

IRG-3. MICROSCALE SOFT MATERIALS

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[6 Graduates Students & 4 Postdoctorals]

GOALS AND INTELLECTUAL FOCUS

This IRG will create and characterize new classes of microstructured materials with tailored optical, mechanical, rheological, and storage properties. These materials will have potential applications as varied as switches for the communications industry to controlled release for consumer products. The basic building blocks will be mesoscale objects of varying sizes and shapes including micron-size spheres, naturally occurring and synthetic rods, and designer vesicles capable of encapsulating a range of materials with useful chemical and physical properties. The IRG brings together an interdisciplinary and collaborative team from five departments with wide ranging expertise in controlling, synthesizing, characterizing, and developing theories for soft materials. The IRG will focus on synthesis of new building blocks, on controlling and understanding self-assembly of complex structures from nanometer to micron length scales, and on characterizing macroscopic and microscopic properties.

This IRG builds on previous success [1-7] and incorporates new investigators (**Hammer, Dai, Discher, Janmey, Nelson**) to both pursue the production of novel colloidal and capsular elements and control the self-assembly of colloidal structures. The expertise gained from these efforts will be combined to produce exciting new microscale soft materials, with potential device applications, composed of capsular elements with controlled mechanical and optical properties. Figure 1 shows a new capsular structure created by **Discher** and **Hammer** in a seed project. It is a self-assembled vesicle, called a "polymersome", with a membrane formed by diblock copolymers that were subsequently crosslinked via interchain polymerization. It is so stable that it can be pulled through the air-water interface, dehydrated, and then rehydrated without loss of internal osmolytes. Figure 2 shows a 20-layer, almost defect free FCC crystal produced by **Yodh** and *Weitz* (Harvard) of one-micron-diameter PMMA spheres formed by directed self-assembly techniques, employing depletion forces and surface templating developed with MRSEC support.

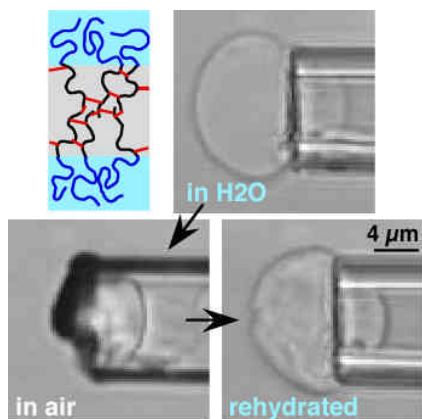


Fig. 1

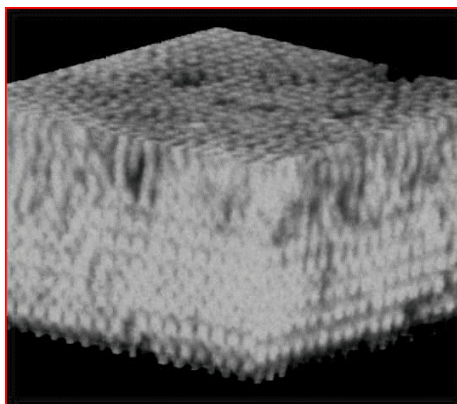


Fig. 2

SELF ASSEMBLY OF MACROMOLECULAR OBJECTS IN SUSPENSION

This effort will create new colloidal materials with novel optical and mechanical properties. It will explore the basic science of colloidal and macromolecular self-assembly via entropic, Coulombic, lock-and-key, and other forces. It will provide predictive guidance for the macroscopic assembly of complex systems from a variety of building blocks.

A. Rods and rod-sphere mixtures

Mixtures of hard rods and spheres of comparable diameter exhibit a rich variety of entropically driven phases [8], including lamellar phases with alternating layers of rods and spheres. The addition of a sufficient concentration of polyvalent ions to aqueous suspensions of charged rods induces formation of tight bundles [9] in a process that is still under study [10]. With increased availability of both biologically and non-biologically based rods, the time is now right for a broad study of rod-sphere systems. These systems offer a vast unexplored phase space that will reveal new avenues to controlled self-assembly of potentially useful anisotropic structures.

Yodh and **Janmey** plan a vigorous exploration of the phase behavior of suspensions of rods and spheres as functions of concentration, size, polydispersity, and type of rods and spheres and as functions of concentration and type of polyvalent ion. Rods will be TMV, fd, and M13 viruses, silicated boehmite [11], and organic dendrimer-based rods. Spheres will range from submicron-size polymers (PEO) and dendrimers, to micron-scale polystyrene, silica, and PMMA balls, to vesicles and emulsion droplets prepared by **Yodh**, **Hammer**, and **Discher**. Specific studies to be undertaken include (1) the interplay of entropic attraction between rods induced by small-sphere depletants and effective Coulomb attraction induced by polyvalent ions, (2) the effect of polyvalent ions on the phase behavior of rods and spheres of comparable diameters, and (3) the effect of polydispersity on phase behavior. **Dai** will use nonlinear optical techniques to measure adsorption of molecules on the surfaces of rods and spheres and thereby provide information about surface charge density and the strength of Coulomb interaction. **Percec** will synthesize organic rods of different flexibility and polydispersity with lengths varying from 100-1000 nm and diameters varying from 5 to 10 nm from taper-shaped molecular building blocks such as alkyloxy dendrimers with polymerizable linking groups. The dispersion of these rods in organic solvents, with and without dispersed spheres, will permit the study of anisotropic colloidal systems without the complications brought about by mobile charges and the Coulomb interaction. Furthermore, the use of organic solvents will permit novel cross-linking chemistries being developed by the **Berry-Sneddon-Webster** seed (Section 11) to be used to create new macroporous materials. Carbon nanotubes are another class of rigid molecular rods that can be dispersed in organic solvents. This IRG will work closely with IRG-2 (**Fischer**, **Johnson**) to produce aligned phases of nanotubes.

The combination of methods assembled in this proposal will allow characterization of single samples of these materials from the macroscopic scale via light scattering, low-angle X-ray scattering (**Heiney**), and microscopy to the scale of polymer subunits via neutron scattering and atomic-force and electron microscopy. Drawing on experience gained in the study of oppositely charged colloidal particles and lipid bilayers [3,4] (Section 5, Fig. 5.5), **Lubensky** and **Nelson** will develop theories for the interplay between entropic and Coulomb forces in rod-sphere systems.

They will also develop semi-microscopic and phenomenological theories for the phase behavior of these systems.

B. Rods, spheres, and ferrofluids

Ferrofluids [12] can act as a colloidal solvent, or emulsion droplets filled with ferrofluid can act as magnetic colloidal particles. The ability to tune magnetic alignment, and thus magnetic dipole-dipole interactions, with external magnetic fields opens new possibilities for the creation of colloidal systems with unusual phase behavior, non-equilibrium states, and rheological properties

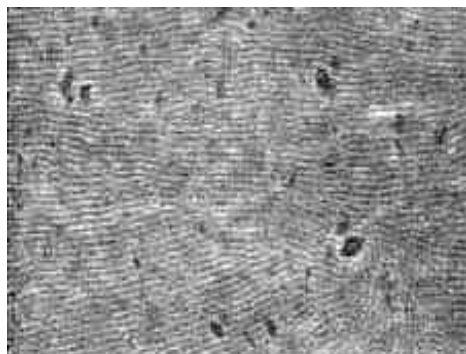


Fig. 3. Microscope image of a lamellar phase in a suspension of 800nm fd viruses in a ferrofluid.

[13]. **Yodh, Janmey, and Lubensky** will carry out a wide-ranging experimental and theoretical study of ferrofluidic colloids. They will investigate binary mixtures of magnetic and nonmagnetic spheres in varying concentrations. In zero field, these systems should resemble standard hard-sphere colloids. In nonzero field, magnetic particles will experience dipole-dipole interactions, which are longer-range, more directional, and potentially stronger than the nonmagnetic interactions. Thus magnetic particles, even in

small concentrations, should affect the mechanical, rheological, and dynamical response of complex fluids at nonzero field in novel ways.

Ferrofluid solvents and particles should also have interesting effects on the rod-sphere systems discussed in the previous section. For example, in mixtures of rods and magnetic particles, there should be competition between the tendency to form alternating rod-sphere lamellae in zero field and the tendency of dipolar spheres to form columns in nonzero field. What happens when a zero-field lamellar structure is subjected to a field? What structures will self-assemble in a field? What kinds of metastable states are there? What kind of rheological response will these systems exhibit? What happens when non-magnetic rods are dispersed in a ferrofluid host? Preliminary studies (Fig. 3) show the formation of a lamellar phase consisting of layers of rods separated by distance several times the rod lengths.

C. Self-assembly via biological crosslinking

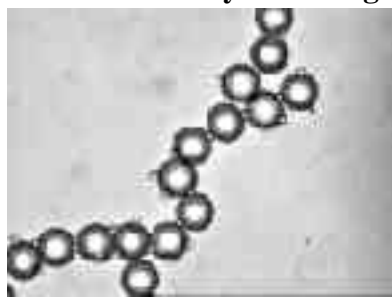


Fig. 4. A chain of linked colloidal spheres.

Hammer will explore directed self-assembly of colloidal particles with attached lock-and-key molecules [14], which provide exquisite selectivity and a broad range of affinities from low (selectin-carbohydrate) to intermediate (antigen-antibody) to high (biotin-avidin). By derivatizing colloidal spheres, micron-scale fibers, polymersomes, and other objects with appropriate crosslinking molecules, **Hammer** will create ordered macrostructures, including linear chains and crystals. An intriguing example of such a structure is a chain of colloidal particles or polymersomes, ordered by the application of two-dimensional optical traps and annealed by chemical crosslinking

between surface macromolecules as shown in Fig. 4. Another is a binary colloidal crystal. The hypothesis is that crystals with two or more distinct particle types per unit cell can form spontaneously if low affinity biospecific crosslinking is used: the low-affinity interactions

preserve selectivity but provide the lability necessary for crystallization rather than trapping in noncrystalline high affinity states.

CAPSULAR STATES OF AMPHIPHILIC BLOCK COPOLYMERS

Lipid-based vesicles are increasingly used in various products ranging from pharmaceuticals and cosmetics to paints and coatings. The essential amphiphilic character of lipids and their resultant rich phase behavior has been mimicked in recent years in block copolymers. Most recently, **Discher**, **Hammer**, and *Bates* (Minnesota) have found that a sub-class of diblocks is capable of forming vesicles [5]. Because the polymers studied thus far are about an order of magnitude larger in molecular weight than lipid molecules, the membranes of these "polymersomes" are significantly more robust than lipid membranes. The enhanced toughness and reduced permeability of polymersomes may prove highly desirable in numerous applications, such as drug delivery, artificial blood, and environmental scavenging, where lipid vesicles prove unstable and leaky. A major effort of this IRG will be the creation and characterization of block-copolymer based vesicles and emulsion droplets with controlled interiors.

Polymersomes and their multicomponent and polymerized generalizations raise a number of theoretical issues of fundamental importance. **Nelson** will investigate the effects of membrane material properties such as composition, phase separation, area compliance, and permeability on polymersome shape and shape transitions [19]. **Lubensky** will study thermal fluctuations and anomalous elasticity of polymerized polymersomes both with and without a fluid membrane layer. *Dan*, (Drexel) will investigate properties of and interactions between inclusions dissolved in membranes, and **Lubensky** and **Nelson** will study their diffusion.

A. Synthesis of new vesicle-forming block copolymers

Rapidly accumulating evidence suggests that other super-amphiphiles, including crosslinkable, di-block, tri-block, and polypeptide-based block copolymers will form vesicles. **Discher** and **Hammer** will systematically tabulate a matrix of vesicle-forming synthetic superamphiphilic copolymers and peptides. The aim is to generate new insights into mechanisms of polymer assembly and to provide predictive guidance in the further synthesis of vesicle-forming polymers. This should enable various device-oriented applications such as bio-mimetic, functionalized shells and "smart" encapsulators of colloids, liquid crystals, and reactive species. To date, vesicle formation has been investigated with materials synthesized both at PENN and elsewhere. *Bates* is supplying diblocks of PEO-polyethylethylene (PEE) and PEO-polybutadiene (PBD) and triblocks of these di-blocks interdispersed with polystyrene. *Tirrell* (CalTech) has supplied amphiphilic polypeptides of comparable molecular weight. **Dutton** (IRG-1) is synthesizing similar amphiphilic polypeptides with the intent of integrating their electron transfer functionalities into polymersomes (see Section 11). **Percec** is supplying a series of amphiphilic dendrimers and intends to synthesize other block copolymers including PEO-[polystyrene; poly(alkyl)methacrylate; or polyacrylic-acid] to systematically examine absolute and relative weight effects on membrane formation. **Percec** and **DeGrado** will also help in production of polymer-peptide conjugates of a general type already known to make vesicles [15]. Studies of commercially available polymers such as pluronics (tri-block PEO-polypropylene (PPO)-PEO), which form lamellar phases at high enough molecular weight, are also underway. Finally, **Discher** and **Hammer** are chemically functionalizing the polymers. Via fluorescein- and biotin-

labeling of PEO-PEE, they have been able to make diffusion measurements on individual vesicles and to attach anti-fluorescein antibodies and avidin-coated colloids.

B. Characterization of individual pristine and mixed polymersomes

A primary goal is to make giant vesicles whose mechanical, chemical, and thermal properties can be characterized on a single-vesicle basis. Current vesicle-formation processes range from electroformation off an electrode to simple self-assembly out of hydrated films. **Discher** and **Hammer** will explore how polymer amphiphiles of different molecular weight and composition can be assembled into vesicles and whether different methods of construction lead to different structures with different material properties. Direct manipulation of individual vesicles with micropipettes will be used to characterize a list of related properties: moduli for membrane bending and stretching, thermal expansivity, permeability, inelastic responses, solubility, and even inter-vesicular adhesion. Additional characterization methods to be employed include modal-contour analysis of thermal fluctuations, birefringence to assess ordering, line-tension determinations during membrane poration, second-harmonic generation from adsorbed probes to assay for adsorption (**Dai**), and simple, visual counting to quantify long-term stability of morphologies. For sub-micron vesicles that may be of particular importance to drug delivery, dynamic light scattering and fluorescence methods will be used to quantify size, aggregation, solute encapsulation, and permeability. Finally, calorimetry and other bulk assays will be applied to centrifugation-concentrated samples.

Multicomponent polymer-polymer and even lipid-polymer membranes are a clear route to property/performance engineering. Indeed, despite the molecular disparity between lipid and the copolymers, fluorescent lipids can be incorporated in polymersome membranes up to at least 15 mol% without compromising stability. Given this, mixtures of block copolymers such as di- and tri-blocks and diblocks with superamphiphilic peptides also seem very feasible. Tri-block copolymers offer particular flexibility for controlling material properties since their center blocks can be chosen to confer fluidity, induce glassy behavior, or drive phase separation. Lastly, polymersomes made from mixtures of polymer and organically soluble liquid crystalline materials have the potential to be piezo-optically responsive. For example, structural changes or even rupture of vesicles whose membranes contain azobenzenes might be induced by UV light, which induces conformational changes in azobenzenes [16].

C. Crosslink polymerization of polymersome membranes

Crosslinking within a vesicle's membrane can considerably enhance its durability with respect to load, temperature, and disruptive solvents. To date, cross-linked lipids do not appear capable of generating fully polymerized vesicles with diameters greater than 100 nm. This may be because strains that accumulate in cross-linking lipids are not sustainable or because smaller lipids translate to reduced reactivity. **Discher** and **Hammer** have found that larger, more reactive superamphiphiles overcome these limitations. A second approach to be tested will employ polymerization of hydrophobic, cross-linkable monomers dissolved in the bilayer core of a giant, lipid vesicle [17]. Current success with cross-linking has begun with a redox initiation reaction on giant polymersomes of PEO-PBD. Preliminary results demonstrate thorough membrane cross-linking while maintaining capsular integrity without shrinkage or tearing, even after vesicle dehydration (see Fig.1). Exposure to organic solvents like chloroform also has no effect. Cross-

linking of pure PEO-PBD imparts a nonzero shear rigidity to the polymersome membrane, mimicking the material fortification provided to biomembranes by membrane skeletal networks. Further, since the reference state of a cross-linked capsule may be tuned between flaccid and spherically-tensed at the time of cross-linking, it will be of interest to examine how the radii of deflated vesicles scale with vesicle area - a 2D analog to the classic polymer scaling problem. High-temperature stability of the chemically cross-linked polymersomes should prove particularly useful in fluctuation analyses and scattering studies of the type carried out on isolated spectrin network shells [18]. Additional measures of in-plane elasticity and ordering will be provided, respectively, by laser tweezing of membrane-attached particles and by birefringence. Considerable effort will go into modulating the crosslink density and thereby membrane properties. Not only can hydrophobic monomers be added to function as cross-link extenders but so can non-reactive superamphiphiles. As crosslink density is increased, there will be a percolative transition from isolated islands to a sample-spanning network of crosslinked polymer, which will be investigated using fluorescent probe diffusion and single-particle tracking.

D. Emulsions and emulsion-processing with amphiphilic block copolymers

Block copolymers used as surfactants in oil-water mixtures (emulsions and inverse emulsions) combined with copolymer crosslinking offer opportunities for the fabrication of a host of novel materials. For example, **Discher** and **Hammer** have crosslinked PEO-PBD at the interface of kerosene droplets emulsified in water. The resulting solid-like monolayer appears to be completely stable in water. This process offers the prospect of encapsulating organically soluble liquid crystals and ferrofluids within water dispersed droplets and producing, for example, permanently stabilized ferro-fluid droplets, which should have higher polarizabilities than entirely solid particles. Vesicles enclosing specified water-soluble encapsulants and having membranes with distinct inner and outer monolayers can be made through the inverse microemulsion process illustrated in Fig. 5. By polymerizing the monolayer membrane in the first emulsion step of the process, it should also be possible to make vesicles with biomimetic fluid-solid composite membranes in which a fluid lipid outer layer laminates an inner skeleton of cross-linked copolymer.

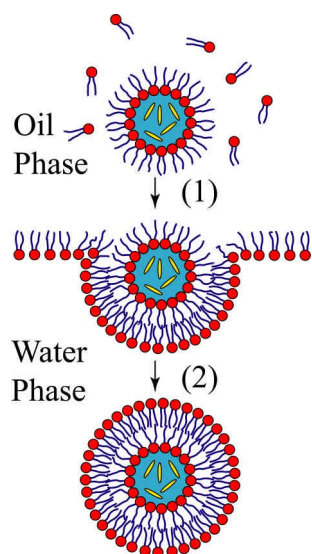


Fig. 5. Inverse microemulsion method of making droplets. Vesicles are formed one layer at a time by (1) adding amphiphile to a mixture of water, carefully layering the suspension on the surfactant layer of an air-water interface, and then (2) gently centrifuging the droplets through the surfactant layer, creating relatively monodisperse vesicles with controlled interior and membrane composition.

RHEOLOGY, DYNAMICS, AND LOCAL FORCES

Colloidal and related systems provide ideal laboratories for the study of fundamental dynamical properties such as diffusion of individual particles, mutual diffusion of collections of particles, and contour fluctuations of semi-flexible rods or polymers. New microscopic visualization, tracking and micromanipulation techniques are revolutionizing our ability to probe local dynamics and structure at the micron scale. A major effort in this IRG will combine microscopic optical measurements with macroscopic rheological measurements to provide insight into molecular origins of the macroscopic responses of complex fluids.

A. Rheology

Janmey and *Kaplan* (Unilever) will use state-of-the-art rheological instruments to measure viscoelastic parameters while at the same time single embedded labeled polymers are imaged by a fluorescence microscope. Measurements will be made of storage and loss moduli of a range of materials fabricated in the IRG, including rod-sphere mixtures, rod suspensions in bundled and gel states, suspensions of magnetic and nonmagnetic spheres, and suspensions of polymersomes. These macroscopic measurements will be correlated with microscopic measurements to be discussed below.

A focus of this work will be the non-linear rheology of biopolymer networks. Whereas aqueous gels formed by synthetic polymers commonly exhibit the linear, entropic elastic response expected for modest deformation of a flexible polymer, cytoskeletal polymers and some extracellular proteins form gels with non-linear elasticity at small strains, with a strong degree of strain hardening. **Janmey** will examine the non-linear viscoelasticity of biopolymer networks to determine how it depends on such factors as mesh size, filament stiffness, degree of crosslinking, solvent viscosity, and temperature using experimental systems already in place. **Lubensky** will define the origin of this non-rubber like elastic response. Characterization of these biopolymer gels may lead to rational design of smart materials that respond to specific stimuli, as chemically sensitive recombinant motor protein constructs can be made to exert internal stresses that contract and stiffen the gels when activated by specific chemical ligands, light, or electric fields.

B. Diffusion and interparticle forces

Laser tweezers can exert controlled forces or confine particles to points or lines in space. Such particles can be tracked with <10 nm precision by optical methods to obtain information about interparticle potentials of mean force in a variety of complex fluid environments. From measurements of the probability that two colloidal particles confined in a linear laser-tweezer trap have particular spatial separations, it is possible to accurately measure their effective pairwise interparticle potential [6]. **Yodh** and collaborators have developed this technique and used it to study effective potentials between two spheres in a variety of complex fluids from colloidal dispersions of smaller spheres to dilute and semi-dilute solutions of DNA. **Yodh, Janmey** and *Pugliano* (RohmHaas) will use laser tweezers to measure interparticle interactions in systems of interest to industry and in the new systems created in this IRG. Examples include interactions between spherical particles in dispersions of rods and in other adsorbing and non-adsorbing polymer solutions and the direct interaction force between two rods. The latter might be measured by optically trapping particles that are fixed to the rods or by observing rod motions by video microscopy on passivated 2-D surfaces. Interactions of particles in the vicinity of or embedded in fluctuating membranes will also be explored as a means to characterize vesicle

membrane properties. These macroscopic measurements will be related to experiments by **Dai**, which characterize local molecular changes on the surface of particles. This will establish a connection between potentials of mean force and local chemical changes.

Particle tracking, which is a powerful tool for studying diffusion in a range of environments with varying heterogeneity, also provides information about macroscopic loss and storage moduli in the emerging field of microrheology [20]. **Yodh**, **Janmey** and *Kaplan* will study diffusion in novel phases of rods and spheres, in polymer networks, in ordered particle arrays, and in semi-dilute F-actin or DNA solutions, which are ideal model systems for studying microrheology as a function of particle size and polymer correlation length. They will study correlated motion of pairs of particles, which should provide more accurate determination of storage and loss moduli than does the motion of individual particles. They will also use particle tracking to probe the dynamics of macro-Rouse polymers formed by tethered linear chains of colloidal particles (**Hammer**), polymersomes, or polymerized vesicles to which a colloidal particle has been attached. **Lubensky** and **Kamien** will investigate theoretical aspects of effective interparticle forces and diffusion of particles in colloidal suspensions and polymer solutions.

ENCAPSULATION, CONSTRAINED GEOMETRIES, AND APPLICATIONS

Collections, including films and periodic arrays, of colloidal particles and emulsion droplets or vesicles with tailored interiors have potential uses in a variety of technological applications including switches of various kinds and optical band-gap devices. The accumulated expertise of this IRG will be combined to create and study new composite capsular states and new arrayed materials. Any technological application of these new materials will require substantial quantities of constituent materials. Thus, efforts will be directed at developing methods of controlled production of large quantities of nearly monodisperse polymersomes and block-copolymer emulsion drops.

A. Encapsulation of micron-sized objects

Discher, **Hammer**, **Yodh**, and **Janmey** will collaborate in the production of micron-sized vesicles from phospholipids and polymers with biological and synthetic self-assembling objects either embedded in their membranes or encapsulated in their interiors or both. A primary goal will be to create “smart” capsules that, like living cells, respond in specific ways to external stimuli. The inverse microemulsion technique outlined in Fig. 5 will be used to encapsulate objects within the vesicle core. Types of materials to be encapsulated include (1) hydrogels, (2) colloidal material that can be induced to crystallize or that can be cross-linked, and (3) ferrofluidic material that can be driven to directed motion using a magnetic field. Active biological agents such as polymerizable actin, myosin motors and/or DNA will also be encapsulated into vesicle interiors, and others such as ionophores will be embedded in membranes. The goal will be to achieve a mimic of a cell in which these “living polymers” respond to environmental factors and induce vesicle shape changes and motion. The possibility of embedding open segments of 5-10 nm lengths of nanotubes prepared by IRG-2 in polymersomes to provide fixed 1.5 nm diameter rigid transmembrane pores will be investigated.

Material encapsulated in vesicle interiors can undergo transformations including phase transitions in response to external stimuli like changes in volume, induced by osmotic deflation or aspiration, or in temperature. These transformations will likely induce shape changes in the vesicle itself.

Discher, Yodh, and Collings (Swarthmore) will incorporate rods, spheres, and liquid crystalline materials within capsules and study their response, including shape change, to external forces. Manipulation of shape can be combined with crosslinking of the polymer membrane to create stable structures with unusual shapes and optical properties. This is rich theoretical territory. **Lubensky, Nelson, and Dan** (Drexel) will combine area-difference elasticity theories with models of particle rheology to develop predictions of vesicle shape transformations.

B. Arrays, films, and templates

A range of practical technologies relies on switches. An electric or magnetic field dramatically alters the mechanical properties of dipolar complex fluids from fluid-like to solid-like. Bragg diffraction of light from ordered particle arrays may be modified via an applied electric field, an applied optical light pulse, temperature, or chemical changes in a solution. An extreme example of this class of material is the photonic bandgap crystal wherein light propagation in any direction is suppressed at specific frequencies. Often practical devices require nearly defect free periodic crystals. **Yodh** has introduced and refined methods of assembling particles on surfaces via depletion forces [7]. These techniques have been used to assemble periodic structures on diffraction gratings or on PMMA surfaces imprinted with either one grating or two crossed gratings that serve as templates for the nucleation of 3D crystals (Fig. 6). These ideas will be used in future work to assemble arrays of particles, vesicles, and emulsion drops. IRG research on vesicle synthesis and on encapsulation of liquid crystals and light sensitive dyes such as Azobenzene provides the constituent materials crucial for “switching”, while research (**Berry, Sneddon, Webster**) on new synthetic chemistries in organic solutions can be used to create inverse structures from the self-assembled three-dimensional templates. A variety of conventional and unconventional applications for structured arrays will be explored. New optical and optoelectronic devices, such as Bragg switches composed of liquid-crystal emulsion droplets, based on these periodic structures will be investigated in collaboration with *Wiltzius* (Lucent) (see Section 15). Phase transitions (e.g. nematic-isotropic transitions) and orientational changes within the droplet induced via photoisomerization [16], pressure (osmotic or mechanical), or external electric fields will provide novel measurable responses for new classes of switches and sensors. Challenges for eventual device application include the high throughput synthesis of nearly monodisperse vesicles with encapsulants, identification of a robust transduction process to focus on, assembly of particles, and characterization of the switches.

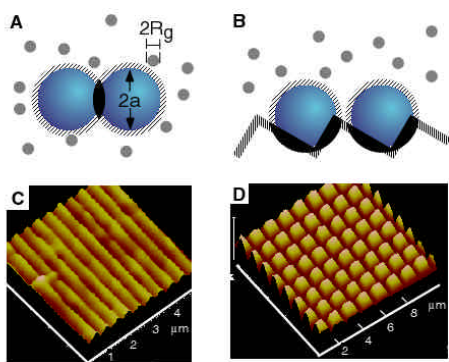


Fig. 6. Increase in excluded volume (black) available to small spheres when large spheres are near each other (A) or near surface grooves (B). AFM image of linear (C) and crossed (D) array of grooves imprinted from an optical diffraction grating.

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