Neutron Scattering and Molecular Simulations: Synergistic Probes of Nanoscale Structure and Dynamics in Complex Polymer-based Materials

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Outline

- Methods
- Examples of Synergism
  - polymer structure
  - polymer dynamics
- Polymer-nanoparticle Composites (PNPCs)
- Self-association of Polymer-grafted Nanoparticles
- Conclusions

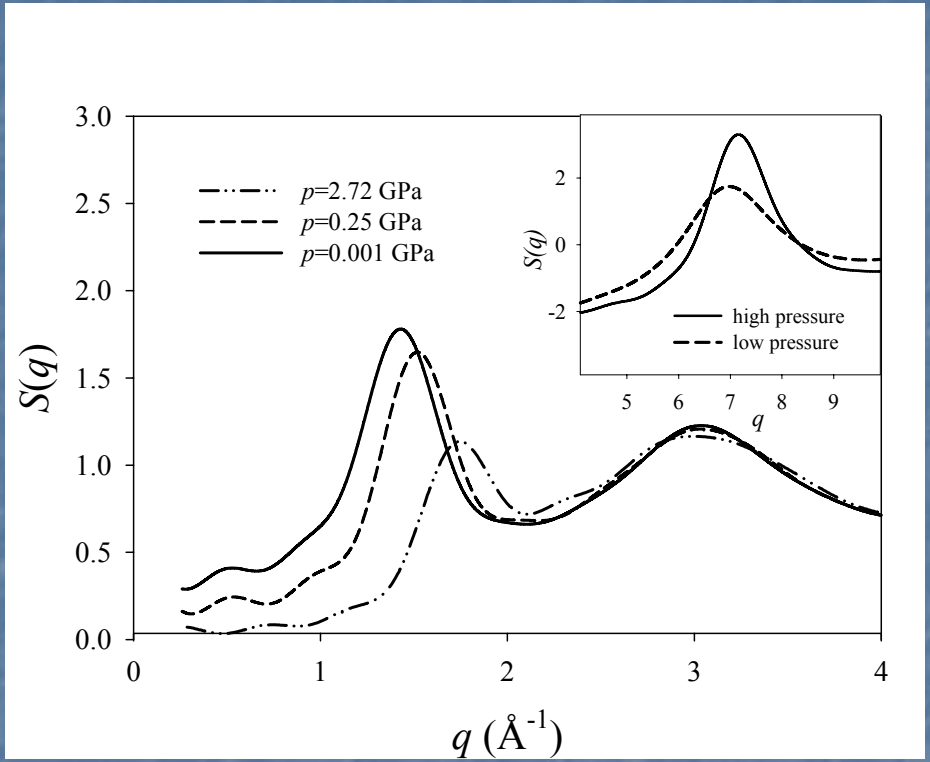
Methods

- Static neutron scattering to determine the static structure factor S(q) with emphasis on nanometer-scale structure

- Dynamic neutron scattering to determine the coherent intermediate dynamic structure factor S(q,t) (NSE) or the incoherent intermediate dynamic structure factor I(q,t) (QENS/FT)

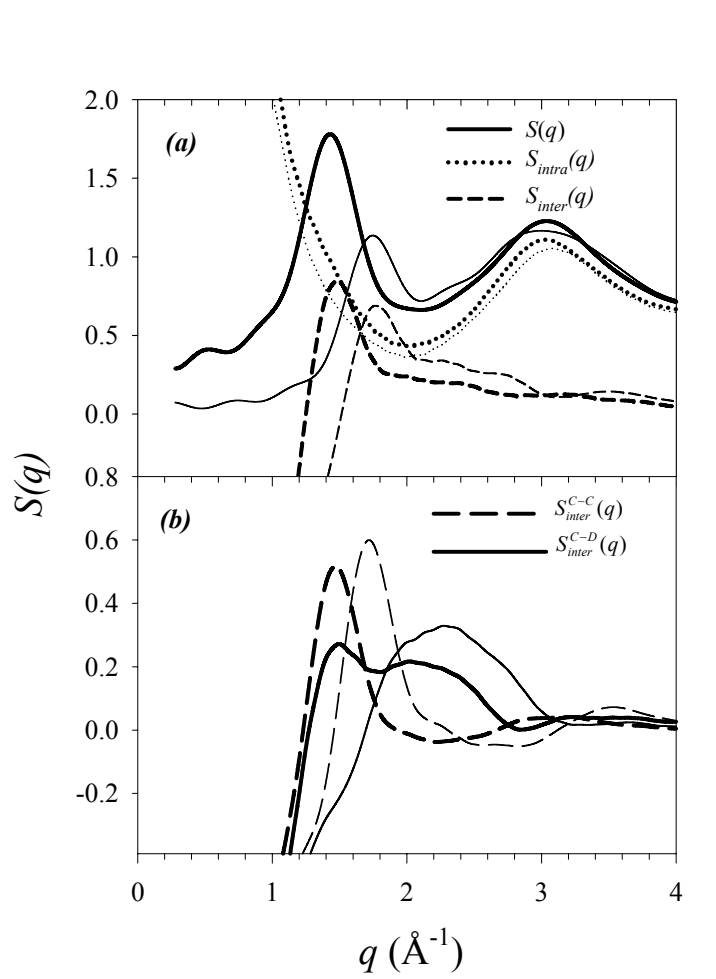
- Molecular dynamics simulations utilizing atomistic models with quantum-chemistry based potentials or multiscale simulations based upon atomistic simulations

Nanoscale Structure of 1,4-PBD Under High Pressure



- Recent neutron scattering studies of polymer melts have shown apparently anomalous behavior in the response of polymer melts to high pressure at the nanometer scale

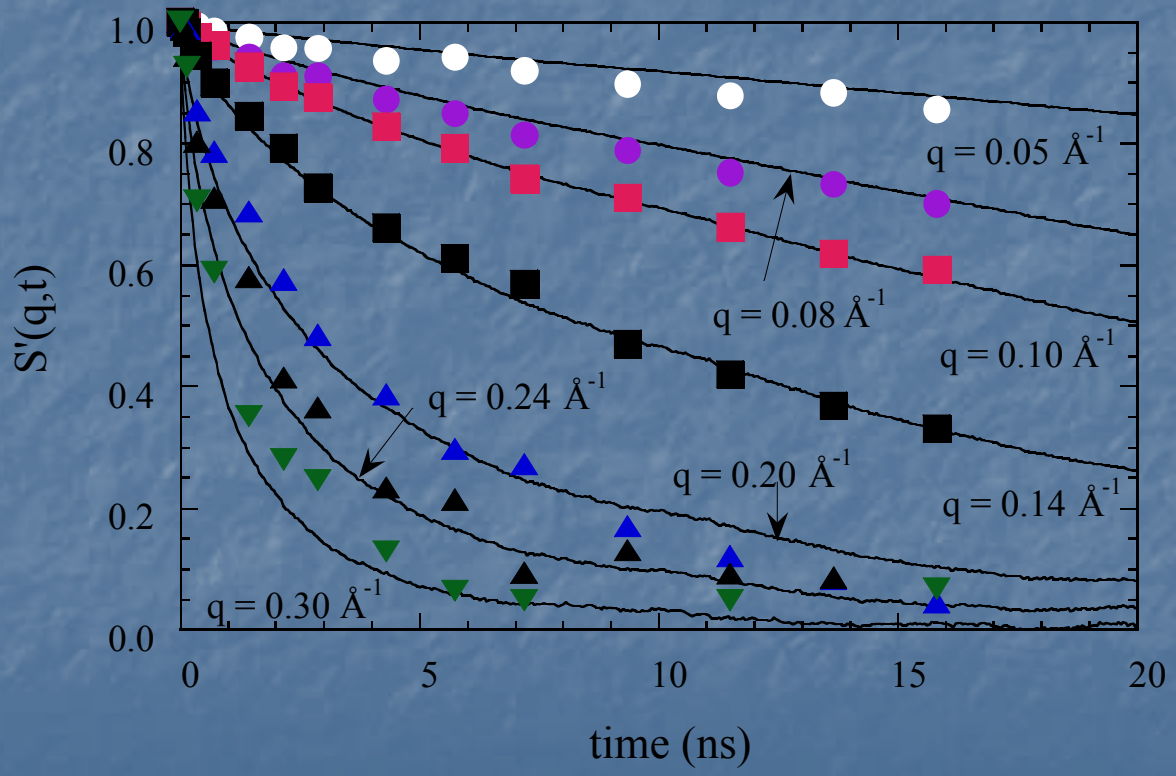
Nanoscale Structure of 1,4-PBD under High Pressure



- Atomistic MD simulations reproduce experimental behavior
- Scattering from the polymer backbone exhibits the expected trends
- Simulations reveal that experimentally observed behavior can be associated with C-D correlations

Single-Chain Coherent Dynamic Structure Factor for PBD (353 K)

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



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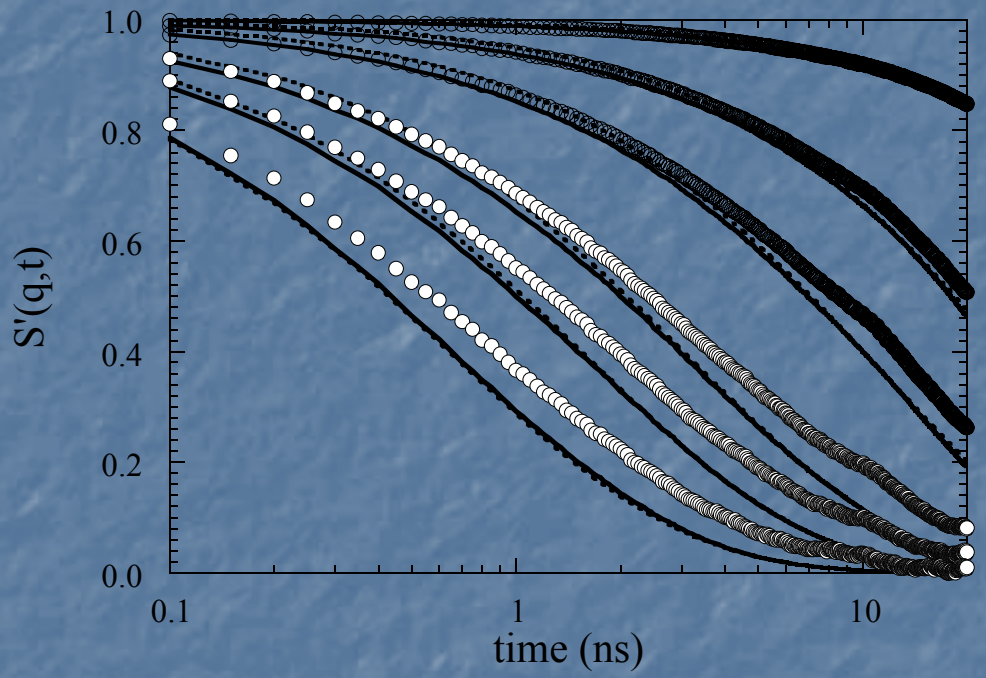
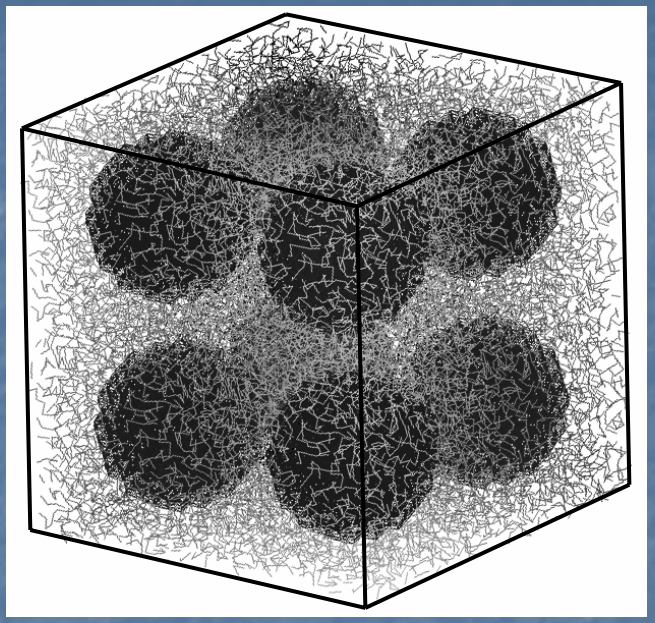
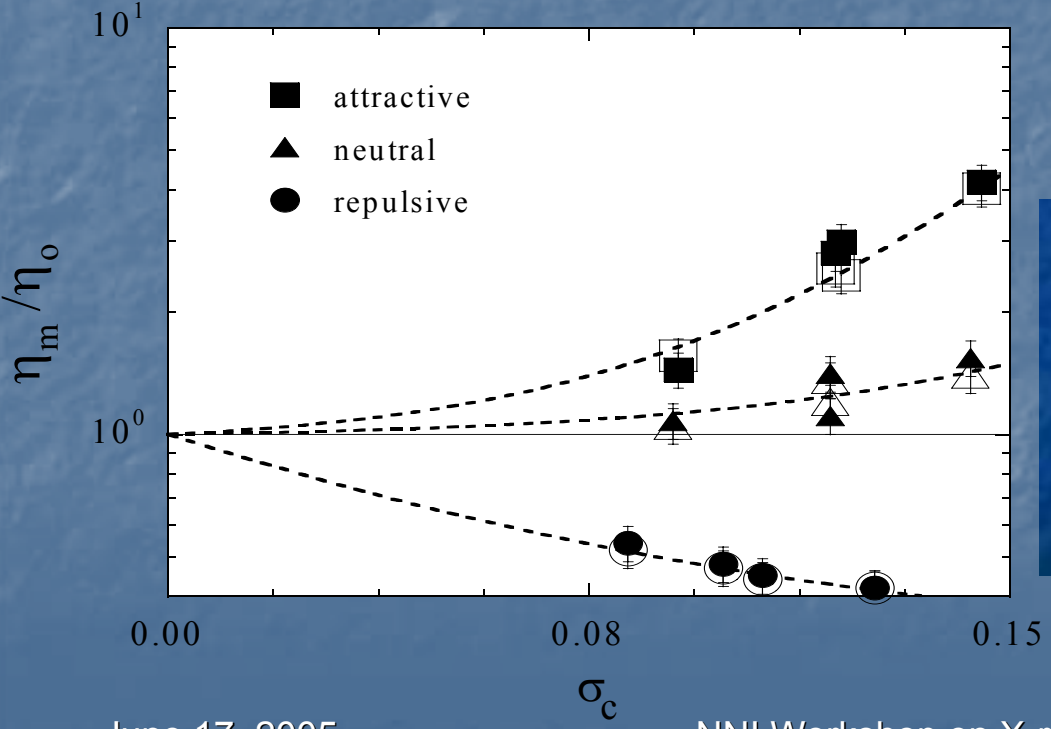


- Why does the Rouse model work so poorly?
  - Chain stiffness
  - Internal viscosity
- Simulations reveal that the discrepancy in S'(q,t) and Rouse predictions are the result of
  - non-Gaussian distributed monomer displacements
  - much of the non-Gaussian behavior results from intermolecular correlations

Polymer-nanoparticle Composites

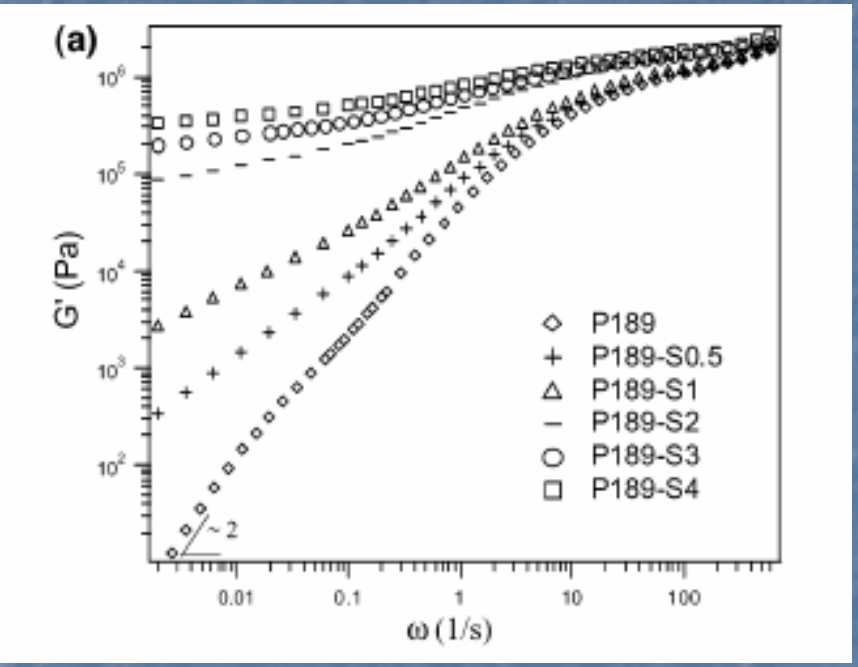
- In order to efficiently design and fabricate PNPCs with desired properties, we must have the ability to predict their structure and response





- maximize interfacial area
- optimize structure
- "externally" control structure

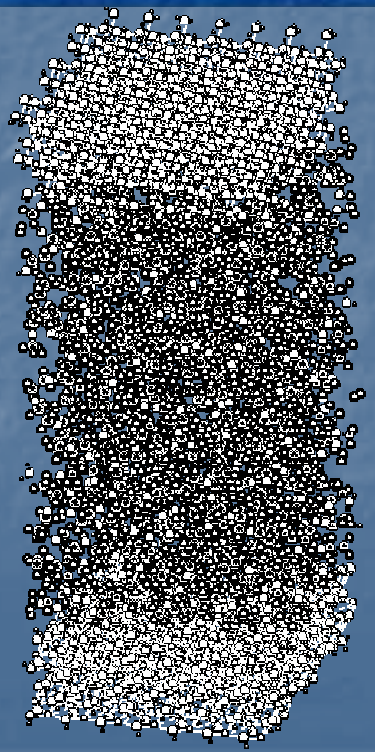
Polymer-nanoparticle Composites

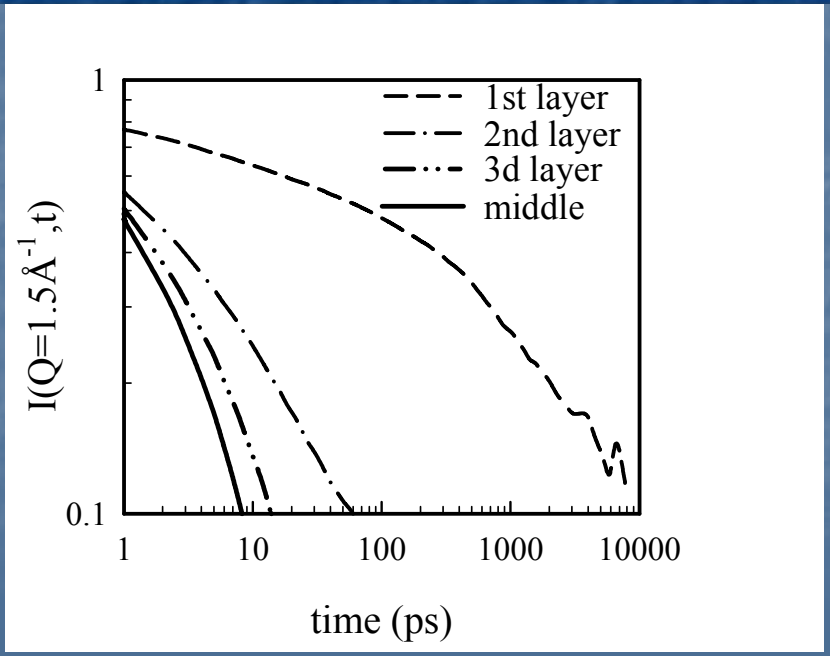


- More dramatic influence on mechanical properties at low loading fractions have been seen experimentally
- The mechanism is unclear
  - Percolation of particles
  - Slowed polymer dynamics
  - Bridging of particles by the polymer
- QENS studies reveal slowing of polymer motion in PNPC's, but it is not dramatic

Polymer-nanoparticle Composites

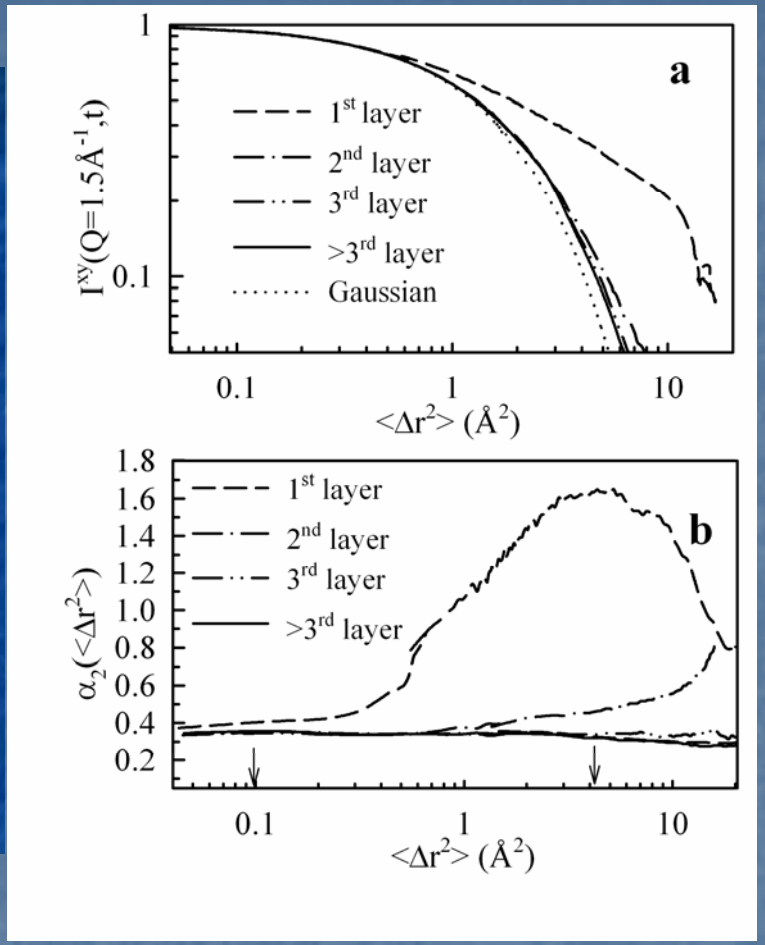
- We have performed simulations studies of 10 chains of PEO (M_w=2380) sandwiched between TiO_2 surfaces of anatase crystal
- Overall slowing of polymer dynamics is consistent with QENS studies
- A dramatic slowing of polymer dynamics is seen for the first layer of polymer, i.e., polymer adsorbed to the surface





Polymer-nanoparticle Composites

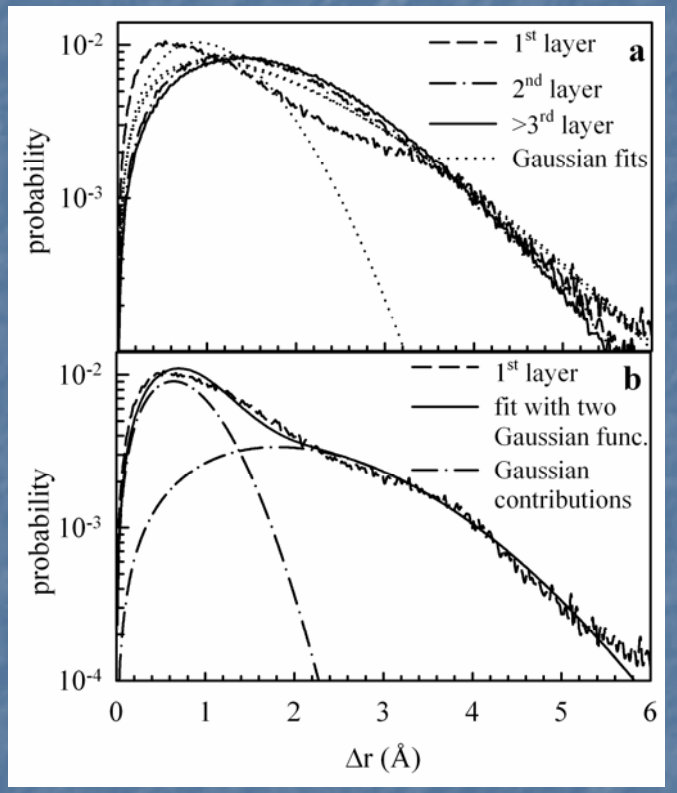
- Slowing in the decay of I(q,t) in for the first layer of polymer is due to
  - Intrinsically slower motion
  - Highly heterogeneous (non-Gaussian) motion along the surface)



Polymer-nanoparticle Composites

- Both the intrinsic slowing and heterogeneity depend upon the strength of interaction between the surface and polymer and the structure of the surface

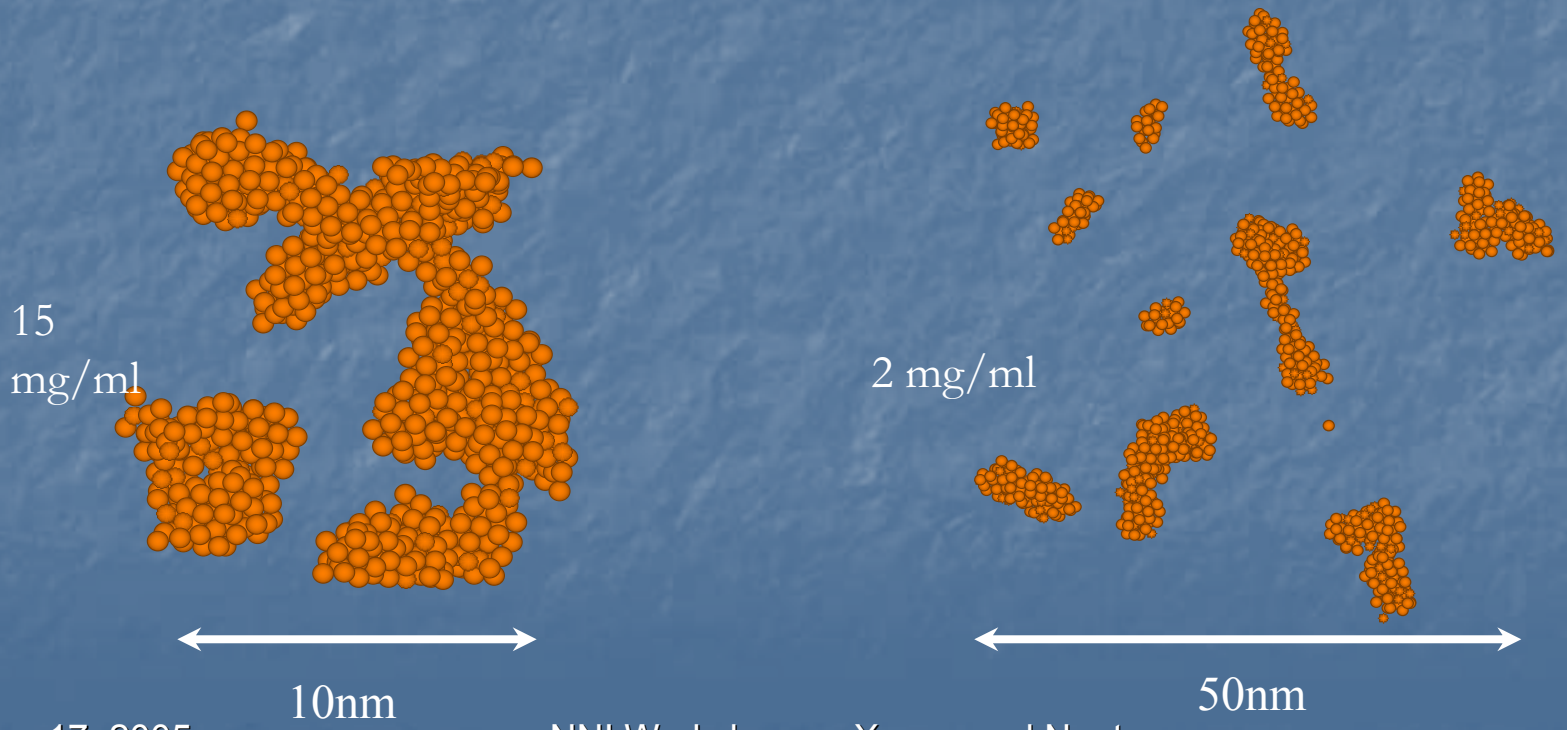
- Hetergeniety largely reflects motion along the surface induced by the structure of the surface



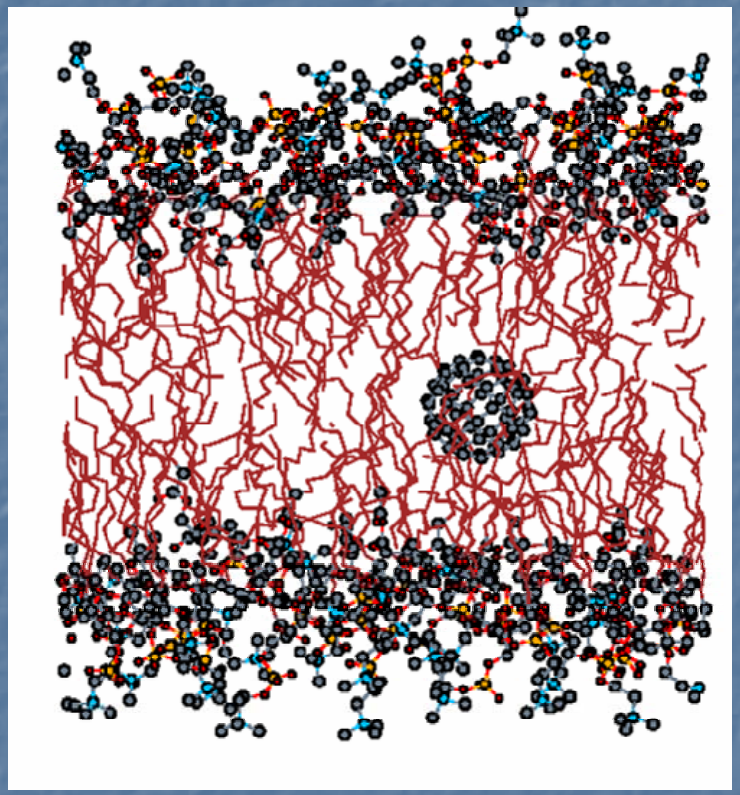
Nanoparticle Self-association

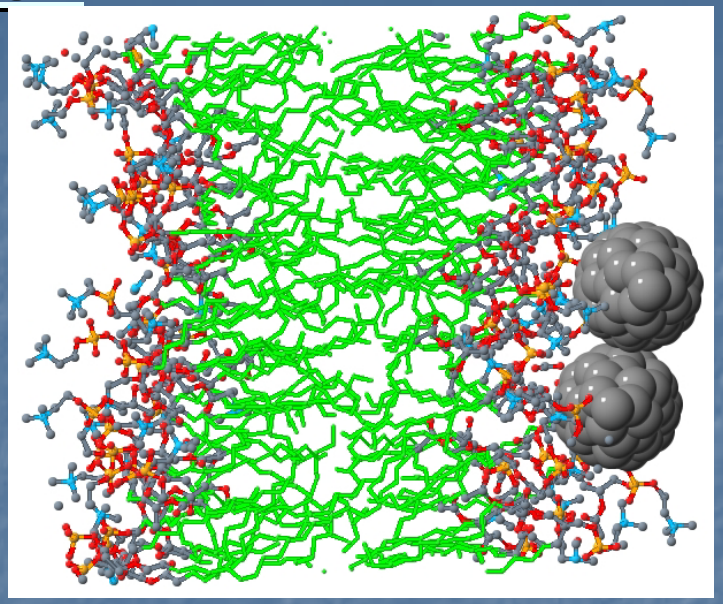
- Interpretation of static and dynamic structure factors in nanomaterials is complex because of the multiplicity of correlations that can be present on the nanometer length scale

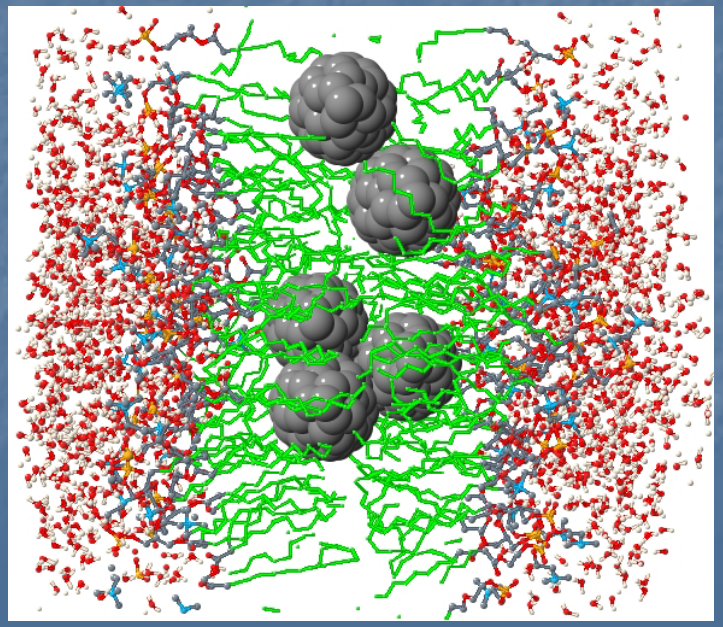
- This is illustrated clearly in efforts to understand the aggregation of C_{60} fullerenes in aqueous solution: Time dependent, model independent



Nanoparticle Self-association

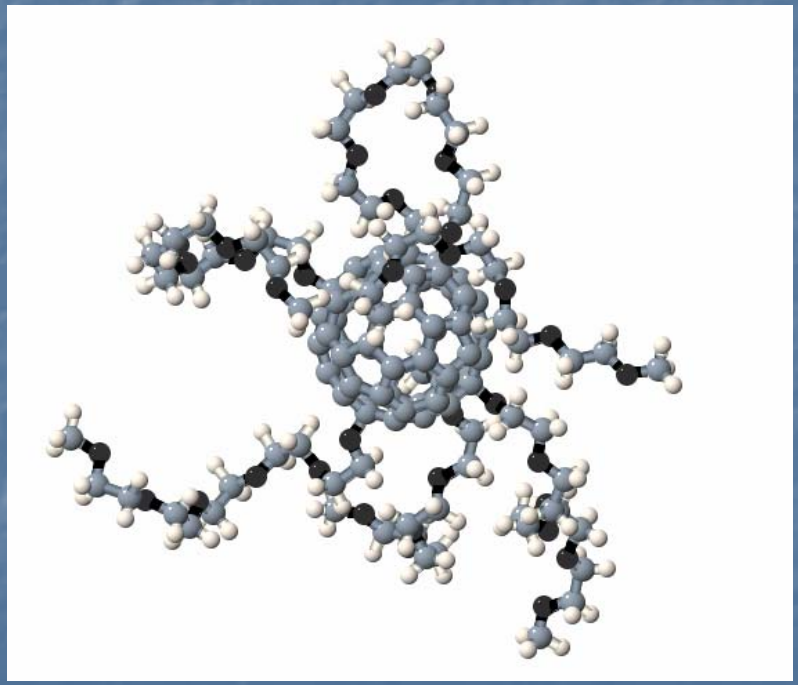






Nanoparticle Self-association

- Conversely, neutron scattering can play a critical role in confirming predictions of molecular simulations



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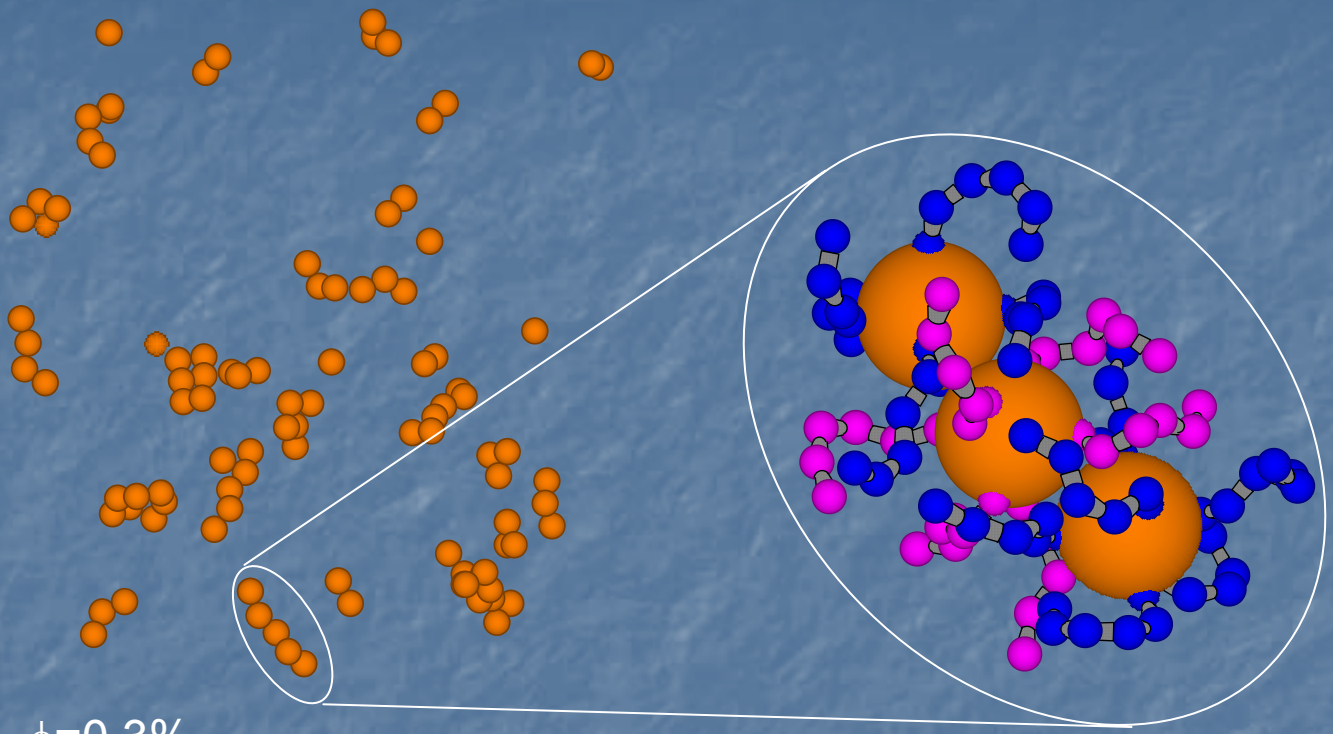
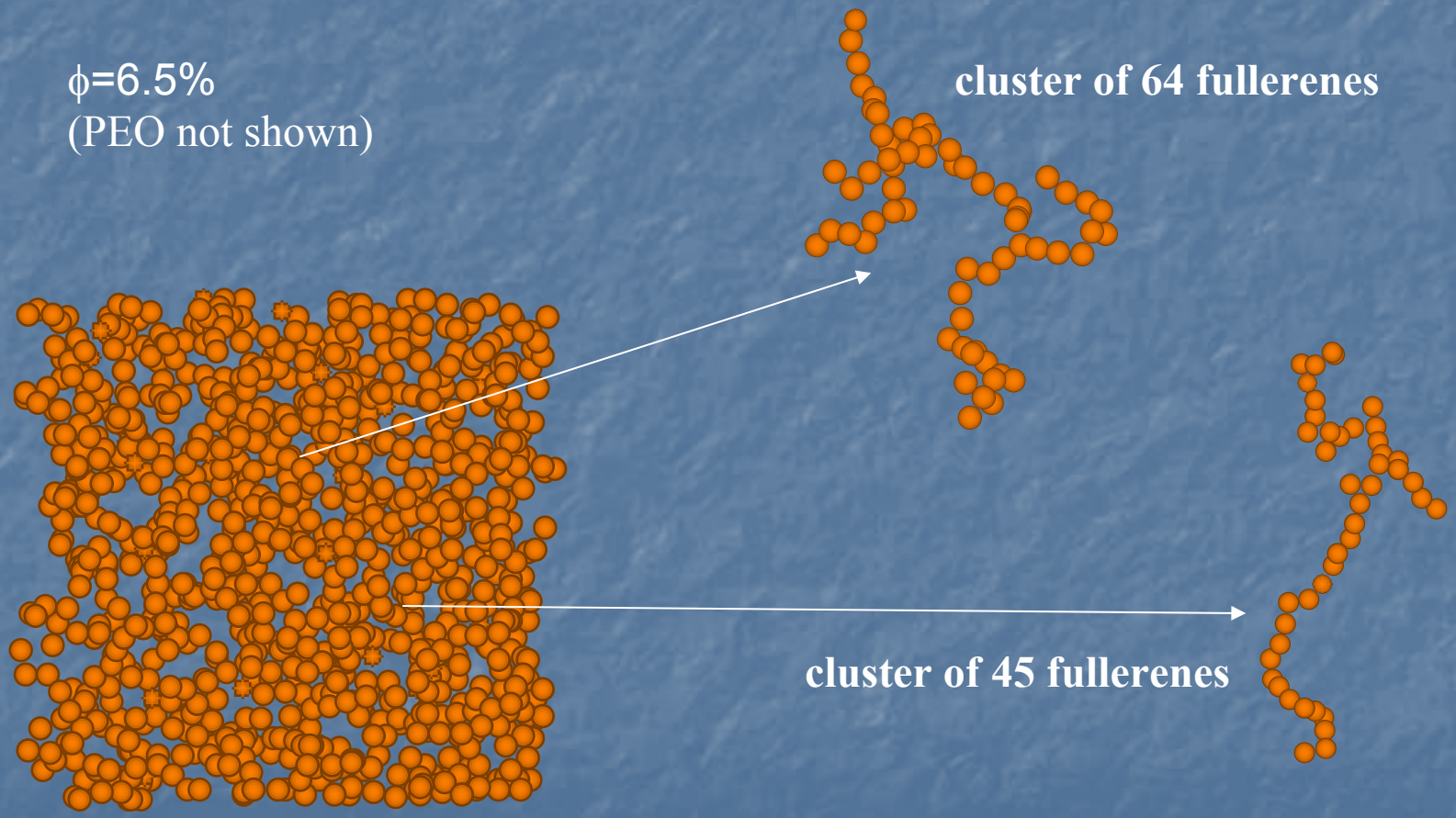


ϕ=0.3%
(PEO not shown)

➢Simulations show that PEO-modified fullerenes neither phase separate nor disperse in water, but rather form chain-like aggregates (6 chains)

Nanoparticle Self-association



Conclusions

- The synergism between static and dynamic neutron scattering and molecular simulations in providing important insight into nanoscale phenomena has been clear established for polymers
  - Interpretation of experimental observations
  - Validation of simulations
  - Mechanistic insight not accessible by either technique alone
- Similar collaborative efforts will be key to unraveling the behavior of polymer-nanoparticle composites and the self-association of polymer-modified nanoparticles, including the interaction of these materials with biological structures