

# Molecular simulation: progress and prospects: CECAM and IRELAND

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## **Introduction**

Very recently Ireland joined the European Centre for Atomistic and Molecular Computations (CECAM) via the Irish Universities Association. CECAM has played a central role in developing molecular and atomistic simulation in the world over the last thirty years. To celebrate this event and ensure that Ireland and its community of simulators benefits to the full from CECAM membership, we are organizing a symposium entitled "Molecular simulation: progress and prospects", to be held May 31 at University College Dublin. An additional motivation for this symposium is that CECAM is about to make a call for a new host location, and Ireland now has a significant chance of being that host since UCD with the strong encouragement of several members of the CECAM council has stated its intention to bid. All of these developments have been warmly welcomed by the heads of research of the Irish universities. We therefore are organizing a one day meeting about how we, both as individual scientists and as different laboratories, may benefit concretely from this development. The meeting will take place Thursday, May 31 2007 at the Complex & Adaptive Systems Laboratory, University College Dublin.

8 Belfield Office Park, Beaver Row

Clonskeagh , Dublin 4

<http://casl.ucd.ie/>

## **Organisers**

Dónal MacKernan, TCD; Niall English, UCD; Nick Quirke UCD

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# 1 Schedule

Timetable			
Presenter	Affiliation	Abstract	Time
Welcome			10.05-10.10
Scott Rickard	UCD	<a href="#">2.21</a>	10.10-10.15
Pietro Ballone	QUB	<a href="#">2.2</a>	10.15-10.45
Simon Elliott	Tyndall	<a href="#">2.6</a>	10.45-11.15
Niall English	UCD	<a href="#">2.7</a>	11.15-11.35
Tea/Coffee break 1			11.35-12.00
Stephen Fahy	UCC-Tyndall	<a href="#">2.9</a>	12.00-12.30
Michael Nolan	UCC-Tyndall	<a href="#">2.16</a>	12.30-12.40
Charles H. Patterson	TCD	<a href="#">2.17</a>	12.40-13.00
Mario G. Del Pópolo	QUB	<a href="#">2.18</a>	13.00-13.20
lunch			13.20-14.10
J-C Desplatt	ICHEC-DIAS	<a href="#">2.5</a>	14.10-14.20
Chaitanya Das Pemmaraju	TCD-CRANN	<a href="#">2.19</a>	14.20-14.40
Isabel Rozas	TCD	<a href="#">2.22</a>	14.40-15.00
Ivan Rungger	TCD	<a href="#">2.23</a>	15.00-15.20
Dermot Frost	TCD	<a href="#">2.10</a>	15.20-15.35
Dónal MacKernan	TCD	<a href="#">2.11</a>	15.35-15.50
Nick Quirke	UCD	<a href="#">2.20</a>	15.50-16.05
Tea/Coffee break 1			16.05-16.20
Damian Mooney	UCD	<a href="#">2.12</a>	16.20-16.35
Jens Nielsen	UCD	<a href="#">2.15</a>	16.35-16.50
Davide Cellai	UCD	<a href="#">2.3</a>	16.50-17.00
francesca Terraneo	UCD	<a href="#">2.24</a>	17.00-17.15
CECAM overview		Dónal Mac Kernan	17.15-17.30
CECAM-Ireland		Nick Quirke	17.30-17.45
Round Table			17.45-18.30
Taslina Akter	UCD	<a href="#">2.1</a>	Poster
Sanket A Deshmukh	UCD	<a href="#">2.4</a>	Poster
Berry Matijssen	TCD	<a href="#">2.13</a>	poster
John Moloney	UCD	<a href="#">2.14</a>	Poster
Gleb Solomentsev	UCD	<a href="#">2.8</a>	Poster

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## 2 Abstracts

### 2.1 Generation of silica deposition model from tetraethoxysilane (TEOS) on flat substrate using Kinetic Monte Carlo Simulation

*Taslina Akter, Thomas McDermott, J.M. Don MacElroy and Damian A. Mooney*

University College Dublin

Ultra-thin, nanoporous silica membranes have the potential to be used in high temperature ( $T > 500C$ ) CO<sub>2</sub> separation processes. Different types of deposition techniques (CVD, PECVD, PVD) have been proposed for the creation of ultra-thin (5-25nm) silica layers on both porous and non porous substrates. In addition to experimental work, the atomistic simulation of the deposition processes can assist in establishing the parameters responsible for key nano-architectural features governing gas permeation. In this work, a kinetic Monte Carlo technique is developed to model the deposition process. This research aims to develop and optimize the SiO<sub>2</sub> nanolayer deposition from TEOS on flat silica substrates under chemical vapour deposition (CVD) and plasma enhanced chemical vapour deposition (PECVD) conditions. Characterization of the deposited layer and comparison with experimental results will also be carried out.

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## 2.2 A Monte Carlo study of an idealised model of bio-membranes

*P. Ballone and M. G. Del Pópolo*

Atomistic Simulation Centre, Queens University, Belfast

The phase diagram of an idealised model recently [1] introduced to simulate bio-membranes has been determined by Monte Carlo simulations. The potential energy is the sum of short range, purely repulsive pair contributions, and spin-spin interactions. These last are of the dipole-dipole form, with however a crucial change of sign.

At low density and temperature the model gives rise to markedly 2D structures, consisting of open extended surfaces and closed vesicles. At high T the stable phase is a homogeneous 3D uid. In between these two extreme conditions the phase behaviour is determined by the relative position and strength of two basic transitions, the first concerning the dipole-dipole part of the Hamiltonian, while the second is analogous to the solid-like to liquid-like transition in 2D.

The possibility of tuning the phase diagram greatly enhances the interest of the model, since it allows to reproduce the so-called main transition (2D solid to 2D liquid) in bio-membranes.

[1] P. Ballone and M. G. Del Pópolo, Phys. Rev. E 73, 031404 (2006).

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### 2.3 Crystallization in the vicinity of dynamical arrest

*Davide Cellai*

University College Dublin

Experiments of colloidal hard particles left undisturbed for a few days after tumbling show different dynamics towards crystallization in different ranges of density: homogeneous nucleation for relatively low densities and heterogeneous nucleation and eventually absence of crystallization for high densities. It appears that the change in the nucleation behaviour is related with the presence of dynamical arrest. We present a lattice model that reproduces the phenomenon by the introduction of a kinetic rule in the dynamical evolution of a lattice model with many-body repulsion. Thus, we use a Monte Carlo algorithm which implements a single-particle move scheme deemed to be representative of the real dynamics of the system. The model also allows us to give a unified picture with experiments in absence of gravity and shows an exponent for the mean squared displacement which can be a signature of universality.

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## 2.4 Molecular Simulation of Temperature-Sensitive Hydrogels: observation of the Lower-Critical-Solution-Temperature

*Sanket A Deshmukh, Thomas McDermott, Savita Kulkarni, Damian Mooney and J.M. Don MacElroy*

University College Dublin

Temperature sensitive hydrogels are highly crosslinked polymers that exhibit a significant volume transition at a well temperature known as the lower critical solution temperature (LCST). On example of such a hydrogel is poly (N-isopropyl acrylamide) (PNIPAM), which undergoes a sharp volume shrinkage in water at 32C, changing from a hydrophilic state below this temperature to a hydrophobic state above it, resulting in the release of the solvent (water) into the surrounding medium. As the LCST of PNIPAM lies close to body temperature one of the most exciting application of these temperature sensitive hydrogels is targeted controlled drug delivery. In this work, we use computer simulation studies in providing a molecular level understanding and evaluation of these hydrogels near LCST not otherwise easily amenable to experimental determination.

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## 2.5 The Irish Centre for High-End Computing: working with the community

*Jean-Christophe (J-C) Desplat*

The Irish Centre for High-End Computing and Dublin Insitute of Advanced Studies

Abstract to Be Announced

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## 2.6 The Electronics Theory Group at Tyndall National Institute

*Simon D. Elliott, Jim Greer, Giorgos Fagas, Panagiotis Drouvelis,*

*Andreas Larsson and Damien Thompson*

Tyndall National Institute

Tyndall National Institute was created in 2004 with the objective of being a focal point for research in Ireland in Information and Communications Technology. The Electronics Theory Group at Tyndall applies computational methods from electronics, chemistry and physics to the design and analysis of nanoelectronic devices, integrated circuit manufacturing, MEMS structures, and microelectronic packaging. This talk will highlight the work of the following group members: Jim Greer, Giorgos Fagas and Panagiotis Drouvelis in the area of molecular electronics and devices, Andreas Larsson in nanoscale clusters, Damien Thompson in molecular assembly and recognition and Simon Elliott in deposition of oxide materials. The group makes heavy use of the Tyndall Beowulf cluster and of national computing resources. More information is available at

<http://www.tyndall.ie/research/computational-modelling-group/>

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## 2.7 Denaturation of hen egg white lysozyme in electromagnetic fields: a molecular dynamics study

*Niall English*

University College Dublin

Nonequilibrium molecular dynamics simulations of hen egg white lysozyme have been performed in the canonical ensemble at 298 K in the presence of external electromagnetic fields of varying intensity in the microwave to far-infrared frequency range. Significant non-thermal field effects were noted, such as marked changes in the protein's secondary structure which led to accelerated incipient local denaturation relative to zero-field conditions. This occurred primarily as a consequence of alignment of the protein's total dipole moment with the external field. The applied field intensity was found to be highly influential on the extent of denaturation in the frequency range studied, and 0.25-0.5 VÅ-1rms fields were found to induce initial denaturation to a comparable extent to thermal denaturation in the 400 to 500 K range. In subsequent zero-field simulations following exposure to the e/m field, the extent of perturbation from the native fold and the degree of residual dipolar alignment were found to be influential on incipient folding. [Back to Home](#)

## 2.8 Using electromagnetic (e/m) fields to probe and influence protein behaviour

*Gleb Solomentsev, Elisa Nogueira, J.E. Nielsen, N. J. English, D. A. Mooney*

University College Dublin

The effect of electromagnetic radiation on biological organisms is a matter of some controversy. A recent study of non-thermal electromagnetic (e/m) radiation effects observed that exposure of a protein to e/m fields induced partial protein unfolding comparable to the initial stages of temperature induced unfolding. The focus of this research project is to further probe these effects. The work is carried out as collaboration between this group and the group of Dr. Jens Nielsen of the Conway Institute. The project combines molecular simulation studies, carried out by myself, and experimental work, carried out by Elisa Nogueira. This poster briefly discusses our methods, some preliminary results, and future studies we hope to carry out.

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## 2.9 Charge Carrier and Phonon Dynamics in Materials

*Stephen Fahy*

Physics Department, University College Cork and Tyndall National Institute

I will present some applications of first-principles band-structure methods to carrier excitation and transport in semiconductors and semimetals, which have recently been done by my research group. A major focus of our programme has been on semiconductor alloys, where we have examined both elastic and inelastic scattering of carriers in SiGe, including both alloy disorder and the electron-phonon interaction contributions. In a rather different view of the electron-phonon interaction, we have also examined non-linear phonon dynamics excited by intense, ultra-short optical pulses in bismuth. [Back to Home](#)

## 2.10 HPC: the Right Tool for the Job

*Dermot Frost*

Trinity Centre for High Performance Computing, Trinity College Dublin

Abstract to be Announced

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## 2.11 Porphyrins, Nanotubes, and Non-Adiabatic Quantum Dynamics: Theory and Experiment

*Dónal MacKernan*

Molecular Electronics and Nanotechnology, School of Physics, Trinity College Dublin

I will extremely briefly present three projects which I am currently working on or just finished. Two were entirely motivated by experiment, while the last sprang from more theoretical concerns.

The first is the application of molecular dynamics simulations to the molecular engineering of nonplanar porphyrin and carbon nanotube assemblies. Of particular interest in this work was the nature and strength of non-covalent interactions existing between a series of nonplanar conjugated tetraphenylporphyrin (TPP) derivatives and carbon nanotubes in solution. The results of molecular simulations on these composite systems in solution were in striking agreement with experiment[1], and revealed a lot of surprising details.

The second pertains to carbon nanotubes. One of the main obstacles to the exploitation of single wall carbon nanotubes (SWCNT) remarkable electronic and materials properties is their tendency to form ropes or bundles, due to a weak Van der Waals attractive interaction. This complicates drastically the processing, and purification of carbon nanotubes into SWCNT's of a given electronic nature (i.e. semi-conducting or metallic), and also leads to a significant deterioration in the material properties of carbon-nanotube composites. An understanding of the "reaction paths" involved in transitions from bundles to isolated SWCNT's in solution is basic to the control of the process, and is the motivation of this work. The results of extensive molecular dynamics studies of this problem have just been completed, and also led to a complementary neutron scattering (diffraction) experiment at the Institut Laue Langevin, Grenoble.

Finally, I will mention the third project. An understanding of the dynamical properties of condensed phase quantum systems underlies the description of a variety of quantum phenomena in chemical and biological systems. These phenomena include, among others, nonadiabatic chemical rate processes involving electronic, vibrational or other degrees of freedom, decoherence in open quantum systems and quantum transport processes. Deriving and constructing an **efficient** propagator and algorithm to study these properties has been at the core of a seven year project. We have now, at last, a code which is several orders of magnitude faster than before - and extremely stable. The form of the propagator is extremely interesting, while the nature of the filter required for long time simulations is based on decoherence properties of the system itself. This code is now ready for "shipping", at least to our friends.

[1] *Molecular Engineering of Nonplanar Porphyrin and Carbon Nanotube Assemblies- a Linear and Non-linear Spectroscopic and Modelling Study*, E. Ní Mhuircheartaigh, S. Giordani, D. MacKernan, S. M. King, Rickard, L.M. Val Verde, M. O. Senge and W. J. Blau, submitted to Phys. Rev B (2007)

[2] *Trotter-Based Simulation of Quantum-Classical Dynamics*, Dónal MacKernan, Giovanni Ciccotti and Raymond Kapral (preprint) (2007)

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## **2.12 From Energy to Enzymes: Molecular Simulation at Chemical and Bioprocess Engineering, UCD**

*Damian Mooney*

University College Dublin

The Materials and Molecular Simulation Group at the School of Chemical and Bioprocess Engineering has been in existence since 1991, founded by Prof. J.M.D. MacElroy, and has grown to its current size of 11, including academic staff, postdoctoral research assistants and PhD students. In this talk an outline of the current research work currently being undertaken will be presented, including investigations on the synthesis of inorganic membranes for CO<sub>2</sub> capture, hydrogels for drug delivery applications and the influence of e/m fields on ionic liquid behaviour.

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## 2.13 Adrenoceptors: homology modelling and molecular dynamics

*Berry Matijssen, Graeme Watson and Isabel Rozas*

School of Chemistry, Trinity College Dublin

Adrenoceptors[1] belong to class A of the superfamily of G protein coupled receptors (GPCRs) that transduce signals across the cell membrane, thus initiating a variety of intracellular biochemical events. The adrenoceptors subtypes ( $\alpha_{1A}$ ,  $\alpha_{1B}$  and  $\alpha_{1D}$ ) are of particular therapeutic interest due to their important role in the control of blood pressure, and in contraction and growth of smooth and cardiac muscle.

Our knowledge of the structure of GPCRs and particularly in adrenoceptors is limited. The only available GPCR crystal structure is that of bovine Rhodopsin, which has been characterised with different resolutions, being the most refined 2.2Å (pdb: 1U19 (fig 1)). Utilising the structural data from this structure we were able to produce homology models of the  $\alpha_{1A}$ -adrenoceptor [2]. By using a similar approach, we have now generated the corresponding homology models for the  $\alpha_{1B}$  and  $\alpha_{1D}$  subtypes. Unfortunately, the

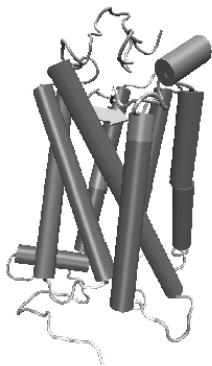


Fig 1. Rhodopsin

Rhodopsin structure is in its inactive conformation, which makes it likely that our homology models are also in an inactive state. Molecular dynamics (performed with the AMBER 7.0 package) can be used to simulate the structural movements of the adrenoceptors therefore, producing structures that can possibly mimic the active form of the receptor.

[1] B. Calzada, A. Arinano, *Pharmacological research*, 44 (2001) 195-208

[2] G. Kinsella, I. Rozas, G. Watson, *Biochemical and biophysical research communications*, 324 (2004) 916-921

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## 2.14 Preparation of Model Microporous Silica for Molecular Simulation Studies of Ultra-thin Oxide Layer Deposition on Porous Substrates

*John Moloney*

University College Dublin

Previous experimental and theoretical studies have demonstrated the incredible potential of ultra-thin, nano-porous inorganic membranes for the purpose of separating key, high temperature, gas mixtures, such as CO<sub>2</sub>/N<sub>2</sub>. These membranes, fabricated using the Chemical Vapour Deposition (CVD) of TEOS (tetraethylorthosilicate) onto a porous Vycor (tm) substrate, exhibited both high selectivities and high fluxes highlighting their potential in next generation CO<sub>2</sub> capture technologies. Because of the complex inter-relationship between the processing parameters of CVD and the resulting nano-architecture, molecular simulation techniques offer a powerful means of elucidating the molecular mechanisms governing membrane synthesis and ultimately gas separation performance. To this end, this work aims to provide a means of developing models for the structure of the substrate itself, the CVD deposition process and the modelling of permeation of selected gas species.

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## 2.15 The interpretation of molecular dynamics simulations of Biomolecules

*Jens Nielsen*

School of Chemistry and Chemical Biology, University College Dublin

The interpretation of molecular dynamics simulations of biomolecules is among the more challenging aspects of computational biology. I will present two examples of comparative molecular dynamics simulations and use these to discuss how and when MD simulations can be used successfully to gain biological insights.

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## 2.16 Defects and Dopants in Metal Oxides: Problems with DFT

*Michael Nolan*

Physics Department, University College Cork and Tyndall National Institute

Density functional theory (DFT) is currently the approach most widely used for studying metal oxides. However, approximate DFT exchange-correlation functionals can exhibit difficulty in describing many interesting and important systems, among these are (i) reduced cerium dioxide (ii) O 2p holes in doped metal oxides and (iii) Cu<sup>2+</sup> states in copper oxides. In this talk I will give a brief overview of our work on these topics and discuss how to go beyond DFT to describe these systems and issues involved with studying metal oxides using approaches beyond DFT. [Back to Home](#)

## 2.17 Strong correlations and stripes in $\text{Ca}_{1.88}\text{Na}_{0.12}\text{CuO}_2\text{Cl}_2$

*Charles H. Patterson*

School of Physics, Trinity College Dublin

The system  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  has been extensively studied by scanning tunnelling spectroscopy (STS) and photoemission as it cleaves readily between CaCl planes to give an atomically smooth, insulating CaCl surface; it is a superconductor with a  $T_c$  of 26 K; it does not undergo lattice distortion when doped. These features make it an ideal candidate for a study of the mechanism of high temperature superconductivity. Recent STS measurements have shown that an electronic stripe structure forms in the CuO<sub>2</sub> planes when it is doped to  $x = 0.12$ . We have performed density functional calculations on  $\text{Ca}_{1.88}\text{Na}_{0.12}\text{CuO}_2\text{Cl}_2$  and find electronic states in CuO<sub>2</sub> planes localized on magnetic anti-phase boundaries at the Fermi level. These states may be the ones observed as stripes by STS.

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## 2.18 Thermal properties of ionic liquids nanodroplets

*Mario G. Del Pópolo and P. Ballone*

Atomistic Simulation Centre, School of Mathematics and Physics

Room temperature molten salts, or ionic liquids, are an important class of Coulombic fluids that have recently experienced a revival of interest due to a myriad of potential applications, ranging from electrochemical systems and devices, to nanostructured materials and chemical synthesis [1]. Although these organic electrolytes share properties with their high temperature (inorganic) counterparts, they also exhibit some remarkable differences. Such differences, that manifest themselves in sub-ambient melting points, result from a peculiar balance between van der Waals and Coulombic forces, and the presence of complex molecular shapes. In this work we will discuss structural, dynamical and thermal properties of 1-butyl-3-methyl-imidazolium triate ([bmim][Tf]) clusters computed using an all-atom empirical potential model [2]. Neutral and charged clusters were considered up to a size (30 [bmim][Tf] pairs) well into the nanometric range. Thermal properties of neutral clusters were investigated in the  $0 \leq T \leq 700K$  range, depicting a near-continuous transition between a liquid-like phase at high  $T$  and a solid-like phase at low  $T$ . The transition takes place at  $T \sim 190K$ , in close correspondence with the bulk glass point  $T_g \sim 200$ . Solidification is accompanied by a transition in the electrostatic properties of the droplet, manifest by the appearance of a small permanent dipole embedded into the solid cluster. The simulation results highlight the molecular precursors of several macroscopic properties and phenomena, and point to the close competition of Coulombic and dispersion forces as their common origin.

[1] Ionic liquids: Industrial applications for green chemistry; R. D. Rogers and K. R. Seddon, Eds.; American Chemical Society: Washington DC, 2002.

[2] Neutral and Charged 1-Butyl-3-methylimidazolium Triate Clusters: Equilibrium Concentration in the Vapor Phase and Thermal Properties of Nanometric Droplets; P. Ballone, C. Pinilla, J. Kohano, and M. G. Del Pópolo, J. Phys. Chem. B, 2007, 111, 4938-4950

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## 2.19 Density Functional and Monte Carlo investigation of ferromagnetism in wide gap Oxides

*C.D.Pemmaraju, R.Hanafin, T.Archer and S.Sanvito*

School of Physics, Trinity College Dublin

Transition metal (Mn, Co, Fe) doped wide gap semi-conducting Oxides such as ZnO, TiO<sub>2</sub>, and SnO<sub>2</sub> are being actively investigated as materials with technological significance for spintronics applications. Cobalt (Co) doped ZnO in particular has been both experimentally and theoretically the most studied oxide Dilute Magnetic Semiconductor (DMS) material. Experimental results in the recent past [1] pointed towards a donor mediated mechanism for long range Ferromagnetism in this material although several inconsistencies in the observations remain unexplained and a clear theoretical understanding on the subject is yet to emerge. Using a combination of Density Functional theory and Monte Carlo methods, we explore both the microscopic and thermodynamic aspects of ferromagnetism in ZnO:Co. Firstly, we present an ab-initio investigation into various microscopic mechanisms for ferromagnetism in ZnO:Co employing a Self Interaction Corrected (SIC) Density Functional method [2] capable of handling strongly correlated materials. Then, we present results from a Monte Carlo study analyzing the feasibility of the donor mediated model for ferromagnetism in ZnO:Co. Finally, using the well known LDA+U method, we look at the electronic and magnetic structure of Wurtzite CoO which might form a magnetic centre in ZnO:Co either as a competing phase or in cluster form.

[1]J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nat. Mater. 4, 173(2005).

[2]C. D. Pemmaraju, T. Archer, D. Sanchez-Portal and S. Sanvito, Phys. Rev. B 75, 045101 (2007)

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## 2.20 The Interaction of Fluids with Surfaces and Nanoparticles

*Nick Quirke*

University College Dublin

The way fluids flow into and fill nanopores is of interest to physicists, chemists, engineers and biologists. Nanoscale flow is dominated by surface properties and these can be studied directly using molecular simulation of model systems. In previous work we have considered equilibrium, steady state and transient flow in carbon nanopores. Recently we have extended our work to polymer surfaces such as PDMS including the effect of oxidation on aqueous flows. In this lecture we review key results concerning flow in nanopores from theory, simulation and experiment, and present new results for dynamical properties of nanomaterials in aqueous solutions.

See for example

S. Supple and N. Quirke, Rapid imbibition of fluids in carbon nanotubes, *Physical Review Letters* 90, 214501 (2003).

V. P. Sokhan, D Nicholson and N. Quirke, Transport properties of nitrogen in single walled carbon nanotubes *J Chem Phys*, 120, 3855 (2004).

S. Supple and N. Quirke, Nanocapillarity: II: Density profile and molecular Structure for decane in carbon nanotubes, *J Chem Phys*, 122, 104706, (2005)

M. Longhurst and N. Quirke, Environmental effects on the radial breathing modes of carbon nanotubes in water, *J Chem Phys* 124, 234708 (2006)

M. Longhurst and N. Quirke, 'Pressure dependence of the radial breathing mode of carbon nanotubes: The effect of fluid adsorption', *Physical Review Letters* 98, 145503 (2007)

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## **2.21 Overview on the Complex and Adaptive Systems Laboratory**

*Scott Rickard*

University College Dublin

Abstract to be Announced

## 2.22 On the nature of hydrogen bonds: an overview on computational studies

*Isabel Rozas*

Medical Chemistry, School of Chemistry, Trinity College Dublin

The nature of Hydrogen bond interactions (HB) is still today the subject of many discussions. We present an overview of computational methods and parameters (interaction energy, HB distance and radii, electron density topological parameters or orbital energies) required for an accurate description of HB systems. As well, different correlations have been found between these descriptors providing a global view of HB interactions. Considering the definitions of covalent and ionic bond, HB interactions could occur between these two extremes. Thus, we look into some of the very strong HBs (LBHB, CAHB, RAHB) and some of the weak HBs (weak donors: C-H or weak acceptors: pi-systems). Other aspects such cooperativity or solvation play also an important role in this versatile interaction.

## 2.23 Electronic transport from first principles: The Smeagol code

*Ivan Rungger and S. Sanvito*

School of Physics and CRANN, Trinity College Dublin

The Smeagol code [1] has been developed to calculate the electronic transport properties of nanojunctions attached to semi-infinite electrodes from first principles. In the first part of this talk the basics of the method are presented. Smeagol is based on the nonequilibrium Green's function (NEGF) technique and uses a Hamiltonian obtained from density functional theory (DFT). It is interfaced with the ab initio LCAO pseudopotential code SIESTA, from which it obtains the DFT Hamiltonian. Smeagol calculates the self-energies describing the semi-infinite leads and then adds them to the Hamiltonian of the scattering region to obtain an effective Hamiltonian for the open system (molecule+electrodes). Moreover the non-equilibrium charge density for a given bias voltage is calculated in a selfconsistent way within the NEGF formalism. Smeagol can be used to treat general transport problems for systems of up to thousands of atoms with arbitrary structure for both electrodes and junction.

In the second part of the talk three examples of practical calculations are presented. The first system is a benzene dithiol molecule attached to gold electrodes. It will be shown that improved agreement with experiments can be obtained by using a self-interaction corrected exchange correlation functional. The second example is a  $Mn_{12}$  based magnetic molecule, where the influence of the local magnetic arrangement of the molecule on the transport properties is studied. As third system Fe/MgO/Fe(100) tunneling junctions are presented. In this system bound states form in the junction, i.e. states that are not coupled to the electrodes. The dependence of the transport properties on the charging of the bound state at finite bias is investigated.

[1]A. R. Rocha, V. M. Garcia-Suarez, S. Bailey, C. Lambert, J. Ferrer and S. Sanvito, Phys. Rev. B 73, 085414 (2006);

<http://www.smeagol.tcd.ie>

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## 2.24 The origin of intermittent sub-diffusive dynamics in nearly-arrested systems

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Unlike thermodynamic phase transitions, dynamical arrest transition is not accompanied by any discontinuity in the thermodynamic derivatives; still, dramatic changes in the physical properties of the system take place. The arrested behaviour in a glass-forming liquid is a well known example of this, but it is now known that many other phenomena in complex matter are quite similar. What is observed is a sharp and reproducible change in the transport coefficients of the fluid on approach to the transition, that leads to a new state. In particular the viscosity diverges, and the diffusion constant vanishes continuously. As the system approaches dynamical arrest, mobility is progressively lost: particle motions become very rare events, and what is more peculiar, they become correlated on a larger and larger scale. A dynamical correlation length can be identified, defining a domain of the system in which the motions are interdependent, so that simple diffusion on that scale is not possible. The dynamics of nearly-arrested systems is observed therefore to be intermittent (particles motions are not regular, waiting times between successive movements encompass a vast range of values) and sub-diffusive (mean-squared displacement growing slower than linearly with time).

We investigate the dynamics of these systems using kinetically constrained lattice models. Studying such simple models, one can deeply understand the fundamental mechanisms governing dynamics; besides, simulating detailed models of systems so close to arrest would be extremely time consuming.

The distribution within the system of dynamically available empty volume and its dynamics prove to be the keys to explain both the intermittent and sub-diffusive dynamics of particles and the successive onset of a diffusive regime, which takes place at a crossover time  $\tau_c$ . In particular, the times elapsed between successive moves are determined by the time it takes to local empty space to return to an already visited site, while the crossover time depends on the average distance between agents of motion in the system, that is identifiable with the correlation length  $\eta$ . If the kinetic constraints are removed, that is in the case of a simple lattice gas, the model results to be analytically solvable and self-consistent: the asymptotic wait time distribution is calculated, and a scaling relation between the linear system size  $\eta$  and  $\tau_c$  is established. The results are universal, because they depend only on the ensemble of return paths of the empty space. Imposing on the system a kinetic constraint (such as Kob-Andersen rule) causes the loss of analytical simplicity. The ideas though are still valid, provided that we correctly identify the local available empty space: the concept of clusters of empty space is thus introduced, and the mechanism which controls particle dynamics is proven to be still valid.

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