QENS and NSE for the Investigation of Dynamics in Soft Condensed Matter

Antonio Faraone

NIST Center for Neutron research

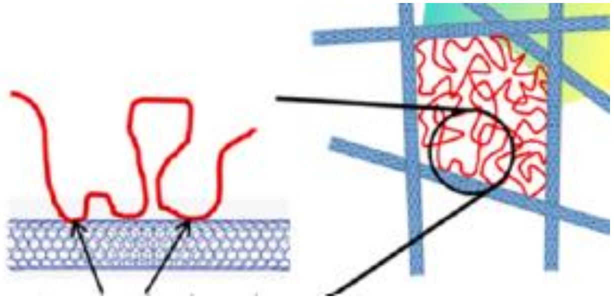
Oxford School on Neutron Scattering, 9/2-12/2019

Outline

- General trends
- Polymer Nanocomposites
  - Introduction
  - QENS role in the study of nanocomposites
  - The role of Nanoparticle size on chain dynamics
  - Chain Dynamics in attractive polymer nanocomposites subjected to large deformations
- Conclusion

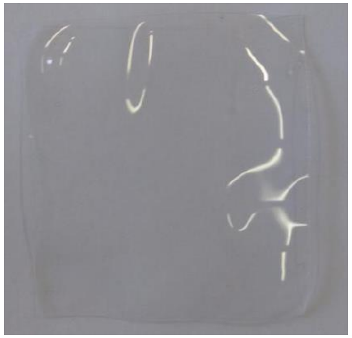
Polymers

Nanocomposites

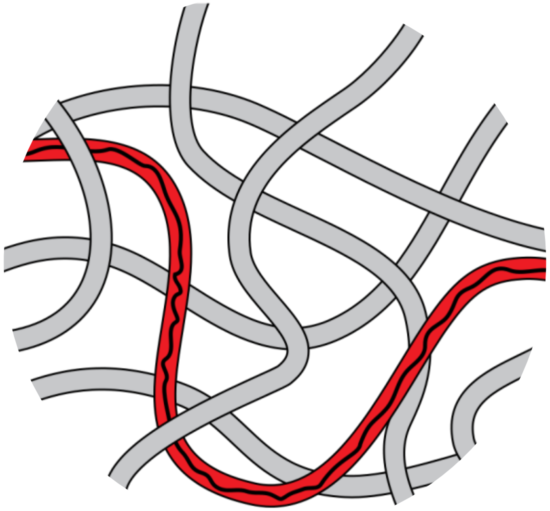


ACS Macro Lett., **3**, 1262 (2014)

Ionomers



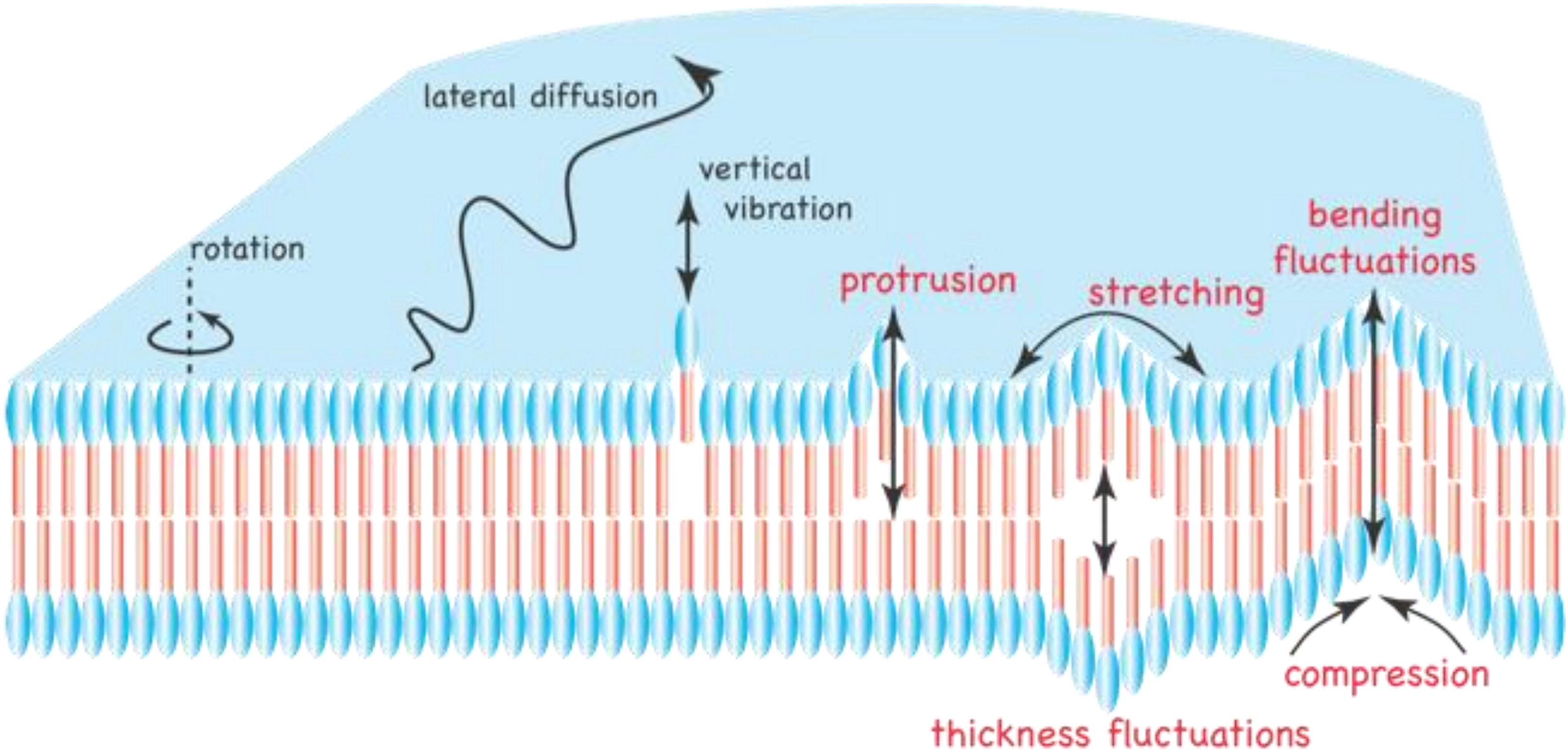
Membranes, **7**, 25 (2017)



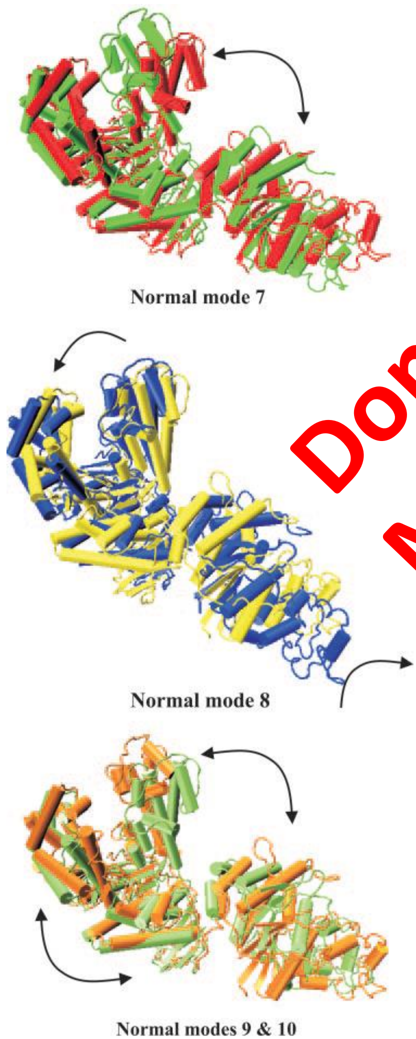
Gels

Adv. in polym. Sci., **174**, 1 (2005)

Membranes

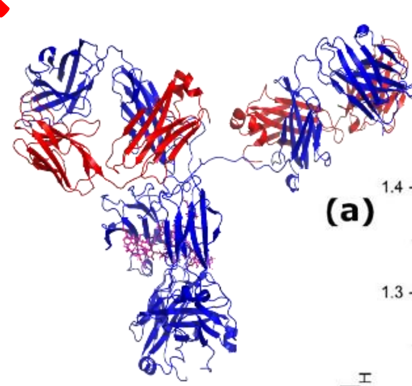

lateral diffusion
vertical
vibration
rotation
protrusion
stretching
bending
fluctuations
compression
thickness fluctuations

Proteins



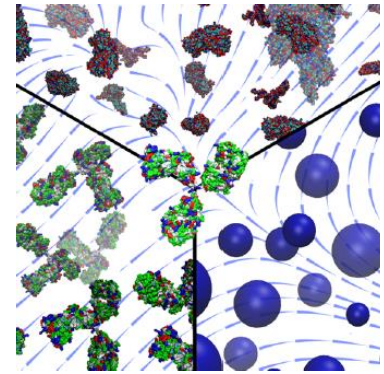
PNAS, 102, 17646 (2005)

Domain Motions

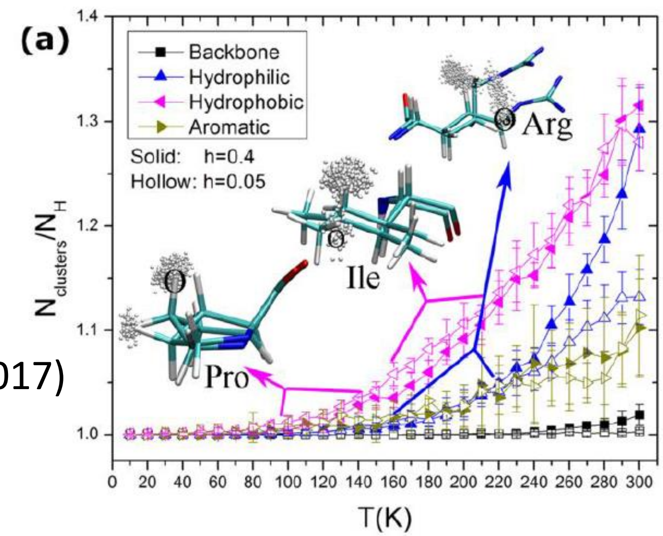


BBA, **1861**, 3638 (2017)

Diffusion



JPCL, **10**, 1709 (2019)



Atomic Motions

More Complex/Realistic Samples

SCIENTIFIC REPORTS

OPEN

Hemoglobin diffusion and the dynamics of oxygen capture by red blood cells

Received: 30 January 2017

Stéphane Longeville[1] & Laura-Roxana Stingaciu[2]

SCIENTIFIC REPORTS

OPEN

Revealing the Dynamics of Thylakoid Membranes in Living Cyanobacterial Cells

Received: 03 June 2015
Accepted: 14 December 2015

Laura-Roxana Stingaciu[1], Hugh O'Neill[2], Michelle Liberton[3], Volker S. Urban[2], Himadri B. Pakrasi[3] & Michael Ohl[1]

THE JOURNAL OF PHYSICAL CHEMISTRY B
Article
Cite This: J. Phys. Chem. B 2019, 123, 6968–6979
pubs.acs.org/JPCB

Chemotherapeutic Targets in Osteosarcoma: Insights from Synchrotron-MicroFTIR and Quasi-Elastic Neutron Scattering

Maria Paula M. Marques,[†,‡] Ana L. M. Batista de Carvalho,[*,†] Adriana P. Mamede,[†] Inês P. Santos,[†] Victoria García Sakai,[§] Asha Dopplapudi,[§] Gianfelice Cinque,[∥] Magda Wolna,[∥] Peter Gardner,[⊥] and Luís A. E. Batista de Carvalho[†]

SCIENTIFIC REPORTS

OPEN

Microscopic diffusion processes measured in living planarians

Eugene Mamontov

NIST
National Institute of Standards and Technology

Insights on the nanoscopic origin of rheological properties in polymer nanocomposites

Acknowledgement

- Erkan Senses

  Chemical and Biological Engineering, Koç University

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- Suresh Narayanan

  Advanced Photon Source, ANL

- Chris Kitchens, Mohamed Ansar

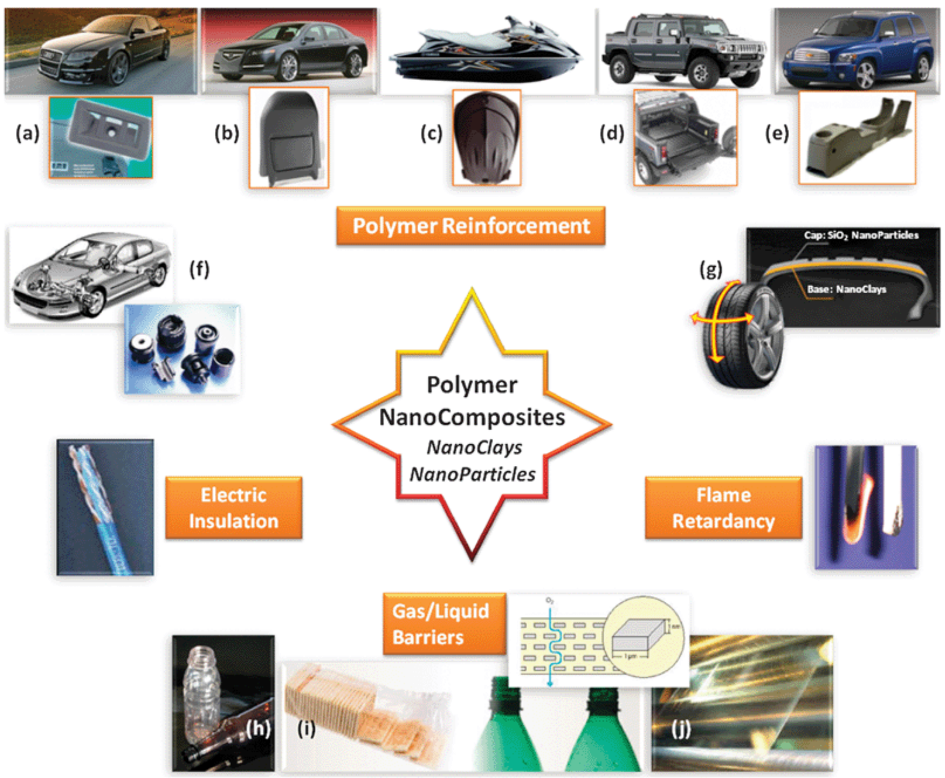
  Chemical and Biomolecular Engineering,

  Clemson University

NIST
National Institute of Standards and Technology

Polymer Nanocomposites (PNC)

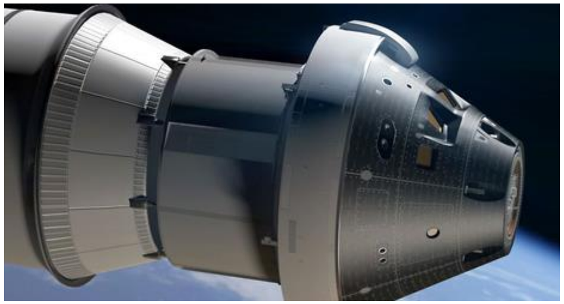
Multifunctionality!



Mechanically **adaptive** composites for improved lifetime and performance

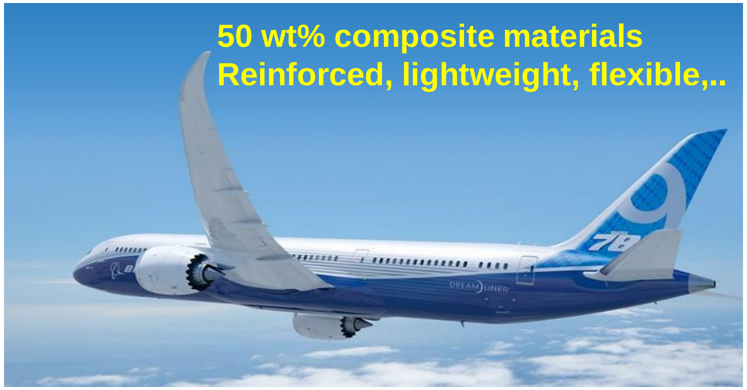
Electrostatic charge dissipation for spacecraft

- Heat & chemical resistance
- Electrically Conductive
- Light weight
- Flexible
- Insulating



Polyimide + 0.03 wt % CNTs

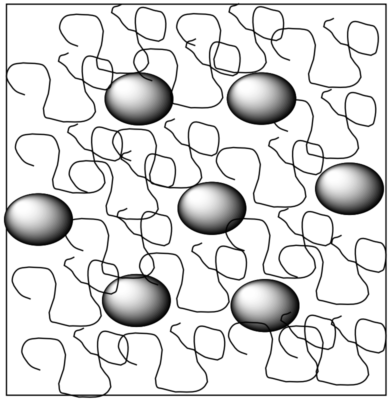
http://www.nasa.gov/exploration/systems/orion/#.VF16wfnF_dg



Boeing 787-Dreamliner

http://www.boeing.com/commercial/787/

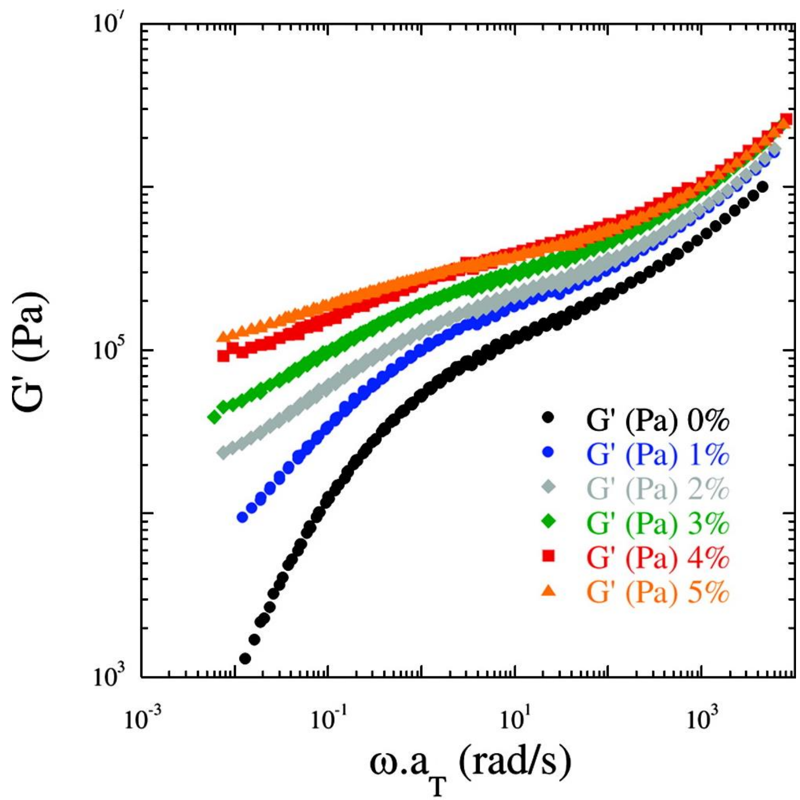
Properties of PNCs

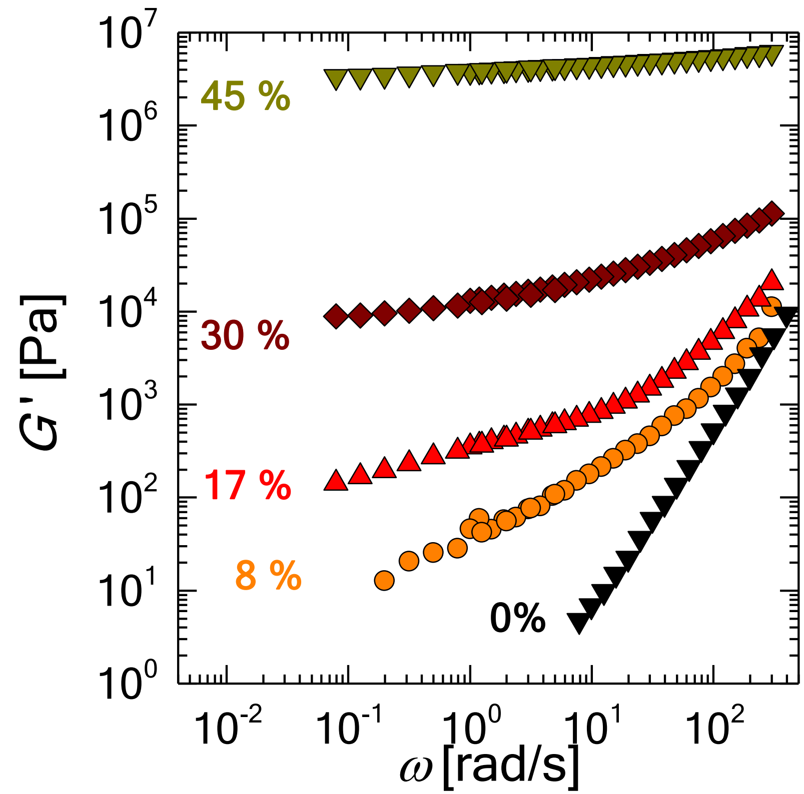


- Polymer matrix
- Nanoparticles: *size, shape, amount*
- Particle dispersion
  - Controlled dispersion
  - Orientation
  - Stability
  - Spatial distribution

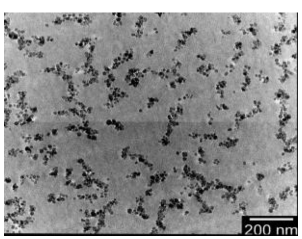
  …
  - History
- Interface and interphase

Mechanical Reinforcement in PNCs



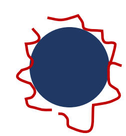


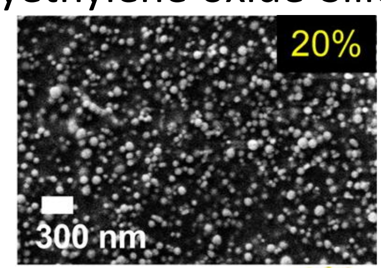
Polystyrene-Silica



Jouault, Nicolas, et al. *Macromolecules* 42.6 (2009): 2031-2040

Polyethylene oxide-Silica





by wt

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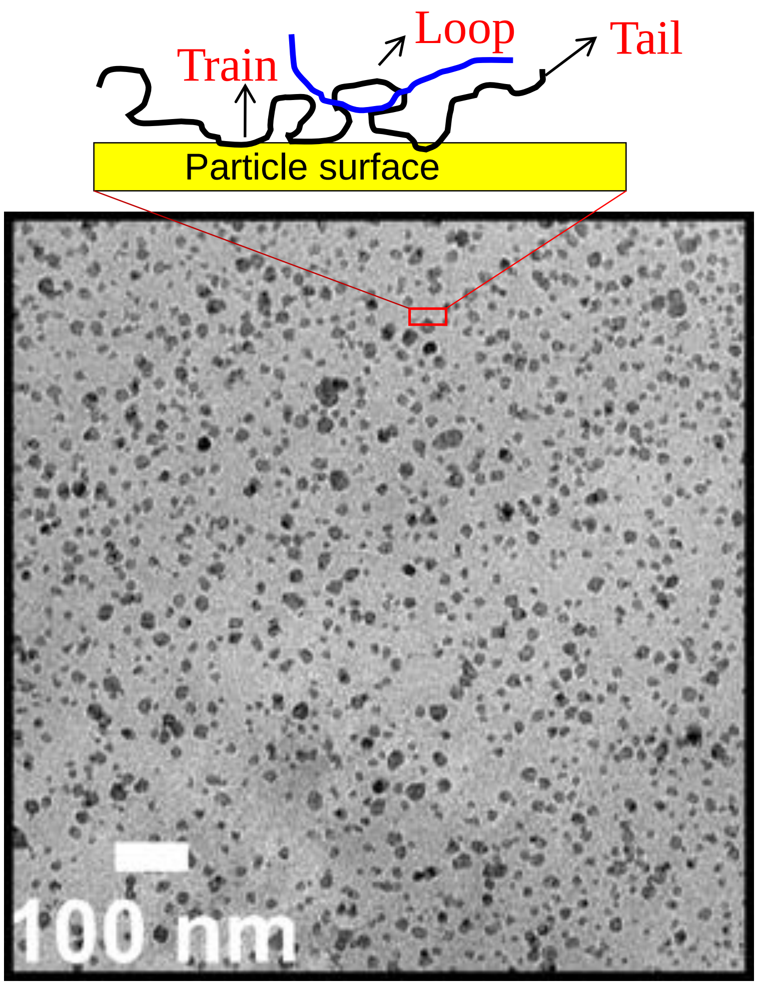
Well Dispersed NP

- NP surface/polymer interaction: Attractive

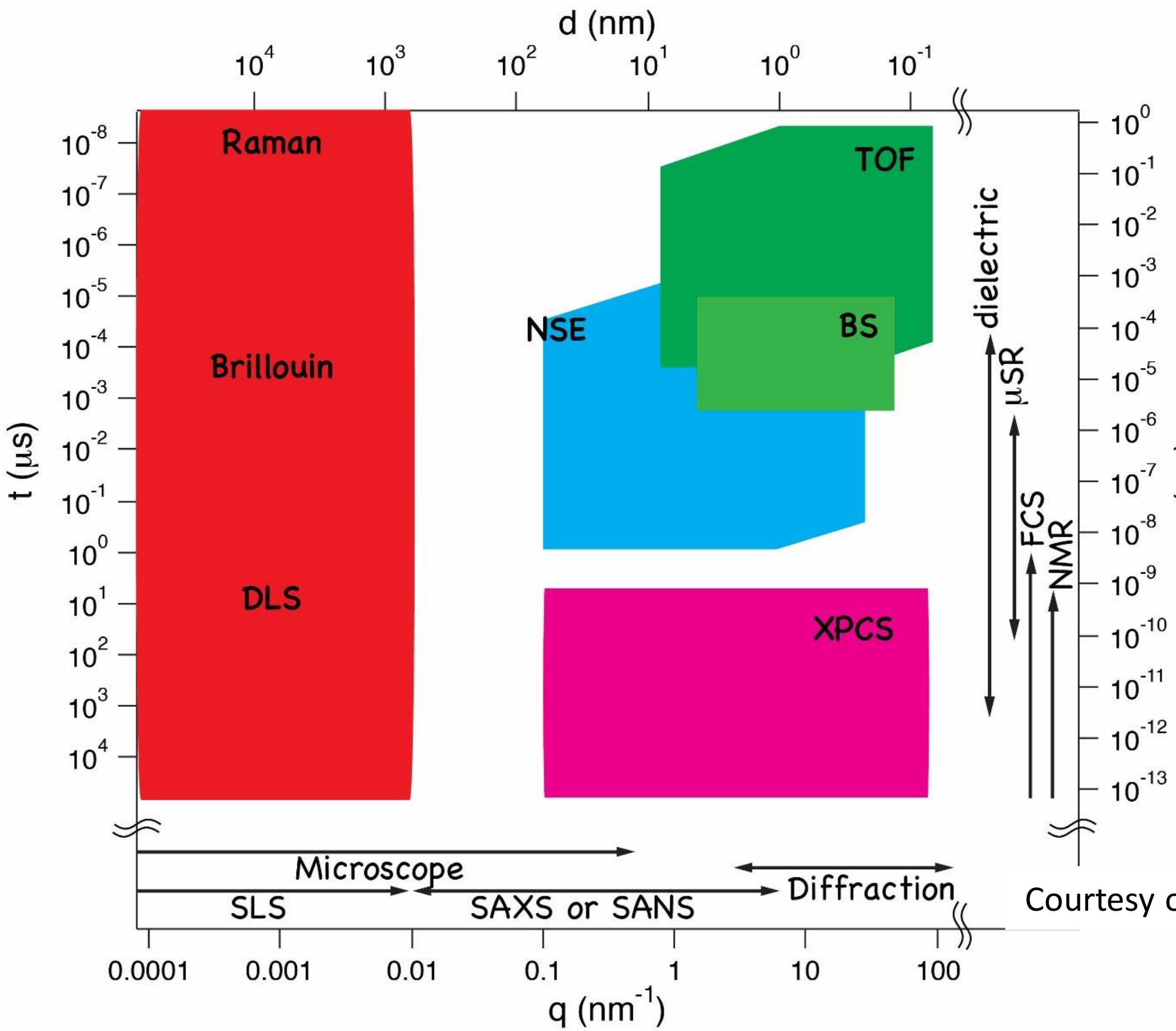
No direct particle contact. Polymer driven Reinforcement



PMMA- SiO_2

J. M. H. M. Scheutjens and G. J. Fleer. *JPC,* **84**, 178 (1980).
M. Krutyeva, et al., *PRL*, **110**, 108303 (2013).

Experimental Techniques



Courtesy of Michihiro Nagao

Scattering techniques, and neutrons in particular, are well suited to investigate the microscopic origin of the rheological behavior.

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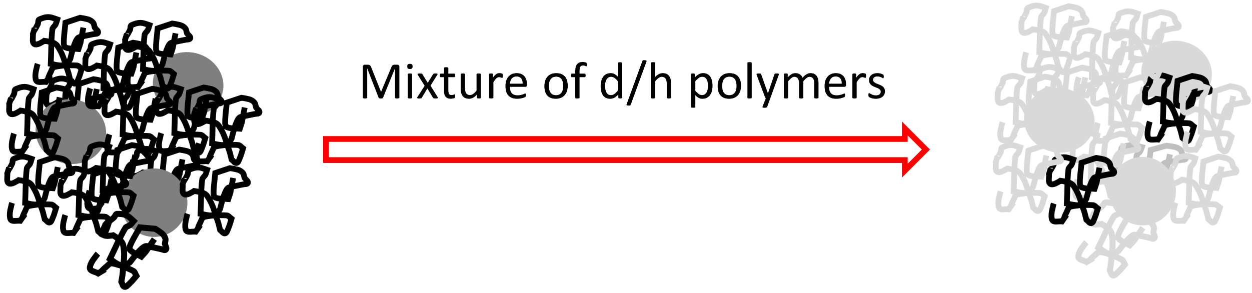
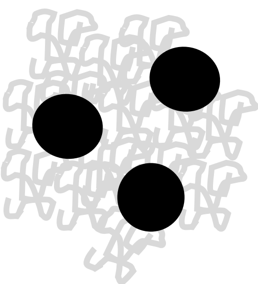
Structure

Isotopic Substitution, contrast matching techniques



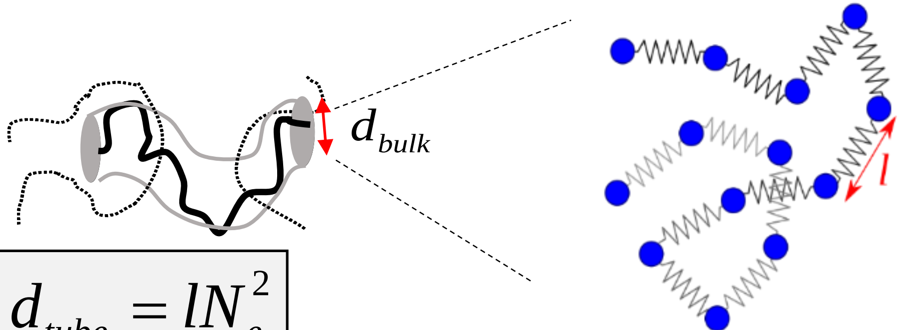
Complementarity with Small Angle X-Ray and microscopy



Microscopic Dynamics

Microscopic chain parameters that determine the macroscopic dynamics:

Length scale **Time scale**



$$\tau_p = \frac{\zeta N^2 l^2}{3\pi^2 k_B T p^2} = \frac{N^2}{\pi^2 W p^2} \qquad p=1,2,\ldots,N$$

$$d_{tube} = l N_e^{2}$$

$$W = \frac{3k_B T}{\zeta l^2} \rightarrow \frac{\textit{Entropic force}}{\textit{Viscous force}}$$

Rouse time p→N $\qquad \tau_R = \frac{1}{\pi^2 W}$

$$G_N^o \propto \frac{1}{N_e} \propto \frac{1}{d^2}$$

Neutron scattering can simultaneously access the length and time scales relevant to Rouse and Reptation motion

D. Richter, M. Monkenbusch, A. Arbe and J. Colmenero, Neutron Spin Echo in Polymer Systems, 2005, 1–221.
Dynamics of Soft Matter, Neutron Applications, Eds: **GARCIA SAKAI**, V., **Alba-Simionesco**, C., **Chen**, S.-H.

Dynamic Neutron Scattering

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \propto \frac{k_f}{k_i} N[\sigma_{coh} S_{coh}(Q,\omega) + \sigma_{incoh} S_{incoh}(Q,\omega)]$$

$$S_{coh}(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} I_{coll}(Q,t)e^{-i\omega t}dt \qquad S_{incoh}(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} I_{self}(Q,t)e^{-i\omega t}dt$$

$$I_{coll}(Q,t) = \frac{1}{N}\sum_i\sum_j \left\langle e^{-i\boldsymbol{Q}[\boldsymbol{r}_i(t)-\boldsymbol{r}_j(0)]} \right\rangle \qquad I_{self}(Q,t) = \frac{1}{N}\sum_i \left\langle e^{-i\boldsymbol{Q}[\boldsymbol{r}_i(t)-\boldsymbol{r}_i(0)]} \right\rangle$$

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Single Chain Dynamics – Neutron Spin Echo

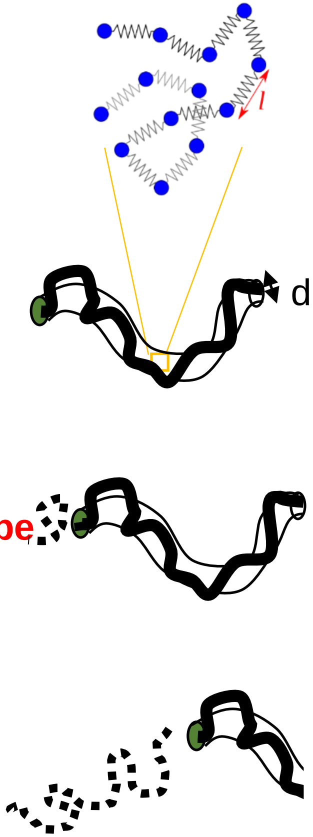
$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \propto \frac{k_f}{k_i} N[\sigma_{coh} S_{coh}(Q,\omega) + \sigma_{incoh} S_{incoh}(Q,\omega)]$$

⇒

Single Chain Dynamics – Neutron Spin Echo

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \propto \frac{k_f}{k_i} N[\sigma_{coh}S_{coh}(Q,\omega)+\sigma_{incoh}S_{incoh}(Q,\omega)]$$

time scale (t) **length scale (1/Q)** **Intermediate scattering function**



$t<t_{entanglement}$
Unrestricted **Rouse** motion within tube

$$\frac{1}{N}\sum_{i,j}^{N}\exp\left\{-Q^2D_Rt-\frac{Q^2l^2}{6}|i-j|-\frac{2Q^2Re^2}{3\pi^2}\sum_{p=1}^{N}\frac{1}{p^2}\cos\left(\frac{p\pi i}{N}\right)\sin\left(\frac{p\pi i}{N}\right)[1-\exp\left(\frac{p^2t}{\tau_R}\right)]\right\}$$

$t_{ent.}<t<t_{Rouse}$
Reptation motion

$$\left[1-\exp\left(\frac{-Q^2d^2}{36}\right)\right]S^{local}(Q,t)+\exp\left(\frac{-Q^2d^2}{36}\right)$$

$t_{Rouse}<t<t_{Terminal}$
Partially escape from the tube

$$\left[1-\exp\left(\frac{-Q^2d^2}{36}\right)\right]S^{local}(Q,t)+\exp\left(\frac{-Q^2d^2}{36}\right)S^{escape}(Q,t)$$

$t>t_{Terminal}$
Center of Mass **Diffusion**

$$\exp\left(\frac{-Q^2d^2}{36}\right)S^{escape}(Q,t)$$

$$S^{local}(Q,t)=\exp\left(\frac{t}{\tau_0}\right)\operatorname{erfc}\left[\left(\frac{t}{\tau_0}\right)^{1/2}\right]$$

$$S^{escape}(Q,t)=\exp(-Q^2D_{rep}t/6)$$

Segmental Dynamics - Backscattering

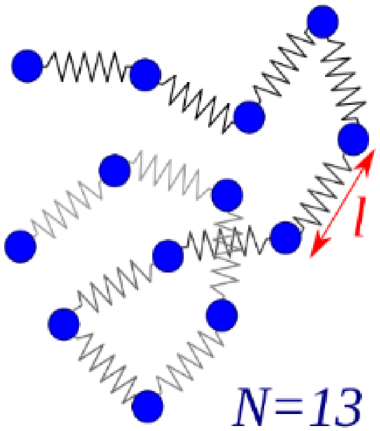
H containing samples

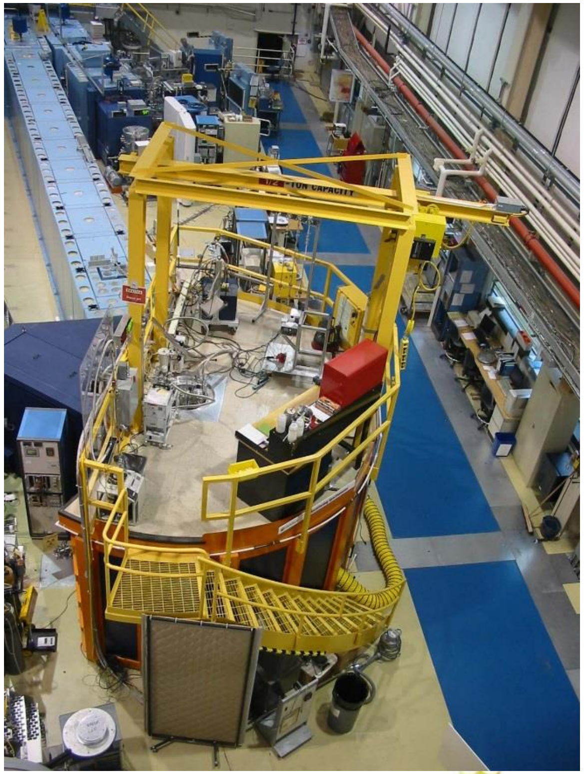
$$\sigma_{incoh}^{H} \gg \sigma_{coh}^{H,D,C,O,Si,Au}, \sigma_{incoh}^{D,C,O,Si,Au}$$

$$\frac{\partial^2\sigma}{\partial\Omega\partial E} \propto \frac{k_f}{k_i} N[\cancel{\sigma_{coh}S_{coh}(Q,\omega)} + \sigma_{incoh}S_{incoh}(Q,\omega)]$$

In the appropriate Q-t range:

Rouse Dynamics





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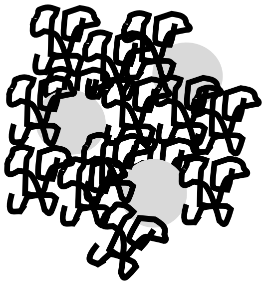
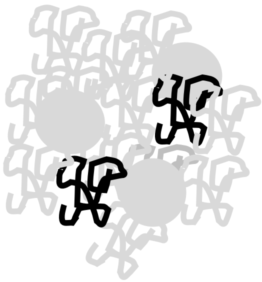
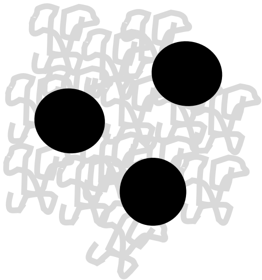
Complementarity



Hydrogenated Polymers:
Single particle segmental dynamics
Backscattering

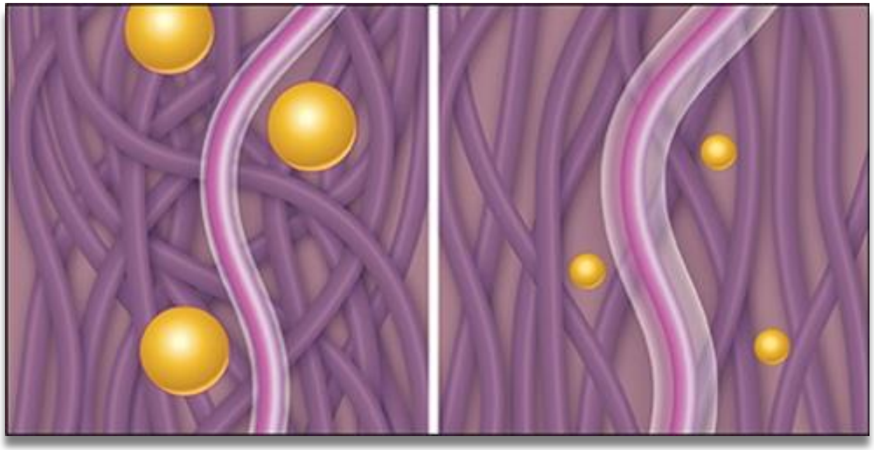


H/D Polymers, contrast match:
Single chain dynamics
Neutron Spin Echo



Nanoparticles dynamics
X-ray Photon Correlation Spectroscopy (XPCS)

The role of Nanoparticle size on chain dynamics

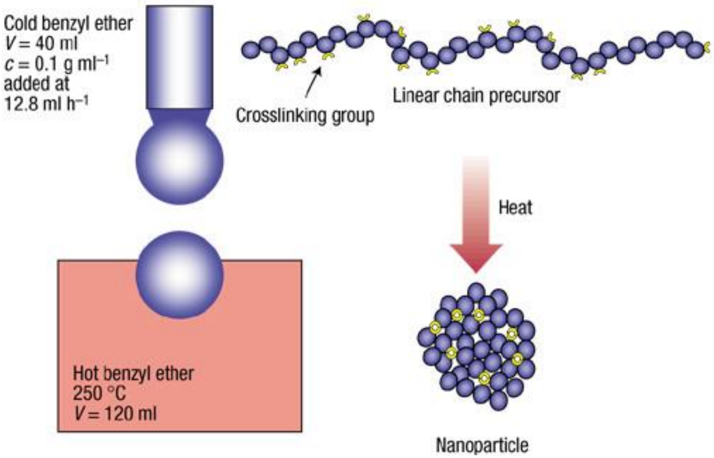


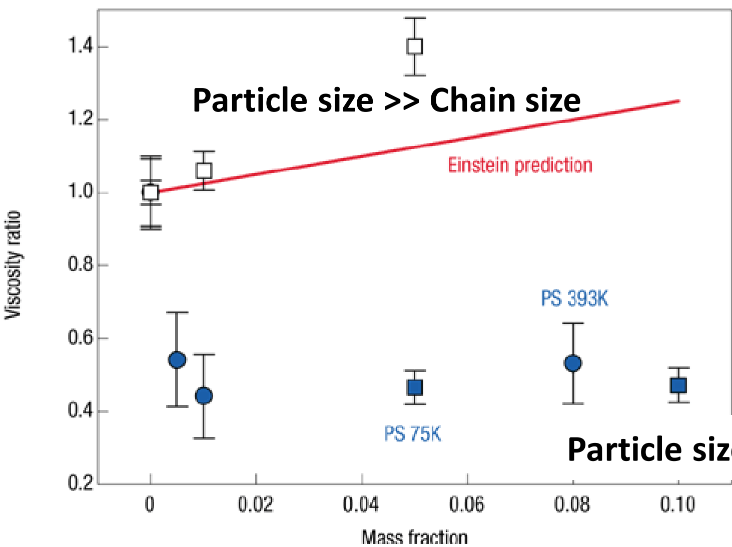
Viscosity Reduction in PNCs

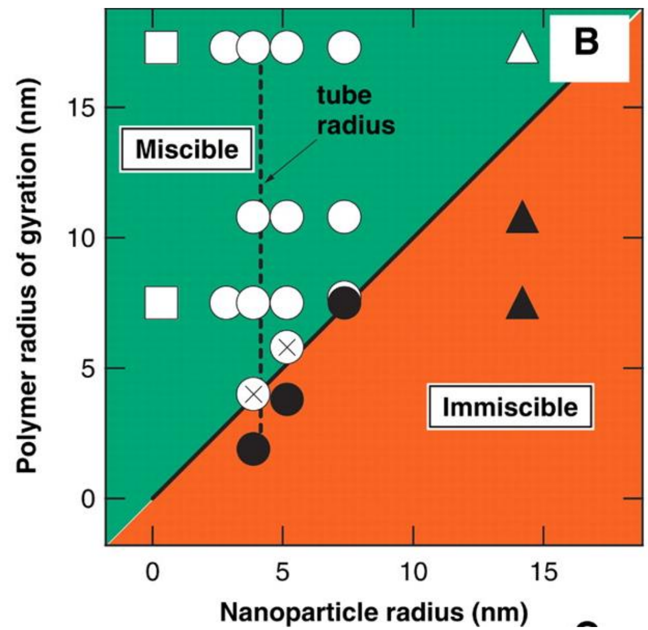
Polystyrene NPs in polystyrene matrix: *athermal*

Mackay, Michael E., et al. *Nature materials* 2.11 (2003): 762-766.

Mackay, Michael E., et al. *Science* 311.5768 (2006): 1740-1743.



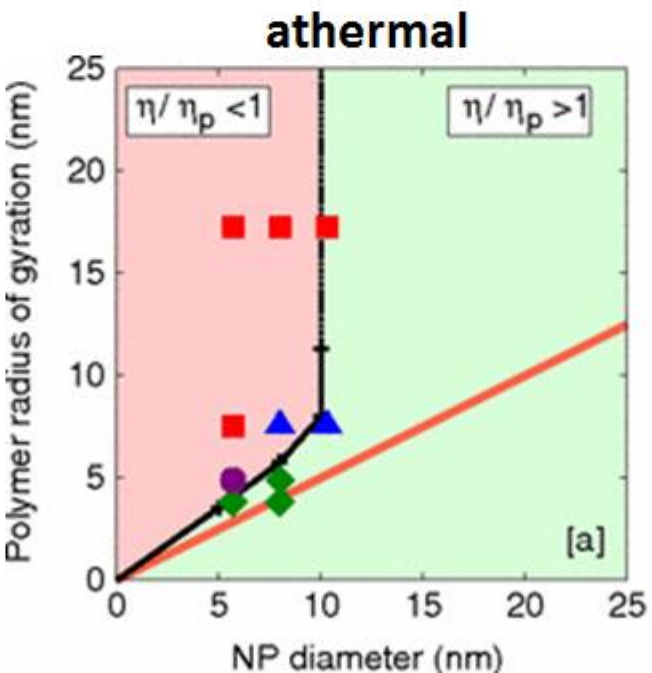


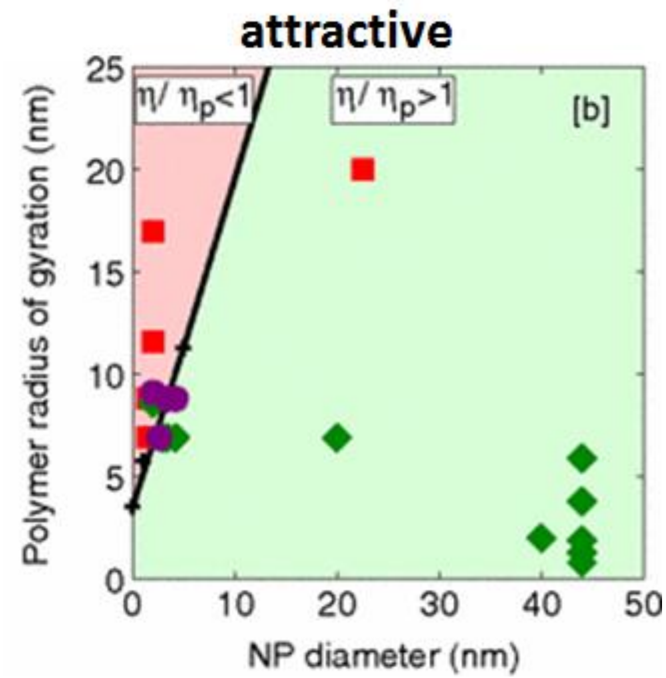


Particle size < Chain size & tube size

Size and Interaction Dependence

Kalathi, Jagannathan T., Gary S. Grest, and Sanat K. Kumar. *Phys. Rev. Lett.*, **109**, 198301. (2012).





- Viscosity reduction independent of polymer size.
- Similar to a plasticizer.
- Valid for sizes up to entanglement mesh size.

Attractive interactions reverse the size effect.

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Need for Experiments

Soft Matter

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Cite this: *Soft Matter*, 2015, **11**, 4123

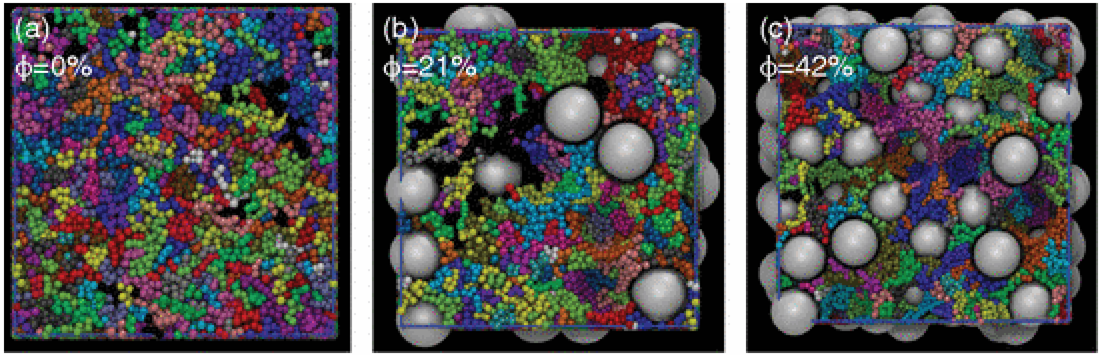
Rouse mode analysis of chain relaxation in polymer nanocomposites

Jagannathan T. Kalathi,[ab] Sanat K. Kumar,*[a] Michael Rubinstein[c] and Gary S. Grest[d]

PRL **109,** 118001 (2012) PHYSICAL REVIEW LETTERS week ending 14 SEPTEMBER 2012

Nanoparticle Effect on the Dynamics of Polymer Chains and Their Entanglement Network

Ying Li,[1] Martin Kröger,[2] and Wing Kam Liu[1,3,*]



nature COMMUNICATIONS

ARTICLE

Received 7 Nov 2014 | Accepted 17 Apr 2015 | Published 5 Jun 2015

DOI: 10.1038/ncomms8198 OPEN

Phase stability and dynamics of entangled polymer-nanoparticle composites

Rahul Mangal[1], Samanvaya Srivastava[2] & Lynden A. Archer[1]

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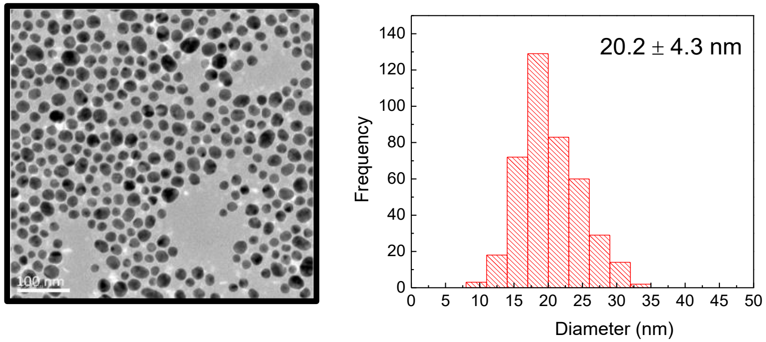
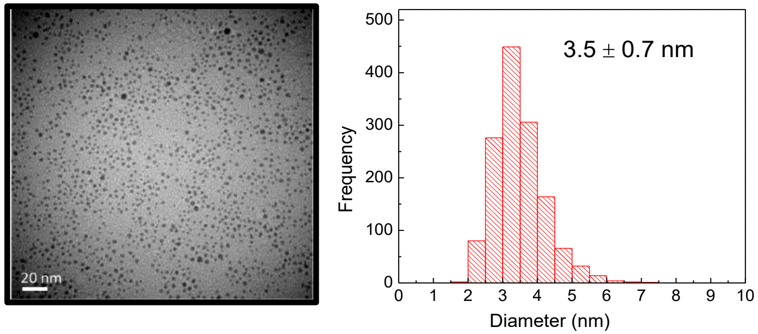
Samples

Large NPs



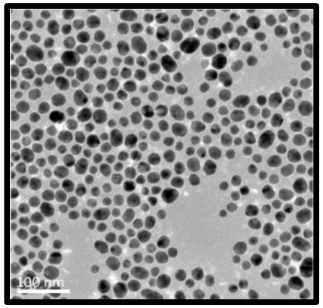
Small NPs

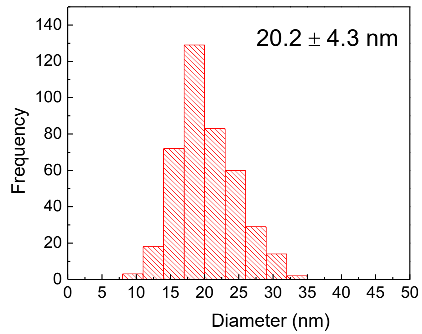


Particles are PEG coated (< 1nm) to provide entropic stabilization

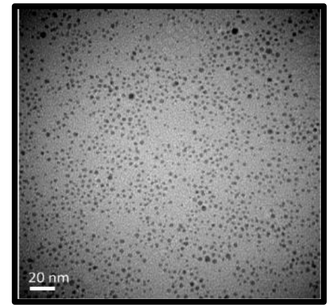
Samples

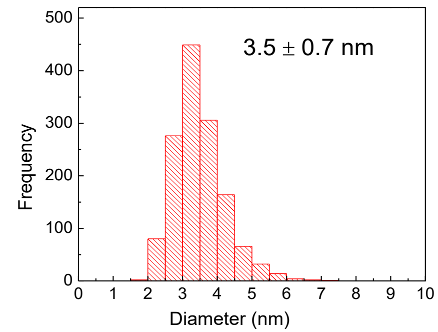
Large NPs





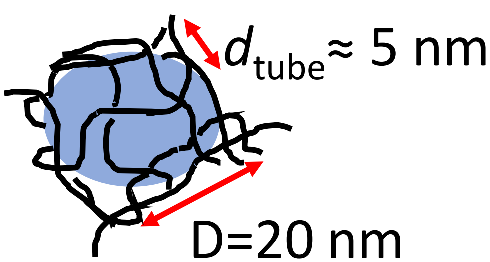
Small NPs

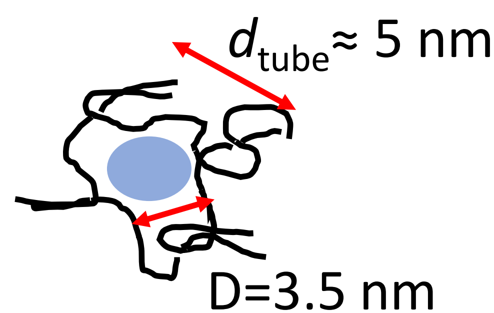




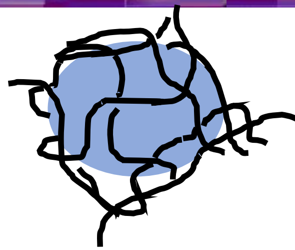
Particles are PEG coated (< 1nm) to provide entropic stabilization

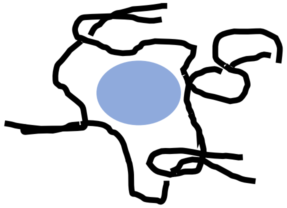
We made nanocomposites with these particles (20 % by volume) and long chain poly (ethylene glycol) (PEG) matrix (35 kg/mol).

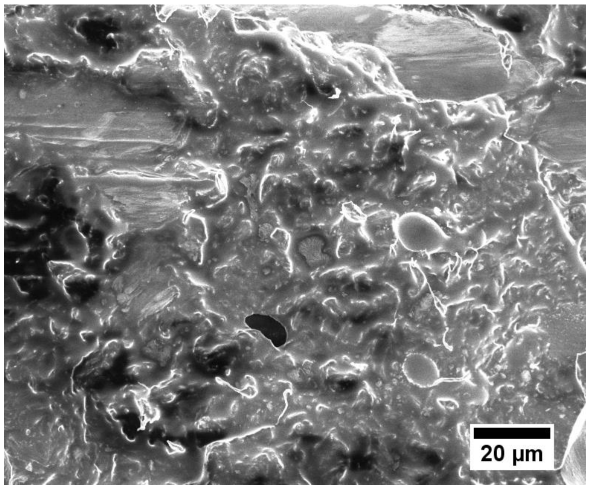


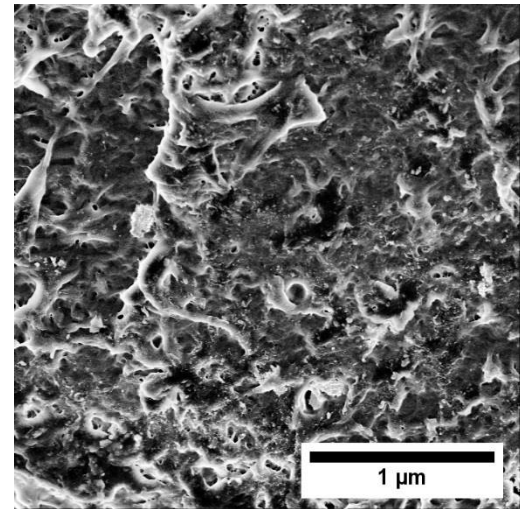


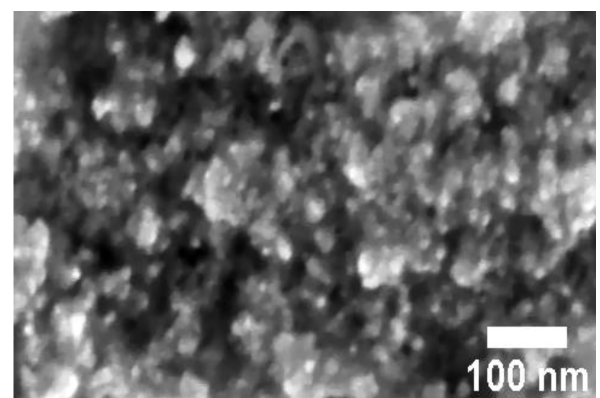
Dispersion





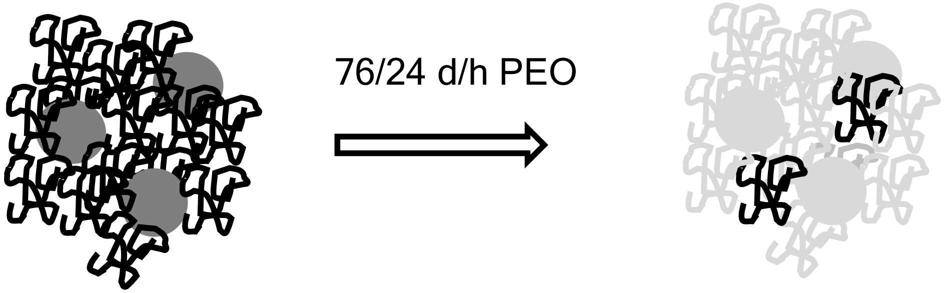


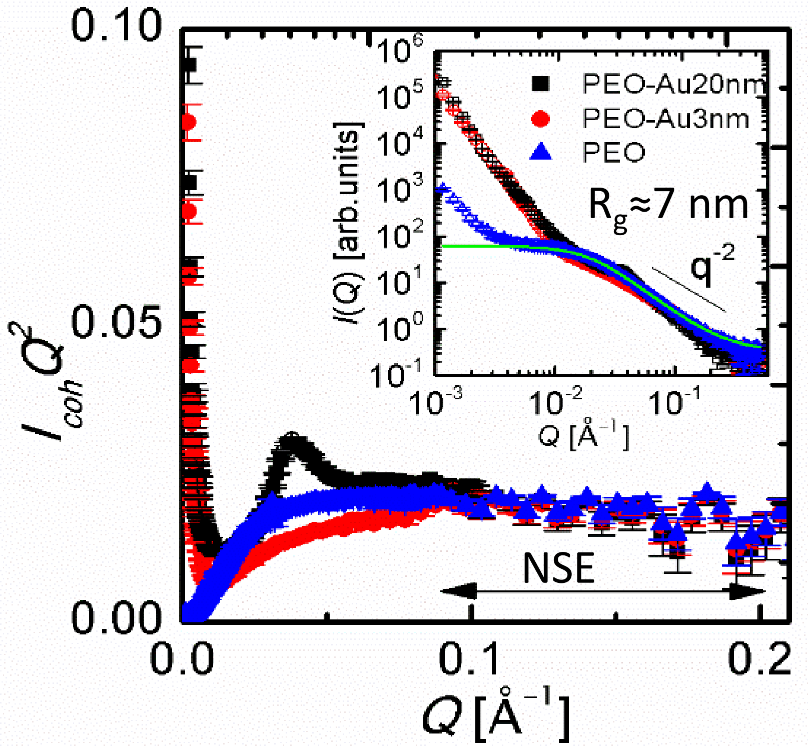




Single Chain Conformation

Contrast Matched PEO/NP (hPEO/dPEO 76 % / 24 %)

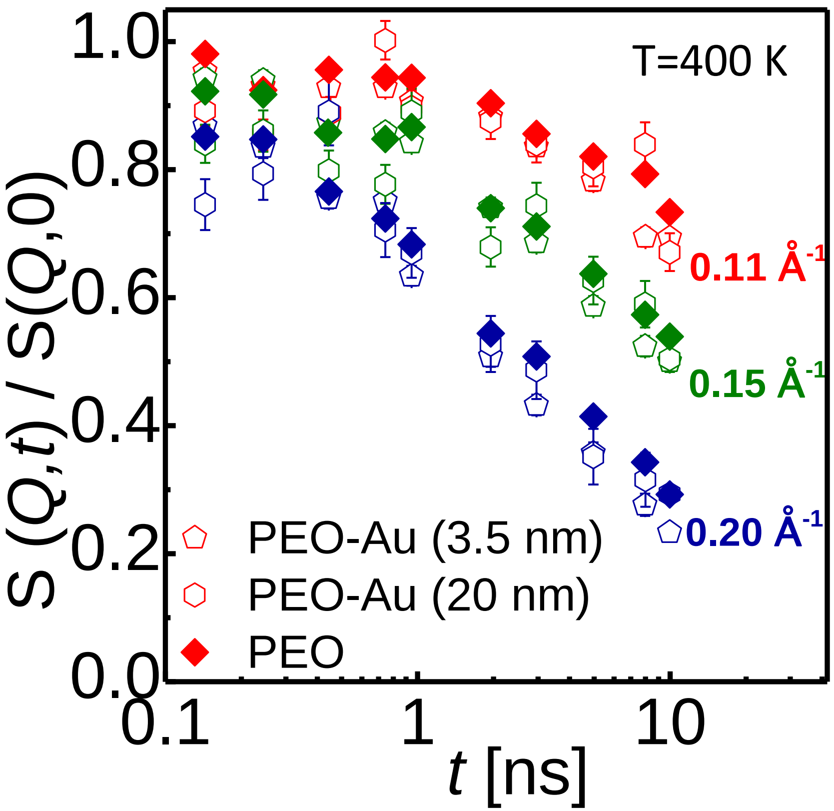


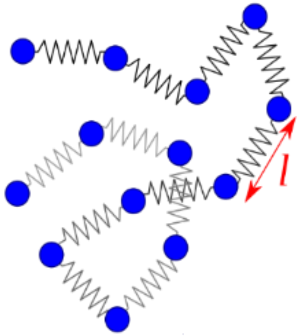


- The PEO in nanocomposites remains Gaussian.
- In the NSE range, we observe the single chain form factor of Gaussian PEO chains.

Fetters, L. J., D. J. Lohse, and R. H. Colby. *Physical Properties of Polymers Handbook*. Springer New York, 2007. 447-454.

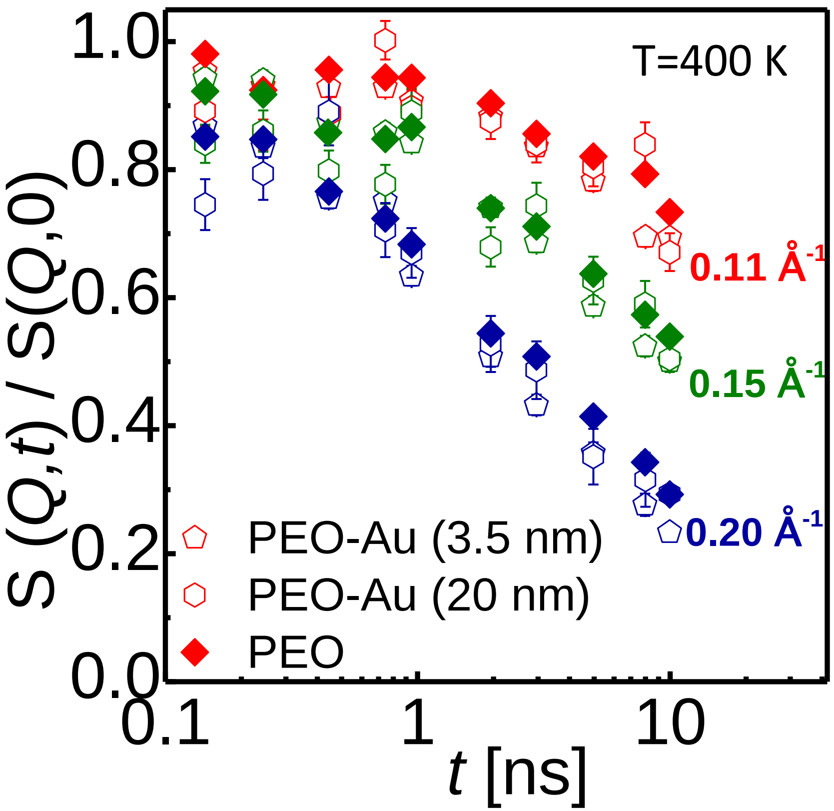
Short time – Rouse Dynamics

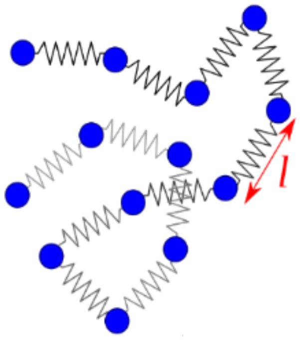




Rouse dynamics is not modified in nanocomposites!

Short time – Rouse Dynamics





Parameters	Definition	Value used	Unit
N	Number of segments	795	-
l	Segment length	0.58	nm
$R_e = \sqrt{Nl^2}$	End-to-end distance	16.35	nm
Wl^4	Rouse parameter	1.51*	nm⁴/ns
$D_R = Wl^4/(3R_e^2)$	Rouse diffusion coefficient	0.0019	nm²/ns
τ_R	Rouse time	4799	ns

*K. Niedzwiedz et al., Macromolecules **41**, 4866 (2008)

Coherent dynamics structure factor for a Rouse motion

$$S_{Rouse}(Q,t) = \frac{1}{N}\sum_{m,n}^{N}\left\{\exp(-Q^2 D_R t - \frac{1}{6}|m-n|Q^2 l^2) - \frac{2}{3}\frac{R_e^2 Q^2}{\pi^2}\sum_{p=1}^{N}\frac{1}{p^2}\cos(\frac{p\pi m}{N})\cos(\frac{p\pi n}{N})[1-\exp(\frac{-p^2 t}{\tau_R})]\right\}$$

$$W = \frac{3kTl^2}{\zeta} \qquad \zeta : monomeric\ friction\ coefficient$$

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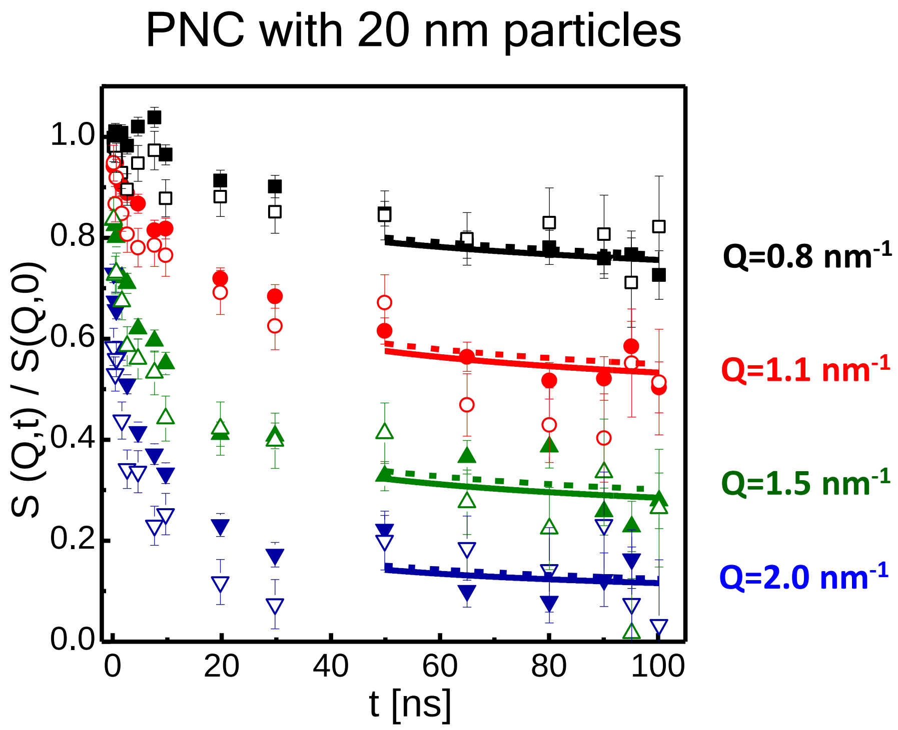
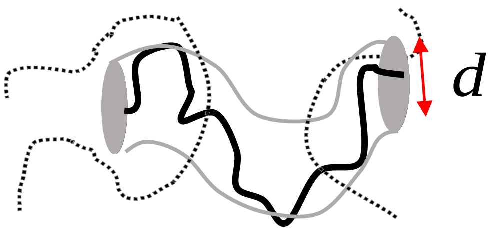
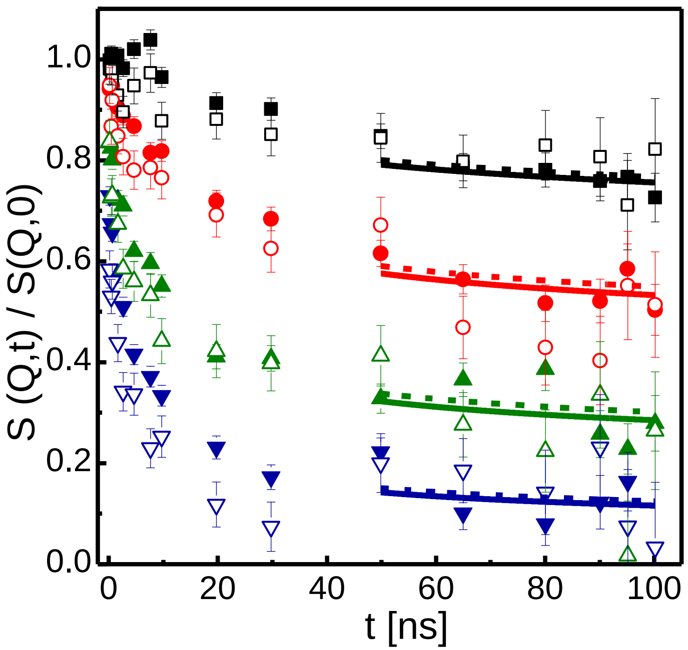
Long time – Confined motion



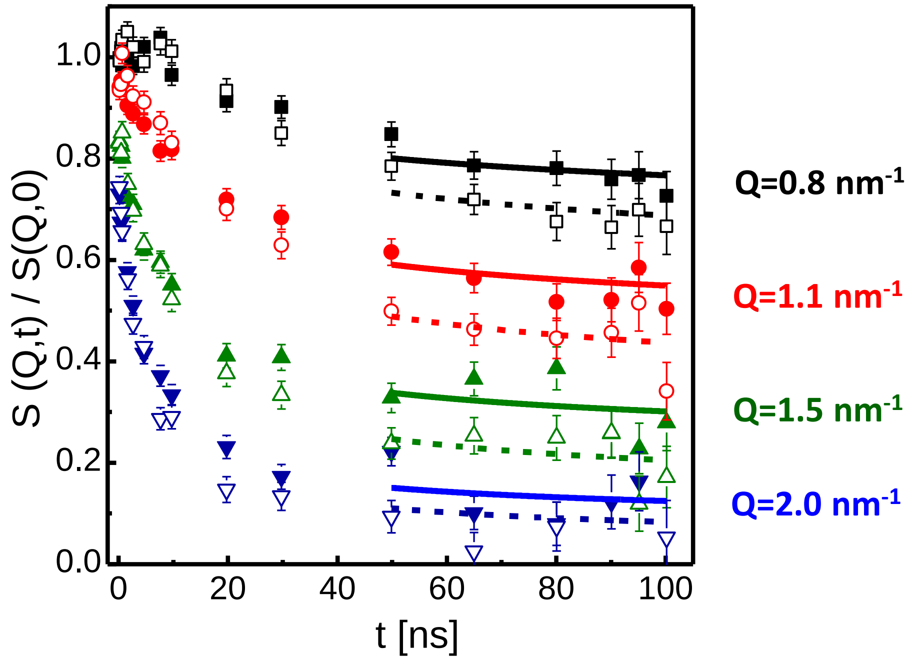


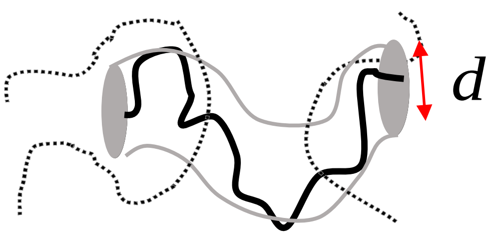
Long time – Confined motion

PNC with 20 nm particles



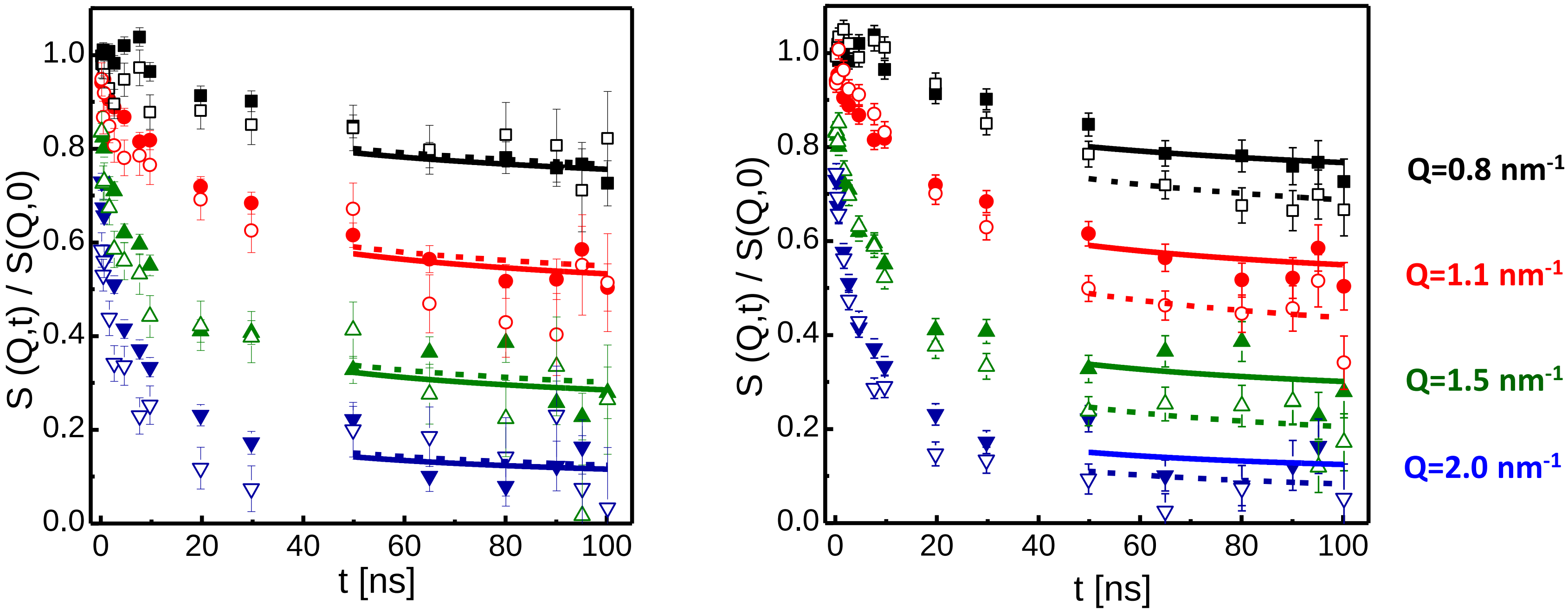
PNC with 3.5 nm particles



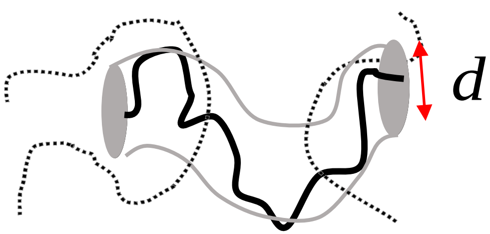


Long time – Confined motion

PNC with 20 nm particles — PNC with 3.5 nm particles



de Gennes formulation



$$\left(\frac{S^{coh}(Q,t)}{S^{coh}(Q,0)}\right)_{\text{Rept.}} = [1-\exp(-\frac{Q^2d^2}{36})]S_{local}(Q,t)+\exp(-\frac{Q^2d^2}{36})S_{esc}(Q,t)$$

$$S_{local}(Q,t)=\exp\left(\frac{t}{\tau_o}\right)erfc(\sqrt{t/\tau_o}) \qquad S_{esc}(Q,t)=1$$

$$\tau_o = 36/(Wl^4\,Q^4) \quad ; \; Wl^4 = 1.51\, nm^4/ns \text{ for PEO @ T=400K}$$

d **is the only fitting parameter!**

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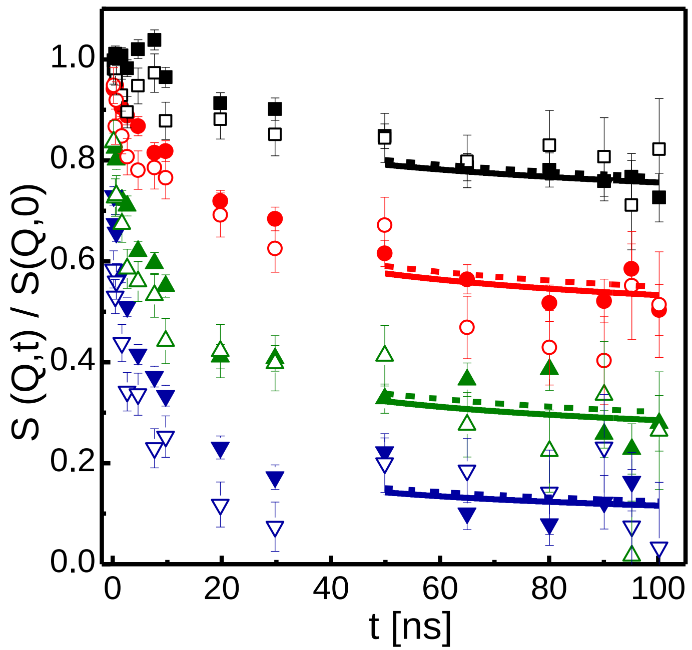
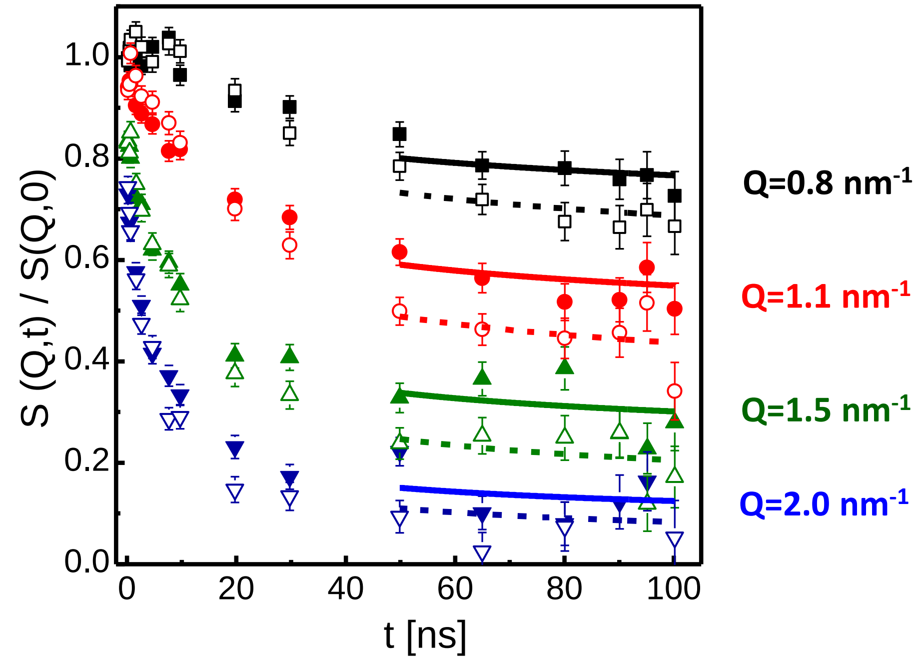
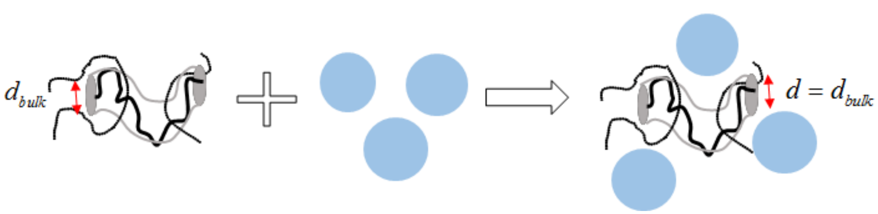
Long time – Confined motion

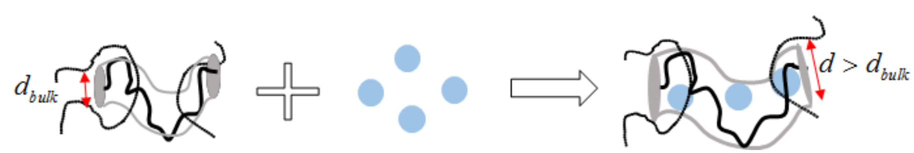
PNC with 20 nm particles



PNC with 3.5 nm particles







$$d_{PEO} = 5.03 \pm 0.1 \text{ nm}$$

$$\approx$$

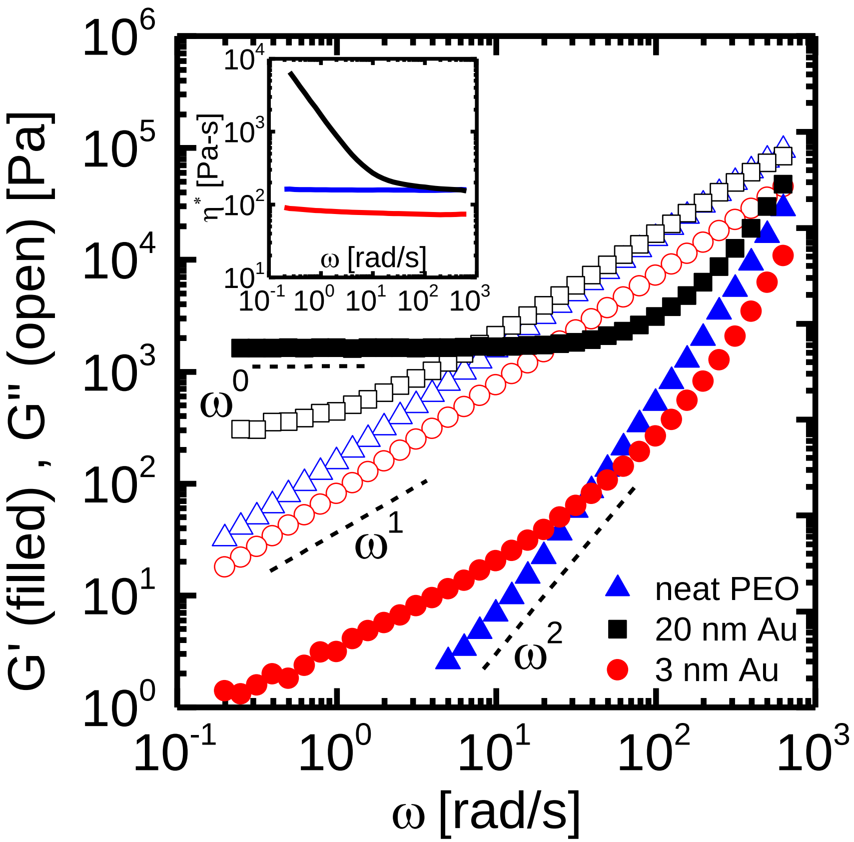
$$d_{PEO-20nmAu} = 5.17 \pm 0.19 \text{ nm}$$

$$d_{PEO} = 5.03 \pm 0.1 \text{ nm}$$

$$<$$

$$d_{PEO-3nmAu} = 6.11 \pm 0.13 \text{ nm}$$

Bulk Rheology



- Strong reinforcing effect of large particles

- Viscosity decreased by half with addition of 20 vol. % small particles

$$\eta_o \propto \tau_d = \frac{3N^3}{W\pi^2}\left(\frac{l}{d}\right)^2$$

$$\eta_{bulk,Au-3nm} / \eta_{bulk,PEO} = (d_{PEO} / d_{PEO-3nmAu})^2$$

$$\approx 0.67 \pm 0.23$$

$$G_N^o \propto \frac{1}{N_{ent.}} \propto \frac{1}{d^2}$$

One would expect to see ~ 60% decrease rubbery plateau.

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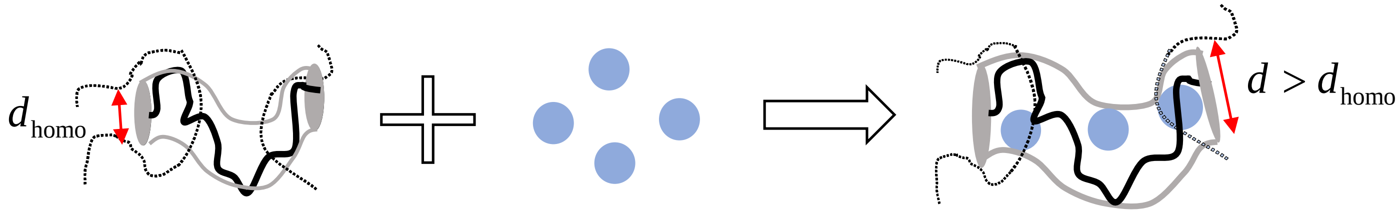
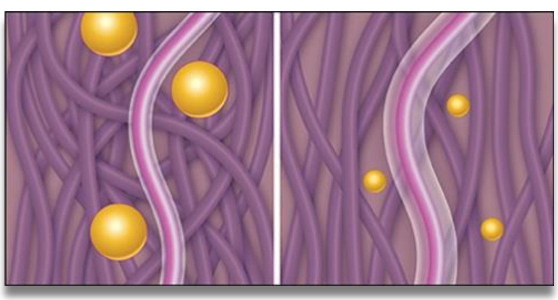
Summary

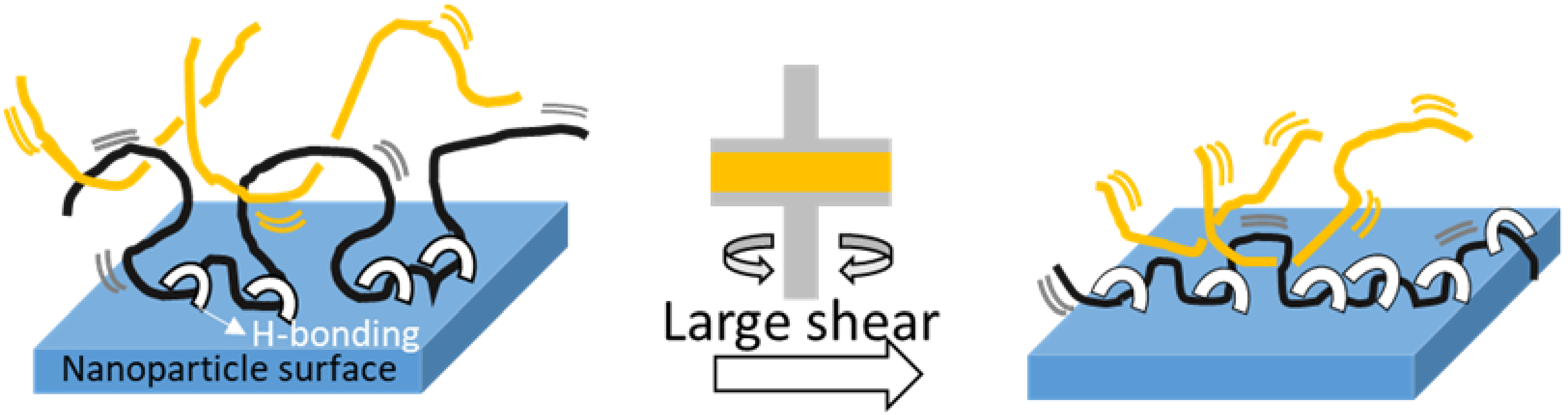


- Chains disentangle when $d_{particle} < d_{tube.}$ First direct experimental evidence.
- Rouse dynamics unaffected (at least in our athermal system).
- An explanation for non-Einstein-like viscosity decrease in polymer nanocomposites.



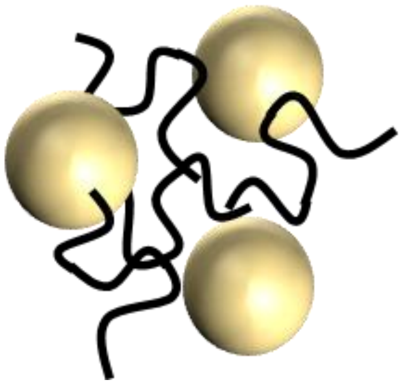
E. Senses, et al., Phys. Rev. Lett, **118**, 147801 (2017).

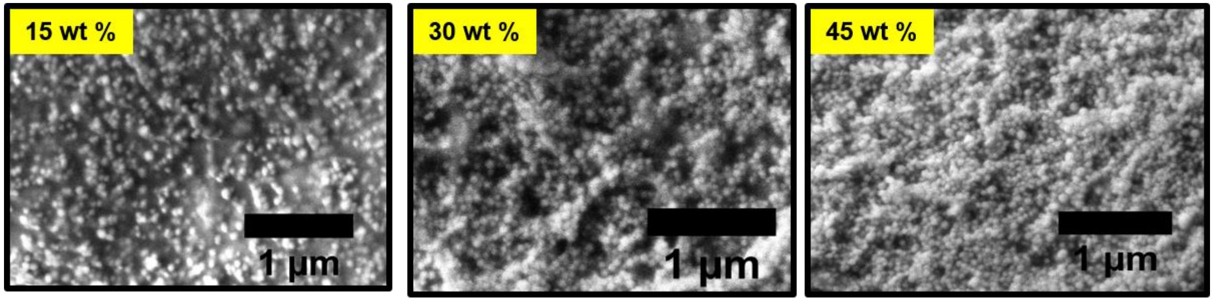
Chain Dynamics in nanocomposites subjected to large deformations



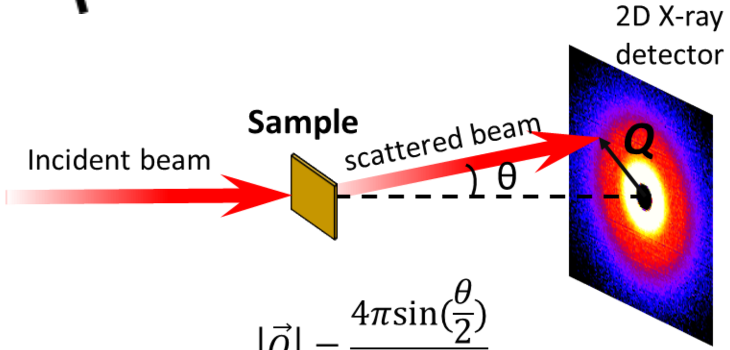
Silica Particles in PolyEthylene Oxide

PEO (35 kg/mol, $R_g \approx 7$ nm) / Silica (55 nm diameter)

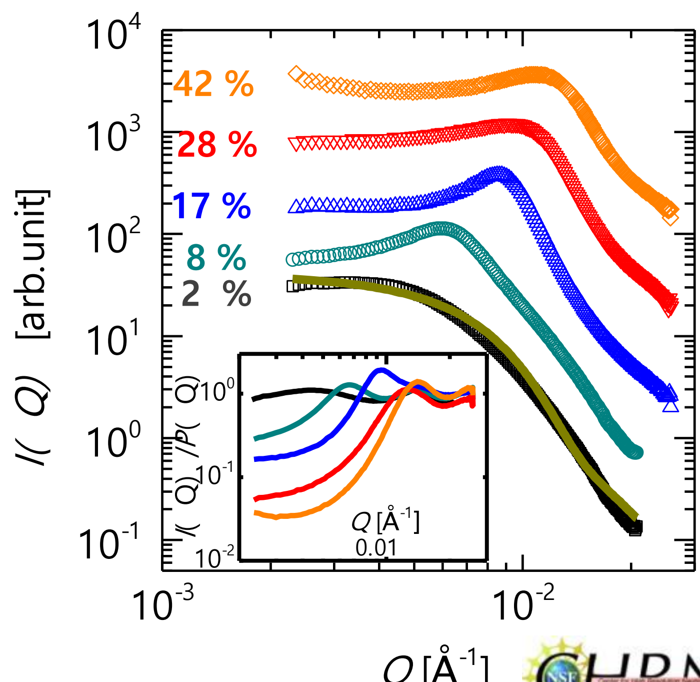




E. Senses, et al., PRL, **119**, 237801 (2017).

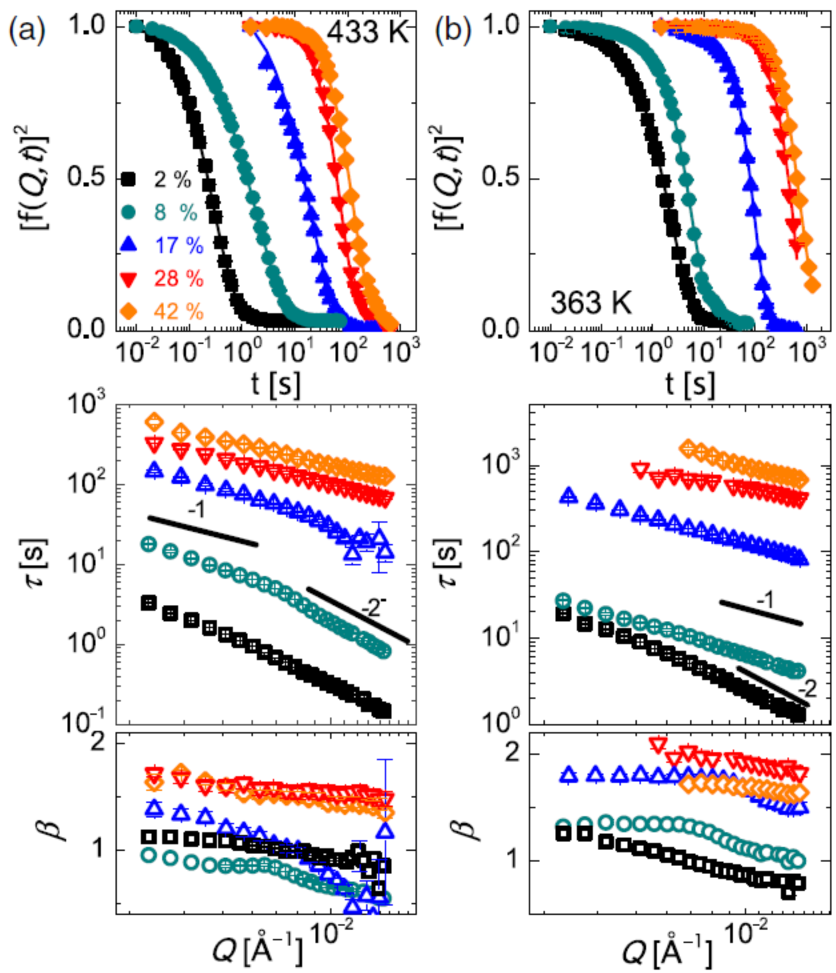


$$|\vec{Q}| = \frac{4\pi \sin(\frac{\theta}{2})}{\lambda}$$



NP % mass (volume)	Face-to-face distance (h) [nm] SAXS	random packing	$h/2R_g$
5 (2.5)	-	93.8	-
15 (7.8)	52.3	48.5	3.74
30 (17.1)	21.8	26.4	1.56
45 (28.3)	14.8	14.9	1.06
60 (41.9)	5.1	7.2	0.51

Nanoparticle Dynamics and Rheology Decoupling



Nanoparticle Dynamics

E. Senses, et al., PRL, **119**, 237801 (2017).

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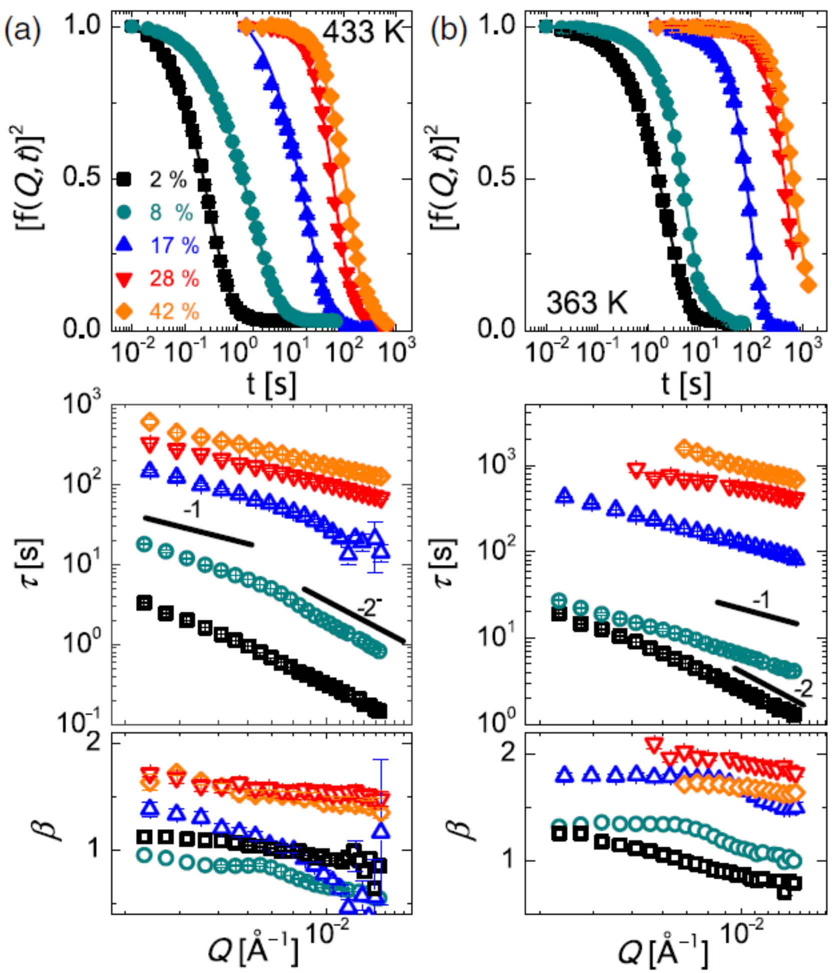
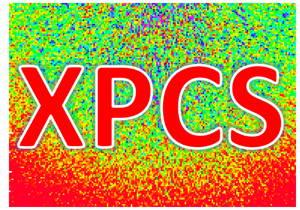
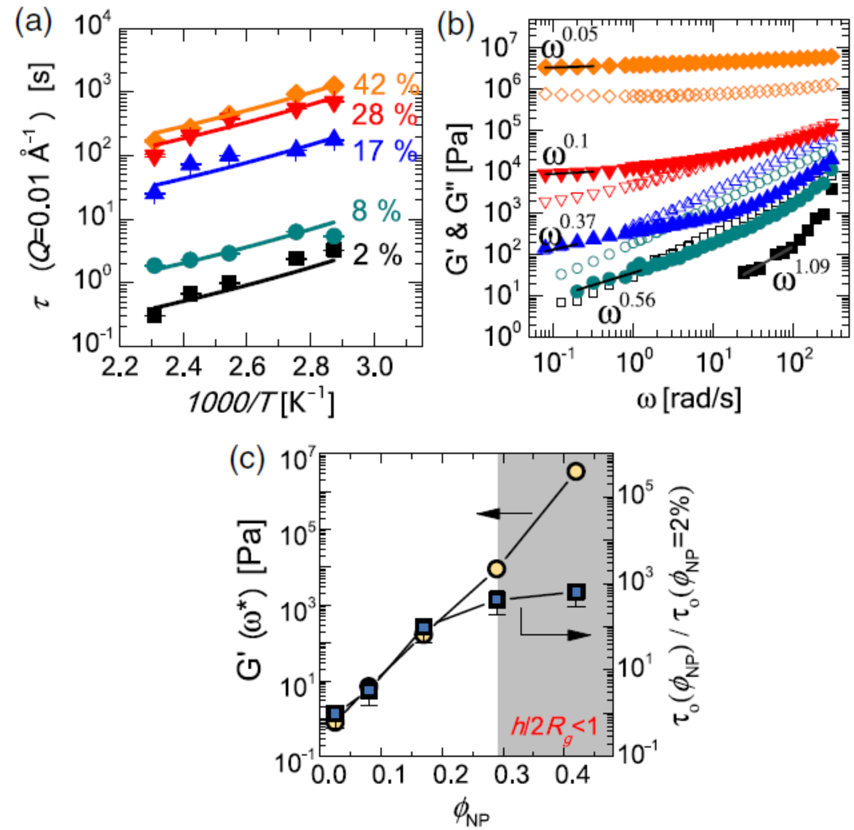
Nanoparticle Dynamics and Rheology Decoupling



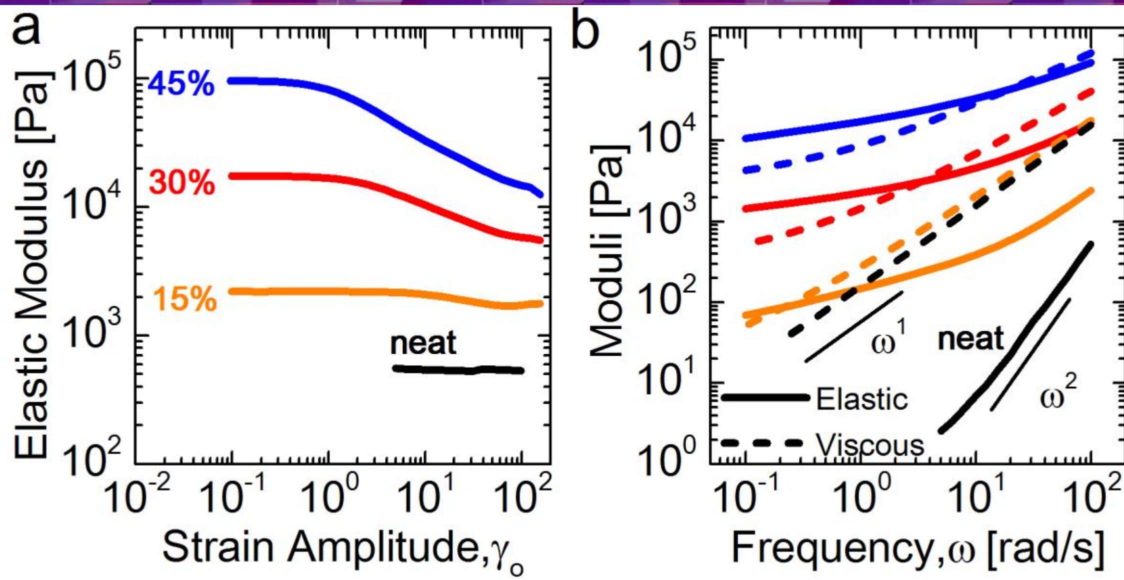


Nanoparticle Dynamics

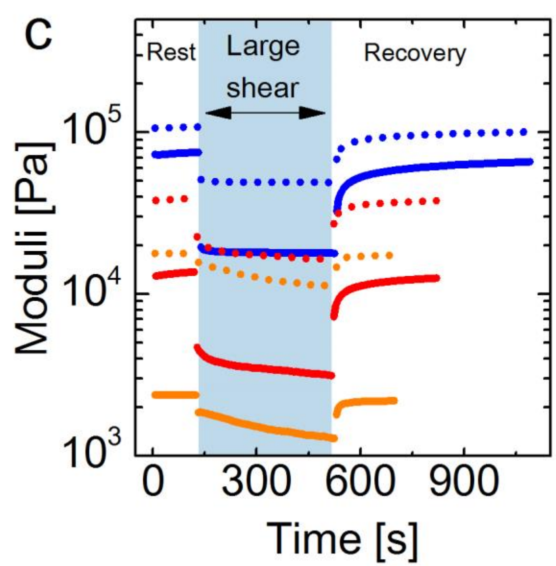


E. Senses, et al., PRL, **119**, 237801 (2017).

Payne effect (Nanocomposites Subject to Large Deformations)



Narrowing linear regime in nanocomposites and large decrease in modulus with strain: **Payne Effect**



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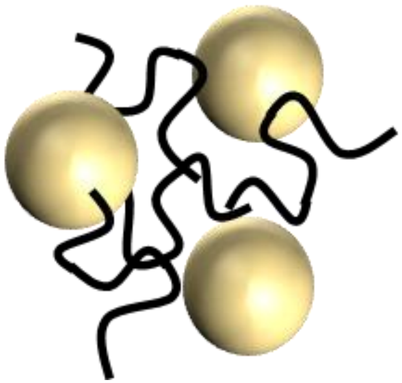
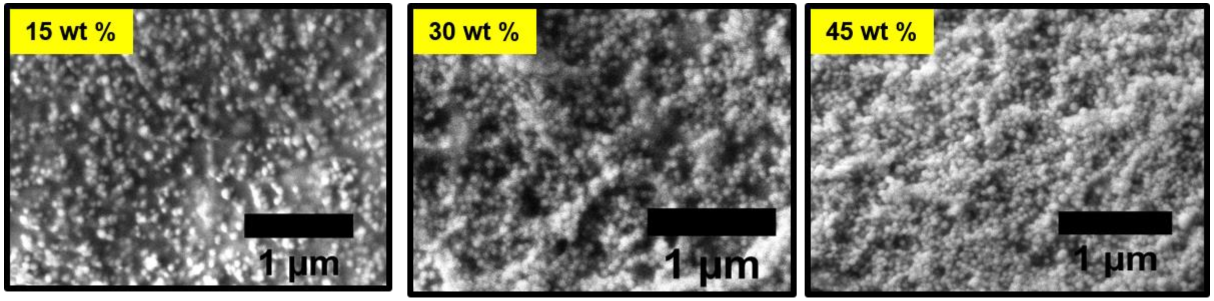
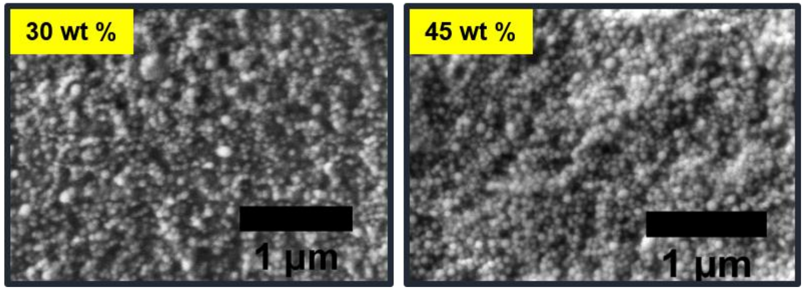
Large Deformation Do Not Affect Structure

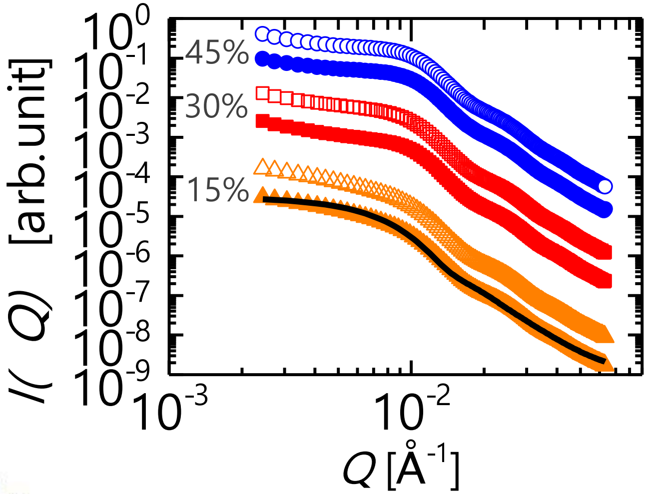
PEO (35 kg/mol, $R_g \approx 7$ nm) / Silica (55 nm diameter)





After
Large Shear

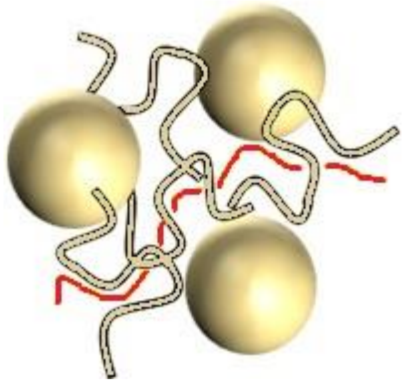


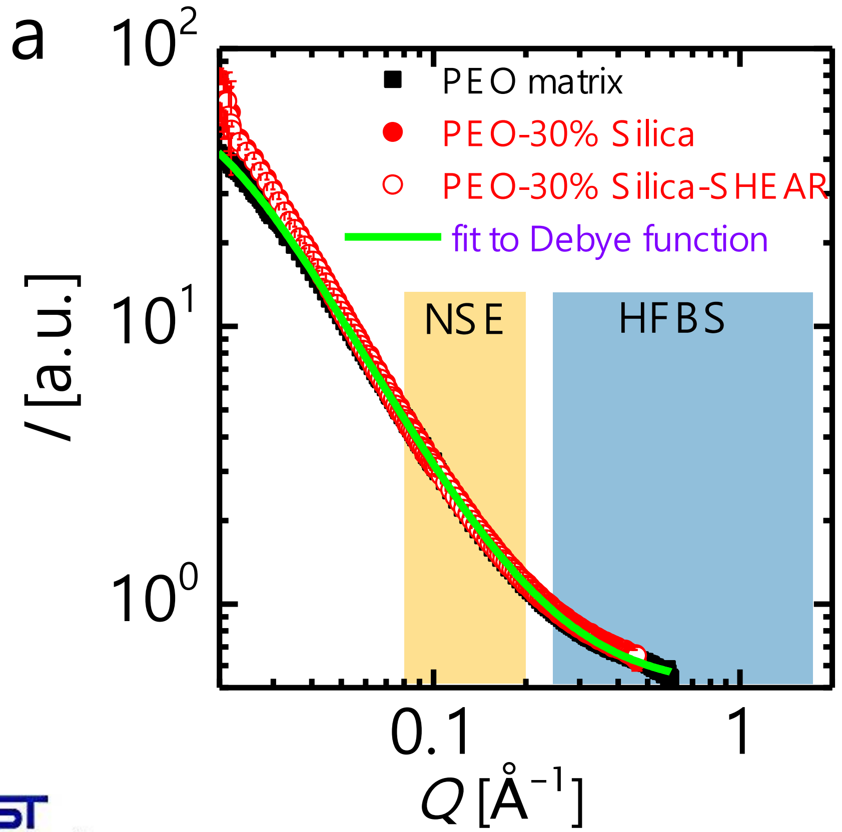


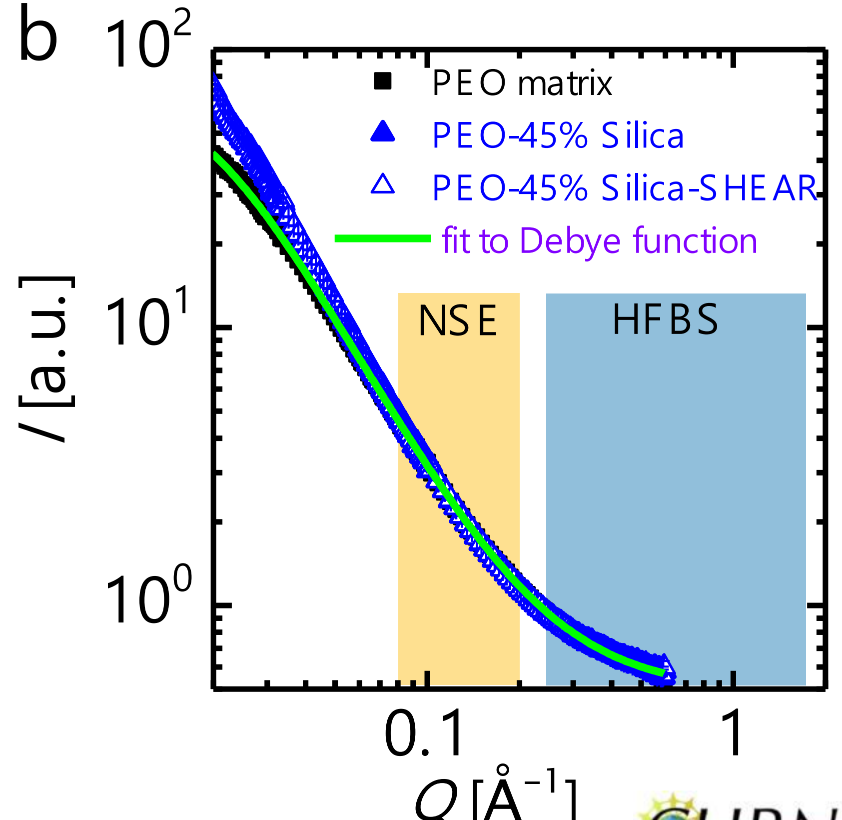
Open Symbols: After Shear

Polymer Chains Conformation

Small Angle Neutron Scattering
contrast matching
h-PEO/d-PEO 48/52 + Silica







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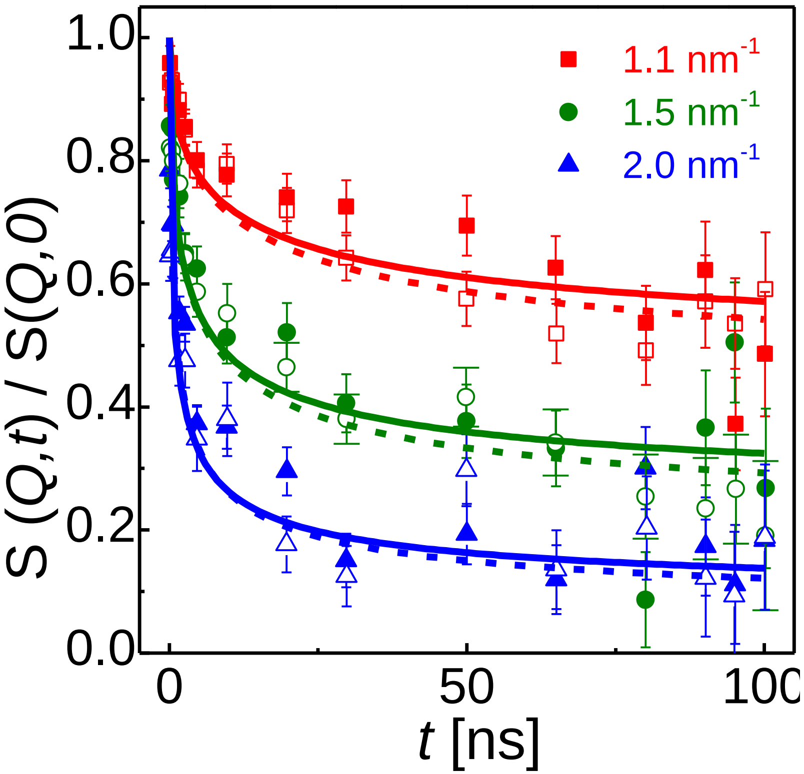
Reptation Tube Diameter



Single-chain dynamic structure factor:

(de Gennes formulation)

$$\frac{S(Q,t)}{S(Q,0)} = [1-\exp(-\frac{Q^2d^2}{36})]S^{local}(Q,t) + \exp(-\frac{Q^2d^2}{36})S^{esc}(Q,t)$$

$$S^{local}(Q,t) = \exp\left(t/\tau_o\right) erfc(\sqrt{t/\tau_o})$$

$$\tau_o = 36/(Wl^4 Q^4)$$

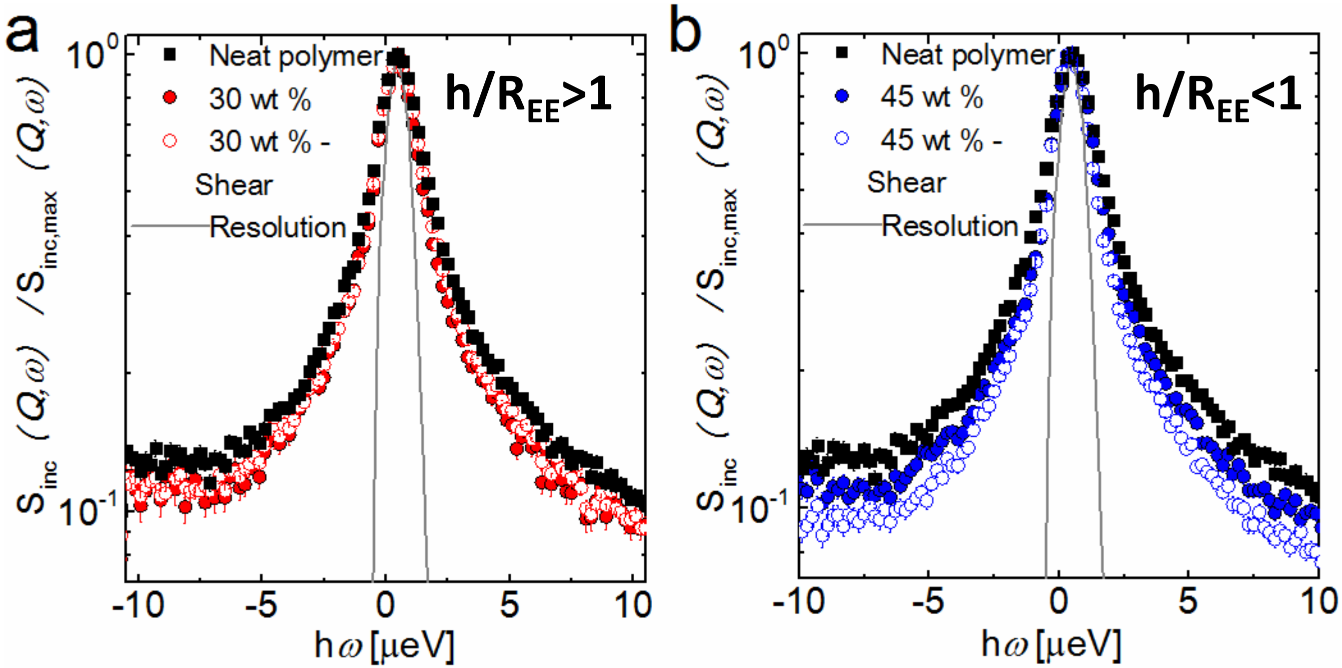
Escape of a chain from its original tube

$S^{esc}(Q,t) = 1$ (for NSE timescale)

Fitting to de-Gennes equation for t>50 ns, the tube diameter is found (≈ 5 nm)

Entanglements are not modified after shear and recovery

Segmental Dynamics



Sample	Wl^4 [nm^4/ns]
Neat PEO	0.182 ± 0.006
PEO-30 % by weight SiO_2	0.140 ± 0.005
PEO-30 % by weight SiO_2-SHEAR	0.138 ± 0.004
PEO-45 % by weight SiO_2	0.129 ± 0.003
PEO-45 % by weight SiO_2-SHEAR	0.106 ± 0.003

Rouse-rate **decreases with nanoparticle** concentration.

It **further decreases after large shear**.

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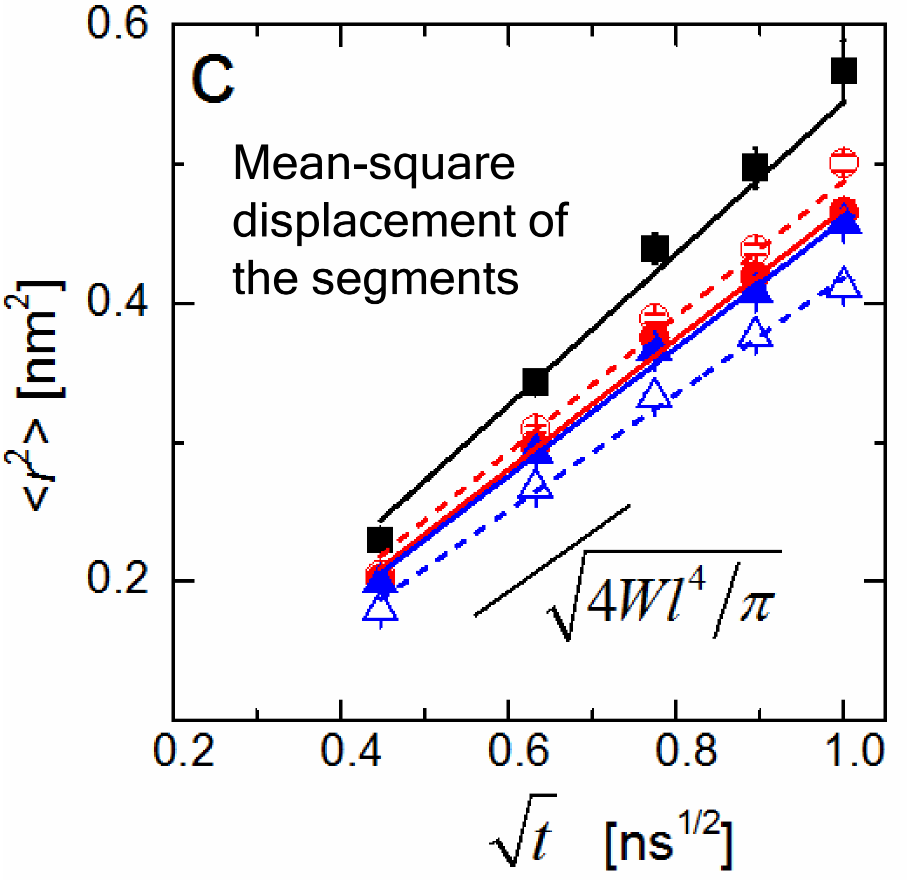
Segmental Dynamics



Fourier transform of the QENS spectra

Gaussian Approximation

Rouse dynamics with characteristic rate: Wl^4

$$S_{self}(Q,t) = \exp\left\{-\frac{Q^2}{6}\langle r(t)\rangle^2\right\}$$

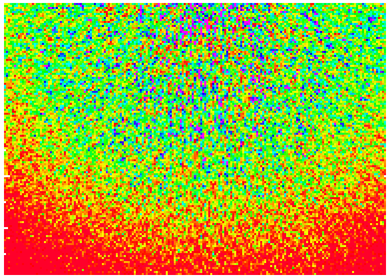
$$\langle r(t)\rangle^2 = 2\sqrt{Wl^4 t/\pi}$$

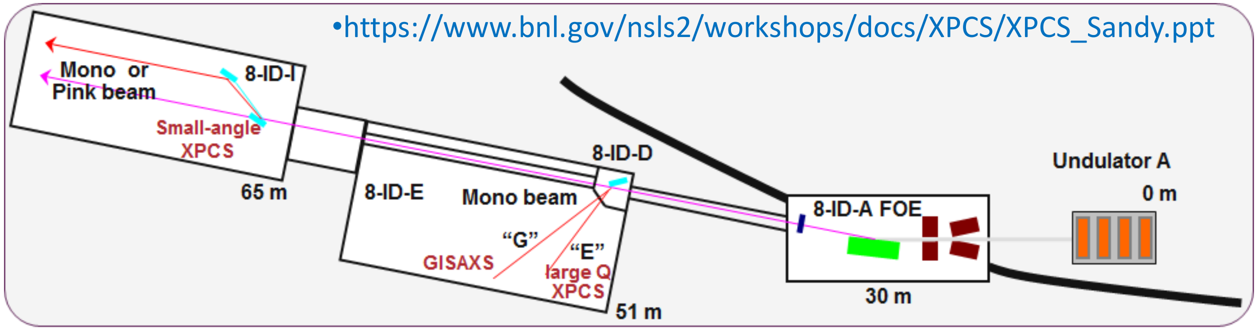
Rouse-rate **decreases with nanoparticle** concentration.

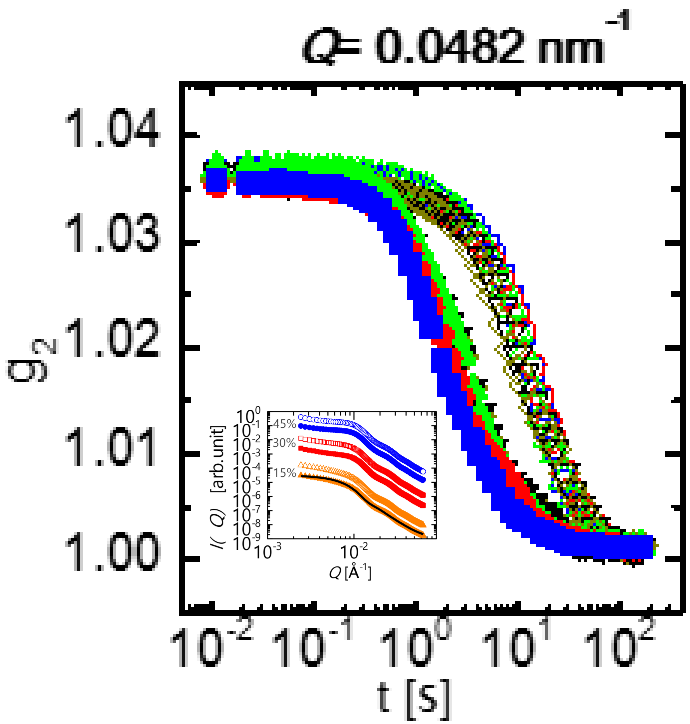
It **further decreases after large shear**.

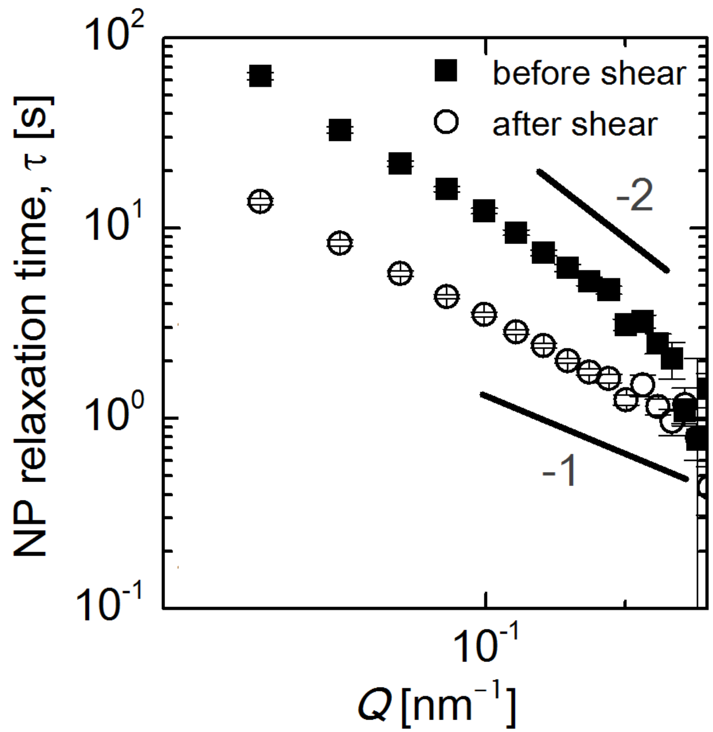
NanoparticleDynamics - XPCS

https://www.aps.anl.gov/Sector-8/8-ID



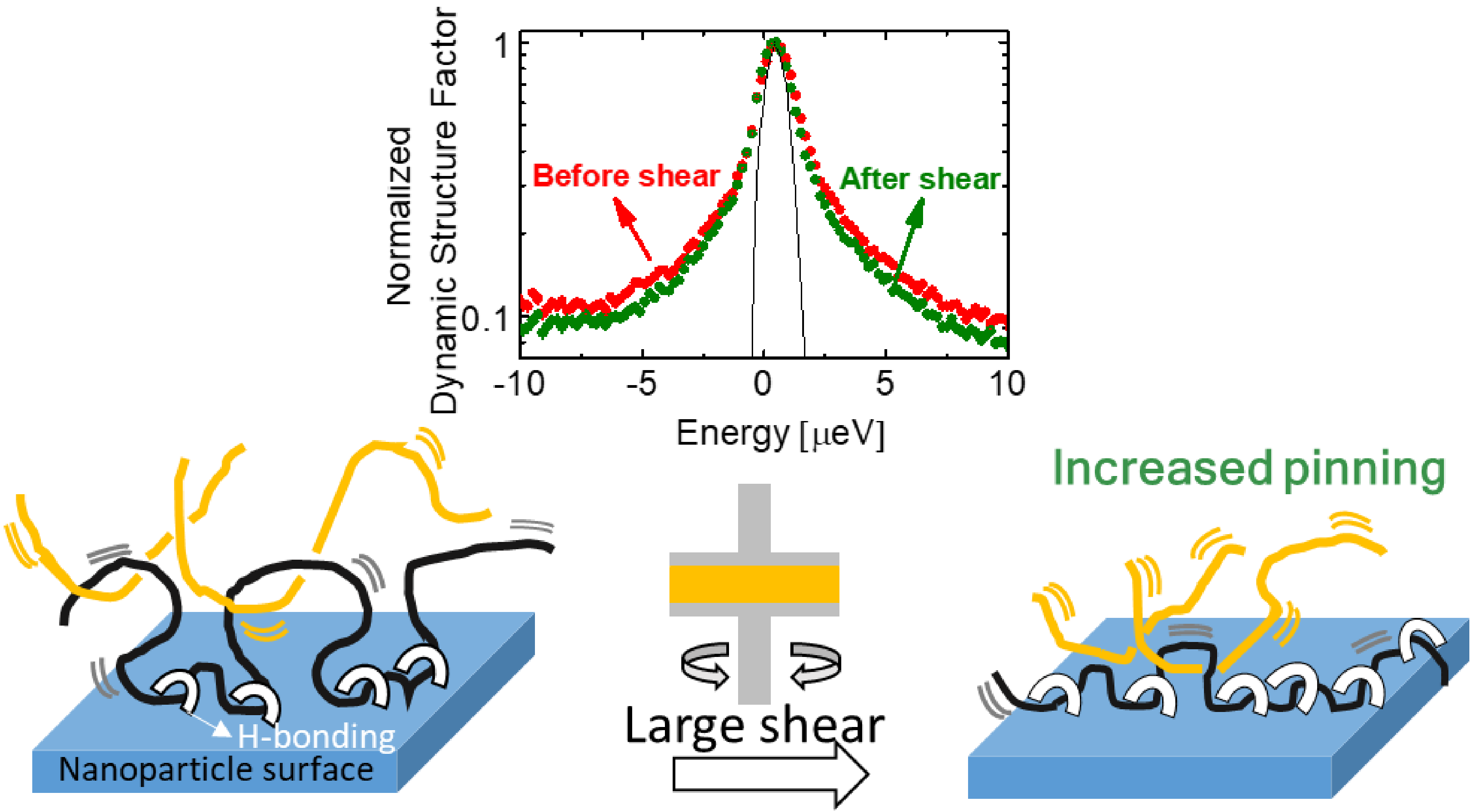






Particles speed-up after large shear

Summary



Backscattering shows enhanced pinning

E. Senses, et al., Soft Matter, **13**, 7922 (2017).

Conclusion

- QENS data indicate that the viscosity reduction in athermal PNC with nanoparticles smaller that the entanglement size originates from a dilation of the reputation tube.
- In attractive PNC subjected to LAOS, an increased pinning which could originate disentanglement of the interphase region, and therefore fluidization, was observed.

Summary

- QENS and NSE provide information on the nanoscopic dynamics in polymer nanocomposites
- These microscopic insights can be related to macroscopic behavior, providing an explanation for the rheological properties
- An accurate knowledge of the structure, the combined use of several methods, and the exploitation of isotopic substitution techniques are key elements of the research.