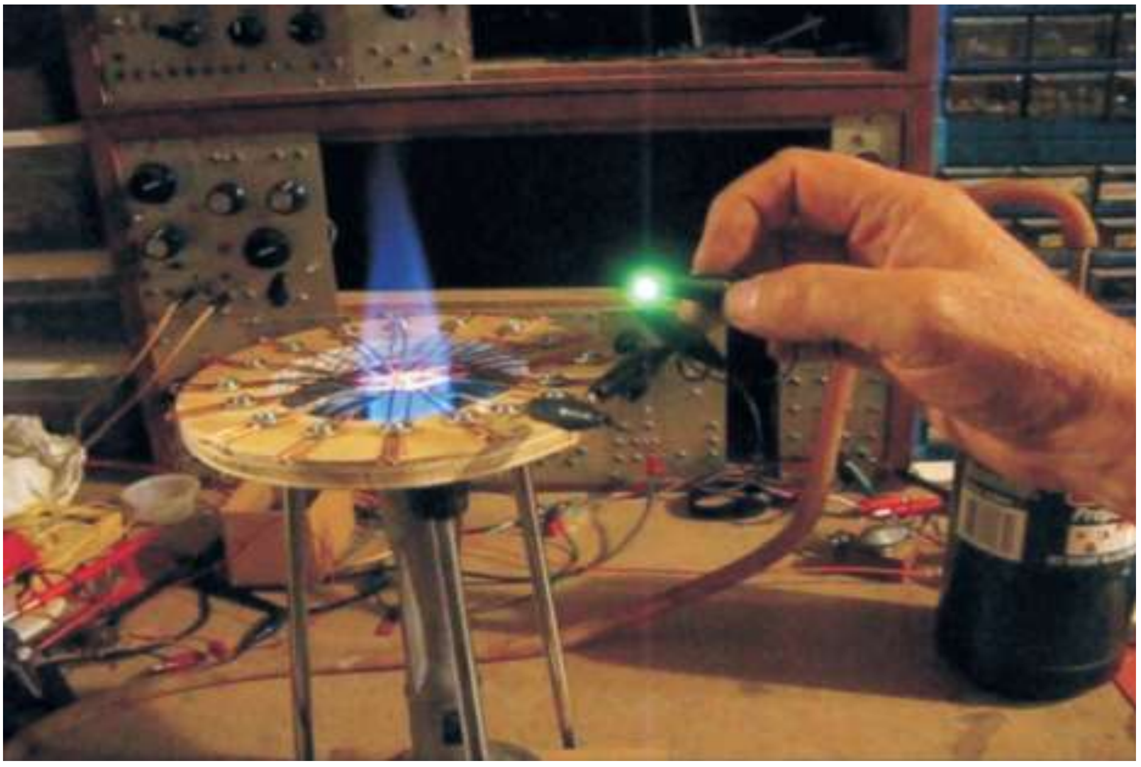
ISTITUTO LOMBARDO
ACCADEMIA DI SCIENZE E LETTERE

Workshop



Modern Aspects of the combined applications of Heat-Electricity-Mechanics

26 ottobre 2017

Milano, Palazzo di Brera, Via Brera 28

Istituto Lombardo Accademia di Scienze e Lettere

The Istituto Lombardo was founded by Bonaparte in 1797 on the model of the *Institut de France* with the task of collecting the discoveries and improving arts and sciences. The Institute became a meeting point for the most famous personalities of the time in the field of sciences as well of letters and arts: Alessandro Volta, Antonio Scarpa, Barnaba Oriani, Andrea Appiani, Vincenzo Monti and others. Alessandro Volta was appointed as first president in 1803. The Institute has constantly maintained its activity counting among its members famous personalities as Alessandro Manzoni (appointed as president in 1859) and also Nobel prizes as Camillo Golgi, Giosuè Carducci and Giulio Natta. During two centuries the members have shared in the activities of the Academy, which are aiming both at publishing original studies (Memoirs and Reports) and at stimulating discoveries through competitions and prizes. The historical and scientific identity of the Institute is completed by a rich library and a precious archive that, among others, counts the complete collection of the Alessandro Volta's original manuscripts.

Conference Presentation

During the last two centuries the interrelationships involving heat and energy, their effects in thermodynamic fields, the electric effects related to temperature gradients, the crucial role of the friction, as well as the applications in technical issues, have been the scenario of relevant scientific developments in Physics, Chemistry and Technology. Recently novel aspects involving that *triade* have arisen and significant improvements are being expected in the strictly scientific field and in the technical applications. A significant European project, having the acronym MAGENTA, in particular involving the Thermoelectricity, has been promoted and includes the participation of Italian scientists, some of them belonging to our Istituto Lombardo. The meeting has the aim of bringing to the attention of the general community the modern aspects of that *triade* and meantime of addressing the scientific status, by gathering distinguished scientists involved in the related fields.

Scientific Committee:
Ferdinando Borsa
Attilio Rigamonti
Andrei A. Varlamov

Program

9.00 **SILVIO BERETTA**
Welcome by the President Istituto Lombardo Accademia di Scienze e Lettere

9.15 **SAWACO NAKAMAE**
SPEC, CEA, CNRS, Université Paris-Saclay, P.I. of the “MAGENTA” project
Magnetic nanaparticle based liquid energy materials for thermoelectric applications

9.50 **ANDREI A. VARLAMOV**
Istituto Lombardo Accademia di Scienze e Lettere, Spin-CNR
History and modern trends in the studies of thermoelectricity

10.25 **ERIO TOSATTI**
Istituto Lombardo Accademia di Scienze e Lettere, SISSA - ICTP di Trieste
The renaissance of friction: from empirism to physics at the nanoscale

11.00 *Coffee break*

11.15 **LUCIANO COLOMBO**
Istituto Lombardo Accademia di Scienze e Lettere, Università di Cagliari
Thermal transport in organic glasses

11.50 **GIORGIO BENEDEK**
Istituto Lombardo Accademia di Scienze e Lettere - Università degli Studi di Milano Bicocca
Graphene as a quantum playground

12.25 **MAURO FRANCESCO SGROI**
Group Materials Lab. Environment & Chemical Analysis C.R.F. S.C.P.A.
Increasing the efficiency of internal combustion engines: heat recovery from exhaust gases by thermoelectric effect

Discussion

13.20 *Lunch*

Summaries

SAWACO NAKAMAE

SPEC, CEA, CNRS, Université Paris-Saclay, P.I. of the "MAGENTA" project

Magnetic nanoparticle based liquid energy materials for thermoelectric applications

Thermoelectric (TE) materials that are capable of converting heat into electricity have been considered as one possible solution to recover the low-grade waste-heat (from industrial waste-stream, motor engines, household electronic appliances or body-heat). Solid semiconductor-based TE-modules were the first to enter the commercial application, and they still dominate the TE-market today. Despite their technical robustness including long life-time, simple use involving no moving parts, TE-technology has long been limited to low-power applications due to their poor efficiency. Closely following the rise of 'nanotechnology' in the 1980's - 90's, there has been a huge increase in the TE materials research in the past 20 years, which has led to some remarkable improvements in thermal-to-electric energy conversion capacity. However, even the most "promising" materials have not yet reached the minimum ZT requirements [1]. Furthermore, solid TE-materials suffer from a variety of practical obstacles such as small sizes, substantial production costs and the use of scarce and/or toxic raw materials, precluding them from wide-scale applications. Clearly, a technological breakthrough in TE-materials research is needed in order to make the thermoelectric technology environmentally friendly and economically viable for its future use.

MAGENTA [2] is a 4-year research & innovation project that aims at bringing a paradigm change in TE-technology by exploiting the magneto-thermoelectric (MTE) property of ionic-liquid (IL) based ferrofluids (FF), i.e., colloidal dispersions consisting of magnetic nanoparticles (MNPs) in non-magnetic ionic liquids. Magnetic nanoparticles are, as the name suggests, a class of nanoparticles (less than 1 μm in diameter) made of magnetic elements such as iron and nickel and their alloys and chemical compounds. They are used in a plethora of technological fields from biomedicine to data storage. However, their use in energy applications remains quite limited so far. Ionic liquids (IL), on the other hand, are enjoying substantial attention in several areas of energy research including thermoelectricity in recent decades [3, 4]. As a thermoelectric material, ILs present many promising features such as high electrical conductivity, large temperature and electrochemical windows, low vapour pressure and toxicity, and raw material abundance [5].

In this presentation, I will discuss MAGENTA's *scientific motivations* (how to produce thermoelectric voltage and current using IL based ferrofluids), *the methodologies* to be used and *the project objectives*; *i.e.*, 1) to provide founding knowledge of novel MTE phenomena in IL based ferrofluids, and 2) to build application-specific MTE prototypes with tailor-made IL-FFs for their use in targeted industrial sectors (cars and portable electronics). Some encouraging preliminary results on liquid thermoelectric materials obtained by the project partners will also be presented.

References:

[1] For thermoelectric devices to be competitive against other renewable energy technology (*e.g.,* geothermal), *ZT* values greater than 4 are considered mandatory. See, for example: C. B. Vining, "An inconvenient truth about thermoelectrics," *Nat. Mater.* 8 (2009), 83.

[2] MAGENTA project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731976

[3] D. R. MacFarlane et al., "Energy applications of ionic liquids," *ENERGY & ENVIRONMENTAL SCIENCE*, 7 (2014) 232.

[4] A. Khan, et al., "Oxygen Reduction Reaction in Ionic Liquids: Fundamentals and Applications in Energy and Sensors" *Sustainable Chem. Eng.*, 5 (2017), 3698.

[5] M. F. Dupont et al., "Thermo-electrochemical cells for waste heat harvesting – progress and perspectives," *ChemCom* (2017), DOI: 10.1039/c7cc02160g.

ANDREI A. VARLAMOV

Istituto Lombardo Accademia di Scienze e Lettere, Spin-CNR

History and modern trends in studies of thermoelectricity

The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the microscopic level of understanding one can say that an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side.

We will start our discussion from the discovery of the phenomenon of thermoelectricity by the Estonian physicist Thomas Johann Seebeck in 1821 and its early manifestations. Today the term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect, and Thomson effect.

Application of magnetic field considerably increases the variety of possible manifestations of thermoelectricity. The most known among them is the Nernst effect which is nothing else as a thermoelectric effect observed when a conducting sample is subjected to a magnetic field and a temperature gradient perpendicular to each other. The crossed electric and magnetic fields should lead to the drift of a charged particle in the direction perpendicular to both of them. In the case of broken circuit condition such motion of the carriers is prevented by the appearance of the temperature gradient in corresponding direction, what is the essence of the Nernst-Ettingshaus effect, reciprocal to the Nernst one.

The theory of thermoelectric and thermomagnetic phenomena in metals and semiconductors, based on the quantum theory of solids, was developed in the middle of XX century. It was found that in metals these effects are negligibly small (for Bi the Seebeck coefficient is maximal and is of the order of 7μV/K).

The magnitudes of thermoelectric signals considerably increases in semiconductors and this allows to use them as the working elements of thermoelectric generators (solid state devices that convert heat flux - temperature differences - directly into electrical energy), for studies of the scattering mechanisms in semiconductors, etc.

Today the interest for the thermoelectricity is very high, especially in view of the possibility to design new artificial materials with tuned high thermoelectric properties: graphene, new generation of superconductors, conducting polymers, electrolytes and ferrofluids. Their non-trivial properties will be reviewed in the second part of our presentation.

ERIO TOSATTI
Istituto Lombardo Accademia di Scienze e Lettere, SISSA - ICTP di Trieste

The renaissance of friction: from empirism to physics — at the nanoscale

Friction and its science hold more than a record. One is longevity: from its very origins, mankind has had to reckon with it. Still today, nonetheless, reducing or increasing friction remain technological and practical objectives of enormous importance — one can read for example that no less than 5% of all energy produced daily degrades into wasted frictional work. Another record is that despite the involvement of great scientist like Leonardo, who already five centuries ago gave friction its first scientific bases, there is still today no proper theoretical formulation of friction, and theorists mostly limit themselves to what P.W. Anderson jokingly defined in a different context "the indignity of numerical simulations".

However, progress in science does not happen because it is necessary, but because it is possible. In the last decades, new mesoscopic and nanoscopic experimental techniques opened new windows on frictional phenomena at the atomic and molecular level. Jump-started by the necessity and indeed the challenge to understand some of that data, theory and simulation progress is moving on along some lines which I shall briefly describe.

LUCIANO COLOMBO
Istituto Lombardo Accademia di Scienze e Lettere, Università di Cagliari

Thermal transport in organic glasses

Glassy materials are condensed matter systems showing physical properties in between solids and liquids. In their structure they retain information about the thermal history they have been subjected to and the way they have been prepared. Formally, this implies that the landscape of their configurational energy is a complex corrugated multi-dimensional surface, showing quite a few basins with different depths, widths, and shapes: the system can be trapped in any of them.

Recently, it has been demonstrated experimentally that ultra-stable glasses (i.e. systems trapped extremely low in the energy landscape) can be grown by physical vapour deposition of organic molecules on a substrate. The physics of such organic glasses is now enriched by a new feature, namely by the anisotropic molecular structure of the basic building block used to assemble the film.

TPD organic glasses have been reproduced by atomistic simulations that mimic vapour deposition and their thermal transport properties have been accordingly calculated. Simulations generate a rational phenomenology providing robust evidence that heat transfer is not isotropic but, rather, that it is correlated to an inherent molecular property, namely the axial structure of the TPD molecule. Temperature effects have been as well investigated, further confirming the picture.

GIORGIO BENEDEK
Istituto Lombardo Accademia di Scienze e Lettere - Università degli Studi di Milano Bicocca

Graphene as a quantum playground.

The modern triathlon “heat-electricity-mechanics” has an indisputable champion, graphene, as a recordman, among all materials in normal conditions, in all three specialties: thermal conductivity, electrical mobility and mechanical strength. On the other hand graphene, being perfectly planar, is the simplest of all possible sp2 pure carbon structures. The graphene family includes curved forms like fullerenes, having gaussian curvature $G > 0$, nanotubes, with $G = 0$ like graphene, and schwarzites with $G < 0$ and vanishing mean curvature. The conjugation of carbon-carbon sp2 bonds makes several global electronic and vibrational properties of graphenes to primarily depend upon the structure topology. Global properties which can be estimated on topological grounds are the growth process, the isomer hierarchy, the vibrational spectrum, the elastic constants, the porosity as a function of the deposition energy, etc. The dynamics of free electrons in graphene is well described by the Dirac quantum-relativistic equation, and some of its consequences like the Zitterbewegung and Klein’s paradox have been proved in graphene. Thus graphene allows for the simulation and validation of fundamental theories in fields hardy accessible to experiments like high-energy physics and cosmology. With some surprising prediction! It is a fact that since the late XIX century topology has become a reference paradigm in many branches of fundamental physics, from Hermann Weyl’s topological theory of electricity and cosmological wormholes, to string theory and present topological field theories in high-energy physics.

MAURO FRANCESCO SGROI

Group Materials Lab. Environment & Chemical Analysis C.R.F. S.C.P.A.

Increasing the efficiency of internal combustion engines: heat recovery from exhaust gases by thermoelectric effect

The concern related to global warming is generating a legislative pressure on reducing CO_2 emissions that is forcing automotive industry to find alternative and more efficient solutions to internal combustion engines. In Europe, the current regulation for passenger vehicles limits the CO_2 emissions calculated as fleet average to 130 g/km and fix a target value of 95 g/km to be achieved by 2021. Car manufacturers will have to pay heavy penalties for each registered vehicle exceeding the CO_2 limits (€95 per exceeding gram by 2019).

Concurrently, the regulations on toxic emissions (CO, NO_x, unburned hydrocarbons, particulate matter) is also becoming more and more stringent and requires complex and costly abatement systems to respect the strict limitations imposed on NO_x and particulate matter emissions.

On the other hand, zero emission electric vehicles, based on batteries, are still not mature enough for a replacement of the internal combustion engine in extra-urban applications, since they are not able to guarantee the driving range required by customers. Hydrogen fuelled vehicles, could meet the same performance of conventional cars, but the cost of materials used in the fuel cell stack is preventing the penetration into the market.

Therefore, even though characterized by low energy efficiency, the internal combustion engine will remain, in the short-medium term, the reference technology for the transport industry but the environmental regulations will impose its hybridization with electric systems. Hybrid architectures allow the circulation in electric mode in urban areas, limiting the local pollution, and increase the efficiency of the car through energy recovery during breaking phases.

An energetic analysis of conventional internal combustion engine reveals that about 70% percent of the chemical energy stored in the fuel is converted in to mechanical energy for traction: the remaining part is dissipated as heat in the exhaust gases (30%) and in the cooling circuit (40%).

So a great amount of thermal energy (tens of kW) is available on a car and its effective recovery can dramatically increase the efficiency of the system. Hybrid systems facilitate this task, since the produced electric energy can be stored in the battery pack.

Thermoelectric generators (TEGs) offer the possibility to directly convert thermal energy into electricity with a reduced complexity and potential low cost. Even though available semiconducting junctions are characterized by low efficiency and limited operating temperatures, coupling a TEG to the internal combustion engine would allow recovering about 1 kW of electric power on a medium size car, with a reduction of CO_2 emissions of about 10 g/km.

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