Research Highlights

2018
## Biocatalysis and Biotechnology (BB)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Department</th>
<th>Expertise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ping Wang*</td>
<td>BBE</td>
<td>Enzymology and biocatalysis, bioconversion and biosynthesis, biomaterials and functional coatings, bioelectrochemical processing, biosensors.</td>
</tr>
<tr>
<td>Mark Distefano</td>
<td>Chem</td>
<td>Organic and biochem., protein conjugates for therapeutic and biotechnology applications.</td>
</tr>
<tr>
<td>Mikael Elias</td>
<td>Biochem</td>
<td>Protein engineering and evolution, molecular modelling and recognition, bioremediation and quorum quenching strategies.</td>
</tr>
<tr>
<td>Wei-Shou Hu</td>
<td>CEMS</td>
<td>Systems biotechnology, biochemical engineering, cell culture bioprocessing, stem cell technology</td>
</tr>
<tr>
<td>Romas Kazlauskas</td>
<td>Biochem</td>
<td>Biocatalytic synthesis of chemical intermediates and biofuels, enzyme modification for new reactions.</td>
</tr>
<tr>
<td>Lawrence Wackett</td>
<td>Biochem</td>
<td>Enzymes in biotechnology, immobilization technology, bioremediation, computer prediction tools for biocatalysis</td>
</tr>
<tr>
<td>Kechun Zhang</td>
<td>CEMS</td>
<td>Synthetic biology, metabolic engineering, protein engineering, biofuels, renewable chemicals.</td>
</tr>
</tbody>
</table>

*Program Leader (Email: ping@umn.edu; Phone: 612-624-4792)

Chemical and fuel bioprocessing; Biocatalyst engineering; Biotransformation and Bioremediation; Enzyme evolution; Bio-based polymers and biocoatings; Pathway engineering; Synthetic biology; Systems biotechnology; Cell culture bioprocessing
Enzymatic Protein Labeling

Fluorescent labeling of CNTF

Mark Distefano is exploring how proteins accelerate chemical reactions and how proteins recognize other molecules with high specificity. This information is useful for drug design and biotechnology applications.

http://www.bti.umn.edu/faculty/biodistefano.html

Protein prenylation is a ubiquitous post-translational modification.
Our Lab aims to decipher the mechanisms by which biological macromolecules evolve, to understand the molecular basis of their biological functions, and to develop new methods for their engineering, with the aim of developing efficient, cost-effective, ecological and sustainable solutions to existing or emerging society issues.

Molecular engineering technology combining structural analysis and phylogeny-inferred information.

Structural and enzymatic characterization of improved variants

Phosphorus is an essential fertilizer for food production, is a very finite resource. Study, and molecular engineering of the bacterial phosphate uptake transporter.

Bioconversion of wastewater into clean water and fertilizer

More info and contacts: http://www.eliaslab.org
Hu Lab

**Systems Design and Cell Engineering**

- **Epigenomics**
- **Transcriptomics**
- **Proteomics**
- **Metabolomics**

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**Mathematical Modeling of Biological Reaction Network**

- **Parameter Estimation**
- **Simulation, Model Exploration**
- **Experimental Validation**

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**Model Prediction, Process Optimization**

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**Chinese hamster**

Genome engineering for biomanufacturing, genome technology for CHO cells

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**Biofilm and antibiotic resistance transmission, microbial invasion**

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**Enterococcus faeaelis**

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**Stem cell engineering for hepatic applications, biomanufacturing, for cell therapy**

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[http://www.cems.umn.edu/people/faculty/wei-shou-hu](http://www.cems.umn.edu/people/faculty/wei-shou-hu)
Ancestral catalyze new reactions

Reconstructed ancestral esterases and hydroxynitrile lyases are more promiscuous than modern enzymes

Kazlauskas Lab

- engineers enzymes to be more stable, to have higher selectivity and even to catalyze new reactions.

http://www.umn.edu/~rjk
Enzymatic rapid test for melamine in milk

Enzymatic water treatment

Molecular modeling

Immobilizing bacteria in fibers

Pool water treatment

Wackett lab

Enzymes, Biocatalysis for pharmaceutical synthesis, Bioremediation, Bioinformatics for genome mining, Plant microbiome engineering

https://cbs.umn.edu/wackett-lab/home
Bioproducts Innovations and Pathway Engineering

Petroleum

Chemical process: Unsustainable, wasteful, low yield, expensive

Glucose

Engineered bacteria

Fermentation process: Renewable, cost-effective,

Our research program combines principles of chemistry, biology and engineering to achieve biosynthesis beyond nature

http://www.cems.umn.edu/about/people/faculty.id21395.html

Zhang Lab

Methyl methacrylate for green PMMA,

Butanediol for sustainable rubber,
Conceiving and realizing nature-inspired multienzyme reaction pathways, Immobilized Biocatalysts, Bioproducts and Biopolymers, Bioenergy, Biosensors and Biomaterials.

http://www.bti.umn.edu/faculty/biowang.html
## Biomedical and Pharmaceutical Materials (BPM)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Department</th>
<th>Expertise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ron Siegel*</td>
<td>Phm¹/BME²</td>
<td>Hydrogels, drug delivery systems, microfabrication</td>
</tr>
<tr>
<td>Effi Kokkoli</td>
<td>CEMS³</td>
<td>Bioadhesion and drug targeting</td>
</tr>
<tr>
<td>Jayanth Panyam</td>
<td>Phm</td>
<td>Multifunctional nanodelivery vehicles</td>
</tr>
<tr>
<td>Wei Shen</td>
<td>BME</td>
<td>Bioactive materials</td>
</tr>
<tr>
<td>Calvin Sun</td>
<td>Phm</td>
<td>Drug crystal and particle engineering</td>
</tr>
<tr>
<td>Raj Suryanarayanan</td>
<td>Phm</td>
<td>Solid state properties of drugs, stability of drug/biomaterial formulations</td>
</tr>
<tr>
<td>Bob Tranquillo</td>
<td>BME/CEMS</td>
<td>Fabrication and characterization of bioartificial cardiovascular replacement tissues</td>
</tr>
<tr>
<td>Chun Wang</td>
<td>BME</td>
<td>Bio-molecular materials, polymer-based DNA and drug delivery, protein-based tissue scaffolds</td>
</tr>
</tbody>
</table>

*Program Leader (Email:siege017@umn.edu)

¹Pharmaceutics; ²Biomedical Engineering; ³Chemical Engineering and Materials Science, ⁴Chemistry

Affiliated Investigators: Chris Macosko,³ Marc Hillmyer,⁴ Theresa Reineke,⁴ Tom Hoye.⁴

- Biomaterials for drug delivery, medical device coatings, and tissue engineering
- Drug/medical device combinations, characterization of drug/materials interactions
- Cell-based fabrication of bioartificial tissues
- Novel tissue mechanical testing and analysis methods
ONLINE COVER Building Blood Vessels. This image shows a cross-section of a tissue-engineered vascular graft. Syedain et al. constructed these tubes from fibrin protein and human skin cells. During culture in a bioreactor, skin cells converted the fibrin into collagen. After removing the cells from the tubes, these grafts were implanted into baboons as arteriovenous grafts. Over the course of 6 months, cells repopulated the grafts and the grafts maintained patency. These grafts offer a biological alternative to synthetic vascular grafts used for hemodialysis access in patients.

[CREDIT: COLE FEAGLER/UNIVERSITY OF MINNESOTA]
A linear relationship exists between indentation hardness and Young's modulus for different pharmaceutical materials.


Forming a sweet salt with acesulfame enabled the successful development of a orally disintegrating tablet of metformin (50 g, 2 months).

• There is spatial heterogeneity in salt disproportionation in tablets as revealed by synchrotron PXRD.

• Disproportionation reaction is initiated at the tablet surface and progresses towards the tablet core.

Compression induced crystallization of amorphous solid dispersions

Cocrystal dissociation in tablet formulations – role of excipients
Spacer between single stranded DNA (ssDNA) and hydrophobic tail affects self-assembly, secondary structure and binding.

Depending on the spacer used ssDNA-amphiphiles self-assemble into spherical micelles and bilayer nanotapes. The nanotapes progress from twisted nanotapes to helical nanotapes to nanotubes.

We can control the diameter and length of the ssDNA nanotubes, and we are exploring both ssDNA micelles and nanotubes for the targeted delivery of oligonucleotides.

Nanotopography-Responsive Myotube Alignment and Orientation as a Sensitive Phenotypic Biomarker for Duchenne Muscular Dystrophy
Freezing-induced nanoparticle concentration at ice boundaries results in particle aggregation and increased size. Presence of a cyroprotectant results in separation of individual particles and prevents aggregation.
Siegel Lab: Biomaterials and Drug Delivery

Hybrid electrospinning of polycaprolactone (PCL) and Gelatin

Left: SEM of NIH 3T3 fibroblasts attached to hybrid nanofiber mat
Right: Live/Dead (gree/red) fluorescent staining indicating biocompatibility
Wang Lab: Polymeric Biomaterials

Biodegradable Polymer Melts for Drug Delivery

✓ Simple to formulate

Polymer melt (solvent-free)  Polymer Drug (soluble)  Polymer Drug (insoluble)

✓ Versatile to use

Injectable depot  Dispersions (in solvent)  Micro-droplet  Nano-droplets
# Coating Process Fundamentals — CPF

<table>
<thead>
<tr>
<th>Investigator</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Lorraine F. Francis*</td>
<td>Solidification, stress development, microstructure, printing</td>
</tr>
<tr>
<td>Marcio S. Carvalho**</td>
<td>Fluid mechanics, rheology, numerical methods</td>
</tr>
<tr>
<td>Satish Kumar</td>
<td>Transport processes, interfacial phenomena, microfluidics</td>
</tr>
<tr>
<td>Alon V. McCormick</td>
<td>Curing, thermodynamics &amp; kinetics, NMR, stress development</td>
</tr>
<tr>
<td>C. Daniel Frisbie</td>
<td>Printing processes, printed electronics</td>
</tr>
<tr>
<td>Chris W. Macosko</td>
<td>Rheology, polymer processing</td>
</tr>
<tr>
<td>Xiang Cheng</td>
<td>Colloids, polymers, rheology, visualization</td>
</tr>
<tr>
<td>Michael Tsapatsis</td>
<td>Zeolite and particulate coatings, membranes, separations</td>
</tr>
<tr>
<td>Wieslaw Suszynski***</td>
<td>Coating process experiments, apparatus, flow visualization</td>
</tr>
</tbody>
</table>

*Program Leader

**Pontifica Universidade Catolica, Rio de Janeiro

***Research Engineer and Coating Process and Visualization Laboratory Manager
Electrostatic Assist of Liquid Transfer between Flat Surfaces: Theory and Experiment

**Goal:** Investigate mechanism of electrostatically assisted liquid transfer by modeling and experiments

**Liquid models**
1. **Perfect dielectric liquid:**
   - Non-conducting liquid
   - No surface charge
2. **Leaky dielectric liquid:**
   - Low-conductivity liquid
   - Charge accumulates at the interface

**Electrostatic forces enhance liquid transfer to the more wettable surface (perfect dielectric)**

**More liquid is transferred to top surface when electric field is present**

- **Without electric field**
- **Leaky dielectric**
- **Perfect dielectric**

**Model predictions agree well with experimental observations**

**Electric fields are a promising strategy for enhancing liquid transfer at high printing speeds**

**Effect of Rheological Properties on Liquid Curtain Breakup**

**Goal:** Study the effect of rheological properties on liquid curtain stability and breakup.

**Method:** Computational model to study breakup dynamics.

**Model for curtain breakup**

**Evolution of free surface as a function of rheological properties.**

**Effect of liquid elasticity on curtain breakup time.**

**Main Results:**

Predictions agree with experimental observations;

Show how liquid formulation may be adjusted to delay curtain breakup.

M. S. Bazzi and M. S. Carvalho, JNNFM, under review, 2018.

Marisa Bazzi (Carvalho)
The dynamics of drop impact on solid surfaces is studied with an experimental setup involving a syringe pump, laser, photo-interrupter, high-speed camera, force sensor, and trigger with delay. The impact force is measured as a function of time and Reynolds number. The impact regimes are classified into inertial, viscous, and elastic impacts based on the Reynolds number range. The equations for the impact force are presented as:

\[ F\equiv \alpha \tau^\beta \quad \text{near } \tau = 0^+ \]

The experimental results show that the impact force scales with the drop velocity, viscosity, and surface tension, and the impact duration is influenced by the Reynolds number. The study is conducted at a drop velocity of \( U_0 = 1.93 \text{ m/s} \), viscosity of \( \nu = 20 \text{ cSt} \), and drop diameter of \( D = 2.2 \text{ mm} \), with a Reynolds number of \( Re = 210 \). The experiments are validated against theoretical predictions and existing literature.

Effect of Rheological Properties on Curtain Coating

**Goal:** Study the effect of rheological properties on liquid curtain stability

**Method:** Rheological characterization, high speed flow visualization.

**Main Result:**

Effect of rheological properties on the different failure mechanism in curtain coating;

Shows how liquid formulation may be adjusted to optimize curtain coating process.


Alireza M. Karim (Francis and Carvalho)
**Goal:** Study effect of rate-dependent rheology on liquid transfer in gravure printing processes

**Method:** Two-dimensional simulation using finite-element method with axisymmetric liquid bridges, neglected inertia and gravity, and moving contact lines

**Results**
- Reduced viscous forces cause enhanced contact-line slip
- Rate-thinning enhances transfer of liquid to a more-wettable plate

**Results**
- Larger cavity angle $\alpha$ improves liquid transfer
- Rate-thinning enhances contact-line motion near the right plate, causing a decrease in liquid transfer

**Goal:** Evaluate effect of particle concentration and size on process limits, particle distribution and orientation on coated films and extrudates.

**Method:** Solve the Navier-Stokes equations for free surface flows coupled with particle concentration and conformation transport equations using the finite element method.

**Main Result:**

Accurate prediction of process limits of particle suspension coating.

Effect of flow conditions on particle distribution and alignment on coated films and particle extrudates.

I. Siqueira, R. Reboucas and M.S. Carvalho, JNNFM, vol.243, 2017
I. Siqueira, R. Reboucas and M.S. Carvalho, AIChE J, vol.63(7), 2017
I. Siqueira and M.S. Carvalho, JFM, vol.825, 2017
R. Reboucas, I. Siqueira, and M.S. Carvalho, JNNFM, vol.258, 2018

R. Reboucas and I. Siqueira (Carvalho)
Modulus and Surface Energy Tunable Thiol-ene for UV Imprinting

**Objective:** expanding the achievable material properties of patterned coatings

**Thiol (T)**

**Ene (E)**

**Acrylate (A)**

**Fluorinated additive (F)**

**Modulus Tunability**

**Strategy:** Adjusting the crosslinking density

**Results:** Modulus decreased over two orders of magnitudes with increasing A%

**Surface Tunability**

**Strategy:** Adding a fluorinated additive

**Results:** Surface energy reduced by half at 1 wt% loading

Yuyang Du (McCormick, Francis)

Capillary-Driven Flow and Drying in Open Microchannels

Objective

• Determine how flow down open capillary channels is affected by liquid properties and channel geometry

Key Results

• Drying generates micro-scale pinning events that impede contact line motion and eventually arrest flow
• Lower drying rates and intermediate channel widths are most conducive to longer flow distances
• The time needed for drying is far greater than the time needed for flow

Robert Lade (Francis, Macosko)

* Lade, Jochem, Macosko, Francis Langmuir in press
## Electronic Materials and Devices (EMD)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Department</th>
<th>Expertise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steven Koester*</td>
<td>ECE (co-leader)</td>
<td>2D materials, transistors, sensors</td>
</tr>
<tr>
<td>Bharat Jalan*</td>
<td>CEMS (co-leader)</td>
<td>Complex oxides, molecular beam epitaxy</td>
</tr>
<tr>
<td>Chris Leighton</td>
<td>CEMS</td>
<td>Electronic/magnetic properties, material growth</td>
</tr>
<tr>
<td>Paul Crowell</td>
<td>Physics</td>
<td>Magnetism, transport, ultra-fast spectroscopy</td>
</tr>
<tr>
<td>Steve Campbell</td>
<td>ECE</td>
<td>Thin-film photovoltaics, 2D materials</td>
</tr>
<tr>
<td>Eray Aydil</td>
<td>CEMS</td>
<td>Thin-film photovoltaics, 2D materials</td>
</tr>
<tr>
<td>Uwe Kortshagen</td>
<td>ME</td>
<td>Nanomaterial devices and synthesis</td>
</tr>
</tbody>
</table>

* Faculty from 4 different departments. Diverse and complementary range of expertise.
* Program Co-Leaders

Synthesis, structural and chemical characterization of materials relevant for a wide range of electronic, optical and magnetic devices. Particular emphasis is placed on the understanding of the fundamentals of electronic structure and transport in electronic and magnetic materials, in addition to the materials science, physics and chemistry of the interfaces and nanostructures that play a vital role in device operation.
Understanding Sources of Disorder in Graphene

- We have quantified the electrostatic potential disorder in graphene arising from ripples caused by thermal expansion mismatch during CVD growth:

- Using Raman spectroscopic mapping we have quantified the doping and potential disorder in graphene associated with thermal expansion ripples.
- This work has potential implications for a wide range of devices, including sensors and varactors based upon CVD graphene.
Physics of Spintronic Devices

- Studying a range of spintronic devices based on integration of ferromagnetic metals with semiconductors, graphene, and normal metals:

  - Heusler-alloy based epitaxial heterostructures
  - Microwave and magneto-thermoelectric measurements
  - Ultralow FMR linewidths in epitaxial Heusler films
  - Anomalous Nernst effect
  - Metallic spin valves (w/ Leighton)

www.physics.umn.edu/people/crowell
Substitutional Doping of WSe$_2$

- WSe$_2$ is one of the few 2D materials that displays natural p-type behavior, yet controlled p-type doping in WSe$_2$ has not been demonstrated to date:

  - Nb increases $p$ by $\sim 10^{12}$ cm$^{-2}$; eliminates ambipolar turnoff.
  - Nb concentration set by position of Nb$_2$O$_5$ source
  - Shape set by H$_2$ flow
  - Results could be important for a wide range of device applications based upon TMDs, including flexible electronics, photonics and thermoelectrics.

- Largest WSe$_2$ crystals ever reported (165 $\mu$m)

Campbell
Transparent, High-Power Electronics using Perovskite Oxides

- Developed a novel commercially viable method for synthesis of thin films of alkaline-earth stannates (BaSnO₃, SrSnO₃) with high mobility, wide bandgap (3 - 4.5 eV) and excellent thermal stability:

  - Conductivity and optical transparency exceeding 10⁴ S/cm and ~85% in 120 nm doped-BaSnO₃ films with sheet resistance ~ 3 Ω/sq..
  - The highest reported electron mobility in SrSnO₃ due to excellent stoichiometry control and low number of defects.
  - These materials are a promising alternative to ITO for transparent conducting oxide (TCOs).

Benchmarked with other TCOs

https://research.cems.umn.edu/jalan/Jalan_research_group/Home.html

Jalan
All-Gas-Phase Deposition of Dense Hybrid Nanocrystal Materials

- “Hybrid NC materials” with potentially new properties can be produced via:
  1. NC gas phase deposition
  2. controlled sintering
  3. matrix infill with (PE)ALD

Materials properties can be tailored through: porosity of NC network (95% – 40%), NC contacts via IPL sintering, NC surfaces and interstices through ALD.

Materials potentially useful for: transparent conductive oxides, photodetectors, interfacial conductors.

http://www.me.umn.edu/labs/ukgroup/index.html

Greenberg, Francis, Shklovskii, Aydil, Kortshagen et al., Nano Lett, 2017

Kortshagen / Aydil
# Flexible Electronics and Photovoltaics (FEP)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Department</th>
<th>Expertise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russell J. Holmes</td>
<td>CEMS</td>
<td>Thin films, LEDs, solar cells</td>
</tr>
<tr>
<td>David Blank</td>
<td>CHEM</td>
<td>Ultrafast spectroscopy</td>
</tr>
<tr>
<td>Chris Douglas</td>
<td>CHEM</td>
<td>Molecular synthesis</td>
</tr>
<tr>
<td>Vivian Ferry</td>
<td>CEMS</td>
<td>Optical materials, plasmonics, metamaterials, nanocrystals</td>
</tr>
<tr>
<td>C. Daniel Frisbie</td>
<td>CEMS</td>
<td>TFTs and printed electronics</td>
</tr>
</tbody>
</table>

*Program Leader

Interested in the design of materials, device architectures, and processes for the realization of flexible electronics and optoelectronics based on organic and hybrid organic-inorganic materials.
Self-aligned Strategy for Printed Electronics

Self-aligned Capillarity-Assisted Lithography for Electronics (SCALE)

Nanoimprinting → Capillary action →

✓ Self-aligned fabrication
✓ High-resolution

Frisbie et al., Adv. Electron. Mater. 2015, 1, 1500137
Self-aligned Strategy for Printed Electronics

Fabrication of graphene micro-supercapacitors by SCALE

- Active footprint: < 1 mm²
- Minimum feature size: 20 μm
- Areal capacitance: 268 μF/cm²
- Fabrication yield: 100% (44/44)

Printing Resistors by Inkjet + Capillary Action

Resistance can be tuned over 5 orders of magnitude with high durability
Decoupling Degradation Mechanisms in OLEDs

- Degradation measurements are an aggregate of the multiple phenomena responsible for electroluminescence (EL) – no clear vector for improvement
- Consider overall EL efficiency as a product of the efficiencies of exciton formation (EF) and exciton recombination (photoluminescence, PL)
- Simultaneous measurements of both EL and PL permit the extraction of both efficiencies - Determine which dominates degradation (here, EF)

Mixed emissive layer (M-EML) OLEDs have longer operational lifetimes than conventional unmixed devices. Simultaneous measurements of electroluminescence (EL) and photoluminescence (PL) can be used to understand improvements in lifetime with increased thickness. M-EML reduces the exciton density, making less severe bimolecular exciton-exciton and exciton-charge degradation processes. Stabilizes the degradation in the M-EML photoluminescence efficiency.
Rubrene is an archetypical organic semiconductor that has been heavily investigated for applications in transistors.

Demonstrate that the normally two-dimension crystal grains observed in thin films can be engineered via additives.

The conjugated molecule Tpbi hinders the attachment of rubrene along the a-axis and permits tuning of crystal shape to a 1D nanocrystal.

## Microstructured Polymers (MP)

<table>
<thead>
<tr>
<th>Investigator</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Chris Ellison*</td>
<td>CEMS</td>
<td>Processing, synthesis, nanostructure</td>
</tr>
<tr>
<td>Frank Bates</td>
<td>CEMS</td>
<td>Thermodynamics, scattering, synthesis, structure and properties</td>
</tr>
<tr>
<td>Kevin Dorfman</td>
<td>CEMS</td>
<td>Theory, simulation, DNA dynamics</td>
</tr>
<tr>
<td>Marc Hillmyer</td>
<td>CHEM</td>
<td>Synthesis and characterization</td>
</tr>
<tr>
<td>Timothy Lodge</td>
<td>CHEM/CEMS</td>
<td>Dynamics, solutions, scattering</td>
</tr>
<tr>
<td>Chris Macosko</td>
<td>CEMS</td>
<td>Rheology, processing</td>
</tr>
<tr>
<td>Mahesh Mahanthappa</td>
<td>CEMS</td>
<td>Synthesis, morphology, self-assembly</td>
</tr>
<tr>
<td>David Morse</td>
<td>CEMS</td>
<td>Theory and modeling</td>
</tr>
<tr>
<td>Theresa Reineke</td>
<td>CHEM</td>
<td>Biomedicine, diagnostics, targeted delivery</td>
</tr>
</tbody>
</table>

*Synthesis, characterization, dynamics, processing, properties, and theory*
Sustainable Polyester Elastomers from Lactones

Hillmyer (UMN), McNeill (ETH), and Coates (Cornell) research groups

Renewable resourced

Excellent elastomers

Biodegradable

Interfacial Crystallization Builds PE/PP Adhesion

Narrow PDI in single site PE lead to perpendicular crystals which trap PP chains.

Oligomers in Zeigler PE move to interfaces and parallel crystals result.

Nanoporous Membranes from Crosslinked Lyotropic Liquid Crystals

- Bottom-up self-assembly of hydrophobic monomer, surfactant, and water
- Crosslinking polymerization with morphology retention

\[
\text{TMA-83u} + \text{HDDMA} \rightarrow \text{H}_2\text{O}
\]

~1.0–2.5 nm nanopores
Tunable Mechanical Properties
Highly Swellable

J. Jennings, B Green, T. J. Mann, C. A. Guymon, MKM, *Chem, Mater.*, 2018, 30, 185
Low Symmetry Phases in Asymmetric Diblock Copolymers

- Strongly segregated micelles in disordered state as $N \to 1$
- Self-consistent field theory (SCFT) reveals many nearly degenerate Frank-Kasper phases

Sequence-dependent persistence length of DNA

- High-throughput data of human DNA stretched in 38 nm nanochannels were obtained using a genome mapping method
- Over 50,000,000 measurements of DNA stretching were obtained on images of over 450,000 molecules

• There is a statistically significant dependence of the stretching of the DNA on the % GC content of the sequence between two fluorescent labels
• The increased stretch is equivalent to an increase in persistence length
• A statistical terpolymer model provides an accurate description of how the persistence length of long DNA depends on sequence

Computer Prediction of One Nanometer Domains

- Sub-10 nm features sizes are required for advanced nanolithography
- Block copolymer self-assembly has demonstrated domain sizes as small as 5 nm
- To shrink these even further, systems with remarkably high $\chi$ are required
- We have simulated oligomers of linear and branched polyols and alkanes
- The results anticipate lamellae with 2 nm period and 1 nm domain sizes
- Synthesis and characterization of these molecules is in progress

Chen, Barreda, Oquendo, Lodge, Hillmyer, Siepmann, ACS Nano 2018, 12, ASAP
Enhanced Mechanical and Adhesion Properties in Sustainable Triblock Copolymers via Non-covalent Interactions

- Incorporation of isosorbide and glucose-based glassy components create sustainable triblock copolymers as alternatives for commodity thermoplastic elastomers and pressure sensitive adhesives

Polymer/Graphene Oxide (GO) Thermosets with GO as a Crosslinker

- GO functional groups exploited in chemical reactions to form covalent bonds
- Synthesized polymer/GO composite elastomers where GO is a multifunctional crosslinker as well as mechanical property enhancer

- \(-\text{NH}_2\) functional polymer
- \(-\text{CONH}\)-functional polymer

- Tortuous and constricted paths
- Gas separation membranes

- Maintains elasticity
- \(\pi-\pi\) interaction assisted chemical reaction
- Crosslink nyons, proteins, etc.

*Journal of Polymer Science Part B* 2017 55, 1406-1413; *Journal of Membrane Science* 2016 518, 131-140
# Nanostructural Materials & Processes (NMP)

<table>
<thead>
<tr>
<th>Investigator</th>
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<tbody>
<tr>
<td>Alon McCormick*</td>
<td>CEMS</td>
<td>Materials and emulsions nanostructure, CryoMicroscopy</td>
</tr>
<tr>
<td>C. Daniel Frisbie</td>
<td>CEMS</td>
<td>Molecular materials and interfaces, molecular electronics</td>
</tr>
<tr>
<td>Wayne Gladfelter</td>
<td>CHEM</td>
<td>Materials chemistry, inorganic chemistry, scanning probe microscopy</td>
</tr>
<tr>
<td>Greg Haugstad</td>
<td>CHARFAC</td>
<td>AFM scanning probe microscopy</td>
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<td>(Director, Characterization Facility)</td>
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<tr>
<td>Christy Haynes</td>
<td>CHEM</td>
<td>Interface of bioanalytical and biomaterials chemistry</td>
</tr>
<tr>
<td>R. Lee Penn</td>
<td>CHEM</td>
<td>Environmental solid state chemistry</td>
</tr>
<tr>
<td>Ilja Siepmann</td>
<td>CHEM</td>
<td>Predictive modeling of phase and sorption equilibria</td>
</tr>
<tr>
<td>Andreas Stein</td>
<td>CHEM</td>
<td>Solid state chemistry of porous materials</td>
</tr>
<tr>
<td>Michael Tsapatsis</td>
<td>CEMS</td>
<td>Materials synthesis, structure elucidation</td>
</tr>
<tr>
<td>Joe Zasadzinski</td>
<td>CEMS</td>
<td>Microscopy of complex fluids</td>
</tr>
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Synthesis, phase behavior, structure, and performance of surfactants and self-assembled molecular and colloid systems
OligoPhenylene Imine (OPI) Wires

Reflectance-Absorption Infrared Spectra (RAIRS)

Step-wise growth on gold substrate

https://frisbie.cems.umn.edu/
Unravelling Tin Precursor Deposition Chemistry Using Computational Methods

Wayne L. Gladfelter, Chemistry, Bharat Jalan, CEMS, Christopher Cramer, Chemistry

**Tin oxide films by CVD**
- Low emissivity windows
- Transparent conducting oxides
- Sensors of combustible gases and CO

**Tin-containing perovskites (e.g. BaSnO₃)**
- High temperature power devices
- All perovskite, transparent electronics
- High mobility 2-D electron gas films

![Graph showing mole fraction vs. temperature](image)

![Diagram of SnMe₄, SnMe₃, SnMe₂, SnMe](image)

![Diagram of Sn(g) and various Sn compounds](image)

![Diagram showing ΔHf° (kJ/mol)](image)
Haugstad research: SPM characterization methods

I. SPM as a complement to other methods
confocal Raman, SEM, TEM and scattering (Xray, ion) on complex materials; under aqueous immersion in some cases.

II. Advanced AFM, contrast mechanisms
visco/elasticity, capillarity, surface energy, polarizability, surface potential.
Exploiting interactions:
attractive vs. repulsive, conservative vs. dissipative, nonlinear dynamics (harmonics, eigenmodes)

III. AFM of difficult condensed matter
Imaging liquid phase droplets or film domains; extremely soft matter (e.g., gels); or weakly bound objects (e.g., physisorbed nanoparticles).

IV. Environmental AFM: real time imaging, analysis of kinetics
In situ crystallization, glass transition, melting, diffusion, hydration;

V. Nano-to-micro scale quantitative properties
tribology, rheology, mechanics, adhesion/cohesion
Haynes Group: Analytical & Biomedical Applications of Nanomaterials Based on Silica Platform

www.chem.umn.edu/groups/haynes

Improved Tissue Cryopreservation using Nanowarming: Inductive Heating of Magnetic Nanoparticles

Perfluorocarbon-Loaded Mesoporous Silica Nanoparticles as NMR Sensors of Abiotic Factors

Silica-coated, pH-sensitive Swelling Polymer for Drug Delivery Applications

The Effect of Surface Charge Density of Silica Nanoparticles on the Interaction with Bacteria

Gao., et al. Sci Transl Med, 2017

Shewanella oneidensis
Dispersion and nanostructural mechanisms (McCormick with collaborators)  
research.cems.umn.edu/mccormick

Making vesicles, liposomes, etc.

Riehm  
Rokke Paul Vizanko  
Lee


Currently also  
Raghavan (Maryland), John (Tulane), Bothun (U Rhode I),  
Corcoran  
Penn

Surfactant blends for rapid dispersion  
DOSS/Tween89/Span80 and Lecithin/Tween80  
Crude oil in Sea water

Wear of nanostructured coatings  
Hubig (Ecolab) Riehm Lee Haugstad Suszynski Luo

Simulating micelle dynamics  
Mycona Morse  
APS March Meeting 2017  
Simulation of Dynamical Processes in Block Copolymer Micelles

Hydration & wear of hydrogel coatings  
Colling  
Zeng  
(Boston Scientific)  
Wormuth  
Haugstad

84 % rh  
82  
81
Single site catalysts: Metal Organic Frameworks (MOFs)

Nanoparticles in WATER

E.g., Vindedahl et al., *Environmental Science: Nano* 2016

Nanoparticles in NONAQUEOUS solvents

E.g., Thompson et al., *Chemistry of Materials* 2016

Green Materials Synthesis: Green Energy

E.g., Pinto et al., *Green Chemistry* 2016

E.g., Burrows, Talmon, *Penn; CrystEngComm* 2014
Computational Screening of Nanoporous Materials for Hexane and Heptane Isomer Separation
Hierarchical screening of all experimentally known zeolites and MOFs for separation of dibranched from monobranched and linear isomers for upgrading of research octane number Chin, Bai, ..., Siepmann & Snurr, *Chem. Mater.* 29, 6315 (2017)

First Principles Molecular Dynamics Study of Choline Chloride/Urea Deep Eutectic Solvent
Simulations of unravel hydrogen-bonded structure and provide insights into mercury solvation Fetisov, ..., *Siepmann, J. Phys. Chem. B* 122, 1245 (2017)

Transferable Potentials for Phase Equilibria. Improved United-atom Description of Ethane and Ethylene
Extensive parameterization including distance between Lennard-Jones sites and partial charges for π-electrons of ethylene yields molecular models that accurately describe C₂H₆/C₂H₄ vapor-liquid equilibria (including concentration dependence of separation factor) and also mixtures with carbon dioxide and water Shah, Tsapatsis & Siepmann, *AIChE J.* 63, 5098 (2017)

Structure and Phase Behavior of Mixed Self-Assembled Alkanethiolate Monolayers on Gold Nanoparticles
Simulations demonstrate that alkanethiolates of different lengths tend to segregate into domains (Janus particles) on the same nanoparticle Fetisov & Siepmann, *J. Phys. Chem. B* 120, 1972 (2016)
**Stein Group: Nanostructured & Nanoporous Materials**

www.chem.umn.edu/groups/stein  
[Email](a-stein@umn.edu)  
(612) 624-1802

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**Solid Adsorbents for Removal of Dilute H₂S from Claus Tail Gas**
(With M. Tsapatsis)

**Stabilizing metal-organic frameworks for high temperature catalysis**
(with R.L. Penn, C. Lu and many ICDC collaborators)

**Modified GO materials for improving fracture toughness at very low loadings**
(with C. Macosko, E. Tadmor)

**Renewable Electricity by High Energy Advanced Thermal Storage**
(with J. Davidson, I. Siepmann)

**All-solid-state potentiometric ion-sensing platform**
(with P. Buhlmann)

**Novel high capacity Li-ion battery cathode materials**
(with D. Truhlar)
NMP Program Review 2018  Collaborations with Dauenhauer, Macosko, Mkhoyan, Siepmann, Stein


Propane/propylene separation membranes Submitted (2018)
Interfacial Dilatational Viscosity

A. Sachan, S. Patton C. Valtierrez-Gaytan B. Stottrup, and J. Zasadzinski

\[
\gamma = \frac{(P_{in} - P_{out})R}{2}
\]

Interfacial Dilatational Rheometer

Phase separation, phase continuity and bubble curvature all play roles in dilatational modulus