Molecular Dynamics Simulations and Neutron Scattering: Polymer Melt and Solution Dynamics

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Polymer Dynamics and Relaxation

Richard H. Boyd and Grant D. Smith

Cambridge University Press (2007)

Bill Gate's Opinion

MD simulation = dissimulation

the act of deceiving deception, dissembling, deceit misrepresentation, falsification - a willful perversion of facts

fakery - the act of faking (or the product of faking)

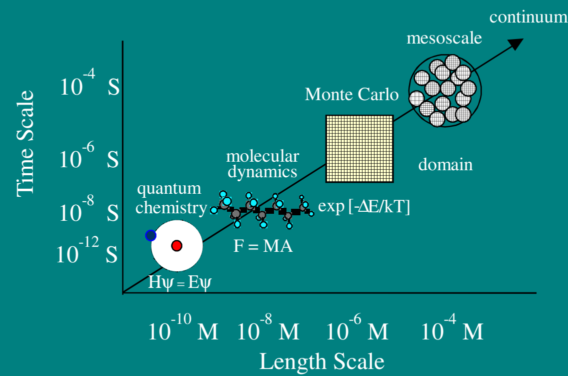
indirection - deceitful action that is not straightforward

Outline

- Molecular Dynamics Simulations
- Force Fields and Force Field Parametrization
- MD Simulations and Neutrons: The Connection
- Local Melt Dynamics: Polyethylene
- Local Solution Dynamics: PEO/water Solutions
- Chain Dynamics: Poly(butadiene)
- Glass and Sub-glass Processes: Poly(butadiene)

MD Background:

Scales of Modeling



MD Background:

Classical Equations of Motion

NVE

H = K + V = total energy = constant

$$K = \sum_i \frac{1}{2} m_i v_i^2 \, , \; V = \sum_{i,j} U(r_{ij})$$

$$\frac{dr_j}{dt} = \frac{\partial H}{\partial p_j} = v_j \, , \; \frac{dp_j}{dt} = -\frac{\partial H}{\partial r_j} = -\frac{\partial V}{\partial r_j} = F_j$$

NVT

$H = K + V + K_s + V_s$ = constant

$K_s = \frac{1}{2} Q p_s^2$

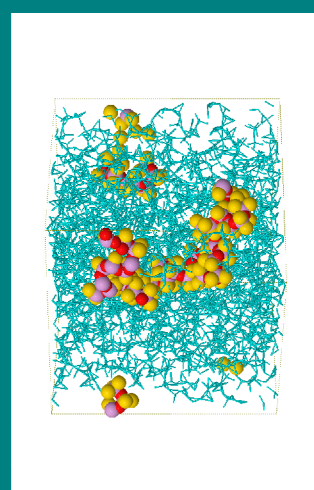
$V_s = (f + 1) k_B T \ln(s)$

p_s = conjugate momentum of thermostat

Q = conjugate mass

s = generalized coordinate of the thermostat

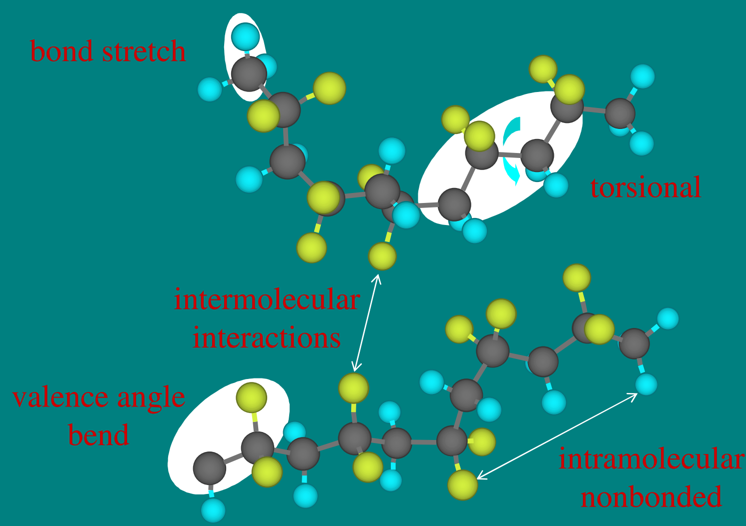
f = number of degrees of freedom



5000 atoms, 4 nm

Force fields

Intramolecular and Intermolecular Interactions



$$V(\vec{r}) = V^{NB}(\vec{r}) + \sum_{bonds} V^{BOND}(r_{ij}) + \sum_{bends} V^{BEND}(\theta_{ijk}) + \sum_{dihedrals} V^{TORS}(\varphi_{ijkl})$$

$$V^{DIS-REP}(r_{ij}) = \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

$$V^{NB}(\vec{r}) = V^{POL}(\vec{r}) + \frac{1}{2}\sum_{i,j=1}^{N} A_{ij}\exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

Force fields: Where do they come from?

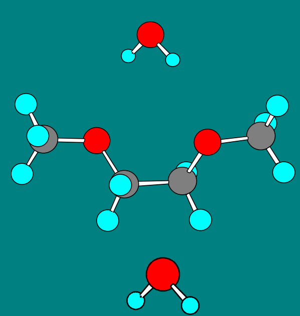
“Generic” (e.g., Dreiding):
Roughly describe a wide range of materials, not parameterized or validated

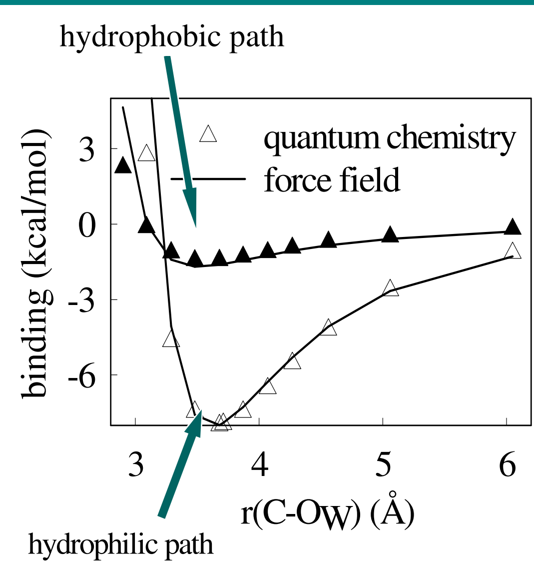
“ Trained” (e.g., AMBER, COMPASS, CHARMM, OPLS)
Parameterized to reproduce the properties of a broad set of molecules such as small organics, peptides or amino acids

“Specialized” (e.g., Atomistic Polarizable Potential for Liquids, Electrolytes and Polymers (APPLE&P))
Carefully parameterized and validated potentials designed to reproduce properties of a small class of specific molecules

Force Field Parametrization:

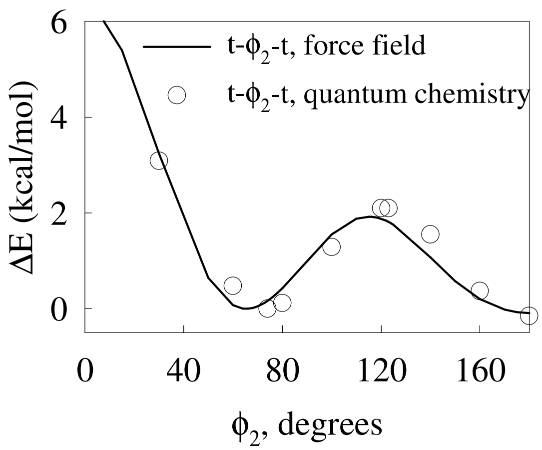
Intermolecular Interactions

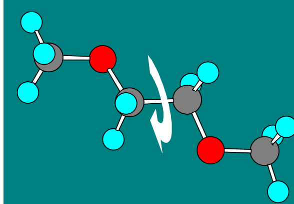




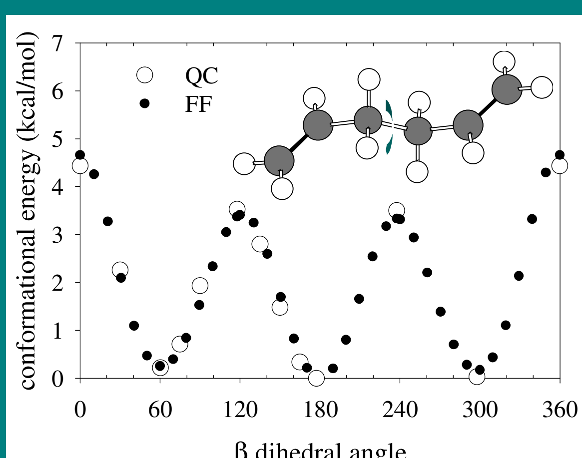
Force Field Parametrization:

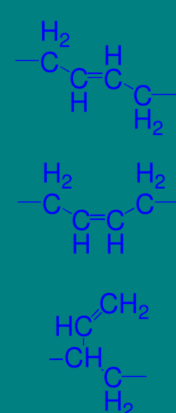
Intramolecular Interactions





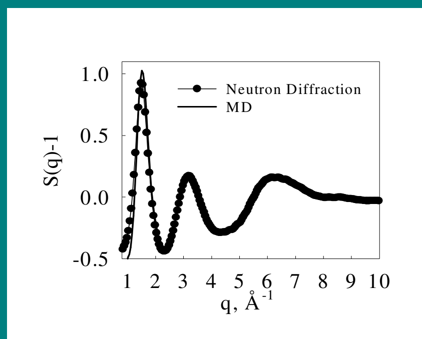
Poly(butadiene)

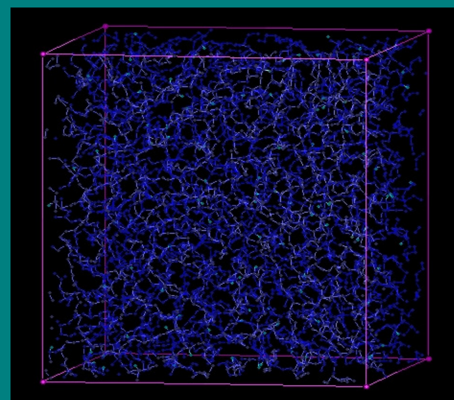




Force Field Parametrization:

Validation: Static Structure Factor

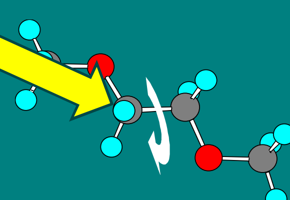


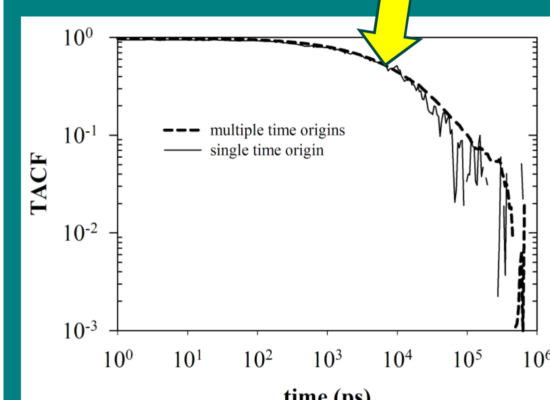


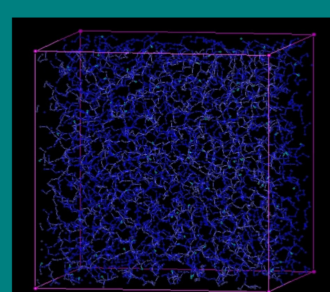
Force Field Parametrization:

Validation: Time Correlation Functions

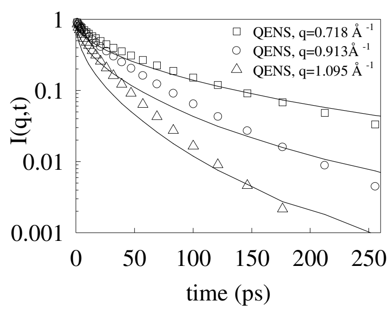
$$TACF(t)=\frac{\langle|\theta(t)||\theta(0)|\rangle-\langle|\theta(0)|\rangle^2}{\langle|\theta(0)|^2\rangle-\langle|\theta(0)|\rangle^2}$$

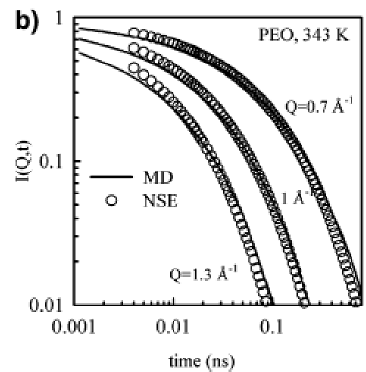






Force Field Parametrization:
Validation: Dynamic Structure Factor for PEO Melt





Incoherent Dynamic Structure Factor, QENS and MD

Coherent Dynamic Structure Factor, NSE and MD

MD-Neutron Connection: Dynamic Structure Factors

Simulation yields intermediate dynamic structure factors (time domain) directly

Coherent scattering

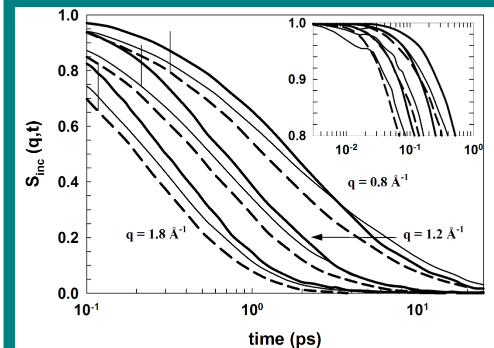
$$s_{coh}(q,t)=\frac{1}{N}<\sum_{j,k}^{N}\exp i\vec{q}\bullet(r_k(t)-\vec{r}_j(0))>=<\sum_{j,k}^{N}\sin q\,|r_k(t)-\vec{r}_j(0)|\,/\,q\,|r_k(t)-\vec{r}_j(0)|\,>$$

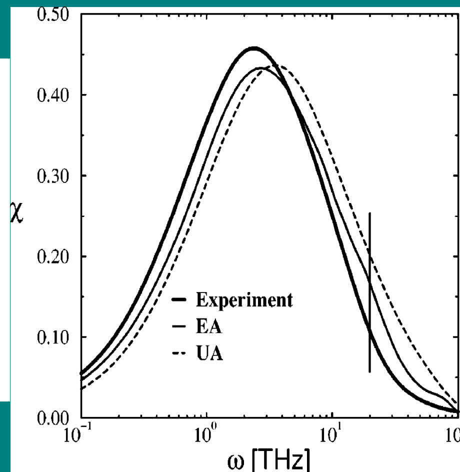
Incoherent scattering

$$s_{inc}(q,t)=\frac{1}{N}<\sum_{k}^{N}\exp i\vec{q}\bullet(\vec{r}_k(t)-\vec{r}_k(0))>=<\sum_{k}^{N}\sin q\,|\vec{r}_k(t)-\vec{r}_k(0)|\,/\,q\,|\vec{r}_k(t)-\vec{r}_k(0)|\,>$$

- Simulation time scales from femtoseconds to microseconds
- Experimental time scales from picoseconds to nanoseconds
- A Fourier-Laplace to frequency domain (or an inverse transform of QENS data) is required for comparison
- Direct comparisons can be made with NSE data

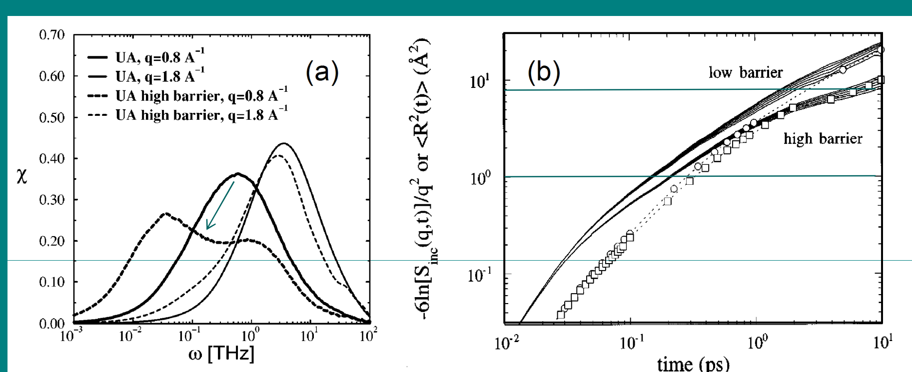
Example: Local Dynamics is a Polyethylene Melt:





MD simulations provide data over a wider range of time
MD simulations are in good agreement with QENS

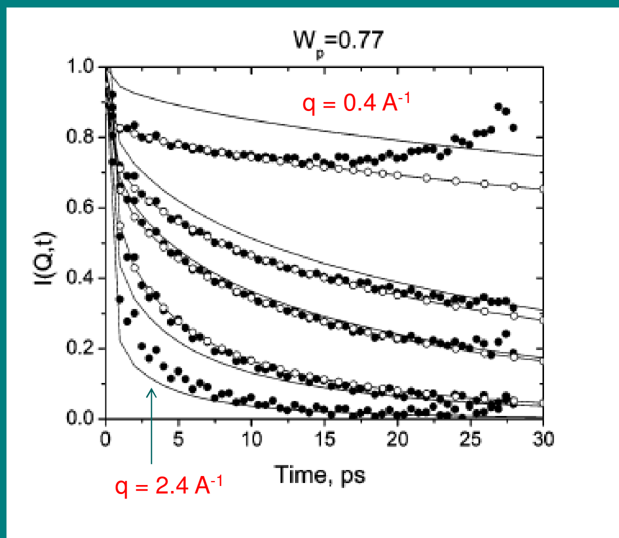
LibLibrations or Conformational Transitions?



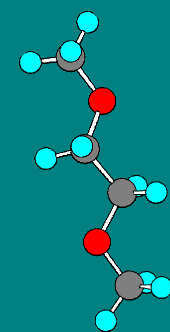
$$s_{inc}(q,t) = \exp\left[-\frac{q^2 < \Delta r_H^2(t) >}{6}\right]$$

PEO/Water Solutions: Local Dynamics

Polymer Dynamics

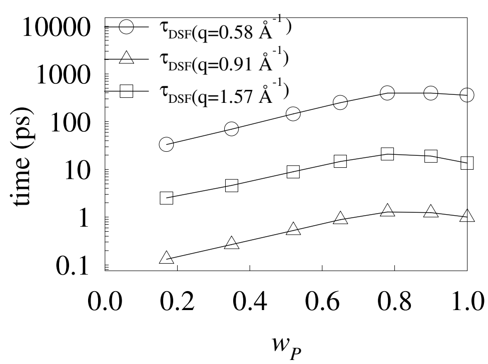


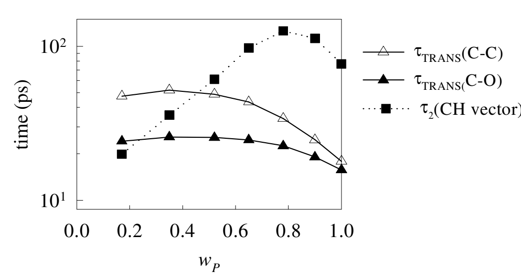
Mw = 500



Low molecular weight PEO exhibits a minimum in local dynamics with concentration

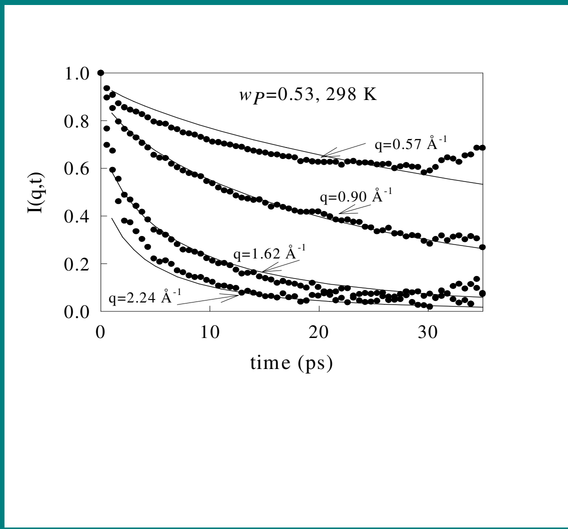
This is due to slowing conformational dynamics and increasing translational/rotational dynamics with dilution



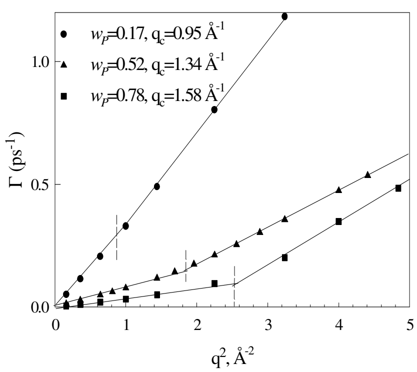


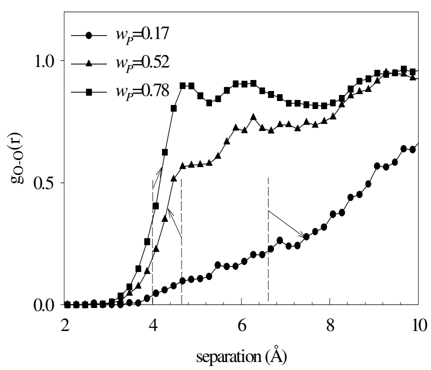
PEO/Water Solutions: Local Dynamics

Water Dynamics



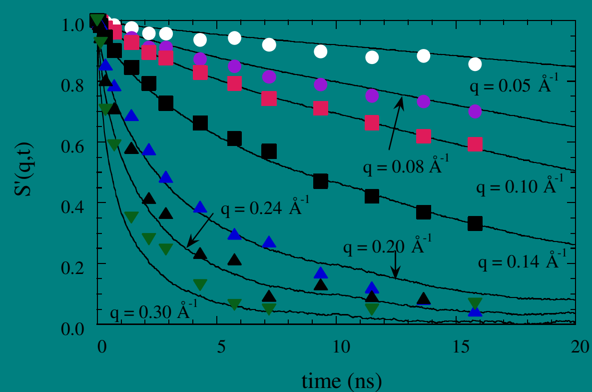
Water quasi-confinement

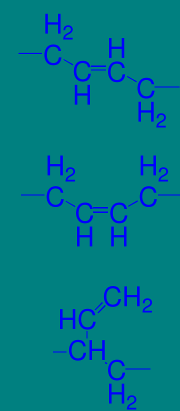




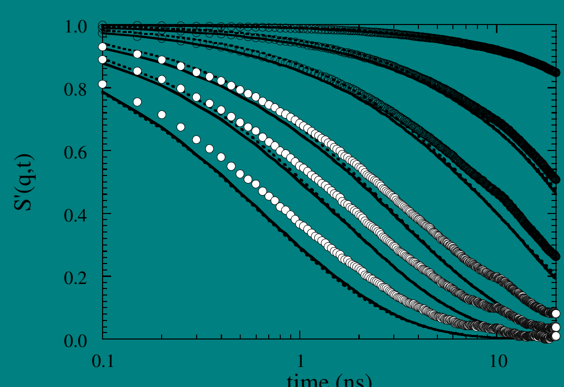
Large Scale Dynamics: Single chain coherent dynamic structure factor for PBD (353 K)

$$S'(q,t) = S(q,t)/S(q) = \sum_{(m,n)} \langle \sin[qR_{mn}(t)]/qR_{mn}(t) \rangle \,/\, \sum_{(m,n)} \langle \sin[qR_{mn}(0)]/qR_{mn}(0) \rangle$$





Why does the Rouse model provide such a poor description of S(q,t)?

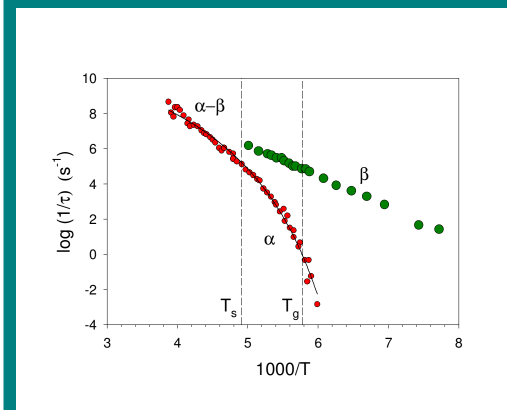


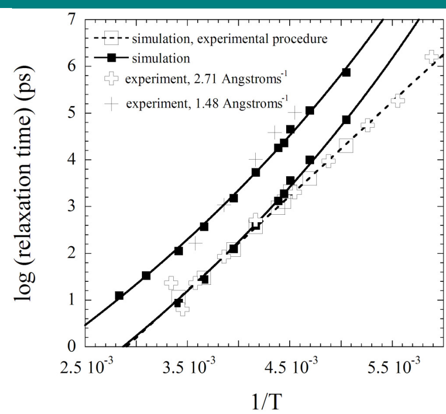
Chain stiffness?

Internal viscosity?

Non-Gaussian displacements?

Can dynamic neutron scattering tell us about the bifurcation of the glass and sub-glass processes?





MD Simulations and Dynamic Neutron Scattering in Polymers

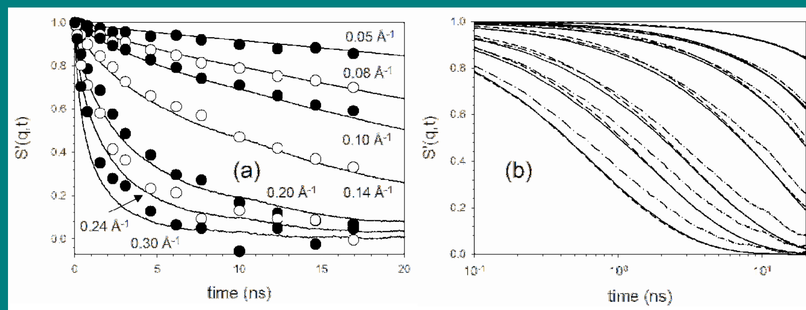
--Natural partners (overlapping time and length scales)

--DNS experiments are important for validation of simulations

--Simulations can direct experiment

--Simulations can help provide mechanistic insight into experimental results

--Simulations can help provide sanity checks for conclusions based on limited (but expanding!) DNS capabilities



0.05 Å-1
0.08 Å-1
0.10 Å-1
0.20 Å-1
0.14 Å-1
0.24 Å-1
0.30 Å-1
(a)
(b)
S'(q,t)
time (ns)