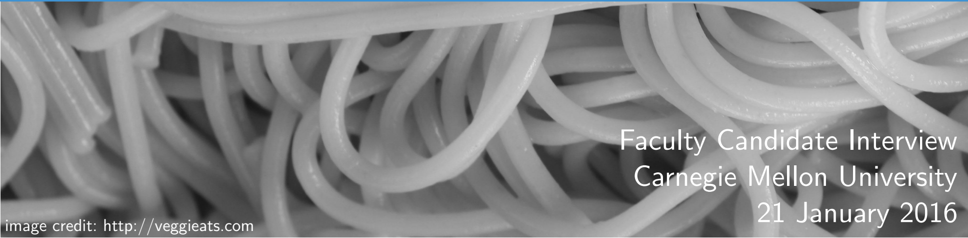
Theory and Simulation of Soft Matter and Complex Fluids

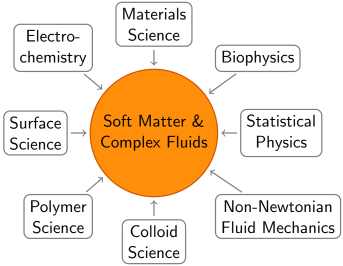
Douglas R. Tree



Faculty Candidate Interview
Carnegie Mellon University
21 January 2016

image credit: http://veggieats.com

What is soft matter?



Materials with degrees of freedom excited by thermal energy

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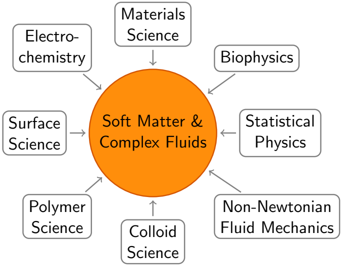
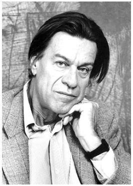


Materials with degrees of freedom excited by thermal energy

An important theme

Mesoscale ordering behavior independent of chemical detail (*universality*)



Pierre-Gilles de Gennes.

Nobel Prize in Physics, 1991.

Image credit: www.nobelprize.org

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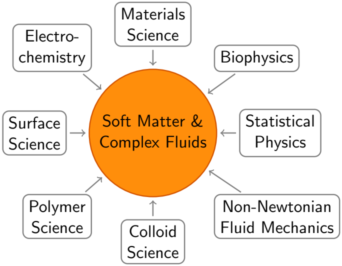

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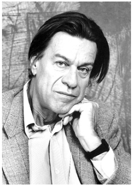

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Can we *engineer* soft materials on the nanoscale?

- Unique combinations of mechanical, electronic and optical properties
- Biomimetic properties: responsive, healable and hierarchical

Why theory? Challenges and opportunities

Key Challenge

Soft matter systems are overwhelmingly complex

- Number of components
- Disparity in length and time scales
- Geometry and topology
- Kinetics v. thermo- dynamics

We need better theories and simulation tools.

Why theory? Challenges and opportunities

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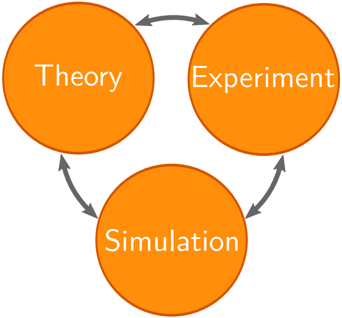
Opportunties

- Scientific understanding
- Accelerate materials discovery
- Enable process design and control



Research approach and strategy

Philosophy

Methods

Competition

Collaboration

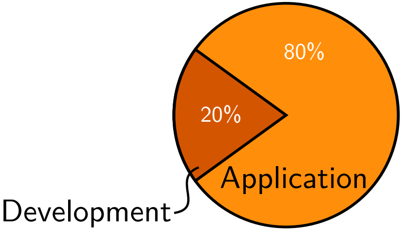
Group

Funding

Strategic Innovation

Develop new methods with the potential to make a lasting impact on

- the fundamentals of soft matter theory
- practical applications in energy, health and industry



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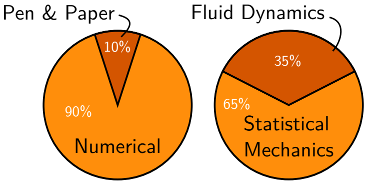
Numerical

- Statistical mechanics (field and particle)
- Fluid dynamics



Pen and paper

- Method development
- Theory and Analysis (PDEs, perturbation theory, scaling theory)

Research approach and strategy

- Philosophy
- Methods
- **Competition**
- Collaboration
- Group
- Funding

- There are many excellent researchers doing soft matter theory

Alfredo Alexander-Katz, John Brady, Kevin Dorfman, Pat Doyle, Jack Douglas, Glenn Fredrickson, Venkat Ganesan, Sharon Glotzer, Mike Graham, Lisa Hall, Arthi Jayaraman, Aditya Khair, Kurt Kremer, Ron Larson, Reid van Lehn, Scott Milner, Corey O'Hern, Monica Olvera de la Cruz, Dave Morse, Athanassios Panagiotopoulos, Juan de Pablo, Jian Qin, Rob Riggleman, Ken Schweizer, Eric Shaqfeh, Charles Sing, Andrew Spakowitz, Zhen-Gang Wang, Jonathan Whitmer...

- Pick problems where (due to complexity) innovative methods are needed

Research approach and strategy

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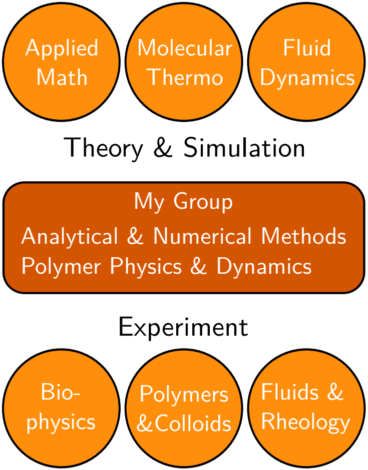


Research approach and strategy

- Philosophy
- Methods
- Competition
- Collaboration
- **Group**
- Funding

- Group size: 8-10 students and postdocs at steady state
- Students: analytical or programming skills
- Resources: offices, computers, moderate HPC resources (GPU cluster)

Research approach and strategy

Philosophy

Methods

Competition

Collaboration

Group

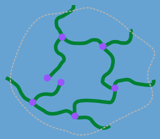
Funding

Broad support

- NSF, DOE, NIH
- DARPA, AFOSR, ONR, ...
- Industry

Future directions

Reversible Network
Materials

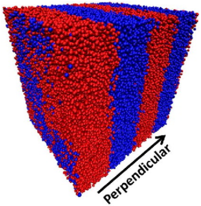


Complexity – process history dependence

Mesostructured fluids are difficult to model

- multiple length scales
- multiple time scales
- emergent order

Coarse-grained particle based



Ramírez-Hernández et al. Macromolecules (2013)

Complexity – process history dependence

Mesostructured fluids are difficult to model

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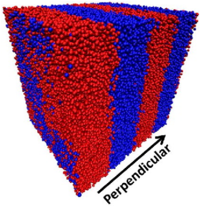
- multiple time scales
- emergent order

Advantages of a field-based approach

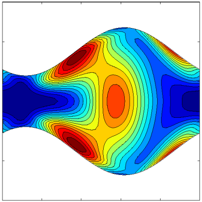
- no molecular degrees of freedom
- incorporation of mature CFD techniques

Coarse-grained particle based



Ramírez-Hernández et al. Macromolecules (2013)

Computational fluid dynamics



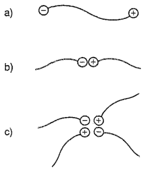
Teran et al. Phys. Fluid. (2008)

Inhomogeneous reversible networks

Reversible networks have properties that are useful for

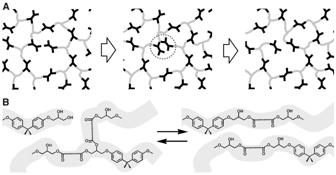
- Thermoplastic elastomers
- Self-healing materials
- Functionalized gels

Physical "crosslinks" (e.g. telechelic ionomers)



Leibler et al. J. Phys. Paris (1993)

Reversible chemical crosslinks (e.g. vitrimers)



Montarnal et al. Science (2011)

The goal

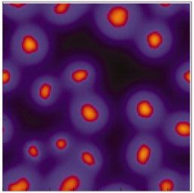
Dynamic control of mechanical properties by reversible chemical and/or physical crosslinks.

Reversible network projects

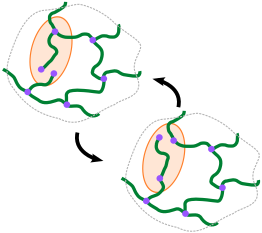
(1) Designing inhomogeneous networks

Go beyond transient network theory

- characterize formation and structure
- predict mechanical/rheological properties
- explore large parameter space



Popov et al. (2007)
J. Polym. Sci. Pol. Phys.



(2) Incorporating chain dynamics

Go beyond mixing rules

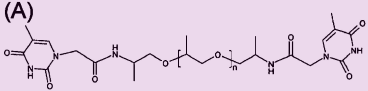
- mean-field dynamics
- topology in field theories

Potential funding: NSF, DMR (Condensed matter and materials theory)

Example – ODT in supramolecular polymers

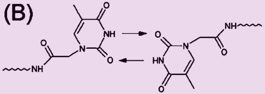
Cortese, Leibler et al. JACS (2011)

(A)

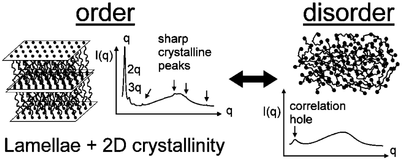


Thy--PPO--Thy

(B)



Weak H-bond



viscoelastic solid $\leftrightarrow$ viscous liquid

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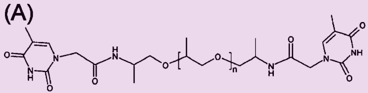

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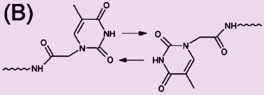

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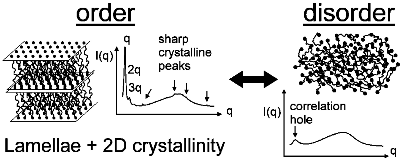


viscoelastic solid ↔ viscous liquid

Quote from Cortese, Leibler et al.

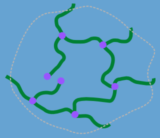
"Development of models ... should pave the way to better control of supramolecular polymers organization and properties."

Open questions

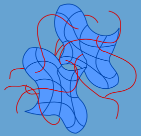
- What nanostructures are possible? How do they affect mechaical properties?
- Is crystallinity required to get microphase separation?

Future directions

Reversible Network Materials



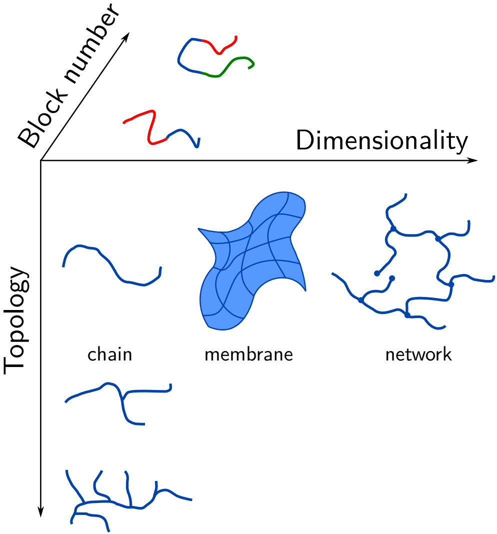
Self-Assembly of Tethered Membranes



Complexity – self-assembly

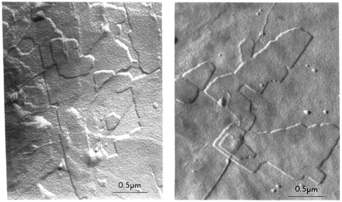
Modeling the self-assembly of complex macromolecules is a challenge

- Many-body problem
- Disparity of length/time scales
- Enormous design space



An emerging class of soft matter: tethered membranes

2D polymers

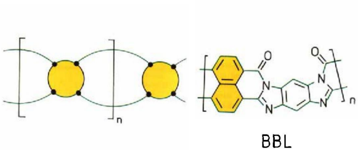


Stupp et al. J. Am. Chem. Soc. (1995)

Covalently bonded, periodic, monolayer (e.g. fisherman's net)

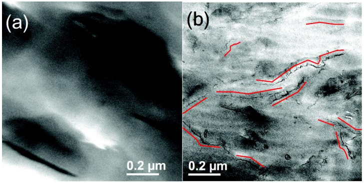
- fillers in polymer blends (thermal, mechanical, electronic properties)
- mass-transport barriers

Ladder polymers



Schlüter. Adv. Mater. (1991)

Polymer/graphene nanocomposites



Kim, Abdala and Macosko. Macromolecules (2010)

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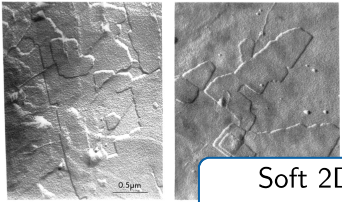

Stupp et al. J. Am. Ch

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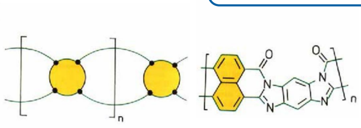
- sport barriers

Soft 2D materials are promising, but we lack efficient simulation methods for characterizing self-assembly

Ladder pol



BBL

Schlüter. Adv. Mater. (1991)

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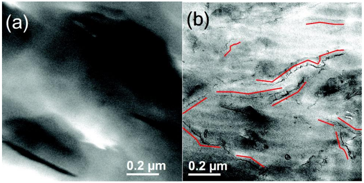
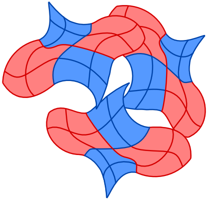


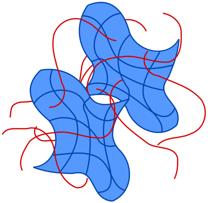
Kim, Abdala and Macosko. Macromolecules (2010)

Membrane self-assembly project

Field-theoretic treatment of tethered membranes

- Efficiently solve the "single-membrane" problem
- Decouple the many-body problem





Applications

- polymer/graphene nanocomposites
- patchy membrane origami
- polymer strips

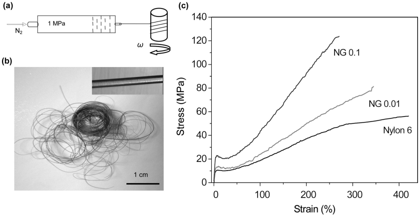
Potential funding sources: DOE (Computational theoretical chemistry), DARPA DSO (Materials with controlled microstructural architecture)

Example – dispersion of graphene in nylon

Goals

- increase tensile modulus
- increase conductivity

In situ polymerization of nylon with graphene oxide (GO)



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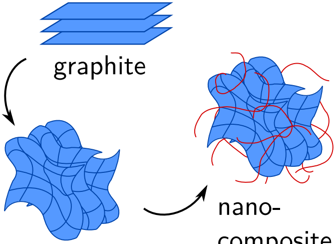
Challenges

- exfoliation (at scale)
- dispersion



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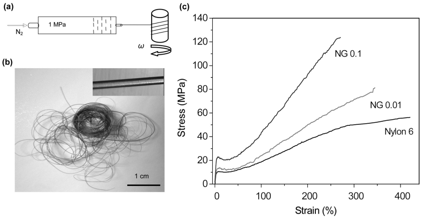

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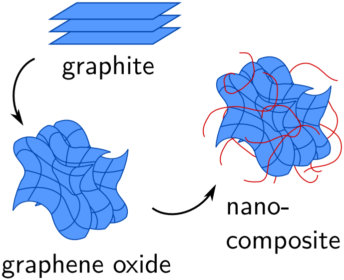

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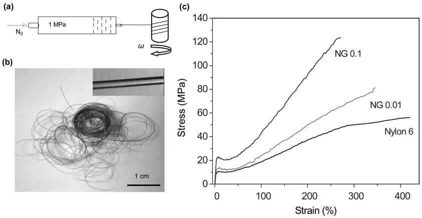

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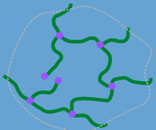
Questions

- How is the phase diagram altered by grafting nylon to GO?
- Are there important mesophases (e.g. nematic)?

Future directions

Reversible Network Materials



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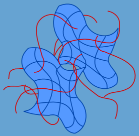
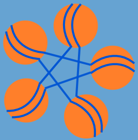
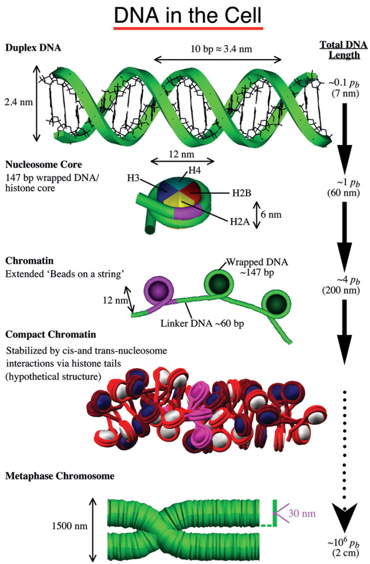


Chromosomes



Complexity – hierarchy



Schlick. J. Biol. Chem. (2011)

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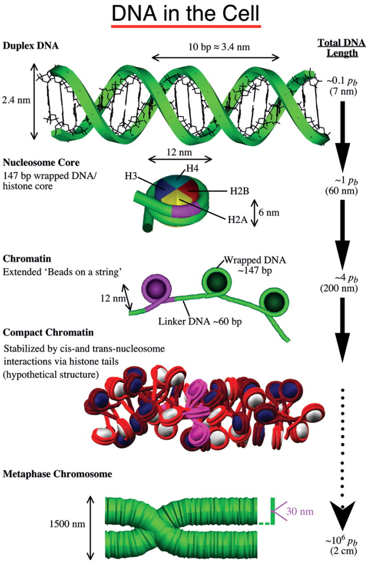
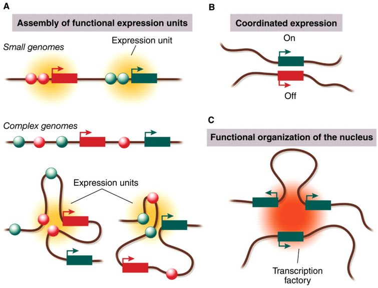


Schlick. J. Biol. Chem. (2011)

- Gene expression is partially regulated by chromosome structure and dynamics
- Chemical alterations of histones changes gene expression (epigenetics)

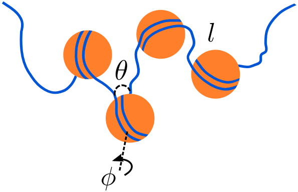


Dekker. Science (2008)

Prevailing models are oversimplified

Small-scale models ...

lack sufficient resolution to capture key phenomena



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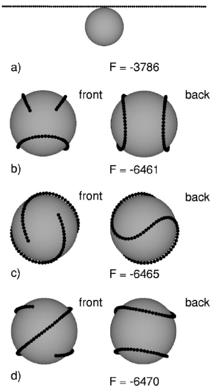

Kunze and Netz. Phys. Rev. E. (2002)

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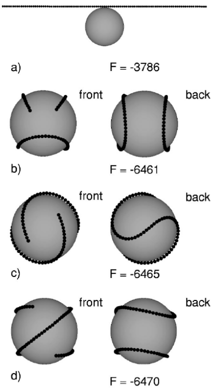
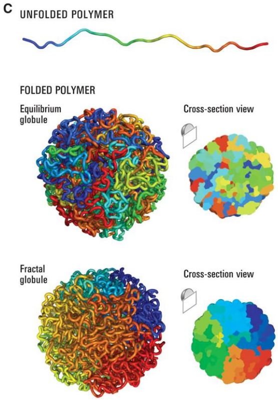


Kunze and Netz. Phys. Rev. E. (2002)

Large-scale models ...

are ad hoc and disconnected from microscopic details

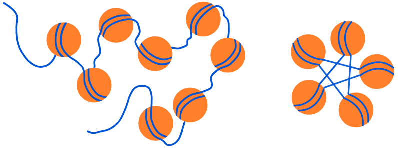


Lieberman-Aiden et al. Science (2009)

Chromosome project

Nature of the chromatin fiber

- Pruned-enriched Rosenbluth method for the long-chain problem
- Remove ad-hoc assumptions of prior fiber models
- Focus on non-equilibrium nature



Inhomogeneous crumpled globule

- Account for fiber inhomogeneities in chromosome structure

Potential funding sources: NIH, NIGMS, (Division of Cell Biology and Biophysics – Biophysical properties of nucleic acids), NSF, Physics (Physics of living systems)

Teaching Interests

Teaching Philosophy

- Pragmatic, organized, prepared
- Goals
  - Rigorous technical training
  - Perspective, critical thinking

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Undergraduate

Flexible, but interested in teaching core courses:

- Thermodynamics
- Transport
- Numerical methods

Graduate

- Statistical Mechanics
- Fluid Dynamics
- Numerical and Analytical Methods
- Thermodynamics

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Course Development

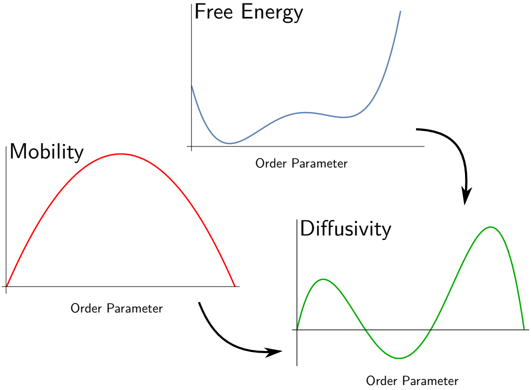
- Polymers and soft materials
- Chemical engineering and society

Backup Slides

Dynamics of inhomogeneous fluids

Origin of inhomogeneous dynamics

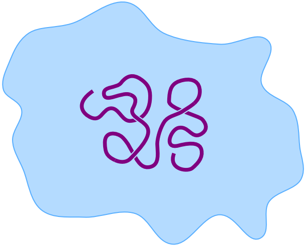
- Thermodynamics (free energy landscape)
- Dissipation (Onsager coefficients)



Two approaches to dissipation

Approach (1): two-fluid model

- phenomenological
- constitutive equations
- mixing rules



$$\Phi = \frac{1}{2}\int d\boldsymbol{r}\left[\sum_i \zeta_i(\{\phi_i\})(\boldsymbol{v}-\boldsymbol{v}_i)^2 + 2\eta(\{\phi_i\})\boldsymbol{D}:\boldsymbol{D}\right]$$

Approach (2): rigorous model

- Field theory (MSR functional)
- Mean field dynamics?

$$Z(t|t_0) = \int D[\rho]D[\omega]D[\boldsymbol{\psi}]D[\boldsymbol{\phi}]e^{-L[\rho,\omega,\boldsymbol{\psi},\boldsymbol{\phi}]}$$

Grzetic, Wickham, Shi. J. Chem. Phys. (2014)

Fredrickson and Orland. J. Chem. Phys. (2014)