Schedule for the 10th Mid-Atlantic Soft Matter workshop, January 11, 2013

Georgetown Univeristy, Institute for Soft-Matter Synthesis and Metrology

8:15 am

Registration and Breakfast

8:50 am

Opening Remarks

9:00 am

Jack Douglas (NIST):
Collective Particle Motion and Structural Relaxation in Strongly Interacting Disordered Materials

9:40 am

Sound-bite Session I

10:10 am

Coffee Break

10:30 am

Jens Rieger (BASF):
Do We Understand Crystallization?

11:10 am

Sound-bite Session II

11:50 pm

Lunch

1:10 pm

John Crocker (U. Penn.):
Interactions, directed assembly and transformations of colloids using DNA handshaking

1:50 pm

Sound-bite Session III

2:20 pm

Break

2:40 pm

Jai Pathak (MedImmune):
*Highly concentrated antibody and protein solutions – **really** complex soft matter*

3:20 pm

Sound-bite Session IV

3:50 pm

Break

4:00 pm

Dan Reich (Johns Hopkins):
Decoupling cell and matrix mechanics in engineered microtissues using magnetically actuated microcantilevers

4:40 pm

Richard Weiss (Georgetown):
Simple Molecules and Simple Chemistry Yield Complex Materials Through Self-Assembly

5:20 pm

Happy Hour/ Reception (Regents Hall)

Jack Douglas, Mat. Sci. and Engineering Division, NIST

Collective Particle Motion and Structural Relaxation in Strongly Interacting Disordered Materials

Most condensed materials at or near equilibrium exhibit a significant fraction of atoms, molecules or particles that strongly interact with each other while being configured geometrically at any instant of time in an 'amorphous' state having a relatively uniform density. For specificity, we are speaking primarily here about glass-forming liquids, the grain boundaries of polycrystalline materials, and the interfacial atoms of nanoparticles; this physical situation also probably applies to many other material systems such as the internal dynamics of proteins, bulk and interfacial water, ionic liquids, dust plasmas, and lipid membranes and these materials are under active investigation. Recently, both simulations and experiments have revealed that the dynamics of diverse amorphous materials of this kind can be characterized by significant heterogeneity in the local particle mobility and by a progressively increasing collective motion upon cooling that takes the unique form of string-like collective particle rearrangements. Simulations of polymer nanocomposites are taken for discussion as a representative class of materials exhibiting this general phenomenon since both the strength of the temperature dependence of structural relaxation time τ (termed the 'fragility' of glass formation) and the spatial extent of string-like cooperative particle motion can be tuned over a large range through the variation of nanoparticle concentration and the thermodynamic interaction of the nanoparticles with the polymer matrix. It is shown that these dynamic string structures can be directly identified within numerical uncertainties with the abstract 'cooperatively rearranging regions' of Adam-Gibbs (AG) model of relaxation in glass-forming liquids and we discuss the assumptions of this frankly heuristic model of relaxation in an effort to establish a firmer conceptual foundation of this model. A relation between the extent of cooperative motion and the rate of structural relaxation means that changes in the fragility of glass-forming liquids with additives, finite size confinement or changes of molecular structure can be completely understood from changes in the strength of the temperature dependence of the extent of cooperative molecular motion. The AG theory also establishes a link between the extent of cooperative motion and the thermodynamics of the material and thus allows for the prediction of changes in the dynamical properties of materials in terms of molecular interactions and structure and thermodynamic conditions based on analytical theory. Such a framework has the potential to greatly aid the design of new materials.

Jens Rieger, BASF SE, Advanced Materials & Systems Research, Ludwigshafen, Germany
BASF Advanced Research Initiative at Harvard University, Cambridge MA

Do We Understand Crystallization?

Crystallization of inorganic (and organic) matter often proceeds via intermediate stages rather than by simple nucleation and growth mechanisms [1]. These precursor stages not only comprise crystal modifications that are less stable than the final one (Ostwalds rule of stages), but also amorphous, hydrated (nano-) particles and emulsion-like precursors have been observed. These precursors tend to aggregate or restructure before being dissolved and entering the next structural stage.

Structural information on all these intermediates – and by which mechanisms they form – is essential for the development of additives to control crystallization processes – either to achieve particles with a certain size distribution, with certain functionalities or "simply" to impede crystallization in water treatment processes such as seawater desalination.

Data on the structural evolution of precipitating $CaCO_3$ and other systems obtained by means of X-ray microscopy and quench cryo-transmission electron microscopy will be presented, emphasizing that the respective particle formation processes do not follow classical nucleation and growth mechanisms[2,3]. Open questions in crystallization will be outlined and discussed.

[1] Horn, D.; Rieger, J. Angew. Chem. Int. Ed. 2001, 40, 4330

[2] Rieger, J.; Frechen, Th.; Cox, G.; Heckmann, W.; Schmidt, C.; Thieme, T. Faraday Discussions 2007, 136, 256

[3] Lee, J.; Saha, A.; Montero Pancera, S.; Kempter, A.; Rieger, J.; Bose, A.; Tripathi, A. Langmuir 2012, 28, 4043

John Crocker, Dept. of Chem. and Biomol. Eng., U. Penn
Interactions, directed assembly and transformations of colloids using DNA handshaking

DNA is a versatile tool for directing the controlled self-assembly of nanoscopic and microscopic objects. The interactions between microspheres due to the hybridization of DNA strands grafted to their surface have been measured and can be modeled in detail, using well-known polymer physics and DNA thermodynamics. Knowledge of the potential, in turn, enables the exploration of the complex phase diagram and self-assembly kinetics in simulation. In experiment, at high densities of long grafted DNA strands, and temperatures where the binding is reversible, these systems readily form colloidal crystals having a range of symmetries. For interactions that favor alloying between two same-sized colloidal species, our experimental observations compare favorably to a simulation framework that predicts the equilibrium phase behavior, crystal growth kinetics and solid-solid transitions. We will discuss the crystallography of the novel alloy structures formed, and the interesting diffusionless transformations they undergo that resemble shape memory alloys.

Jai A. Pathak, Drug Delivery and Device Group, MedImmune

Highly concentrated antibody and protein solutions ***really*** *complex soft matter*

Concentrated solutions of monoclonal antibodies (mAbs) expressed by mammalian cells are being increasingly developed as biological therapeutics. Antibodies are charged macromolecules with dynamic conformations that also possess some characteristics of colloids (size & charge). Intermolecular interactions (van der Waals, electrostatic, excluded volume, hydrophobic, solvation and dipole-dipole) assume increased importance in concentrated solutions (100-200 g/L protein concentration). Moreover, proteins are amphiphiles that possess hydrophilic and hydrophobic surface patches; the latter adsorb readily to air (oil)/water interfaces, where they can partially unfold, a common precursor to protein clustering Equilibrium and non-equilibrium clustering pervade soft matter physics and are observed in systems ranging from colloidal suspensions to mAb formulations. Such adsorption and clustering phenomena pose fundamental scientific challenges that hinder prevention of irreversible clustering for stabilizing antibody therapeutics and manipulation of viscosity challenges for delivery of protein therapeutics. Surprisingly, little work has been done in exploring the cluster size dependence of low-shear viscosity and intrinsic viscosity in protein solutions in a controlled manner, which motivated us to control cluster size of reversible and irreversible clusters formed by globular proteins or monoclonal antibodies over a concentration range of 2 mg/mL - 500 mg/mL and pH from 3-9. We find a marked dependence of low-shear viscosity on cluster size using custom-designed silicon-based microfluidic devices. Measurements of cluster sizes using static light scattering reveal correlation of low shear viscosity and intrinsic viscosity with the mean cluster size. We model the composition dependence of viscosity for the case of equilibrium and non- equilibrium clusters using a model adapted from recent modeling by Minton for protein mixtures. I will also discuss how surface rheology profoundly influences the bulk rheology. Clustering antibody solutions have fascinating bulk and surface rheology: they yield at the interface and in the bulk.

Daniel Reich, Dept. of Physics and Astronomy, Johns Hopkins Univ.

Decoupling cell and matrix mechanics in engineered microtissues using magnetically actuated microcantilevers

Contractile forces generated by cells and the stiffness of the surrounding extracellular matrix are two central mechanical factors that regulate cellular function. Probing these correlations is critical to furthering the understanding of processes such as cellular differentiation and tissue maturation, as well as developing methods to design and benchmark engineered tissues, which hold great promise for organ repair, and as model systems for biomaterials research and drug screening. Recently, new devices based on bio-microelectromechanical systems (bio-MEMS) have provided the potential for improved research tools for tissue biomechanics, notably by enabling construction of 3D microtissues created in patterned poly(dimethylsiloxane) (PDMS) substrates that, for example, overcome

diffusion barriers for soluble factors present in larger samples, or enable measurement of contractility in microtissue arrays. We have developed a 3D microtissue culture system that integrates the advantages of existing bio-MEMS approaches with the capability of applying both static and dynamic external loading to tissue samples via magnetic actuation, enabling simultaneous quantification of both the microtissues contraction forces and stiffness. We have used this system to study the evolution and self-organization of the mechanical properties of fibroblast-populated collagen matrices. For example, by coupling loading studies with transient biochemical treatments that modulate the cells mechanical behavior, we were able to demonstrate that the collagen matrix is the primary determinant of tissue stiffness, and the cells appear to adjust their own stiffness to match that of the matrix. These experiments provide the first measurements that suggest that cellular contractility and matrix stiffness can be decoupled at the tissue level, and illustrate the potential for magnetic control of tailored mechanical input to open new approaches to study cellular and tissue-level mechanobiology.

Richard Weiss, Dept. of Chemistry and I(SM)^2, Georgetown Univ.

Simple Molecules and Simple Chemistry Yield Complex Materials Through Self-Assembly

Basic strategies will be described to produce a variety of soft materials which can be interchanged between ionic and uncharged forms by simple chemical transformations and others that can be induced by addition of small molecular species. All of the systems depend on a form of self-assembly which is induced different stimuli. The strategies will be demonstrated by some of our recent approaches to self-assembling systems that rely on the addition or removal or small molecules (such as a neutral triatomic molecule [1], CX_2 where X = O or S). They will include the formation of reversible room-temperature ionic liquids from amidine/amine mixtures [2], the transformation of low viscosity amino substituted polysiloxanes into very viscous liquids, gels, and rubbers [3], and dispersions made by dynamic crosslinking of partially hydrolyzed poly(vinyl acetates) with borate [4]. In addition, applications of some gels to art conservation [5] and to oil spill recovery will be presented.

[1] Yu, T.; Cristiano, R.; Weiss, R. G. Chem. Soc. Rev. 2010, 39, 1435- 447.

[2] (a) Yu, T.; Yamada, T.; Weiss, R. G. Chem. Mater. 2010, 22, 54925499. (b) Yu, T.; Yamada, T.; Gaviola, G. C.; Weiss, R. G. Chem. Mater. 2008, 20, 5337-5344.

[3] Yu, T.; Wakuda, K.; Blair, D. L.; Weiss, R. G. J. Phys. Chem. C 2009, 113, 11546-11553.

[4] (a) Natali, I.; Carretti, E.; Angelova, L.; Baglioni, P.; Weiss, R. G.; Dei, L. Langmuir 2011, 27, 1322613235. (b) Angelova, L. V.; Terech, P.; Natali, I.; Dei, L.; Carretti, E.; Weiss, R. G. Langmuir 2011, 27, 1167111682.

[5] (a) Carretti, E.; Bonini, M.; Dei, L.; Berrie, B. H.; Angelova, L. V.; Baglioni, P.; Weiss, R. G. Acc. Chem. Res. 2010, 43, 751760. (b) Angelova, L. V.; Terech, P.; Natali, I.; Dei, L.; Carretti, E.; Weiss, R. G. Langmuir 2011, 27, 1167111682.

Soundbite Talks: *MASMX*

Session I

1. Jie Chen (NCNR,NIST)
   Dynamic property change across the Widom line of a sticky hard sphere system
2. Jonathan Bauer (University of Delaware)
   Hydrodynamic study of ellipsoids in corner flow with leakage
3. Frederick R. Phelan Jr. (NIST)
   Molecular Modeling of Polymeric Materials for the Materials Genome Initiative (MGI)
4. Armstrong Mbi (Georgetown University)
   Particle Size Segregation in binary glassy silica colloids
5. Nicos Martys (NIST)
   Rheology of Suspensions: Application to Cement-Based-Materials
6. Luz J Martinez-Miranda (University of Maryland, College Park)
   Interaction of discotic organic molecules and ZnO nanoparticles
7. Ryan McAllister (Georgetown University)
   Exploring Mechanotransduction in Breast Cancer Cells with Dynamic 3D Matrix Stiffness
8. Robert J. Polackwich (Georgetown University)
   Measuring Cell Generated Forces in 3D Collagen Networks
9. Jillian Emerson (University of Delaware)
   Phase separation in poly(3-hexylthiophene)/polystyrene thin films
10. Ryan Murphy (University of Delaware)
    B-PEO block copolymer micelle dynamics upon cosolvent removal

Session II

1. Divya K. P. (Georgetown University)
   A Two Photon Active Molecular Probe for the Detection of Zinc Ions Under Cellular Environment
2. Wei-Fan kuan (University of Delaware)
   Effects of Copolymer/copolymer Blends on the Conductivity of Block Copolymer Electrolytes
3. Kathryn Whitaker (University of Delaware)
   Silica nano-shells: A model suspension for colloidal microrheology
4. Duncan Kilburn (Johns Hopkins University)
   Exploring the folding landscape of RNA in crowded solutions.
5. P. Douglas Godfrin (University of Delaware)
   Structure, Dynamics, and Rheology of Clusters in Colloidal Dispersions and Protein Solutions
6. Joonwoo Jeong (University of Pennsylvania)
   Observation of liquid crystals in spherical and elliptical confinements
7. Mark Panczyk (University of Delaware)
   2D Assembly and Dynamics of Dicolloid Particles
8. Ajay Mallia (Georgetown University)
   Reversible gel to gel phase transitions within fibrillar Networks of (R)-18-(n-alkylamino)octadecan-7-ols in their carbon tetrachloride gels
9. Xin Zhang (University of Maryland)
   Nanoparticles Templated using a Block Copolymer Film through Coulombic Interactions

10. Pramukta Kumar (Georgetown University)
Shear-Driven Aggregation Dynamics in Colloidal Fiber Suspensions

11. Peter Beltramo (University of Delaware)
The "music" of colloidal ellipsoids

12. Ting Ge (Johns Hopkins University)
Entanglements and Mechanical Failure of Polymer Glasses

13. Yong He (Georgetown Universtiy)
Synthesis and properties of polysiloxane ammonium salts

14. Samuel M. Stavis (NIST)
Evaluation of Measurements of DNA Size in Nanofluidic Slits

Session III

1. Ruiliang Bai (University of Maryland/NIH)
NMR Water SelfDiffusion and Relaxation Studies on Sodium Polyacrylate Solutions and Gels in Physiologic Ionic Solutions

2. John Royer (NIST)
Shear Induced Diffusion of Cubic Colloids

3. Justin Stimatze (Georgetown University)
Simulating fiber motion in shear flow using Dissipative Particle Dynamics

4. Lora Angelova (Georgetown University)
Polymeric Gels for Conservation of Art

5. Matthew Lohr (University of Pennsylvania)
Dynamic and Vibrational Properties of Quasi-2D Attractive Colloidal Suspensions

6. Bob Leheny (Johns Hopkins University)
XPCS studies of nanoparticle motion in entangled polymer solutions

7. James Shaw (Bruker Nano)
AFM Nanomechanical Mapping of Live Escherichia coli Cells with Peak Force Tapping Technology

8. Tatiana Perevozchikova (National Institute of Standards and Technology/ University of Delaware)
Conformation of Monoclonal Antibodies during Freeze-Thaw Cycle studied by SANS

9. Annie Lu (University of Maryland)
Microfluidic Droplet Coalescence Induced Assembly of Microparticulate Dimers with Bi-functional Compartments

10. Suman Samai (IIT Kharagpur)
Does crystal or gel matter to stereochemistry of a reaction? Silver complexation-promoted solid-state [2+2] reaction of an unsymmetrical olefin

Session IV

1. Hao Shen (NIST NCNR)
Structural Characterization of Polymer Solar Cells by Small Angle Neutron Scattering

2. zengjiang wei (Research Institute of Materials Science, South China University of Technology, Guangzhou, China && Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, USA)
The ionic migration enables the self-healing of hydrogels

3. Ming Luo (University of Delaware)
Manipulating Nanoscale Morphologies in Block Copolymer Thin Films Using Gradient Approaches

4. Rana Ashkar (University of Maryland at College Park/ NIST)
Exploring the orientational order of carbon nanotubes under elongational flow

5. Marguerite Brown (Georgetown University)
   Birefringence in Microtubules under confinement

6. WONSEOK HWANG (University of Maryland, College Park)
   iso-Polypropylene / a-Polypropylene Block Copolymer Blends with Low Molecular Weight Functionalized iso-Polypropylene Homopolymer

7. Michael J. A. Hore (National Institute of Standards and Technology, Center for Neutron Research)
   Quantitatively Determining Polymer Brush Behavior on Gold Nanorod Surfaces

8. Mohan Zhang (Georgetown University)
   Derivative of Ricinoleic Acid as Low Molecular Mass Organic Gelator

9. Max Watson (National Institute of Standards and Technology)
   Simulations of Concentrated Antibody Solutions and Neutron Spin-Echo Experiments on Lipid Bilayer Vesicles

10. Nestor Valdez (NIST)
    Relation between intermediate order and local density fluctuations for a colloidal system with competing interactions