

Report of
AIMR/UCL Materials Workshop
November 21-22, 2013

PROGRAMME

Thursday, November 21 Morning Events

9.15 – Meet with Prof Shluger at the Royal National Hotel, London

9.30 – 10.15 – Tour of LCN

10.15 – 11.45 – Individual meetings with LCN researchers

11.45 – 12.00 – Walk to the Senate House

12.00 – 13.00 – Lunch at the Chancellor's Hall, 1st Floor, Senate House

13.00 – 14.00 – General Meeting and presentations at the Chancellor's Hall, 1st Floor, Senate House

14.00 – 14.15 – Walk back to the Physics Building

Thursday, November 21 Plenary Talks: room E3/E7, Physics

Chair: Prof Alexander Shluger

14.15 – 15.00 **Richard Catlow** “Predictive Modelling of Catalytic and Energy Materials”

15.00 – 15.45 **Kazue Kurihara**: “Surface forces measurement for characterising solid-liquid interfaces and confined liquids”

15.45 – 16.15 **Coffee Break**

16.15 – 17.00 **Tadafumi Adschiri**: “Supercritical route for nanoparticles”

17.00 – 17.45 **Valery Smyshlyaev**: “Mathematics related to Materials Science (at UCL and beyond)”

Friday, November 22 Oral Presentations:

Wilkins Garden Room, South Cloisters

Chair: Prof. Masaru Tsukada

9.00 – 9.30 **Steve Bramwell**: “Monopoles and Magnetism in Spin Ice”

9.30 – 10.00 **Seigo Souma**: “Spin-helical Dirac-cone surface states of 3D topological materials”

10.00 – 10.30 **Yaroslav Kurylev**: “Mathematical theory of metamaterials and cloaking”

10.30 – 11.00 **Coffee Break**

11.00 – 11.30 **Geoff Thornton**: “Support-morphology induced modification of adsorbate bonding to nanoparticles”

11.30 – 12.00 **Taro Hitosugi**: “STM/STS studies of perovskite oxide heterostructures”

12.00 – 12.30 **Ian Ford**: “Microscopic measures of dissipation”

12.30 – 13.30 **Lunch**

Chair: Prof. Geoff Thornton

13.30 – 14.00 **Shigemi Mizukami**: “Mn-based metallic magnets as spintronics materials”

14.00 – 14.30 **Peter Sushko**: “Optical transitions in LaCrO_3 , $\text{LaFe}_{1-x}\text{Cr}_x\text{O}_3$ and $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ studied using an embedded cluster method”

14.30 – 15.00 **Zhongchang Wang**: “Atom-by-Atom Structural and Electronic Analysis of

Interfaces and Grain Boundaries in Electronic Materials”

15.00 – 15.30 **Coffee Break**

15.30 – 16.00 **Akihiko Hirata:** “Local structure analysis of metallic glasses”

16.00 – 16.30 **Neal Skipper:** “Dissolution of Carbon Nanotubes and Graphene”

16.30 – 17.00 **Kazuto Akagi:** “Toward a theoretical design of aqua-solid interfaces”

17.30 Posters with buffet dinner and wine reception in South Cloisters

1. **Yasmine Al-Hamdani:** “Tuning the adsorption and dissociation of water over chemically doped benzene and graphene”
2. **Kazuto Akagi:** “Toward a theoretical design of aqua-solid interfaces”
3. **Nobuaki Aoki:** “Re-Dispersion of Flocculated Nanoparticles Using Back Pressure Valve”
4. **Naoki Asao:** “Metallic glass nanoparticles as effective catalysts for selective molecular transformations”
5. **David Santos Carballal:** “Theoretical study of the equilibrium inversion degree and the electronic structure of FeM_2X_4 spinels (M = Cr, Mn, Fe, Co, Ni; X= O, S)”
6. **Bo Chen:** “Three-Dimensional Structure Investigation and Analysis of Barrier Anticorrosive Marine Coatings by Ptychographic X-ray Tomography”
7. **Clair Chew:** “Thin films of transparent conducting doped SnO_2 and gold nanoparticles”
8. **Robert Darkins:** “Stress in titania nanoparticles: An atomistic study”
9. **Al-Motasem El-Sayed:** “Intrinsic and extrinsic electron trapping in silicon dioxide”
10. **David Gao:** “Theoretical Treatment of Organic Molecules on Bulk Insulators: Growth and Nucleation”
11. **Steven Hepplestone:** “Defects at metal/semiconductor interfaces”
12. **Daisuke Hojo:** “Self-Assembly and Reassembly phenomena of Organic-Inorganic Hybrid Nanocrystals in Highly Ordered Nanocrystalline Multi/Monolayer”
13. **Rastko Joksimovic:** “Surface forces between mica surfaces confining ceria nanoparticles dispersions and frictional properties”
14. **Navaratnarajah Kuganathan:** “Ru-loaded nanoporous oxide $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ ”
15. **Kazue Kurihara:** “Interfacial Water Studied by Surface Forces Measurement”
16. **Thomas Mellan:** “DFT calculations elucidate cathode material for lithium-air battery of the future”
17. **Shigemi Mizukami:** “Mn-based metallic magnets as spintronics materials”
18. **Daniel T. Payne:** “Two-photon photoemission from the $\text{TiO}_2(110)$ surface”
19. **Steven Schofield:** “Two-dimensional Atomic-scale Quantum Dots on $\text{Si}(001):\text{H}$ ”
20. **Georg Schusteritsch:** “First-principles-based structure prediction of interfaces in strontium titanate”
21. **Gabriele Tocci:** “Structure and dynamics of water on graphene and boron nitride from ab-initio molecular dynamics”
22. **Zhongchang Wang:** “Atom-by-Atom Analysis of Functional Ceramics Interfaces and Grain Boundaries”
23. **Chi Ming Yim (Oliver):** “Strain and substrate effects on nanoparticle adsorption”
24. **Kazue Kurihara, Motohiro Kasuya, and Masashi Mizukami:** “Interfacial Water Studied by Surface Forces Measurement”

***** Individual meetings with LCN researchers*****

Prof. Kotani, Prof. Tsukada – Prof Valery P. Smyshlyaev, Applied Mathematics

Prof Kurihara – Dr Bart Hoogenboom

Prof Adschiri – Prof Neal Skipper Dr Souma – Dr Chris Howard

and Dr Mark Ellerby

Dr Hitosugi – Dr Steven Schofield

Dr Mizukami - Dr Hidekazu Kurebayashi

Dr Wang – Dr Peter Sushko

Dr Hirata – Prof. Chris Pickard and Dr Georg Schusteritsch

Prof. Akagi – Prof Angelos Michaelides

*****Summary of presentation *****

November 21, Plenary Talks

Predictive Modelling of Catalytic and Energy Materials

Richard Catlow (Department of Chemistry, UCL)

Computer modelling techniques are now used very widely in chemical, physical and biological sciences, especially in understanding the behaviour of complex systems at the molecular level [1].

This lecture will highlight their application to materials chemistry where the impact has been substantial in recent years. Special emphasis will be given to three important and topical areas:

- Crystal structure prediction
- Guiding and understanding synthesis
- Modelling nucleation and growth
- Understanding reactivity at the molecular level

Applications to oxides, microporous silicates sulphides and molecular crystal will be discussed.

Future prospects and developments in the field will be considered.

[1] S. M. Woodley and C. R. A. Catlow, Nature Materials, 7, 937 (2008)

Surface forces measurement for characterising solid-liquid interfaces and confined liquids

Kazue Kurihara AIMR, Tohoku University

Surface forces measurement determines the force-distance profiles by using a spring balance, enabling one to study the origins of interactions and interfacial properties such as the surface potential and the adsorption at the solid-liquid interfaces. Advantages of this measurement are large surface area studied and high resolution in distance. Taking advantage of large surface area, various shear devices were developed for studying confined liquids. Among them, our original contribution is the development of Resonance Shear Measurement (RSM) for Nano-rheology and Nano-tribology of Confined Liquids. There is a drawback of the conventional surface forces apparatus (SFA). This is applicable only for transparent samples. We have developed the Twin-path SFA for opaque samples including metal.

This paper describes the principles of the measurement techniques we developed and their applications: (1) RSM for characterizing confined liquids such as ionic liquids and water; (2) Twin-path SFA applied for electrochemical SFA and spectroscopic SFA.

Supercritical route for nanoparticles

Tadafumi Adschiri (AIMR, Tohoku University)

Variety of composite materials has been developed so far, but in many cases trade-off of the functions are of important issues: fabrication becomes difficult due to the significant increase of viscosity, and transparency of the polymer is sacrificed. To overcome the trade off, control of the nano-interface is the key, but nanoparticles are easily aggregated in polymer matrix because of the higher surface energy of NPs, and thus it has been considered a difficult task. Organic functionalization of inorganic nanoparticles is required to have higher affinity between NPs and polymers. The organic modification, NPs should be dispersed in an organic solvent with high concentration, which is difficult. For fabricating multi-functional materials, we proposed a new method to synthesize organic modified nanoparticles (NPs) in supercritical water (Fig.1). Since the organic molecules and metal salt aqueous solutions are



Figure 1 Flow reactor apparatus for supercritical hydrothermal synthesis (ITEC Co., LTD, Japan).

miscible under the supercritical state, and water molecule works as an acid/base catalyst for the reactions, organic-inorganic conjugate nanoparticles can be synthesized under the condition (Fig.2). The hybrid NPs show high affinity with the organic solvent or the polymer matrix (Fig.3). This method enables self-assembly of NPs through the organic linkers to form crystal of NPs as shown in Fig.4. This controllable functionalization of NPs leads to fabricate the organic inorganic hybrid nanomaterials with the compatible (trade-off) functions. Hybrid polymer with high loading of BN achieved extremely high heat transfer coefficient (40 W/m/K) in vertical

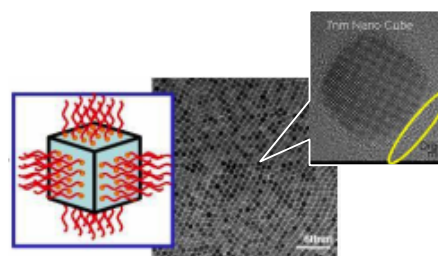


Figure 2. Organic-inorganic hybrid nanoparticles



Figure 3. Dispersion of decanoic-acid-capped ceria NPs dispersed in cyclohexane

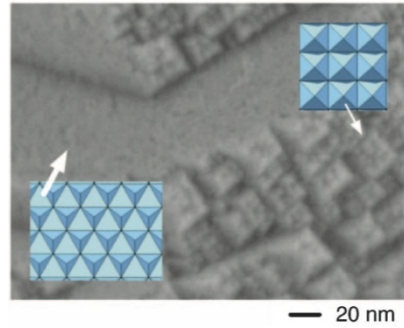


Figure 4 Nanoassembled 3D structure comprising primary octahedral CeO_2 nanocrystal

direction to the sheet with maintaining the flexibility (Fig.5). In case of Al_2O_3 loaded resin, due to the organic surface modification of NPs, more than 80 vol % of high loading could be achieved with keeping the fluidity (low viscosity), which enables transferring this soft-seramics to the package of semiconductor device without the damage of electric circuit (Fig.5).

Now, we are challenging to establish a new science for the highly concentrated nano particulate system (prediction of phase equilibrium/fluid dynamics) through the collaboration between materials science and mathematics in WPI-AIMR.

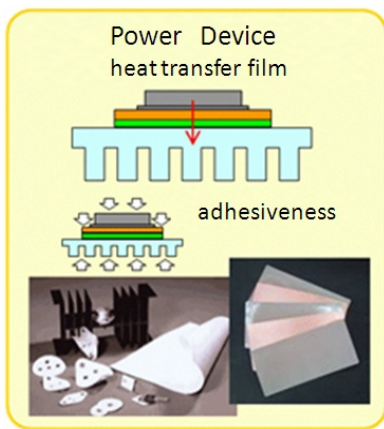


Fig. 5 Flexible heat transfer sheet. Thermal conductivity: 40W/m/K

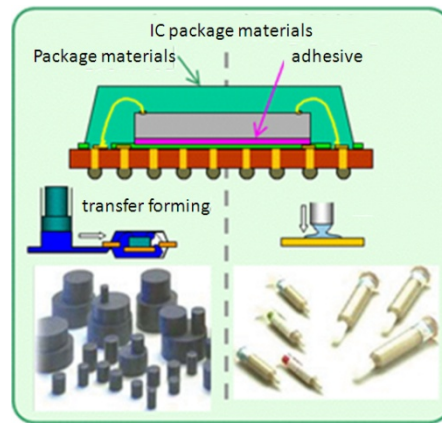


Fig. 6 High heat transfer- low viscosity package materials

Mathematics related to Materials Science (at UCL and beyond)

Valery Smyshlyaev (Applied Mathematics group, UCL)

First, a brief overview of broad international activities and of interdisciplinary communities concerned with mathematical aspects of Materials Science over about the last two decades was given. One broad direction relates to multiscale mathematical modelling, where deriving refined upscaled models remains a great challenge for mathematics. Some examples were given from recent and current activities where the mathematical approach not only subjects ideas based on physical intuition to scrutiny of rigorous mathematical analysis and hence assists in assessing the accuracy of the physical models (and of their possible limitations), but also leads to rigorously deriving novel mathematical models displaying new physical effects as well as designing new efficient numerical schemes. This prompts in turn development of an interesting mathematics. Some specific recent and current activities at UCL Mathematics resonating with materials were also briefly reviewed and mentioned. These included two-scale analysis of microresonances and of their relation to "negative" materials, band-gaps in photonic crystal fibres near a critical dispersion line, rotational elasticity and analogies with neutrino models, fluid-structure interactions, biological materials (e.g. biofilms), and finally a mathematical theory of cloaking metamaterials (as discussed in more detail in the talk of Y. Kurylev).

November 22, Oral and Poster presentations

Monopoles and Magnetricity in Spin Ice

Steven T. Bramwell (Department of Physics&Astronomy and LCN, UCL)

The analogy between spin configurations in spin ice materials like $\text{Ho}_2\text{Ti}_2\text{O}_7$ and proton configurations in water ice, H_2O , has been appreciated for many years (see Ref. [1] for a review). However it is only in the last few years that this equivalence has been extended into the realm of electrodynamics [2,3]. In this talk I shall describe our recent experimental work that identifies emergent magnetic charges ("monopoles"), transient magnetic currents ("magnetricity") and the universal properties expected of an ideal magnetic Coulomb gas (magnetic electrolyte - "magnetolyte"). These universal properties include the Onsager-Wien effect, "corresponding states" behaviour, Debye-Huckel screening and Bjerrum pairing [4-8]. I will describe experimental results for both traditional spin ice materials ($\text{Ho}_2\text{Ti}_2\text{O}_7$, $\text{Dy}_2\text{Ti}_2\text{O}_7$) and a recently discovered system ($\text{Dy}_2\text{Ge}_2\text{O}_7$). Finally I shall report new experimental results that show how hitherto unexplored regimes of spin ice behaviour may be accessed in the laboratory.

[1] Bramwell and Gingras, *Science*, 294 1495 (2001)

[2] Castelnovo et al., *Nature* 451 42 (2008)

[3] Ryzhkin, *JETP* 101 481 (2005);

[4] Bramwell et al. *Nature* 461 956 (2009)

[5] Fennell et al., & Bramwell *Science* 326 415 (2009)

[6] Giblin, Bramwell et al., *Nature Physics* 7 252 (2011)

[7] Zhou, Bramwell et al., *Nat Comm.* 478, 1483 (2011)

[8] Bovo et al., *Nat. Commun.* 4, 1535 (2013)

Spin-helical Dirac-cone surface state of 3D topological materials

S. Souma (AIMR, Tohoku University)

Three-dimensional topological insulators (TIs) exhibit a novel quantum state with metallic topological surface state (SS) which disperses across the bulk band gap generated by a strong spin-orbit coupling. In this talk, we show the systematic spin- and angle-resolved photoemission [1] study on several topological insulators Bi₂Se₃, Bi₂Te₃, TlBiSe₂, and PbBi₂Te₄, all which exhibits a single Dirac-cone surface state but with different hexagonal warping strength [2-6]. Divergent research activities on topological aspect of matter have lead to the prediction for various different kinds of material class such as topological crystalline insulator [7], topological superconductor [8], and so on. We experimentally found that the known band-inverted semiconductor SnTe exhibits double Dirac-cone surface state protected by mirror symmetry, indicating this material indeed belongs to the predicted topological crystalline insulator [9].

[1] S. Souma *et al.*, Rev. Sci. Instrum. **81**, 095101 (2010). [2] T. Sato *et al.*, Phys. Rev. Lett. **105**, 136802 (2010). [3] S. Souma *et al.*, Phys. Rev. Lett. **106**, 216803 (2011). [4] S. Souma *et al.*, Phys. Rev. Lett. **109**, 186804 (2012). [5] T. Arakane *et al.*, Nature Commun. **3**, 636 (2012). [6] S. Souma *et al.*, Phys. Rev. Lett. **108**, 116801 (2012). [7] Liang Fu, Phys. Rev. Lett. **106**, 106802 (2011). [8] L. Fu and C. L. Kane, Phys. Rev. Lett. **100**, 096407 (2008). [9] Y. Tanaka *et al.*, Nature Phys. **8**, 800 (2012).

Mathematical Theory of Metamaterials and Cloaking

Yaroslav Kurylev (Applied Mathematics group, UCL)

In this talk we consider several mathematical blueprints for physical designs based on the ideas of the transformation optics. These ideas go back to the paper by Greenleaf-Lassas-Uhlmann (2002) which suggested a construction of a counterexample for the uniqueness in a conductivity inverse boundary value problem. In 2006, Pendry-Schurig-Smith suggested an electromagnetic device to cloak an interior of a ball from an external observer. It has turned out that, independently, they used the same construction, albeit in the context of electromagnetism, as GLU. Later, together with Greenleaf, Lassas and Uhlmann, we have developed these ideas much further. In particular we introduced a notion of a double cloak which allows to cloak active sources inside the cloaked ball. We suggested and analysed different methods to approximate an ideal cloaking material which is highly singular with regular cloaking metamaterials including some isotropic ones. The study of these approximations has led us to analyse cloaking effects in quantum physics, in particular, almost trapped states and Schrodinger-hat phenomena. In addition, we showed that dealing with an approximate cloaking metamaterial, it is possible to build up an almost ideal sensor, i.e. the one that can register the external signals but is effectively not visible by an external observer. It should be noted that in the case of an ideal cloak, an observer inside the cloaked region is also unable to "see" what is going on outside and the phenomena of an invisible sensor uses a delicate balance of a resonance inside the cloak and the incoming wave. At last, we have shown how to use a cloaking metamaterial in order to "change the topology" of the space suggesting the so-called electromagnetic wormhole.

Support-morphology induced modification of adsorbate bonding to nanoparticles

Geoff Thornton (Chemistry Department & LCN, UCL)

The effect of the surface morphology of an oxide support on metal nanoparticle adsorption has been investigated using scanning tunneling microscopy (STM) and X-ray photoelectron microscopy

(XPEEM) near-edge X-ray absorption fine structure (NEXAFS). Pd nanoparticles grown on $\text{TiO}_2(110)$ were used as the model system, with their reactivity probed via the adsorption of CO. NEXAFS from a single nanoparticle indicate that the molecules are bonded with their molecular axis more or less along the nanoparticle normal. STM shows that the (111) top facets of the nanocrystals are curved, due to the underlying substrate step-edges. At a CO coverage of half monolayer, two types of CO overlayers form in addition to those normally observed on the native Pd(111) surface. DFT calculations suggest that the formation of these additional CO overlayers arises from the strain that arises on the top facet due to the presence of the substrate step-edges.

STM/STS studies of perovskite oxide heterostructures

Taro Hitosugi (AIMR, Tohoku University).

The scanning tunneling microscopy/spectroscopy of $\text{LaAlO}_3/\text{SrTiO}_3$ system revealed that a TiO_x layer of the SrTiO_3 substrate transferred to the topmost surface across the LaAlO_3 layer. This results indicate that we have successfully synthesized a new oxide nano material, a TiO_x layer that can be viewed as a graphene-like one unit-cell TiO_x sheet. These findings on atomic-scale nature of perovskite growth lead to preparation of higher-quality thin films and interfaces exhibiting novel electronic and magnetic properties.

Microscopic measures of dissipation

Ian Ford (Department of Physics&Astronomy, UCL)

The second law in classical thermodynamics provides a yes/no indicator of the natural direction of evolution of a macroscopic physical system in contact with an environment, but in nanosystems the law becomes only a statistical indicator. Because of fluctuations, there is a chance that the system or experimental tools will not respond as desired, and we can lose control of thermodynamic processing. However, there are measures of dissipation, or irreversibility, at such scales that allow us to quantify the loss of directionality and hence to design process protocols that optimise control. I shall describe the stochastic entropy production, and its partition into three components, to illustrate how they provide an insight into thermodynamic behaviour at the nanoscale.

Mn-based metallic magnets as spintronics materials

Shigemi Mizukami (AIMR, Tohoku University)

Spin-transfer-torque magnetoresistive random access memory (STT-MRAM) is one of the candidates for a high capacity and fast nonvolatile memory. Exploration of key materials is one of the challenging issues for realization of STT-MRAM. We demonstrated that an interesting candidate of such materials is a Mn-Ga alloy. We also discussed epitaxial films of C38 structured MnAlGe ternary alloys and Mn_3Ge in this talk.

Character of the optical transitions in strained LaCrO_3 , $\text{LaFe}_{1-x}\text{Cr}_x\text{O}_3$ and $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solutions studied using an embedded cluster method

Peter V. Sushko (Department of Physics&Astronomy, UCL)

We explore how the optical properties of complex oxides can be modified in order to provide greater efficiency in capturing solar energy. To this end, we investigate theoretically optical absorption in strained epitaxial LaCrO_3 films deposited on various substrates [1], as well as in $\text{LaFeO}_3\text{-LaCrO}_3$ and $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ solid solutions [2]. We use an embedded cluster method, together with an accurate electrostatic embedding potential [3] and hybrid density functionals, which provide a reliable description of band gaps in insulators and wide band gap semiconductors. The effects of the thermal disorder are taken into account with the help of *ab initio* molecular

dynamics simulations.

Our results provide valuable insight into the origin of the optical absorption spectra and allow for the assignment of their individual features. In particular, we show that the optical absorption spectrum of LaCrO_3 includes distinct contributions associated with two types of the intra-Cr $t_{2g} \rightarrow e_g$ (2.7, 3.6 eV), inter-Cr $t_{2g} \rightarrow t_{2g}$ (4.4 eV), and O $2p \rightarrow \text{Cr } 3d$ transitions. The onset of the O $2p \rightarrow \text{Cr } 3d$ charge transfer gap is between 4.6 and 5.0 eV, in contrast to earlier reports which put it at ~ 3.4 eV. The magnitude of the charge-transfer gap depends on the lattice strain and can be varied by ~ 0.2 eV by judicious choice of the substrate. On the contrary, the energies of the Cr $d-d$ transitions are strain insensitive. In the case of the $\text{LaFe}_{1-x}\text{Cr}_x\text{O}_3$ and $(\text{Fe}_x\text{Cr}_{1-x})_2\text{O}_3$ solid solutions, an additional absorption band with an onset of ~ 1.7 eV appears and is attributed to Cr $t_{2g} \rightarrow \text{Fe } t_{2g}$ transitions. The dependence of the optical absorption spectra on Fe:Cr ratio is determined by the relative positions of the occupied and unoccupied metal d states and the spin structures of the constituent materials. The optical absorption spectra reconstructed from individual transitions are in good agreement with the experimental data in all three systems.

- [1] P. V. Sushko, L. Qiao, M. Bowden, T. Varga, G. J. Exarhos, F. K. Urban III, D. Barton, S. A. Chambers, Phys. Rev. Lett. 110, 077401 (2013).
- [2] Y. Wang, K. Lopata, S. A. Chambers, N. Govind, P. V. Sushko, J. Phys. Chem. C (published online).
- [3] I. V. Abarenkov, Phys. Rev. B 76, 165127 (2007). P. V. Sushko, I. V. Abarenkov, J. Chem. Theory Comput. 6, 1323 (2010).

Atom-by-Atom Structural and Electronic Analysis of Interfaces and Grain boundaries in Electronic Materials

Zhongchang Wang (AIMR, Tohoku University)

In the talk, I tried to convince audience that the combined studies of the scanning transmission electronic microscopy and first-principles calculations can provide insight into complex atomic structure and electronic properties of functional interfaces and grain boundaries, which could be applicable to many other functional systems with interface problems. I listed two cases: (1) the insulator-to-metal transition driven by an insulating layer in Ruddlesden-Popper phase, and (2) direct atomic-resolution imaging of ordered defect superstructure at individual grain boundaries. In the first case, I first show direct atomic-resolution imaging and spectroscopy of the Ruddlesden-Popper phase especially for the fault region and then explain the unexpected transition from insulating ground state to metallicity as the stacking layer of SrTiO_3 in the superlattice comprising periodically n layers of SrTiO_3 and one layer of La-doped SrO as the n goes beyond four. In the second case, I demonstrated in detail the determination of a whole new class of defect complex at GB, which forms an ordered defect superstructure comprised of Ca and Ti impurities, Mg vacancies, Ca interstitials and Ca vacancies. The questions from the audience are mainly on the origin of the impurity segregation into the GB and I explained it to them.

Local structure analysis of metallic glasses

Akihiko Hirata (AIMR, Tohoku University).

Local atomic configuration of metallic glasses is one of the long-standing problems in materials science. So far, the local atomic configurations have been determined experimentally using average structural information from large volumes using conventional diffraction and spectroscopic methods. Three-dimensional atomic positions have been achieved only by using simulation methods such as reverse Monte Carlo and molecular dynamics (MD). Therefore direct experimental evidence of local atomic order in metallic glasses is much needed. For this purpose we have developed

Angstrom-sized beam electron diffraction (ABED) technique using an aberration-corrected scanning transmission electron microscope. The obtained results were compared with the ABED simulation from the structural model calculated using an *ab-initio* MD method.

Using the novel ABED technique, we have investigated distortion manner of atomic clusters in metallic glasses by detecting diffraction from a single atomic cluster. It is well known that an icosahedron has been considered to be a representative local environment in glass and liquid states after Frank's proposal in 1952. We are now able to directly access to the single icosahedron and evaluate it experimentally. Also we employed *ab-initio* energy calculation and homology analysis for each atomic cluster as complementary computational methods. As a result, all the icosahedra we observed were distorted and the distortion is not simply from atomic size difference. The computational homology analysis indicates that all the atomic clusters are different from the perfect icosahedron and considerably distorted in a similar way. The interconnecting-network of such distorted atomic clusters should give rise to the long-range disorder in metallic glasses.

Dissolution of Carbon Nanotubes and Graphene

Neal Skipper (Department of Physics and Astronomy, UCL)

Nanostructured forms of carbon such as the fullerenes, nanotubes and graphene are relatively insoluble in common organic and aqueous solvents. However, these materials can be reversibly reduced by the solvated electrons formed in metal-ammonia solutions [1], and the resulting nanocarbon salts (fulleride, nanotubide and graphenide) are then soluble in common aprotic solvents such as THF, DMF and NMP [2-4]. These solutions have great practical potential as a means to purify and process nanotubes and graphene in particular. Neutron scattering in conjunction with isotope labelling has proven to be a very powerful method for understanding the structure of both the host metal-ammonia solutions and also the dissolved nanocarbons. We will discuss the methodology and analysis, including the use of small angle neutron scattering, necessary to study these complex fluids. In the case of single walled nanotubes, in situ small-angle neutron scattering demonstrates the presence of dissolved, unbundled nanotubides in solution, at concentrations reaching at least 2 mg/mL. Our ability to isolate individual nanotubes is confirmed by atomic force microscopy. In the case of graphenes our experiments show that >95 vol % of the solute is present as single-layer graphenide sheets. These charged sheets are flat over a length scale of >150 Å in solution and are strongly solvated by a shell of solvent molecules. Atomic force microscopy on drop-coated thin films corroborated the presence of monolayer graphene sheets. Our dissolution method thus offers a significant increase in the monodispersity achievable in graphene solutions.

[1] H. Thompson, J. C. Wasse, N. T. Skipper, S. Hayama, D. T. Bowron, A. K. Soper, Structural Studies of Ammonia and Metallic Lithium-Ammonia Solutions. *J. Am. Chem. Soc.*, 2003, 125, 2572–2581.

[2] C. A. Howard, H. Thompson, J. C. Wasse and N. T. Skipper, Formation of Giant Solvation Shells around Fulleride Anions in Liquid Ammonia. *J. Am. Chem. Soc.*, 2004, 126, 13228–13229.

[3] S. Fogden, C. A. Howard, R. K. Heenan, N. T. Skipper, M. S. P. Shaffer, Scalable Method for the Reductive Dissolution, Purification, and Separation of Single-Walled Carbon Nanotubes. *ACS Nano*, 2012, 6, 54–62.

[4] E. M. Milner, N. T. Skipper, C. A. Howard, M. S. P. Shaffer, D. J. Buckley, K. A. Rahnejat, P. L. Cullen, R. K. Heenan, P. Lindner, and R. Schweins, Structure and Morphology of Charged Graphene Platelets in Solution by Small-Angle Neutron Scattering. *J. Am. Chem. Soc.*, 2012, 134, 8302–8305.

Toward a theoretical design of aqua-solid interfaces

Kazuto Akagi (AIMR, Tohoku University):

In this talk, origin of the electric double layer structure in NaCl/Al(111) and NaCl/Au(111) systems is shown based on first-principles molecular dynamics calculations in order to see how the picture of aqua-metal interface widely varies reflecting the character of components. In the latter half, a universal concept in aqueous systems, which shows a certain type of hydrogen-bond network structures play a role of effective repulsive potential to hydrogen ions, is introduced.

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Surface forces between mica surfaces confining ceria nanoparticle dispersions and frictional properties (poster presentation)

Rastko Joksimovic (AIMR, Tohoku University)

Contributing authors: M. Mizukami, K. Kurihara (Kurihara lab); D. Hojo, T. Adshiri (Adshiri lab)

The poster presents the fusion research between the Kurihara and Adshiri labs, both of the soft materials group. Ceria cubic nanocrystals with a size lower than 10 nm and coated with decanoic acid were produced in the Adshiri lab by a simple approach using organic-ligand-assisted supercritical water as the medium. We have then investigated the properties of ceria nanocrystals under confinement since it is known that nanosystems and molecules confined in very thin films between two solid substrates can form ordered structures and present interesting lubricant properties. The particular effects of nanomaterials under confinement are well accessible by surface force and resonance shear measurements.

We have observed a long-range repulsion between the surfaces during the first approach. Interestingly, this force disappears starting from the second approach, which indicates that an irreversible rearrangement occurs due to the compression. As for the shear measurements, we have shown that the resonance peak at contact is significantly reduced by the presence of a particle layer, which means that the friction is reduced and the particles present interesting lubrication properties. Based on AFM results on the adsorption behavior of the particles on mica, a model has been proposed for the compression process.

Re-Dispersion of Flocculated Nanoparticles Using Back Pressure Valve with Small Orifice Channel (poster presentation)

Nobuaki Aoki (AIMR Tohoku University),

This poster describes an easier and more effective method for producing a colloidal solution in which flocculated nanoparticles become re-dispersed by using a back pressure valve as shown in Fig. 1. Initially, a solution of nanoparticles (CdSe/ZnS-core/shell quantum dots) is left to flocculate by storing water-soluble nanoparticles (modal diameter 13.5 nm) for 2 days at 40°C. A large shear stress is applied to the solution in a back pressure valve for re-dispersing the flocculated particles. The clearance of the flow path in the valve decreases with increasing primary pressure. The re-dispersibility is evaluated through the measurement of their size distribution and zeta potential using dynamic light scattering (Zetasizer). The results show that the method re-dispersed the flocculated particles and reduces their modal diameter from over 6000 nm to 21.0 nm. Additionally, increasing the pressure decreases the particle diameter after the re-dispersion. In addition, we identify the mechanism of re-dispersion in this valve from the ratio of the applied shear stress or the colliding force against the channel wall compared to the van der Waals interaction energy. From the results, shear stress dominates the re-dispersion of flocculated particles. Moreover, we can

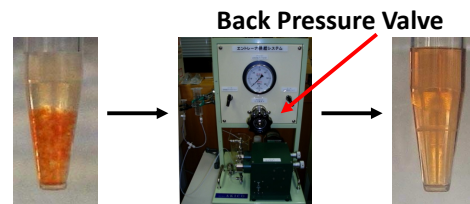


Fig. 1 Nanoparticle re-dispersion through a continuous process including a back pressure valve.

predict the particle diameter after the re-dispersion from the ratio of the shear stress to the van der Waals interactive energy)

Self-Assembly and Reassembly phenomena of Organic-Inorganic Hybrid Nanocrystals in Highly Ordered Nanocrystalline Multi/Monolayer (poster presentation)

Daisuke Hojo, Takanari Togashi, and Tadafumi Adschiri (AIMR, Tohoku University)

Uniform and highly ordered nanocrystalline multilayers were obtained after tetrahydrofuran annealing of pre-assembled nanocrystals on the substrate surfaces. As a result of the rearrangement process during solvent annealing, cerium oxide hybrid nanocrystals were correctly positioned in the nanocrystalline film layers because of high carrier ability and the high affinity of the solvent to the nanocrystals. It was also found that solvent annealing had almost no effect on the nanocrystalline monolayer macroscopically, indicating that nanocrystals chemisorbed on the modified substrate surface did not move freely as compared with nanocrystals on top of the pre-assembled nanocrystals. A sufficiently highly ordered nanocrystalline structure was self-assembled in the concentrated solvent and thus printed to such a sticky surface from a face-down configuration that prevented the random deposition of nanocrystals, resulting in the uniform and ordered nanocrystalline monolayer of macroscopic size.

Metallic glass nanoparticles as effective catalysts for selective molecular transformations (poster presentation)

Naoki Asao (AIMR, Tohoku University)

The chemical fabrication of metallic glass nanoparticles (MG-NPs) was reported. Using commercially available Pd, Ni, and P precursors, size-controlled Pd-Ni-P nanoparticles were obtained by a one-pot solvothermal synthesis procedure. The formation of a dense amorphous structure was indicated by high resolution TEM, selected area diffraction, and XRD pattern. Differential scanning calorimetry identified typical metallic glass properties. Notably, the supported MG-NPs showed remarkable catalytic properties and durability in methanol electro-oxidation in alkaline medium. These results indicate the potential use of Pd-based MG-NPs as fuel cell catalysts.

Interfacial Water Studied by Surface Forces Measurement (poster presentation)

Kazue Kurihara, Motohiro Kasuya, and Masashi Mizukami

Interfacial water plays important roles in physical, chemical, biological, and technological processes, e.g., self-assembly of biomolecules such as lipids and proteins in living systems, lubrication, and electrochemistry (electrolyte-electrode interfaces). The molecular level pictures of interfacial water, within several nanometers from the surface, have been gradually established for interfaces such as water/ mica, water/air, and water/hydrophobic surfaces, although there has been controversy among them. For example, the distance range where the surface has an effect on the structure and properties of water has a large variation from monolayer to more than micrometer for various surfaces such as silica, polymers, and gels. Therefore, the important and interesting question remaining is the effect of chemical and physical conditions especially on the range of interfacial water. For such a purpose, surface forces measurement is the most powerful method because it can continuously study the structure and properties of a liquid between surfaces as a function of the surface separation. Interfacial water, formed by adsorption or phase separation (prewetting transition), on a silica surface in water–cyclohexane binary liquids, and water between silica surfaces were studied using the surface forces and resonance shear measurements.