



COMPLEX FLUIDS AS SCAFFOLDING FOR FORMATION OF NANOPARTICLE ARRAYS

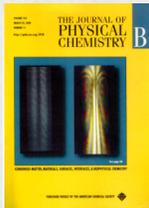
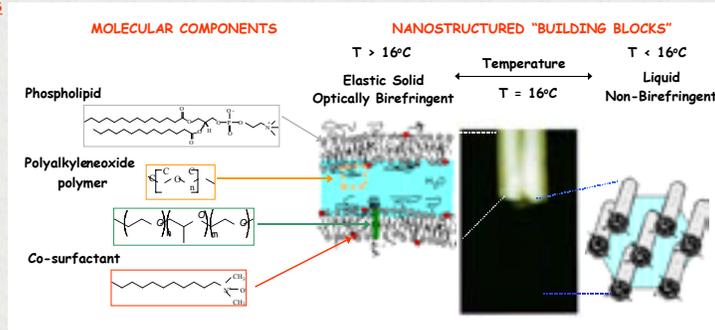
Millicent A. Firestone, Dixy E. Williams, Soenke Seifert, Roseann Csencsits
Materials Science Division
Argonne National Laboratory, Argonne, Illinois, 60439 USA



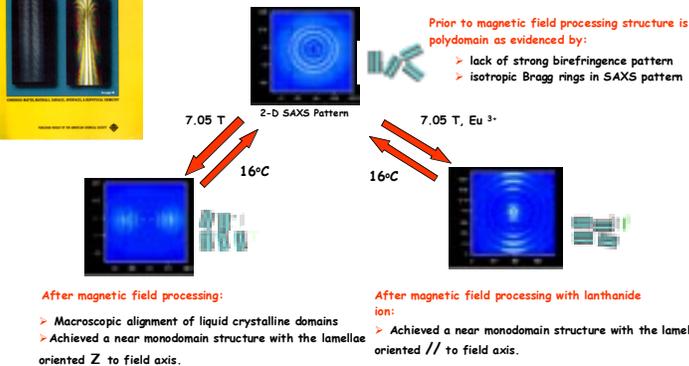
NANOSTRUCTURED MATERIALS BASED ON COMPLEX FLUIDS

We are exploring the potential of complex fluids, a type of soft condensed matter (non-covalent, self-assembled aggregates) formed by the spontaneous organization of amphiphathic molecules in a solvent, as nanoscale "building blocks", templates, and scaffolds for the fabrication of functional materials.

For this work we are using a biomimetic complex fluid developed here at Argonne. This material is a quaternary mixture of a phospholipid, a polymer comprising polyethylene glycol terminally grafted to a lipid headgroup (or alternatively, introduced as a triblock copolymer (PEO-PPO-PEO)), and a zwitterionic co-surfactant. These solid amphiphilic components, when dispersed in water at room temperature (in ca. a 1:4 ratio of organic solids to water), self-assemble to form a gel consisting of ordered microdomains of lamellae, having a tunable lattice dimension in the range of 14 - 25 nm. Furthermore, this material undergoes an phase transition at 16°C, converting to a lower viscosity state that adopts a hexagonal arrangement of tubules with a lattice constant of 34.5 nm.



ACTIVE PROCESSING OF COMPLEX FLUIDS WITH MAGNETIC FIELDS



ENHANCING STRUCTURAL ORDERING IN SELF-ASSEMBLED NANOSTRUCTURED MATERIALS

The harnessing of self-assembly to produce functional aggregates poses a significant challenge, since frequently it leads to disordered (polycrystalline) structures, limiting the utility of these materials. Although much effort has been directed at the study of the design principles of self-organizing molecular assemblies, considerably less attention has focused on the use of post-assembly processing as a means of converting poorly organized materials, such as complex fluids, into useful/functional materials of well-defined structure. In this work, we explore the use of magnetic field induced processing as a means of enhancing the structural ordering in our biomimetic complex fluids. Macroscopic orientation of the lamellae can be achieved via magnetic field processing of the complex fluid. The lamellar domains preferentially orient perpendicular to the applied field. The directional alignment can be flipped by 90° with the lamellar domains oriented parallel to the field by modifying the composition through the addition of lanthanide ions (Eu³⁺). The induced alignment does persistent outside the field for several months if the sample is stored at temperatures above 16°C. The field-induced anisotropy can be erased by simply cooling below the phase transition and rewarming thereby offering potential opportunities for a magnetic field writeable media.

NANOPARTICLE ARRAYS

There has been increasing interest in the development of facile methods for the fabrication of nanoparticle-based materials. Here, we describe the use of the lamellar gel phase of the complex fluid as a scaffolding for the spatial compartmentalization and organization of inorganic nanoparticles. Specifically, we show that by controlling the size and surface chemistry of the nanoparticles, site-directed localization of the particles into one of the three physicochemically distinct regions of the complex fluid has been achieved.

Small angle X-ray scattering studies, conducted at The Advanced Photon Source, have been used to characterize the composite structure. Specifically, small angle diffraction measurements show that the lamellar structure of the complex fluid is retained upon fabrication of the composite, small angle scattering in the low Q region shows that the nanoparticles remain non-aggregated (discrete) and approximately the same size as that determined by TEM prior to introduction into the complex fluid. The scattering profiles do, however, indicate strong interactions between particles when they are incorporated

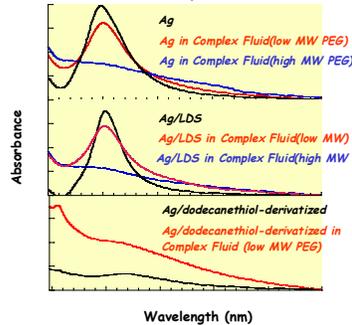
into the hydrophilic domains. Comparison of the surface plasmon resonance of the various silver nanoparticles dispersed in conventional solvents to those contained within the complex fluid was used to determine the region of spatial localization in the lamellar gel phase. Silver particles rendered hydrophobic by capping with an alkane thiol insert into the hydrocarbon bilayer region. Surfactant-stabilized and underivatized silver nanoparticles reside in the aqueous channels, with the latter particles preferentially interacting with polymer chains/charged membrane interface region. The spectroscopy data also indicates that interparticle interactions between encapsulated hydrophilic silver nanoparticles is significantly enhanced by increasing the

polymer repeat units. Most importantly, this work shows that complex fluids can serve not only as passive scaffolding in which to produce periodic arrays of encapsulated nanoparticle guests, but also an active host matrix capable of modulating the interactions between guests, and hence their physical and chemical properties (e.g., optical and electronic properties).

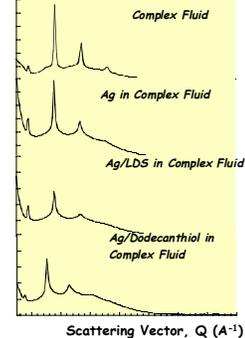
Fabrication Strategy



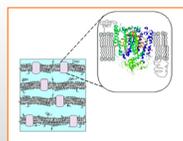
Surface Plasmon Resonances of Silver Nanoparticles



Synchrotron Small Angle X-ray Scattering



FUTURE DIRECTIONS



Complex fluids and inorganic oxide-reinforced complex fluids will be used as platforms for the fabrication of biomolecule-based materials (e.g., protein arrays). This will allow us to adapt & implement natural molecular "machinery" (proteins, enzymes, bacteria, cells) in "non-traditional" uses such as nano-photonics, energy storage & transduction or nano-mechanical devices.

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