CeFEMA

Center of Physics and Engineering of Advanced Materials

Newsletter February 2016

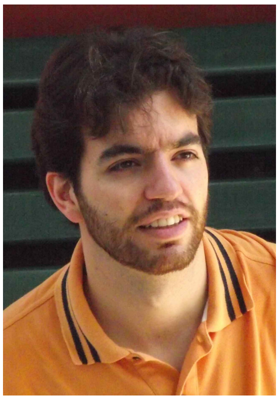
Editorial

PEDRO JOSÉ SEBASTIÃO

This is the second number of CeFEMA newsletter, where we aim at reporting the most recent research activities of CeFEMA to a broad community, be it academic or entrepreneurial, which might be interested in materials science and condensed matter physics. In this number are presented a theoretical work of CeFEMA researchers on systems away from equilibrium and works related to the development of membranes for wine quality improvement and new ceramics materials for dental care.

A step away from equilibrium

PEDRO RIBEIRO



In nature no system is at strict equilibrium. Yet, most of what we know of matter concerns its equilibrium properties. The very notion of a matter phase refers to equilibrium states such as solids, liquids or gases. However, key thermodynamic concepts, such as temperature and entropy, are hard to reconcile with non equilibrium quantum dynamics. So, why do equilibrium descriptions work so well? How does temperature emerge from the microscopic laws, ruled, ultimately, by quantum mechanics? What lyes beyond equilibrium matter phases? Which new properties can be expected? And, how can we use them in technology for energy harvesting, sensing, quantum computing, etc.? These are some of the questions we presently address at CeFEMA.

The fundamental and technological challenges

When modelling complex systems it is impossible and even useless to track all microscopic details. Instead one focus on a small set of degrees of freedom, that are the relevant variables at a certain energy scale, and fix thermodynamic quantities, such as temperature, pressure or stoichiometry, appealing to a weakly coupled external environment. The program of understanding what happens as we perturb a system slightly away from equilibrium has been a tremendously successful way of understanding equilibrium phases of matter and their properties. Questions that arise as we step far away from equilibrium are of a rather different nature and a systematic program to study quantum non-equilibrium matter has not yet emerged. Moreover, a system can be away from equilibrium in many different ways. A first set of problems relate to the emergence of an equilibrium state from out of equilibrium initial conditions. In open systems this is achieved by changing energy or particles with an environment. However some quantum systems seem to reach some form of equilibrium even in the absence of an environment. The conditions for this to happen have been recently reexamined and are currently under debate. They help to explain why the equilibrium description is so successful, how temperature emerges, and when such assumptions can fail. Another set of non-equilibrium problems is due to the presence of various environments at different thermodynamic potentials in such a way that the system cannot be at equilibrium with all of them. Under these conditions particle or energy currents may ensue. This is a ubiquitous situation for many technological applications. The study of how the quantum mechanics gives rise to classical thermodynamic concepts such as entropy production, work and the existence of local temperatures is an active research field. Yet, a different set of questions arise when dealing with quantum technologies. A delicate balance is needed between being able to interact with a quantum system and screening it sufficiently from its environment so that decoherence does not render the evolution essentially classical. Coming up with new ways of protecting quantum states while still being able to manipulate them efficiently is a great challenge, required to developed useful quantum computers. These are exciting times as progress in the manipulation and control over quantum devices has rendered these different sets of questions at experimental reach. At the technological level, the progressive miniaturization of devices has made their quantum mechanical description unavoidable. Progress in the understanding of non equilibrium processes in nano devices, in particular in those interfacing spin end electronics, is of immediate interest for data storage, sensing and information processing.

Our work at CeFEMA

The research being developed at CeFEMA touches a number of these questions. We are particularly interested in exploring electronic matter away from equilibrium as a root to new and yet unknown regimes with properties unreachable under equilibrium conditions. At a fundamental level we are investigating how to extend the notions of quantum phases of matter and phase transitions to open quantum systems away from thermal equilibrium. We explore new non equilibrium phases and identify the role of currents to enhance and stabilize ordered states, such as superconductors and magnets. Our topics also include the characterisation of current carrying states, the role of different electronic environments, the study of entanglement entropy production and the establishment of topological order. Advances in these topics have potential applications in nano-engines for energy harvesting, cooling and spin caloritronics.

Development of membrane based processes for wine quality improvement

Vitor Geraldes

Different membrane unit operations are being gradually adopted by the wine industry to replace more conventional processes, in different parts of the wine production process. Wine tangential microfiltration and tartaric stabilization by electrodialysis [1], for instance, are now well established technologies that are ubiquitous in the wine manufacturing process. The success of these technologies is grounded on factors such as gentle wine processing, low energy consumption and less pollution generation. Membrane processes have also been used to improve the wine quality. Reverse osmosis is used now widely to concentrate grape must [2], in order to increase the final alcohol concentration of wine. The final adjustment of the alcohol concentration is also performed combining reverse osmosis of the wine with distillation of the permeate [3]. Beyond these well-established membrane technologies, there are still opportunities to develop new membrane-based operations to improve the wine quality. The excess of volatile acidity in wines, for instance, is an economic worldwide problem, causing in many cases the loss of large volumes of wine, contributing to the increase on waste generated by the industry as well as profit loss. Typically, the volatile acidity, which comprises mainly acetic acid and ethyl acetate, can occur at any point in the wine production process, even during the harvest, occurring anytime when there are contamination with acetobacters and contact with atmospheric oxygen. Biologic wines are significantly exposed to this problem, for obvious reasons. In the MemChem group of CeFEMA we have been investigating an hybrid process that combines electrodialysis and nanofiltration to remove volatile acidity from wines [4]. In particular, this year, we have been focused on the selection of the best polyamide-based membrane that selectively permeates the acetic acid and ethyl acetate, without losing valuable organoleptic compounds [5]. This process is still under optimization, but it is already used in industrial tests by the company Wineinova (wineinova.com) and a triennial report was already submitted this year, by this company, to the Instituto do Vinho e da Vinha (IVV). The main objective of these industrial tests is to demonstrate that the process is effective, improves the overall quality of the wine and is well accepted by the wine producers.

Another important problem that is been addressed, in collaboration with Wineinova, is the membrane treatment of wine with Brett off flavor. This off flavor is caused by 4-ethylphenol (4-EP) and 4-ethylguaiacol (4-EG) compounds in concentrations less than 1 mg/L, produced Brettanomyces/Dekkera yeasts, mainly during the wine ageing in oak barrels. Diluting contaminated with uncontaminated wine is not usually a good solution to solve this problem, because the concentration of 4-EP and 4-EG normally exceeds the sensory threshold concentration by more than a factor of two and the fraction of the contaminated wine frequently is very large. This is a severe problem worldwide, which has no satisfactory solution yet and is responsible for economic losses that range into the hundreds of millions of dollars annually. Nanofiltration of the wine followed by adsorption of the off flavor compounds, using activated carbon or other adsorbents, has been tried [6], but the overall quality of the wine decreases dramatically, because valuable aroma compounds are removed also. An innovative and proprietary membrane-based process to remove Brett off-flavour has been developed and already tested by Wineinova with promising results, but research is still necessary to increase efficiency of the method and to reduce the production cost. A master thesis is under way this year, with a collaboration between Wineinova and IST, to optimize this new process of ellimination of the Brett off flavor, by reducing the water and energy consumption to minimal levels and identifying the best integration strategy of the membrane operations.

[1]M. Norberta de Pinho (2010). Membrane Processes in Must and Wine Industries. Membrane Technology: Membranes for Food Applications, Volume 3, 105-118
[2] M. Norberta de Pindo, *et al.* U.S. Patent No. 8,945,645. 3 Feb. 2015
[3] Fernando da Silva Gonçalves, *et al.* U.S. Patent Application 10/561,540
[4] Vítor Geraldes *et al.* PT 105008 (2013)
[5] Joana Viais Temido, MSc Thesis, IST (2015)
[6] Ugarte P, *et al.* Am J Enol Vitic **56**, 30-36 (2005)

Dental wear studies

Mafalda Guedes
Célio Figueiredo-Pina

Ceramic materials offer the possibility of recreating the functionality and aesthetics of natural teeth and are widely used in dental restoration, without constraints regarding the size of the denture element. Common uses include fillings, veneers, crowns, bridges and implants. However, the typical brittle behaviour and low fracture toughness values often determine the premature collapse and early replacement of all-ceramic prosthesis. The development and selection of prosthetic ceramics with high reliability and low cost is therefore of great importance to the dental community. In this context the Nanomatter group develops work in the field of dental materials in two main areas: tribological characterization, and development of new dental ceramic with improved mechanical properties.

Dental wear results from the forces associated with mastication, together with the chemical and thermal aggressive environment of the oral cavity. It is a natural and unavoidable physiological process, particularly at the occlusal surfaces. However, wear between restorations and natural teeth can introduce pathological damage, leading to lack of contact between opposing teeth (or teeth/restoration) and disturbance of the mastication process efficiency. An ideal restorative material should therefore present tribological behaviour similar to that of dental enamel (regarding surface roughness, coefficient of friction and wear mechanism), in order to avoid excessive dental abrasion. Wear tests are mandatory to dismiss the possibility of tooth pathological wear and constitute an important tool regarding selection of dental materials. Also, wear studies enlighten the clinical management of tooth wear, in the sense that they tutor minimization of causal factors, while comparing new and traditional restorative dental materials for replacement of missing tooth tissue. Aiming to contribute to these goals, the Nanomatter group carries out comparative studies to understand the friction and wear behaviour of human teeth against available restorative materials. This work has been carried out in a partnership with ZIRCLAB, a Portuguese manufacturer of ceramic dental materials.

The work of the Nanomatter group on dental wear targets the effect of surface veneers that usually coat the commercial materials used in dental crowns. These coatings are applied to approximate the colour and translucency of restoration materials to those of patient's natural teeth. Commercial systems studied so far include zirconia, alumina and lithium disilicate, either uncoated or veneered with fluorapatite or feldspar porcelain. A number of liquid media with different pH values, the effect of the presence of microbiota and the effect of temperature have already been tested. Attained results have allowed ranking pairs of commercial dental material regarding their resistance to wear in several service conditions. The most important conclusion drawn so far regards the effect of the presence of a veneer layer: the application of coating results in an increase of the overall wear of restoration/tooth couples tested. While no measurable wear was found both for unveneered zirconia, alumina or disilicate plates, a significant wear rate results whatever the applied veneer. Likewise, antagonist tooth cusps used against veneered materials show higher mass loss than tooth cusps used against unveneered plates. These results suggest that the application of coatings to zirconia dental crowns should be avoided in areas where effective contact between natural teeth and the artificial crown takes place during mastication. As a practical result of such findings, ZIRCLAB changed its coating procedures and now advices their dentist clients to use unveneered tooth crowns in occlusal surfaces.

CG Figueiredo-Pina *et al.*, J. Mechanical Behavior of Bio Materials 53, 226-238 (2016)
M Guedes *et al.* Bulletin of Materials Science **37**, 695-703 (2014)
CG Figueiredo-Pina*et al.*, Wear **297**, 872-877 (2013)

Events

2015

Mathematica
First course in Mathematica lectured by Pedro Ribeiro, on 6, 13, and 20th of October, Total time 4h30 (1h30 min/session). This course was received with great success by CeFEMA students and researchers.

Mini-Workshops
Theoretical Condensed Matter Physics
IST, January 6, 2015

Theoretical Condensed Matter Physics
IST, December 18, 2015

Seminars
Feb. 12$^{\text{th}}$ Dr. Héctor Ochoa Donostia International Physics Center (DiPC), San Sebastián, Spain
July 22$^{\text{th}}$: Aldona Balčiūnaitè, Department of Catalysis, Center for Physical Sciences and Technology, Vilnius, Lithuania
Nov. 5$^{\text{th}}$: Cláudia Cardoso Centro S3, CNR-Istituto Nanoscienze, Modena, Italy
Dec. 4$^{\text{th}}$: Gisele Iulianelli IMA - UFRJ, Rio de Janeiro, Brasil

2016

CeFEMA seminars
Inter-group seminars scheduled for March, April, May, October, November and December.

Workshop
Correlations, integrability, and criticality in quantum systems
Évora, Portugal, 24-28 October 2016

Mathematica
A repetition of this course is likely to happen during 2016 in a date to be announced in the CeFEMA website.

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