



# Nanoparticle Dynamics in Polymer Matrices

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

LAMMPS, Aug 2015

### Polymer Nano Composites: Integration of Nano Properties in Organics with Polymer Mechanical Properties

Mechanical, Thermal

 Super-light, super-strong materials

Optical

- Flexible photovoltaic
- **Organic Electronics** 
  - Next-generation carbonbased electronics
  - High energy density capacitors

Biomedical

 Recognition and biomarkers









Images:www.nano.gov

# Nanoparticles (NPs) in Polymer Matrix Significance

Nanocomposites
 Mechanical
 Thermal
 Electrical
 Responsive media

#### Outline

- Dynamics of linear polymers
- > Nanoparticles in linear polymers
- Nanoparticles in ring polymers

#### Computational Challenge: Accessing Long Time Scales

### The Polymer

• Polymers are simultaneously hard and soft -Unique Viscoelastic Behavior



• Motion of a polymer chain is subject to topological constraints

#### Polymer Characteristic Length Scales

• Simple Liquids

– D ~ M^-1 ,  $\eta$  ~ M

- Short Polymer Chains (M < M<sub>e</sub>)
  - Longest relaxation time  $\tau_R \sim M^2$
  - Intermediate  $t^{1/2}$  time regime in mean square displacement

$$- D \sim M^{-1}$$
,  $\eta \sim M$ 

• Long Polymer Chains (M > M<sub>e</sub>) - Reptation



$$D \sim M^{-2}$$
$$\eta \sim M^{3}$$
$$\tau_{d} \sim M^{3}$$

Characteristic signature of reptation – intermediate  $t^{1/4}$  regime

**Computational Challenges in Polymers** 

- Longest relaxation time  $\tau \sim N^3$
- Chains are Gaussian coils R ~  $N^{1/2}$

- Number of chains must increase as  $R^3 \sim N^{3/2}$  so polymer chains do not to see themselves through periodic boundary conditions

- Double chain length cpu required increases by at least a factor of  $2^{4.5} \sim 23$ 
  - 1-2 month simulation becomes 2-4 years
- Number of processors limited: ~500-1000 particles/processor
- Imagine adding the NPs.....

# Polymer: Bead-Spring Model

• Short range - excluded volume interaction

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left\{ (\sigma/r)^{12} - (\sigma/r)^6 + \frac{1}{4} \right\} & r \le r_c \\ 0 & r \ge r_c \end{cases}$$

• Bonded interaction - FENE spring  

$$U_{\text{FENE}}(\mathbf{r}) = \begin{cases} -0.5kR_o^2 \ln\left(1 - (r/R_o)^2\right) & r \le R_o \\ \infty & r > R_o \end{cases} \quad \mathbf{k} = 30\varepsilon/\sigma^2, \, \mathbf{R}_o = 1.5\sigma$$

• Energy barrier prohibits chains from cutting through each other - topology conserved

$$m_i \frac{d^2 \vec{r_i}}{dt^2} = -\vec{\nabla} \cdot U_i - m_i \Gamma \frac{d\vec{r_i}}{dt} + \vec{W_i}(t) \qquad \text{Time step } \Delta t \sim 0.01\tau, \ \tau = \sigma (m/\epsilon)^{1/2}$$

## Nanoparticles in Polymers



- Weakly interacting mixtures of nanoparticles (NPs) in linear (N=10-400) and ring (N=800) polymer melts
- NPs of diameter  $\sigma_{NP}$  are well dispersed

LAMMPS: neighbor skin multi comm\_modify mode multi

# Motion of Unentangled Polymer



• Once polymer move their own size, unentangled polymers move like simple liquids

### State of the Art: Motion of Entangled Polymer



- t<sup>1/4</sup> motion is clearly seen for inner monomers
- Second t<sup>1/2</sup> region still unresolved

### Nanoparticles in Polymer Nanocomposite

- Stokes-Einstein relates particle diffusion to viscosity of media  $D = kT/f\pi\eta\sigma_{NP}$ , f=4,6 depending on slip
- What is the relevant viscosity? Macroscopic viscosity Local viscosity ~ σ<sub>NP</sub>
- How does presence of NP affect motion of the polymer?

# Small NPs in Polymer Nanocomposite

#### **Theoretical Prediction**

- Effective viscosity corresponds to a section of the chain with  $\sigma^2_{NP} = N_{NP} \sigma^2$
- Stokes-Einstein with the Rouse viscosity  $\eta = \eta_1 N_{NP}$ gives  $D_{NP} \sigma^3_{NP}$  constant



#### Large NPs in Polymer Nanocomposite



#### **Mobility of Large NPs:**

-slowed by chain entanglements

-not describable by the Stokes-Einstein relationship

Kalathi et al. PRL 2014

### Viscosity of Polymer Nanocomposites



- Small, neutral NPs act akin to plasticizers
  - -reduce the viscosity of polymer melt
- Effect persists for NPs whose sizes are as large as chain size or entanglement mesh size
- Increasing polymer-NP interactions reduces plasticizer
   effect

Tuteja et al., Macromolecules 38, 8000 (2005) Kalathi, PRL 109, 198301 (2012) Polymer Nanocomposites: Correlate microscopic dynamics with macroscopic response

- Nanoparticle Mobility affected by Polymer
- Polymer Mobility affected by Nanoparticles
  - Reduce number of effective entanglements
  - NPs increase or decrease viscosity, depending on their size, interactions

### Topology Effects: Ring Polymers

• Long linear polymers entangle and are forced to move ('reptate') along their contours

Branched polymers relax via a hierarchy of modes from dangling ends moving inward
Mystery: How do ring polymers relax without beginning or end?





#### **Conformation of Ring Polymers**



- Rings more compact, less entangled than linear chains
- Radius of Gyration  $R_g^2 \sim N^{2/3}$  for rings

~ N for linear

J. Halverson et al. J. Chem. Phys. 134, 204904 (2011)

#### Mean-Squared Displacement of NPs



•  $t < t_e$ , sub-diffusive motion due to coupling with dynamics of the subsections of polymer chains for both linear/ring •  $t > t_e$ , *MSD* different

for linear/ring

T. Ge et al, in prep (2015)

#### Effects of NPs Size



#### Nanoparticle

- Trapped by the entanglement mesh in linear polymers
- Shorter subdiffusive regime in rings
- No entanglement mesh

T. Ge et al, in prep (2015)

#### Fickian Diffusion of Nanoparticles



- Crossover occurs as NP motion couples with coherent motion of chain subsections of size  $R_g \sim \sigma_{\rm NP}$
- Rings:  $D \sim \sigma_{NP}^{-3.2}$
- Linear: D~  $\sigma_{NP}^{-4.5}$
- Crossover to Stokes-Einstein  $\sigma_{PH}$ >20 $\sigma$

# Highlights

- Small nanoparticles:
  - Diluent, decrease viscosity
  - Relaxation times and their diffusivities are completely described by the local, Rouse dynamics of the polymer
- Nanoparticles ~ Mesh size
  - Significantly slowed by chain entanglements, and is not describable by the Stokes-Einstein relationship
- NPs always reduce the number of entanglements
- Subdiffusive regime suppressed in ring melts compared to linear

# Acknowledgements

#### Collaborations:

- J. Kalathi and S. Kumar (Columbia University)
- T. Ge and M. Rubinstein (University of North Carolina)
- K. Schweizer and U. Yamamoto (University of Illionis)
- K. Kremer and J. Halverson (Max Planck, Mainz)
- A. Grosberg (New York University)

Funding:

- Center for Integrated Nanotechnologies (CINT)
- DOE (BES)

#### **Computer Resources:**

- Advanced Scientific Computing Research (ASCR) Leadership Computing Challenge (ALCC) at the National Energy Research Scientific Computing Center (NERSC)
- Sandia National Laboratories