coast (Fig. 5), shows the best general performance. The 24 hours accumulation forecast for Castelbuono and Polizzi reach almost the 100 percent of the values of observations. Despite the good general performance, none of the PBL schemes result to be better of the others, but all produce about the same results.
Conclusion

The WRF meteorological model has been used to analyze a severe weather event occurred in Sicily on 25 November 2016 in order to evaluate the role played by PBL schemes in the forecast of convective systems. The PBL schemes tested during this case study have been the Yonsei University (YSU), the Mellor-Yamada-Janjic (MYJ) and the version 2 of the convective asymmetric scheme (ACM2). These schemes have been selected because each of them use a different physic description of the turbulent transport. The precipitation fields forecast by WRF using the three PBL schemes, have been compared with the map of observed precipitations obtained by Regional Department of Civil Protection. Significant differences were quite clear especially in the North-East sector, because the PBL scheme used. Using the precipitation data observed by all the weather stations we have evaluated the PBL schemes using statistical index. We obtain that in this case the best performance were obtained by MYJ scheme. The aim of the study was to understand the influence that the only PBL parameterization has in forecasting heavy precipitation and to show how important is its choice. Difference of 160 mm in 24 hours, obtained just changing the PBL scheme, demonstrate that the choice of each parameterization of WRF model should be always carefully assessed for each geographic domain where it runs.

References


Bi Nanoparticle preparation by Laser Ablation for X-Ray imaging and Radiotherapy

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Abstract

Bi nanoparticles were obtained by laser ablation in water and characterized by using different physical techniques (Raman, UV-VIS, XRD and EDX). Their shape, estimated by SEM measurements, was approximately spherical with a diameter of about 25 nm, and a solution concentration of about 1 mg/ml was prepared. The high Z of the nanoparticles in the solution shows effects of surface plasmon resonance, high mass absorption coefficient for X-ray interaction and high electronic and nuclear stopping powers for electron and ion beams. Such biocompatible solution can be injected in living systems, such as mice, in order to study the presence of up-take in different organs with high contrast spatial localization in the tissues where nanoparticles are confined. The results indicate that nanoparticles can be employed as high contrast medium for high resolution imaging in biological systems as well as target for exposition to ionizing radiation during radiotherapy or to visible light during thermal therapy of diseased cells.

Keywords: Laser, plasma, ion source, implantation, accelerator.

Introduction

The main purpose of radiotherapy is to maximize the dose of radiation delivered to the tumors and at the same time minimize the level of harm to the surrounding healthy tissues by reducing the dose they receive. The methods used to achieve this goal were mainly focused on the use of the latest technologies and computers, such as modulated intensity radiotherapy (IMRT) and volumetric modulated bowel therapy (VMAT). A complementary approach to potentially reaching this aim involves the localization of high atomic number (Z) elements and compounds in target tumor tissue prior to irradiation. The presence of high Z atoms in the target leads to an increase in the cross-section of the photoelectric effect and the generation of low-energy free radicals (photoelectrons and electrons Auger). These low energy free radicals have elevated linear energy transfer rates (LET), and as a result can cause DNA damage through the generation of reactive oxygen species. Moreover, it has recently been reported that metallic nanoparticles chemically sensitize DNA molecules and make them more susceptible to radiation damage. If the cell sustains sufficient DNA damage it may compromise its ability to replicate and / or activate cell death paths. This line of inquiry began with the use of iodine compounds of the type normally used as contrast agents for radiology imaging. Recently, metallic nanoparticles (NP) have been used for this purpose [1]. NPs have several advantages over iodine since they have a higher Z number and thus a greater likelihood of photoelectric interactions, which is approximately dependent on Z; accumulate more readily and to a greater degree in tumor tissue, and sensitize DNA molecules. One of the metal most recently used for dose improvement is bismuth (Bi) [2-3]. Bismuth is a pentavalent post-transition metal, it has an atomic number of 83, it is a brittle metal with white color when freshly produced, but its color turns pink as a consequence of the surface oxidation. Bismuth compounds are used in cosmetics, as pigments, and a few pharmaceuticals, notably bismuth subsalicylate, are used in medicine to treat certain for different purposes. Even if bismuth is an heavy metal, it has an unusually low toxicity. Bismuth, as a dense element of high atomic weight, is used in bismuth-impregnated latex shields to shield from X-ray in medical examinations, such as TC, mostly as it is considered non-toxic. The mass absorption coefficients of X-ray and the stopping power for electrons and ions versus the energy shows a significant increase of the values for heavy Bi element demonstrating the best behavior for its use as contrast medium and as targeting elements in biological cancer tissues for appropriate radiotherapy exposures [4]. Several nanoparticulated TC contrast agents are based on iodine, gold and silver nanoparticles, core-shell iron oxide / tantalum oxide nanoparticles and others alloy nanoparticles [5-6]. Nanoparticulated TC contrasts bearing bismuth, in particular bismuth sulphide nanoparticles, have received special attention due to a combination of low price, low tox-
icity and high x-ray attenuation coefficient.

Materials and Methods

Metallic bismuth nanoparticles (Bi-NPs) were prepared using the technique of the pulsed laser ablation in liquids. A Nd:YAG laser was employed at 1064 nm wavelength, 3 ns pulse duration, 100 mJ maximum pulse energy, 1 mm² focused spot and 10 Hz repetition rate. The metal, as sheets of about 3 cm² surface and 1 mm thickness, was placed on the bottom of a glass beaker. A volume of 5 ml of distilled water was added and 1 µg of tensioactive was employed as stabilizer in order to avoid fast particle coalescence. Using 70 mJ pulse energy and an irradiation time of 10 min and covering the Bi sheet surface with 4 mm liquid, the ablated mass was of 4 mg, thus in these conditions a solution concentration of 4 mg/5 ml, that is 0.8 mg/ml, was obtained. The ablation yield, in terms of removed mass per laser shot, was controlled by the laser fluence and solution concentration, because the increment of the laser fluence enhances the ablation yield while the high solution concentration absorbs laser energy and decreases the ablation yield. Generally we use an exposition times of the order of 20 min. A scheme of the used set-up is reported in Figure 1a. The Bi laser ablation in water was evaluated in term of removed mass per laser shot as a function of the laser pulse energy, as reported in Fig. 1b. Fig. 1c shows the Bi-NPs in water after 10 min of laser irradiation time (C=0.8 mg/ml). The removed atoms in the laser-generated plasma and in the water environment condense in nanometric particulate. The nanoparticles tend to aggregate forming micrometric nanoparticles but the presence of the tensioactive liquid stops the aggregation phase. The produced solution of Bi-NPs in water changes color during the laser ablation from white transparent to white opaque, to brown and to dark brown color at high concentration. The Bi-NPs were characterized at the Department of Physics Sciences of Messina University (MIFT) laboratories and at the Messina IPCF CNR ones by using FESEM microscopy, X-rays, UV-Vis absorption. In particular the bismuth nanoparticle solutions were diluted with water before taking the UV-Vis absorption spectra. Deionized water was used as reference. To observe the Bi-NPs morphology and composition a drop of the resulting solution was dried onto a silicon or glass substrates and a field emission scanning electron microscope (FESEM), operating at 1.5 and 3.0 kV. The prepared Bi-NPs were injected in specific organs of living systems (mice) and their spatial location and contrast were controlled using the fluorescence induced by a (20 ± 45) kV X-ray tube of the Bruker-in vivo MS-FX PRO system.

Results

The presence of the metallic nanoparticles in the solution induces surface plasmon resonance (SPR) absorption effects showing absorption wavelength bands depending strongly on the particle shape, dimensions, concentration and nature of liquid medium. The resonant absorption is due to the light induction of dipole and electron oscillations on the surface of the metallic nanoparticles. Fig. 2 reports the UV-Vis absorption spectrum of the diluted aqueous solution of Bi-NPs containing the tensioactive stabilizer. It shows a poorly resolved shoulder at about 269 nm; this feature can be assigned to the SPR absorption peak of the Bi NPs that gradually broadens as the size of Bi NPs decreases. Since the Bi clusters with diameter below 10 nm do not show any SPR absorption band, while the larger nanoparticles (> 100 nm) show a strong absorption peak at about 280 nm [7], our spectrum seems to indicate that the Bi-NPs shape is a sphere, with a diameter greater than 10 nm but smaller than 100 nm, in agreement with the SEM.
Fig. 2: Absorbance measurements vs. wavelength for the Bi-NPs solution in water

Fig. 3 (a, b, c, d) report a lot of SEM images of the Bi-NPs deposited with the solution on the Si substrate after prolonged drying (6 h). The nanoparticles have spherical shape with a diameter distribution going from about 10 nm to 100 nm and an average value of about 25 nm. The use of Bi-NPs as contrast medium in living tissues was tested in mice injecting the prepared biocompatible solution in some organs and observing the Bi fluorescence image induced by the Bruker X-ray tube.

Fig. 4a shows the image when the solution was injected in the heart. The image shows very well the organ (observed in dark gray scale such as X-ray transmission) and the nearest blood irrigated tissues as very bright due to the X-ray induced fluorescence. Fig. 4b reports the image when the solution was directly injected directly in the Sx kidney. The image illustrates very well the organ (observed in gray scale such as X-ray transmission) and the nearest blood irrigated tissues are very bright due to the X-ray induced fluorescence. The obtained medical images are well contrasted and the interested organ shows high spatial resolution of the zones where the Bi-NPs are localized. The aim of the study was to distinguish the interested organ in order to be observed in detail before that a successive radiotherapy procedure can be applied on the diseased tissues.

Figure 3: SEM photos of the dried Bi-NPs deposited on a silicon surface (a, b)

Figure 4: X-ray fluorescence image showing the Au-NPs for an injection of solution in heart(a) and Sx kidney(b)

Discussion and Conclusions

Due to the high-Z of the Bi element, the high X-ray absorbance in the tissues containing this element, the high stopping power of electron and ion beams, the high UV absorption and the high fluorescence yield induced in such structures, permit to use them as a probe to localize the oligoelement in biological tissues. Thus the fluorescence imaging technology is one of the main methods used in the study of molecular events in vivo and has important applications in life science research. The results have showed that the Bi-NPs have good biocompatibility and safety, and does not affect normal organ functioning. Mice are alive after injection of the solution in the blood-
stream through the tail vein. Measurements of the Bi-NPs up-take and decay are in progress.

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**References**


Dynamical investigation of cavitation bubble following pulsed laser induced damage on Ag target

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Abstract

Pulsed-laser assisted nanoparticle synthesis in liquids (PLAL) is a versatile tool for colloidal nanoparticle synthesis with ligand-free surfaces. The chemical-physical properties of the prepared nanoparticles are strongly dependent on the plasma expansion and cavitation bubbles in the liquid but some aspects of nanoparticles formation are poorly understood. It is generally accepted that the laser-induced cavitation bubble plays a significant role in nanoparticles formation. In this work, the initial growth and collapse stages of bubbles after pulsed laser ablation of a 3D silver target in water were investigated. The cavitation bubble dynamics results different using a high purity-flat and a rough-damaged silver target where the roughness is induced by a treatment of the target surface by means of the 1064 nm line of a nanosecond pulsed laser. Even if cavitation bubble dynamics significantly changes, the ablation efficiency remain almost unchanged.

Keywords: Pulsed Laser Ablation in Liquid, Cavitation Bubble, Shadowgraphy.

Introduction

Pulsed laser ablation in liquids (PLAL) is a versatile technological approach to produce a large variety of nanoparticle colloids. It is a low-cost method because chemical precursors are replaced by bulk materials, other expensive chemicals are rarely used and manual operation and the experimental set up are minimal. These features improve reproducibility of the synthesis and the biocompatibility of the products [1, 2]. It is well known that plasma expansion and cavitation bubbles dynamics strongly influence the nanoparticles properties, mainly in terms of dimensions and size distribution. However, being a multiscale process in which many phenomena are involved, it is particularly difficult to resolve a functional relationship between them. Initially, a laser pulse interacts with a bulk target, creating a hot and dense plasma. The subsequent rapid expansion process results in plasma quenching and in a shock wave emission that leads to a bubble formation and expansion for a sub-millisecond time scale, until energy is dissipated and the bubble collapses [3, 4]. Among the different mechanisms involved, the laser-induced cavitation bubble plays a significant role and acts as a kind of nanoparticle reactor in which the nanoparticles are formed. The reaction conditions inside the bubble nanoparticle are strongly time-dependent and cover a broad temperature range during expansion and shrink phases, reaching $10^4$ K and $10^4$ Bar [5]. Then, the observation of bubble dynamics throughout the entire process can help to understand its role in the nanoparticle formation mechanism [6]. In this work, we present and discuss the results obtained following the cavitation bubble dynamics ablating a flat and a rough-damaged silver target. To this purpose, we developed a custom designed shadowgraphy system with a flow ablation chamber in which it is possible to exchange the liquid between two pulses, avoiding the screen effect due to nanoparticles scattering and absorption of the laser light. A correlation between the cavitation bubbles dynamics and nanoparticles ablation efficiency is studied.

Methods and materials

Fig.1 shows the setup used for cavitation bubble imaging. In this setup, a nanosecond-pulsed laser has been focused on a Ag target placed inside a custom made ablation chamber that is filled by Milli-Q water. The light source and the camera used for the acquisition of bubble images are placed in a direction parallel to the sample surface. The laser for the ablation is a Nd:YAG ns-laser pulse with a Gaussian beam profile (Innolas SpitLight DPSS250-100) operating at 1064 nm wavelength, 9 ns pulse duration, 0.1 Hz repetition rate and at 20 mJ
energy pulse. The measured laser spot diameter is around 0.4 mm.

![setup](image)

**Figure 1:** *Photo of the setup used for bubble image acquisition.*

The setup for shadowgraph measurements consists of a white LED source, the water chamber, a CCD camera with a teleobjective to collect the shadow of the bubble, a filter for cut-off the scattered laser light and a pulse generator to synchronize the camera with laser pulses. Shadowgraphy image are taken by a Basler acA1600-60 with a gate time of 10 µs and an intrinsic delay of 43 µs; hence we collected a picture for every laser pulse, changing the delay of the camera. The water layer above the target was 5 mm and it was continuously refreshed during ablation by means of a peristaltic pump that run maintaining a constant flow of 25 ml/min. In this way during experiments the particles produced from ablation flow out from the chamber and the experimental conditions are maintained the same for every pulse. Accumulation of persistent gas bubbles is minimized by a vertical, upward flow of the liquid, while the laser beam is coupled horizontally.

**Results and discussion**

The temporal resolved shadowgraph images of the cavitation bubble produced during the laser irradiation of a flat 3D Ag target are shown in Fig. 2. The bubble is formed immediately after the laser pulse irradiation, it expands reaching its maximum size at around 100 µs and then shrinks to collapse after 200 µs from the laser irradiation. The first bubble, formed in the 53-173 µs delay time, shows a well-defined and sharp boundary. The second bubble emerges after the collapse of the first one (in the 213-253 µs delay time). Then, the process repeats several times. After the first collapse, rebounds of smaller bubbles with irregular shapes are observed.

An appropriate description for such a motion is made by the Rayleigh-Plesset equation which takes into account the bubble radius change as a function of time:

$$R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} \left( P_B(t) - P_l - \frac{2\sigma}{R} - \frac{4\eta \dot{R}}{R} \right)$$  \hspace{1cm} (1)

where \( R, P_B, P_l, \sigma, \rho, \) and \( \eta \) denote the bubble radius, the internal pressure, the surrounding liquid pressure, the fluid surface tension, the liquid mass density and the dynamic viscosity of the liquid, respectively [7].

Target exposure to the laser beam determines a change in the surface of the target as a result of material removal. These changes are more evident upon increasing laser shots number. It is known that the efficiency of nanoparticle productivity is influenced by focusing conditions which changes as the material is removed. However, also the cavitation bubbles dynamics emerging from the laser-ablated target could be remarkably modified. Then, it was considered interesting to study the cavitation bubbles dynamics involved during the ablation of a rough-damaged target. So, we stroked the target in the same point with 1000 laser shots, creating a crater on the surface of our target, then we follow the cavitation bubble dynamic expansion as already done for Ag flat target. In this case, an irregular shape is already visible as soon as the first bubble expands (from 53 up to 93 µs). Otherwise, in the shrinking phase (from 113 to 153 µs), the dynamic occurs in a completely different way: the bubble seems to be composed by a trapezoidal section near the target surface and an hemispheric feature above it (see Fig. 3).

![bubble dynamic](image)

**Figure 2:** *Dynamic evolution of cavitation bubble when the laser is focused on a flat target surface.*
Moreover, the lifetime of the first bubble is also reduced respect to what observed for the undamaged target (the lifetime decreases from 200 down to 170 µs). A material rebound on the crater edge is also visible. On the overall, bubble shape results quite different in the two investigated cases. This behavior could be explained in terms of hydrodynamic effects during the bubble expansion [8]. However, even if preliminary, such evidence is important to provide precise information about single reaction steps occurring during the ablation process.

Now, in order to investigate the influence of the cavitation bubble dynamics on the nanoparticles ablation efficiency we analyzed, by a 3D confocal microscope, the crater profiles obtained for several number of laser shots (10, 50, 100, 250, 500, 1000). In Fig. 4 is shown the crater depth obtained after the target exposure at 250 pulses. Analyzing the crater profile, the ablated mass was quantified. We found that the ablated volume increases linearly as a function of the pulses number (from 15 µg for 10 pulses up to 928 µg for 500 pulses). Hence, within this range of depth, no significant change in the ablation efficiency was observed. However, the observed bubble dynamics changes could influence Ag nanoparticles morphological properties in terms of size and distribution. A systematic study of nanoparticles properties is necessary to better understand all these mechanisms.

Conclusion

In this work, a custom designed setup with a flow ablation chamber was used to examine cavitation bubble dynamics in laser ablation of silver target in water. Cavitation bubbles, generated by a laser pulse, undergo several repeated expansions and shrinkage. Moreover, we have observed that, during the ablation process, the target surface is reached several times by the laser beam and this causes target inhomogeneities. These latter influence cavitation bubble shape and dynamics. Particularly, we found that the cavitation bubble dynamics results different using a high purity-flat and a rough-damaged silver target. Even if cavitation bubble dynamics significantly change, the ablation efficiency remain almost unchanged.

References


Moment tensor inversion of the 1978 Ferruzzano earthquake (Southern Italy) by analog historical seismograms

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Abstract

The knowledge of historical earthquakes is crucial for understanding regional tectonics and seismic hazard. The more recent developments concerning moment tensor inversion of modern seismograms and processing of old recordings offer the opportunity to estimate source parameters of historical earthquakes. This study shows the methodology and the results of complex analog seismic data modeling and the analysis of the earthquake occurred in Southern Italy on 11 March 1978. We re-analyzed this event applying a modern-standard time-domain analysis to the original analog data to determine the focal mechanism, the depth and the seismic moment. Our focal mechanism solution shows a normal faulting (strike $185^\circ$, dip $69^\circ$, rake $-86^\circ$) in a very good agreement with the study area seismotectonic frame.

Keywords: Historical seismograms, moment tensor inversion, waveform analysis, Southern Italy.

Introduction

Southern Italy represents one of the most interesting sector of the Mediterranean region both for the several destructive earthquakes (e.g. 11 January 1693, I=XI MCS $M_w=7.4$; 5 February 1783, I=XI MCS $M_w=7.1$; 28 December 1908, I=XI MCS $M_w=7.1$, [1]) occurred in the last centuries and for the geodynamic framework characterized by the transition between the compressive domain, due to the NW-SE convergence Nubia-Eurasia, and the extensional domain due to the southeastward rollback of the Ionian lithospheric slab. Both the activation mechanisms of the several strong earthquakes and the description of the regional seismotectonic and geodynamic frame are strongly debated in the literature.

High energy earthquakes ($M>5$) are direct expressions of the regional scale processes hence they are a key information for understanding the complex seismotectonic processes, the regional strain release and for characterizing seismic hazard of the study area [2]. Only a small number of moderate-to-strong earthquakes were recorded in Southern Italy in the last thirty years (recording period of modern standard broadband seismometers) while, numerous earthquakes with $M>5$ were occurred in Southern Italy in the early seismic instrumental times 1900-1980 [3]. These events are mainly unexplored because of the limits of data management and analyze techniques. The most recent development about the waveform inversion technique [4–6] and a more accurate knowledge of the recording parameters of old instruments allow to explore these historical events by using data coming from the seismographs operating since the beginning of XX century.

This study shows the methodology of complex analog seismic data analysis and the result obtained for the earthquake occurred in Calabria (Southern Italy) on 11 March 1978, prior to the installation of the global digital seismic network. Contrasting and poor resolved solutions of this event have been reported in the literature[7, 8]; it is therefore interesting to analyze it by one of the most recent technique of waveform inversion for historical earthquakes [5, 6]. With this study we also test, for the first time on an italian seismic event, the method performance.

The 11 March 1978 earthquake ($M_w=5.2$), know as Ferruzzano earthquake, were recorded by more than hundred seismic stations [9] but the instruments operating at the time were analog mechanical pendulums writing on paper, especially. With the aim to test the methodology for studying the Italian historical earthquake, the choice to explore an event occurred in the late 1970’s has been guided by a major knowledge of the technical features of the seismic stations operating at the time. In the early 1960’s the deployment of the World Wide Standard Seismograph Network (WWSSNN) equipped by highly sensitive electrodynamic sensors with galvanometric amplified recordings on paper allowed homogeneous global data coverage. But the real breakthrough came only in the 1990’s with the development of high resolution digital broadband recordings with large dynamic range.
Data collection and waveform inversion method

We collected for the Ferruzzano earthquake 25 original analog seismograms from 17 seismic stations equipped with three component long- and short-period instruments. Most of the records have been collected from stations located in Europe because they were preserved in the best condition and were most easily accessible. The availability of historical records has been improved thanks to the SISMOS database [10, 11] that collected and scanned original seismograms of Italian historical earthquakes. Because the period band of long-period seismograph records is more suited for the earthquake analysis only 11 seismograms could be used. Also not all records have enough high quality for successful vectorialization, digitized seismograms often have steps and distortion due to the writing mechanism. The information of the instruments (free period, damping and magnification, the component orientation), that were documented manually, sometimes do not fully correspond to the real values or are not available, so biasing the restitution to true amplitudes of the seismic records. For this reason only 8 seismograms from six stations have been digitized.

Figure 1: Recording geometry for digitized historical seismograms of the 11 March 1978 earthquake. The black triangles and the red star indicate the stations and epicenter locations, respectively.

Figure 1 shows the station geometry for digitized seismograms. For TRI station three components of motion are preserved, while for EBR only single horizontal trace is available and for all the other stations just vertical traces are obtained. It is obvious that considerable azimuthal gaps were left but for an historical earthquake this amount of data is very valuable. Each of these seismograms have been digitized manually using the tool of GIMP (GNU Image Manipulation Program) by redrawing the whole traces and, corrected from curvature, resampled and converted to modern seismological format by TESEO a GIMP plug-in made up by INGV [12]. Figure 2 shows an example of original seismogram of the 11 March 1978 earthquake recorded by the galvanometric Sprengnether seismograph at the LJU station (plot a) and the respectively converted digital trace (plot b).

Modern moment tensor inversion techniques require to rotate the horizontal NS and EW component seismograms into radial (P-SV) and transverse (SH) components. This is difficult for historical records because of imprecise alignment and magnification correction between horizontal components. Also, single components of the instruments may be lost or the instrument consisted of only one component. For this reason one of the peculiarities of the algorithm we used for historical data is to work directly on the seismogram components. Feasibility and effectiveness to determine the parameters of an historical earthquake based on limited dataset is supported by the most recent literature (e.g., [4–6, 13]), that proves the capability of this technique to obtain reliable results. Following [5] we apply a modern standars time-domain analysis technique to the Ferruzzano earthquake to estimate the source parameters of the event. This technique analyze the least-squares misfit among observed seismograms and their synthetic predictions within a long period passband (20 to 50 s) and, use original waveforms without previous rotation of the horizontal seismograms. In this way errore-prone step in the processing sequence are avoid and single horizontal seismograms can be used. Finally, the individual instrument characteristics were processed to pole and zero type transfer functions [14] and then convolved the instrumental response to the synthetic waveforms.

Results and discussion

The inversion of the 1978 Ferruzzano earthquake is based on 8 seismograms from six different stations, the individual traces are weighted to balance the different amplitudes and improve the overall fit of the waveforms (Fig. 3). For the parameter selected, the best solution indicates normal faulting (strike/dip/rake of 185/69/-86 and 354/22/259 for the two nodal planes) and a seismic moment of \( M_0 = 0.128 \times 10^{24} \) Nm (\( M_w = 4.7 \)). The non-double-couple (CLVD) component of the inverted moment tensor is small (12%) indicating that this earthquake can be adequately modelled as a simple faulting event. The best solution is obtained at a depth of 8 km, more shallow than [7] and [8]. The misfit error as function of depth shows that the solution is stable around the minimum (Fig. 3).
Waveform matches (Fig. 3) between the corresponding predictions and the observations are good and reproduced adequately. $P$ waves are very well fitted at each station. For the Italian station TRI (only for the EW component) we observe effects of limited bandwidth and low resolution, since the recordings underestimate amplitudes near the first arrival of long-period surface waves, for this reason we excluded this trace from inversion. The obtained magnitude ($M_w=4.7$) is smaller than that ($M_w=5.2$) proposed by [7] and [8], we supposed that possible regional seismic attenuation could affect the propagation wave paths and recorded amplitudes. The presence of asthenospheric mantle material at shallow
depths beneath the Appennines and in front of the Ionian slab could cause inefficient wave propagation paths [15], from the earthquake hypocenter to the used stations. Our solution is characterized by a good match between synthetic and observed seismograms and, with respect to the other solution reported in the literature, it also shows a good agreement with the regional geologic contest.

Future steps

Working with historical seismograms is a very challenging task and there are several aspects to take into account. To recover and analyze by means of modern waveform inversion techniques the past earthquakes is very important for the knowledge improvement because they allow to recover an irreplaceable data amount and to obtain information actually not available from recent seismicity. This study allowed to test the above described modern-standard time-domain analysis technique for the first time on an Italian historical seismic event and re-evaluate the source parameters of the Ferruzzano earthquake. Further efforts will be done to collect other original seismograms from different archives in order to have a greater number of data suitable for the inversion procedure and a better azimuthal coverage. Moreover additional tests will be performed to investigate the wave propagation paths along the Appennines that could have influenced the magnitude estimate. The good results obtain in this study demonstrate the value of the preservation of historical seismic data and the capability of modern-standard time-domain technique to properly analyze them. Following this first study other investigations will be carry out to analyze italian earthquakes of the early XX century.

References


Reports
Ph.D. Students
Cycle XXXII
Design of an Electromagnet for Laser-generated Plasma diagnostics

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Abstract

In this paper, we propose a plasma diagnostic method with magnetic fields perpendicular to the direction of propagation of the particles in a laser-generated plasma. The design of the electromagnet requires accurate simulations, conducted with COMSOL Multiphysics simulation software. Here are illustrated the advantages of using magnetic fields that are adjustable from the outside, compared to fixed ones, and a careful study of their realization. The ultimate aim is to obtain a useful device for the characterization of plasmas generated by low-intensity laser pulses, of the order of $10^{10}$ W/cm², and its subsequent application for the characterization of plasmas at higher temperatures, generated by higher laser intensity.

Keywords: Laser-generated Plasma, Magnetic Field, Electromagnet, Plasma Diagnostics.

Introduction

When a laser with a very high intensity ($\geq 10^{18}$ W/cm²) is focused on a solid target, photons, electrons, protons and ions emerge from the irradiated material with very high energy. High ion accelerations are possible under Target Normal Sheath Acceleration (TNSA) or Radiation Pressure Acceleration (RPA) [1], and to date the highest energies observed for protons are in the order of dozens of MeVs [2]. Ion acceleration by laser-generated plasmas has become relevant scientifically in recent decades, due to the high number of application fields, such as Laser Ion Source, medical applications, hadron research, and more [3].

Plasma diagnosis is therefore important for knowing the properties of the ion beams generated in the laser-matter interaction. In this paper, we propose the design of an electromagnet for the study of a low-intensity laser plasma of about $10^{10}$ W/cm². Recent studies on the application of magnetic and/or electrical fields have been conducted for the characterization of non-equilibrium plasmas generated by low intensity lasers [4, 5].

Magnetic Field can be applied to charged particles of a laser-generated plasma with axial symmetry to the latter, obtaining increments in the detection yield and in the particles energy like reported in literature [6]. If the magnetic field have a transversal symmetry to ions beam of non-equilibrium plasma, charged particles are separated in accordance with Lorentz’s Force, and circulate with a radius:

$$r = \frac{m v}{z e B} \quad (1)$$

where $m$ is the mass, $v$ is the velocity, $z$ is the charge state of ion investigate, $e$ is the elementary charge and $B$ is the magnetic field module applied. Therefore heavier ions, but with the same charge state, will have higher radius, and thus will be less deflected. At the same time, ions with higher charge state, but with the same mass, will be deflected more. It is clear that a device is based on this physical principle will separate the same ion, with the same charge state, according its own velocity.

By positioning a high-resolution detector at a given angle, for example 30°, if we change the magnetic field applied by the electromagnet, it is possible to have a device that works as a filter for the ratio linear momentum to charge state, from the eq. (1):

$$p/z = reB \quad (2)$$

where $p = mv$ is the linear momentum. The product $r \cdot e$ is fixed and $B$ is controlled by the user. By using Time Of Flight technique (TOF), it is possible to evaluate the velocity of the ions that travel a known distance:

$$v = \frac{L}{TOF} \quad (3)$$

where $L$ is the distance between the target and the detector, and $TOF$ is the time of flight, measured with a fast storage oscilloscope. Thus, it is possible from eq. (2) and (3) to have information on charge-to-mass ratio, and by varying the magnetic field we can reconstructed the distribution of the charged particles velocity in non-equilibrium plasma, as will be presented.
Material and Methods

A Nd:YAG laser was employed to generate a non-equilibrium plasma in vacuum chamber at low pressure of about $10^{-6}$ mbar. The laser beam, with fundamental wavelength of 1064 nm, pulse duration of 3 ns, and variable energy from 1 to 300 mJ, was focused with optical lens on a target. The product plasma travel in vacuum for 90 cm before to be detected. Charged particles of plasma, in their flight, pass through a system of two pinholes (with a respectively diameter of 3 and 1 mm) to generate a tight and collimated ions beam [7]. The collimated ions beam is detected by 32 faraday cups, distributed with an angle of $90^\circ$, each distant $2.9^\circ$ from the other. They are placed on a mobile sleigh, in the horizontal plane on the ion trajectory, that permits to investigate different angle from $0^\circ$ to $180^\circ$, (Figure 1). The faraday cup signal is sent to a fast storage oscilloscope; however, since collimators cut down ionic current, it is necessary to work with high input impedances of the megaOhm order. In this way we get a signal amplification, but a slow discharge of the RC circuit.

![Figure 1: Picture of chamber where are placed the 32 faraday cups.](image)

Results and Discussion

As previously reported, if there is not a magnetic field in the system we can study the angular distribution of particle emitted from target, when the laser beam shoot it. In Figure 2 is shown the angular distribution for Aluminium ions.

![Figure 2: Experimental data (in black) and fit (in red) of the angular distribution for Al-ions, emitted from a target of pure Aluminium.](image)

The angular distribution reported in Fig. 2 shown the profile of the ions beam after it passes through the collimation system. The data was obtained evaluating the maximum yield detected with a faraday cups placed at a certain angle vs. the angle of detection. Fit of experimental data was done using a Normal Distribution:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$ (4)

where $\mu$ is the mean or expectation of the distribution, and $\sigma$ is the standard deviation. The correlation between the Full Width at Half Maximum (FWHM), $\Gamma$, and the standard deviation is $\Gamma = 2\sqrt{2\ln 2} \cdot \sigma$, so we obtain from the fit $\Gamma \approx 6.33^\circ$. This means that the two pinholes generate an ions beam of Gaussian-shaped, which have very narrow angular aperture, but also with low currents. For more heavy ions we aspect smaller angular distributions, according to literature [8].

When a Magnetic Field, orthogonal to particle direction, is applied to plasma plume, the ions are deflected according to Lorentz’ force, shown in eq. (1). In this way, it is possible to evaluate some of important features about the charged particles that constitute the non-equilibrium plasma, such us velocity, energy, charge state, and more. Figure 3 shown the simulation, performed with COMSOL Multiphysics simulation software [9], for first charge state of Aluminium and Tantalum, in the interest system.
Figure 3: COMSOL Multiphysics simulations about Al$^{1+}$-ions and Ta$^{1+}$-ions, in the system of interest, with a transversal magnetic field module of 0.18 Tesla.

The simulations were performed using a Coulomb-Boltzmann distribution for the energy of particles [10], introducing a plasma temperature of 30 eV and a plasma potential of 50 V (with energy ranging from 100 to 700 eV). The magnetic field is fixed with dimensions of 25x25x10 mm; it has a value of 0.18 Tesla, in the centre of system. This study would be fine if we use the 32 faraday cups of this device. However, due to the low number of ions that out of the two pinholes and their subsequent separation due to magnetic field, the spectrometer resolution is very low. A solution designed for this device could be to work with a Windowless Electron Multiplier (WEM) placed at 30 degree angle, varying the magnetic field. In this way, we can work with a small number of ions and with a high resolution. Thus, Figure 3 shown a good deflection for aluminium ions (up to 30° angle deflection), due their small mass. However, when the mass goes up, like in tantalum case, we need more intense magnetic field to reach 30° angle deflections.

To use this device as a spectrometer, it is necessary to design an electromagnet with appropriate characteristics. For this design, we have used the COMSOL Multiphysics simulation program. The electromagnet consists of an iron core, having a “C” shape. The iron core design is shown in Figure 4.

The core structure consists of three pieces. The central part is the one on which the coil made of copper is inserted.

Figure 4: Design of the iron core of the electromagnet.

Various simulations with COMSOL Multiphysics were performed to evaluate the value of the magnetic field in the iron core cavity. In Figure 5 is shown a simulation of this electromagnet.

Figure 5: Simulation of electromagnet with 1000 copper windings cross by 5 current’s Ampere, and magnetic field in the core cavity.
The electromagnet consists of 1000 copper windings. The diameter of the copper wire section is 1.6 mm, in which a current intensity of 5 Ampere is simulated. The simulation was carried out using the B-H curve for iron, so to obtain non-linear solutions when a current is flowed into the solenoid. The magnetic field obtained in the center of the iron core cavity is shown in Figure 5. It reaches the maximum value of 0.31 Tesla, that value is sufficient to deflect also heavy ions at 30° angle. In this way, we can obtain a device with a high resolution, and the correlation between the magnetic field and the TOF for ions, may be indicative of the velocity distribution of plasma ions, similar like in the Ion Energy Analyzer case (IEA) [11]. In Figure 6 a picture of the electromagnet is shown.

![Picture of the electromagnet.](image)

The Figure 6 shows an assembly with 1200 copper windings with a wire’s diameter of 1.25 mm. The next step will consist in the calibration of this assembled magnet, before its use for the study of plasmas generated by laser.

**Conclusion**

In this paper, we have introduced a device to characterization of laser-generated plasma in vacuum. The use of fixed magnetic fields can be a valid analysis when we work with small detectors that cover large angles. However, when high resolution measures are required, other types of detectors, often bulky, must be used. This means that it is more convenient to vary the magnetic field rather than the detection angle of the detector. Accordingly, by designing an appropriately studied electromagnet, it is possible to vary the magnetic field by varying the current flowing into the coil of the electromagnet. Thus an accurate study of the properties of the charged particles of the non-equilibrium plasma becomes quick and easy.

**References**


Random bit generators based on skyrmions

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Abstract

Magnetic skyrmion are topologically protected non-uniform configuration of the magnetization which can behave as particles. They can be easily manipulated (nucleated, shifted and detected) by spin-polarized current, and for this reason they offer a wide range of applicability fields. In this work, we study the skyrmion dynamics driven by the spin-Hall effect in a synthetic antiferromagnet within a micromagnetic framework. We show that, in presence of thermal fluctuations at room temperature, the skyrmion motion is not deterministic. This feature, combined with a properly designed device, could be exploited for using skyrmions as building blocks of random bit generators.

Keywords: Magnetic Skyrmion, Spin-Hall effect, Micromagnetic modeling, bit generator.

Introduction

The skyrmion, proposed in the context of particle physics, \cite{1} has been stabilized in magnetic materials exhibiting properties such as topological protection\cite{2}, \cite{3}. Magnetic skyrmions range in sizes from 10 nm to approximately 100 nm depending on material parameters. They can be created and annihilated by spin currents and magnetic fields, and they can be easily moved by an electrical current \cite{2} - \cite{7}. Skyrmions are also chiral, which means the skyrmion has a definite “sense of rotation”. In other words, the skyrmion and its mirror image cannot be brought to coincide with each other by translation and rotation. A fundamental interaction for stabilizing a magnetic skyrmion is the Dzyaloshinskii-Moriya interaction (DMI) \cite{8}, \cite{9} arising from inversion symmetry breaking in material with high spin-orbit interaction (bulk DMI) or from the interface between a ferromagnet and material with high spin-orbit interaction (interfacial DMI) \cite{3}, \cite{10}, \cite{11}. Most bulk DMI materials belong to the category of B20 compounds and they host Bloch skyrmions, while in multilayered heterostructures Néel skyrmions can be stabilized \cite{3}.

In order to manipulate skyrmions, spin-polarized current can be used. For instance, single skyrmion nucleation has been predicted by the use of a perpendicular spin-polarized current \cite{12}. Skyrmion motion has been driven by spin-transfer torque, and, more efficiently, by pure spin currents generated by the spin-Hall effect (SHE) \cite{11}. Skyrmion detection can be performed by optical techniques, such as neutron scattering, or, in the real space, by the Lorentz transmission electron microscopy \cite{6}, as well as electrically by a magnetic tunnel junction read-head \cite{13}.

Because of their small size, their stability, the demonstration of their individual creation and annihilation, and their facile movement with low current, they are being investigated for information storage (memory). In fact, the most promising technological applications of skyrmion is in racetrack memory \cite{14}, where the presence of a skyrmion code the bit “1”, while its absence code the bit “0” \cite{11}. However, several further uses of skyrmion has been predicted, such as in microwave oscillator and detectors \cite{15}–\cite{17}, or in logic gates \cite{18}. In this report, we predict the use of skyrmions in random bit generators \cite{19}.

A random bit generator is a system whose output consists of fully unpredictable (i.e., statistically independent and unbiased) bits\cite{19}. Here, we provide, by means of micromagnetic simulations, the proof of concept of a random bit generator based on magnetic skyrmions. We exploit the stochastic behavior of skyrmions in presence of thermal fluctuations to achieve the generation of random bits, here represented by the skyrmion. In particular, we drive the skyrmion motion by the SHE in a synthetic antiferromagnetic (SAF) device \cite{20} composed of one input branch and two output branches. We show that, under the same current, skyrmions, which are continuously nucleated in the input branch, are divided randomly in the two output branches. Our results pay the way for the design of a novel application of skyrmions as well as of a new generation of random bit generators.
Device and Modeling

Micromagnetic simulations of a multilayered nanowire with two output branches have been performed (see Figure 1(a)). It is composed of a 3 nm thick Platinum heavy metal (HM) (lower HM) with on top two perpendicular CoNi ferromagnetic layer (FMs) separated by a thin Ruthenium (Ru) layer designed to provide an antiferromagnetic exchange coupling [21] (see Figure 1(a)), and a second HM on top of the whole stack (upper HM) [22].

The device is 1900 nm long and the width of the input and output branches is 320 nm. The thickness of both ferromagnets and Ru layer is 0.8 nm. The physical parameters of CoNi layers taken from [23], [24], and equal for both ferromagnets, are: saturation magnetization $M_s = 600$ kA/m, exchange constant $A = 20p J/m$, uniaxial perpendicular anisotropy constant $k_u = 0.5 M J/m^3$, and damping $\alpha_G = 0.1$. The interlayer exchange coupling (IEC) constant $A_e x$ is fixed to $-5.0 \times 10^4$ J/m$^2$ [23], [24]. We use a discretization cell of $4 \times 4 \times 0.8$ nm$^3$, and introduce a Cartesian coordinate system with the x-, y- and z-axes lying along the length, the width and the thickness of the device, respectively (see inset Figure 1(a)). The numerical study is carried out by means of a self-implemented micromagnetic solver (it includes the SHE, IDMI and IEC) and post-processing tools [25]-[27].

The total micromagnetic energy density of the system under investigation is (the superscripts $L$ and $U$ refer to lower and upper FMs):

$$
\epsilon_{tot}^{L,U} = A(\nabla \cdot m)^2 + \epsilon_e^{ex}
+ D^{L,U}[m^{L,U}_z \nabla \cdot m^{L,U} - (m^{L,U}_x \cdot \nabla) m^{L,U}_y]
-k_u (m^{L,U}_z \hat{z})^2 - \frac{1}{2} \mu_0 M_s m^{L,U} \cdot H^{L,U}_m
$$

where $m_x$, $m_y$ and $m_z$ are the x-, y-, and z-components of the normalized magnetization, respectively. The interlayer exchange energy is given by $\epsilon_e^{ex} = -(A_e x / \xi Ru) \cdot (m^L \cdot m^U)$ (same contribution for both FMs), where is the thickness of the Ru layer [28]. $D$ is the parameter taking into account the intensity of the IDMI. More specifically, $D^L (D^U)$ refers to the lower (upper) FM. According to our definition, $D^L$ and $D^U$ are materials properties (they are not related to the multilayer geometry), i.e. in the specific case where both lower (HM/FM) and upper (FM/HM) interfaces are the same (see inset Figure 1(a)), one would have $D^L = D^U$. We fixed $D^L = D^U = 2.5$ mJ/m$^2$ [22].

The Pt/FM interface produces the lower IDMI, while the upper IDMI derives mainly from an upper HM. $\xi$ is the unit vector along the z-direction, $\mu_0$ is the vacuum permeability. $H_m$ is the magnetostatic dipolar field, which is computed by considering both ferromagnetic layers. The boundary conditions related to the IDMI are [29], [11]:

$$
\frac{dm^{L,U}}{dn^{L,U}} = \frac{1}{\xi_e^{L,U} (\hat{z} \times n^{L,U})} \times m^{L,U}
$$

where $n$ is the unit vector normal to the surface and $\xi_e^{L,U} = 2A/D^{L,U}$ is a characteristic length.

We wish to underline that, when considering the dynamical analysis, the presence of two HMs gives rise to a lower and upper SHE when an electric current is passed through them (the electrical current here denotes a flow of electrons). In order to model this behavior, it is necessary to introduce two spin-Hall angles, $\theta_{SH}^L$ and $\theta_{SH}^U$, for the lower and upper FMs, respectively (see inset Figure 1(a)). As for $D^L$ and $D^U$, according to our definition, the two spin-Hall angles are only linked to material properties. We fixed $\theta_{SH}^L = \theta_{SH}^U = 0.10$ [24].

![Figure 1](image)

**Figure 1:** (a) 2D view of the SAF multilayer under investigation, where the input branch and two output branches are indicated. Inset: 3D sketch of the input branch, where the ferromagnets (FM), separated by a Ru layer, are sandwiched between different heavy metals (HM). (b) Snapshot representing examples of the spatial distribution of the magnetization for SAF Néel skyrmion (Skx). A color scale, linked to the z-component of the magnetization, is also indicated.

The thermal effects are accounted into the micromagnetic solver as a stochastic term $h_{th}$ added to the deterministic effective magnetic field in each computational cell $h_{th} = (\chi / M_S) \sqrt{2(\alpha K_B T / \mu_0 \gamma_0 \Delta V M_S \Delta t)}$ with $K_B$ being the Boltzmann constant, $\Delta V$ the volume of the computational cubic cell, $\Delta t$ the simulation time step, $T$ temperature of the sample, and $\chi$ a three-dimensional white Gaussian noise with zero mean and unit variance [30].
Results

We carry out a micromagnetic study at room temperature $T = 300$ K and zero external. We apply an electrical current $jHM$ only though the lower HM. All the results are shown for $jHM = -2.0 \times 10^8 \text{ A/cm}^2$, but similar results are obtained for current densities in the range $-2.25 \times 10^8 \text{ A/cm}^2 \leq jHM \leq -0.25 \times 10^8 \text{ A/cm}^2$.

We perform micromagnetic simulations within a simulation time of 60 ns, where we continuously nucleate a single Néel skyrmion in the input branch. In order to simulate such a periodic nucleation, we modified our micromagnetic code such that, every 5 ns, a skyrmion is nucleated in the input branch.

We observe that the skyrmions divide randomly in the two output branches (see example in Figure 2). This is because of the stochastic behavior of skyrmions in presence of thermal fluctuations [13].

![Figure 2: Example of spatial distribution of the magnetization for the lower ferromagnetic layer after 30 ns. Two skyrmions went to the upper output branch, three skyrmions went to the lower output branch, while another skyrmion is coming from the input branch.](image)

Conclusion

We have shown via a full micromagnetic simulations the possibility to move randomly skyrmions in presence of spin-Hall effect and thermal fluctuations in a synthetic antiferromagnets. We have observed that, under the steady action of the current, skyrmions stochastically divided in the two output branches of our device starting from a continuous nucleation in the input branches. Our results open the path for the designing of random bit generators based on skyrmions.

References


Temperature-Dependent FTIR-ATR Spectral Variations in pure 1-propyl Alcohol: a 2D Correlation Spectroscopy and Statistical Analysis

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Abstract

In this work, the temperature-dependent middle-infrared (MIR) spectral variations of pure 1-propyl alcohol have been studied by 2-dimensional (2D) correlation spectroscopy over a range between 253 K and 347 K. Experimental data were used as dataset for the computation of the synchronous and asynchronous correlation maps, which contain the modulated intensity profile induced by the perturbation variable (temperature). The original absorbance dataset, composed of 10 spectra, was recorded in the 400 - 4000 cm$^{-1}$ region using the attenuated total reflectance geometry (ATR), although only the 2700 - 3700 cm$^{-1}$ region was studied in detail (-CH and -OH stretching region). Furthermore, the position of isosbestic point was calculated with high accuracy by mathematical manipulation of the raw data.

Keywords: FTIR - ATR, 1- Propanol, 2D Correlation Spectroscopy Analysis, Isosbestic point.

Introduction

The study of H-bond (HB) dynamics in liquids (e.g. polymers, alcohols, etc.) represents a challenging task for most research groups. As is well known, it plays a fundamental role in driving some important biological phenomena and it is the main cause of water diffusion mechanism in polymers. Alcohols represent an example of amphiphilic hydrogen-bonded liquids containing both polar hydrophilic hydroxyl and nonpolar hydrophobic alkyl functional groups, which are the responsible for the bio- compatibility of these systems respect to a given chemical environment. For this reason, understanding the properties associated to the $\nu_s(\text{OH})$ in alcohols and how these oscillators are correlated to different functional groups of the same sample can provide useful informations in terms of diffusion performances and chemical affinity. Here, we focused our attention on an important example of aliphatic alcohol named 1 - Propanol (or 1 - Propyl Alcohol (1PR)). 1PR is an isomer of propan-2-ol and it is usually used as solvent in the pharmaceutical industry and for resins and cellulose esters (fig. 1).

Only in recent years, due to its high "octane number" (118) has it been used also as engine fuel, despite its high production costs.

In order to characterize the temperature dependent variation of the OH stretching band (3000-3700 cm$^{-1}$) and the "in-phase" and "out-of-phase" intensity changes respect to the $=\text{CH}_2$ and $=\text{CH}_3$ modes (2700 - 3000 cm$^{-1}$) we analysed the FTIR-ATR spectra of 1PR by means of 2D correlation spectroscopy. This technique allowed us to compute correlation intensity among different functional groups as a function of T.

Recently, the physical structure of 1PR has been widely studied by means of different approaches based on infrared, Raman and microwave spectroscopy [1, 2]. The results reveal that 1PR can be found (in liquid state) in two different conformations: -trans and -gauche, which differ in the relative position of the hydroxyl group compared to the methyl group. For the 1PR molecules in gauche conformation, the hydroxyl and methyl groups are separated by an angle of about 180°, whereas, in the second configuration, the same groups are spatially closer. In 1963, P. J. Krauger [3] demonstrated that the fundamental OH stretching mode of 1PR in a CC\textsubscript{4} solution can be considered as the mathematical convolution of three sub-bands, each of which is associated to three different structural conformations (2 to trans-conformation and 1 to the gauche). Furthermore, we will see that 3 kinds of O-H oscillators coexist in the investigated liquid with different cooperativity.

Each absorption band has a unique temperature evolution due to structural modifications which oc-
cour by increasing/decreasing the temperature applied. The aim of this work was to study this evolution as a function of T, trying to obtain useful information about the structural and dynamical properties of 1PR. Finally, the isosbestic point in the 3000 - 3700 cm\(^{-1}\) wavenumber region was also calculated by means of a statistical approach recently proposed by Vardevanyan et. al.

Material and Methods

Material

1 - Propanol was purchased from Sigma - Aldrich (Steinheim, Germany) with a 99.5 % purity level and used without any further purification. FTIR - ATR measurements were performed between 253 and 347 K.

Methods

FTIR - ATR measurements

The FTIR-ATR spectra of 1PR were collected over a wavenumber range between 400 - 4000 cm\(^{-1}\) using a Bomem DA8 Fourier Transform Spectrometer. It is equipped with a Globar source (10 - 1000 cm\(^{-1}\) emission range) and a DTGS detector. A horizontal ATR Ag-based crystal was positioned in the sample compartment of the BOMEM DA8 and fixed by means of a proper support. 100 scans were carried out to reduce the thermal noise with a spatial resolution of 2 cm\(^{-1}\).

2D Correlation Spectroscopy Analysis

An accurate comparison of the spectral intensity variation profile due to a temperature-perturbation was evaluated by the 2D correlation spectroscopy technique (2DCorrS), first proposed by Noda in 1986. Basically, starting from a set of raw data (experimental spectra), affected by some external perturbations (e.g. temperature), we can estimate the so-called synchronous and asynchronous maps which contain all the information on the intensity correlation between the temperature-dependent input data. Generally speaking, the spectral intensity can be defined as \(I(\nu, t)\), where \(\nu\) is wavenumber and \(t\) is the external variable (temperature in this case). Then, the correlation function between two different spectra \(\tilde{I}(\nu_1, t)\) and \(\tilde{I}(\nu_2, t)\) can be written as:

\[
\Lambda(\nu_1, \nu_2) = \langle \tilde{I}(\nu_1, t) \cdot \tilde{I}(\nu_2, t) \rangle
\]  
(1)

where \(\tilde{I}(\nu_1, t)\) and \(\tilde{I}(\nu_2, t)\) represent the dynamical spectra defined as \(\tilde{I}(\nu, t) = I(\nu, t) - \bar{I}(\nu)\).

\(\bar{I}(\nu)\) can be considered as the reference spectrum of the system which can be chosen arbitrarily. Eqn. (1) can be rewritten as a complex function and splitted into two different contributions called synchronous \((\phi(\nu_1, \nu_2))\) and asynchronous \((\varsigma(\nu_1, \nu_2))\) parts of the correlation function:

\[
\Lambda(\nu_1, \nu_2) = \phi(\nu_1, \nu_2) + i\varsigma(\nu_1, \nu_2)
\]  
(2)

For a set of discrete intensity columns (10 in this case, one for each spectrum) and assuming that measurements are approximately equidistantly spaced in T, we can compute the synchronous and asynchronous maps using the following relations:

\[
\phi(\nu_1, \nu_2) = \frac{1}{k-1} \sum_{m=1}^{k} \tilde{I}(\nu_1) \cdot \tilde{I}(\nu_2)
\]  
(3)

\[
\varsigma(\nu_1, \nu_2) = \frac{1}{k-1} \sum_{m=1}^{k} \tilde{I}(\nu_1) \cdot N \cdot \tilde{I}(\nu_2)
\]  
(4)

Where \(k\) is the number of measurements and \(N\) is the Hylbert-Noda trasformation matrix. The first term of the correlation function (eqn. 3) describes the coincidental variation of the intensity associated to the original dataset; in other words, peaks on the synchronous map develop only if the band intensities of the measured spectra at \(\nu_1\) and \(\nu_2\) increase or decrease together. On the other hand, the second term (eqn. 4) shows the "out-of-phase" or non-sequential intensity changes of the measured data.

Results and Discussion

Fig. 2 shows the FTIR - ATR spectra of 1PR in a wavenumber region between 2700 - 3700 cm\(^{-1}\) over the whole range of temperature (253 - 347 K).

![Figure 2: FTIR - ATR spectra (2700 - 3700 cm\(^{-1}\)) of 1 - Propyl Alcohol collected over a temperature range between 253 and 347 K.](image-url)

In all the presented spectra a base-line correction was applied by manually located baseline anchor points (no. 13-14). These points were properly located on
raw data and subsequently connected by interpolation, giving as a result the subtracted spectra. Finally, all spectra were properly normalized. In fig. 2 we can distinguish three different peaks in the 2700 - 3000 cm\(^{-1}\) range due to the methyl groups vibrations centred at 2872 (\(\nu_s(CH_2)\)) and 2963 (\(\nu_{as}(CH_2)\)) cm\(^{-1}\), and one due to the methylene mode at 2935 cm\(^{-1}\). Furthermore, the multi-component broad band centred at 3330 cm\(^{-1}\), due to hydroxyl oscillators, was also detected.

At first glance, all the presented spectra show a specific temperature evolution characterized by a decrease/increase of the absorption peak intensities, and by a shift of the \(\nu(OH)\) towards higher energy. This wavenumber shift can be attributed to a modification of the relative percentage of the -OH modes ranging from "strongly arranged" to "free" OH oscillators (between 3000 and 3450 cm\(^{-1}\)), induced by the increasing temperature. In order to take into account this variation, we carried out a deconvolution of the OH stretching absorption band in three sub-bands, according to the three different structural conformations of the OH stretching mode in 1PR, centred at 3219, 3329 and 3443 cm\(^{-1}\). For each sub-band, the percentage area (number of relative oscillators) was calculated in order to evaluate the population of each "arrangement" with increasing temperature. Here, we report these results over a T range between 297 and 347 K, as example.

In the synchronous spectrum we can identify two broad bands due to the presence of the O-H and =CH\(_2\) -CH\(_3\) oscillators, labelled "A" and "C", respectively. The development of these bands indicates that the investigated region is quite susceptible to a temperature perturbation. In fact, we can observe 4 different "auto-peaks" (peaks appearing on the diagonal position (\(\nu_1 = \nu_2\)) centred at 2874, 2933, 2962 and 3334 cm\(^{-1}\) (white circle) due to changes of single band intensity. For this reason, "auto-peaks" do not provide useful information about the correlation between different peak intensities of the original dataset. In addition, 7 pairs of negative cross-peaks are observed, 4 on bands "A" and "B" and 3 on band "C". The presence of 4 negative (green circles) cross-peaks in bands "A" and "B" at (3337,3284), (3337,2986), (3337,2931) and (3337,2877), imply that peaks at 3284, 2986, 2931 and 2877 change intensity in the opposite direction to that of the peak at 3337 cm\(^{-1}\) with increasing temperature. In particular, the opposite variation of 3337 and 3284 intensity, both associated to different conformations of the O-H
bond network in 1PR, reveal the presence of an isosbestic point somewhere between these two frequency values. Finally, the last 3 peaks (blue circles) are due to strong cross-correlation between =CH\textsubscript{2} and -CH\textsubscript{3} functional groups.

Information about the unsynchronized (or sequential) cross-correlation profile were obtained by the analysis of the asynchronous spectrum displayed in the triangle below the diagonal line of fig. 4. In particular, the two negative cross-peaks (band "D") at (3246,3377) and (3211,3377) (light blue circles) suggest that, with increasing temperature, the intensity at 3246 and 3211 decrease predominantly (or faster) respect to the increase of the 3377 cm\textsuperscript{-1} absorption peak. This means that there is an initial breaking of the highly cooperative OH oscillators followed by the formation of "free" O-H, as expected. In addition to this, we can distinguish 6 different positive cross-peaks related to the out-of-phase intensity changes between the O-H and the =CH\textsubscript{2} and -CH\textsubscript{3} oscillation modes. accordingly, peaks associated to high cooperative O-H groups (3211 and 3246 cm\textsuperscript{-1}) decrease before the increase of both methyl and methylene groups of 1PR implying that, with increasing temperature, =CH\textsubscript{2} and -CH\textsubscript{3} stretching vibrations are effected by temperature less than OH stretching modes.

A statistical approach, firstly proposed by P. O. Vardevanyan et. al, was used to calculate the isosbestic point (IP) in the O-H stretching mode region (3000 - 3700 cm\textsuperscript{-1}) with high accuracy. Let $I_i(\nu)$, with $1 < i < 10$, be the $i-th$ spectrum of the original dataset. They demonstrated that the mean square deviation $\sigma(\lambda)$ (MSD) of all spectra can provide the position of the isosbestic point by calculating its minimum value. In order to do this we computed $\sigma(\lambda)$ with ORIGIN software by using the following algorithm:

$$
\sigma(\lambda) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (I_i(\lambda) - \bar{I}(\lambda))^2}
$$

where $\bar{I}(\nu)$ represents the average spectrum of the origin set of measured data. In fig. 5 we report the MSD profile and its first derivative in the wavenumber region between 3000 and 3700 cm\textsuperscript{-1}. As we can see, a clearly visible minimum of the MSD function was detected. In order to evaluate the frequency associated with that value with high precision, we calculated the first derivative (bottom figure) trying to figure out where this function crosses the zero line. As a results, we found the presence of an isosbestic point at 3332 cm\textsuperscript{-1} in the region between 3150 - 3400 cm\textsuperscript{-1}, which is in accordance with the 2D correlation results in the same region. At this point in 1PR no intensity variation was observed with increasing temperature.

Conclusions

In this work, the FTIR-ATR technique was used to evaluate the temperature dependent intensity variation of hydroxyl and methyl groups in 1-propyl alcohol. In order to do this, 2D correlation spectroscopy was also used revealing features otherwise unrecognizable. In particular, the intensity correlation profile was calculated as a function of T revealing how the OH and =CH\textsubscript{2} and -CH\textsubscript{3} modes are strongly affected by temperature. Peaks at 3284, 2986, 2931 and 2877 were found to change intensity in the opposite direction to that of peak at 3337 cm\textsuperscript{-1} with increasing temperature. Finally, the isosbestic point in the O-H stretching region was also evaluated by means of a statistical approach proposed Vardevanyan in 2015 showing an IP centred at 3332 cm\textsuperscript{-1} implying the presence of at least two different OH arrangements.

References


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Abstract

Graphene shows astonishing properties that can be exploited in many applications, for example high performance microcircuits. Many physicochemical procedures are being used for the production of such devices, one is the local reduction of graphene oxide to graphene by means of laser ablation. Of course, it is necessary to investigate the structure of the irradiated samples to get detailed insights into the as-produced material. For this reason, micro-Raman spectroscopy is used as a characterisation technique either for its non destructive nature and for its ability to distinguish between the plethora of existing carbon materials. We report the results we got by irradiating GO with a Nd:YAG laser (1064 nm) using different laser fluences: 15 J/cm$^2$, 7.5 J/cm$^2$ and 5 J/cm$^2$. We studied the laser-induced changes in the main Raman contributions of graphitic materials: the $D$, $G$ and $2D$ bands. We used as figure of merit (FOM) parameters the intensity ratios $I_D/I_G$ and $I_{2D}/I_G$ computed for the different laser treated samples, finding out that higher fluences do not lead to a better reduction process.

Keywords: graphene, laser ablation, Raman spectra.

Introduction

In 1935 Peierls [1] stated that 2D crystal could not exist since they are thermodynamically unstable. The discovery of graphene in 2004 by Novoselov et al [2] gave a huge thrust through the search of 2D materials, since they show astonishing physicochemical properties [3], the electrical ones being of great potential for use in microelectronics [4][5]. However, high resolution transfer printing methods are needed to produce high quality microcircuits [6], so many procedures have been used. One chance is to adopt a top–down approach, using as a starting material graphite oxide (GO). The oxidation of graphite is obtained with strong oxidizing compounds (like KMnO$_4$) [7]. However this procedure induces modifications of graphite structure since epoxy and hydroxyl groups occur in the basal plane, while carboxylic groups arise at the edges [8][9]. These defects are responsible for the insulating or semiconducting properties of GO. The reduction of graphite oxide can be accomplished with dehydration, thermal reduction, UV-assisted photocatalysis [10] and finally laser ablation [11]. However high intensity laser beams ($I \sim 10^{10}$ W/cm$^2$) induce changes in the composition, foil thickness, mechanical properties and morphology [12], i.e. light treatment induces many defects on the material. This means that a thorough and reliable structural analysis is needed to understand the quality of the graphene produced by laser ablation. In this perspective, micro-Raman spectroscopy is fundamental owing to its sensitiveness to geometric structure, allowing its use for the study of carbon allotropes (i.e. diamond, carbon nanotubes [13], buckminster fullerene [14], graphene nanoribbons [15], etc.). In this work we report on the results of a micro-Raman investigation on laser irradiated GO samples, using different laser fluences.

The Raman spectra of pristine and defected graphene

Pristine graphene is characterised by a Raman spectrum where two main contributions occur: the $G$ band (1582 cm$^{-1}$) and the $2D$ band (around 2700 cm$^{-1}$) [16]. (Fig. 1, top, shows an example of this spectrum, taken from [17]).
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Figure 1: Raman spectra of pristine (top) and defected (down) graphene [17].

The G band arise from a $E_{2g}$ symmetry phonon mode which is due to an in plane vibration of $sp^2$ carbon networks, while the 2$D$ peak is the overtone of the D peak (a defect induced contribution that is not present in pristine graphene). The latter peak originates from a process where no defects are required for its activation, so the 2$D$ peak is always present [16]. In high quality graphene a single G peak and a sharp 2$D$ peak, roughly four times more intense than the G peak, occur. As concerns few layers and/or defected graphene, both the G and 2$D$ regions are affected by many defect-induced contributions [17]: 1350 cm$^{-1}$ (D band), 1620 cm$^{-1}$ (D' band), 2445 cm$^{-1}$ ($D + D''$ band), 2925 cm$^{-1}$ ($D + D''$ band) and 3160 cm$^{-1}$ ($2D'$ band) [16]. This means that the intensity ratio for the D, G and 2$D$ Raman bands can be used to verify the graphene quality: minimum of $I_D/I_G$ and maximum of $I_{2D}/I_G$ characterise the highest quality of graphene and, in the perspective of the present work, provide information on the best conditions for the GO-to-graphene reduction. In fact, the first ratio relates to the in-plane crystallite sizes [16], while $I_{2D}/I_G$ is used to distinguish a single layer, from bilayer from few (less than 5) layers [17].

Experimental

Material Synthesis

The graphite oxide (GO) foils were prepared using the Hummer method as described in detail in [18].

Laser treatment

We used a Nd:YAG laser with the following characteristics: fundamental wavelength of 1064 nm, 3 ns pulse duration, 300 mJ maximum pulse energy, 1 mm$^2$ spot size focus, about $10^{10}$ W/cm$^2$ intensity. It can be used in single pulse or up to 10 Hz repetition rate. The ablation of GO occurred in a sample chamber using a transparent window and an external lens with 50 cm focal length. Different laser pulse energies have been employed: 150 mJ, 75 mJ and 50 mJ, with a fluence of 15 J/cm$^2$, 7.5 J/cm$^2$ and 5 J/cm$^2$, respectively. A scheme of the experimental set up is reported in Fig. 2.

Characterisation

Raman microscopy was used to investigate the structural transformations in GO samples. Raman measurements were performed with 532 nm excitation light by using the LabRam HR800 (Horiba Jobin Yvon) spectrometer with the 1800 gr/mm grating and a CCD camera cooled with liquid nitrogen. The laser power used was 1 mW and the spectra were taken with the 50x objective lens. The overall integration time was 100 s.

Results and Discussion

Different laser fluences (5 J/cm$^2$, 7.5 J/cm$^2$ and 15 J/cm$^2$) have been used to irradiate the GO samples in air atmosphere. We measured the Raman spectra of all the ablated samples and compared them to the reference one. The results are shown in Fig. 3.
Figure 3: Raman spectra of GO reference sample (black line), 5 J/cm² irradiated area (red line), 7.5 J/cm² irradiated area (blue line), 15 J/cm² irradiated area (green line). The spectra are normalized with respect to the G peak intensity.

Two different regions can be recognised: the medium-Raman-shift region (below 2000 cm⁻¹) and the high-Raman-shift region (above 2000 cm⁻¹). The D and G bands dominate the first area, while a broad bump occurs in the high Raman shift region. The reference spectrum is characterised by a similar intensity of both the D and G peaks while the high frequency bump has a low intensity. The latter observation underlines that the sample is made up by several layers and that defects (e. g. structural, chemical, etc) are present (otherwise a sharp 2D peak would be visible). As concerns the irradiated samples, the D peak has a higher intensity the G peak, emphasising that a higher quantity of defects is present with respect to the reference sample, although the 2D peak is more intense.

These qualitative observations are supported by the values of intensity ratios \( I_D/I_G \) and \( I_{2D}/I_G \), that we used as figure of merit (FOM) of our study. Minimum of \( I_D/I_G \) and maximum of \( I_{2D}/I_G \) indicate that the ablation procedure lead to a better quality graphene. The intensity ratios for the spectra of Fig. 3 are reported in Tab. 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( I_D/I_G )</th>
<th>( I_{2D}/I_G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.96</td>
<td>0.68</td>
</tr>
<tr>
<td>5 J/cm²</td>
<td>1.14</td>
<td>0.78</td>
</tr>
<tr>
<td>7.5 J/cm²</td>
<td>1.17</td>
<td>0.69</td>
</tr>
<tr>
<td>15 J/cm²</td>
<td>1.17</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table 2: Computed values of the intensity ratios \( I_D/I_G \) and \( I_{2D}/I_G \) for the Raman spectra shown in Fig. 3.

These results confirm that irradiated GO samples are thinner but have more defect with respect to the reference sample. We believe that there are two possible reasons for this observation. First of all, the laser treatment was carried out in air atmosphere, so oxide species can be created (CO, CO₂) inducing more structural and chemical defects [19]. Finally, the irradiation causes the removal of layers (so the \( I_{2D}/I_G \) ratio increases) but more edge defects occur.

Conclusions

Nanosecond laser pulses were used to reduce locally graphite oxide to graphene. Our results show that the as produced graphene is not of high quality for two main reasons. On the one hand, it is made up by too many layers (low intensity of the 2D peak), on the other hand the D peak is higher in the irradiated samples than in the reference one. The latter can be ascribed to the presence of either edge – defects and oxidized chemical species, since the irradiation was performed in ambient atmosphere. We believe that better results should be get if the whole procedure is carried out in inert atmosphere or in vacuum. If this will be the case, nanosecond laser irradiation could compete with pico and femtosecond laser pulses treatments.

Acknowledgements

The authors want to thank Mariapompea Cutroneo and Vladimir Havranek, from the Nuclear Physics Institute (Rez, Czech Republic) for proving the graphene oxide samples and Professor Lorenzo Torrisi, from the MIFT Department of the University of Messina, for performing the laser irradiations. This research was supported by University of Messina Research e Mobility 2016 Project (project code RES AND MOB 2016 TORRISI). The research has been also carried out at CANAM infrastructure LM2015056 and Czech Science Foundation (GACR No. 16-05167S).
References


SEMINARI
DEL DOTTORATO DI RICERCA
IN FISICA
(Svolti nel 2017)
Chemical reactions driven by an electric field

Dr. Giuseppe Cassone

Institute of Biophysics - Czech Academy of Sciences, Brno

Abstract

Methanol is employed as a primary reactant in order to produce a multifaceted set of important chemical compounds, from hydrocarbons to di-hydrogen or dymethyl ether, just to cite some of the accessible derivates. In this respect, the importance of the simplest alcohol is remarked by the envisaged possibility to base on it the world economy by the Nobel laureate G. A. Olah [1]. Among the chemical pathways that stem from methanol, formaldehyde synthesis covers a privileged role due to its manifest economic importance, but it requires the presence of specific catalysts and it is industrially achieved only in the gas phase.

Ab initio molecular dynamics studies have succeeded in predicting complex chemical reactions of organic molecules under extreme conditions of confinement and pressure. Moreover, the remarkable catalytic capabilities of static electric fields has been demonstrated by a series of similar quantum-based molecular dynamics investigations. However, the detailed action of the field is not understood and only very recently the first experimental evidence that electric fields are able to control chemical reactions has been provided [2].

In this talk I will present, inter alia, a recently published ab initio molecular dynamics study of liquid methanol under the effect of static electric field [3]. It turns out that an extremely simple, but so far unreported, chemical reaction occurs at ambient temperature: $2\text{CH}_3\text{OH} \rightarrow \text{H}_2\text{CO} + \text{CH}_4 + \text{H}_2\text{O}$. This reaction has been characterized by exploiting not only the standard Density Functional Theory tools but also a newly developed scheme for definition of efficient reaction coordinates [4] capable to reveal unexpected microscopic mechanisms and, at the same time, providing an accurate free-energy landscape, fully including the effect of the chemical environment and of the thermodynamics.

References


An interferometric technique for the study of gas-liquid and liquid-liquid interfaces

Prof. Mario Corti

CNR-Istituto per i Processi Chimico-Fisici

Abstract

A new interferometric technique to study gas-liquid and liquid-liquid interfaces is described. Bubbles and drops, either standing by buoyancy or attached to an electrode by surface forces, are subjected to a varying-frequency external excitation, either electric or acoustic, inducing a discrete spectrum of stationary oscillation modes of the interface. Amplitudes, frequencies and widths of such frequency modes are measured by a simple interferometric
technique and give direct information on the nature of the interface. Results regarding adsorption of surfactants, proteins and nanoparticles will be presented.

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**DOTTORATO DI RICERCA IN FISICA DELL’UNIVERSITÀ DEGLI STUDI DI MESSINA**

23 Marzo 2017, ore 15.00, Sala seminari, CNR-IPCF
V.le F. Stagno d’Alcontres 37, S. Agata, Messina

**The Mpemba paradox in granular gases**

Dr. Andrés Santos

*Departamento de Física, Universidad de Extremadura, Badajoz, Spain*

**Abstract**

The Mpemba effect is a counterintuitive phenomenon according to which, given two samples of fluid, the initially hotter one may cool more rapidly than the initially cooler one [1, 2]. A necessary condition for the effect to take place is that the thermal rate of change depends not only on the instantaneous temperature but also on additional variables. In this talk, it will be shown that the Mpemba effect is present in granular gases, both in the uniformly heated and in the freely cooling systems [3]. By assuming that the most relevant variable to determine the thermal rate of change, apart from the granular temperature itself, is the excess kurtosis of the velocity distribution of the grains, analytical quantitative predictions for how differently the system must be initially prepared to observe the effect are obtained. An inverse Mpemba effect [4] (whereby a cooler fluid heats more rapidly than a hotter one) is also predicted in the case of uniformly heated systems. The theoretical predictions are numerically confirmed by the direct simulation Monte Carlo method and by molecular dynamics.

**References**


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**DOTTORATO DI RICERCA IN FISICA DELL’UNIVERSITÀ DEGLI STUDI DI MESSINA**

29 Marzo 2017, ore 15.00, Sala seminari, CNR-IPCF
V.le F. Stagno d’Alcontres 37, S. Agata, Messina

**Hyperbolic metamaterials: Ultra-anisotropic materials for nano-biophotonics**

Prof. Giuseppe Strangi

*Department of Physics, Case Western Reserve University, Cleveland-USA*

**Abstract**

Hyperbolic metamaterials (HMM) are non-magnetic anisotropic nanostructures that can support highly confined wave-vector modes in addition to surface plasmon modes within the structure due hyperbolic dispersion. This class of materials feature hyperbolic (or indefinite) dispersion because one of their principal components has the opposite sign to their two. Their properties include the strong enhancement of spontaneous emission, diverging density of states, negative refraction, enhanced superlensing effects and extreme sensitivity for sensing applications. Such metamaterials represent the ultra-anisotropic limit of traditional uniaxial crystals, having dielectric properties in one direction ($\epsilon > 0$) but metallic properties in the other ($\epsilon < 0$) and supporting high-wavevector propagating waves (bulk plasmon modes) due to hyperbolic dispersion. The design, fabrication and characterization of grating-coupled HMMs in a wide wavelength range, from visible to near infrared will be presented. I will also discuss current and potential applications of HMMs in nanophotonics and bio-medical research.
References


Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
3 Maggio 2017, ore 15.00, Sala seminari, CNR-IPCF
V.le F. Stagno d’Alcontres 37, S. Agata, Messina

Silicon Nanowires: the route from synthesis towards applications

Dr. Maria José Lo Faro

CNR-Istituto per i Processi Chimico-Fisici

Abstract

Silicon nanowires (NWs) are attracting the interest of the scientific community as building blocks for a wide range of future nanoscaled devices. We demonstrate the synthesis of NWs by a cheap, fast and maskless approach compatible with Si technology, using metal-assisted chemical etching of Si substrates catalyzed by thin metallic layer. This is a powerful technique to obtain high density and low-cost Si NWs with high and controllable aspect ratio. NWs obtained by this method have tunable nanometer-size diameter, suitable to observe quantum confinement effects, indeed a bright room temperature PL in the visible range is reported. Moreover Si NWs maintain the same crystalline structure and doping of the starting substrate, a fundamental feature for devices implementation. The realization of Si NWs-based light emitting devices has been demonstrated, showing an efficient room temperature electroluminescence emission at low voltage. We fabricated a low-cost multiwavelength light source working at room temperature, achieved combining Si NWs and carbon nanotubes (CNT). The NW/CNT hybrid system exhibits a tunable emission both in the visible range, due to Si NWs, and in the IR from CNT, and the conditions leading to the prevalence of the visible or the IR signal have been identified opening the route towards silicon photonics. Furthermore we combined the high aspect ratio of NWs with plasmonic effects, investigating the structural and optical properties of Si NWs decorated with metallic clusters for sensing applications.

Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
9 & 11 Maggio 2017, ore 15.00, Incubatore d’Impresa Aula HT1C-1, Università degli Studi di Messina
V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina

Introduzione alla relatività Einsteiniana

Prof. Liliana Restuccia

Dip. MIFT, V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina
Abstract


Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
15 & 16 Maggio 2017, ore 15.00, Incubatore d’Impresa Aula HT1C-1, Università degli Studi di Messina
V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina

Termodinamica irreversibile classica ed applicazioni
Prof. Liliana Restuccia
Dip. MIFT, V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina

Abstract

S’introducono le leggi della Termodinamica dei mezzi continui in formulazione di campo. Si sceglie lo spazio degli stati definente il mezzo di cui si vogliono studiare le proprietà meccaniche, termiche, viscoso, .... Si analizza la disuguaglianza entropica e si trovano le equazioni fenomenologiche e le relazioni di Onsager-Casimir. Si costruisce la teoria costitutiva, che permette di bilanciare il sistema di equazioni descrittive il mezzo.

Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
23 Maggio 2017, ore 15.00, Incubatore d’Impresa Aula Magna, Università degli Studi di Messina
V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina

Modelling Ionic Conductivity in Materials. Glasses, Ionic Liquids and Ionogels
Dr. Radha D. Banhatti
Laboratory for Functional Materials, Division of Materials Chemistry, Zagreb, Croatia

Abstract

In this talk, I will present in brief the MIGRATION concept which was developed for modelling conductivity and permittivity spectra of materials with structural disorder. The model formulation generates a time-dependent correlation factor using simple physical picture to describe relaxations following an ionic hop in a dynamically varying potential landscape. Using linear response theory, this function can be Fourier transformed to yield scaled model conductivity and permittivity spectra. The model parameters help us examine features of spectra such as the shape of the spectra, scaling, length scales for localised diffusion, and temperature-dependence of DC conductivity. A few examples where the model has been successfully employed to understand ion transport will be given. As part of my ongoing NEWFELPRO project, I examine these features in mixed glass former systems where we can correlate local structure obtained from Raman and NMR techniques to the spatial extent of local hops of the ion. In ionic liquids, both neat and contained in supramolecular gelator matrix, the shape of the spectra is first modelled. Using this, one can model the high-frequency conductivity and extract the activation energy of elementary displacements. This helps in modelling DC conductivity, and in constructing model conductivity isotherms. Remarkably, even in iron phosphate glasses which show polaronic conduction, the MIGRATION concept has been able to provide insights, revealing that the model is applicable whether the hopping species is an ion or an electron, since the hop produces disturbance in the neighbourhood in the form of a polarising field. Insights gleamed from this are discussed.
**Abstract**

The modern scientist spend more time in front of a laptop, the approach "simulate and analyse" has become increasingly using. To solve realistic problems they need not only fast algorithms but also a combination of good tools and fast computers. Parallel computing may be defined as coordinated computation on independent processors devoted to a single task. In this talk the scientific parallel computing is introduced and some examples are shown to illustrate as the use of parallel computing makes it feasible and realistic some simulation.

Hyperbolic metamaterials: Ultra-anisotropic materials for nano-biophotonics

Prof. Giuseppe Strangi

Department of Physics, Case Western Reserve University, Cleveland-USA

Abstract

Hyperbolic metamaterials (HMM) are non-magnetic anisotropic nanostructures that can support highly confined wave-vector modes in addition to surface plasmon modes within the structure due hyperbolic dispersion. This class of materials feature hyperbolic (or indefinite) dispersion because one of their principal components has the opposite sign to their two. Their properties include the strong enhancement of spontaneous emission, diverging density of states, negative refraction, enhanced superlensing effects and extreme sensitivity for sensing applications. Such metamaterials represent the ultra-anisotropic limit of traditional uniaxial crystals, having dielectric properties in one direction ($\epsilon > 0$) but metallic properties in the other ($\epsilon < 0$) and supporting high-wavevector propagating waves (bulk plasmon modes) due to hyperbolic dispersion. The design, fabrication and characterization of grating-coupled HMMs in a wide wavelength range, from visible to near infrared will be presented. I will also discuss current and potential applications of HMMs in nanophotonics and bio-medical research.

References


Disentangled UHMWPE and its composites
Dr. Sara Ronca
*Department of Materials, Holywell Park, Loughborough University, Leicestershire, UK*

Abstract
Il polietilene ad altissimo peso molecolare (UHMWPE) possiede proprietà meccaniche eccezionali, ma il suo utilizzo è limitato a causa dell’altissima viscosità del fuso, che ne rende estremamente difficile la manifattura con tecniche tradizionali. Il presente seminario verterà su come sia possibile sintetizzare l’UHMWPE in condizioni di reazioni tali da renderlo più facilmente processabile, non solo come omopolimero, ma anche in vari tipi di composti.

Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
4 Luglio 2017, ore 9.00, Incubatore d’Impresa Aula Magna, Università degli Studi di Messina
V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina

Plasma Physics by Laser and Applications 2017 (PPLA 2017)
Prof. Prof. David Neeley
*Central Laser Facility, Rutherford Appleton Laboratory, STFC, Didcot, Oxon, UK*

• Prof. István Földes
*Wigner Research Centre for Physics of the HAS, Hungary*

• Prof. Danilo Giulietti
*Physics Department of the University and INFN, Pisa, Italy*

Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
11 Settembre 2017, ore 15.00, Incubatore d’Impresa Aula HT6-1, Università degli Studi di Messina
V.le F. Stagno d’Alcontres 31, 98166 S. Agata, Messina

Polymer Optics and Photonics: Part 1: Photosensitive Polymers
Prof. Alexandra Trofimova
*General Physics Department, Belarusian State University, Minsk, Belarus*

Abstract
Photosensitive polymer materials undergoing certain changes in their optical properties upon light impact provide key functions of many modern optical devices and technologies. The lectures discuss the direct connection between these photoinduced changes in polymers and their certain optical applications. The polarization optics of polymers is given the most attention, including polarization phase recording and LC-display technologies.
Polymer Optics and Photonics: Part 2: Application of polymers in optics

Prof. Alexandra Trofimova
General Physics Department, Belarussian State University, Minsk, Belarus

Abstract

Photosensitive polymer materials undergoing certain changes in their optical properties upon light impact provide key functions of many modern optical devices and technologies. The lectures discuss the direct connection between these photoinduced changes in polymers and their certain optical applications. The polarization optics of polymers is given the most attention, including polarization phase recording and LC-display technologies.

Polymer Optics and Photonics: Part 3: Polarization optics of polymers

Prof. Alexandra Trofimova
General Physics Department, Belarussian State University, Minsk, Belarus

Abstract

Photosensitive polymer materials undergoing certain changes in their optical properties upon light impact provide key functions of many modern optical devices and technologies. The lectures discuss the direct connection between these photoinduced changes in polymers and their certain optical applications. The polarization optics of polymers is given the most attention, including polarization phase recording and LC-display technologies.

L’esperimento ALICE al Large Hadron Collider del CERN e le collisioni nucleari ad energie ultra-relativistiche

Prof. Francesco Riggi
Università di Catania e Sezione INFN, Catania

Abstract

Il Large Hadron Collider (LHC) del CERN ha iniziato a fornire dal 2009 fasci di protoni e di ioni pesanti, per lo studio delle collisioni protone-protone, protone-nucleo e nucleo-nucleo ad energie ultra-relativistiche. L’esperimento ALICE è una delle grandi facilities realizzate a LHC, dedicato in particolare allo studio della
materia nucleare in condizioni estreme. La Collaborazione ALICE comprende oggi oltre 1500 persone, afferenti a 150 Istituzioni di 40 Paesi diversi, con una forte componente italiana. L’apparato ALICE ha una struttura complessa, costituita da 18 diversi rivelatori, che sfruttano la maggior parte delle tecnologie disponibili oggi per la rivelazione delle particelle prodotte nelle collisioni nucleari ad altissima energia. In questo seminario sarà presentato lo status dell’esperimento, in relazione alla strategia di utilizzo, anche negli anni futuri, del Large Hadron Collider, una breve rassegna dei risultati scientifici ottenuti in questi anni e le attività di upgrade in corso per l’ulteriore ottimizzazione dell’apparato sperimentale.

Dottorato di Ricerca in Fisica dell’Università degli Studi di Messina
21 Dicembre 2017, ore 15.00, Sala seminari, CNR-IPCF
V.le F. Stagno d’Alcontres 37, S. Agata, Messina

Protein Dynamics and Allosteric Properties in the Terahertz Regime
Dr. Valeria Conti Nibali
Lehrstuhl für Physikalische Chemie II, Ruhr Universität Bochum, Germany

Abstract
Allostery is defined as any process in which an event at one site of a protein (e.g. the binding of a ligand) impacts the structure and or dynamics of another site, thereby affecting its binding affinity towards a specific ligand and as a consequence modulating the protein activity. Such a process involves a long-range communication between the two sites that can be mediated both by changes in structure and in dynamics. Over recent years the role of protein dynamics in allostery has been widely investigated in the picosecond-to-millisecond time scale, while the potential relation of faster intramolecular vibrations in the terahertz (THz) frequency range to allosteric effects is almost unexplored. Recently, the importance of these fast fluctuations has become a topic of intense debate for several processes occurring in biomolecules, e.g. in mediating efficient protein-ligand binding and in initiating and modulating slower dynamical processes. In the framework of molecular recognition, shedding light on the role of the THz dynamics of proteins could provide significant insights into the fine determinants of dynamic allostery. In this contribution, we present a molecular dynamics simulations study of two model PDZ domains with differential allosteric responses. By characterizing the dynamic modulation of the protein induced by ligand binding, and focusing on the THz frequencies as opposed to a lower frequency regime, we identify a response nucleus that is visible only in the THz regime. The overlap between the known allosterically responding residues of the investigated PDZ domains and the response nucleus highlighted here suggests that fast THz dynamics could play a role in allosteric mechanisms. The characterization of the THz dynamics by means of the proposed computational approach might provide a robust basis for the interpretation of the experimental results obtained with the emerging THz spectroscopy techniques.
Organizzazione del Dottorato di Ricerca in Fisica

Cicli XXXI, XXXII, XXXIII
ORGANIZATION AND PERSONNEL

Ph.D. Coordinator: Prof. Lorenzo Torrisi

Reference Teachers for the different specialization:

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Area di Fisica Nucleare e Subnucleare

Prof. Paolo Giaquinta e Santi Giarritta Prestipino
Area di Fisica della Materia - Aspetti Teorici

Prof. Giuseppe Carini
Area di Fisica della Materia - Fisica dei Sistemi Disordinati

Prof. Francesco Mallamace
Area di Fisica della Materia - Fisica dei Liquidi e dei Sistemi Complessi

Prof. Fortunato Neri
Area di Fisica della Materia - Nanosistemi e Fotonica

Prof. Salvatore Magazù e Domenico Majolino
Area di Fisica della Materia - Biofisica

Prof. Lorenzo Torrisi
Area di Fisica della Materia e Area di Fisica Nucleare - Fisica dei Plasmi

Prof. Domenico Majolino, Salvatore Magazù e Lorenzo Torrisi
Area di Fisica Applicata - Fisica applicata ai Beni Culturali, Ambientali e Medicina

Prof. Giancarlo Neri
Area di Fisica Applicata - Geofisica
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FISICA NUCLEARE E SUBNUCLEARE
FISICA DELLA MATERIA
FISICA APPLICATA

⋆⋆⋆ Area di Fisica Nucleare e Subnucleare ⋆⋆⋆
Referenti Proff. ri A. Trifirò e G. Mandaglio

Lezioni di interesse generale (12 ore):
1. Dinamica delle Reazioni Nucleari (4 ore);
2. Risonanze barioniche e sezioni d’urto adroniche (4 ore);
3. Fisica delle particelle con sonde elettromagnetiche e leptoniche (4 ore);

Lezioni di Interesse Specialistico (Moduli ciascuno di 10 ore; tot. 80 ore):
1. Teoria delle Reazioni Nucleari;
2. Reazioni di multiframmentazione o formazione di nuclei superpesanti;
3. Teoria delle Interazioni Fondamentali;
4. Fasci Ionici in Plasmi prodotti da Laser;
5. Rivelazione e analisi dei prodotti di reazione in Fisica Nucleare, Subnucleare e Astrofisica;
6. Risonanze barioniche e sezioni d’urto adroniche in Fisica delle Particelle;
7. Acquisizione, elaborazione dei dati e procedure di simulazione nei processi nucleari;
8. Emissione di fotoni e particelle in processi nucleari;

⋆⋆⋆ Area di Fisica della Materia ⋆⋆⋆
Aspetti Teorici
Referente Prof. S. G. Prestipino

Lezioni di interesse generale (14 ore):
1. Teoria e simulazione di liquidi atomici e molecolari: metodi, modelli, sistemi.

Lezioni di Interesse Specialistico (Moduli ciascuno di 10 ore, tot. 70 ore):
1. Modellizzazione, diagramma di fase e proprietà di trasporto di liquidi a legami idrogeno (Teoria e simulazione da principi primi);
2. Interazioni localizzate e processi di autoaggregazione in fluidi macromolecolari;
3. Formazione di aggregati in liquidi con interazioni microscopiche antagonistie;
4. Diagrammi di fase non convenzionali in fluidi semplici;
5. Teoria della nucleazione di solidi cristallini da fasi liquide;
6. Anomalie termodinamiche in sistemi metastabili;
7. Metodi avanzati di simulazione numerica.

*** Area di Fisica della Materia ***
Fisica dei sistemi Disordinati
Referente Prof. G. Carini

Lezioni di interesse generale (14 ore):
1. Disordine e Localizzazione (3 ore)
2. La transizione vetrosa (3 ore)
3. Dinamica Ionica in sistemi disordinati (4 ore)

Lezioni di Interesse Specialistico (Moduli ciascuno di 10 ore, tot. 30 ore):
1. Dinamica vibrazionale e rilassamenti in solidi amorfi;
2. Spettrosopia dielettrica in materiali a conduzione ionica;
3. Spettrosopia Meccanica in polimeri.

*** Area di Fisica della Materia ***
Fisica dei Liquidi e dei Sistemi Complessi
Referente Prof. F. Mallamace

Lezioni di interesse generale (12 ore):
1. Networking, Percolazione e Mode Coupling (4 ore);
2. Granular Materials e Arresto Dinamico (4 ore);
3. Scaling Law e Processi di Universalità (4 ore);

Lezioni di Interesse Specialistico (Moduli ciascuno di 10 ore, tot. 60 ore):
1. Econofisica;
2. Acqua e soluzioni;
3. Networks;
4. Levy flights e processi di turbolenza;
5. Universalità dei Jammings;
6. Polimeri e polielettroliti (sol-gel transition).
Lezioni di interesse generale (12 ore):

1. Materiali nano strutturati (4 ore);
2. Sistemi quantistici complessi (4 ore);

Lezioni di Interesse Specialistico (Moduli ciascuno di 24 ore, tot. 72 ore):

1. Nanomateriali e dispositivi:
   - Sintesi di nano sistemi (8 ore);
   - Materiali a bassa dimensionalità (8 ore);
   - Plasmonica e SERS (8 ore).
2. Diagnostica di nano e microsistemi:
   - Micro-imaging (8 ore);
   - Spettroscopia Elettronica (8 ore);
   - Microscopia (8 ore);
3. Processi fisici su scala nanometrica:
   - Fotonica (8 ore);
   - Intrappolamento ottico (8 ore);
   - Scattering ed assorbimento di luce (8 ore).

Lezioni di interesse generale (10 ore):

1. La visione moderna della biofisica molecolare (5 ore): organizzazione della materia biologica e termodinamica dei processi biologici (5 ore);
2. Caratterizzazione strutturale e dinamica di sistemi di interesse biofisico mediante tecniche spettroscopiche complementari e tecniche simulative.

Lezioni di Interesse Specialistico (Tot. Moduli 50 ore):

1. Proprietà chimico-fisiche delle biomolecole e influenza del solvente (e.g. folding, unfolding e misfolding delle proteine, etc...) (5 ore).
2. Caratterizzazione strutturale di sistemi di interesse biofisico (e.g. macromolecole, membrane, etc...) mediante tecniche PCS, SANS/SAXS, X-Radial Diffraction, NMR, microscopia e spettrometria di massa (15 ore).
3. Caratterizzazione dinamica di sistemi di interesse biofisico (e.g. macromolecole biologiche, sistemi host-guest, idrogels, etc...) mediante spettroscopia Raman e IR (10 ore).
4. Scattering elastico, quasi-elastico e anelastico di neutroni per la caratterizzazione dinamica di sistemi di interesse biofisico (e.g. polisaccaridi, proteine, etc...) (10 ore).

5. Tecniche calorimetriche e reologiche per la caratterizzazione di sistemi di interesse biofisico (5 ore).

6. Caratterizzazione strutturale e dinamica di sistemi di interesse biofisico mediante metodi computazionali (5 ore).

⋆⋆⋆ Area di Fisica della Materia e Area di Fisica Nucleare ⋆⋆⋆
Fisica dei Plasmi
REFERENTE PROF. L. TORMISI

Lezioni di interesse generale (4 ore):
1. Plasmi LTE e NLTE e Fisica Sperimentale associata (4 ore).

Lezioni di Interesse Specialistico (Tot. Moduli 16 ore):
1. Tecniche Diagnostiche di plasmi laser (6 ore);
2. Laser ion sources (5 ore);
3. Laser particle acceleration (5 ore).

⋆⋆⋆ Area di Fisica Applicata ⋆⋆⋆
Fisica Applicata ai Beni Culturali, Ambientali e Medicina
REFERENTI PROFF.RI D. MAJOLINO, S. MAGAZU, L. TORMISI

Lezioni di interesse generale (12 ore):
1. Le tecniche spettroscopiche nel campo dei Beni Culturali (10 ore);
2. Monitoraggio Ambientale (2 ore).

Lezioni di Interesse Specialistico (Tot. Moduli 22 ore):
1. Diffrazione di neutroni per la caratterizzazione microscopica di reperti archeologici (2 ore);
2. Lo scattering di neutroni a piccolo angolo per la caratterizzazione mesoscopica di reperti archeologici (2 ore);
3. L’assorbimento di raggi X da luce di sincrotrone per la caratterizzazione superficiale di reperti archeologici (2 ore);
4. Spettroscopia a raggi X-caratteristici (4 ore);
5. Spettrometria di massa (2 ore);
6. Tecnica LAMQS (Laser Ablation coupled to Mass Quadrupole Spectrometry) (4 ore);
7. Analisi e Trattamento di Materiali biocompatibili (2 ore);
8. Tecniche di monitoraggio inquinamento dell’aria ed elettromagnetico (4 ore).
Lezioni di interesse generale (4 ore):

1. Ricerche di geofisica e geodinamica nella regione calabro-peloritana e nel complesso Tirreno-Ionio (2 ore);
2. Studi della sismicità e della pericolosità sismica con particolare riferimento all’impiego di metodologie fisiche (2 ore).

Lezioni di Interesse Specialistico (Moduli ciascuno di 9 ore, tot. 18 ore):

1. Geofisica (9 ore);
2. Sismologia (9 ore).
Collegio dei Docenti del Dottorato di Ricerca in Fisica
## Collegio dei Docenti del Dottorato di Ricerca in Fisica
### Cicli XXX, XXXI, XXXII, XXXIII

<table>
<thead>
<tr>
<th>Docente</th>
<th>e-mail</th>
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</thead>
<tbody>
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Tesi ed Argomenti di Ricerca
Studenti del Dottorato di Ricerca in Fisica
2017
## Tesi degli Studenti del Dottorato di Ricerca in Fisica
### Ciclo XXX

<table>
<thead>
<tr>
<th>DOTTORANDO</th>
<th>TITOLO DELLA TESI</th>
<th>TUTOR CO-TUTOR</th>
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<tbody>
<tr>
<td>Dr. Cannavò Antonino <a href="mailto:acannavo@unime.it">acannavo@unime.it</a></td>
<td>Wide-bandgap detectors for low-flux radiations and laser-generated plasma diagnostics</td>
<td>Prof. L. Torrisi</td>
</tr>
<tr>
<td>Dr. Ceccio Giovanni <a href="mailto:gceccio@unime.it">gceccio@unime.it</a></td>
<td>Ion source by Laser-generated plasmas and relative diagnostics</td>
<td>Prof. L. Torrisi</td>
</tr>
<tr>
<td>Dr. Macrì Vincenzo <a href="mailto:vmacri@unime.it">vmacri@unime.it</a></td>
<td>Coherent Resonant Coupling of States with Different Excitations Numbers in Hybrid Quantum Systems</td>
<td>Prof. S. Savasta</td>
</tr>
<tr>
<td>Dr.ssa Ruello Giovanna <a href="mailto:gruello@unime.it">gruello@unime.it</a></td>
<td>Pressure dependence of the intermediate-range structure and the boson peak in oxide glasses</td>
<td>Prof.ssa G. D’Angelo</td>
</tr>
<tr>
<td>Dr. Sanzaro Salvatore <a href="mailto:ssanzaro@unime.it">ssanzaro@unime.it</a></td>
<td>Newly-Designed Spongy TiO$_2$ Layers by Modified Sputtering Methods for Hybrid PhotoVoltaics</td>
<td>Prof. F. Neri</td>
</tr>
<tr>
<td>Dr. Vasi Sebastiano <a href="mailto:vasis@unime.it">vasis@unime.it</a></td>
<td>Thermodynamics of Water and Biosystems</td>
<td>Prof. F. Mallamace</td>
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### VALUTATORI dei lavori di TESI

<table>
<thead>
<tr>
<th>DOTTORANDO</th>
<th>REFEREE</th>
</tr>
</thead>
</table>
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2) Prof.ssa Elvira Fortunato, *University of Lisbon*, Portugal |
| Dr.ssa Ruello Giovanna | 1) Dr. Lorenzo Ulivi, *CNR -IFAC - Ist. di Fis. Appl. Nello Carrara*, *Via Madonna del Piano 10*, 50019 Sesto Fiorentino, Italy  
2) Dr.ssa Silvia Caponi, *CNR - Ist. Off. dei Mat. – IOM e/o Dip. di Fis. e Geol.*, *Via Pascoli - 06100 Perugia*, Italy |
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2) Prof.ssa Elvira Fortunato, *University of Lisbon*, Portugal |
| Dr. Vasi Sebastiano | 1) Prof.ssa Carla Andreani, *Università degli Studi di Roma Tor Vergata*, *Italia*  
2) Prof. Antonio Cupane *Università degli Studi di Palermo*, *Italia* |
### Argomenti di Ricerca del Dottorato di Ricerca in Fisica

Cicli XXXI, XXXII, XXXIII

<table>
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<th>DOTTORANDO</th>
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<tr>
<td>Dr. Cannuli Antonio <a href="mailto:acannuli@unime.it">acannuli@unime.it</a></td>
<td>Dispositivi sample-environment per applicazioni biofisiche e spettroscopia neutronica</td>
<td>Prof. S. Magazu</td>
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<tr>
<td>Dr. Castorina Giuseppe <a href="mailto:giuseppe.castorina@unime.it">giuseppe.castorina@unime.it</a></td>
<td>Sviluppo di un modello fisico-matematico ad area limitata per previsioni meteorologiche</td>
<td>Prof. S. Magazu</td>
</tr>
<tr>
<td>Dr. Colombo Franco <a href="mailto:colombofranco64@gmail.com">colombofranco64@gmail.com</a></td>
<td>Tecniche di analisi di dati mediante wavelet</td>
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<tr>
<td>Dr.ssa Restuccia Nancy <a href="mailto:nrestuccia@unime.it">nrestuccia@unime.it</a></td>
<td>Impiego di Nanoparticelle in Radioterapia e Diagnostica</td>
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<td>Dr. Santoro Marco <a href="mailto:masantoro@unime.it">masantoro@unime.it</a></td>
<td>Sintesi e caratterizzazione di materiali nanostrutturati</td>
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<tr>
<td>Dr.ssa Scolaro Silvia <a href="mailto:silscolaro@unime.it">silscolaro@unime.it</a></td>
<td>Processi di fratturazione e campi di sforzo sismogenetico nell’area del mediterraneo centrale</td>
<td>Dr.ssa B. Orecchio</td>
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### CICLO XXXII

<table>
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<tr>
<th>DOTTORANDO</th>
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<tbody>
<tr>
<td>Dr. Costa Giuseppe <a href="mailto:gcosta@unime.it">gcosta@unime.it</a></td>
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</tr>
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</table>

### CICLO XXXIII

<table>
<thead>
<tr>
<th>DOTTORANDO</th>
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<th>PROFESSORE DI RIFERIMENTO</th>
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<tbody>
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</tbody>
</table>
PUBBLICAZIONI
DEGLI
STUDENTI DEL DOTTORATO
DI RICERCA IN FISICA
2017
PUBBLICAZIONI 2017 XXX Ciclo

Antonino Cannavò


*****

Giovanni Ceccio


Vincenzo Macrì


Giovanna Ruello


Salvatore Sanzaro


Sebastiano Vasi


*****
PUBBLICAZIONI 2017 XXXI Ciclo

Antonio Cannuli

Giuseppe Castorina
Franco Colombo


Nancy Restuccia


Marco Santoro


Silvia Sciaro

PUBBLICAZIONI 2017 XXXII Ciclo

Giuseppe Costa


Israa Medlej


Valeria Indelicato


Giuseppe Paladini


Valentino Romano

1. V. Romano, “Atomic packing and low energy vibrations in $\text{B}_2\text{O}_3$ glasses”, Messina Ph.D. Activity Report 2016, ISSN 2038-5889


Galleria Fotografica degli Studenti del Dottorato di Ricerca in Fisica 2017
Ph.D. Student Cycle XXX
Ph.D. Student Cycle XXXI

Antonio Cannuli

Giuseppe Castorina

Franco Colombo

Nancy Restuccia

Marco Santoro

Silvia Scolaro
Ph.D. Student Cycle XXXIII

Cristiano Calabretta
Sveva Longo
Francesco Patti
Alessio Settineri
Daniele Spucches
Alta Formazione
Ricerca Scientifica
E
Relazioni Internazionali
Alta Formazione, Ricerca Scientifica e Relazioni Internazionali  
Via Consolato del Mare 41 (Palazzo Mariani)

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I Corsi di Dottorato di Ricerca, raggruppati in Scuole, hanno il compito di organizzare e gestire, sia a livello nazionale che internazionale, la formazione superiore finalizzata allo svolgimento di attività di ricerca di elevato livello e rappresentano, propriamente, il terzo livello degli studi universitari. I Corsi di Dottorato hanno durata triennale/quadriennale e prevedono la frequenza obbligatoria. Requisito di ammissione è il possesso della Laurea Specialistica e/o Magistrale o il Diploma di Laurea conseguito prima dell’entrata in vigore del D.M.5009/99 ovvero di altro titolo di studio conseguito all’estero e riconosciuto idoneo, oltre il superamento delle prove di esame previste dai Bandi di concorso emanati dall’Università e pubblicati nella Gazzetta Ufficiale della Repubblica Italiana. Almeno la metà dei posti messi a concorso è coperta da borse di studio in parte finanziate dal MIUR e dall’Ateneo, in parte da altre Università o Enti esterni pubblici o privati. Il titolo di Dottore di Ricerca si consegue all’atto del superamento dell’esame finale che consiste nella discussione della Tesi di Dottorato e che può essere ripetuto una sola volta. È possibile, inoltre, ottenere la menzione del Doctor Europaeus nel caso in cui parte degli studi siano stati condotti all’estero.

http://www.unime.it/didattica/corsidottorato/doceuropaeusweb.pdf
http://ww2.unime.it/dottoratofisica

Post-Dottorato di Ricerca

Le borse di studio post-dottorato vengono assegnate, con un concorso per titoli, ai possessori del titolo di Dottore di Ricerca. Hanno una durata biennale e prevedono un’attività di ricerca da svolgersi non solo in strutture dell’Università di Messina ma anche presso i laboratori stranieri con i quali siano in corso attività di collaborazione.

Perfezionamento Estero

Le borse di perfezionamento estero hanno una durata annuale e vengono assegnate, con un concorso per titoli ed esami, ai possessori della Laurea Specialistica e/o Magistrale o il Diploma di Laurea conseguito prima dell’entrata in vigore del D.M.5009/99 ovvero di altro titolo di studio conseguito all’estero e riconosciuto idoneo; di età inferiore ai 29 anni che documentino un impegno formare di attività di perfezionamento presso istituzioni estere o internazionali di livello universitario.

Borse Private

Le borse private, o alla memoria, vengono finanziate da soggetti privati esterni all’Università e prevedono anch’esse lo svolgimento di un particolare progetto di ricerca specificato nel bando di concorso.
Alta Formazione, Ricerca Scientifica e Relazioni Internazionali
Via Consolato del Mare 41 (Palazzo Mariani)

Delegato alla Ricerca
Prof. Salvatore Cuzzocrea
salvatore.cuzzocrea@unime.it – 090 676 5208

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