Molecular Dynamics Polymer nano-composites

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Workshop on GPU Programming for Molecular Modeling 2013

August 5,2013

Wesleyan University

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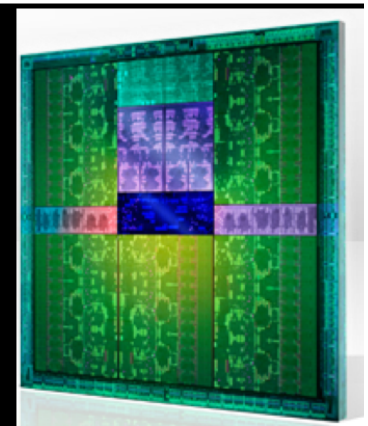
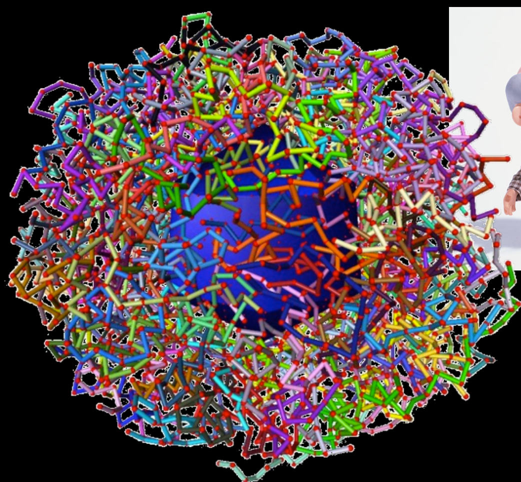
ESPE
B.S.
Electronic Engineering

Prof. Francis Starr
Wesleyan University

GPU Projects:



- MD program



Motivation

Computational Model

Key Algorithms

GPU Challenges

- STRINGS program

Motivation

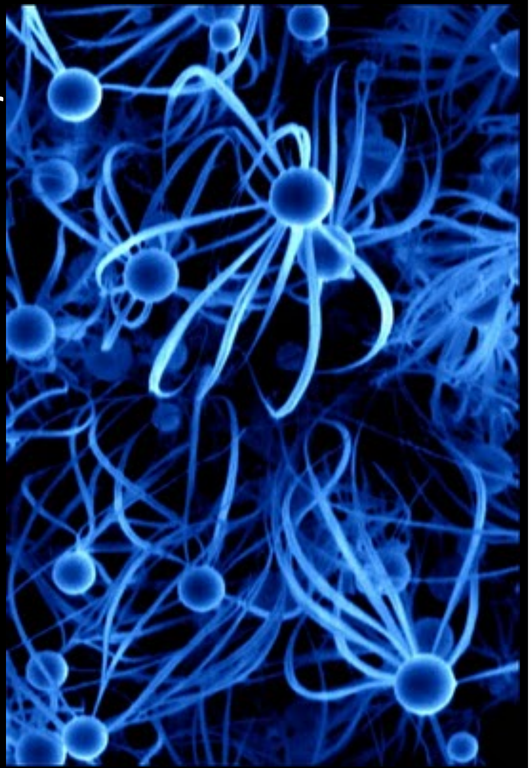
Computational Model

Key Algorithms

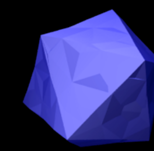
GPU Challenges

Polymer Nano-composites

- ✓ Polymer-Nanocomposite = Polymer + Nanoparticles
- ✓ Additives to polymer common to change properties or cost
- ✓ Only small concentration of NP needed (<15%)
- ✓ Substantial improvements possible for:
  - Tensile strength
  - Thermal stability
  - Heat distortion temperature
  - Chemical resistance
  - Electrical conductivity
  - Optical clarity
- ✓ Polymer nanocomposites are typically glasses



http://www.zeitnews.org/node/1163



What is the problem?

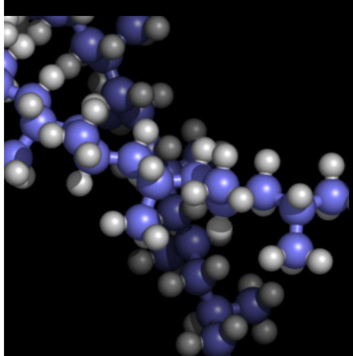
- ✓ How can we understand and manipulate the dynamics and glass transition of polymers by adding nanoparticles (NP)?

Why do we care?

- ✓ Polymers are a $2.4 trillion industry
- ✓ Fundamental insight into the origin of the glass transition

"The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition."

Philip W. Anderson (1995)
(Nobel Laureate 1977)



Cooperative Motion
in polymer nano-composites

Beatriz A. Pazmiño[1], Francis W. Starr[1], Jack F. Douglas[2]

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NIST

Wesleyan University

Cooperative Motion
in polymer nanocomposites

What is the specific relationship with their dynamical properties?

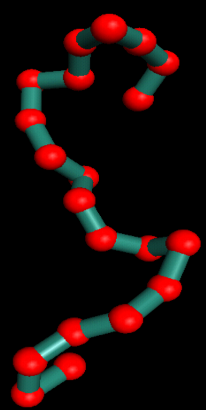
Wesleyan University

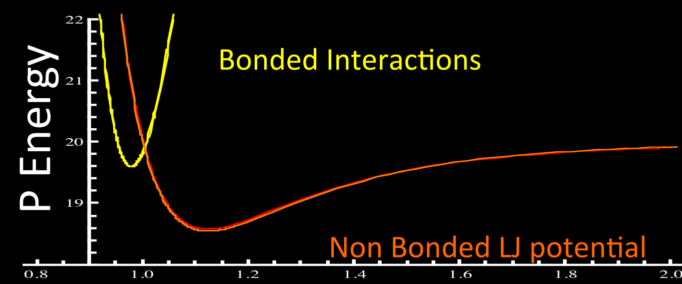
Tool — **Molecular Dynamics Simulation**

-Polymer Model

Chain of (LJ) monomers

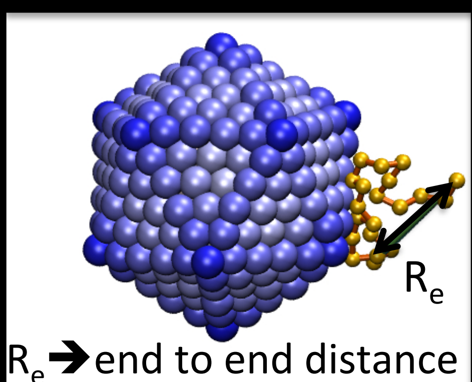
Inhibit crystallization Phys. Rev. A 33, 3628 (1986)





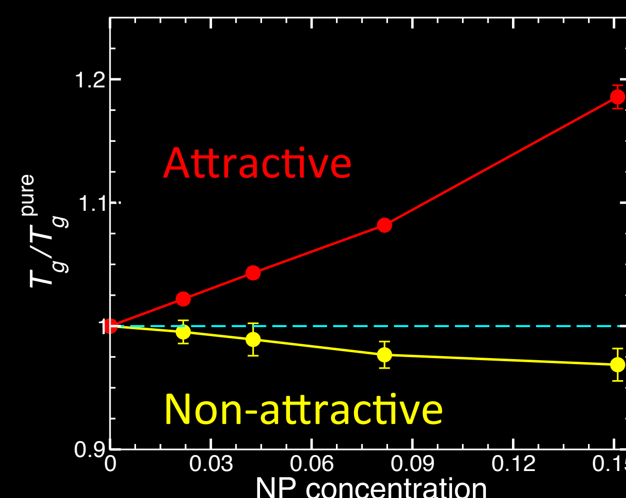
-Nano-particle Model

Icosahedral Macromolecules 35, 4481 (2002)



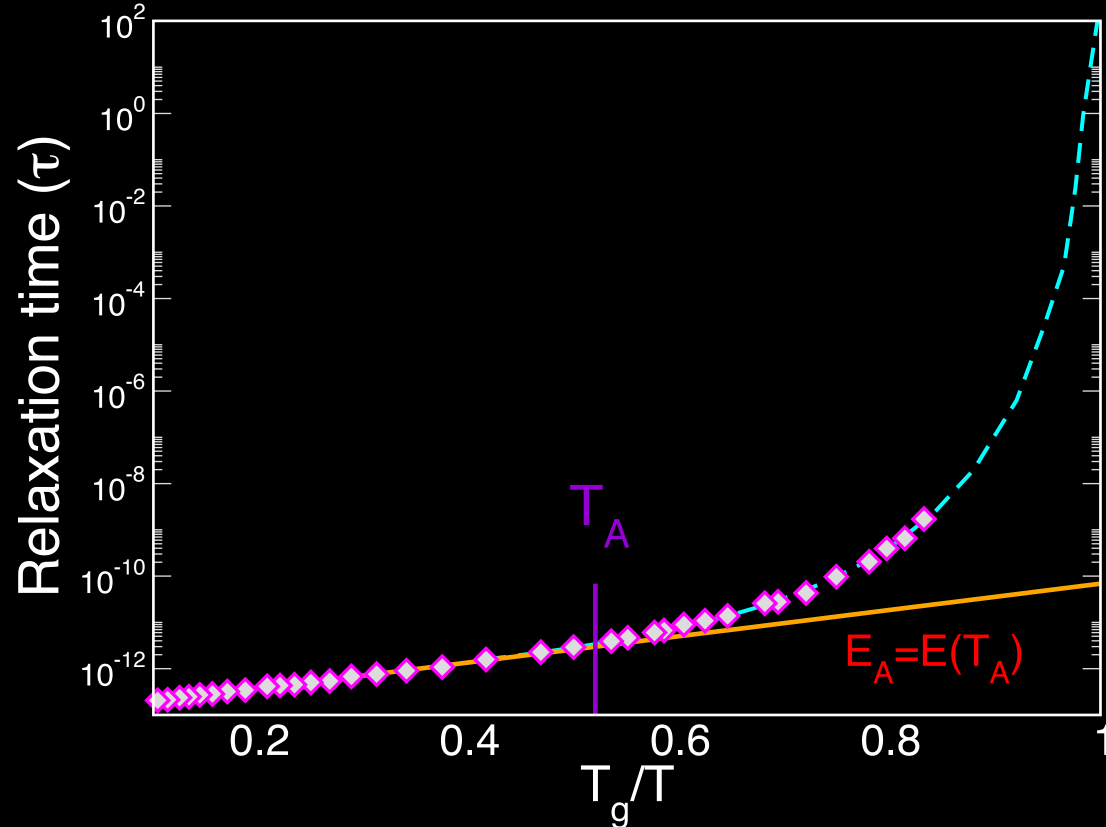
Surface Interactions:

- Attractive
- Non-attractive



Ideal Mono-dispersion of Nanoparticles

NP concentration $\phi < 15\%$



$$\tau = \tau_0 e^{\frac{E(T)}{T}}$$

$$E(T) = T \ln\left(\frac{\tau}{\tau_0}\right)$$

Activation Energy

Relaxation time can be parameterized by the Activation Energy

Can we describe AE in a more detailed way?

Adams and Gibbs Theory

J. Chem. Phys. **43**, 139 (1965)

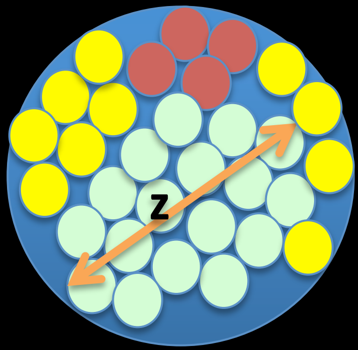
- Assumptions:
  - Relaxation time is an activated process

$$\tau = Ae^{z\frac{\Delta u}{k_B T}}$$

Where the activation energy is extensive in the size of CRR z

  - The size z increases as temperature decreases

Cooperatively Rearranging Regions
(CRR)

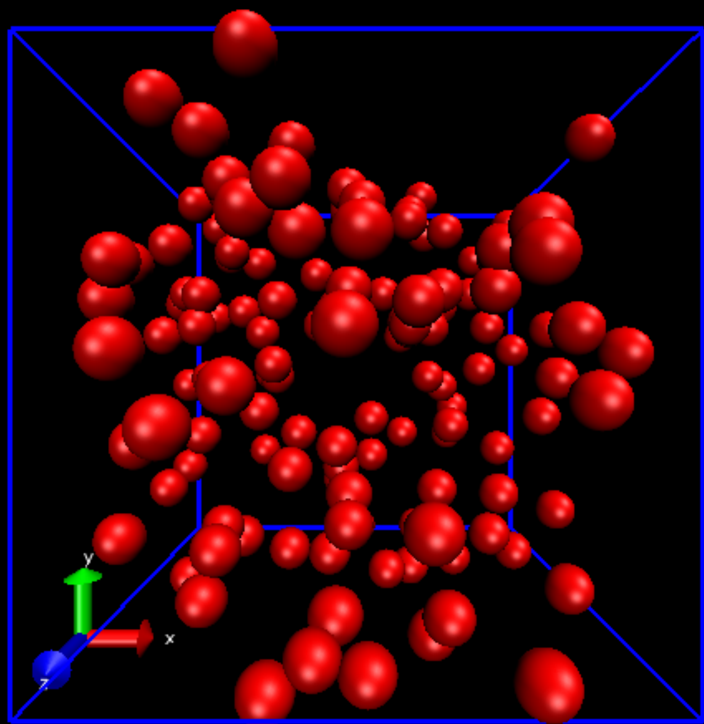


Probability of rearrange ~ size z
Energy Barrier ~ size z

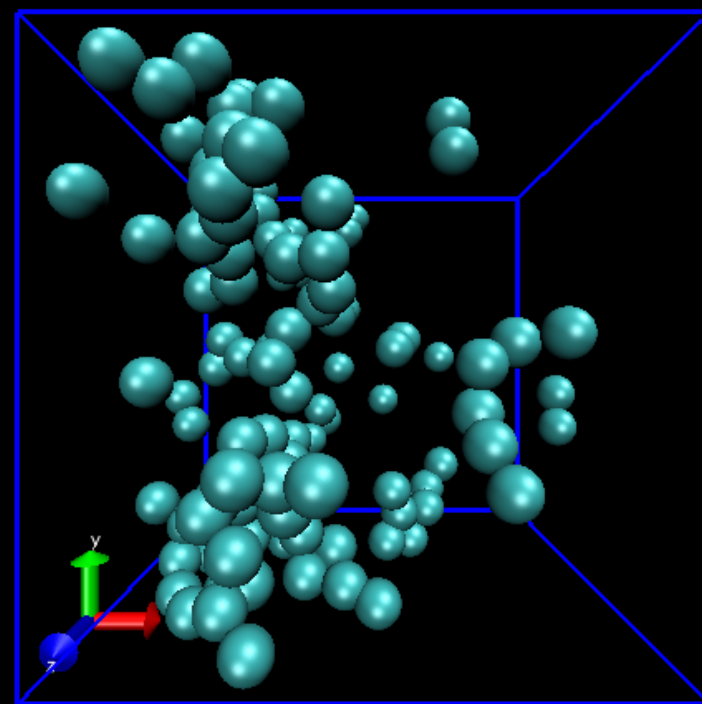
- Flaws:

The shape of CRR is poorly defined!

Cooperatively Rearranging Regions (CRR)



Most mobile particles hi T



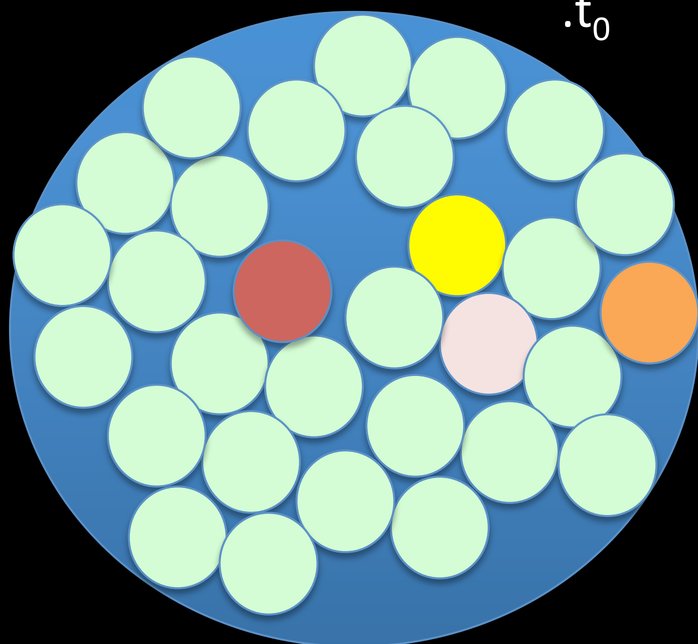
Most mobile particles lo T

Not all of particles move cooperatively

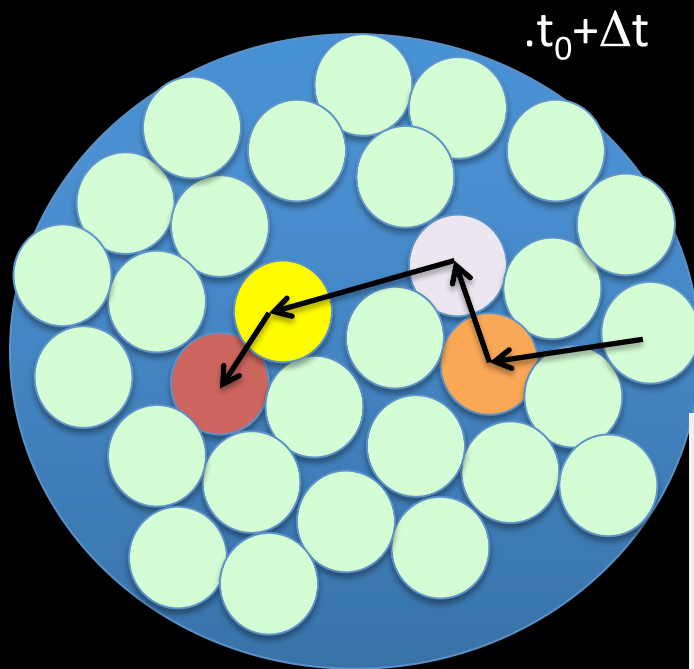
Below T_A : ~~Cluster of most mobile~~ particles increases

Cooperatively Rearranging Regions

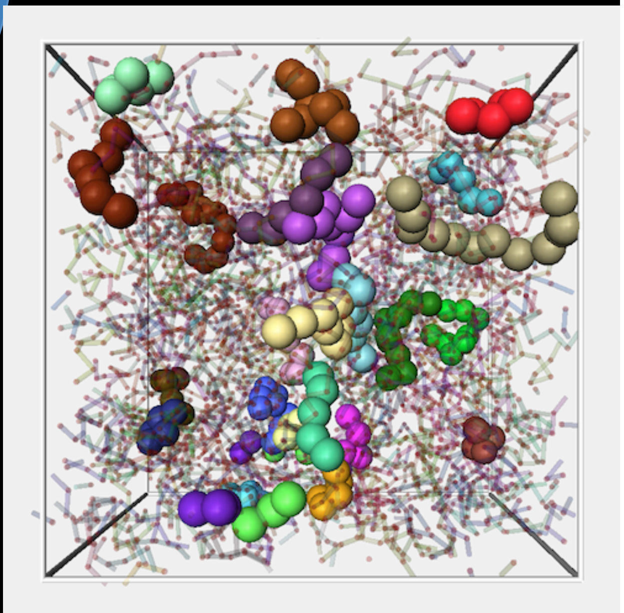
(CRR)



Cooperatively Rearranging Regions (CRR)



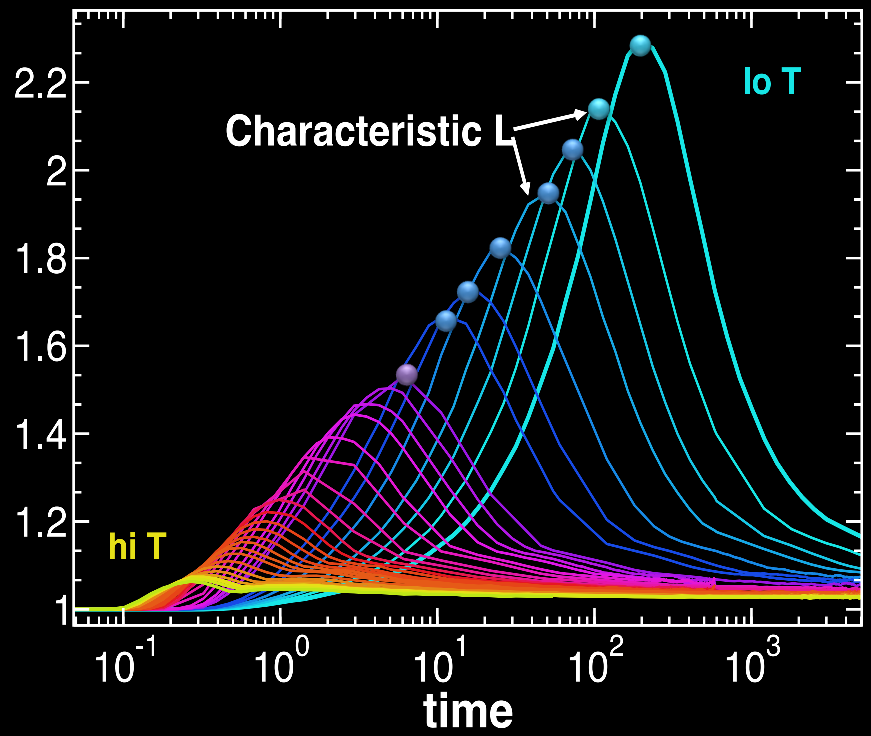
Soft Matter, 2013,9, 241-254

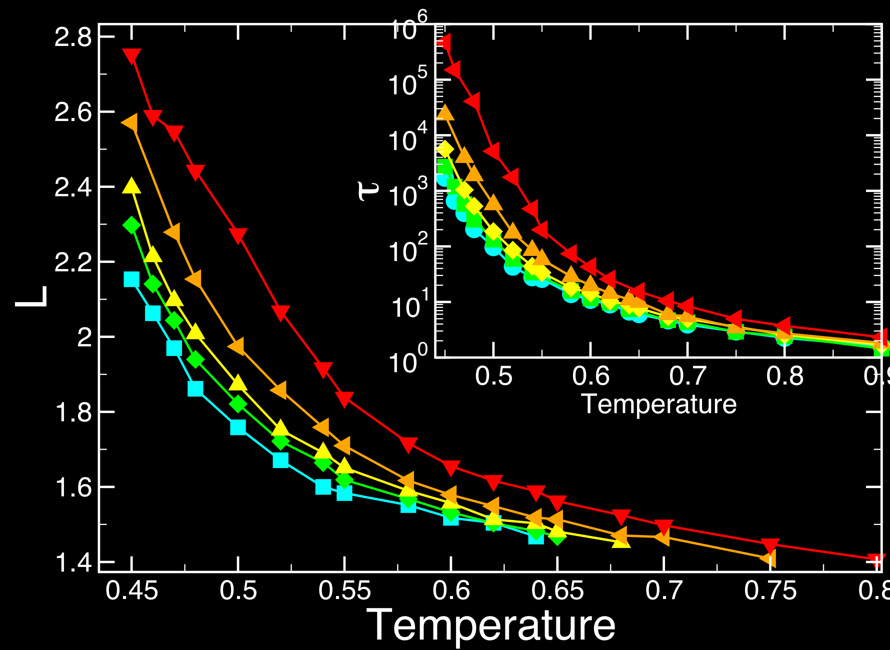


String-like motion
Phys. Rev. Lett. 80, 2338–2341 (1998)

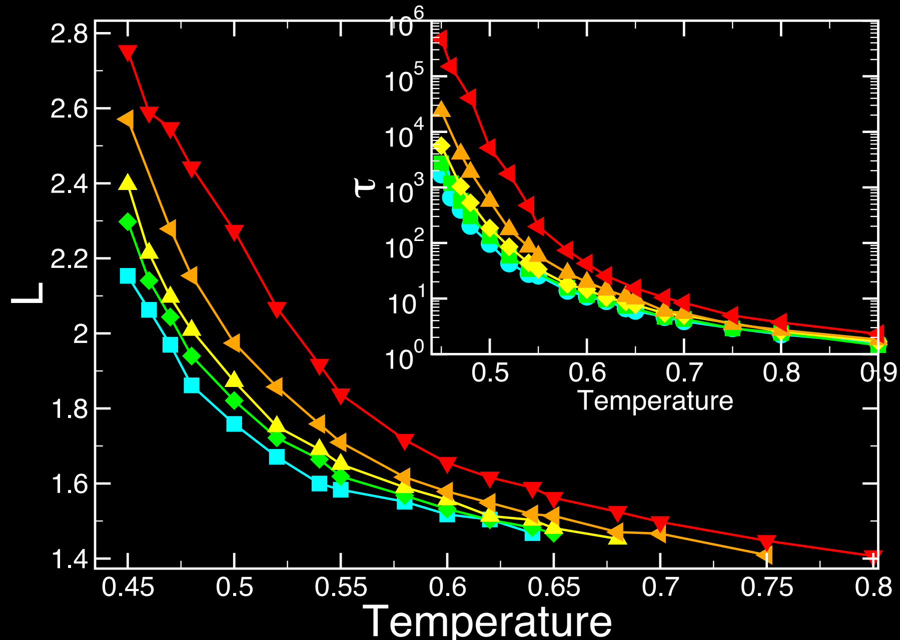
Cooperatively Rearranging Regions

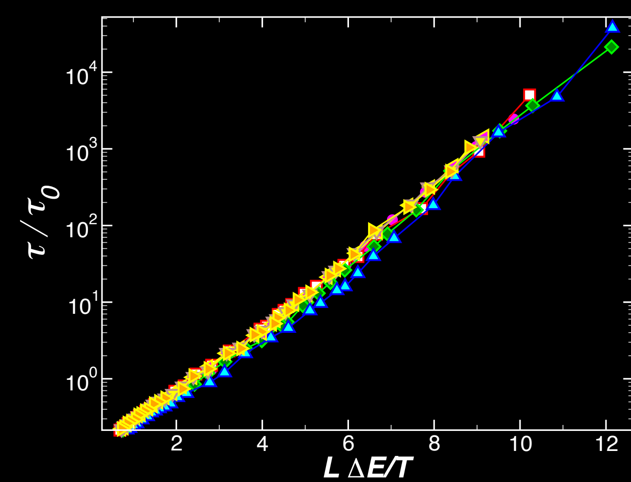
"string like motion"





Cooperatively Rearranging Regions
“string like motion”





References:
Phys. Rev. Lett., 2011,106, 115702
Soft Matter, 2013,9, 241-254

Length of the string like motion can be use as the size of CRR

Goal

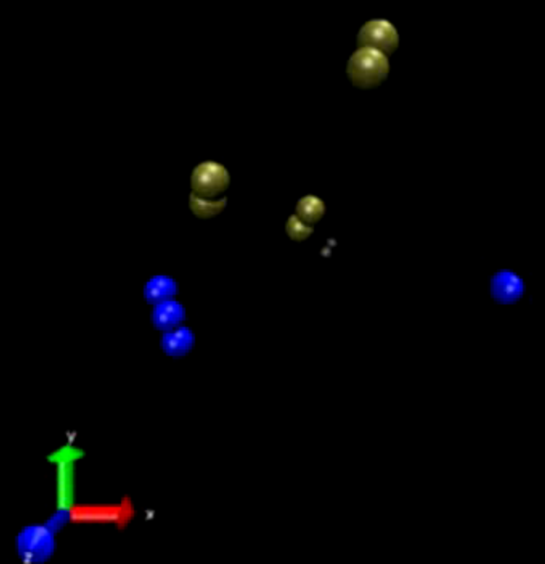
Explain L(T) ⟺ Activation Energy ⟺ Relaxation Time

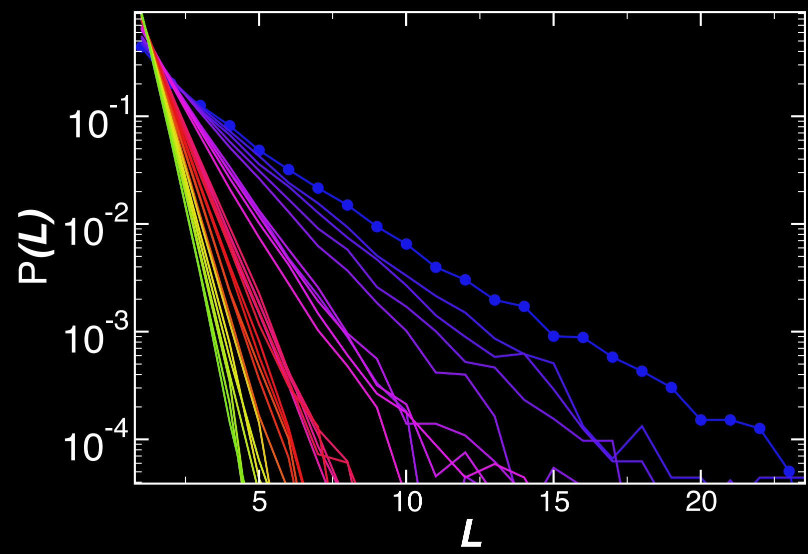
How do we explain the change in L(T)?

What do we know?

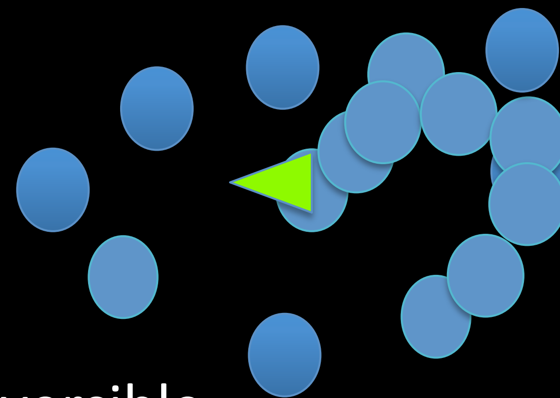
They are dynamical chains

Their lengths have a exponential distribution

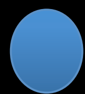
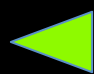
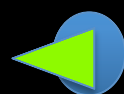




Strings as equilibrium polymers?

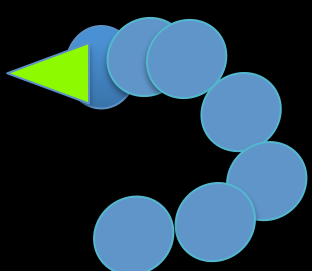


Let's consider:

- Monomers 
- Initiators 
- Monomer and Initiators react irreversible
- Only initiated units  form chains in chemical equilibrium

Equilibrium Polymerization Model

J. Chem. Phys, Vol. 111, No. 15, pp. 7116–7130



$$\langle l(\Phi)\rangle = \frac{1}{1-\Phi+\frac{r}{2}}$$

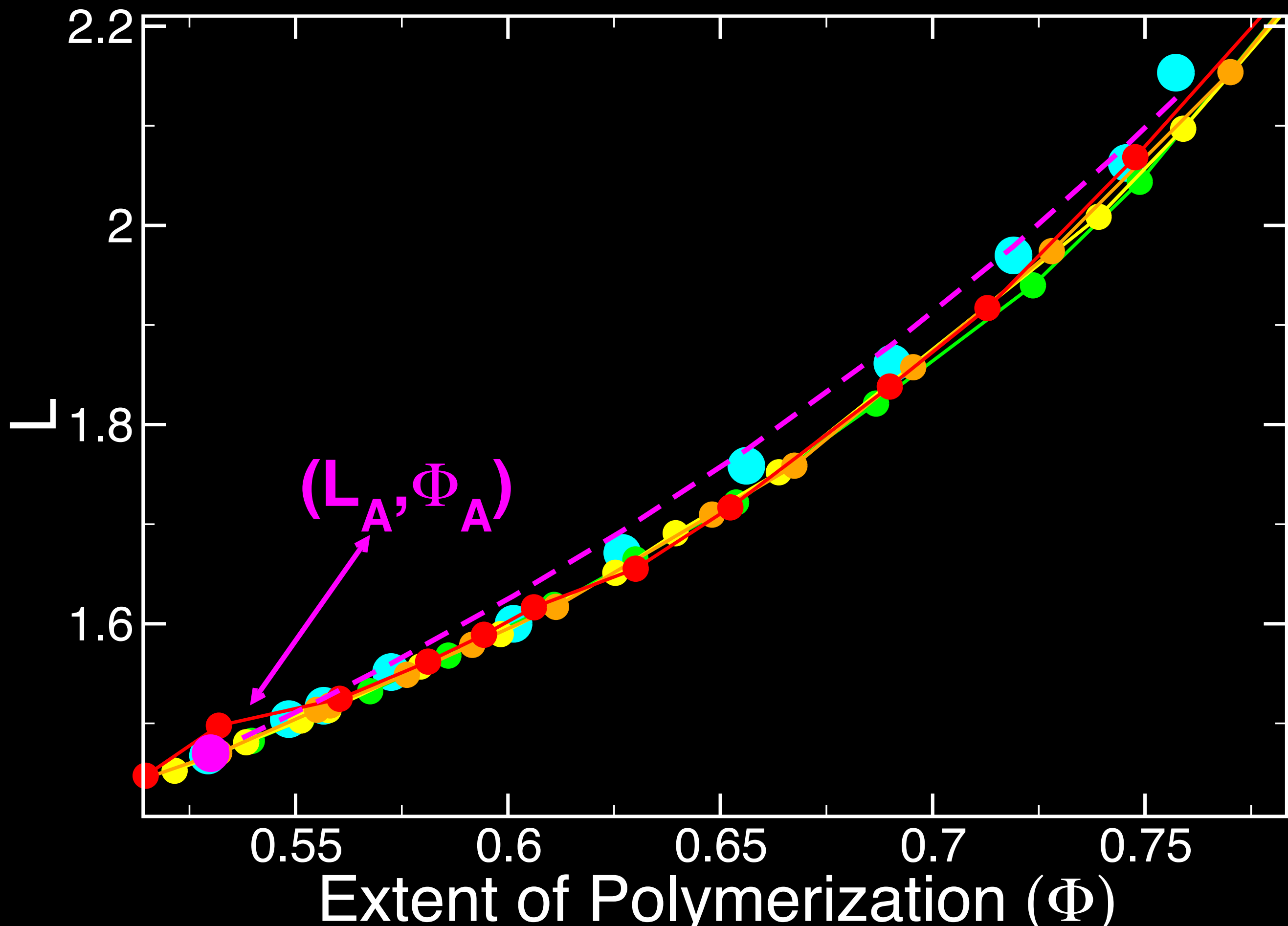
where:

Φ Extent of polymerization

r initiator concentration

l length of the polymer

Strings as an equilibrium polymer?



$$L(\Phi) = \frac{L_A\left(1-\frac{\Phi_A}{2}\right)}{1-\left(\Phi-\frac{\Phi_A}{2}\right)}$$

Pazmino et. al., "Self-Assembly Model for Correlated Motion in a Glass-Forming Polymer Melt" in preparation

String-like motion "only in polymer melts?"

Simulations:

- ✓ Kob-Anderson model *Physics Letters A 350 (2006)*
- ✓ Interfacial dynamics of grain boundaries
- ✓ Interfacial dynamics in nanoparticles
- ✓ Proteins
- ✓ Water *(to be published)*
- ✓ Lipids *(in press)*

Experiments:

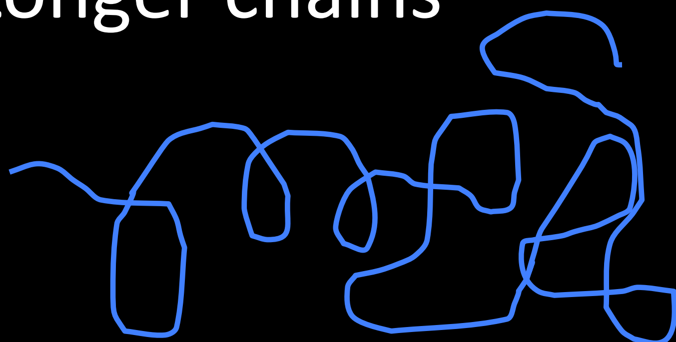
- ✓ Strings have been observed experimentally in the amorphous interfacial region of crystals
- ✓ Particle tracking measurements of colloidal particle

Phys. Rev. Lett. 107 (2011)

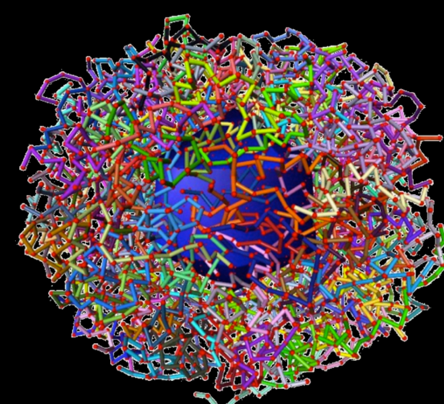
Polymer Dynamics

Computational Demands:

- Lower temperatures
- Longer chains

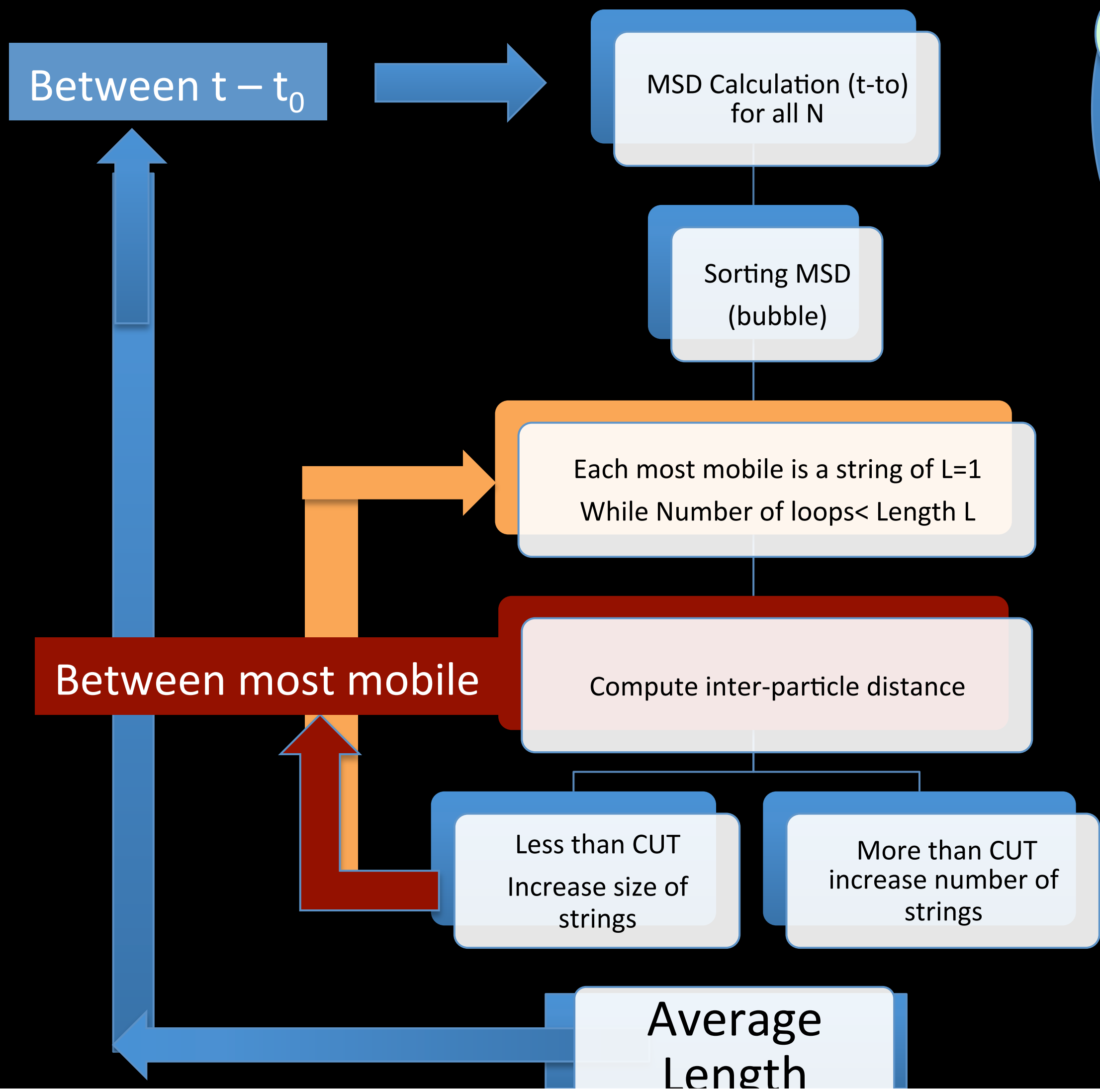


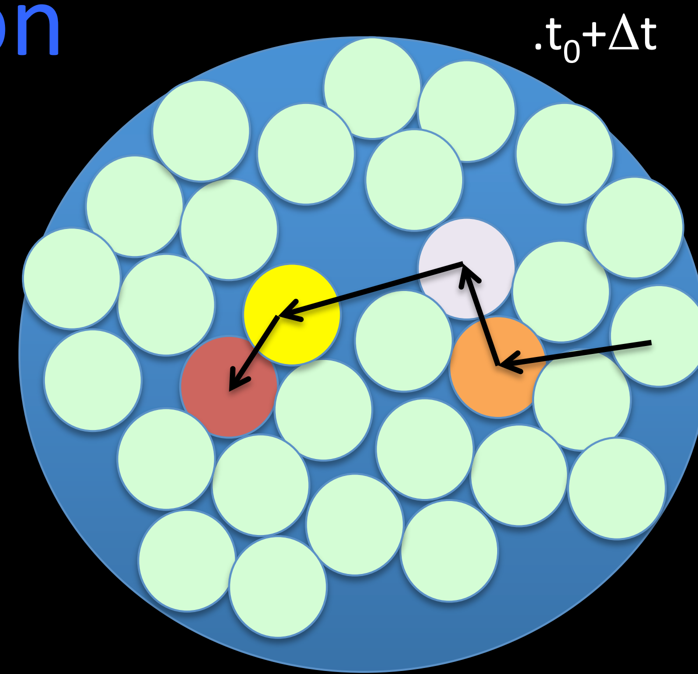
- Polymer nano-composites :
  - Less than 1% vol frac.
  - More than (35,000 particles)



String Length Calculation

Serial Key algorithms





String Length Calculation
GPU Challenges

- Make independent threads (Single MSD particle a thread?)
- Memory Allocation

  First Target systems

Particles	400*175 = 70,000	Time steps	100
	200*700 = 140,000		800

  – Using single float precision

  3*4Bytes*70,000*2=1680MB vs 100 t.s 5.6GB
- How to scale to much bigger systems
- Among many others!!

Possible starting points…

- Single MSD particle a thread?
- Arrange Memory to sort at each Δt
- Flag identification of Inter-particle distance among all, at all t
- Reduction scheme to average most mobile

THANKS!