Psi-K Workshop on Encapsulated Nano Phase Change Materials

The Psi-K Workshop on Encapsulated Nano Phase Change Materials took place between the 13th - 15th September 2017 at the University of Warwick, UK. The workshop sought to address strategies for the computational modelling of nano phase-change materials (NPCMs) and related phenomena. The limitations of currently available modelling tools, as well as possible solutions, were reviewed. Topics considered included the thermodynamics and kinetics of nano-crystalline phase change processes and the connection between theory and experiments via computation of spectral properties. Our aim was to motivate collaborations and further advancements in the methodologies for modelling NPCMs.

The Psi-K funding allowed the inclusion of a range of international experimentalists and theorists to be invited, along with recently appointed lecturers within the UK.

Atomic bonding in phase-change materials was presented as an important theme, Professor Wuttig proposing that none of the current bonding models are capable of describing such systems, and Prof. Elliot asking “what have the bonds ever done for us?”.

A large part of the meeting was given to materials that form within carbon nanotubes (CNTs), *so-called* nano-confined materials. This section included Dr Medeiros’ description of his prediction, and the subsequent experimental verification by Dr Sloan, of helical nanowires of tellurium inside CNTs.

Prof Mousseau from Montreal presented an interesting talk on the kinetic Activation-Relaxation Technique, some of which was recorded for the French media.

Several follow up discussions are scheduled to take place, including new collaborations, and reciprocal visits to groups in the US and France.

The organisers are also grateful to the Engineering and Physical Sciences Research Council’s Collaborative Computational Project 9 for financial support.

Organisers:

Andrew J Morris (School of Metallurgy and Materials, University of Birmingham, UK)
David Quigley (Department of Physics, University of Warwick, UK)

Programme

Wednesday 13th September

13:00 - 14:00	**Arrival and registration**
14:00 - 14:15	**Introduction & Welcome**

Session 1 - Phase change materials

14:15 - 15:05	**Mattias Wuttig - Phase Change Materials by Design: The Mystery of Resonance Bonding**
15:05 - 15:40	**Gabriele Sosso - The Crystallization Kinetics of GeTe Nanowires - Insights from Large Scale Atomistic Simulations**
15:40 - 16:15	***Coffee***
16:15 - 17:05	**Stephen Elliott - Structure of amorphous phase-change materials: What have the bonds ever done for us?**

Dinner in Rootes Restaurant from 19:00

Thursday 14th September (AM)

Session 2 - Encapsulated nanowires

09:00 - 09:50	**Jeremy Sloan - Crystallography and Functional Evolution of Atomically Thin Confined Nanowires**
09:50 - 10:25	**Mark Wilson - The Formation of Unique Crystal Structures in Confined Environments**

Coffee

11:00 - 11:50	**Eric Faulques - Recent progress in characterization and modelling of functional nanowires**
11:50 - 12:25	**Elena Besley - Electron beam induced chemical reactions and nano-catalysis in confined environments**
12:25 - 13:00	**Paulo V. C. Medeiros - Efficient and Accurate *Ab Initio* Structural Predictions of CNT-Encapsulated Extreme Nanowires**

Lunch in Rootes Restaurant

Session 3 - Advanced sampling for structural transformations/phase change

14:00 - 14:50	**Normand Mousseau - Carbon diffusion in Iron : A Kinetic Activation-Relaxation Technique Study**
14:50 - 15:40	**Jutta Rogal - Atomistic mechanisms and kinetics during phase transformations in metals**

Coffee

Session 4 - Poster session

16:00 - 17:30	**Posters (all contributions welcome)**

Conference dinner in (Chancellors Suite) 19:00

Friday 15th September

Session 5 - Functional properties of nanostructures

09:00 - 09:50	**Chris Ewels - Semi-automatic routes to confined structure prediction in nanocarbons**
09:50 - 10:25	**Nicola Bonini - Transport in nanomaterials from first-principles**
10:25 - 11:00	**Andrij Vasylenko - Regulation of electronic and thermoelectric properties of SnTe and HgTe nanowires via their encapsulation within single-walled carbon nanotubes**

Coffee

Session 6 - Large length scale simulation methods

11:30 - 12:05	**Gabor Csanyi - Gaussian Approximation Potentials for Materials Research**
12:05 - 12:40	**Lionel Truflandier - An overview of the CONQUEST code capabilities: Molecular dynamics and applications**
12:40 - 13:00	**Conclusions & Discussion**

Lunch in Rootes Restaurant followed by departure

Abstracts

Phase Change Materials by Design: The Mystery of Resonance Bonding

Mattias Wuttig
RWTH Aachen University of Technology, Germany

Phase change media utilize a remarkable property portfolio including the ability to rapidly switch between the amorphous and crystalline state, which differ significantly in their properties. This material combination makes them very attractive for data storage applications in rewriteable optical data storage, where the pronounced difference of optical properties between the amorphous and crystalline state is used. This unconventional class of materials is also the basis of a storage concept to replace flash memory. This talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that only a rather small group of materials utilizes resonant bonding, a particular flavour of covalent bonding, which can explain many of the characteristic features of phase change materials. This insight is employed to predict systematic property trends and to explore the limits in stoichiometry for such memory applications. It will be demonstrated how this concept can be used to tailor the electrical and thermal conductivity of phase change materials. Yet, the discoveries presented here also force us to revisit the concept of resonance bonding and bring back a history of vivid scientific disputes about ‘the nature of the chemical bond’.

The Crystallization Kinetics of GeTe Nanowires - Insights from Large Scale Atomistic Simulations

Gabriele Sosso
Department of Chemistry, University of Warwick, UK

The usage of phase change materials in the form of nanowires (NWs) represents an attractive option to deal with the ever-growing need of phase change memories (PCMs) for smaller cell size and lower power consumption. In fact, NWs typically show e.g. a larger degree of crystallinity and a much greater potential to be employed in multibit cells if compared with the traditional 3D design of PCMs. And yet, a number of functional properties of phase change material NWs remain largely unexplained: as an example, the origin of the reduction of the resistance drift observed experimentally in NWs with respect to the bulk is not entirely understood. In the last few decades, atomistic simulations, and particularly first principles, Density Functional Theory (DFT) calculations, have provided invaluable insight into many a property of phase change materials. However, phenomena such as crystal nucleation and growth remain well beyond the reach of conventional first principles calculations. This is mainly because of the limitations of e.g. DFT in terms of system size (typically 10^2 particles) and simulation length (typically 10^2 picoseconds). This is why we have taken advantage of a machine learning-based interatomic potential for the prototypical phase change material GeTe. We have previously employed such a potential to perform large scale (10^4 particles, 10^4 picoseconds) atomistic simulations aimed at investigating the crystallization kinetics of GeTe from the supercooled liquid phase - and in the case of heterogeneous crystal growth as well. Here, we focus on the crystallization kinetics of ultrathin (9 nm in diameter) GeTe nanowires: we show that the melting temperature of these objects is about 100 K lower than that of bulk GeTe, which leads to a reduction of about a factor two of the maximum crystallization speed. Furthermore, we pinpoint the structural origin of the reduction drift mentioned above, at the heart of which stand a smaller population of Ge-Ge homopolar chains - if compared to the bulk case. These results allow for a direct comparison of the crystallization kinetics and of the ageing process in GeTe NWs with respect to its bulk counterpart - and with the heterogeneous crystal growth scenario as well, thus adding yet another piece to the comprehensive picture of crystal nucleation and growth within PCMs.

Crystallography and Functional Evolution of Atomically Thin Confined Nanowires

J Sloan,[1] A Vasylenko,[1] C. Slade,[1] SR Marks,[1] RJ Kashtiban,[1] M. Burdanova,[1] PVC Medeiros,[2] J Wynn,[2] IA Pantazi,[2] S Kret,[2] P Dłużewski, AM Sanchez,[1] E Faulques,[4] DC Smith,[5] J-L. Hughes,[1] D Quigley,[1] AJ Morris.[2]

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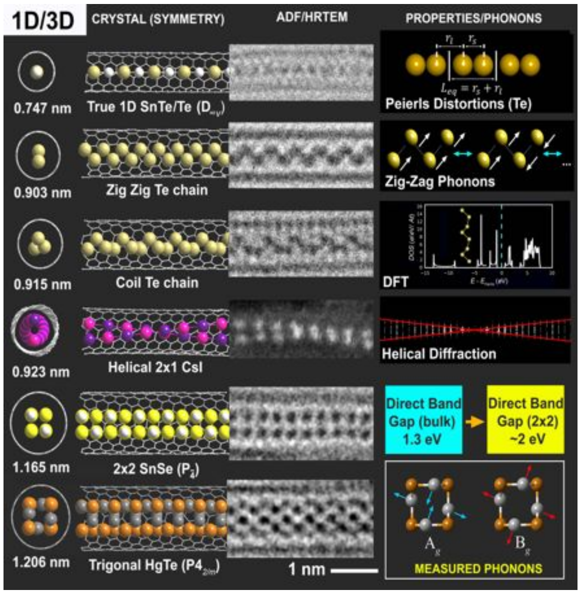

Figure 1. Evolution of polytype, symmetry and function of atomically thin nanowires with SWNT diameter and filling composition for SnTe, Te,[4] CsI,[2] SnSe[5] and HgTe[6,7] True-1D or near 1D crystals.

A logical extension to fabrication of monolayer 2D materials such as graphene and the 2D layered Transition Metal DiChalcogenides (TMDCs) is creation of atomically regulated nanowires as thin as a single atom column in width.[1,2] In close concert with increasing nanotube diameter, the number of columns of atoms per nanowire accommodated in cross section changes along with symmetry and functionality (Figure 1).[1-7] We and others have created atomically regulated nanowires by confining them within the smallest diameter carbon nanotubes, and are investigating their structural and electronic properties. In terms of their experimental characterisation, these materials provide the ultimate benchmark for testing the highest resolution imaging methodologies, in particular aberration-corrected Transmission Electron Microscopy (ac-TEM) and Scanning Transmission Electron Microscopy (ac-STEM).[2,4-7] A wide variety of different types of materials can be inserted into SWNTs, including ionic halides,[1,2] metals,[1,3] semi-metals,[6,7] semi-conductors,[7] ferro-magnetic materials,[1] and Phase Change Materials[5,8] and others.[5] Imposition of low-dimensional symmetry induces novel phonon characteristics in several of these materials, making them accessible to Raman spectroscopy.[3,6,7] All of these aspects, and many more, can be modelled either *ab initio* or *a posteriori* by state-of-the-art Density Functional Theory methods[3-5] which allow for both predictive modelling and diagnostic interpretation of existing and novel low-dimensional systems, allowing for the creation of an effectively unlimited palette of atomically regulated crystals whose structures can be synthesized, predicted (and then synthesized), their properties modelled and measured, their phase-change characteristics mapped on an atom-column by atom column basis. The extraordinary collective potential that these nanomaterials represent, the techniques used to investigate them and the progress made so far will be introduced in the presentation.

References

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[3] A. Vasylenko et al Phys. Rev. B, 95, (2017).
[4] P. V. C. Medeiros et al ACS Nano (2017)
[5] R. Carter et al Dalton, 43, 7391 (2014).
[6] J. H. Spencer et al ACS Nano, 8, 9044 (2014).
[7] J. H. Spencer et al RSC Adv. 6, 95387 (2016).
[8] C. Giusca et al Nano Lett. 13 4020 (2013).

The Formation of Unique Crystal Structures in Confined Environments

Mark Wilson.
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Carbon nanotubes (CNTs) offer a potentially stable and controllable confining environment in which novel (and potentially technologically useful) crystalline materials may be grown. In this presentation models will be developed to understand the filling of CNTs by both (relatively simple) molten salts and by near-spherical fullerenes. Molten salts represent a potentially useful class of filling material as their relatively low surface tensions allow salts to fill the CNTs without simply crushing them (as would, for example, most liquid metals). Many salts form inorganic nanotubes (INTs) which may have unique low-dimensional morphologies not simply related to known bulk polymorphs, and potentially offer unique mechanical and electronic properties. Atomistic simulation models, in which the atom interactions are treated utilizing relatively simple potential energy functions, are developed and applied to understand the INT formation and stability. Further developments include the CNT flexibility (deformability) and allowing the CNT to be considered as insulating or metallic. INT morphologies are classified by reference to folding two dimensional sheets. The distribution of INT morphologies formed can be controlled using the CNT diameter and by applying a potential difference to the CNTs. Filling the CNTs with mixed metal salts highlight the potential application of the CNTs as nano-sieves. The salts may interact with the CNT to effectively repair defects. Fullerenes are shown to fill the CNTs to form highly ordered close-packed structures stabilised by the high deformability of the CNT. The coherent motion of the internal fullerene structure and the eccentric deformations of the CNT are found to be highly correlated.

Recent progress in characterization and modelling of functional nanowires

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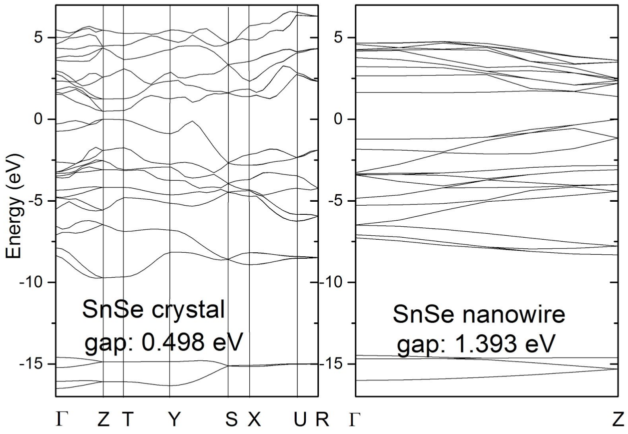
Functional nanowires are expected to be important components in the future for optronics, photonics, thermoelectrics, spintronics, and nanoelectronics. Lower spatial dimensions as well as confinement result in substantial modifications of the structure and electronic properties of functional nanomaterials, as compared to those in their bulk forms. Nanowires can be obtained for example by top-down fabrication with electro-chemical methods allowing easy control of shaping. Metallic nanostructures with extraordinary quantized properties can be formed this way [1]. At the opposite side bottom-up techniques have proven unprecedented effectiveness for elaboration of very small diameter nanowires. A significant progress has been made in designing and modelling atomic-sized organic nanowires and nanoribbons grown on clean metallic surfaces by molecular self-assembly under ultra-high vacuum [2]. Other recent advances include works on hybrid nanowires obtained by filling small-diameter (~1 nm) carbon nanotubes with functional crystals [3]. All these approaches provide unique possibilities for 1D controlled growth of metals, polymers, insulators or semiconductors having no analogues in the 3D world. The intercalation of several topological insulators (SnTe, SnSe, GeTe, HgTe..) in single walled carbon nanotubes is of particular interest. Inside the carbon walls these atomic nanowires are self-contained. They weakly interact with the outer environment and possess extreme physical properties. Density functional theory (DFT) calculations of the electronic and vibrational structures of these nanowires after encapsulation were performed with SX, PBE, and PBEsol methods [4,5]. The nanostructures are found to be stable with drastically changed electronic band gap [6] and can be envisioned for various nanoscale applications.



Example of DFT calculations of band structure in bulk and nanowire SnSe crystals with functional sX-LDA

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2. N. Kalashnyk, et al. On-surface synthesis of aligned functional nanoribbons monitored by scanning tunnelling microscopy and vibrational spectroscopy. *Nat. Commun.* **8**, 14735 (2017). doi: 10.1038/ncomms14735
3. J.H. Spencer, J. M. Nesbitt, H. Trewhitt, R.J. Kashtiban, G. Bell, V. G. Ivanov, E. Faulques, J. Sloan, D. C. Smith. Raman spectroscopy of optical transitions and vibrational energies of 1nm HgTe extreme nanowires within single walled carbon nanotubes, *ACS Nano* **9**, 9044-9052 (2014). doi: 10.1021/nn5023632, and references therein.
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Electron beam induced chemical reactions and nano-catalysis in confined environments

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Chemical reactions of molecules and metal clusters, taken place in confined environments of carbon nanotubes and activated by the high-energy electron beam (e-beam) of transmission electron microscope (TEM), are fundamentally limited by the element and electron energy-specific interactions of the material with the e-beam. We examine the key mechanisms controlling the interactions between the e-beam and C–H bond present in all organic molecules. We identify the low atomic weight of hydrogen as the principal cause of instability of organic molecules resulting in facile displacement of atomic hydrogen by the e-beam. It is demonstrated theoretically and proven experimentally[1] that exchanging all hydrogen atoms within molecules with the deuterium isotope, and therefore doubling the atomic weight of the lightest atoms in the structure, leads to a more than two-fold increase in the stability of organic molecules in the e-beam. This affects the e-beam induced chemistry of organic molecules inside carbon nanotubes.

Catalysis of chemical reactions by nanosized clusters of transition metal atoms holds the key to the long-term provision of sustainable energy. However, the atomistic pathways of chemical transformations facilitated by nanocatalysts remain largely unknown due to uncertainties associated with the highly labile metal nanoclusters changing their structure during the reaction. We explore[2] reactions of nm-sized clusters of technologically important metals in carbon nanotubes using TEM, employing the e-beam simultaneously as an imaging tool and stimulus of the reactions. The carbon nanotube serves as a ligand to which metal nanoclusters bind and as a source of carbon for transformations catalysed by the metals. Different metal nanoclusters exhibit different ability to bond with carbon and catalytic activity with key features mirroring heterogeneous catalysis.

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Efficient and Accurate *Ab Initio* Structural Predictions of CNT-Encapsulated Extreme Nanowires

Paulo V. C. Medeiros[1], Jamie M. Wynn[1], Andrij Vasylenko[2,3], Samuel Marks[2], Charlotte Slade[2],
Quentin M. Ramasse[4], Jeremy Sloan[2], David Quigley[2,5], and Andrew J. Morris[1,6]

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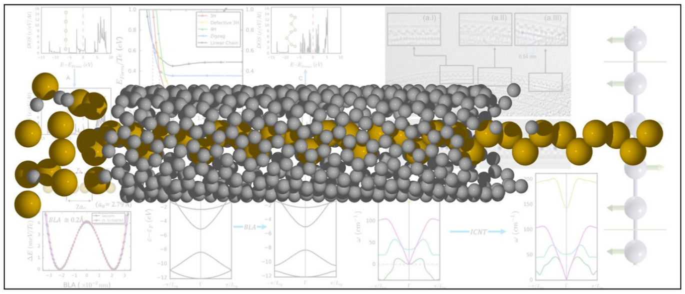
Extreme nanowires (ENs) [1] are atom-wide structures that are periodic along one single direction in space. They represent the smallest possible 1D crystals, and their reduced dimensionality often leads to material properties that (i) are highly sensitive to seemingly minor changes in their atomic structures [2], and (ii) can differ drastically from the ones exhibited by their bulk counterparts – when such bulk structures even exist [2]. A practical route to synthesising such materials is *via* encapsulation inside carbon nanotubes (CNTs) [2, 3], which offer excellent shielding from the external environment and, in many cases, interact only minimally with the encapsulated ENs except for providing a potential energy landscape that quenches otherwise unstable transverse vibrational modes [2].

In this talk, we will discuss our recent developments [2] in the high-throughput *ab initio* structural prediction of CNT-encapsulated ENs, including the introduction of implicit nanotubes (ICNTs), as well as methods to calculate their encapsulating diameter-dependent periodicity and to correct mismatch-induced unphysical strains. We apply these methods to the study of encapsulated Te [2], CsI [4] and SnSe [4] ENs, including the assessment of their structural stability through the use of ICNTs. Our methods provide a fully *ab initio* framework to efficiently predict novel EN structures with high enough accuracy to identify fine structural features such as Peierls distortions, while naturally allowing for chemical interactions between ENs and CNTs.



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[3] J. Sloan et al., Chem. Commun. **0**, 699−700 (1999).

[4] Paulo V. C. Medeiros, Charlotte Slade, Samuel Marks, Jamie M. Wynn, Andrij Vasylenko, David Quigley, Jeremy Sloan, and Andrew J. Morris, *In preparation*.

Carbon diffusion in Iron : A Kinetic Activation-Relaxation Technique Study

Normand Mousseau,
Université de Montréal, Canada

Carbon is an essential component to steel. As it diffuses through the Fe network, it also affects the global materials' properties facilitating, for example, corrosion and embrittlement. Using the kinetic Activation-Relaxation Technique (k-ART), a kinetic Monte Carlo (KMC) algorithm with on-the-fly catalogue that allows to obtain diffusion properties over large time scales taking into account long-range elastic effects coupled with an EAM forcefield, we characterize carbon motion in buk Fe, to (100), (110) and (111) surfaces and various high-angle grain boundaries (GB). Following carbon diffusion over time scales of up to one second and more, we produce a detailed picture of the evolution of the energy landscape for thse systems that show unexpected a number of results such as, for example, that contrary to general understanding, although C diffusion is necessarily faster than in the bulk and can even be slower by one to two orders of magnitude as a function of the GB. This result, and others presented in this talk, demonstrate the need for such study.

This work was done in collaboration with Oscar Retrepo, Mickaël Trochet (Université de Montréal), Charlotte Becquart (Université de Lille), Othmane Bouhali (Texas A&M University at Qatar) and Fedwa El-Mellouhi (Qatar Environment and Energy Research Institute)

Atomistic mechanisms and kinetics during phase transformations in metals

Jutta Rogal
Department of Atomistic Modelling and Simulation, Ruhr-Universität Bochum, Germany

Atomistic modelling of the dynamics of phase transformations is a particularly challenging task. If the mechanism of the phase transformation is governed by so-called rare events then the timescale of interest will reach far beyond the capabilities of regular molecular dynamics simulations. In addition to the timescale problem the simulations provide a vast amount of data in a high-dimensional space that requires the projection into a low-dimensional space and the identification of suitable reaction coordinates.

One example are the atomistic rearrangements during solid-solid phase transformations in bulk systems which involve massive structural changes including concerted multi-atom processes. The interface between two structurally different phases leads to a complex energy landscape that needs to be explored during the dynamical evolution of the interface. Here, we employ an adaptive kinetic Monte Carlo (AKMC) approach to investigate such processes at the interface between the body-centered cubic and A15 phase in molybdenum.

A second example is the initial nucleation and growth during solidification in metals. Here, we investigate the atomistic mechanisms of nucleation in nickel for various undercoolings using transition path sampling (TPS). The analysis of the path ensemble reveals a non-classical behaviour with mainly non-spherical nuclei, and shows that the nucleation initiates in regions with high orientational order that also predetermine the selection of specific polymorphs.

Semi-automatic routes to confined structure prediction in nanocarbons

Chris P EWELS[1], Dmitry V. Rybkovskiy[2,3], Jeremy RIO[1], Dogan ERBAHAR[1,4],
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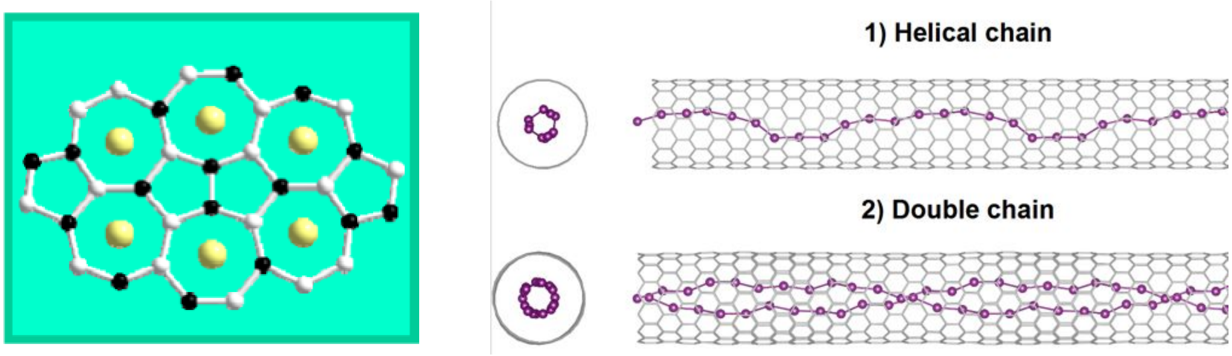
Novel phase stability depends on a number of factors: in this talk we explore two of these, namely charge transfer and local confinement. There is great interest, particularly from the theoretical modelling community, in designing new 2D nanocarbon structures. We discuss some of the proposals (such as haeckeliates, pentagraphene, …) and evaluate criteria such as energy funnels for determining whether such materials are experimentally viable[2]. Routes such as stabilization through counter-ion charging are explored.

We are also exploring crystal filling in 1D carbon nanotubes in conjunction with experimental colleagues. In this part of the talk I will discuss our latest results with new approaches to semi-automatic structure determination, notably using Iodine as an example test system[3], with the intention to revisit prior 1D crystal filling assignments. New constraint algorithms, with and without HRTEM input, appear to converge rapidly on stable confined structures.



(left) Metal borocarbide structures mimic Haeckelites[1],
(right) Simulated iodine filling in CNTs using new constrained "ab-initio" algorithms[3]

[1] Full publication list with links at www.ewels.info
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Transport in nanomaterials from first-principles

Nicola Bonini
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Understanding and modelling transport and energy dissipation phenomena in nanostructured materials is a key issue for the design of high-performance devices for nano-electronics and energy conversion technologies.

Here we present a first-principles study of transport in graphene-based materials and bulk semiconductors. Modelling these phenomena requires an accurate description of the electronic and vibrational properties of these systems, including electron-phonon and phonon-phonon interactions. For this we use density functional theory, and carrier scattering rates are then computed using perturbation theory. Electrical and thermal transport properties are calculated via the exact solution of the Boltzmann transport equation.

Our results provide a detailed characterization of the inelastic relaxation mechanisms that determine the dynamics of charge and heat carriers, of crucial importance to assist the interpretation of spectroscopic measurements. We also discuss the relevance of these findings to model and understand the transport properties of graphene and doped semiconductors.

Regulation of electronic and thermoelectric properties of SnTe and HgTe nanowires via their encapsulation within single-walled carbon nanotubes

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Cavendish Laboratory, University of Cambridge, UK

Nanostructuring offers a unique possibility for manipulation of a materials' properties by reduction of their dimensionality. Effects of nanostructuring - electronic band engineering, modulation of scattering characteristics - enable fine tuning of the materials' electrical and thermal conductivity [1-4]. Here we elucidate how by using the extreme nanostructuring, encapsulation of the nanowires within single-walled carbon nanotubes (SWCNTs) of different diameters from 7 to 14 Å, one can manipulate the emerging structure of the one-dimensional materials SnTe and HgTe and utilize nanostructuring effects for enhancement of the nanowires' electrical and thermoelectric properties. To demonstrate this we exploit Ab initio Random Structure Searching for establishing the structures of the nanowires SnTe and HgTe encapsulated within SWCNTs. Further, from ab initio calculations of electronic band structure, electron-phonon and phonon-phonon scattering, and solving Boltzmann transport equation we evaluate electrical and thermal conductivity and thermoelectric figure of merit of the resulting nanowires.

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Gaussian Approximation Potentials for Materials Research

Gabor Csanyi
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I will briefly introduce our Gaussian Approximation Potential (GAP) framework for building interatomic potentials. GAP is a model utilizing machine learning technology, in particular Gaussian process regression, using a symmetry-invariant description of the atomic environment called SOAP (Smooth overlap of atomic positions), which in turn are the rotationally invariant combinations of the spherical harmonic expansion coefficients of the neighbour density. I will show models in a series of increasingly complex materials that are trained on density functional calculations and approach the DFT potential energy surface systematically.

An overview of the CONQUEST code capabilities: Molecular dynamics and applications

Lionel A. Truflandier, Teruo Hirakawa, Ayako Nakata , Jianbo Lin, Tsuyoshi Miyazaki , David R. Bowler

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Sustained by the fast increase of investments in high performance computing (HPC) technologies, quantum mechanics accuracy for many-atoms systems, as achieved in mean-field electronic structure method(s), is about to reach the mesoscale within this century. This implies the development of advanced parallelized program with appropriate theoretical frameworks and numerical algorithms. Whereas standard approaches for solving electronic structure present (at least) a computer effort scaling with the cube of the number of electrons, solutions to get across this cubic wall are now well established for ground-state properties, and allow to reach *asymptotically* the linear-scaling regime[1]. In this talk, the formalism and the main technical points related to the ground-state search as implemented in the linear-scaling DFT code CONQUEST[2] will be briefly explained. The capabilities of the code will be reviewed with a special emphasize on the recent (linear scaling) molecular dynamics implementation[3] and the possibility of computing free energy profiles using the blue moon ensemble. Examples for molecular reactivity in liquid water will be presented. Within the field of low-dimensional materials, I will sum-up the recent application of CONQUEST to investigate the structural and electronic properties of Si/Ge core-shell nanowires. This work is currently performed at NIMS by the Japanese team.

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Poster abstracts

Predicting the structure of germanium telluride nanowires encapsulated inside carbon nanotubes from first principles

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The quasi-1D structures formed by the insertion of materials into carbon nanotubes can differ dramatically from bulk phases in their structures and properties. Many of these encapsulated nanowire (ENW) structures have considerable technological potential, in areas such as phase-change memory and gas sensing. However, the structures of ENWs can also bear little resemblance to their bulk forms. We have therefore adapted the ab initio random structure search (AIRSS) method for the prediction of the structures of nanowires encapsulated inside carbon nanotubes. The AIRSS method has previously proven itself as a powerful and effective tool in the prediction of both bulk materials [1] and defect complexes [2]. Using AIRSS, we have predicted the structure formed by germanium telluride ENWs as a function of the radius of the encapsulating nanotube. Germanium telluride is a well-known phase change material, so the extent to which its behaviour changes when strongly confined to one dimension is of considerable interest. We use simulated TEM imagery to show that our results are consistent with experimental evidence [3].

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Ab Initio Study of Ag_2Se Extreme Nanowires

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As the relentless downsizing of silicon-based devices drives current silicon-based technology to its physical limit [1], much focus has been given to the research of different classes of materials to allow miniaturisation to continue whilst maintaining efficiency demands. One-dimensional ``extreme” nanowires (ENWs) encapsulated within carbon nanotubes (CNTs) are promising candidates for this task. These materials are structurally stable, and exhibit tunable electronic and phase-changing properties [2]. Thus they are also promising candidates in phase-change memory devices.

We employ *ab initio* methods for the discovery of CNT-encapsulated ENWs. Our structural searches are based on *Ab Initio* Random Structure Searching (AIRSS) [3], and to complement this we also perform composition ``swaps” based on previously predicted 1D structures from our group’s database [4]. Our method has been previously validated with experiment[2].

In this work we investigate the encapsulation of silver selenide (Ag_2Se) nanowires in CNTs. Our calculations indicate that a metal-insulator transition arises when different geometries of 1D Ag_2Se crystals are encapsulated inside CNTs.

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AR-TEM and STEM Studies of Encapsulated SnSe in Narrow to Medium Diameter SWCNTs

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Encapsulated SnSe in medium to narrow single wall carbon nanotubes (SWCNTs) has been imaged and analysed using Atomic Resolution Transmission Electron Microscopy (AR-TEM) & Scanning Transmission Electron Microscopy (STEM) at 80kV. The discovery of this new form of confined SnSe offers another dimension in the investigation of this compound as a nano-Confined Phase Change Material (nC-PCM)1 as opposed to other types of crystalline fillings.2-4 SWCNTs are thermally stable up to temperatures of 1400K, which makes them particularly suitable for investigations into the properties and structural transformation of nC-PCMs.5 The van der Waals forces at the internal surfaces of the SWCNTs act to constrain the encapsulated material to confined surfaces with cross-sections down to 1nm2. This results in structures that can often vary wildly from that of the bulk form of the material. Bulk SnSe was Vapour Phase Transported (VPT) and deposited inside SWCNTs, with diameters in the range (0.7 – 1.7) nm, via the sublimation method. This method utilises a silica quartz double ampoule sealed under vacuum, with the filling material and the SWCNTs separated by a neck in the ampoule. The threshold for knock-on electron beam damage is 86keV, which is above the energies used for these studies. Although SWCNTs are only selectively sensitive to electron beam irradiation below the energy threshold, the SnSe has been observed to dissociate under high dose conditions. The previously reported 2x2 cubic structure of encapsulated SnSe in narrow SWCNTs has been observed (Fig. 1), as well as a new, currently undefined, structure. Presented here are models and images of these structures. Phase contrast (TEM) studies have also shown the formation of more bulk-like rocksalt SnSe structures in the wider SWCNTs (Fig.2). This is as expected from previous findings and theory, which have also reported the existence of a distorted orthorhombic layered nC-SnSe structure. In addition, whilst the theory is clear in regards to the reported cubic SnSe, the connection between experiment and theory has yet to be confirmed for the new structure. Reported here HRTEM Filter script developed by D. R. G. Mitchell.6 using the is evidence of quantitative filling of SWCNTs with SnSe, alongside some examples of in situ and ex situ phase change behaviour and associated data. These results also form the basis for studies into further nC-PCMs, such as GeTe and PbTe. In particular, investigations into the variation of the structure of the encapsulated material as a function of the diameter of the NT, and the effect that this has on in-situ phase changes. STEM imaging was enhanced by the use of a standard Average Background Subtraction Filter (ABSF), in order to uniformly reduce the noise in these images without adding spurious information,

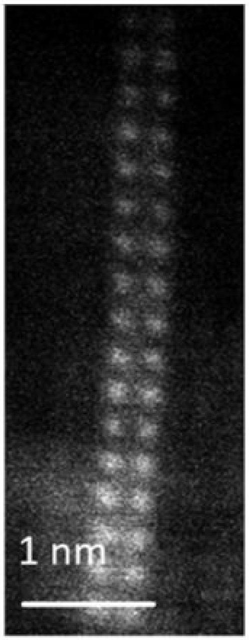

Fig. 1
STEM image of the 2x2 cubic structure of nC-PCM SnSe in a SWCNT. The structure was imaged at 80kV. The image has been Wiener filtered to reduce noise.

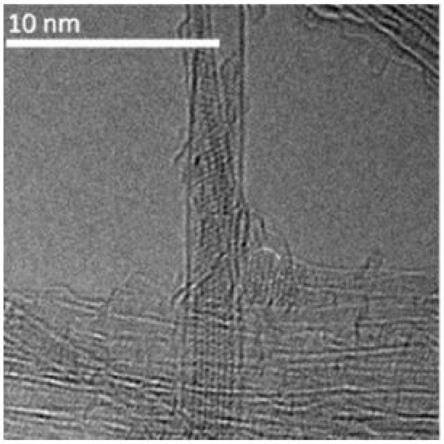

Fig. 2
AR-TEM image of nC-SnSe in a wide diameter and (superimposed) narrower diameter SWCNT. The thicker SWCNT encapsulates a bulk-like rocksalt form of SnSe, with the thinner, overlaying SWCNT confining a cubic structure. The image was obtained at 80kV.

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A machine-learned interatomic potential for Ge-Sb-Te phase-change materials

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We present a machine-learned interatomic potential for Ge-Sb-Te phase-change materials . The fit of a high-dimensional potential energy surface for more than two atomic species is a challenge for most approaches. Our potential was generated within the Gaussian Approximation Potential (GAP) framework from a database of Density Functional Theory (DFT) calculations. The potential is transferable and is able to provide an accurate description of the local structure of several different compositions and phases over a wide range of thermodynamic parameters. These include the liquid and amorphous phases of the canonical Ge2Sb2Te5 composition and most of the known stable and metastable crystalline phases in the ternary system. The potential opens the door to high-throughput and large-scale computational investigations of the Ge-Sb-Te phase diagram and can be a significant tool in the rational design of new materials for phase-change applications.

Ab Initio Structure Prediction of Carbon-Nanotube Encapsulated Nanowires: Coping with Incommensurability

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The encapsulation of materials within single-walled carbon nanotubes (CNT) affects their behaviour and structure dramatically relative to the bulk. In many cases, such encapsulated nanowires (ENWs) even exhibit long-range ordered one-dimensional phases that do not, *or cannot,* exist in three dimensions. Moreover, many are of considerable technological interest, especially in the case of the so-called *nano phase-change materials*, whose properties make them potential candidates for next-generation information storage technologies.

The computational problems faced in ENW structure prediction are different from those of 3-dimensional bulk structures. Since the encapsulated wires will have a different periodicity to the encapsulating CNT, one must know the periodicity of the predicted wire *before* one may accurately predict its existence in a CNT: which begs the question. Our method is a two-step process which predicts the structure of a wire in an implicit (non-periodic) nanotube, before fully relaxing within an explicit tube. This not only allows us to perform the first truly *ab initio* quantitative structure prediction calculations for ENWs, but from the implicit tube calculation, obtain a bulk modulus correction to obtain a more accurate formation energy from the explicit tube calculation.

To illustrate the capabilities of the method, we present results from AIRSS searches on encapsulated nanowires of silver chloride and many other metal halides. I present a “trick” inspired by perturbation theory to obtain the *ab initio* Raman spectrum of encapsulated nanowires that would otherwise be computationally intractable to perform.

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