Where Scattering and Modeling Meet: Structure and Dynamics of Poly Dots

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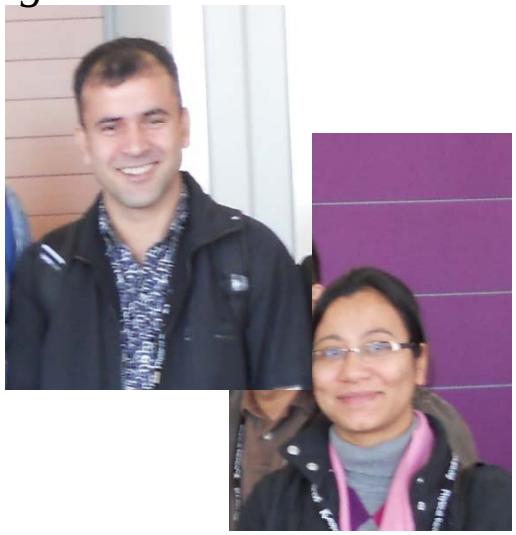
Acknowledgements

Prof .Uwe H.-F. Bunz U of Heidelberg

Prof Rakchart Traiphol Naresuan University, Thailand

Dr. Yunfei Jiang Behr Ltd

Dr. Gary S. Grest Sandia National Laboratory



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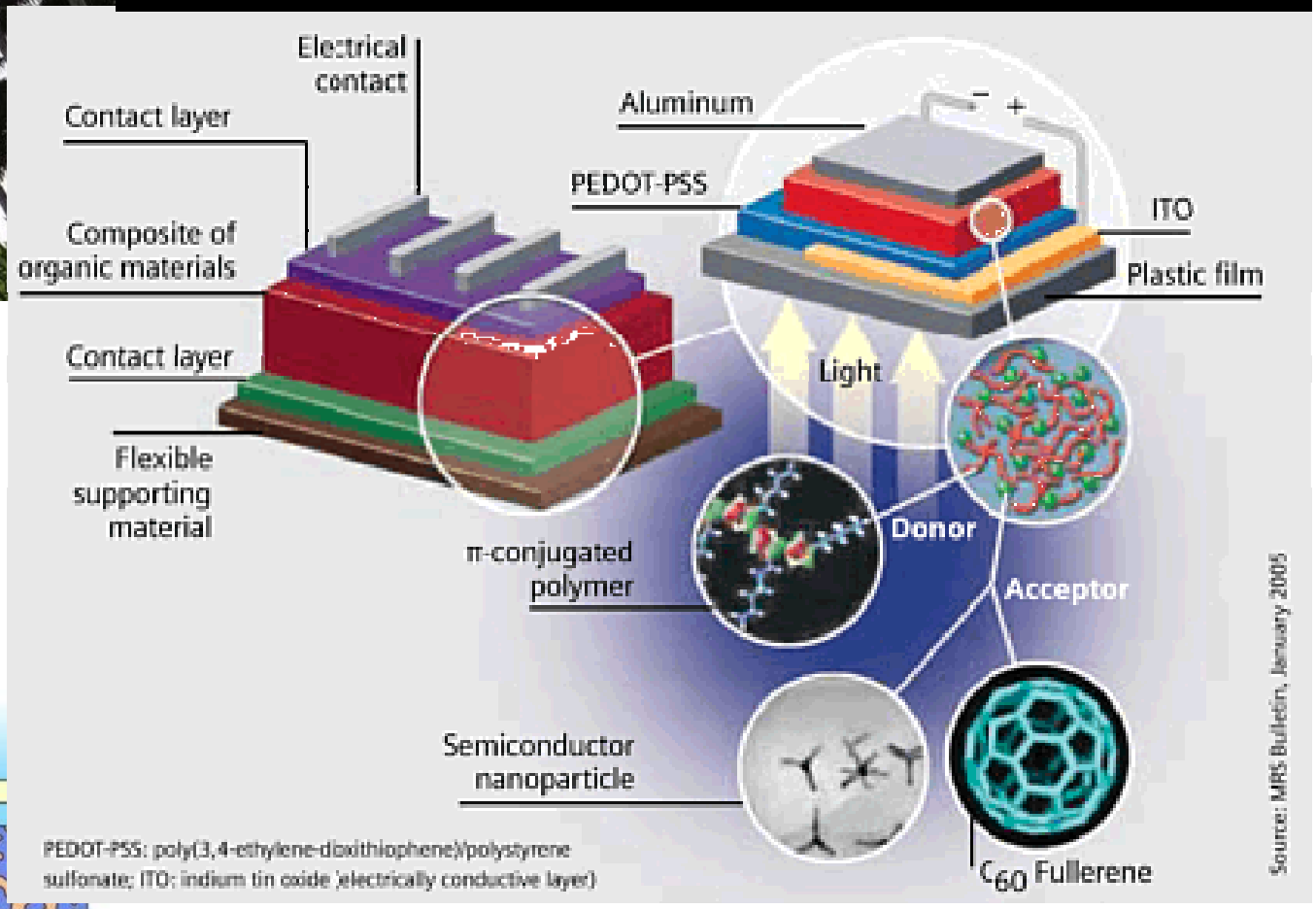
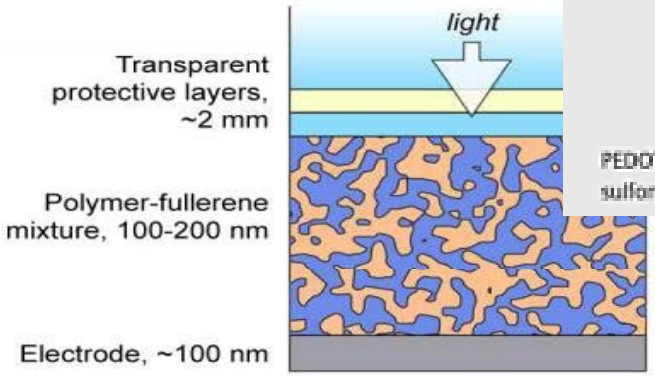
Clemson University

Resources

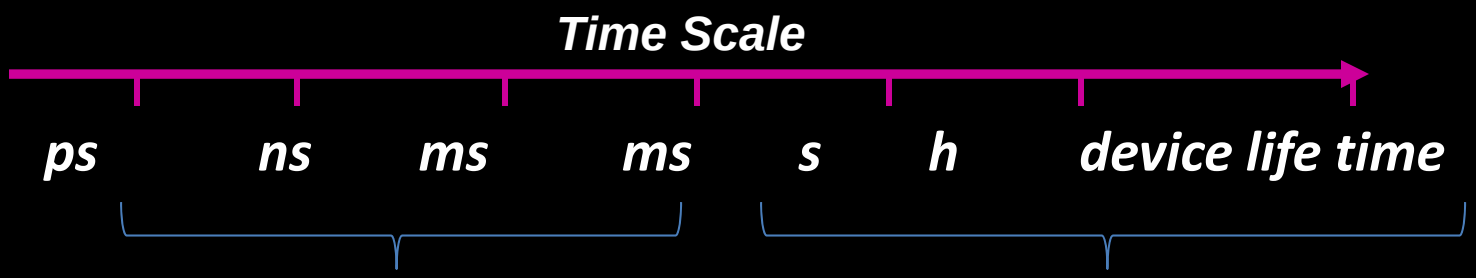
$$	NSF
$$	Clemson University
CINT,	SNL
Neutrons:	NIST, SNS. Lujan Center
Comp Time:	Palmetto Cluster, Hopper NERSC DOE

Organic Photo Voltaic Technology





Dynamics in Complex Fluids



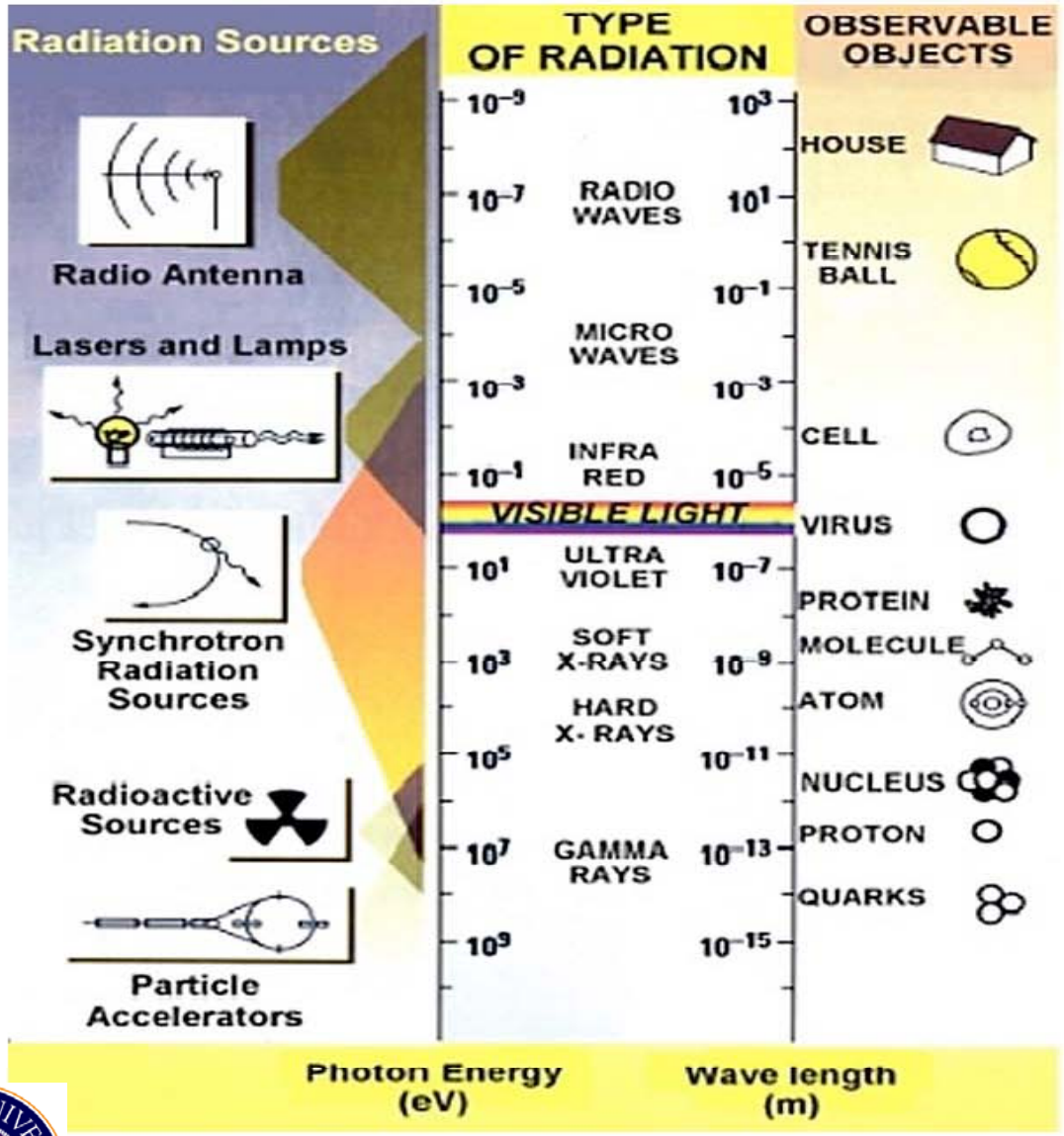
*Electron Dynamic
*Dynamics of segments
*Solvent Dynamics

*Charge Transport

*Macroscopic Structure Evolution
*Interfacial Reengagements
*Macroscopic Solvent D

Quantum --- Atomistic -----Coarse Grained -----Continuum

Multiple Length Scale in Scattering



Wavelength

≈

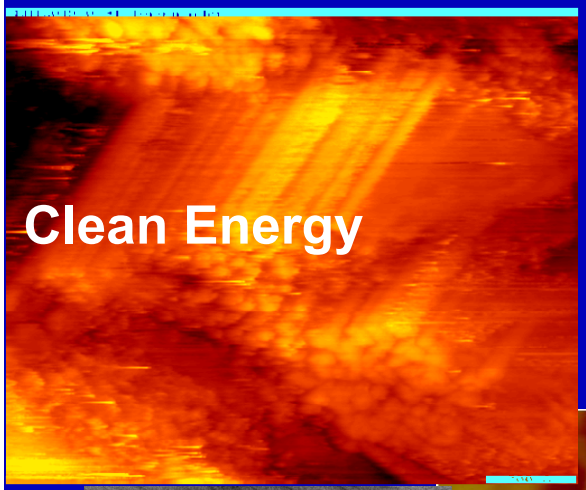
Object Size

≈

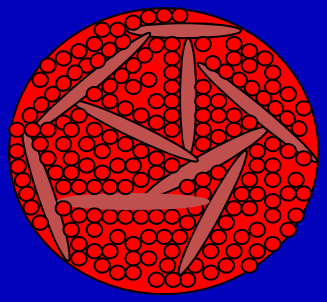
Angstroms for Condensed Matter Research

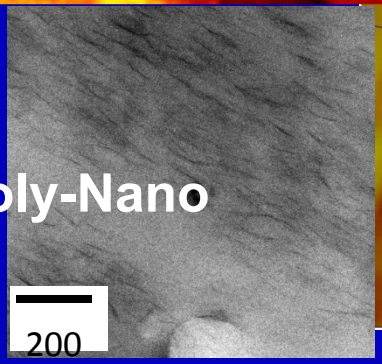
$$\lambda[\text{Å}] = \frac{12.398}{E_{\text{ph}}[\text{keV}}$$

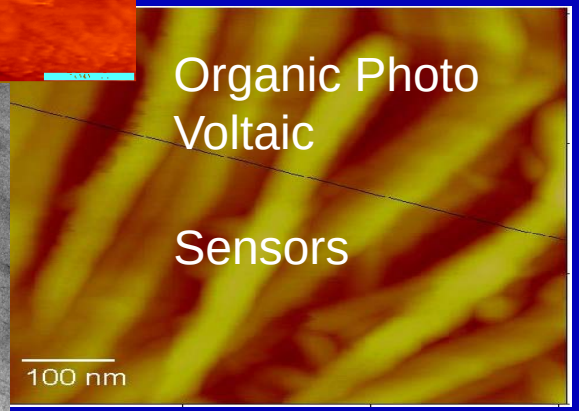
Responsive Soft Materials



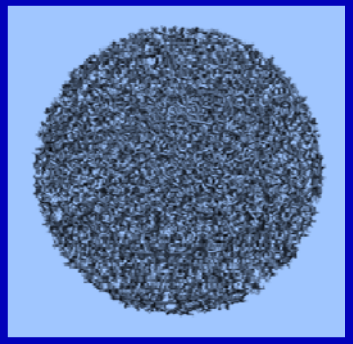
Soft Colloids







Poly Dots



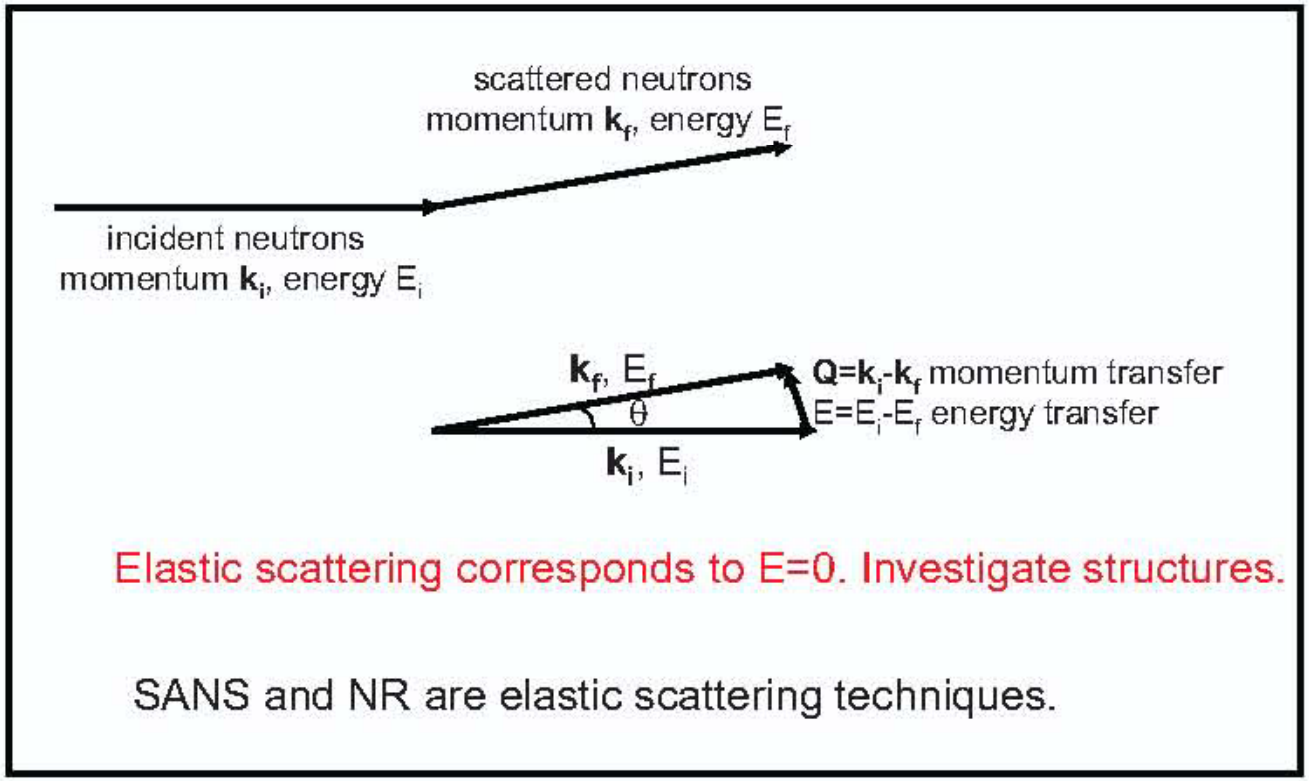
>Elastic and Inelastic Scattering

Lujan, HFIR, SNS, NIST

>Computational Studies

CINT

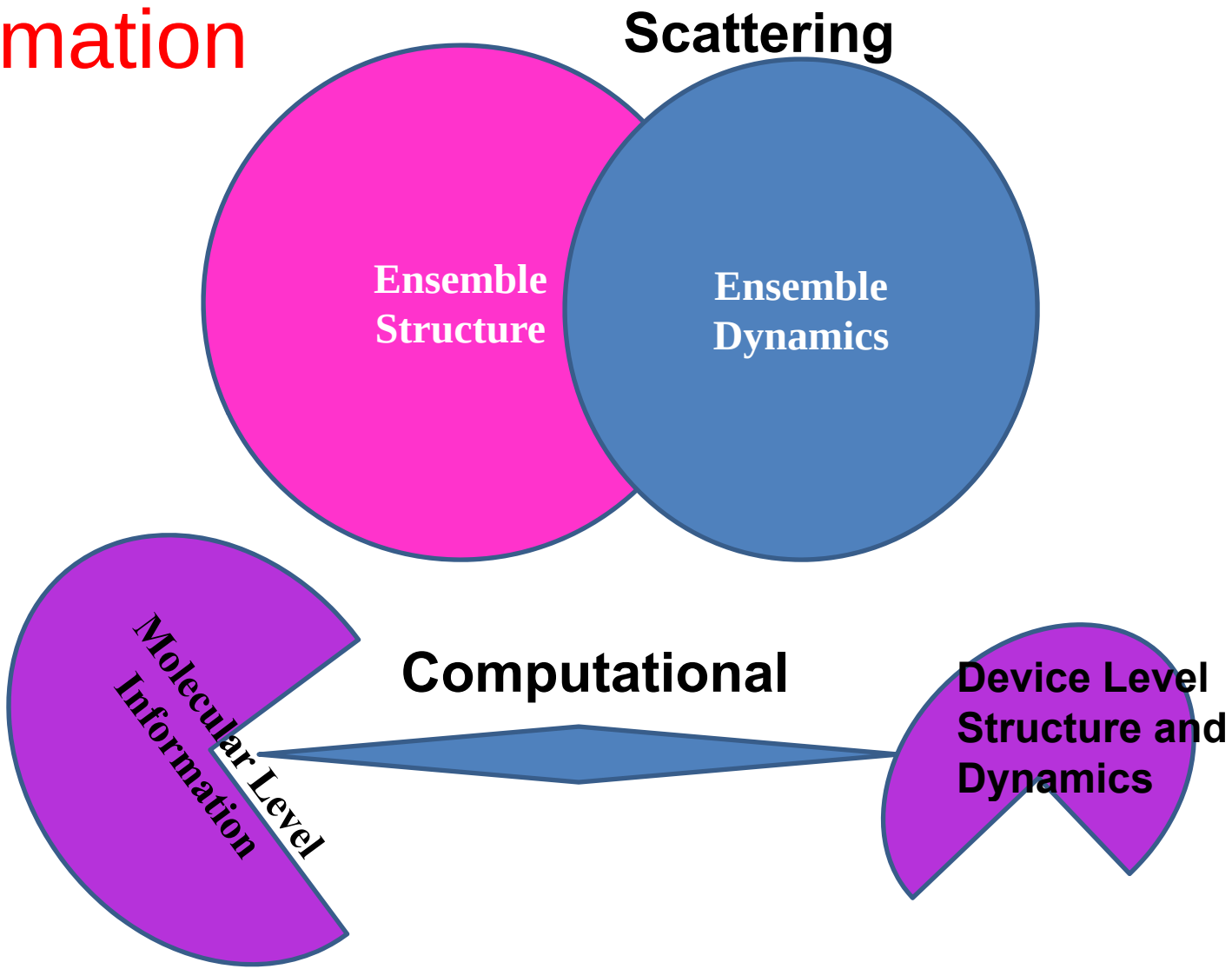
A Few Words on Scattering



Elastic: Correlations
Inelastic: Dynamics

=> Ensemble Average

Multiple Scale Information



PHYSICAL REVIEW VOLUME 136, NUMBER 2A 19 OCTOBER 1964

Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN

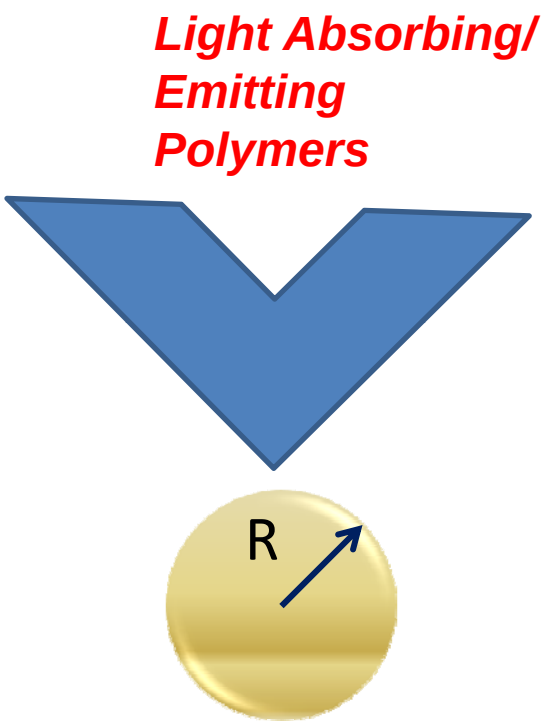
VI. CONCLUSIONS

A classical 864-body problem with a truncated two-body interaction of the Lennard-Jones type, with periodic boundary conditions is, by itself, a problem of interest, in which case the assumptions involved reduce simply to the assumptions in solving the set of differential equations as a set of difference equations.

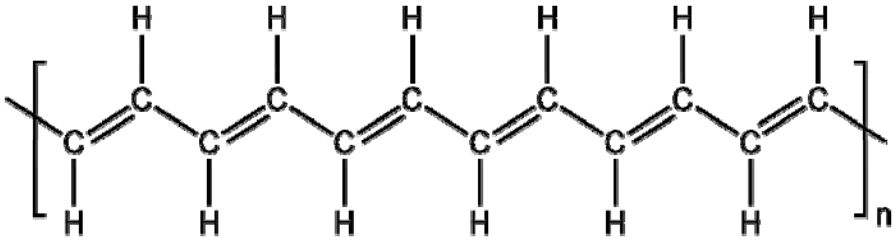
The question of identifying such a system with a physical system like liquid argon is very difficult to answer on the basis of the limited amount of information presented in this paper. Firstly, the value of the diffu-

Poly Dots Overview

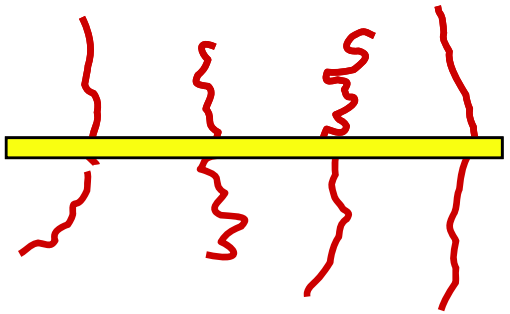
- Conjugated Polymers
- Poly Nano Dots
- Structure
- Dynamics



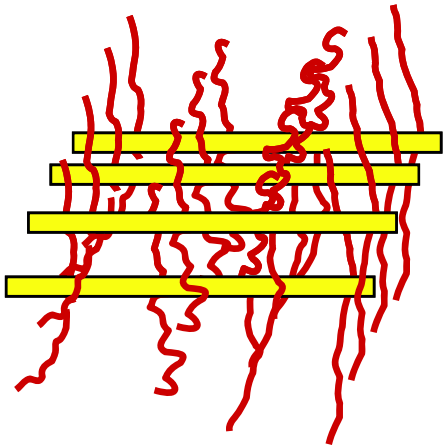
Conjugated Polymers



e⁻ in a 1-D Box



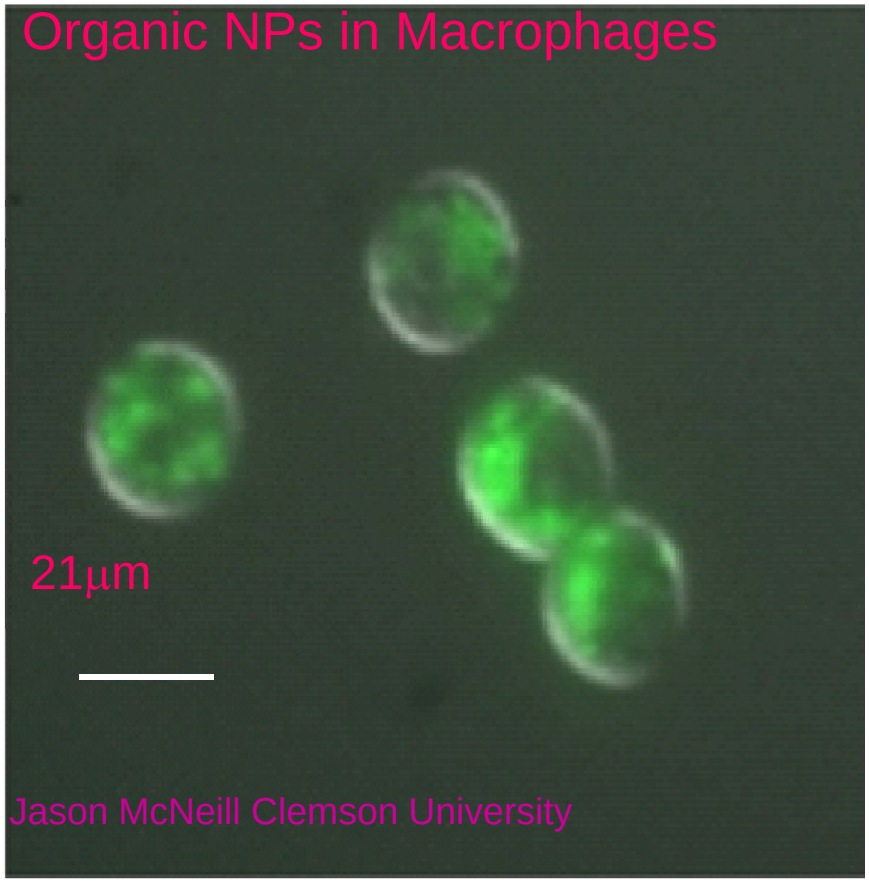
- Organic Electro-Optical Devices



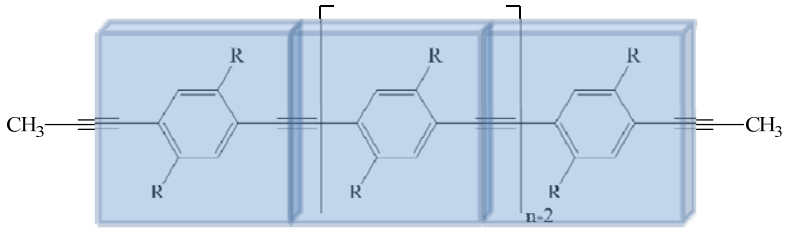
Self assembled Nano Clusters

Optically Active Polymer Nano Particles

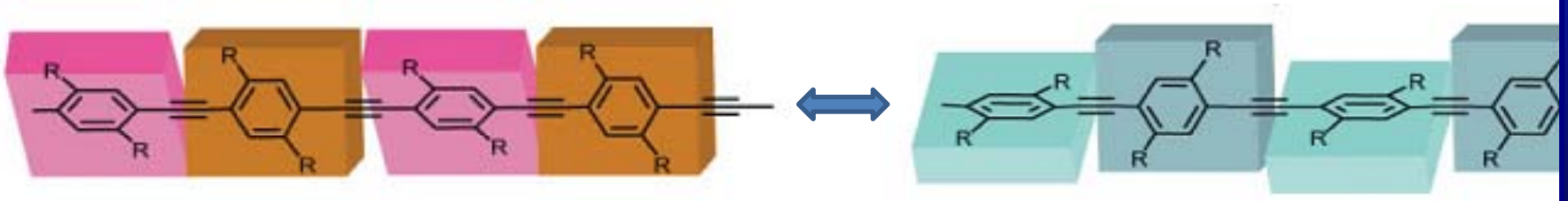
- Cellular-Imaging
- Cellular Targeted Treatments
- Sensing
- Building Blocks for Devi



Poly Dots Parent Polymer



poly(para-phenyleneethynylene) (PPE)



Conformation → Conjugation length (L) → Emission and absorpt properties

Bunz, U. H. F., *Macromolecular Rapid Communications* 2009, *30* (9-10), 772-805.

Poly Nano-Dots: Wish List

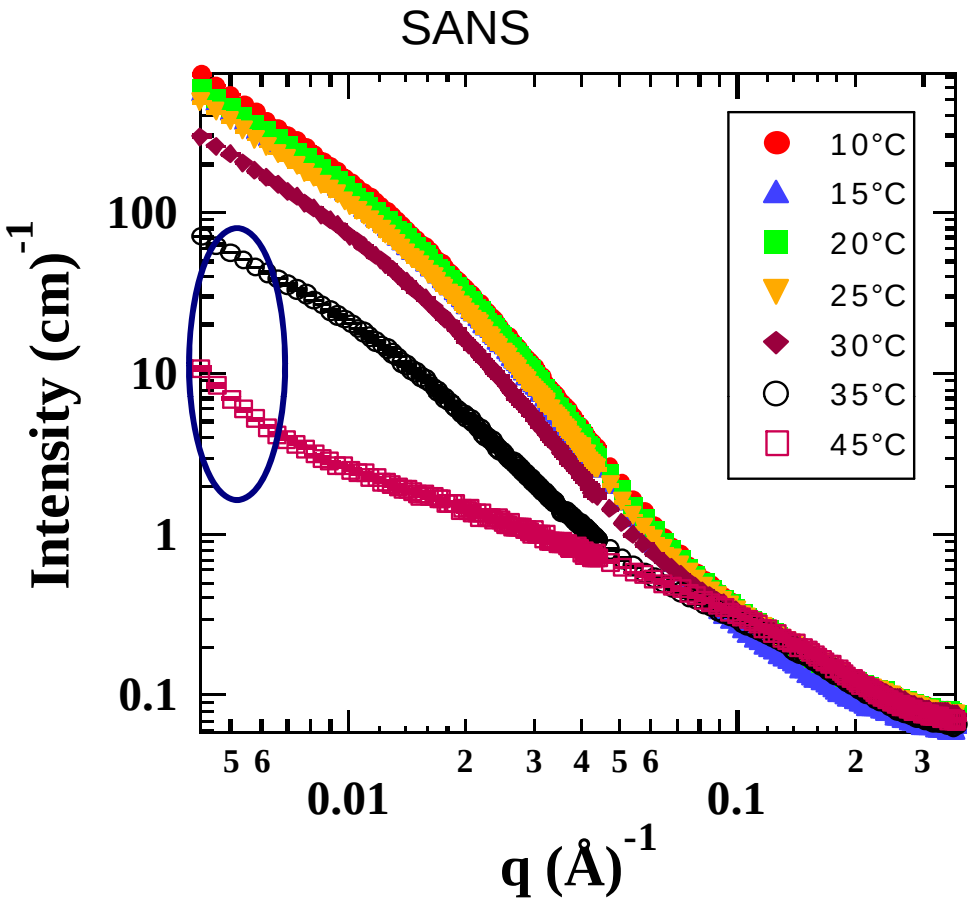
- Remain in Confined Geometry:
  - for extended time
  - while passing across membranes
  - while assembled into devices
- Remain fluorescent in confined NP geometry.
- Remain optically active upon integration.

Challenges

- Conjugated polymers are often rigid:
  folded into a nano particle does not yield a stable state

- Conjugated polymers are highly interacting
  Integration may result in lost of optical activity

Single Molecules in Toluene



Solutions: Rod-like particle

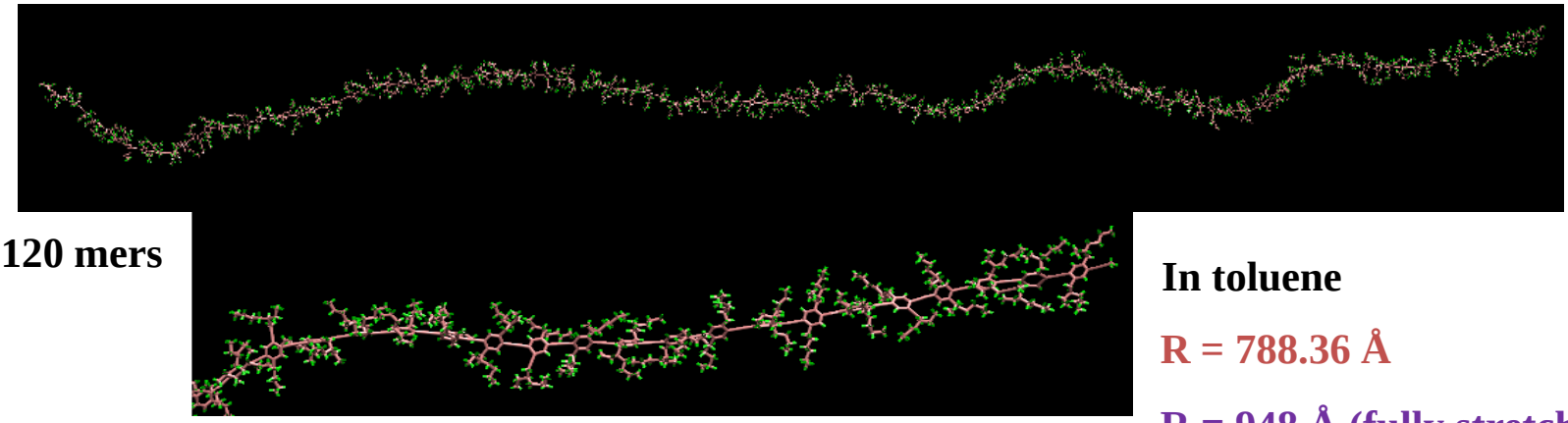
$$I(q) = L\frac{\pi}{q} I_c(q)$$

$$I_c(q) = (\Delta\frac{b}{V})^2 A\int_0^D 2\pi r dr \gamma_{co}(r) J_0(qr)$$

❖Single Molecules are Fully Extended!

Flexible and Semi Flexible Polymer Conformations

Conformation of a single Molecule

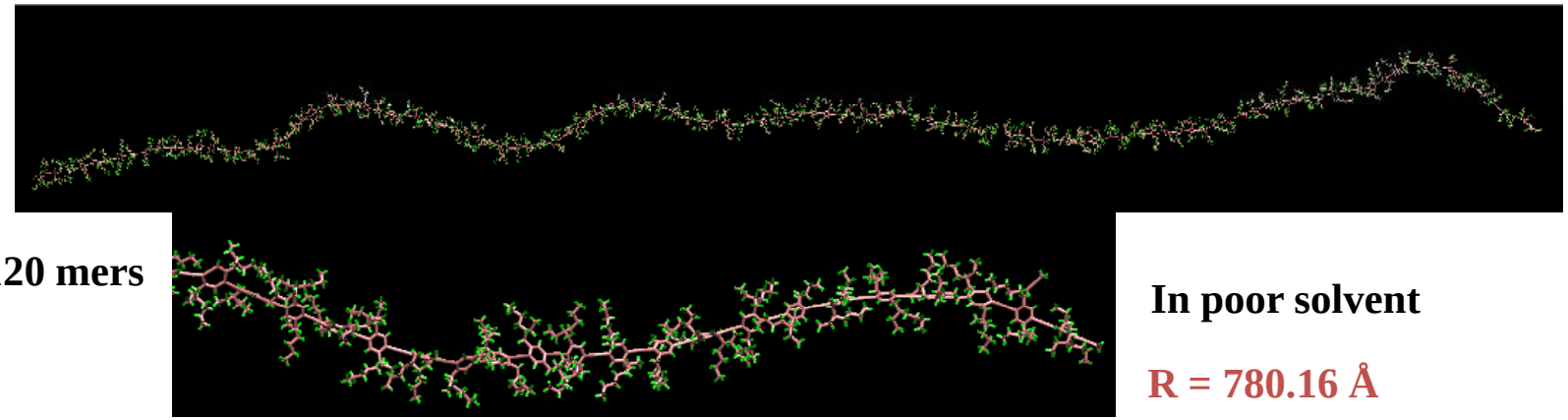


120 mers

In toluene

R = 788.36 Å

R = 948 Å (fully stretched)



120 mers

In poor solvent

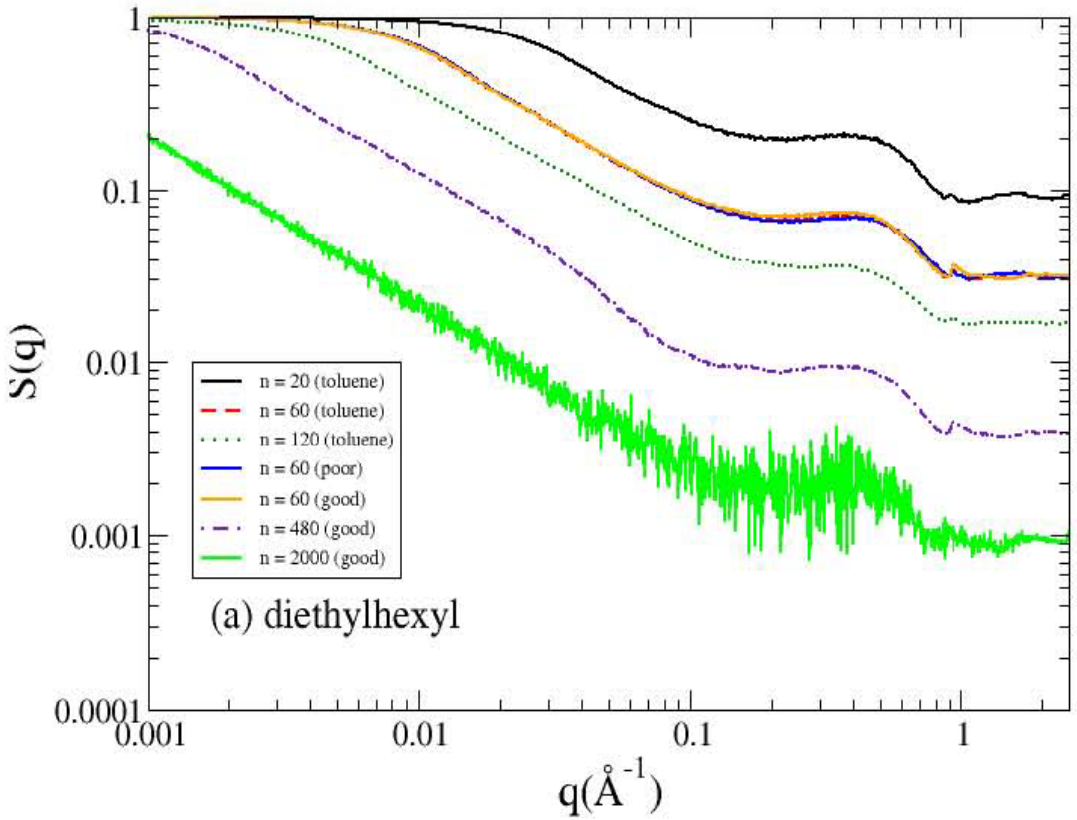
R = 780.16 Å

R = 948 Å (fully stretched)

Extended conformation up to N=2000 in all solvents

Maskey,S.; Pierce,F.;Perahia,D.;Grest,G.S. J. Chem Phys. 2011

Structure From MD Simulations



❖**Molecules are stretched out in good solvents**

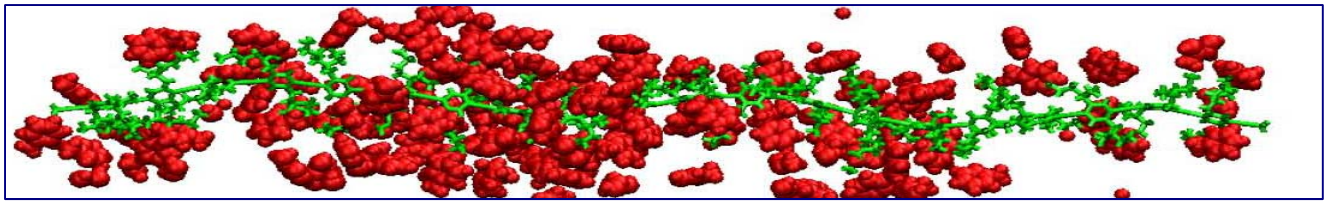
❖Backbone is stretched out

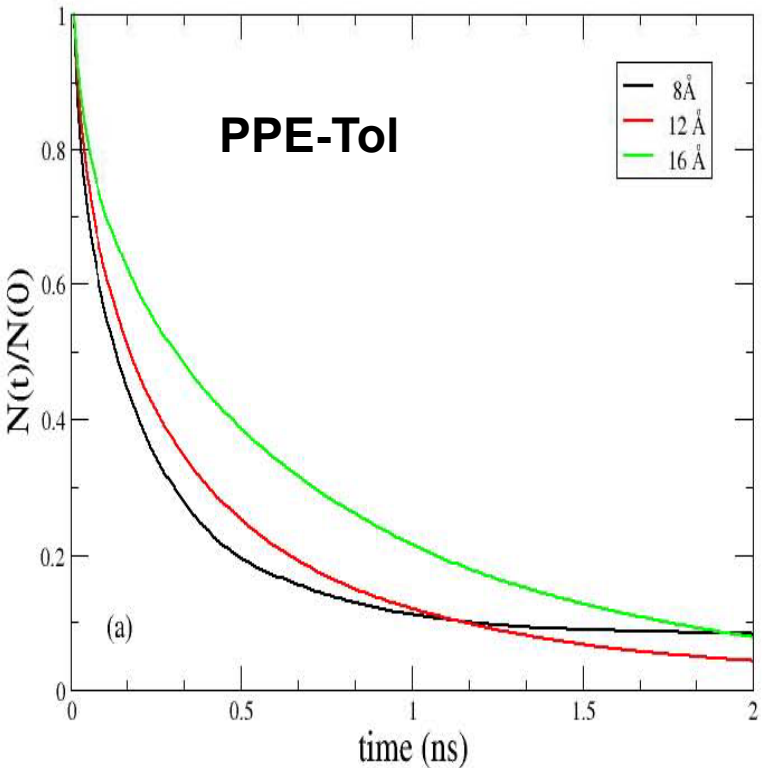
❖ Side chains lie away from the backbone

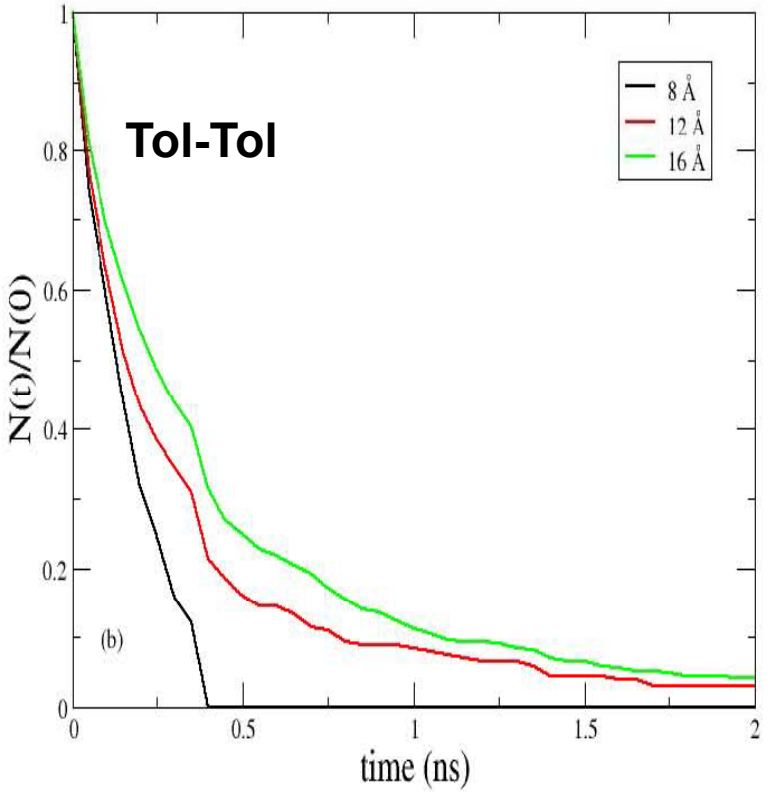
❖ Aromatic rings are not co-planar

Where are the solvent molecules?

Solvent-Molecule Resonance Time

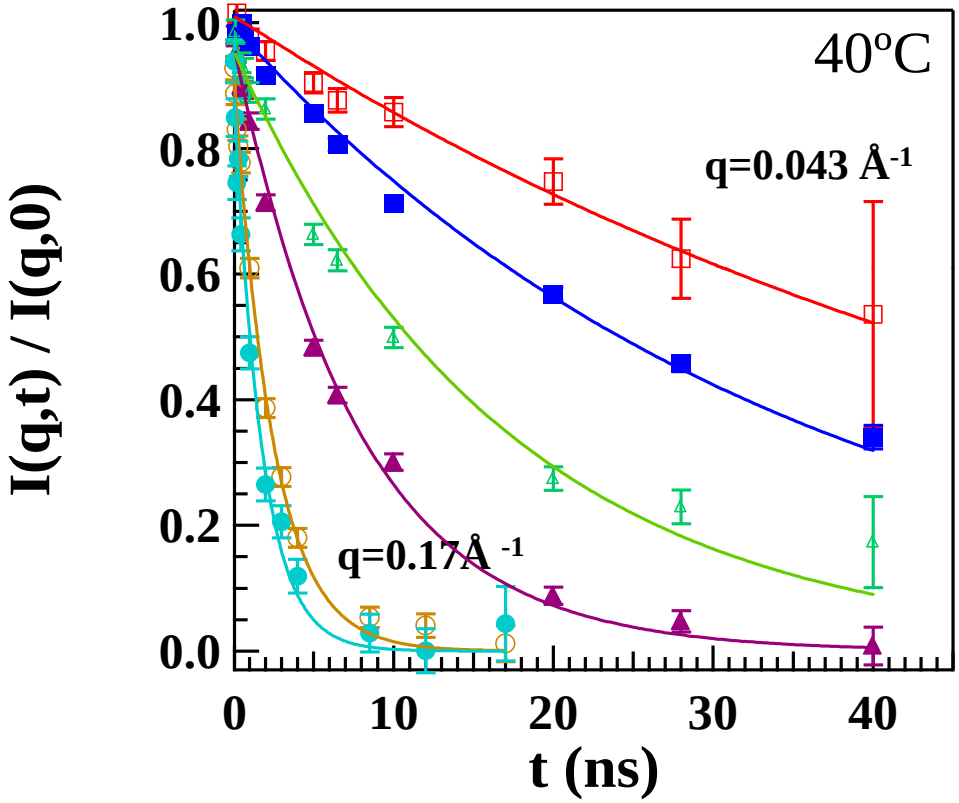


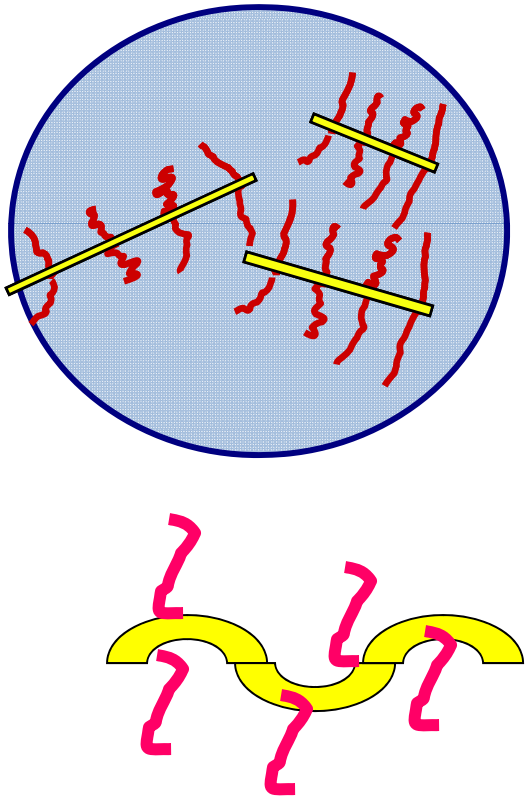




❖Fraction of tol resides next to the PPEs longer than tol-tol in neat toluene

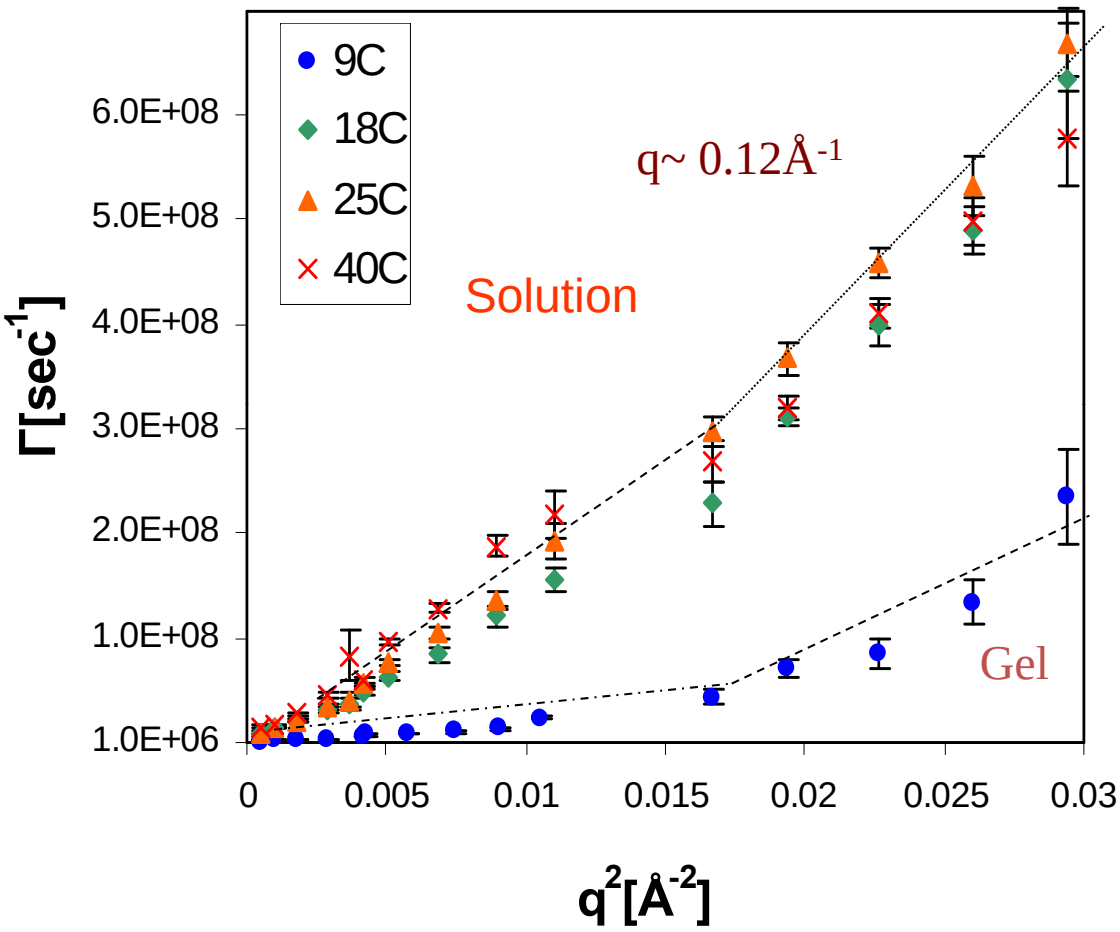
Single Molecules in Toluene: NSE Dynamics

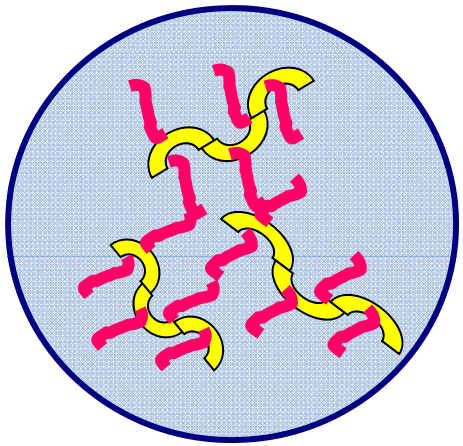




$$S(q,t)/S(q,0) = A \exp[-D_{eff}(q)\, q^2\, t]$$

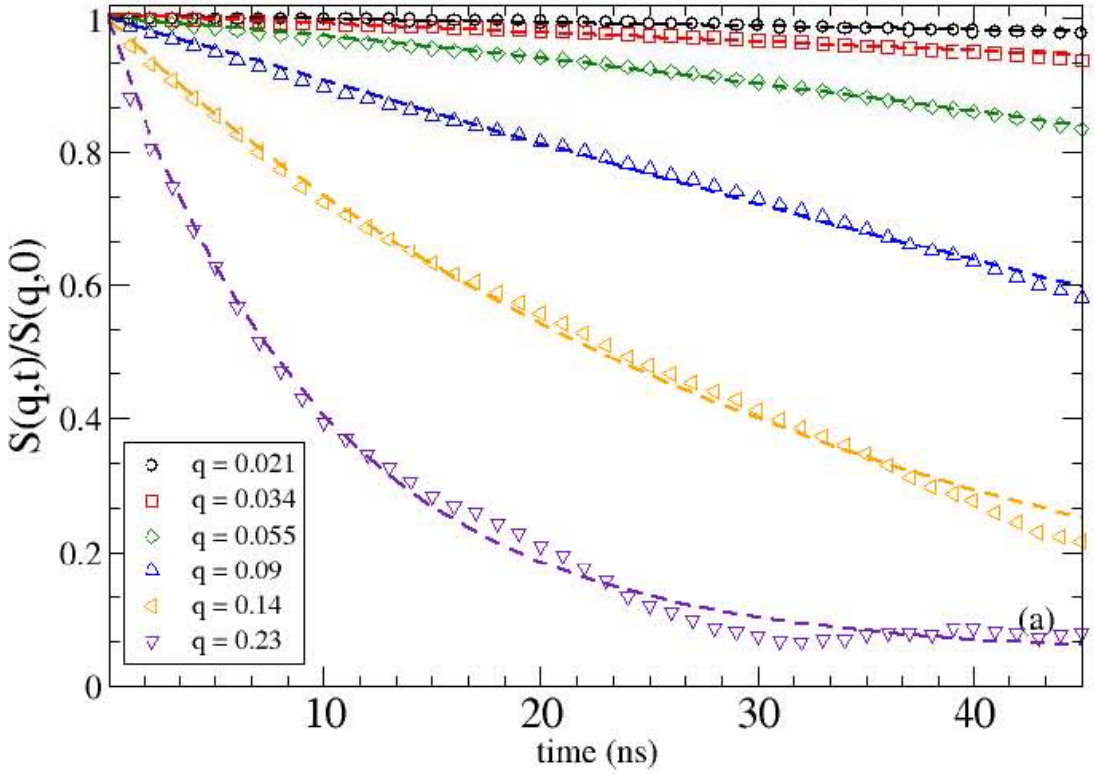
Effective Diffusion





❖Dynamics with a characteristic length scale that corresponds to the rigid segment of PPEs measured by SANS

Dynamics of A Single Molecule



- Effective Diffusion on the Order of Magnitude of the Experimental Results
- The side chains are significantly more dynamic than the backbone

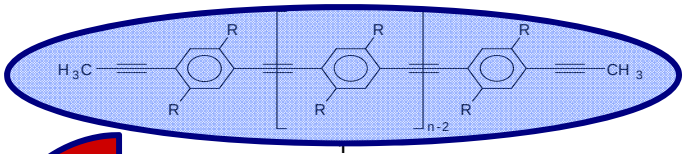
Isolated Conjugated Polymer in Solvents

- PPE molecules remain extended
- No correlations are observed within the backbone
- The polymer backbone remains dynamic
- Toluene is associated with the PPE backbone.

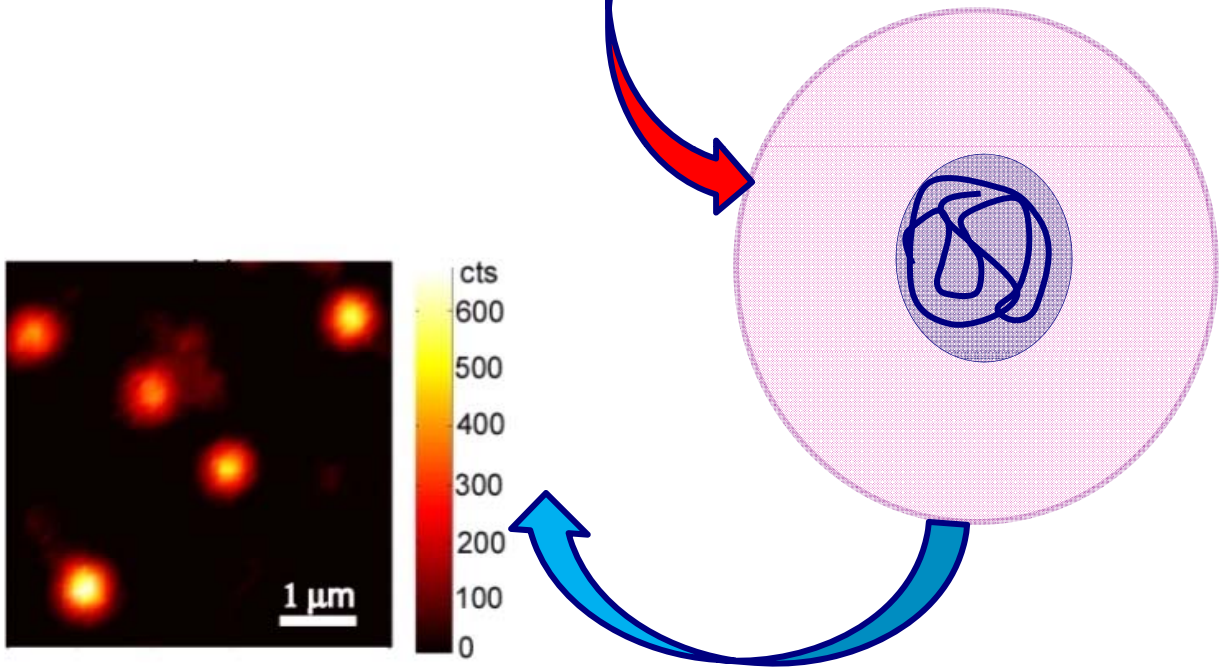
What is Next? Assembly of the PPEs

Poly Dots

Good Solvent



Poor Solvent

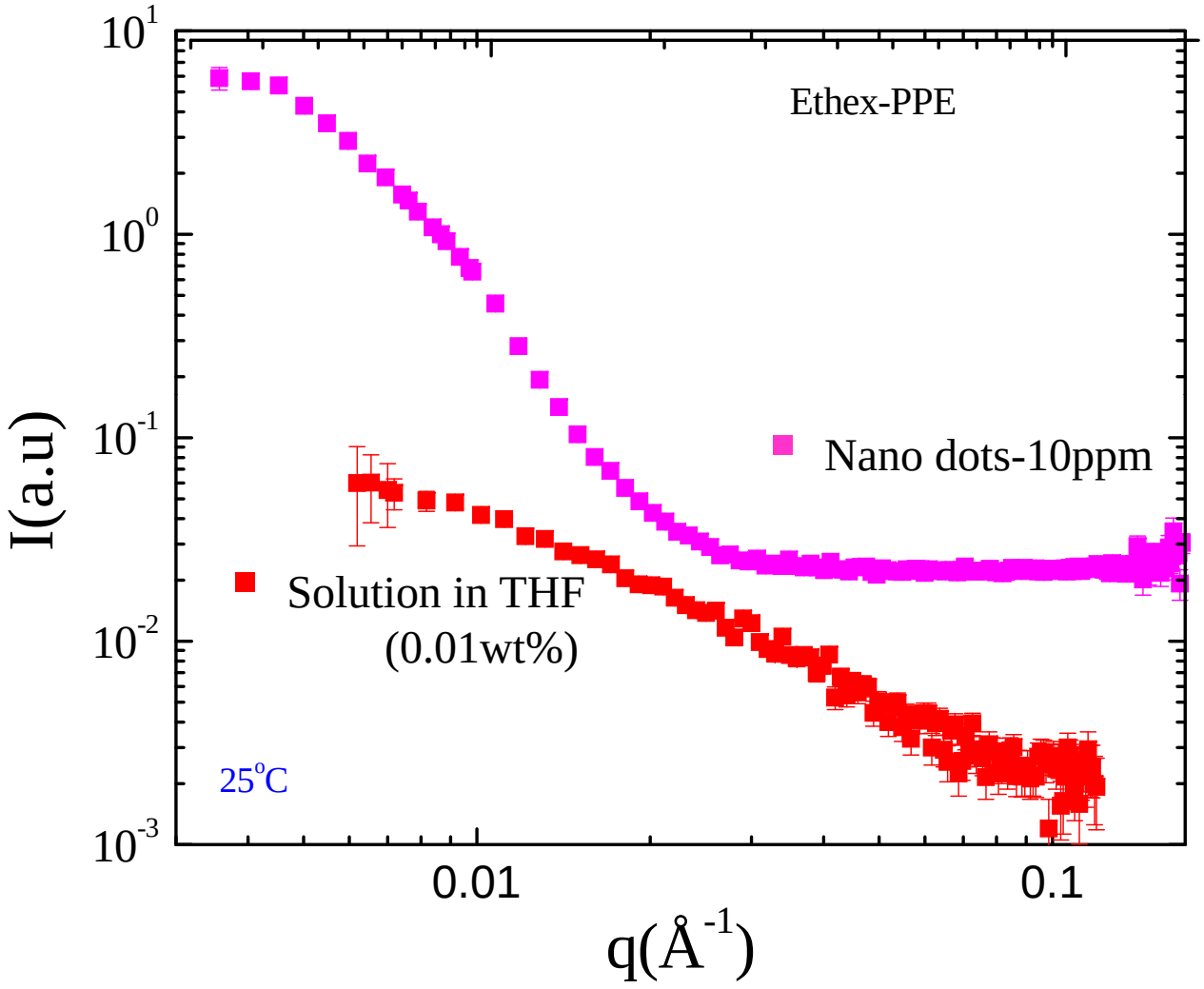


What affect the:

- Conformation
- Dynamics
- Stability

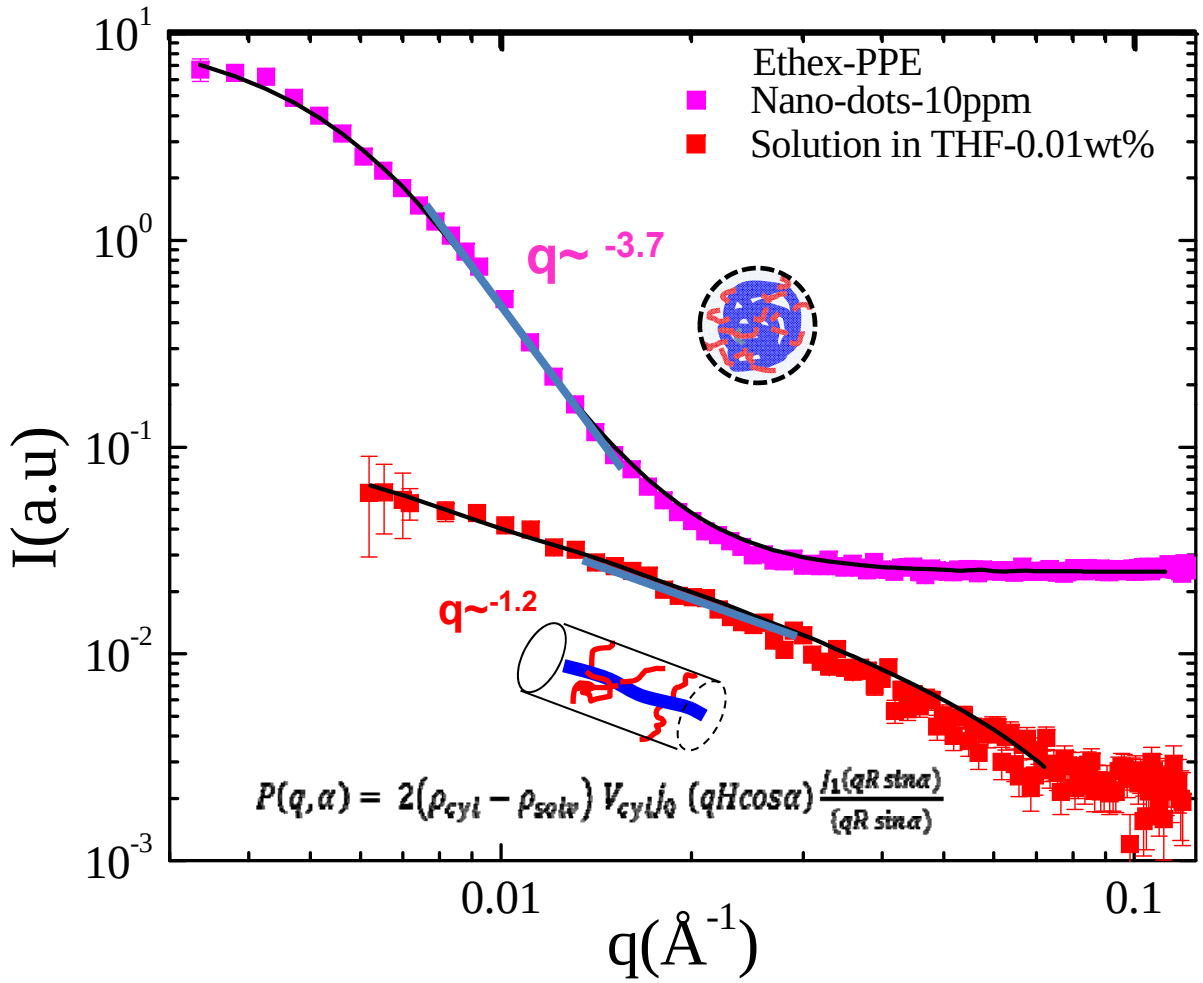
?

Scattering: SANS ⇔ Structure

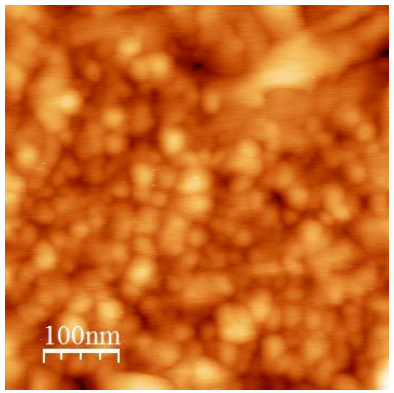


- Line shapes and intensities are different

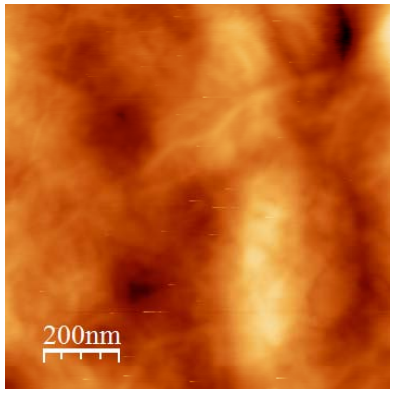
Shape of a Poly Dot



Ethx-PPE- NP-10ppm



0.01wt% solution from THF



- In good solvent, stretched out conformation of the PPE
- Nano dots assume hard sphere shape in water

Open Questions

Internal Structure

- Correlation between the aromatic rings
- Correlations between the side chains
- Density away from the surface

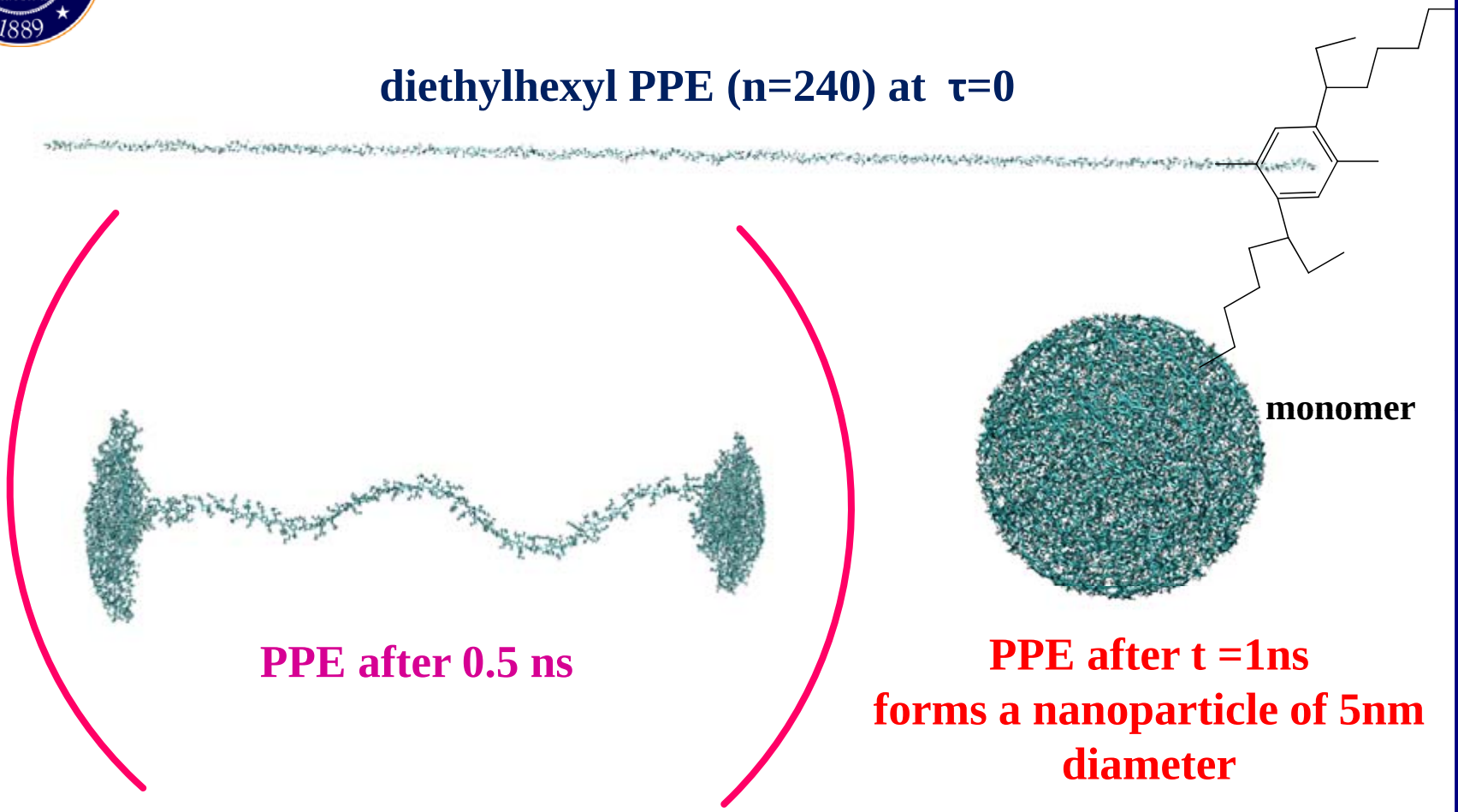
Internal dynamics

- Backbone
- Side chain
- Dynamics away from the interface

Forces: What hold the NP together?

Formation in Simulation

diethylhexyl PPE (n=240) at τ=0

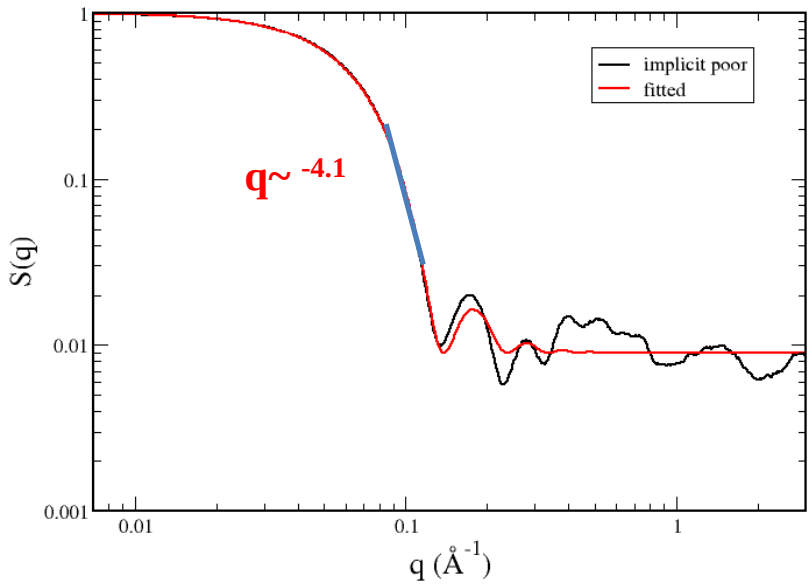


- Polymer chain was enclosed in a large sphere and radius of the sphere v
decreased as a function of time until nanoparticle of desired diameter v
formed.

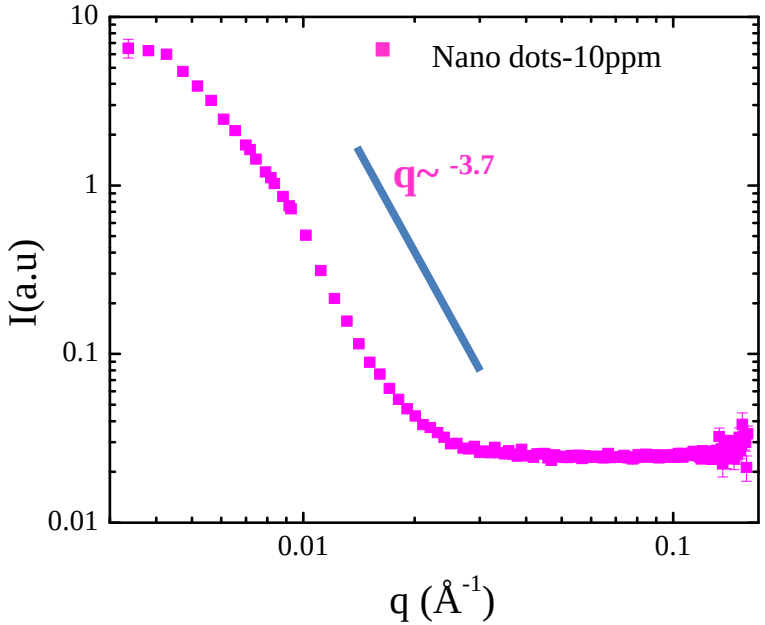
Maskey,S.; Pierce,F.;Perahia,D.;Grest,G.S. CSRI Summer Report ,Sa

Structure of Poly dots

Simulation



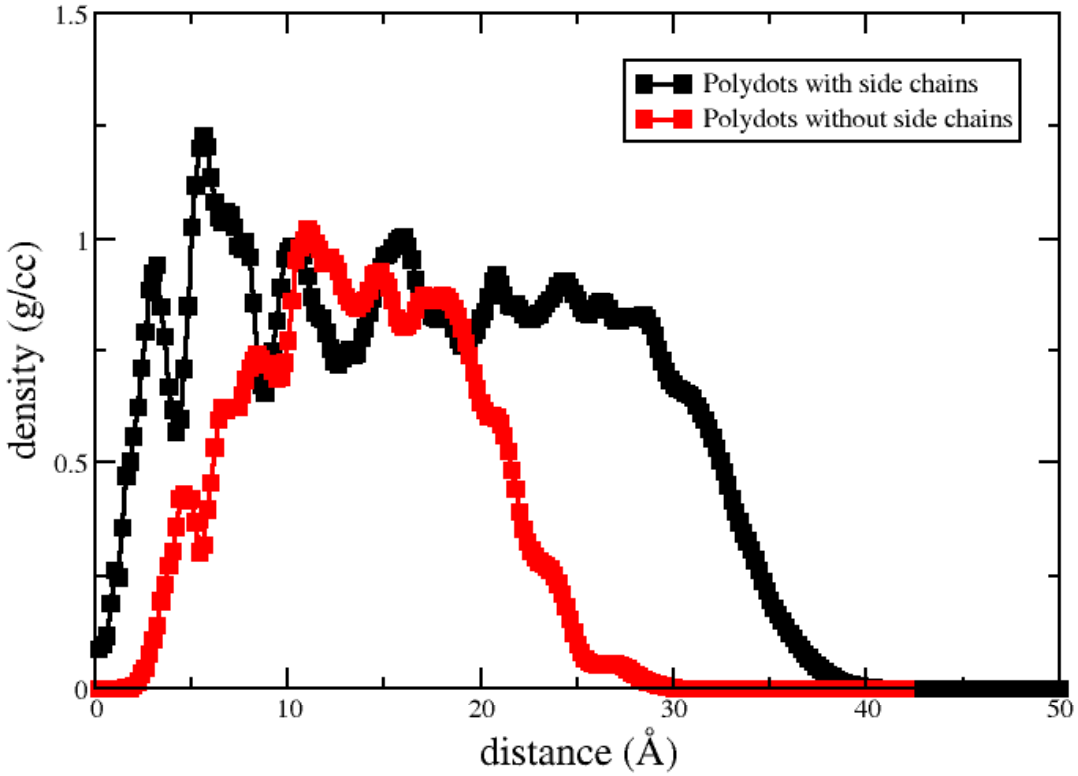
Experimental



- Experimental and computational results:

  poly dots are spherical in shape

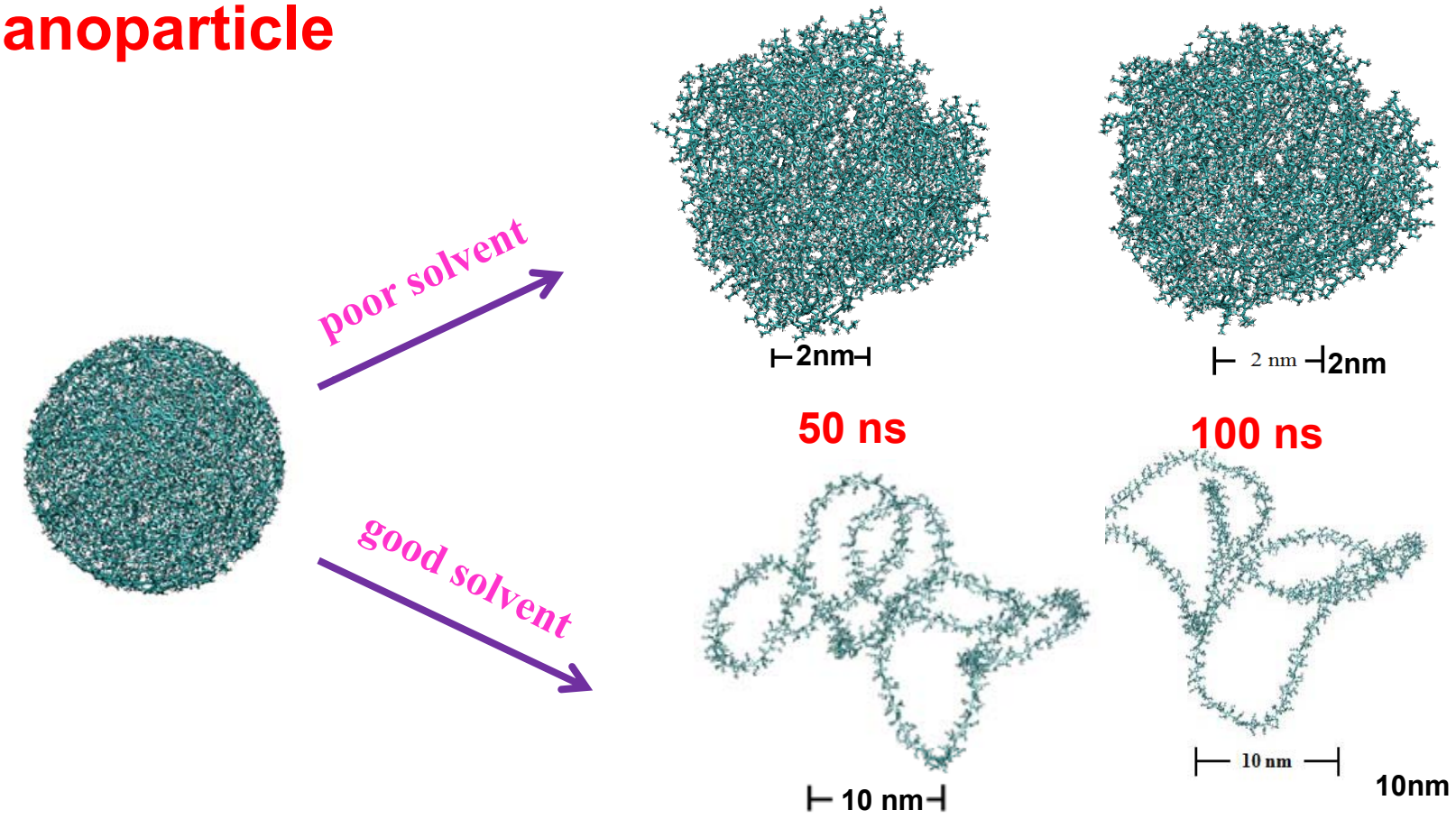
Structure of Poly dots



A full sphere with a bit of a density decrease at the interface

Time Evolution of Nanoparticles

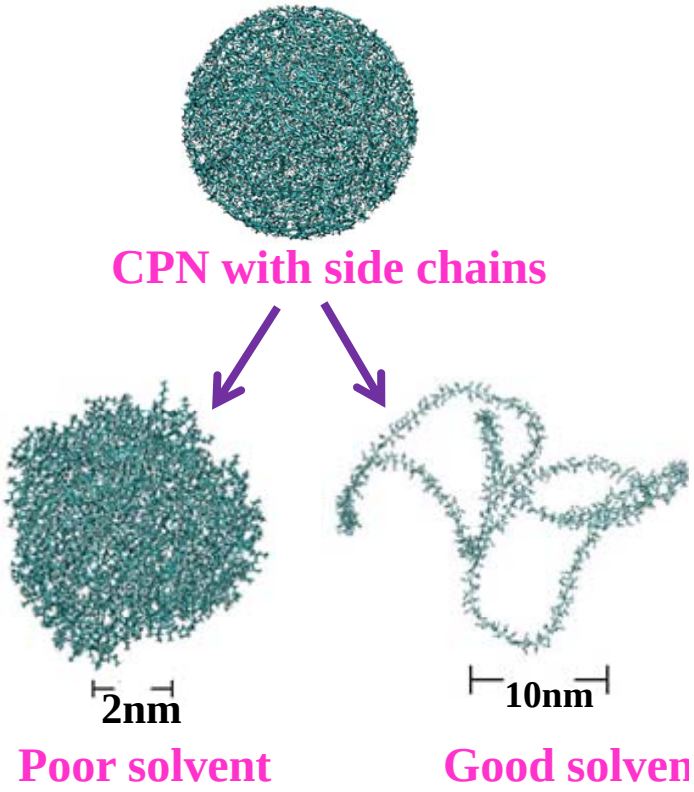
Nanoparticle

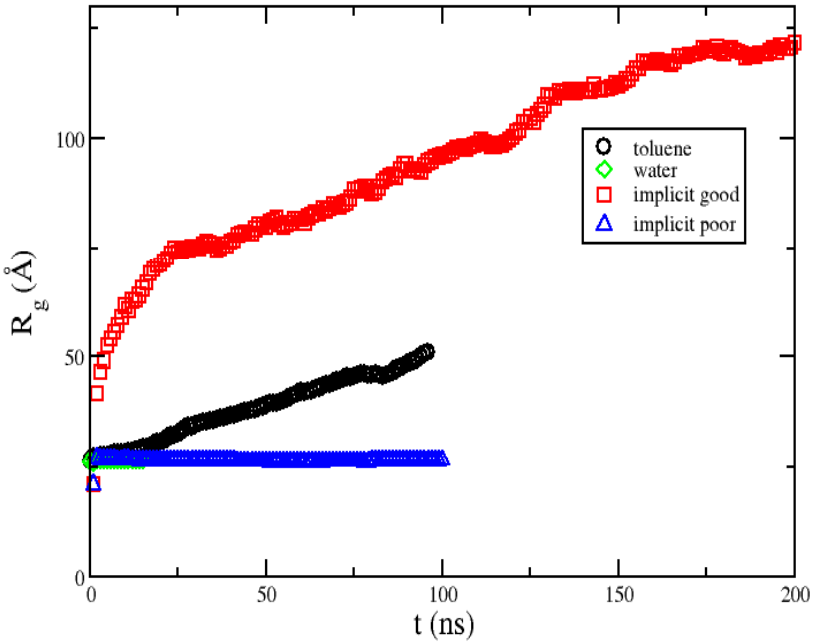


- In poor solvent, nanoparticle unravels at beginning but remains steady wi time
- In good solvent, nanoparticle keeps on unraveling with time

Maskey,S.; Pierce,F.;Perahia,D.;Grest,G.S. CSRI Summer Report ,Sa

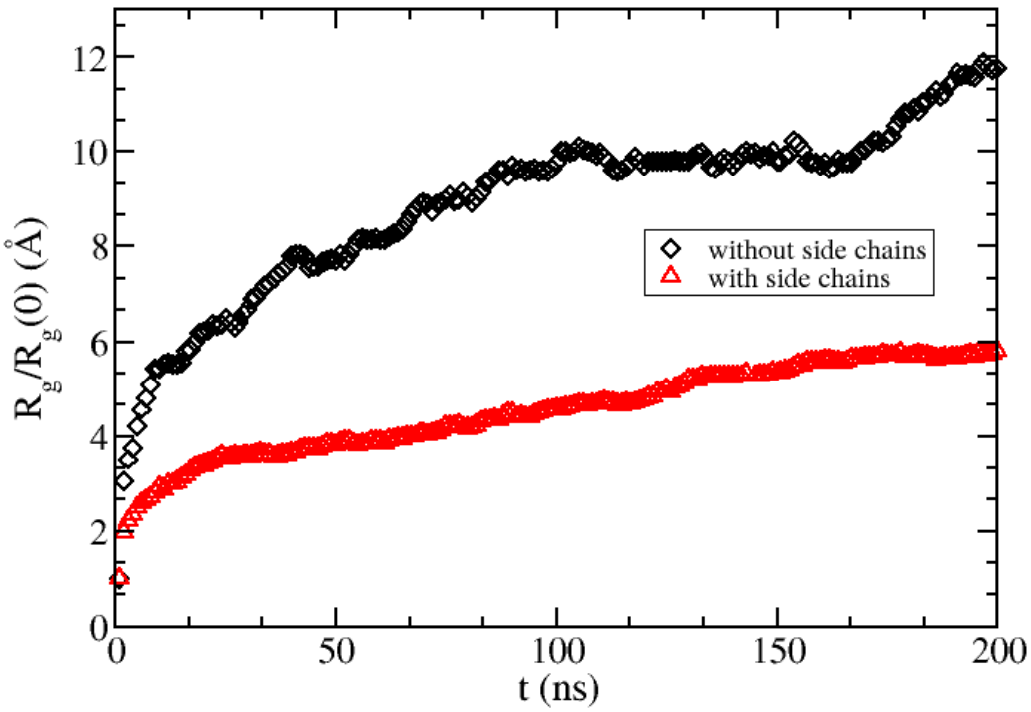
R_g as a Function of Time





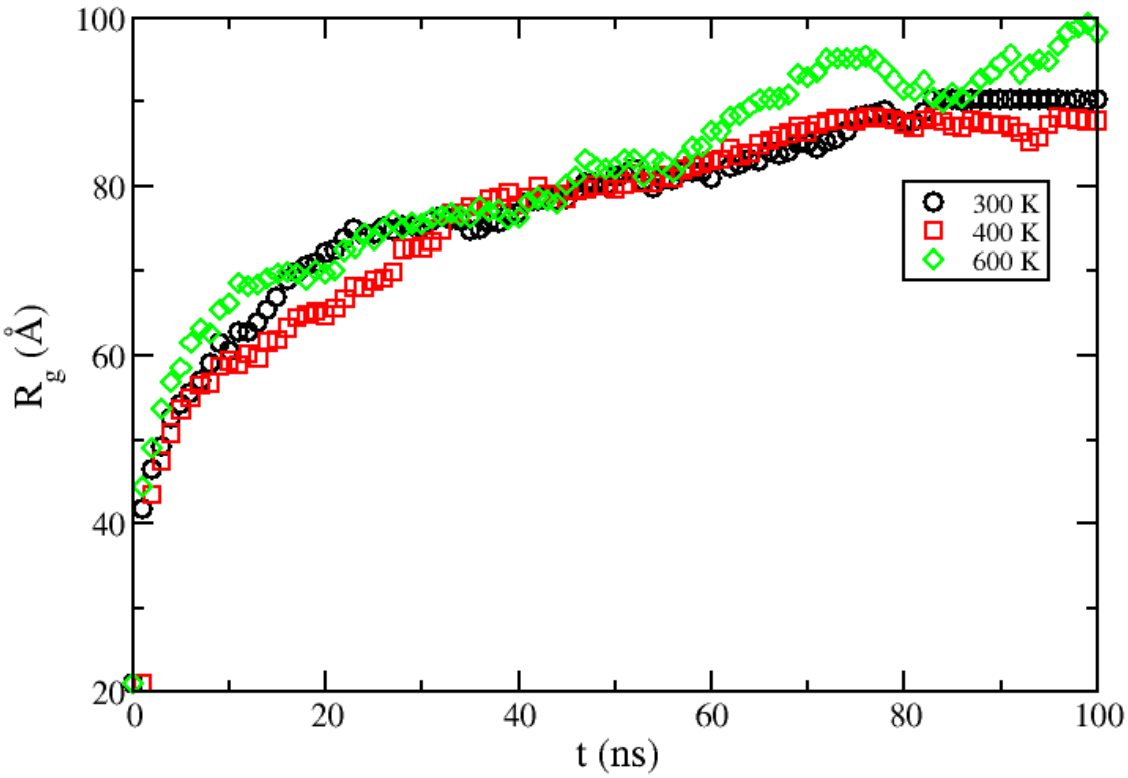
Maskey,S.; Pierce,F.;Perahia,D.;Grest,G.S. CSRI Summer Report ,Sandia 2010.
Maskey,S.; Pierce,F.;Perahia,D.;Grest,G.S. To be submitted

Side Chain Effects



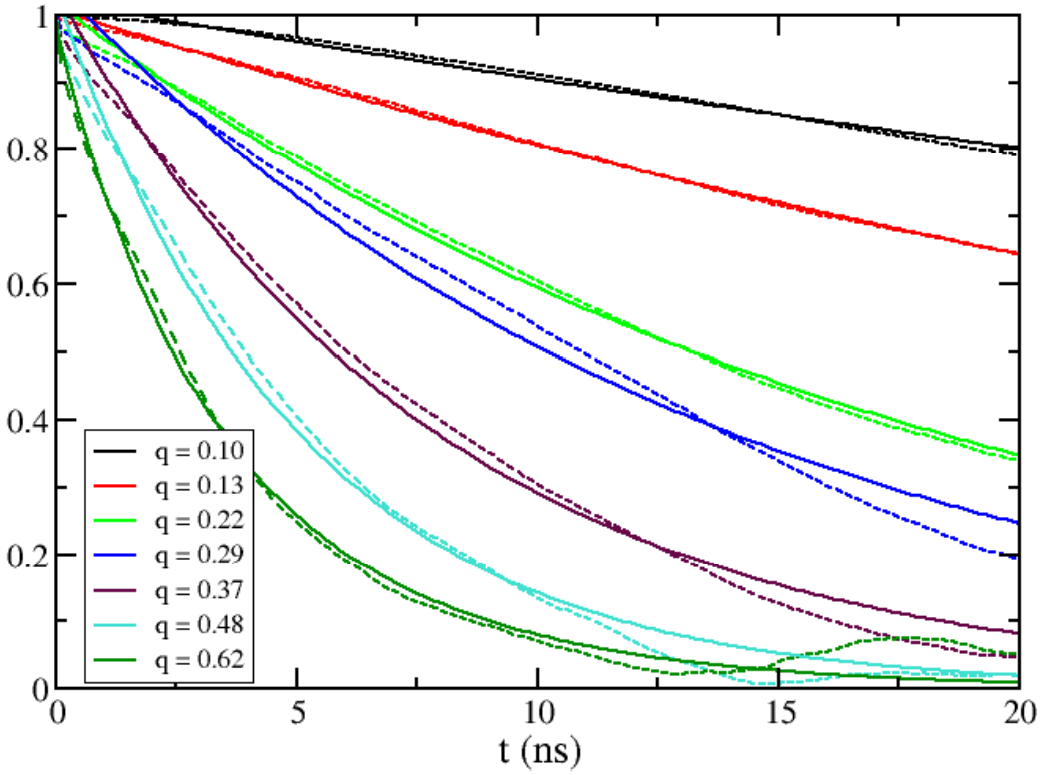
- Rg increases as a function of time in good solvent.
- Rg remains constant in poor solvent.

NP Stability



❖Temperature has very little effect

Dynamics



- The side Chains Remain Dynamics
- Limited motion is observed for the backbone

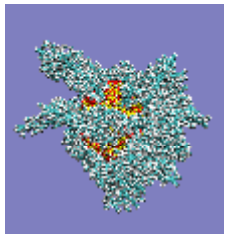
Summary

- Poly Dots are spherical objects
- No Internal Correlations within the backbone
- Remain Dynamic in Confinement

- Future:
  - Effects of the chemistry of the side chains
  - Assembly

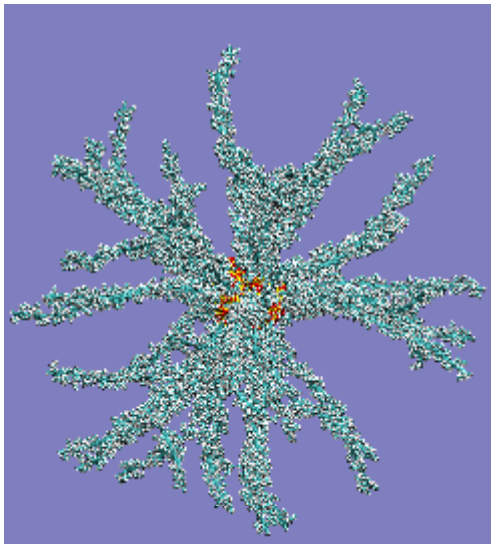
Silica-NPs Grafted with PPEs in Poor Solvent

T= 300 K
t= 20 ns



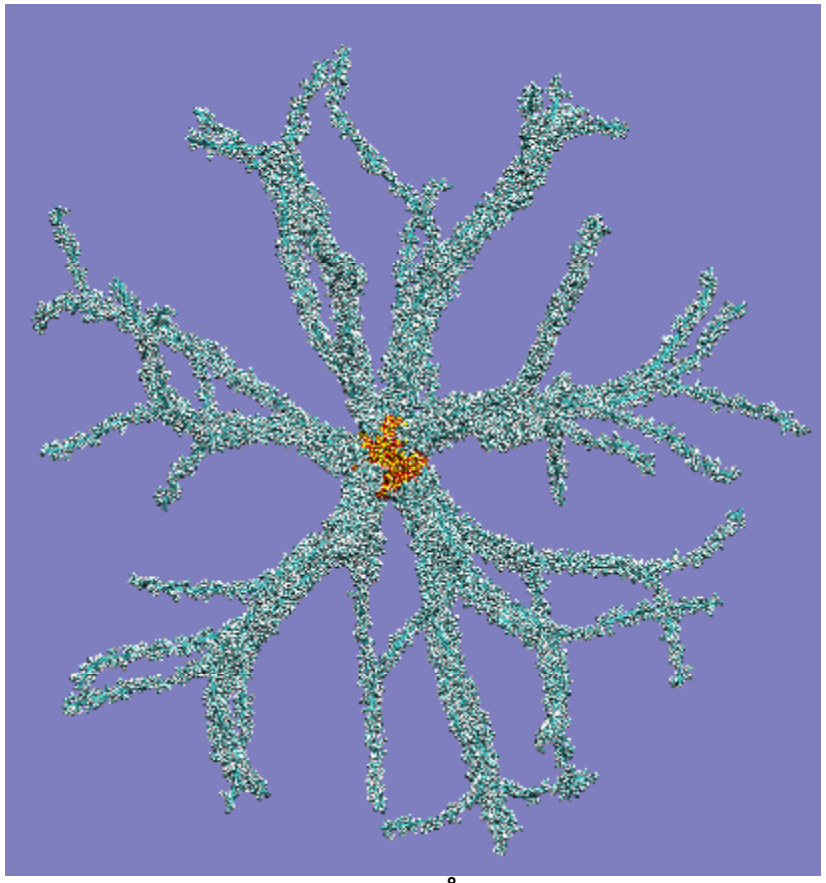
150 Å

6 monomers of PPE



350 Å

20 monomers of PPE



650 Å

40 monomers of PPE

- Clusters of PPE chains are formed in poor solvent.
- With increase in molecular weight, the clusters become more distinct and PPE chains are branched.