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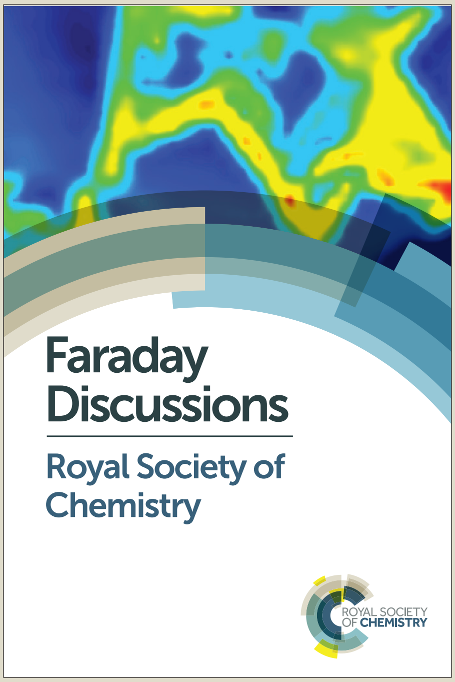

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Nanoparticles and self-organisation: the emergence of hierarchical properties from the nanoparticle soup (i.e., the small is getting bigger). Concluding remarks for FD 181

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Some four years ago, one of the participants in this Discussion (Prof Nicholas Kotov) predicted that: *" within five years we shall see multiple examples of electronic, sensor, optical and other devices utilizing self-assembled superstructures.*"[1] Although this prediction came partially to fruition, we have witnessed an unprecedented interest in the properties of materials at the nanoscale. The point highlighted by Kotov, however, was the importance of self-assembly of structures from well characterised building blocks to yield hierarchical structures, hopefully with predictable properties, a concept that is an everyday pursuit of synthetic chemists. This Discussion has brought together researchers from a wide range of disciplines, i.e., colloid science, modelling, nanoparticle synthesis and organisation, magnetic and optical materials, and new imaging methods, within the excellent traditional Faraday Discussion format, to discuss advances in areas relevant to the main theme of the meeting.

Imaging

The spectacular development of imaging technology has had a profound influence in our understanding of the physics and chemistry of process at the nanoscale, from the initial work of high resolution TEM and Z contrast imaging highlighted in the Faraday discussion of 1991 on *The Chemistry and Physics of Small Metallic Particles*,[2] to current applications as a powerful analytical tool in material characterisation.[3,4] It is only recently, however, that imaging of nanoscale object dispersed in a solvent has become possible. The conflict between vacuum requirements for transmission electron microscopy and the presence of solvents for in-situ imaging was initially solved by encapsulation of the liquid sample within a micro-flow cell employing for example, silicon nitride membranes as windows for liquid containment in the high vacuum environment in HRTEM. In his introductory *tour de force* lecture, Alivisatos explained contemporary efforts to circumvent these problems and described the use of laminated graphene layers for the entrapment of liquid films.[5] In this configuration, the sealing and hence, the integrity of the liquid pocket in the vacuum environment is ensured by the van der Waals interactions between the adjoining graphene sheets. This elegant arrangement allows high TEM contrast for nanoparticle samples present in a liquid environment and importantly, the capabilities of modern instrumentation for ultrafast image acquisition allow visualising process at the nanoscale in real time. Alivisatos showed the multiple applications of this imaging technique to follow diffusion events and the dynamics of artificial molecules by following nanoparticle (NP) trajectories. Other topics covered included an analysis of interaction potentials as a function of distance, electrostatic screening and nanoparticle growth.

The application of the complementary technique of environmental scanning electron microscopy (ESEM) to follow in-situ superlattice formation was discussed during the meeting by Kunstmann-Olsen et al. This work originates from the intriguing patterns of NP organisation that are observed on solvent evaporation, some of which have been attributed to entropy driven phenomena. The authors the changes in organisation as solvent evaporates were followed and hence, particle crowding takes place on the support. The importance of NP-support interactions were in evidence when comparing the behaviour of hydrophobic and

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hydrophilic substrates and crimpled support resulted in the formation of linear NP arrays. Notably, the use of ESEM allowed observing the intermediate stages of assembly in-situ and in real time.

Synthesis, morphology and properties

A myriad of shapes of nanoparticles has been reported in the literature and wet chemistry synthetic routes can produce almost any conceivable morphology. Even using exactly the same preparative conditions but chemicals from different batches from the same manufacturer can lead to completely different geometries. This has been observed in the case of CTAB for the synthesis of nanorods, an important material in cancer phototherapy. It is recognised that adsorption phenomena for different surface orientations can determine the final morphology. Petit investigated the "wet" chemical synthesis of Pt nanocubes, showing that the order in which the reactants are mixed determines the final geometry. This demonstrated that the stronger adsorption of hydrogen on Pt(100) compared with a Pt(111) surface stabilises this NP termination thus forcing growth in a cubic geometry. An unusual result is the realisation that the order in which the reagents are added determines shape: in order to obtain nanocubes, reduction of the Pt complex precursor must take place before adding a stabilising capping agent. Understanding the nature of the rate determining steps of deposition in the mechanism of NP growth is a general problem highlighted by this paper.

Size control and stability are recurrent themes in NP research. A strategy for controlling size is to carry out the reduction steps in a confined space employing, for example, reverse micellar microemulsions. Koper et al described NP syntheses employing bicontinuous microemulsions and demonstrated that size control can be predicted by a judicious choice of amphiphile head group and chain length. Importantly, this method allows the preparation of concentrated NP dispersions without significant aggregation. NP aggregation can represent a formidable obstacle for their use in biological environments. For example, the stability of citrate gold particles in aqueous electrolytes, mainly due to electrostatic repulsion, becomes compromised as the electrolyte concentration increases, leading to a decrease in Debye length with the resulting predominance of London dispersion interactions. In this case, achieving surface compatibility and avoiding non-specific interactions with biological material becomes of paramount importance. The determination of the state of charge of nanoparticles in solution presents difficulties since traditional methods, such as conductivity measurements, cannot easily separate the properties of the NPs and those of the base electrolyte present. The paper submitted by Philipse et al. discussed the possibility of a new approach to analyse the state of NP charge based on measuring the equilibrium difference of ionic concentrations between bulk solution and that of a small reservoir containing the nanoparticle dispersion.

Functionalisation with thioalkylated poly(ethylene glycol) is known to stabilise nanoparticles in aqueous electrolytes[6] and this surface termination is now being extensively investigated for biomedical applications.[7] In relation to this, mono-, di-, trithiol PEGylated Au nanoparticles were investigated by Graf et al. who demonstrated the remarkable stability increase in concentrated electrolytes achieved when Au NP are capped with polyvalent ligands. These results are noteworthy for improving the biocompatibility of nanoparticles and cellular components. An example of how size can be greatly controlled by the capping ligands present during synthesis was shown by Okram el al. Ni NPs prepared with octylamine (OA) as capping agent were highly polydisperse whereas a uniform preparation was observed when OA and trioctylphophine were jointly employed.

Self-organisation

Several papers dealt with soft interactions between nanoparticles. Silicon oil, polydimethylsiloxane (PDMS) droplets and O/W mini-emulsion, serving as platforms for the controlled adsorption self-assembly of microgels, were investigated by Schurtenberger et al. as models for the synthesis of colloidal molecules. Although colloidal molecules were not obtained, this work is interesting in showing the importance of controlling the number of interaction sites and interfacial curvature. The behaviour of shell nanoparticles at a liquid interface was modelled by Del Gado et al. PEG was employed as the stabilising brush polymer and as discussed above, a polymer of relevance for NPs applications in biomedicine. The appropriate repulsive potential to describe interactions between nanoscale objects was the subject of several discussions during the meeting. It was recognised that changes in the functionality of this term for different length scales may be necessary for a better computer modelling fit of experimental results. Two repulsive terms were employed, the classical Lennard-Jones potential:

$$U_{\mathrm{ij}} \propto r_{\mathrm{ij}}^{-12}$$

and the Gaussian Core Model (GCM):

$$U_{\mathrm{ij}} \propto \exp[-(r_{\mathrm{ij}}/\sigma)^2]$$

(r_{ij}=distance between particles, σ=particle diameter), the latter representing ultrasoft interactions. The conclusions of the extensive Monte Carlo simulations presented to analyse kinetics of interfacial adsorption, surface crowding and surface diffusion will be of interest to experimentalists since they provide a way of analysing the complexities of adsorption of nanoscale objects at interfaces.

Monte Carlo simulations were also employed by Bianchi et al to investigate self-organisation of patchy nanoparticles. These materials display surface regions containing groups or structures (patches) that provide specific interactions resulting in directional assembly of structures.[8] The interest in these materials is the possibility of predicting nanostructures made from them by the synthesis of appropriate polymers. The work presented concentrated in analysing how connectivity and directionality is affected by flexibility of the patchy structure, a question that is of great significance to synthetic chemists developing these materials. Another approach for the use of patchy materials was described in the paper by Ravaine et al. by considering that both enthalpy and entropy are driving forces for self-organisation. It has been known for some time that the latter contribution results from the collective behaviour of the system and is not dependent on the specific chemical nature of the surfaces. These very interesting ideas were further developed in this work by growing polystyrene nodules on silica particles, using them as masks to force the formation of surface dimples and demonstrating the further growth of nanostructures onto these.

Superlattices, nanoparticle assembly, electrical and optical properties

Korgel et al. presented the unusual and counterintuitive order-disorder phase transition property of a superlattice of Au nanoparticles capped with ocatadecanethiol. Using small angle X-ray scattering, it was unexpectedly demonstrated that a disorder-to-order transition occurred at 45-50 °C whereas the reverse process was observed at 45-50 °C. These transitions were reversible and indicated that the superlattice became more ordered on melting of the alkane chains. This important paper generated a justifiable great deal of interest and was extensively discussed. As the author indicated, the observed effect is probably due to the disruption of the alkane bundles attached to the gold cores, thus allowing core-core interactions to become predominant and leading to an ordered structure on melting of the methylene chains.

Two elegant contributions discussed the use of capillary forces to create well-defined NP assemblies. Isa et al illustrated the trapping of particles by controlled solvent evaporation into features engraved on a substrate. The effect of trap depth on the forces responsible for trapping was calculated and the trapping of more than one particle could be predicted. Fery at al. employed a simple dip-coating technique to confine nanorods in the grooves of a wrinkled substrate. The nanorods assembled by this simple technique showed strong plasmonic coupling, demonstrating the integrity of the nanostructures produced.

Mechanical properties of membranes obtained by self-assembly of nanoparticle sheets were investigated by Wang et al. The fracture strength can give a measure of the interactions between particles. A similar analysis for the same material can be found in Ref. 9. Bending and scrolling of free-standing nanoparticle monolayers by e-beam exposure was also described. The Young modulus calculations for nanoparticle membranes that were presented by Salerno et al. cannot unfortunately be compared with the above results since the mechanical properties measured corresponded to nanoparticle films deposited on a polymer and only fragmented layers were investigated, i.e., outside the elastic limit calculated by Salerno et al.

An interesting application of nanoparticles for making electrical contacts using Cu nanoparticles was presented by Kotov et al. Stable Cu NPs are notoriously difficult to prepare but the technique employed seems to have circumvented instability problems. The novel strategy described for making internal contacts in batteries could find important applications in the rapidly developing modern battery industry. Equally important is the development of nanomaterials for photonic applications and the paper by Teranishu et al., on the synthesis and properties of Cu_7S_4 nanodisks, represents a very nice example of how the optical properties of semiconducting materials with a high concentration of holes can be tuned by chemical assembly.

Magnetic nanomaterials

Magentotactic bacteria, i.e., bacteria that can recognise earth's magnetic field, owe their properties to the biological of magnetic particles (magnetosomes) present within the cell as linear structures. The work presented by Faive et al. queried why magentosomes are organised in an energetically unfavourable geometry. It was argued that the simple chain formation observed must result from active transport and it was concluded that cellular filaments play a central role in chain organisation.

Klajn et al. discussed the self-assembly of magnetic nanocubes and demonstrated that beautiful nanorope structures were formed under the influence of an applied magnetic field. The chirality leading to these structures was investigated by Monte Carlo simulations and the observed structures resulted from a balance between van der Waals and magnetic interactions. The possibility of altering the structures formed by including photoresponsive ligands containing an azobenzene group was explored. On UV irradiation, the *trans* form switches to the *cis* form bringing about a large change in dipole moment and a remarkable change in chain length of the assembled material was observed. These preliminary experiments open up multiple possibilities for the development of controllable photomechanical structures.

A study of properties of magnetic NPs in an ionic liquid was presented by Perzynski et al. where phase separation due to strong magnetic interactions was observed. These were related to NP size, counterions derived from the aqueous preparation technique of the NPs and the inevitable presence of water in the ionic liquid. The variables determining the self-assembly of magnetic nanoparticles and the choice of appropriate materials were clearly mapped by Puri et al. and several examples of organisation determined by applied magnetic fields were presented during this session. Velev et al. demonstrated the formation of microfilaments in solution of lipid coated γ-Fe_2O_3 that did not redisperse when the magnetic field was switched off suggesting a magnetophoretic assemble mechanism. Disch et al. used not only static magnetic fields to organise anisotropic hematite nanoparticles with spindle geometry but importantly, the effect of rotating magnetic fields was investigated. The former led to parallel orientation of the particle in the substrate whereas the latter resulted in a film of vertically orientated particles. This inventive research adds a new interesting procedure to the currently available nanoparticle assembly toolbox.

Final comments: What if? (The "blue sky" conundrum)

This Discussion highlighted the wide gamut of techniques, basic concepts and disciplines that are being currently deployed in efforts to understand and progress the area of nanoparticles and their organisation. Listening to the presentations and discussions during the Chicago meeting, one could not fail to realise the extensive interdisciplinary nature of this area of research and the excitement it generates. Imaging techniques allow us to visualise what some time ago were only models; this possibility represents a step change in methodology.

The discussion of some topics pointed to areas where additional research would be useful. For instance, there are still grey areas in our understanding of the distance dependence of the interaction energy between nanoparticles. It is to be expected that we will witness a rapid development of a large number of applications of nanoparticles in biomedicine and diagnostics. Nanophotonics is another area of active research where nanoparticles occupy a unique strategic position. In industrial applications, nanoparticles are currently already employed in fuel cells and new developments, for example, in nanoalloys, represent an important industrial objective for the area of transport and indeed, for electrocatalytic syntheses.

The above description can map the likely development of some of the topics we discussed in Chicago. My view, however, is that this is only one side of what is desirable. Sometimes it is convenient to ask, where are we going? What would constitute a step change in scientific knowledge? What are the general questions that can have profound ramifications in many aspects of scientific endeavour? My view of one such key research area is the understanding of the emergence of hierarchical properties of assemblies from knowledge of the individual properties of the building blocks, in this case, nanoparticles and/or nanostructures.

Although it is not possible or reasonable to deny the important beneficial societal consequences of scientific research, we have not yet achieved a reasonable balance between the support of intellectual curiosity and utilitarian science. This is more important when considering the training of young researchers, a question that impinges on the development of future leaders in what is regarded as desirable science-based economies. The development of nanoscale science represents an interesting example of this duality and I would suggest that it is not only important to provide a solid foundation in the required elements of scientific research, but also we should also encourage, through appropriate funding, young researchers to explore the question: what if?

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