Carlos Nieto de Castro

IONIC LIQUIDS AND NANOMATERIALS

Fundamental Tools for Chemistry Redesigning?

FACULDADE·DE·CIÊNCIAS UNIVERSIDADE·DE·LISBOA

CENTRO DE CIÊNCIAS MOLECULARES E MATERIAIS

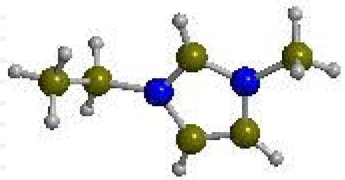
Objective

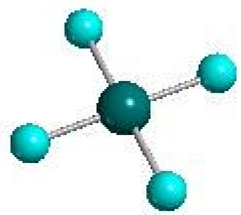
- To make an introduction to ionic liquids, nanomaterials and nanofluids
- To emphasize the difficulties encountered in measuring thermophysical properties well and with a certified accuracy (uncertainty)
- To illustrate the plethora of applications of both fields
- To foresse the impact of these areas in 21st century chemistry and chemical engineering

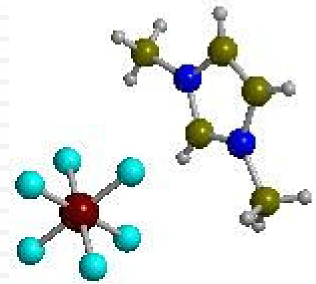
Outline

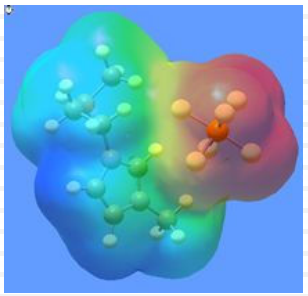
- Ionic Liquids
- Nanomaterials
- Nanofluids
  - IoNanoFluids
  - Bucky Gels
- Applications
- Problems in the Measurement of Thermophysical Properties
- Chemistry Redesigning?

IONIC LIQUIDS

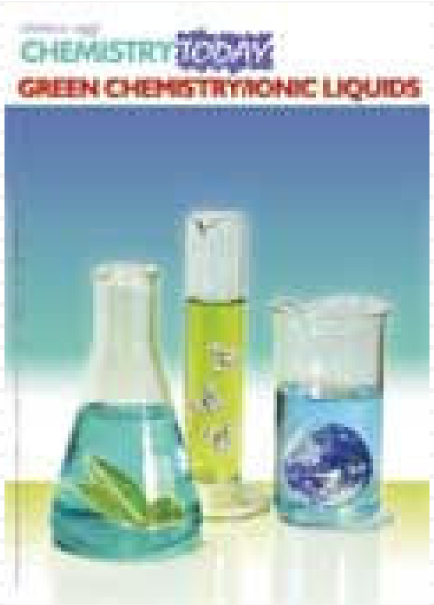








$[bmim][PF_6]$



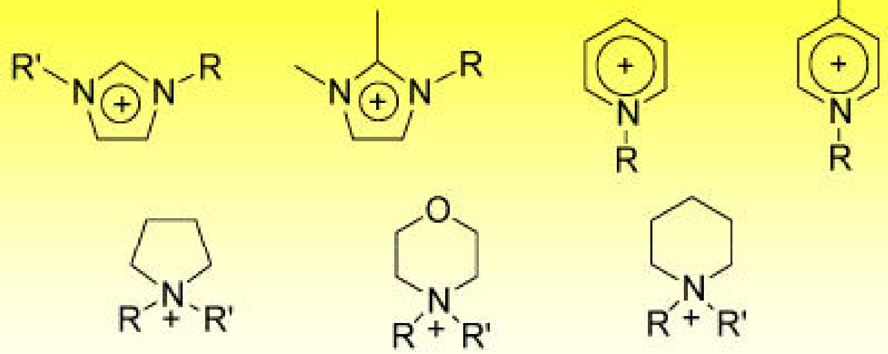
Why Ionic Liquids?

- Low temperature ionic liquids (LTIL's) are innovative fluids for chemical and materials processing, generally non-flammable and non-volatile at ambient conditions, and thus, perceived as "green" solvents.
- However, to implement new processes, it is necessary to prove that they are competitive with the traditional processes, not only from the point of view of final products, but for all the technological operations involved in the processes.
- The optimal technological design of green processes requires the characterization of the ionic liquids used, namely values of their **thermodynamic, transport and dielectric properties**

Ionic Liquids

Ionic Liquids - commonly defined as materials that are composed of cations and anions which melt at or below 100 °C

Cations



R , R' : Ethyl, Propyl, Butyl, Pentyl, Hexyl, Octyl, etc.

Anions

Cl^-, Br^-, PF_6^-, SbF_6^-, BF_4^-, OTf^-, $MeSO_4^-$,

NO_3^-, $N(CN)_2^-$, SCN^-, $Co(CO)_4^-$

World interest has grown exponentially in the last years

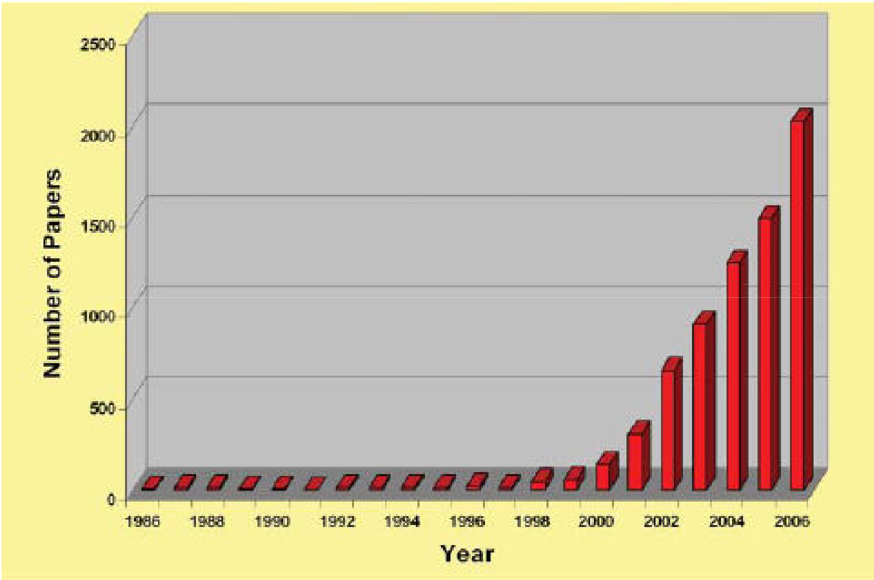


Fig. 15 Steeper than exponential growth of ionic liquid publications, 1986–2006.[59]

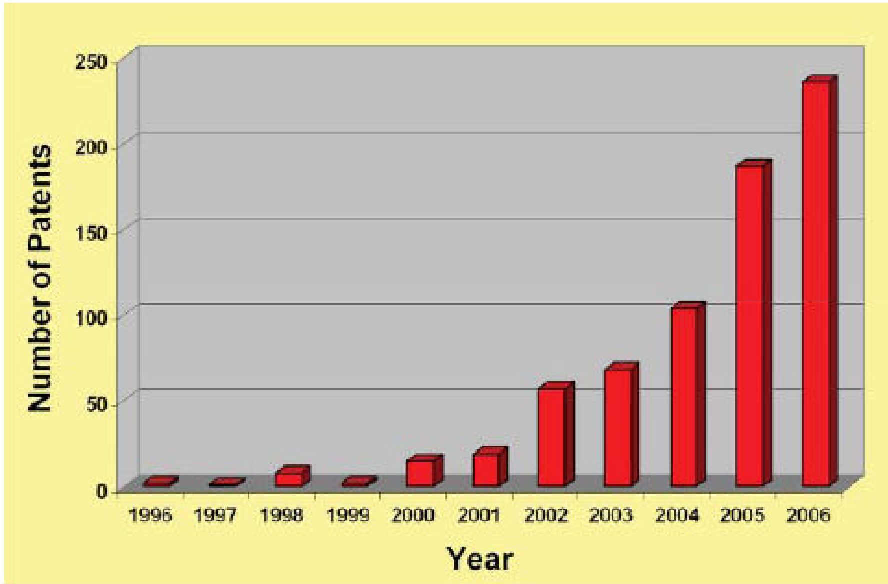


Fig. 16 Annual growth of ionic liquid patents, 1996–2006.[59]

In "Applications of ionic liquids in the chemical industry", Natalia V. Plechkova and Kenneth R. Seddon, Chem. Soc. Rev., 2008, 37, 123-150

IL Properties

- **RTILs** possess a unique array of physico-chemical properties that make them suitable in numerous **task-specific applications** in which conventional solvents are non-applicable or insufficiently effective.
- Such properties include:
  - **high thermal stability,**
  - **high electrical conductivity,**
  - **large electrochemical window** (the electrochemical window is the range within which cations and anions are inert toward electrochemical oxidation and reduction),
  - low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment,
  - **very good solvents properties** for a wide variety of organic, inorganic and organometallic compounds: in some cases, the solubility of certain solutes in RTILs can be several orders of magnitude higher than that in traditional solvents.
- Moreover, by fine-tuning the structure, these properties can be tailor-designed to satisfy the specific application requirements.
- As a result, ionic liquids are very popular materials and they enjoy a plethora of applications in various domains of physical science

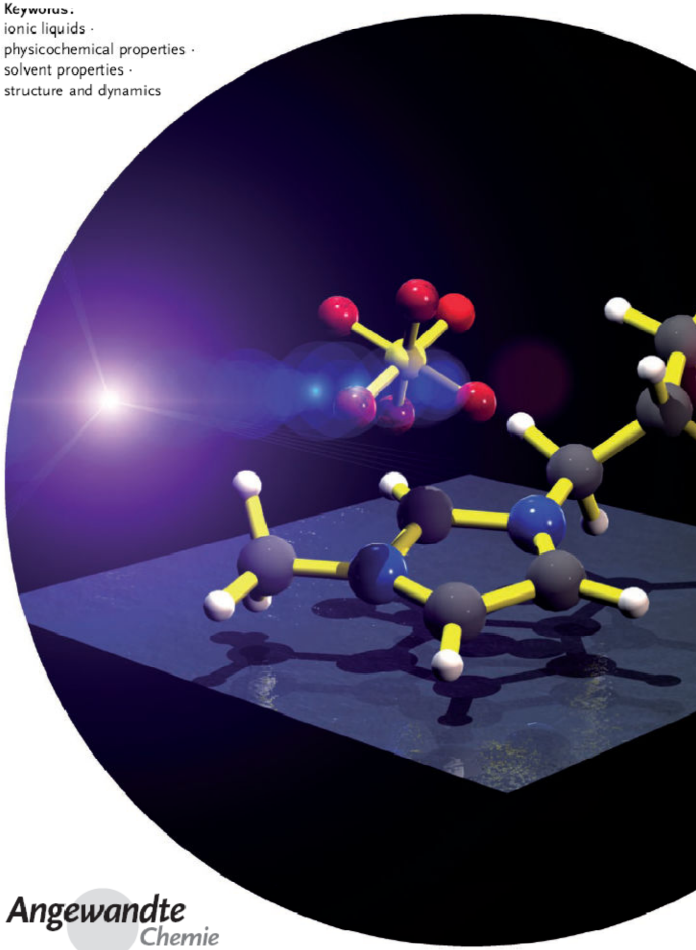
Ionic Liquids

DOI: 10.1002/anie.200604951

Understanding Ionic Liquids at the Molecular Level: Facts, Problems, and Controversies

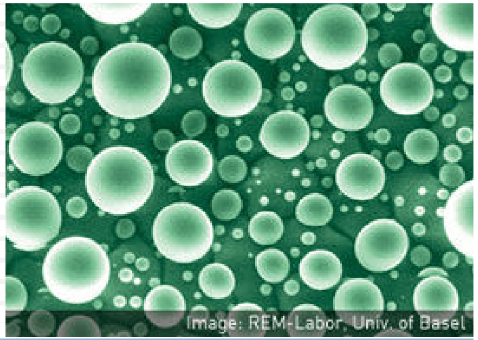
*Hermann Weingärtner** Ruhr-University of Bochum

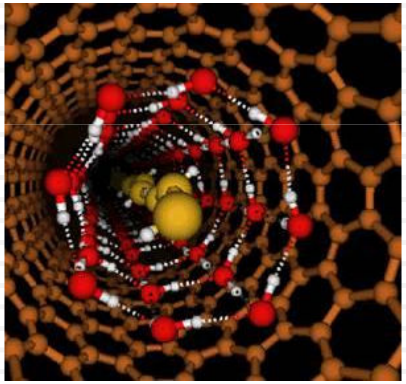
Keywords:
ionic liquids ·
physicochemical properties ·
solvent properties ·
structure and dynamics

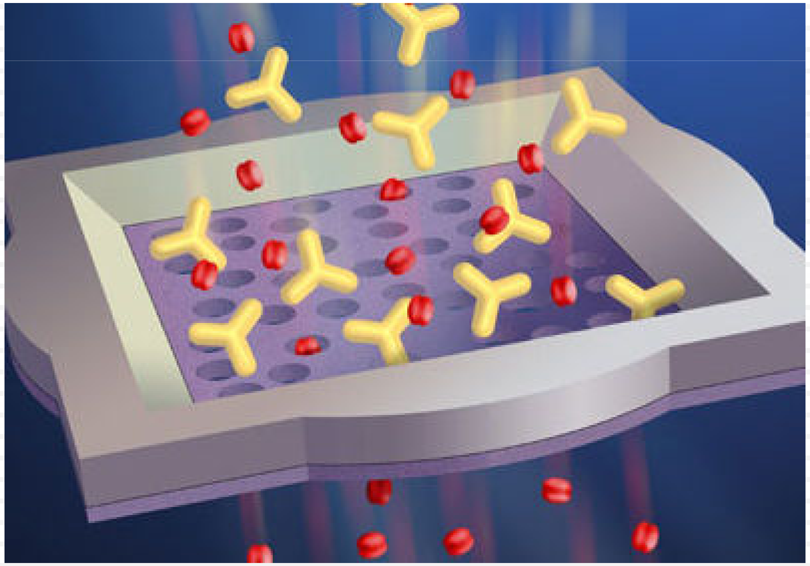


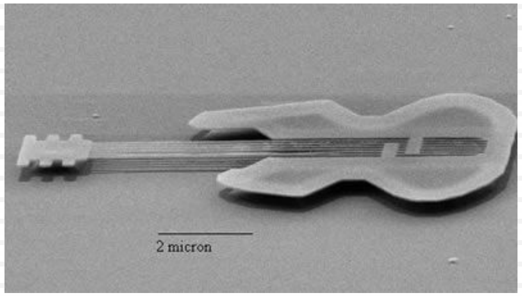
- Because it is impossible to experimentally investigate even a small fraction of the potential cation–anion combinations, a molecular-based understanding of their properties is crucial.
- However, ***the unusual complexity of their intermolecular interactions renders molecular based interpretations difficult, and gives rise to many controversies, speculations, and even myths about the properties that ILs allegedly possess.***
- Herein the current knowledge about the molecular foundations of IL behavior is discussed.

Nanomaterials









Nanomaterials

The particles of nanomaterialscan be produced in several shapes (BN nanoparticles, p.ex.):

- Spheres
- Nanotubes
  - Single wall
  - Multiwall
  - Banboo structured nanotubes
  - Collapsed nanotubes
- Nanowires
- Nanofibers

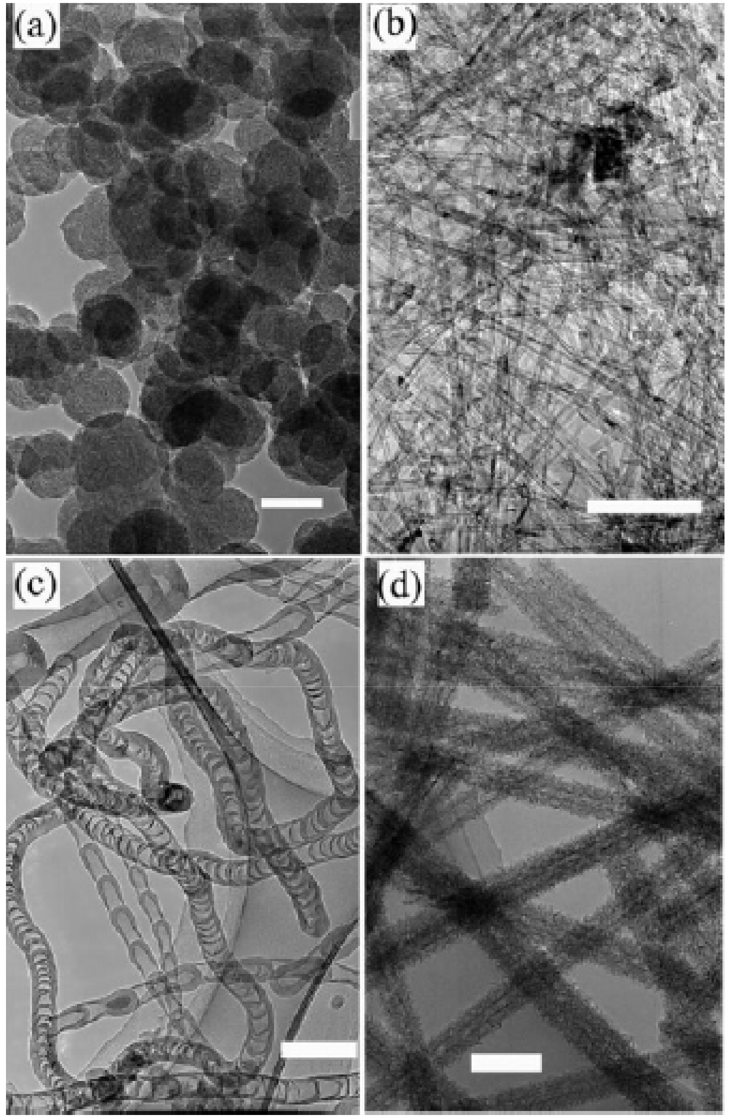
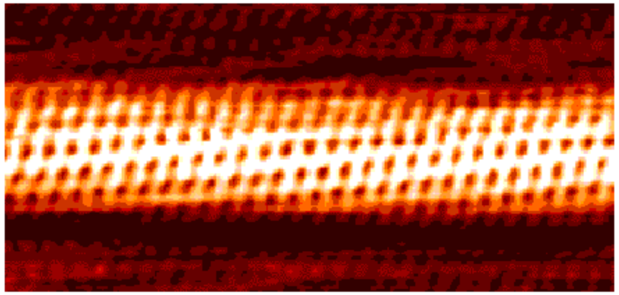


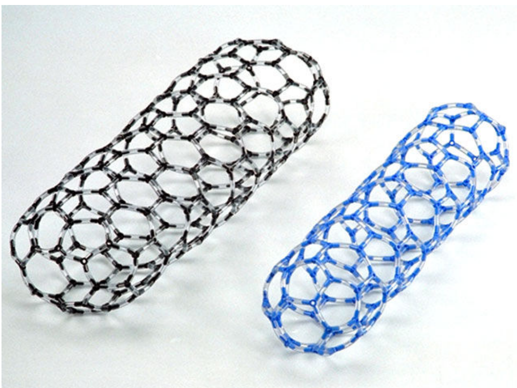
Figure 1. Transmission electron microscopy images of the nanostructured BN materials used for thermal conductivity measurements: (a) spherical nanoparticles; (b) structurally perfect nanotubes; (c) bamboo-structured nanotubes; (d) collapsed nanotubes. The scale bar is 200 nm.

Nanotubes (Different length scales)

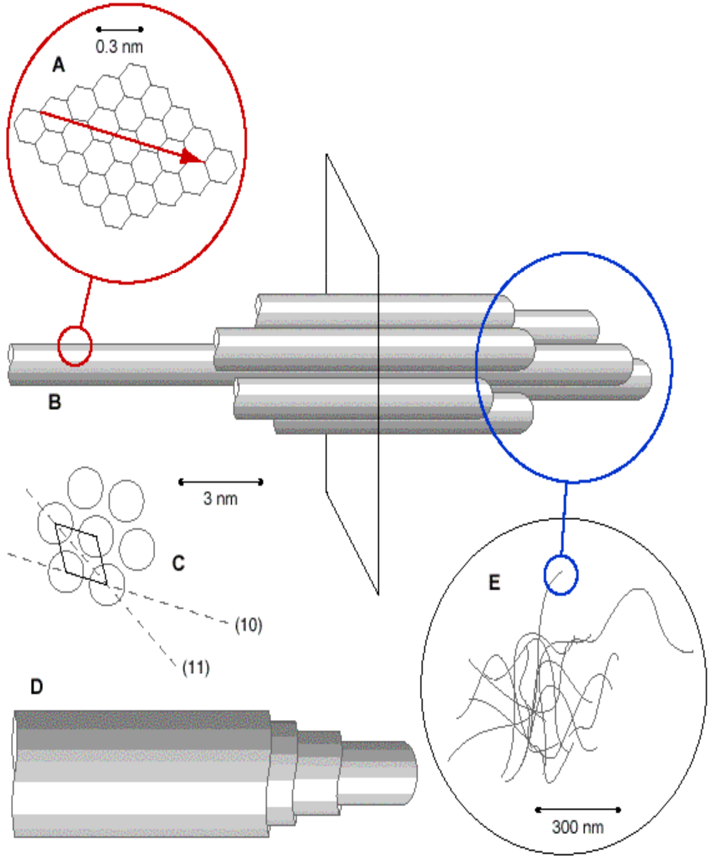


Atomic resolution scanning tunneling microscopy image of an individual (11,7) SWNT.

M. Di Ventra, S. Evoy and J. R. Heflin, Jr., “Introduction to Nanoscale and Technology”, Kluwer Academic Publishers, Boston, 2004



(a) Shows the wrapping of a graphene sheet into a seamless SWNT cylinder.
(b) and (c) show the aggregation of SWNTs into supramolecular bundles. The cross-sectional view in (c) shows that the bundles have triangular symmetry.
(d) A MWNT, another nanotube polymorph composed of concentric, nested SWNTs.
(e) At the macromolecular scale.



Why Nanomaterials?

- The discovery of carbon nanotubes (CNT's) in 1991 has led to speculation that this new class of one-dimensional carbon, having potential applications in electronic, optical, and energy conversion devices, could have a thermal conductivity equal to or greater than that of diamond and graphite, and that their thermal properties had a tremendous interest for basic science as well as for those technological applications, with transport properties metallic or quasi-metallic.
- The accurate measurement of thermal and electrical conductivity of carbon nanotubes (SWCNT's, MWCNT's and nanofibers) requires a mix of ingenuity and nanotechnology, namely for sensor designing and construction, and some **limiting approaches to modelling the heat transfer that might question the accuracy of the measurements**.

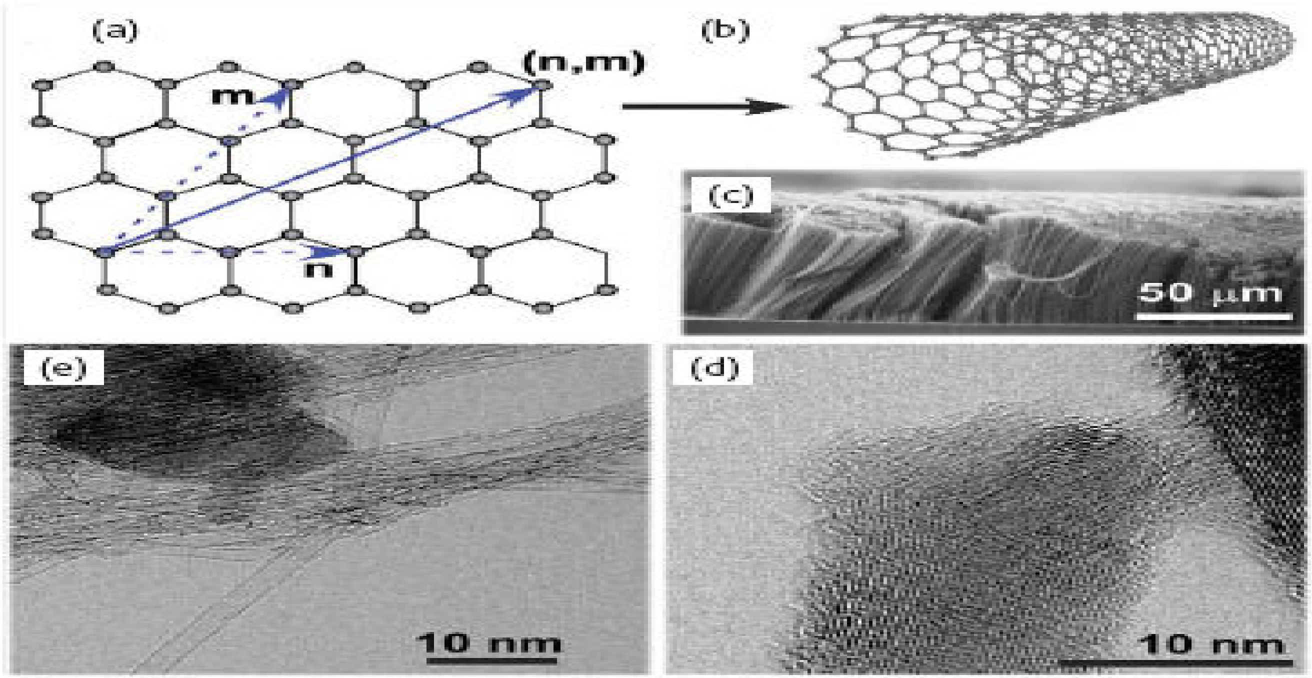


Fig. 1 Structure and morphology of CNTs. (a) Schematic of a graphene sheet and a CNT roll-up vector. The roll-up vector (n,m) is perpendicular to the axis of the CNT. (b) A three-dimensional model of a SWNT. (c) A scanning electron microscope (SEM) image of a vertically aligned array of MWNTs grown on a Si substrate. (SEM image courtesy of M. Stadermann, O. Bakajin and A. Noy, LLNL.) Transmission electron microscopy (TEM) images of (d) MWNTs and (e) SWNTs. (TEM images courtesy of J. Plitzko and A. Noy, LLNL.)

… By now, the CNT has firmly established itself as the iconic molecule of nanoscience …

Aleksandr Noya *et al.*, "Nanofluidics in carbon nanotubes", Nanotoday, Vol. 2, N#6, Dec 2007, 22-29

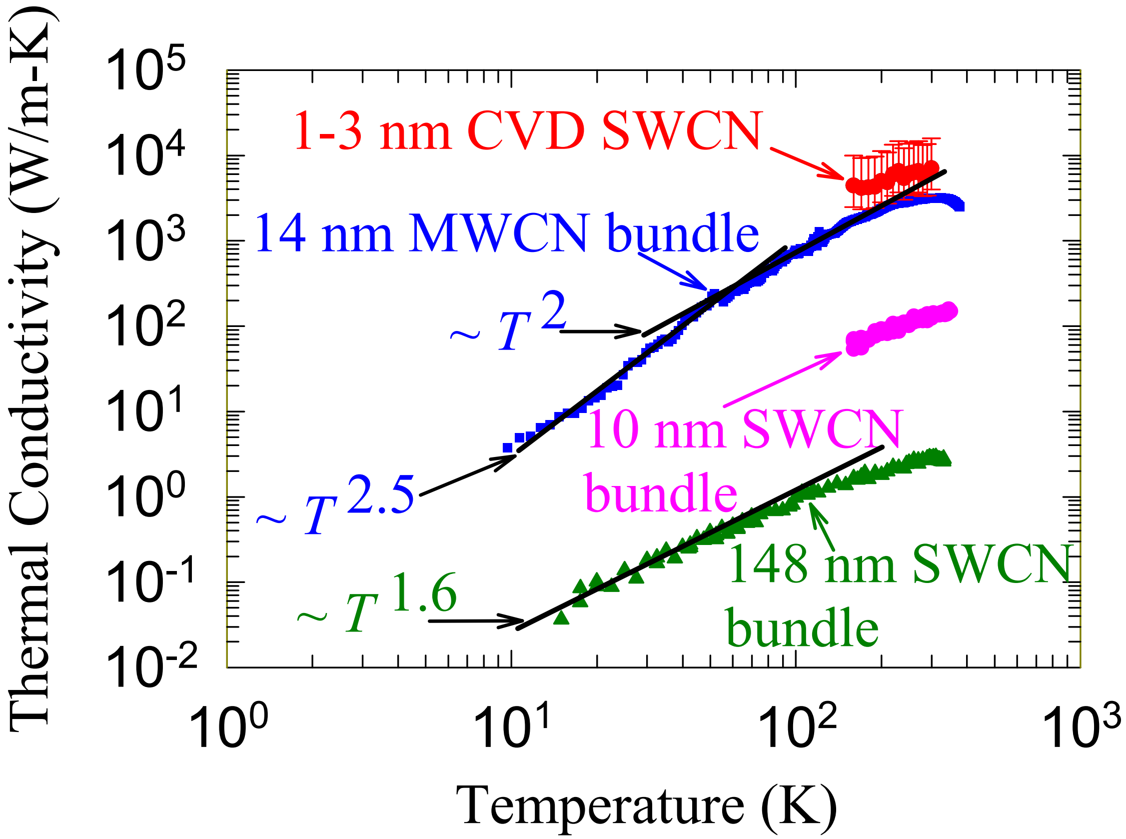
Current awareness

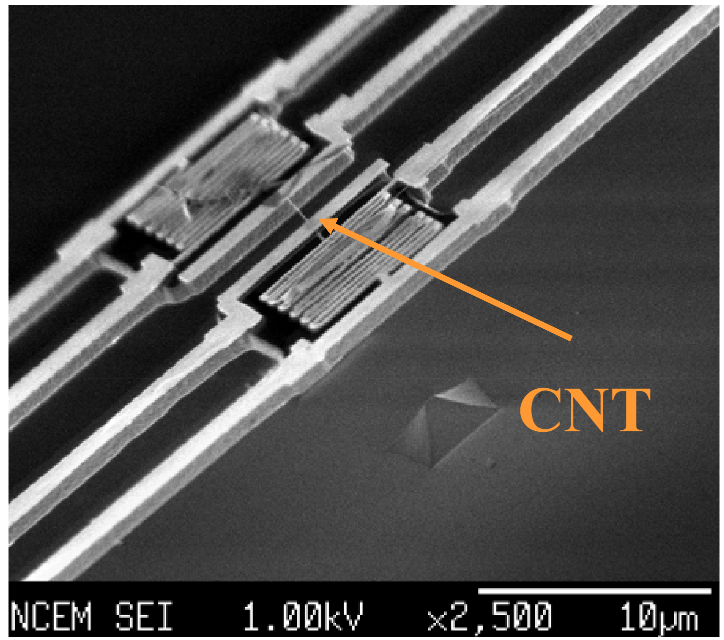
- Today, the remarkable, unique, and phenomenally promising properties of these nanoscale carbon structures have placed them right among the hottest topics of materials science.
- So why are they only at number eight in this list? Well, there still remains much to sort out in their synthesis, purification, large-scale production, and assembly into devices.
- And there's also the very frustrating inability to manufacture uniform samples of nanotubes with the same properties.

Jonathan Wood, Editor, "The top ten advances in materials science", Materials Today, Jan-Feb 2008 Vol. 11, 40-45

Thermal Conductivity of Carbon Nanotubes

MEMS device





An individual nanotube has a high $\lambda \sim$ 2000-11000 W/m-K at 300 K. That of a CN bundle is reduced by thermal resistance at tube-tube junctions, Li Shi, The University of Texas at Austin. (2007)

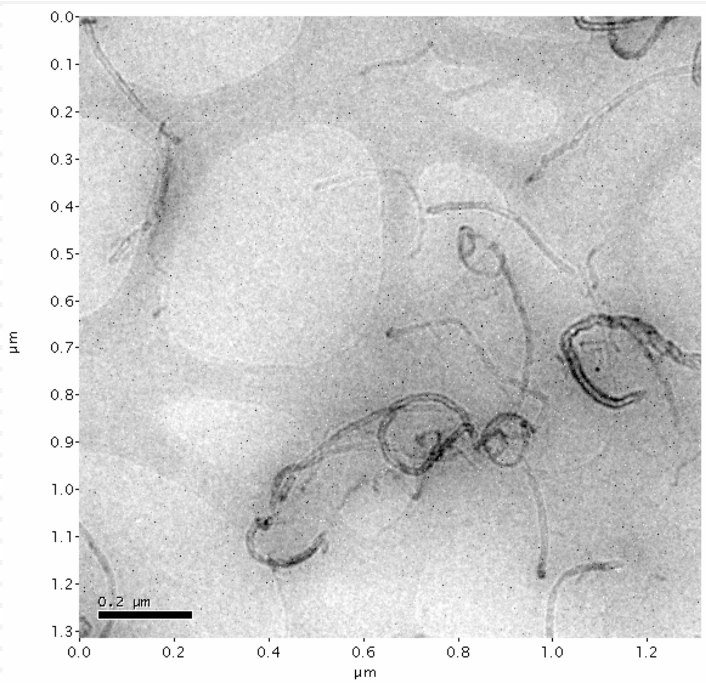
Problems

- Sample fabrication (*in situ?*)
- Rigorous definition of geometry (dimensional measurements)
- Anisotropy of single nanotubes
- Accuracy of heat dissipation calculation
- Contact resistances

- BUT the way is promising!

Nanofluids and Bucky gels

IoNanoFluids

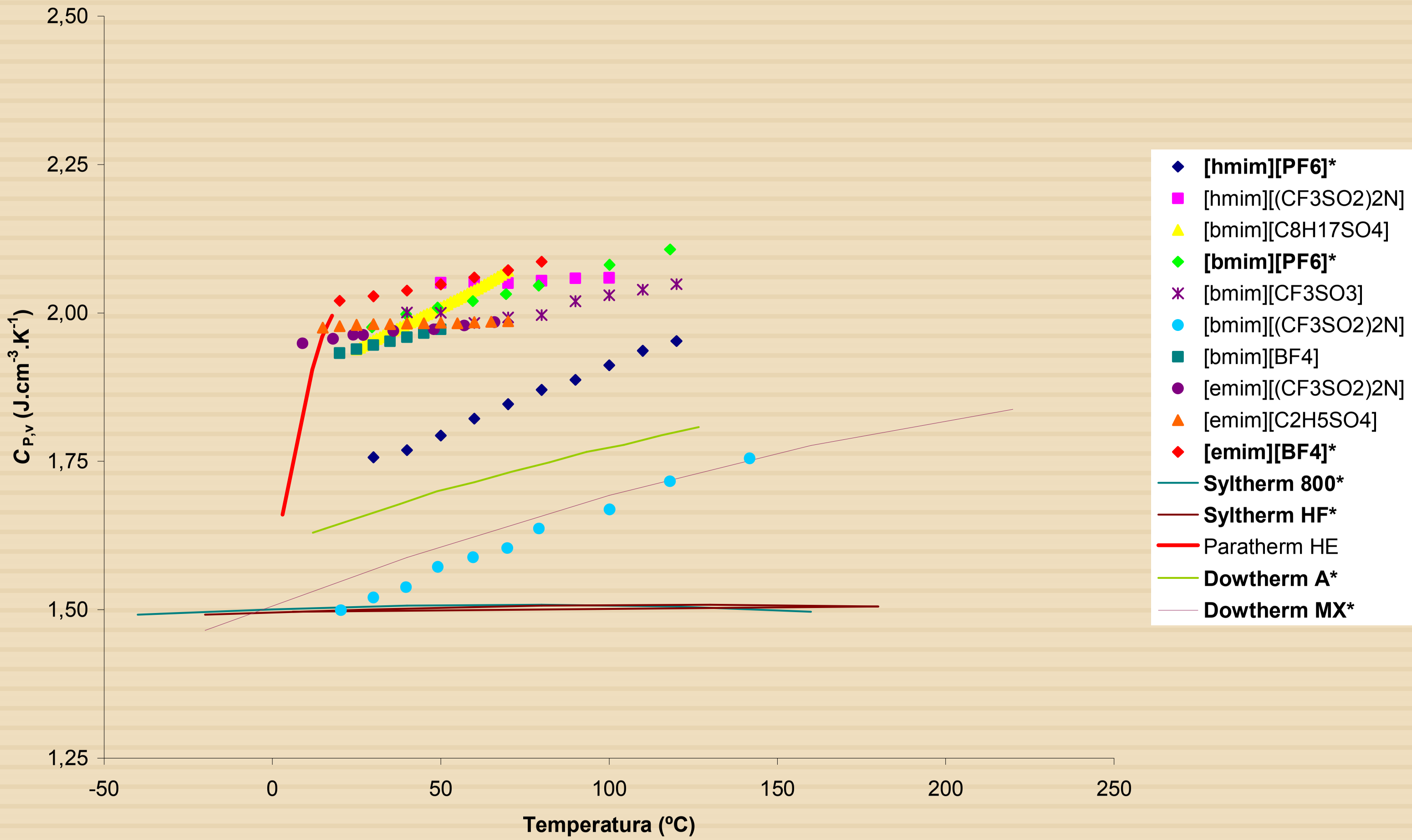


TEM Image of a Bucky gel of o ionic liquid and MWCNT's

Nanofluids

- Several applications for thermal management have been presented, were SWCNT's or MWCNT's are dissolved or suspended in common solvents - **nanofluids**, to enhance the thermal conductivity of the media, namely liquids used in convective and boiling heat transfer – **IoNanoFluids.**
- The huge potential of nanofluids led recently to consider them as "the cooling medium of the future".
- Ionic liquids alone have a significant heat capacity per unit volume, bigger than most thermal oils used in engineering applications (Dowtherm, Syltherm, Partherm, etc.)

Graphical representation $C_{P,v}$ vs T

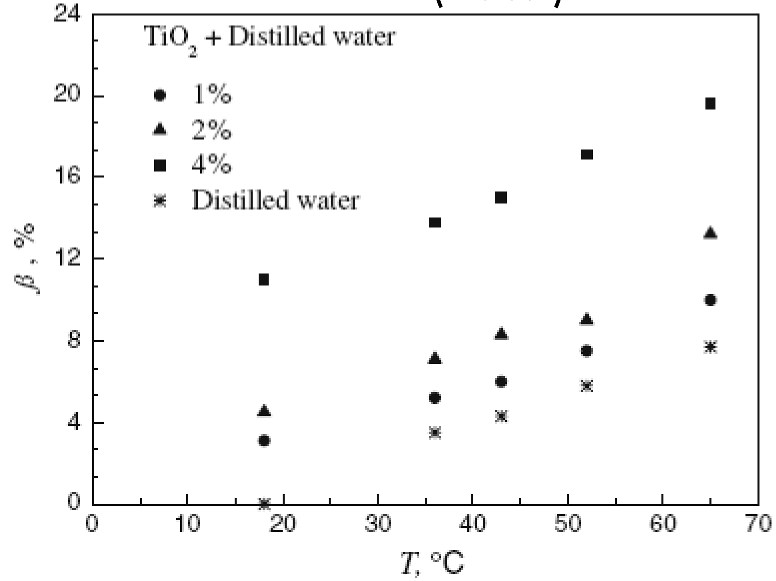


França et al., Ionic Liquids: The Influence of Their Thermophysical Properties in Chemical Process Design, **EUCHEM 2008 Conference on Molten Salts and Ionic Liquids**, August 24-29, 2008 • Copenhagen • Denmark

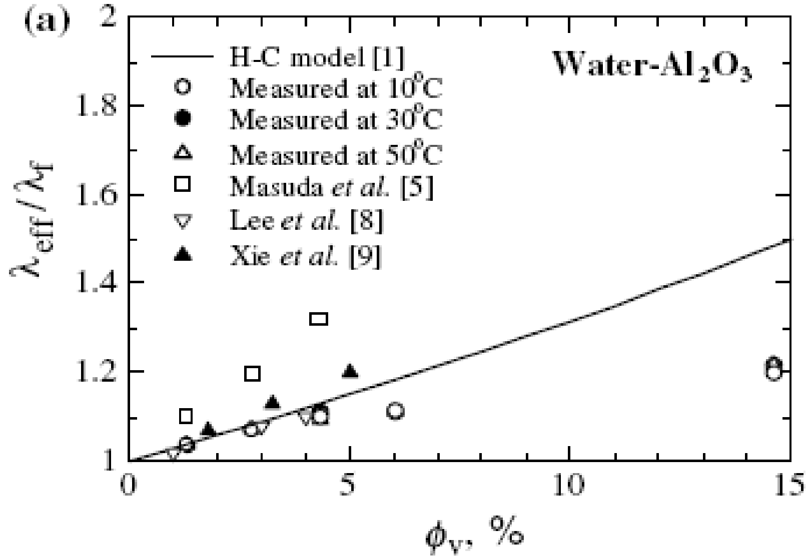
Why are nanofluids important?

- Its importance in the area of **thermal management** arises from the fact that **small amounts** of nanomaterials added to normal fluids seem to enhance the thermal conductivity of the media
- Is this enhancement significant?
  - Some authors say it can be up to 300% - Choi *et al.* (1999), Kumar *et al.* (2004), Liu *et al.* (2005), Araki et al. (2007), Murshed *et al.* (2008)
  - Others state that they only found increases of the order of 5% or less - Assael *et al.* (2005), Fujii *et al.* (2007)
- **Which are right**?
- Probably both, because the systems were different, the concentration range of nanoparticles also and there is a possibility of nanoparticle aggregation and separation in the emulsions/suspensions studied.
- Also in some studies, electrical insulation of the probes used was not accounted for!

Araki et al. (2007)



Fujii *et al.* (2007)



Murshed *et al.* (2008)

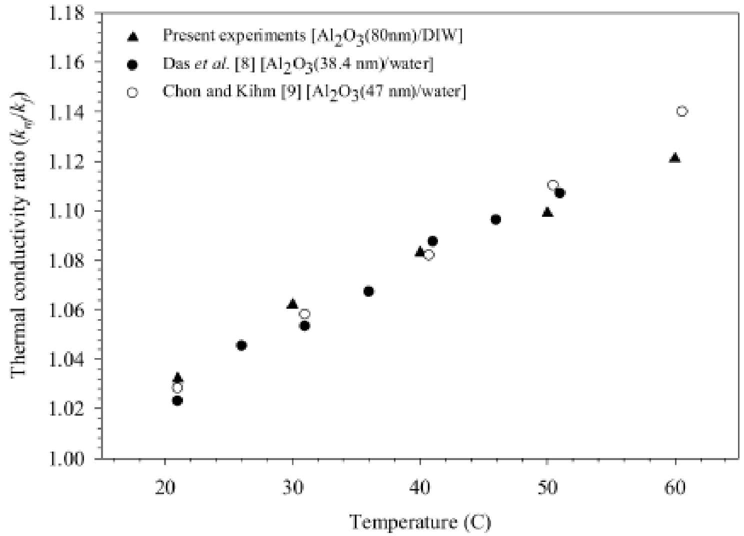


Fig. 7. Thermal conductivity enhancement with temperature for Al_2O_3/water-based nanofluids.

Assael *et al.* (2005)

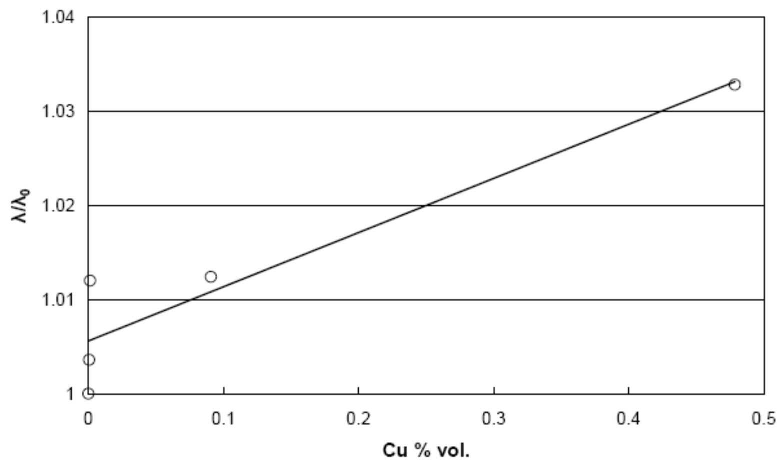


Figure 1. Thermal Conductivity enhancement of Cu suspensions in ethylene glycol.

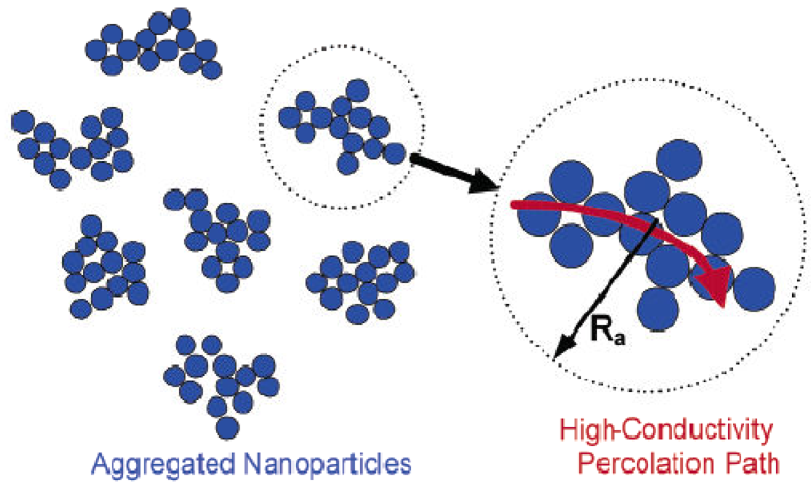
Is Aggregation important to the mechanism of thermal transport?

Prasher *et al.*(2006)

Keblinski *et al*, Thermal conductance of nanofluids: is controversy over?

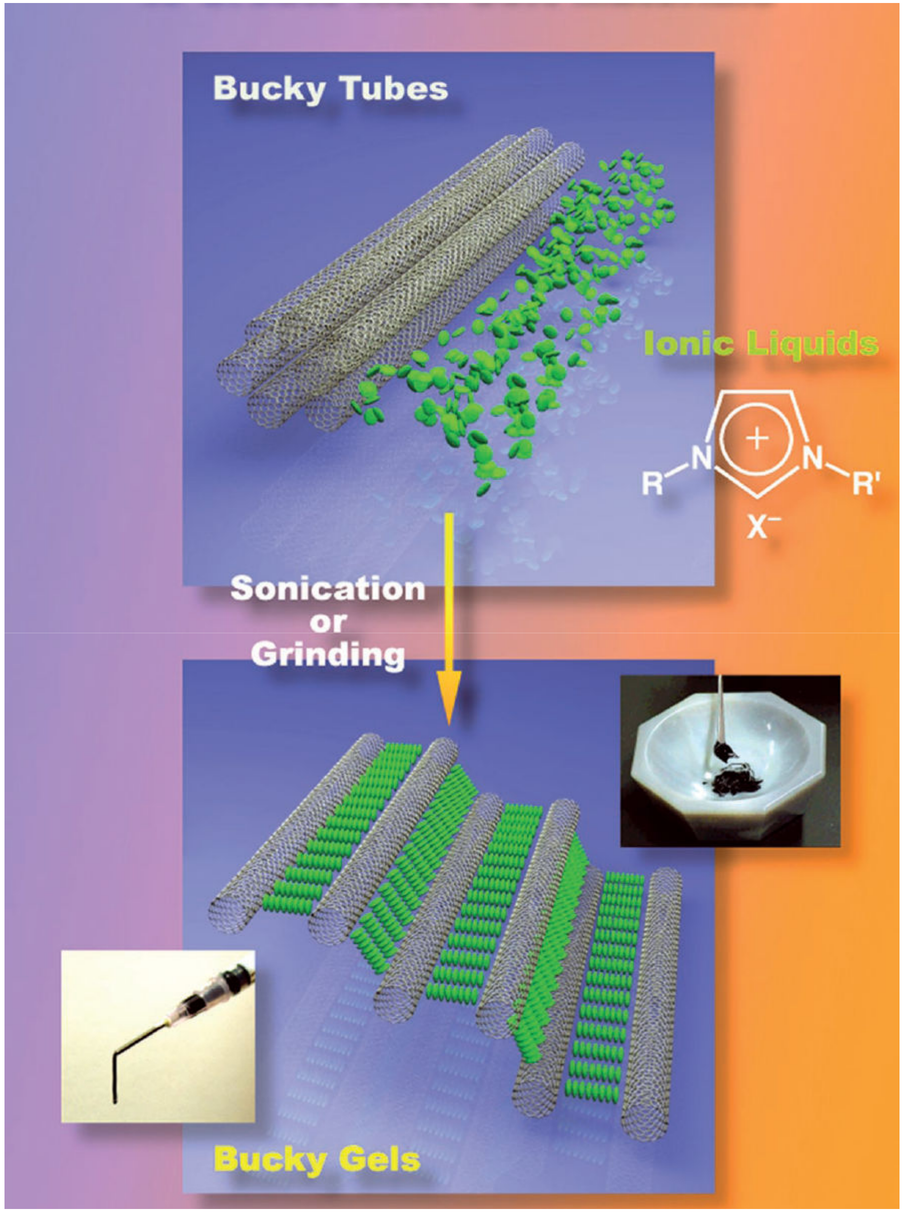
J. Nanopart. Res., (2008), 10, 1089-1097

- The thermal conductivity enhancement can be explained within two lines of reasoning:
  - It is enhanced by micro-convection caused by Brownian motion of the nanoparticles
  - It is enhanced by the aggregation of the nanoparticles leading to local percolation behaviour and inducing preferred paths for heat conduction
- Probably both!



Bucky Gels

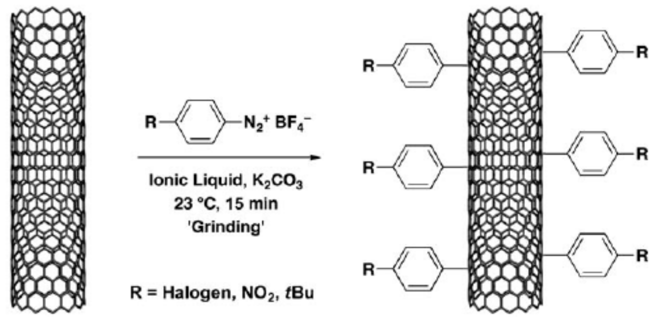
- The discovery that carbon nanotubes and room-temperature ionic liquids can be blended to form gels that may be used to make novel electronic devices, coating materials, and antistatic materials, opens a completely new field – **Bucky Gels**
- "Bucky gels" are blends or emulsions of ionic liquids with nanomaterials, mostly nanocarbons (tubes, fullerenes, spheres)
- Aida and co-workers (2003) prepared "bucky gel" stable materials by grinding suspensions of high-purity SWCNT's in imidazolinium cation-based ionic liquids and enhanced recently the possibilities of ionic liquids for design of soft materials based on CNT's



Soft Functional Materials

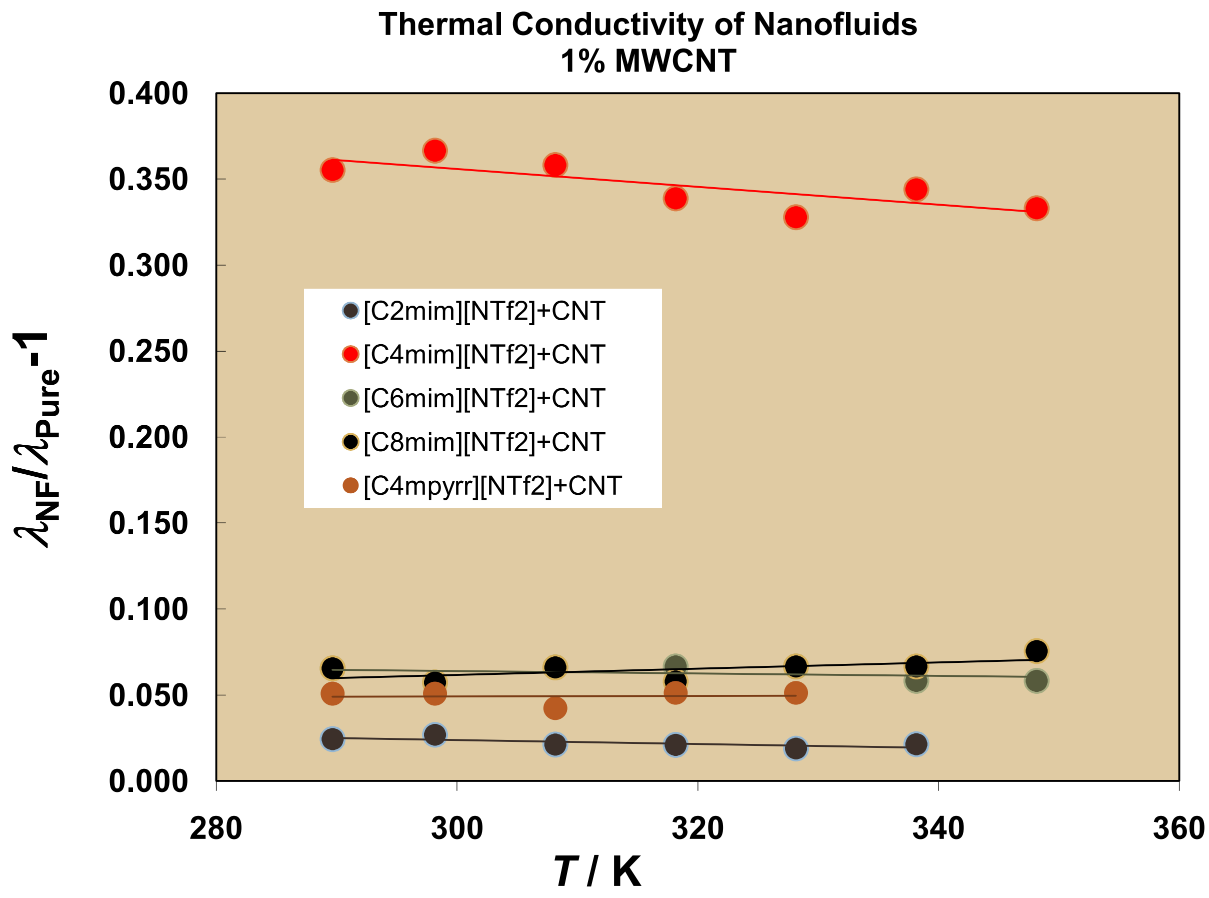
The possibility of using ionic liquids with nanoparticles dispersed can be used in the functionalization of the nanomaterials, namely SWCNT's, MWCNT's and fullerenes (C_{60}, C_{80}, etc.) --- many applications

Fukushima & Aida (2007)



Thermal Conductivity Enhancement in Nanofluids / Bucky gels

Ribeiro et al, Thermal Conductivity of Bucky gels, **EUCHEM 2008 Conference on Molten Salts and Ionic Liquids,** August 24-29, 2008, Copenhagen, Denmark



Possible explanation

- Because carbon nanotubes in the "bucky gels" are considerably more untangled when compared to CNT's in the absence of the ionic liquid, they give much finer bundles that physically cross-link due to the cation-π interactions between the imidazolium ions of the ionic liquids and the carbon nanotube surfaces.
- Ionic liquids are nonvolatile, the "bucky gels" are thermally stable and do not shrivel, even under vacuum.

Applications

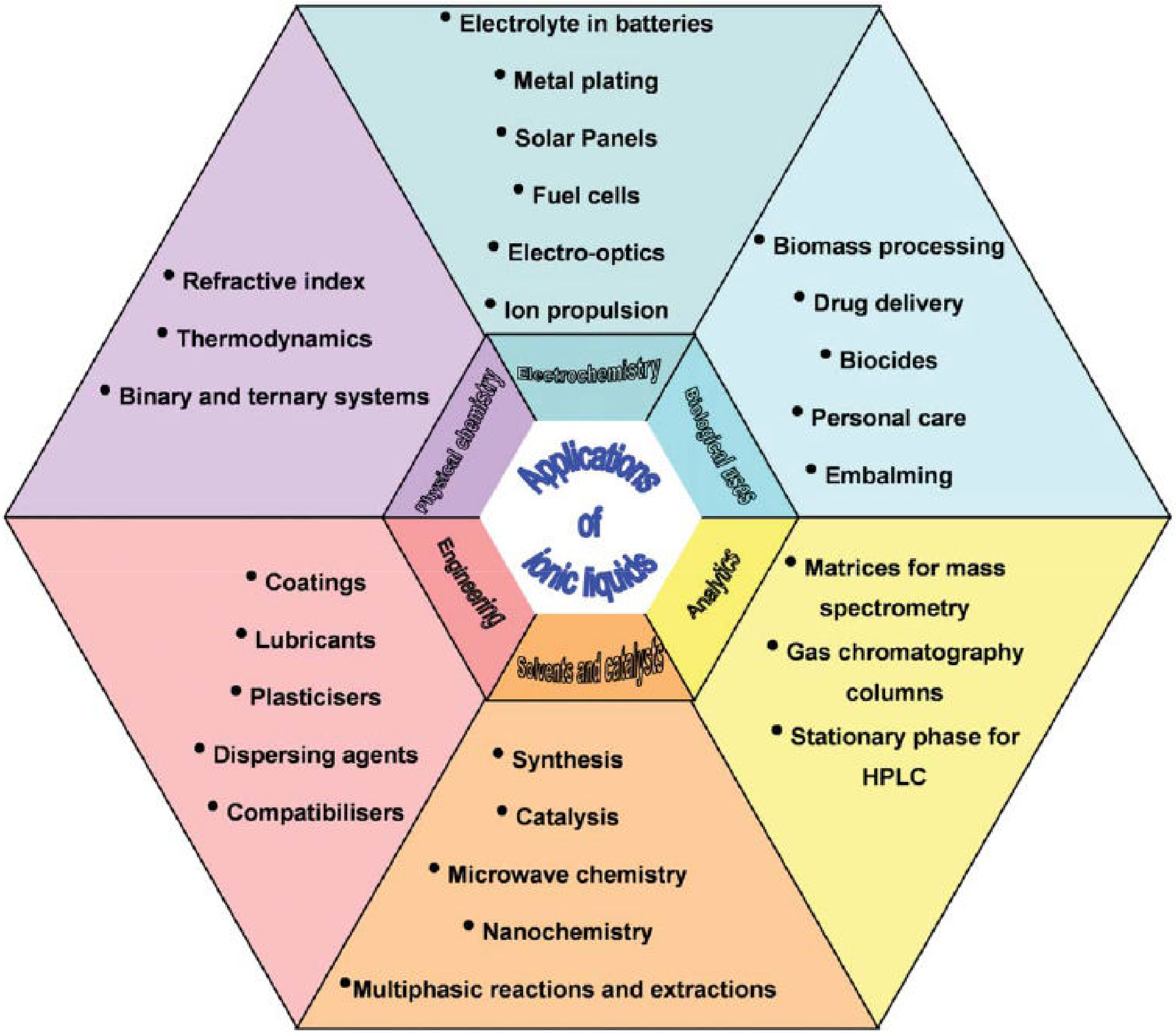
Some references to applications of

Ionic Liquids and Nanomaterials

Applications of Ionic Liquids

- Heat transfer fluids
- Azeotrope Separation
- Lubricants
- New Materials
  - Electrolytes for industry
  - Liquid crystals
  - Supported Liquid Membranes (SILM's)
    - Gas separations
    - Separation of organic and biomolecules
    - Sensors (oxygen, organic vaporss)
    - Reactors
  - New materials for GC, HPLC, e CE
  - Plasticizers, dispersants ans surfactants
  - Antimicrobial agents, embalming and tissue preservatlves
  - Anticorrosive coatings for electrochemical depositions
- Industrial processes

Future


Applications of ionic liquids
Electrochemistry
Electrolyte in batteries
Metal plating
Solar Panels
Fuel cells
Electro-optics
Ion propulsion
Biological uses
Biomass processing
Drug delivery
Biocides
Personal care
Embalming
Analytics
Matrices for mass spectrometry
Gas chromatography columns
Stationary phase for HPLC
Solvents and catalysts
Synthesis
Catalysis
Microwave chemistry
Nanochemistry
Multiphasic reactions and extractions
Engineering
Coatings
Lubricants
Plasticisers
Dispersing agents
Compatibilisers
Physical chemistry
Refractive index
Thermodynamics
Binary and ternary systems

Applications of Nanomaterials

- Clever clothes
- Light paint, heavy savings
- Screensavers
- Nano batteries
- Nanotube filter
- Chip technology
- Transistors, MEMS, etc
- Mini machines
- Optical devices
- Composites
- Nanofilms

Ink on Egyptian papyrus dating from about 1200BC containing nanoparticles of soot.

Liquids and Nanomaterials – one example

- Development of Functionalized Nanomaterials/Ionic Liquids Systems For Solar Energy Thermal Conversion
- The functionalization of carbon nanotubes (MWCNT's) with organic molecules can be used to develop new molecules suspended in ionic liquids to produce TISS (thickness insensitive spectrally selective) paint coatings for photothermal solar energy conversion. The new ionic liquids developed were based on crystal violet and methylene blue

Portugal

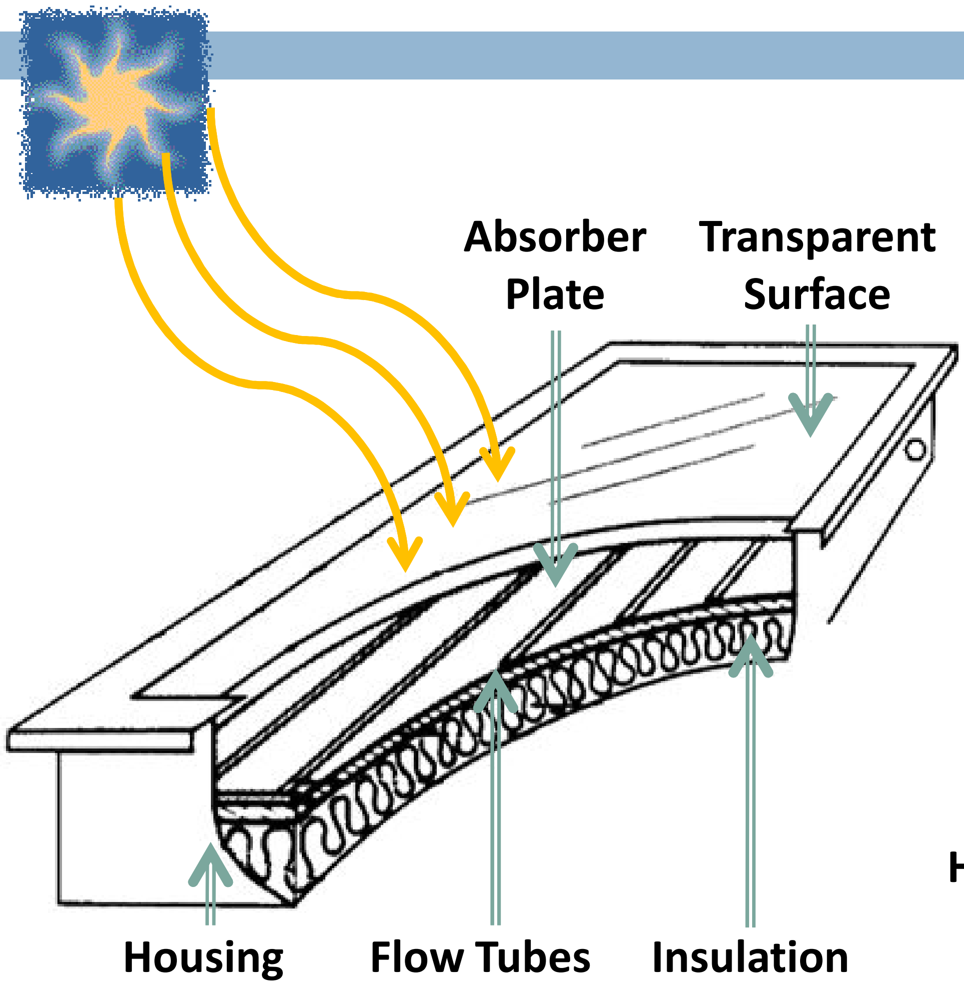
In my country there are 220 sunny days a year

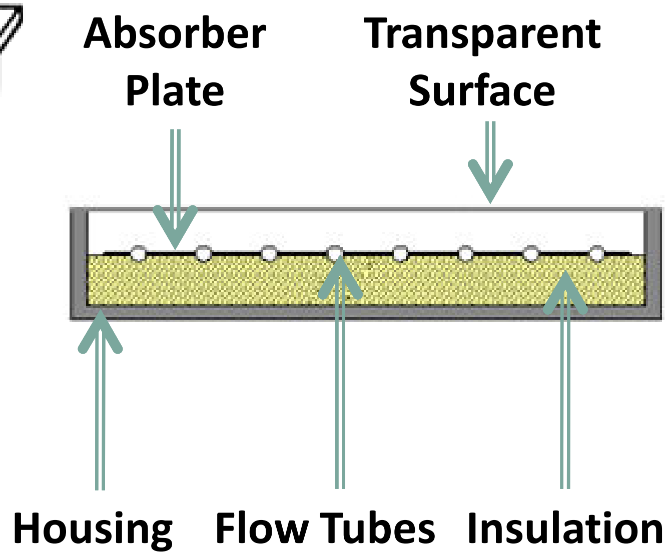
World's Largest Solar Photovoltaic Power Plant, *Serpa (east Alentejo)*
52 000 Solar Panels – 11MW

- Preparation of pigments for solar collector panels, based in complex systems of nanomaterial/ionic liquid: **Bucky gel**

- Preparation and characterization of spectrally selective paint coatings for photothermal energy conversion

Flat Plate Solar Collector





Paints

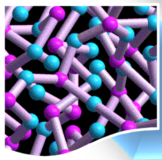
Resin: Organic material responsible for adhesion, viscosity, chemical resistance, etc.

Solvent: Volatile vehicle that adjusts the viscosity, flow and application properties

Pigment: granular solids adding colour, hiding power, toughness and other characteristics

Filler: Insoluble inorganic powder that increases the volume and provides hiding power

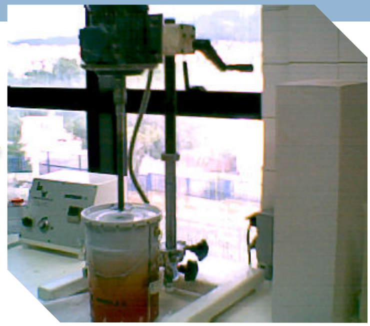
Additives: Added in very small amounts, improve several properties of coatings



Hardener: Catalytic or reactive agent which when added to resin causes crosslinking of chains leading to hard, insoluble films

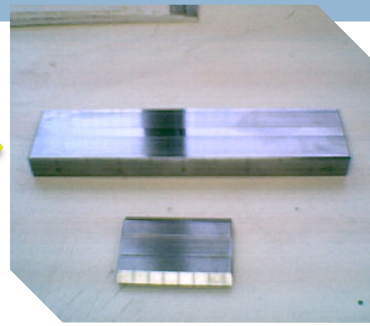
Paint Preparation

Weighting of raw materials



Dispersion

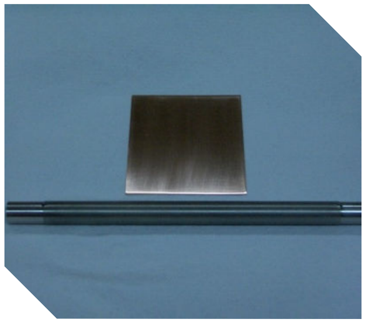
Grinding by ball mill



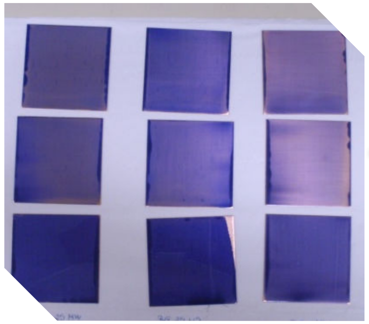
Particle size measurement

Filtration

Viscosity and density measurement

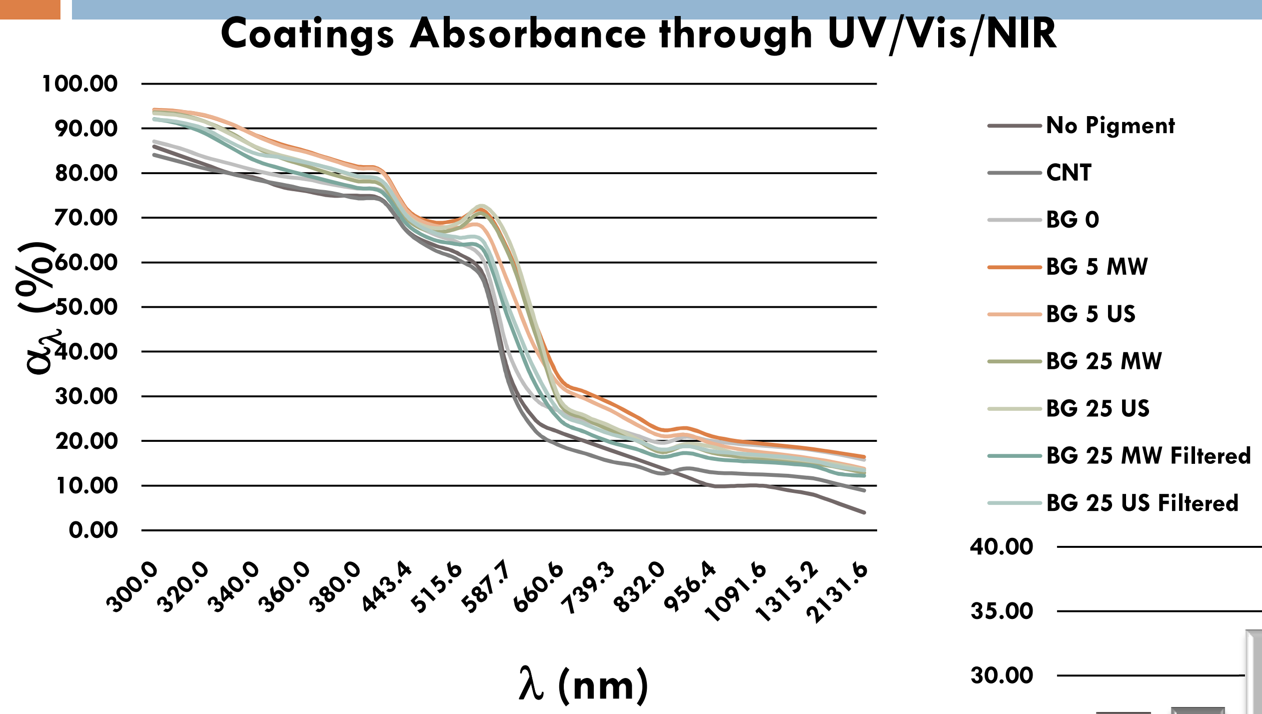


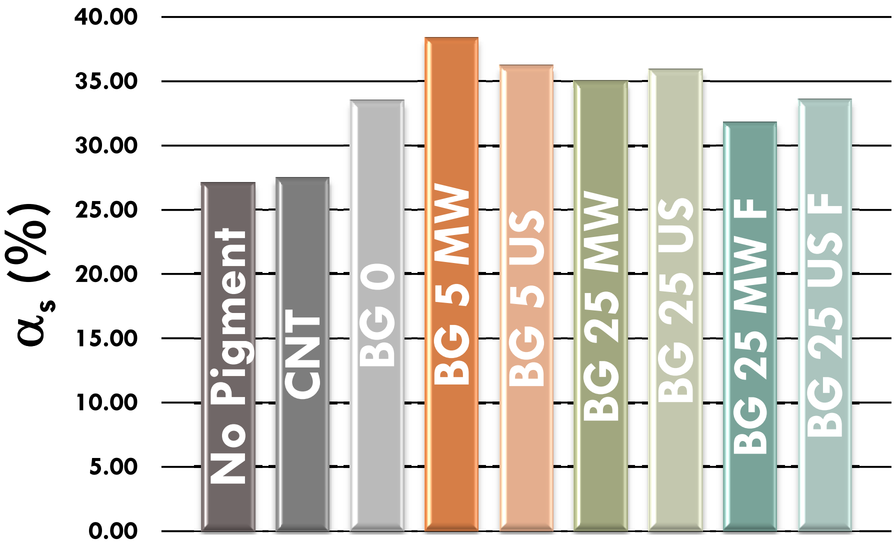
Paint Application



Coating Characterization

Coating Characterization: Solar Absorbance





Conclusions of this study

- Paint coatings with bucky gels have a spectrally selective behaviour
- The addition of only 2.5% (w/w) of pigment:
  1. Enhances the Solar Absorbance
  2. Doesn´t greatly affect the Thermal Emittance
- Coating with best performance is BG 5 MW
- Coatings with higher thicknesses give higher absorbance's and emittances, but similar efficiencies (α_s/ε_T)

Problems in the Measurement of Thermophysical Properties

Are Properties well measured?

- Most of the properties, namely thermophysical properties like viscosity and thermal conductivity have been measured using other liquids approach
- People has forgotten about the structure and properties of ionic liquids / nanofluids and their impact in methods of measurement, like
  - Sample preparation
  - Mathematical modelling
  - Chemical reactivity

What characteristics of IL's can affect measurements?

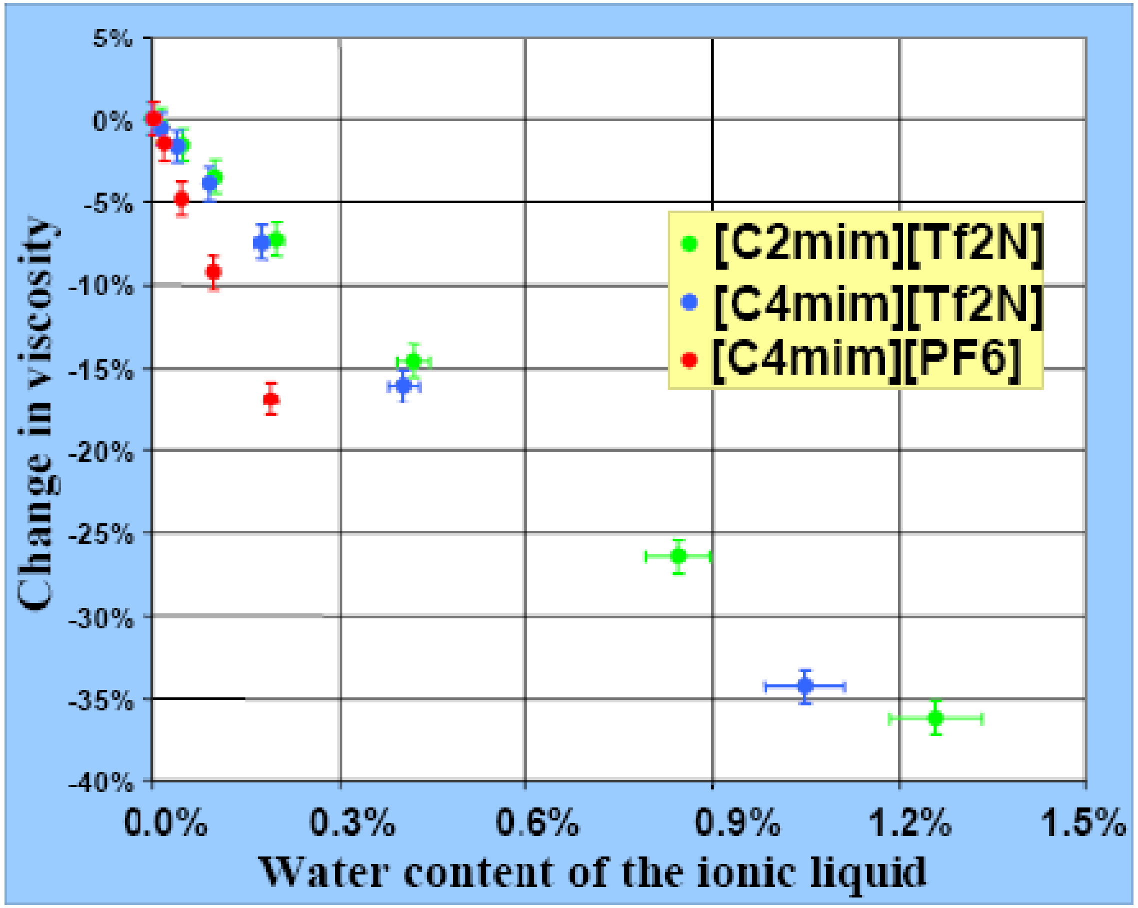
- Low to high viscosity, as the ions are not mutual independent, for most of the cases, and can form aggregates,
- Cations and anions have completely different sizes
- Reaction with water is possible,
- High solubility of water in IL's, affecting the properties,
- Moderate to high heat capacity per unit volume.

Some examples

- Effect of water on the viscosity
- Thermal conductivity measured with non-isolated HW probe
- Available data (ILThermo)

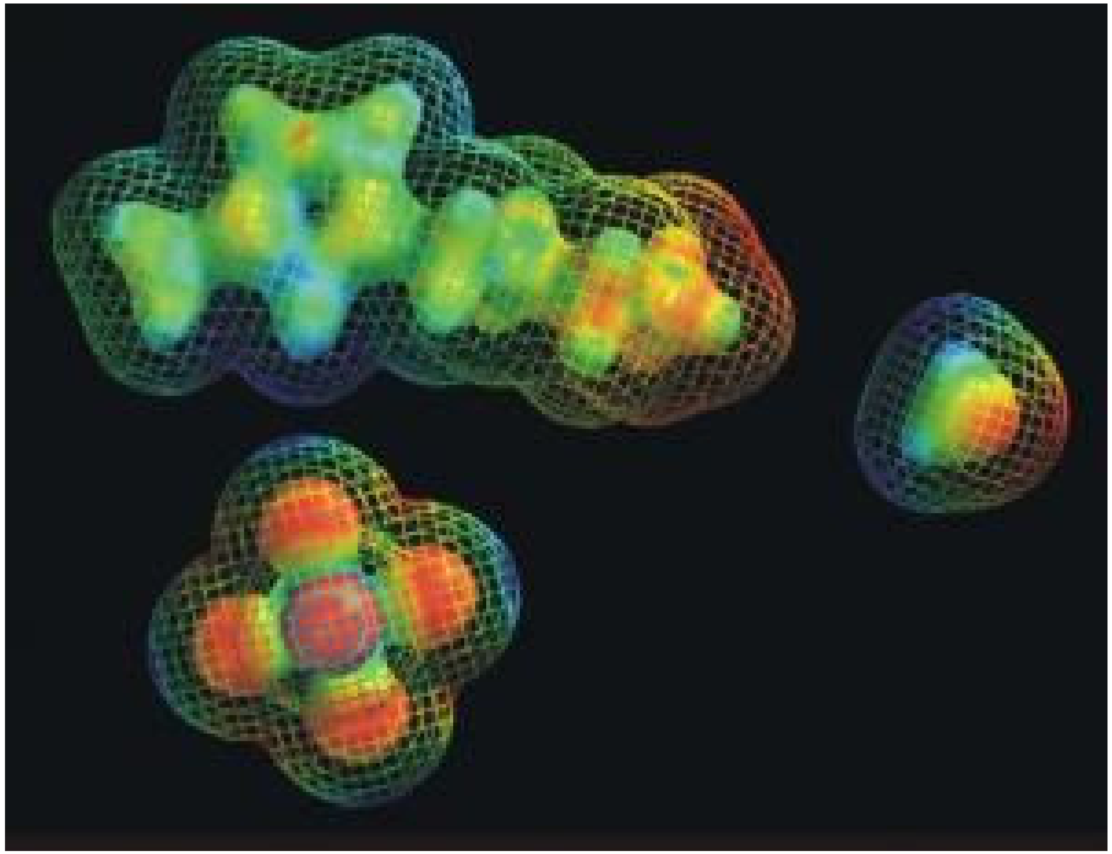
Effect of Water on Viscosity

J. A. Widegren, A. Laesecke, J. W. Magee *"The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids"* Chem. Comm. (12): 1610-1612 (2005)



Molecular "space filling" models demonstrate the difference in size for the positively charged "anion" (top image) and the negatively charged "cation" (bottom left) that combine to form a promising ionic liquid. It is still a mystery how the much smaller water molecule (right) can have such a large effect on the viscosity of such ionic liquids…

[C4mim][PF_6]



$[C_6mim][Tf_2N]$ – our data

Effect of water in the viscosity of $[C_6mim][Tf_2N]$

Experimental values with water contents between 119.3± 30 ppm and 196.4 ± 3 ppm, corrected to 10 ppm (dry samples) using NIST data

Nieto de Castro & Santos, Chemistry Today, 25, n°6, 20-23 (2007)

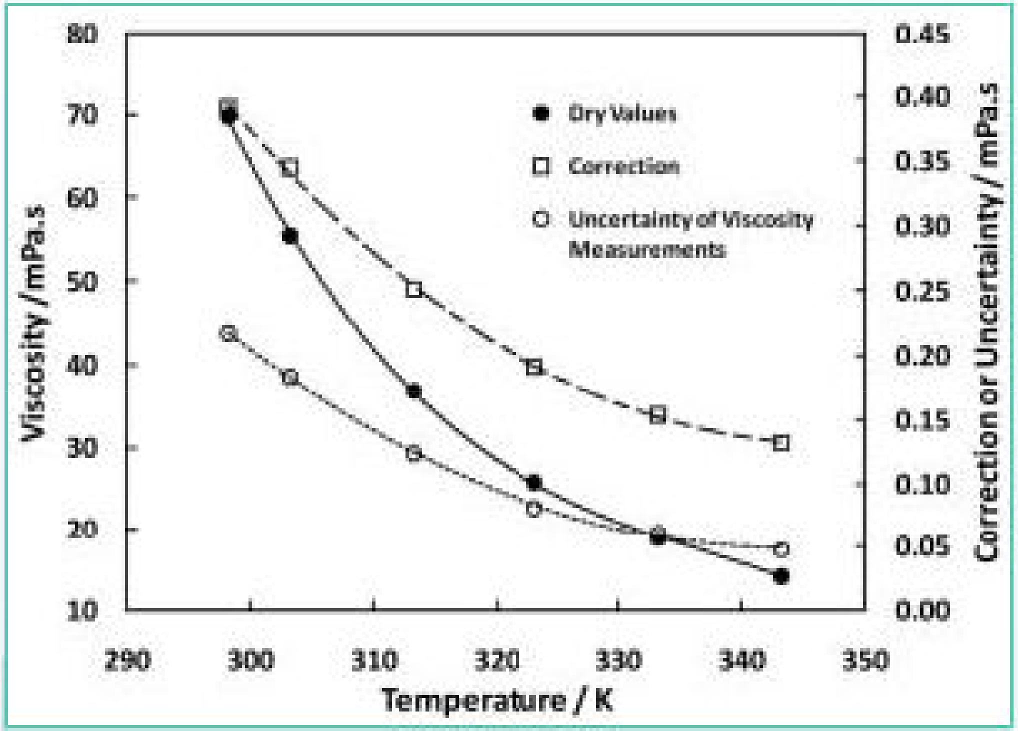
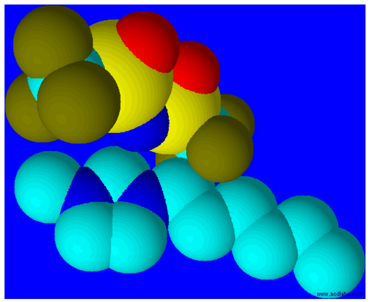
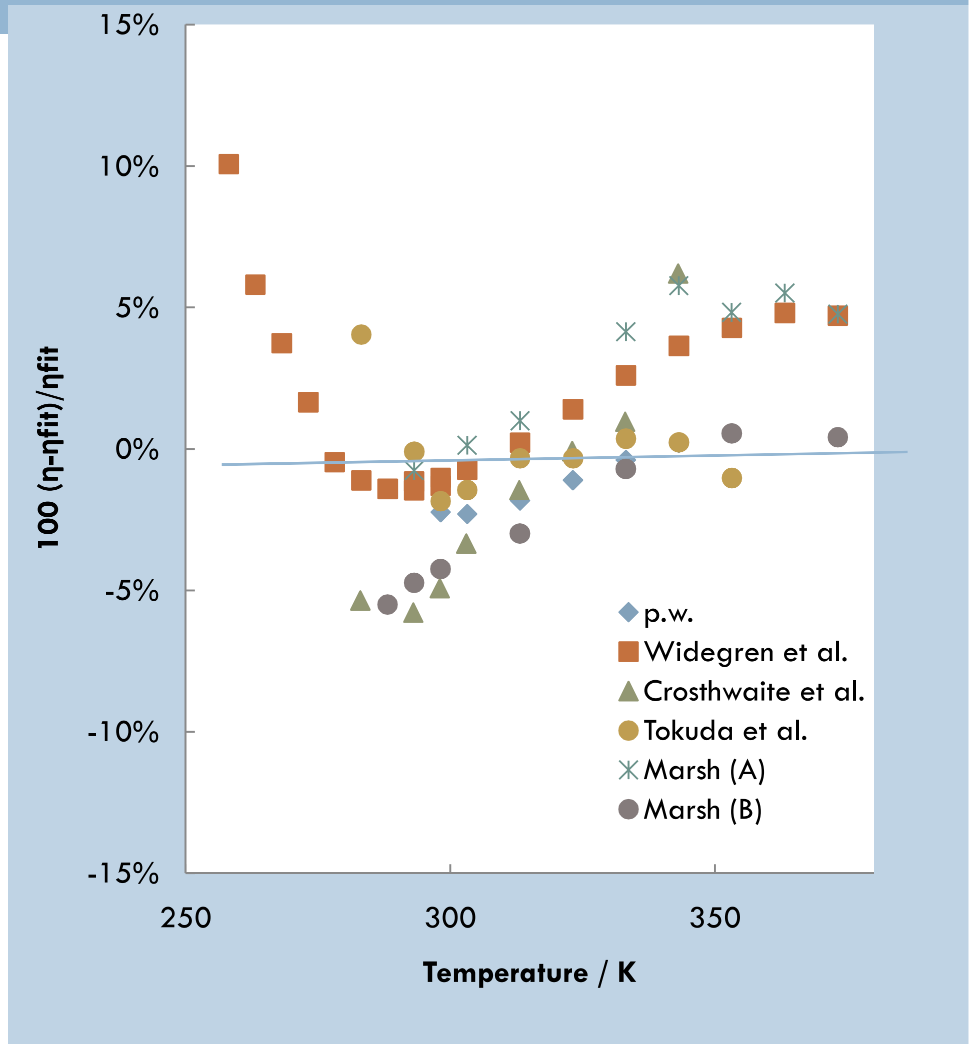


Figure 2. The viscosity of (hmim)(Tf2N) between 298 K and 343 K. Dry values mean experimental values corrected to zero water content in the sample, after (12). Lines are just trend quadratics

[C_6mim][Tf_2N]

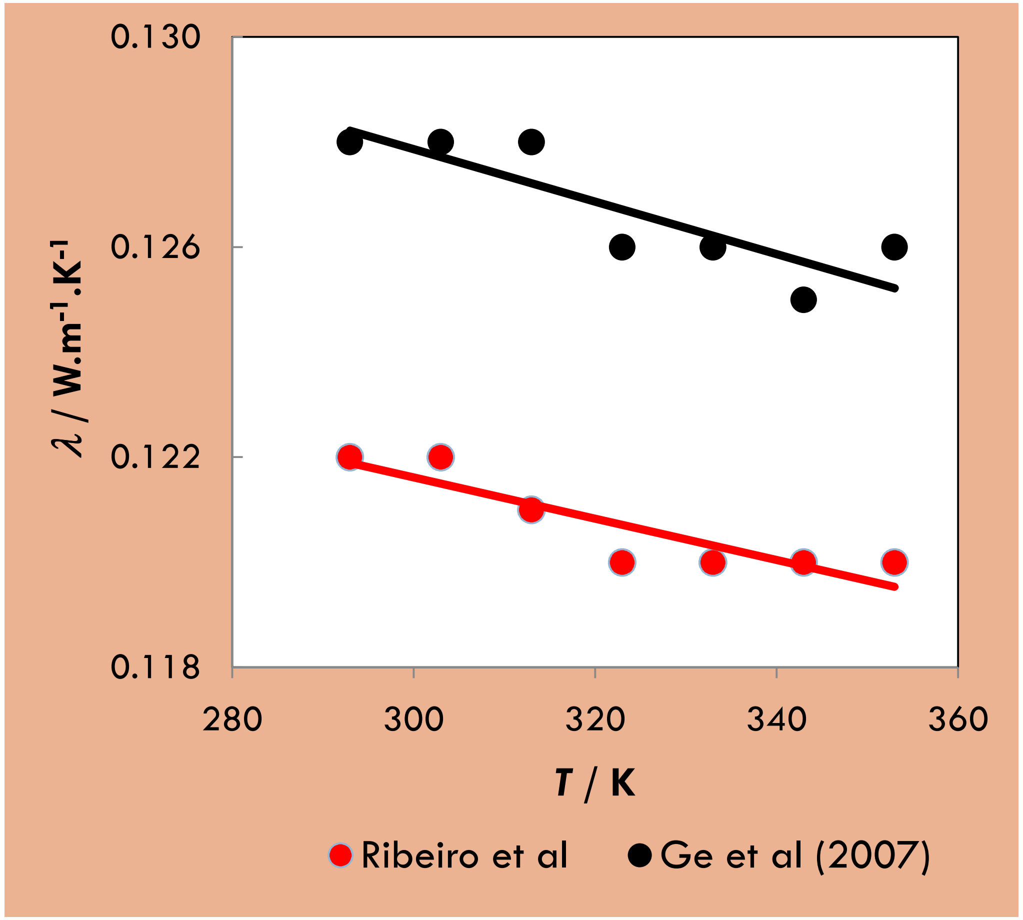
- IUPAC project
- All the participants aware of water absorption problem!
- But discrepancies are still there





Thermal conductivity of $[C_6mim][Tf_2N]$

Measurements made with the same equipment, with (Ribeiro *et al* (2008) and without (Ge *et al*, 2007) insulated probe



BUT…

- When the ordinary transient hot-wire is applied to measure the thermal conductivity of electrical conducting liquids, several problems are encountered:
  - The contact between the bare metallic wire and the conducting liquid provides a secondary path for the flow of current in the cell and the heat generation in the wire can not be defined unambiguously.
  - Polarization of the liquids occurs at the surface of the wire, producing an electrical double-layer.
  - The electrical measuring system (an automatic Wheatstone bridge) that detects the changes in the voltage signals in the wire is affected by the combined resistance/capacitance effect, caused by the dual path conduction

Solutions?

- Three main solutions have been developed in the past to overcome these problems
  - One is the production around the wire of an electrical insulating coating
    - Ceramic coating
    - Oxide formation by anodizing the metallic wire at its surface
  - The second, the polarization technique, consists in polarizing with a DC current of high impedance the wire against the cell wall
  - Using AC driven measurements
- Any of these solutions permits the measurement of the thermal conductivity of electrically conducting and polar liquids with accuracies comparable to those obtained with non-polar or non-conducting liquids, and consequently can be applied to LTIL's

Nunes, *et al.*, "*Accurate Measurements of Physico-Chemical Properties on Ionic Liquids and Molten Salts*", in Ionic Liquids and Molten Salts: Never the Twain?, Eds. K. E. Seddon and M. Gaune-Escard, John Wiley (2008), in press

Getting data from ILThermo

- Data bases are very useful
- Let us look to density of $[C_6mim][Cl]$
- Not better than 3% accuracy!

T / K	ρ / kgm-3 /uncert.	Method	Ref
298.15	1041 / 3%	VT	Gomes et al (2006) PCL
298.15	1040 /2.7%	VT	Gomes et al (2006) (JCED)
298.15	1030 /10%	Pycnometer	Huddleston et al (2001)

Getting data from ILThermo

- Data bases are very useful
- Let us look to viscosity of $[C_6mim][Cl]$

T / K	η / Pa.s /uncertainty	Method	Ref
298.15	1809 /2%	Capillary	Gomes et al (2006) (JCED)
298.15	0.716 /10%	Capillary	Huddleston et al (2001)

Same Liquid?

Getting data from ILThermo

- Data bases are very useful
- Let us look to surface tension of $[C_6mim][Cl]$

T / K	σ/ kgm-3 /uncertainty	Method	Ref
298.15	0.0425 / 3%	Ring Tensiometer	Huddleston et al (2001)
298.15	0.0411 /5%	Pycnometer	Ghatee &Zolghadr (2008)

What Can We Do?

- It is evident that:
  - **Accurate measurements of the thermal properties**, namely viscosity and thermal conductivity of ionic liquids / bucky gels and thermal conductivity of nanomaterials, are a must
    - Probably new methods are needed, namely for solid aggregates
    - Transient-hot wire, with isolated wires (or polarizing techniques) can be used to ionic liquids and nanofluids, including "bucky" gels
  - **Standardization/Intercomparisons** are also necessary, namely for ionic liquids and nano-carbons (tubes, wires, spheres, bucky balls, etc…)
  - **Chemical and physical characterization of the samples** to be used is a must, while handling in controlled atmospheres can be necessary for some ionic liquid systems
  - **Systems are much more complex than the ones used before. It is therefore necessary to have an interdisciplinary approach, where physics, chemistry and molecular sciences have to work together**

Last but not the least

- Can we measure temperature at the nanoscale?
- The absolute temperature definition (second law of thermodynamics) needs a continuum…
- Local measurements and thermal equilibrium can be well defined?
- Are there thermometers available?
- Can we calibrate them or trace them to ITS?

And what about safety?

- These new materials/chemicals create some problems to our health
- REACH and EEA will contribute to protect us, but in the laboratory we must be very careful
- Toxicity and skin and lung adsorption are not yet dominated, as normally happens in new fields

Are we redesigning CHEMISTRY?

Future

- Would the merging research in two of the most promising fields of 21st century – ionic liquids and nanomaterials – change our way of thinking and making chemistry?
- From all that has been said, chemistry and the molecular sciences will change the world in the next decades
- New materials, new properties, new applications!
- Can we do it, without abandoning our exigency for accurate and reliable measurements?

- Chemistry must be redesigned?

- Chemistry is in the heart of innovation!

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