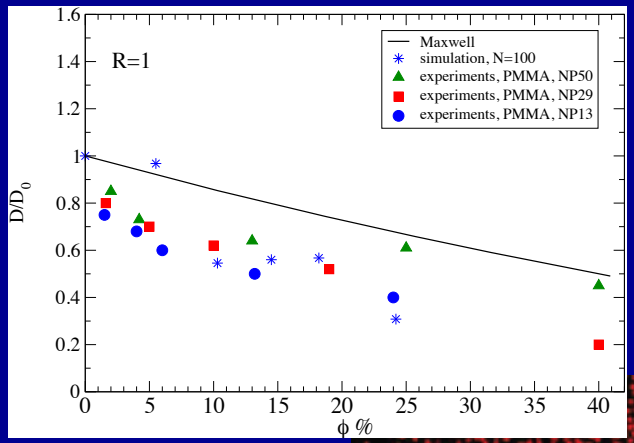
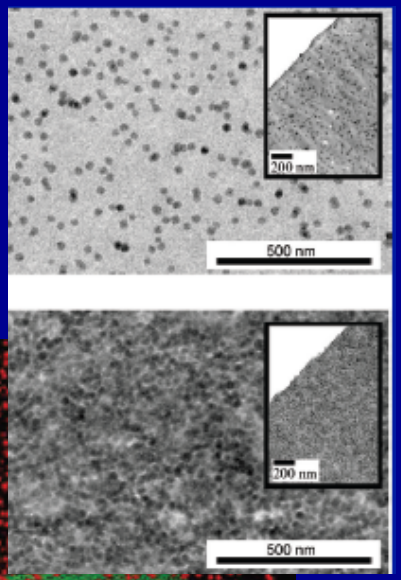
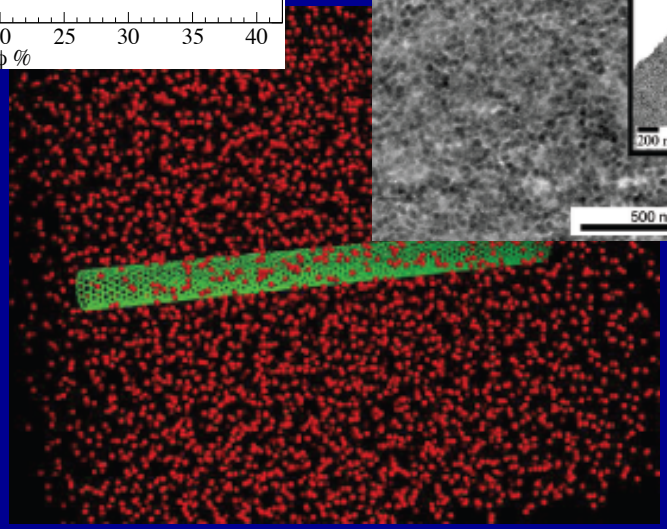
Unusual Dynamic Processes in Polymer Nanocomposites







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Acknowledgements

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  - Molecular dynamic simulations
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  - Graphene oxide nanocomposites

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  - Structure/processing in C_{60} nanocomposites

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  - Materials and characterisation

University of Pennsylvania

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- Sangah Gam, Chia-Chun Lin, Philip Griffin
  - Silica nanocomposites

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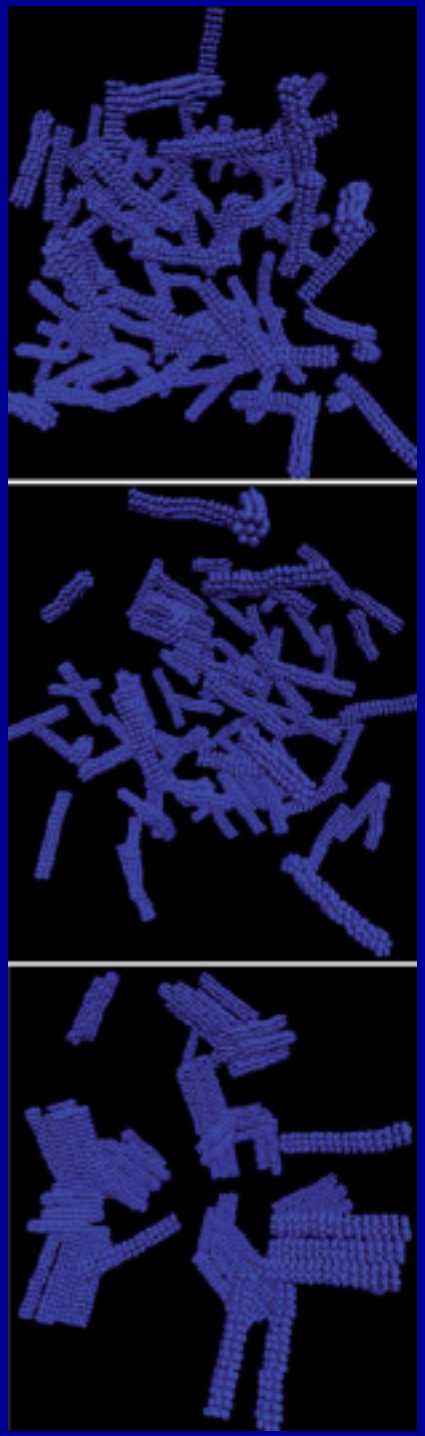
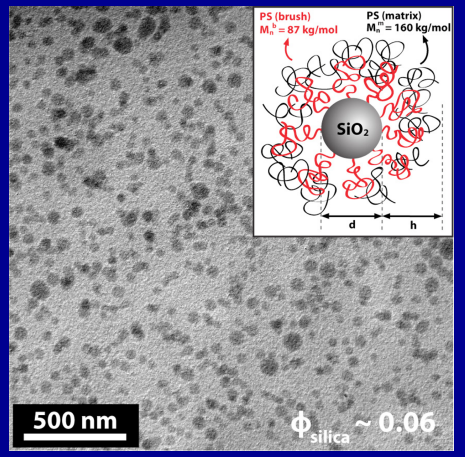
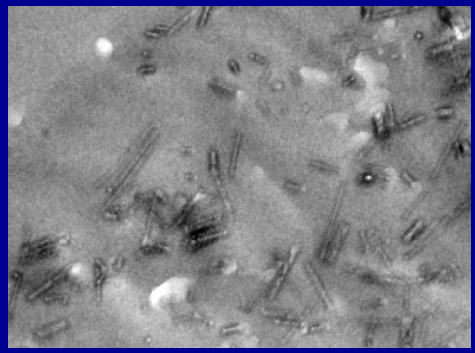
Dynamics are important for polymer processing …

- Dispersion/orientation of nanoparticles during processing depends on dynamics of polymers and nanoparticles
- Dynamics characterised by the viscosity and the diffusion coefficient







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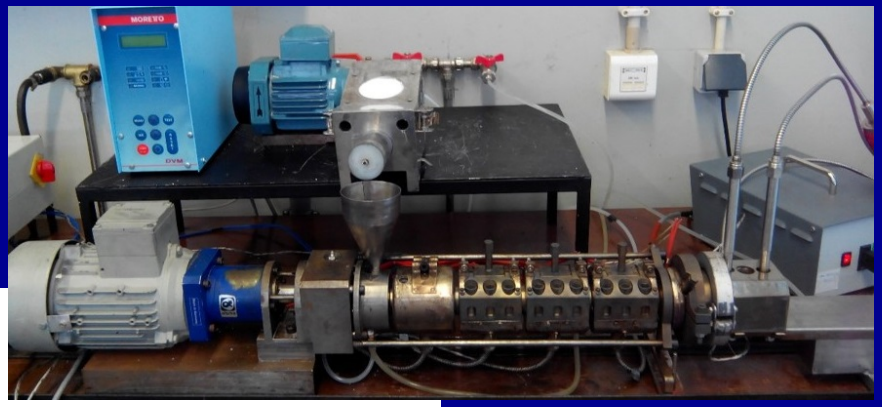
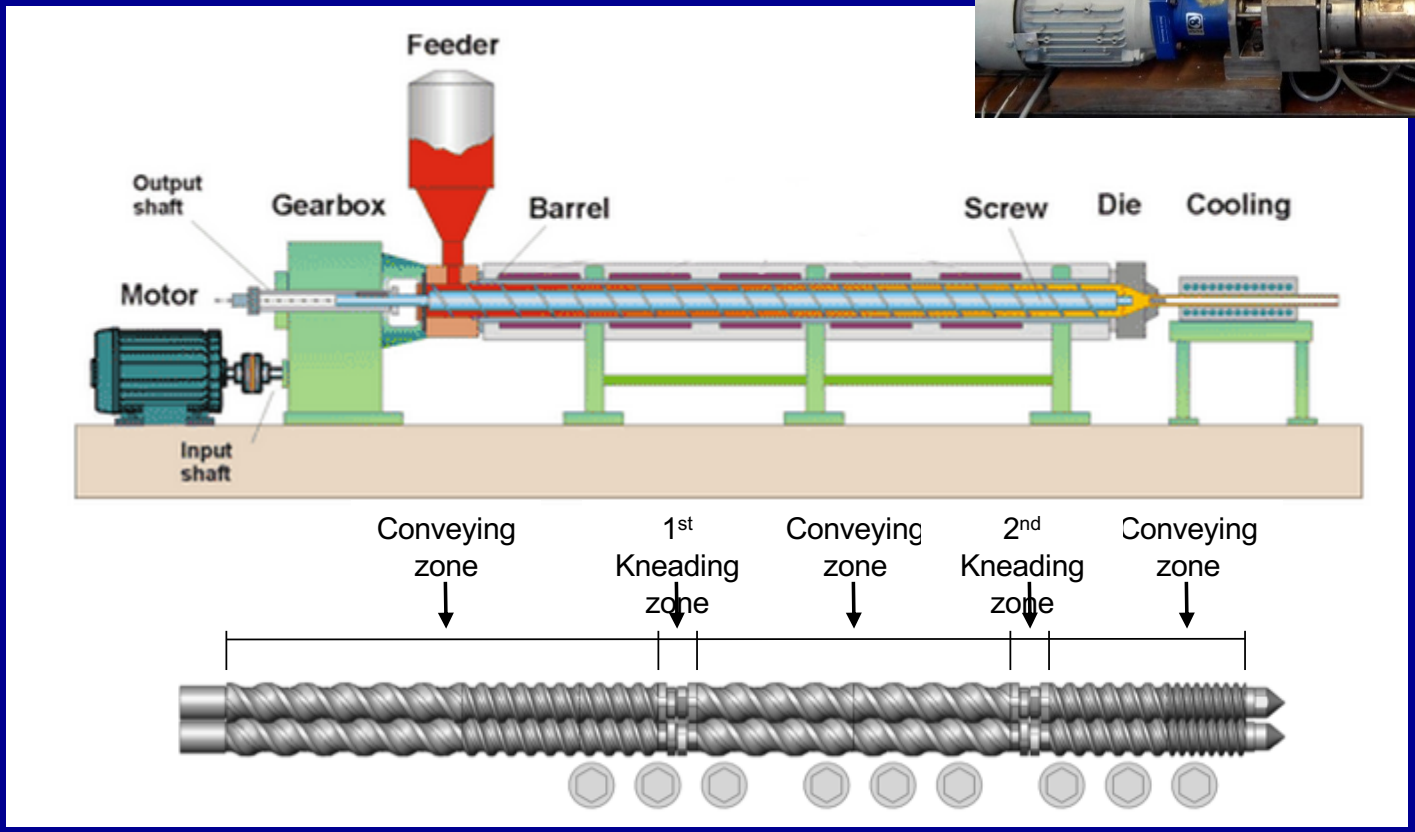
Morphology evolution of PS-C_{60} composites along the barrel of a twin screw extruder





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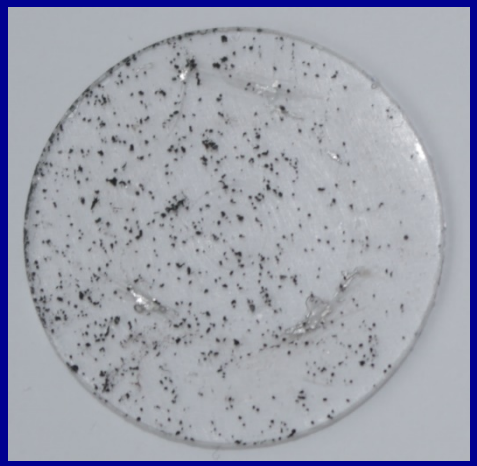
Does sample preparation impact on the morphology?

Formulation:
1.0% C_{60} / 99.0% PS

Solvent-processed composite



Mechanically mixed powders

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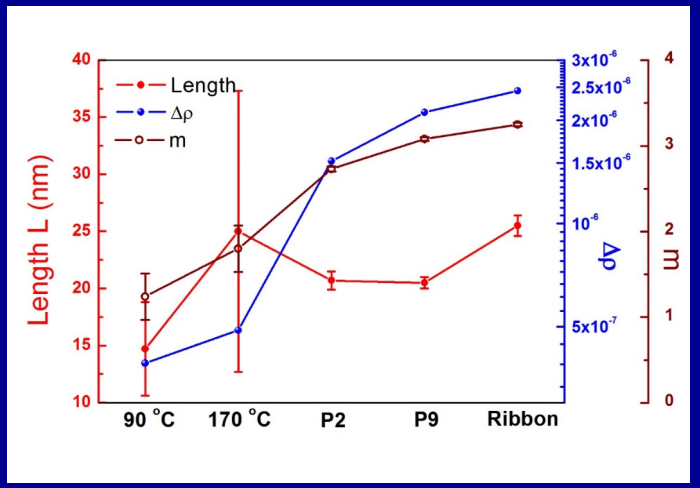
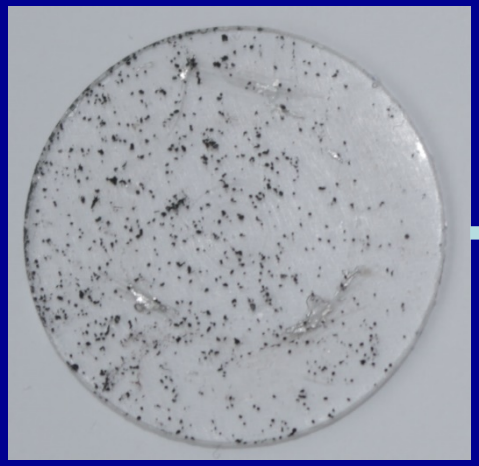
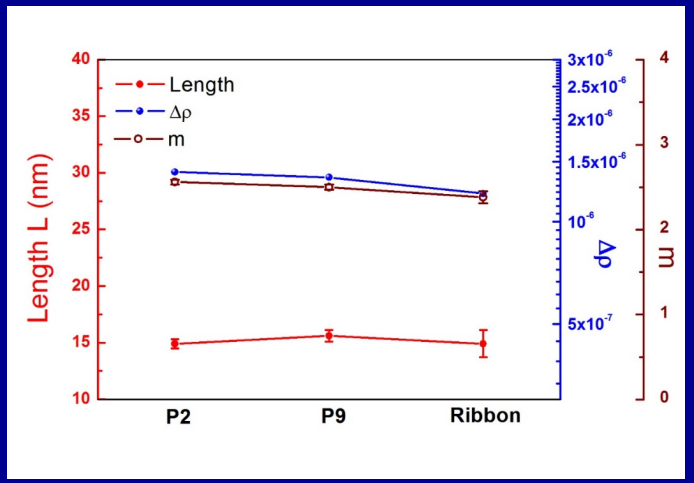
Solvent processed mixture evolves toward that from mixed powder







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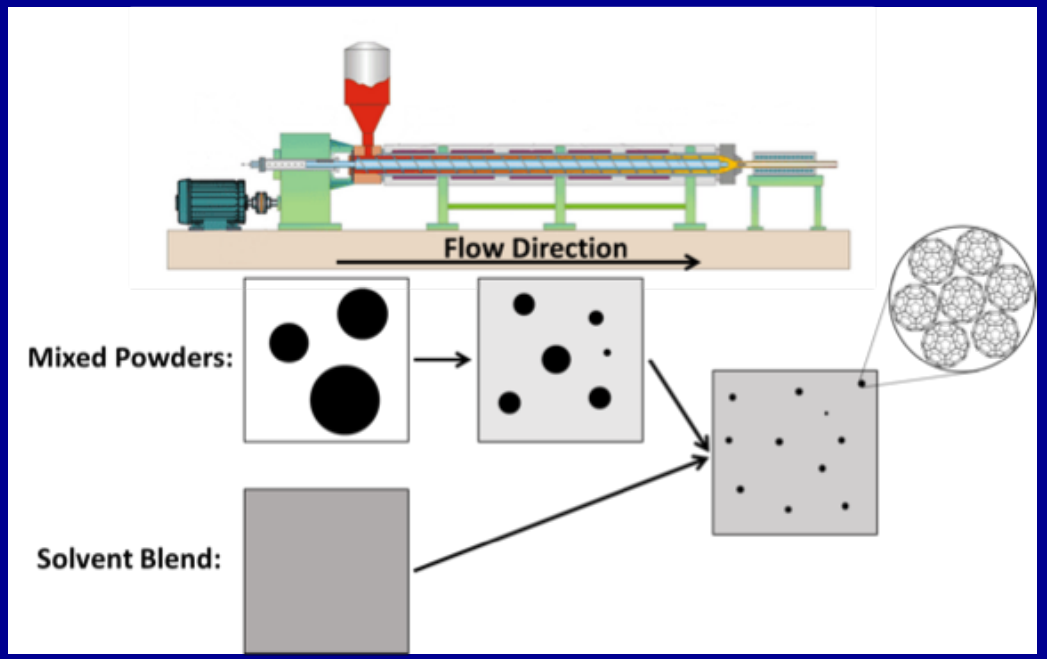
Morphology of PS-C_{60} composites is determined by coupling between thermodynamics of mixing and rheology

Dynamics characterised by diffusion coefficient

Dynamics characterised by viscosity



Bernando *et al*, Macromolecules 2017, 50, 3301−3312

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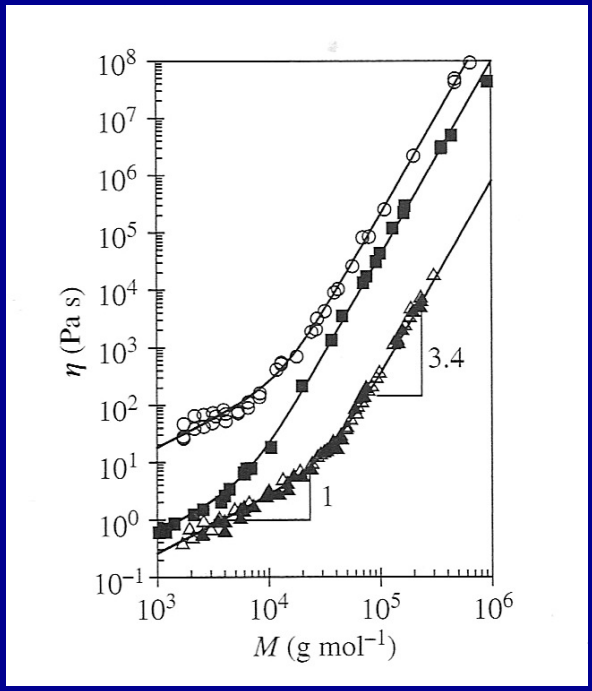
Viscosity and diffusion strongly correlated in polymer melts

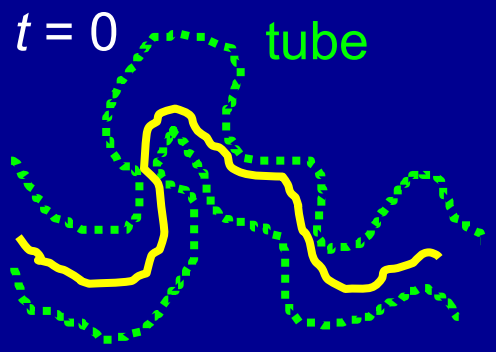
- Diffusion represents chain motion but is difficult to measure
- Viscosity is easy to measure

Polymer viscosity scales with molecular weight



From Colby and Rubinstein: *Polymer Physics*

- "Entangled" polymers
  - effect of surrounding polymers modelled by motion in a tube



  - Viscosity ~ M^3
  - Diffusion ~ M^{-2}

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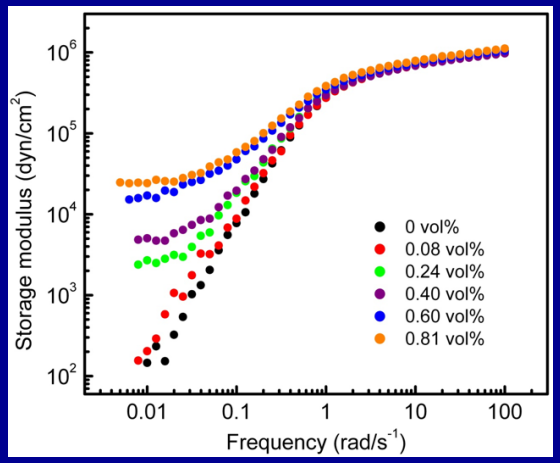
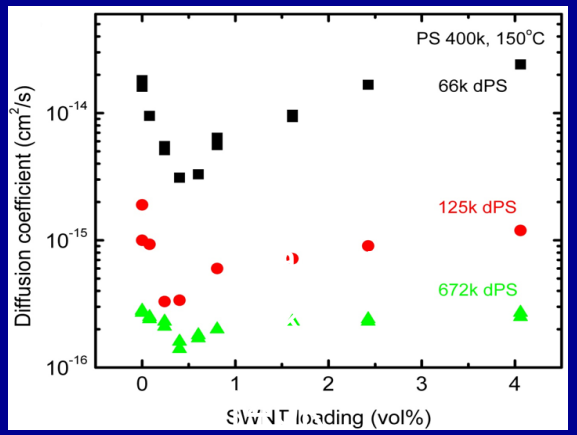
Viscosity/diffusion in CNT nanocomposites

- Nanoparticle dispersion and orientation dependent on dynamics not stress relaxation
- Diffusion becomes a more important characteristic
- Impacts upon polymer – polymer welding
- Can processing be used to manipulate dispersion/orientation?



viscoelasticity



diffusion

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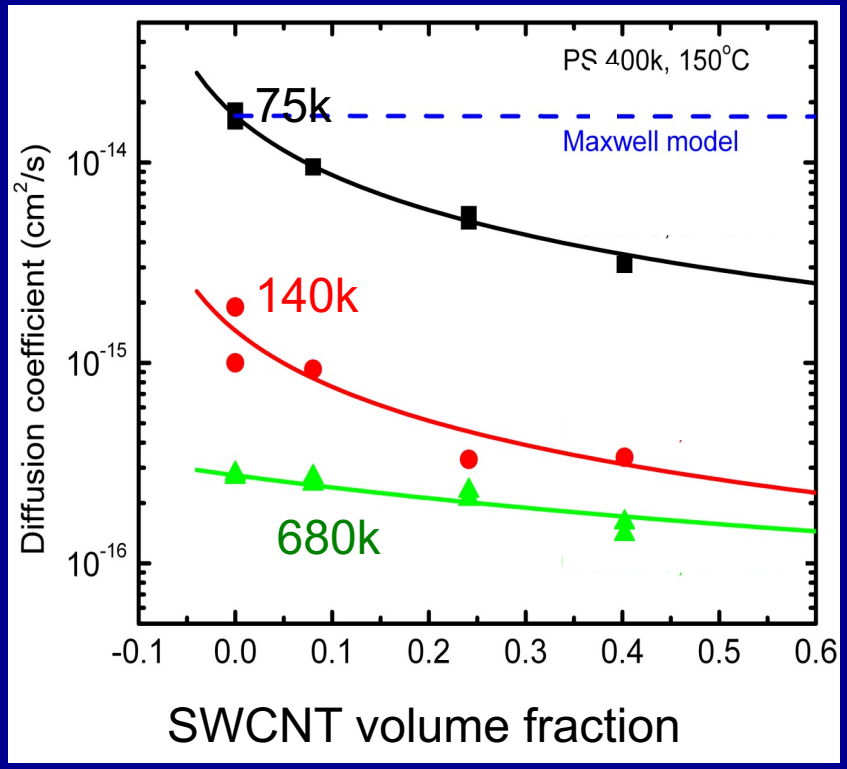
SWCNTs slow polymer diffusion at low volume fractions



- Maxwell model
  - decrease in diffusion due to presence of obstacles
- Polymer diffusion decreases more significantly than Maxwell model prediction

Mu et al, Macromolecules 2011,191, 44, 191

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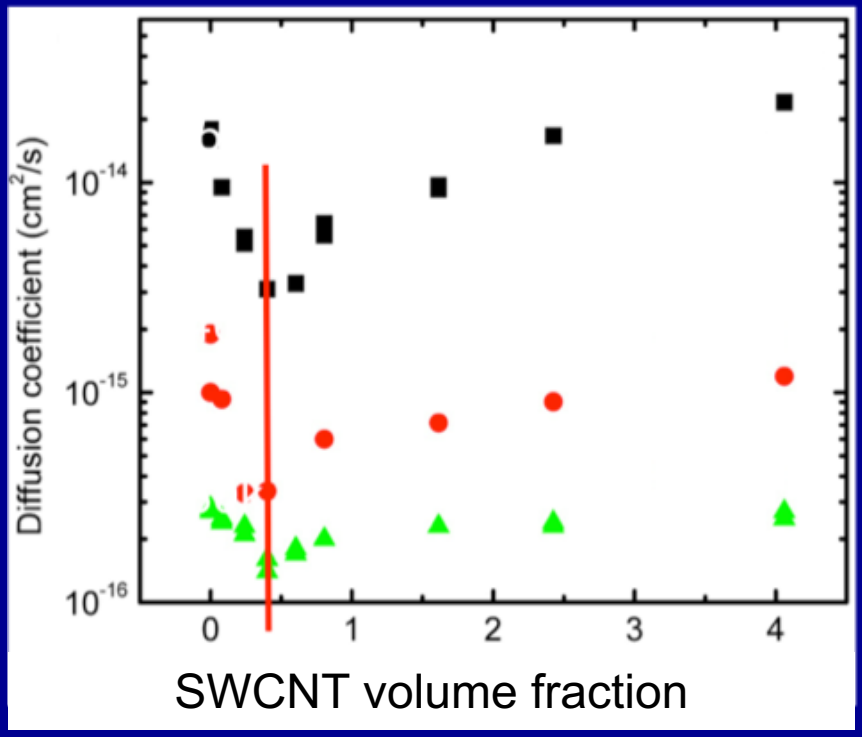
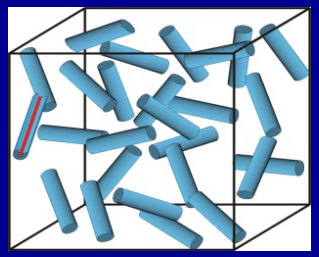
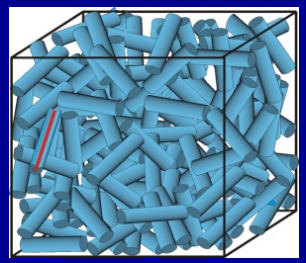
Tracer diffusion recovers above critical volume fraction







- D_{min} at critical volume fraction of SWCNT 0.4 vol%
  - independent of polymer molecular weight
  - correlates with SWCNT percolation
- SWCNTs have a more dramatic influence on *D* of shorter tracers

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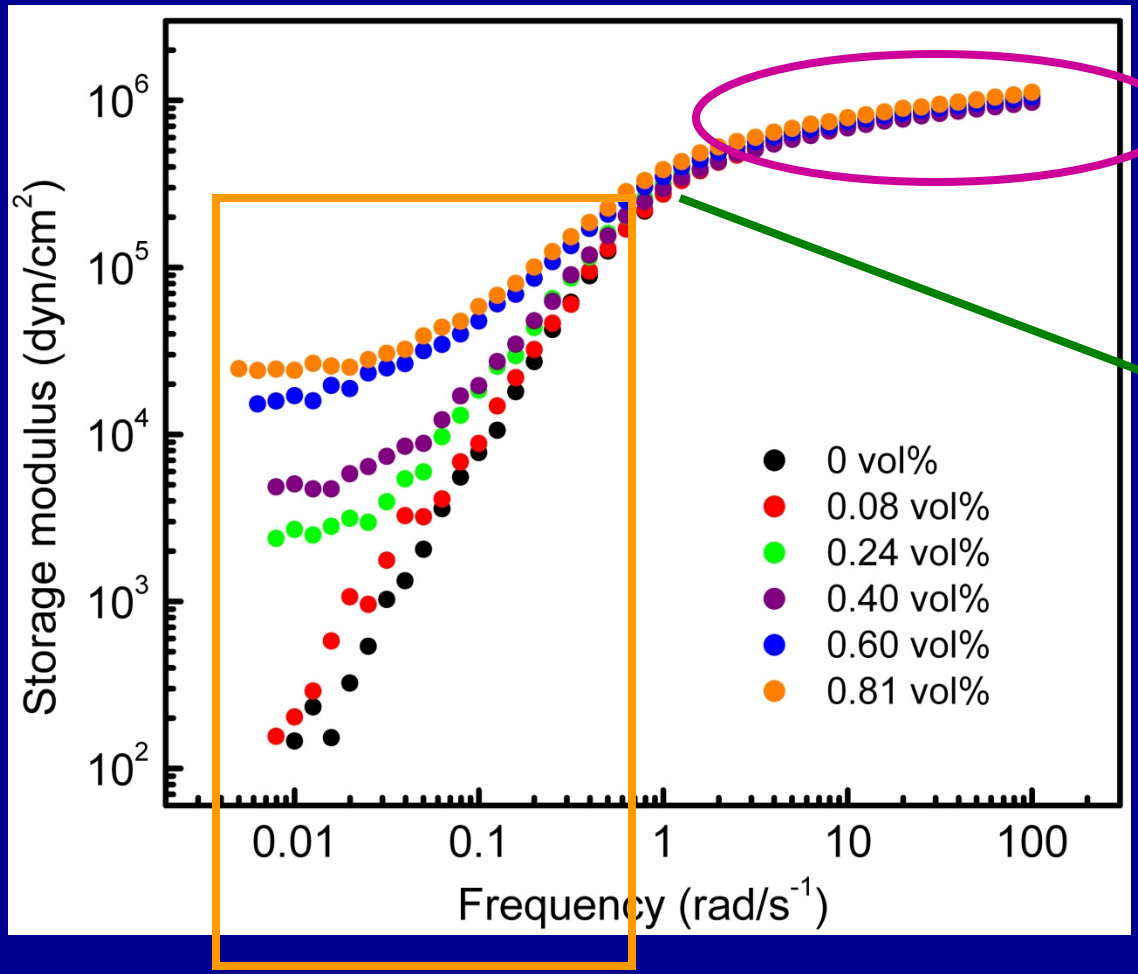
Diffusion is decoupled from viscoelasticity in nanocomposites

SWCNT/480k PS, 200 ºC



Plateau modulus
M_e = constant

Relaxation time
~ 8 sec
independent of
SWCNT
concentration

Low frequency modulus scales with square of nanotube concentration

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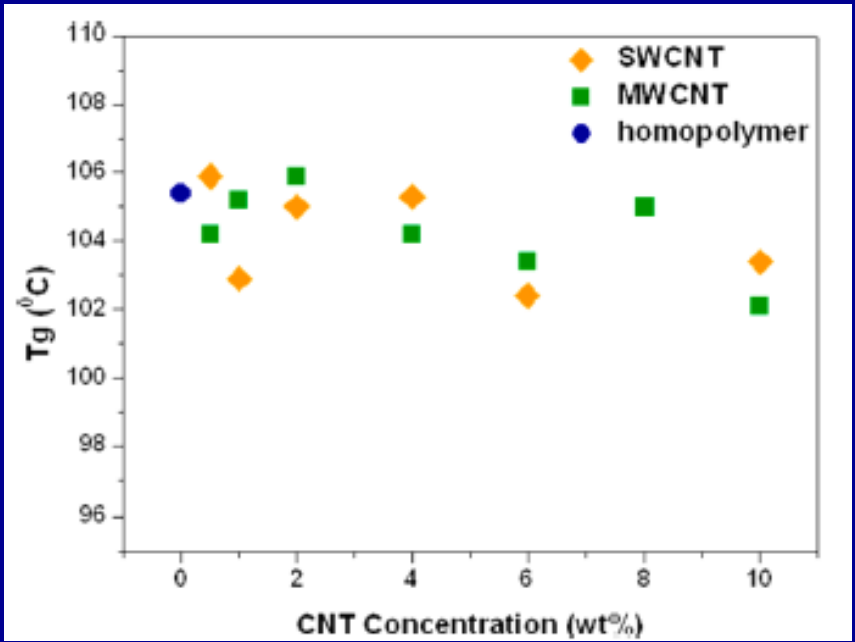
The glass transition temperature



- No significant change in T_g as measured by DSC
- Width of transition, 6 - 7° , also independent of CNT concentration

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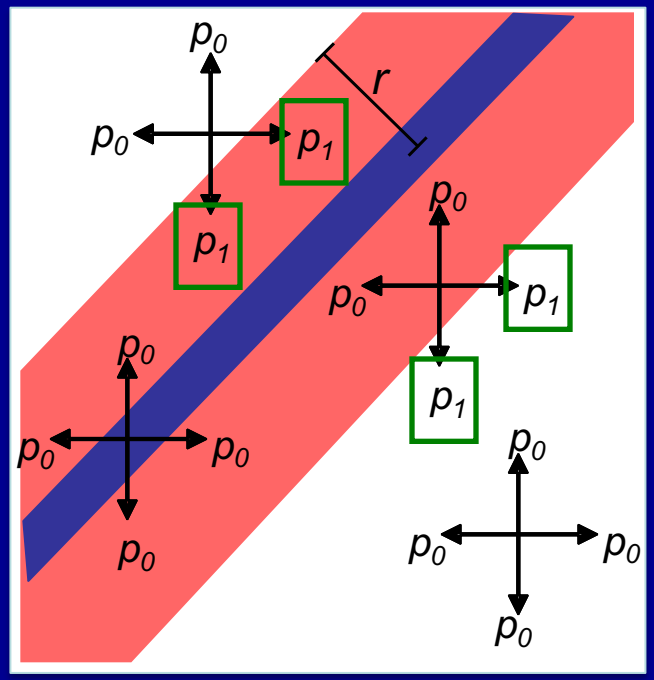
A phenomenological trapping model for diffusion



Jump probability: $p_o > p_1$

- SWCNT (blue) creates a trap region
- Inside and outside traps
  - probability of hopping between sites constant, p_o
- Jump probability smaller for hop into or out of trap, p_1
- Consistent with both viscoelasticity and diffusion observations

Mu et al, Macromolecules 2011,191, 44, 191

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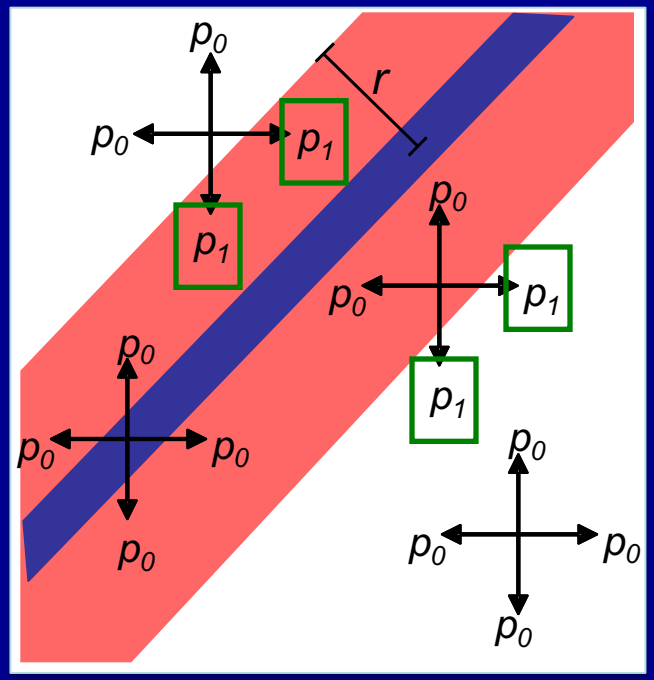
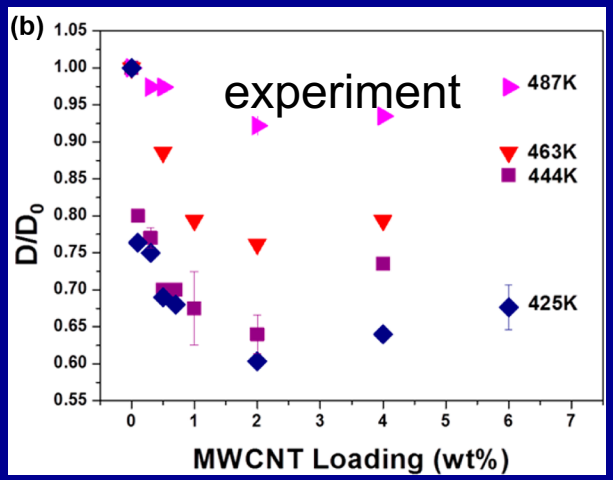
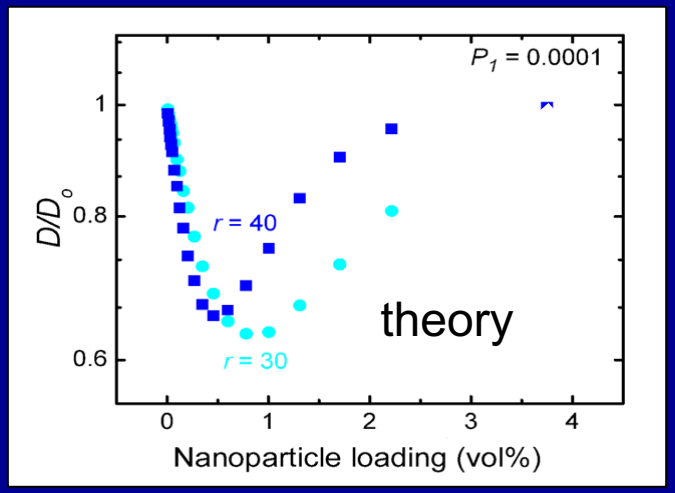
A phenomenological trapping model for diffusion



Jump probability: $p_o > p_1$





Is there a molecular basis?

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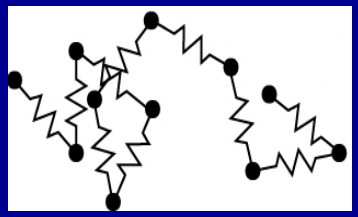
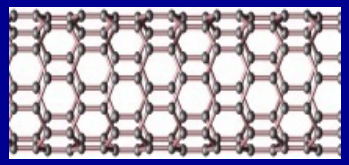
What can we learn from molecular dynamics simulations?

- Bead-Spring model



- Atomistic model for SWCNT



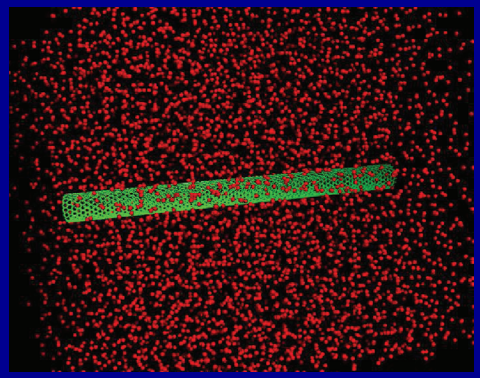
  - SWCNT diameter ~ Kuhn length
  - Fixed SWCNT spans simulation box
  - Volume fraction of SWCNT ~ 0.4%

Unconnected beads interact through Lennard-Jones potential

$$U(r) = 4\varepsilon\left(\frac{\sigma_{ij}^{12}}{r^{12}} - \frac{\sigma_{ij}^{6}}{r^{12}}\right)$$

connected beads interact through harmonic potential

$$U(r) = \frac{K}{2}(r - r_0)^2$$



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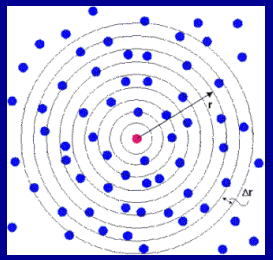
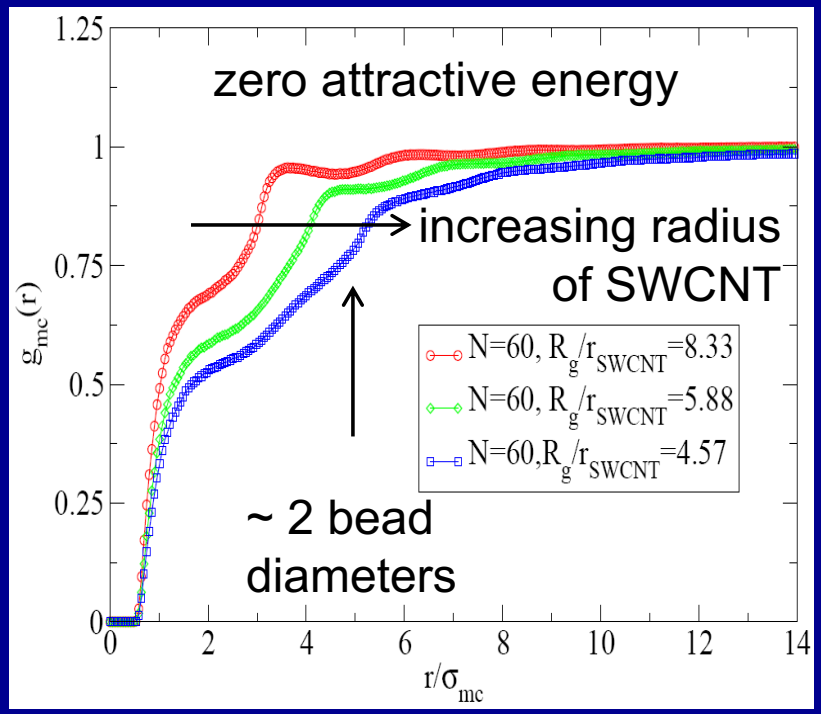
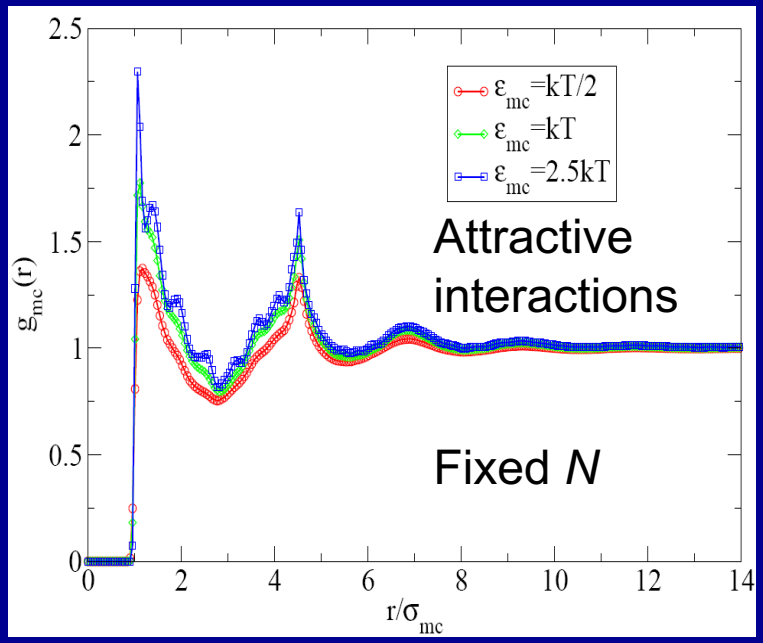
Local structure: radial distribution function $g(r)$







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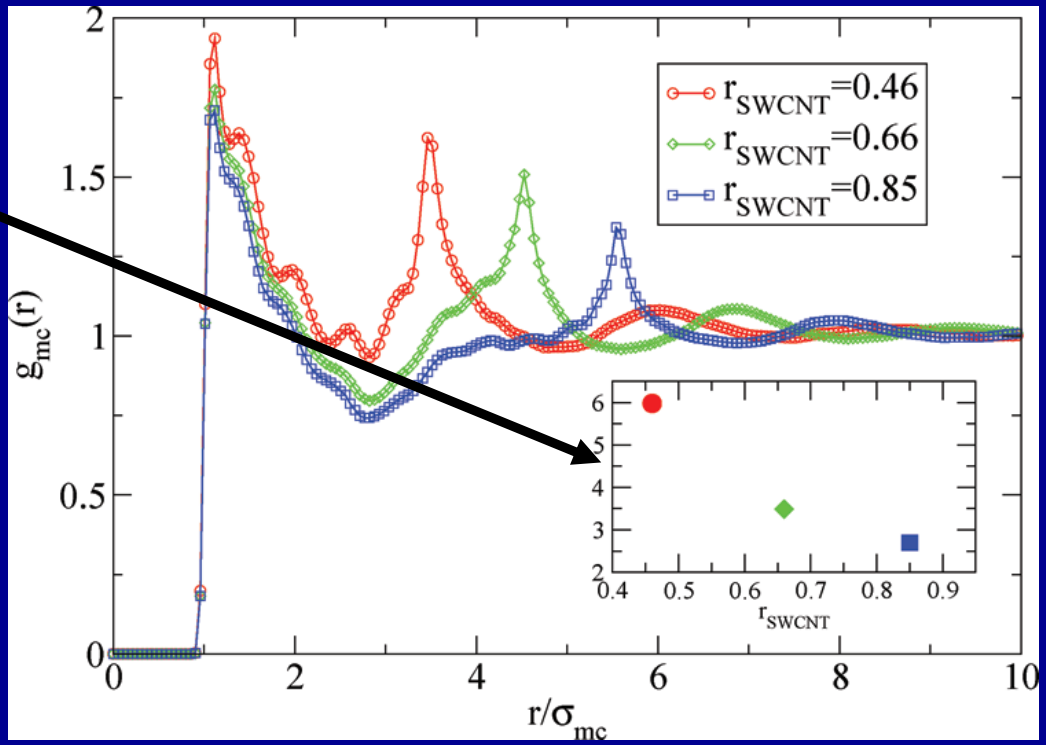
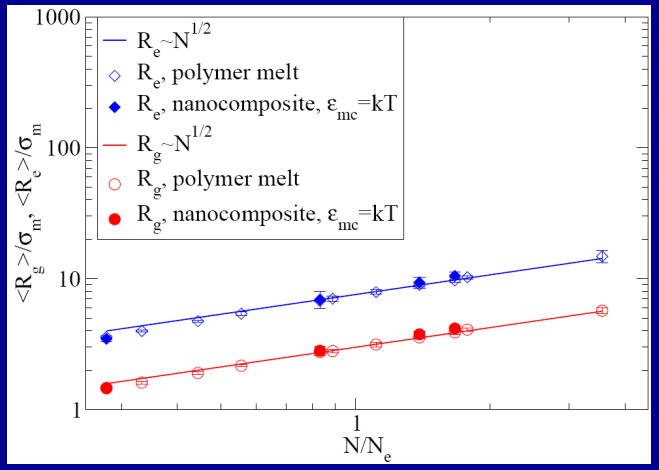
Impact of curvature

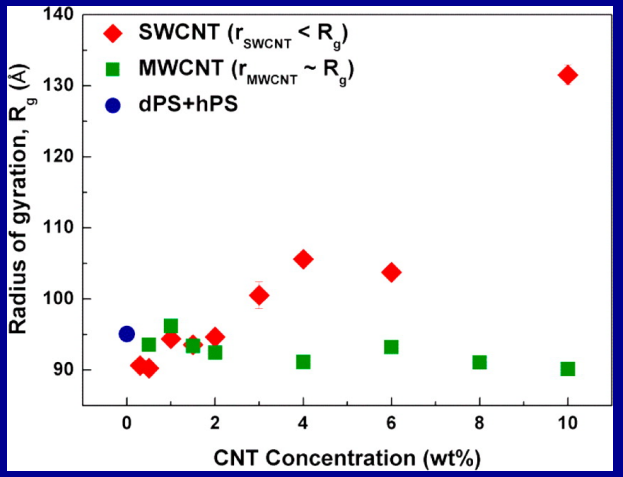
- For a fixed degree of polymerisation
  - Interfacial volume per SWCNT decreases with increasing radius of SWCNT



Affect of SWCNT on chain dimensions

- Both radius of gyration and r.m.s. end-to-end distance unaffected by a single SWCNT
  - Equivalent to nanocomposite with 0.4% volume fraction SWCNTs
  - overall chain configuration well described by Gaussian statistics





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Modelling: Karatrantos et al. *Macromolecules*, 44, 9830, 2011
Experiments: Tung et al. *Macromolecules*, 46, 5345, 2013

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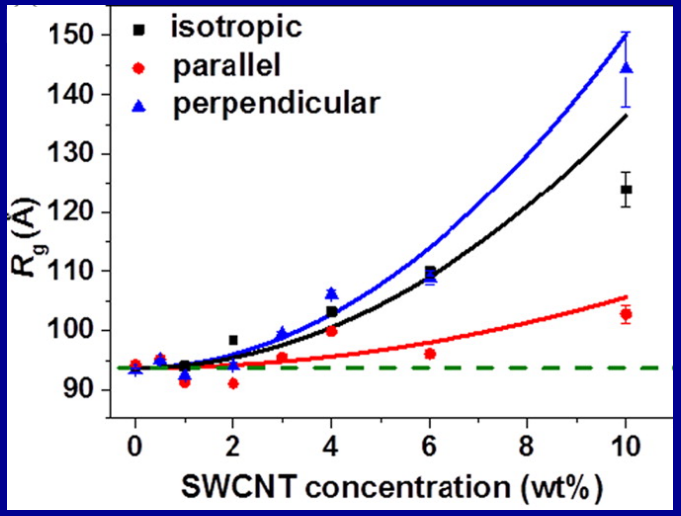
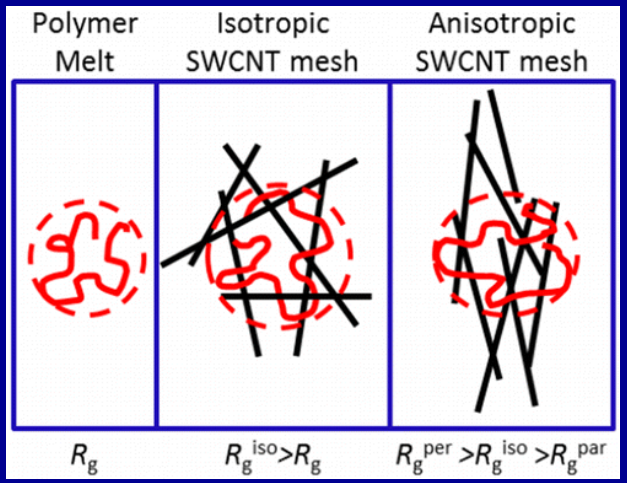
Chain confirmation is anisotropic

- If CNTs randomly aligned
  - Experiments average over all orientations
  - Cannot distinguish behaviour parallel and perpendicular to individual CNTs
- Use an aligned mesh of CNTs





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Tung et al. *ACS Macro Letters*, 4, 916, 2015

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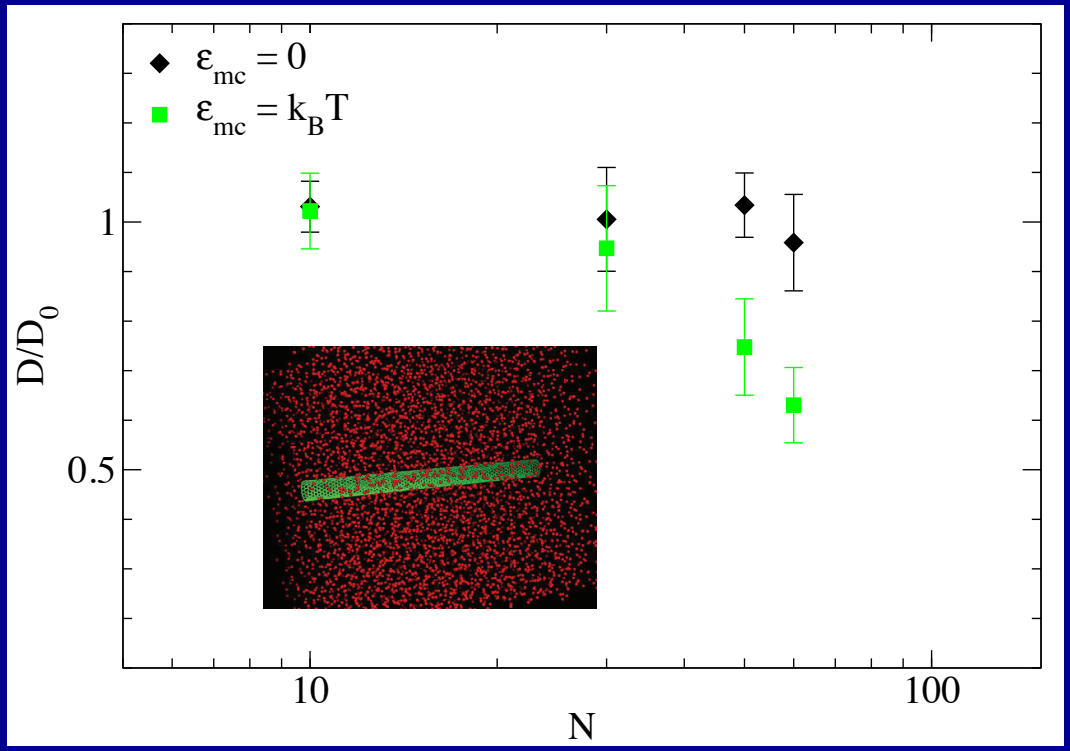
The impact of interactions on polymer dynamics in the presence of a SWCNT



- Reduction in *D* for higher molecular weight chains when $k_B T$ attractive interaction between polymer and SWCNT

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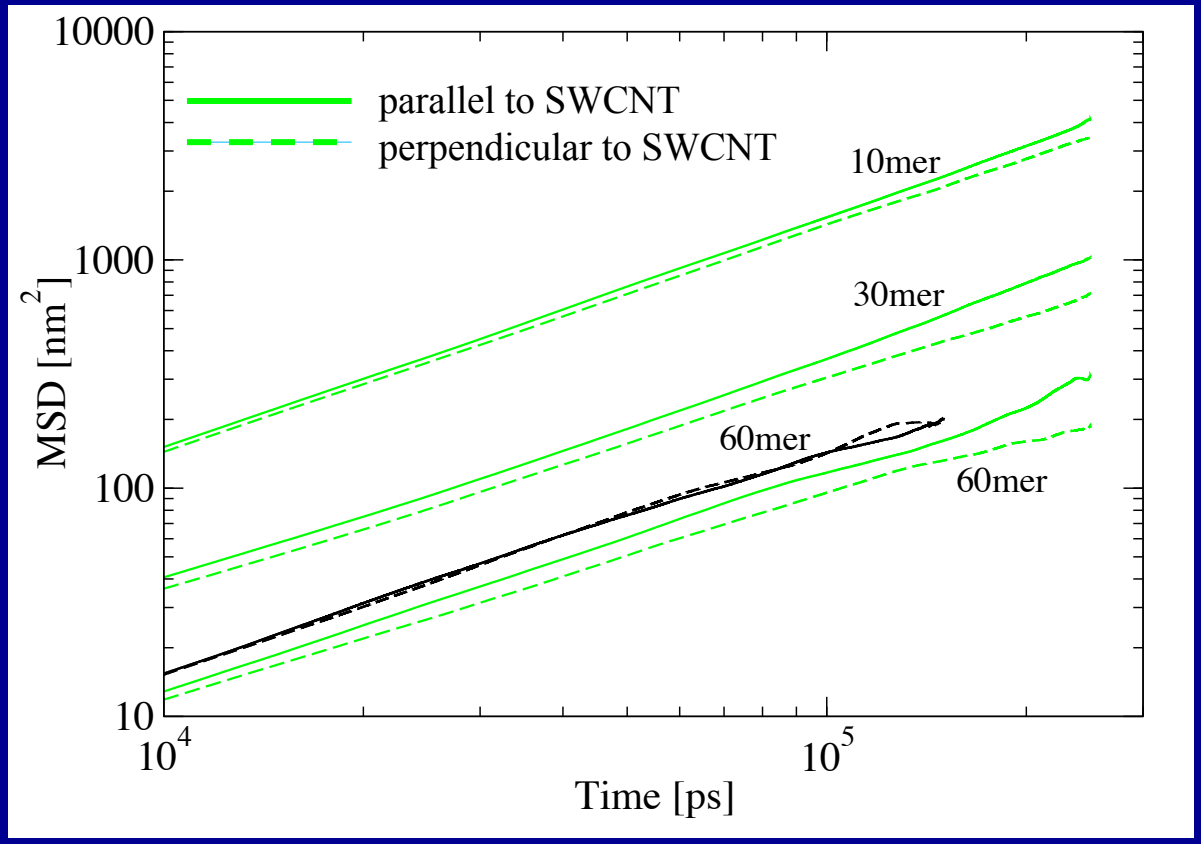
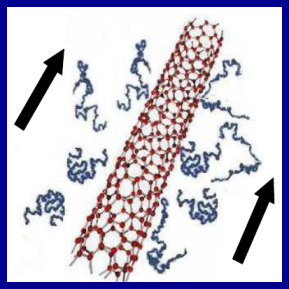
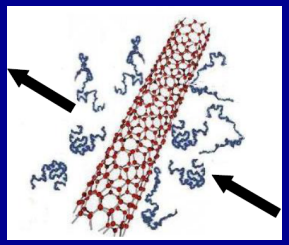
Dynamic anisotropy



dynamics parallel to SWCNT





Dynamics perpendicular to SWCNT

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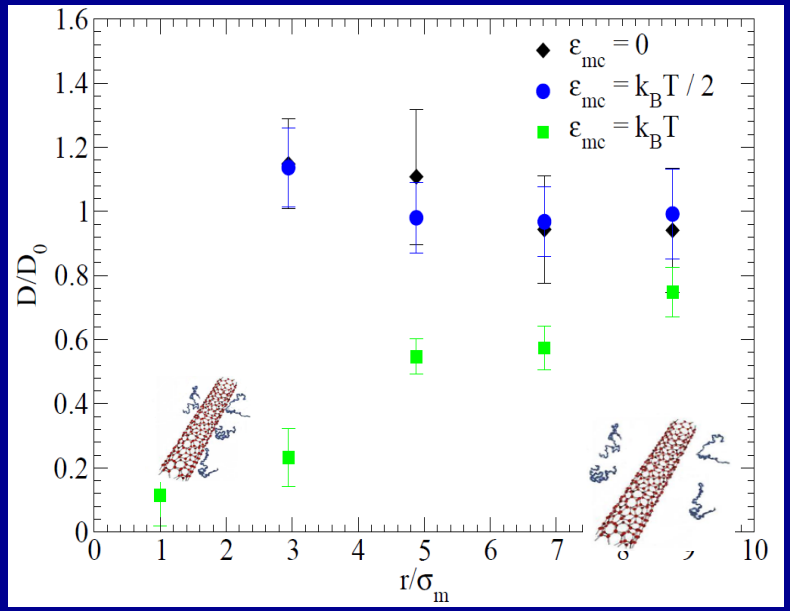
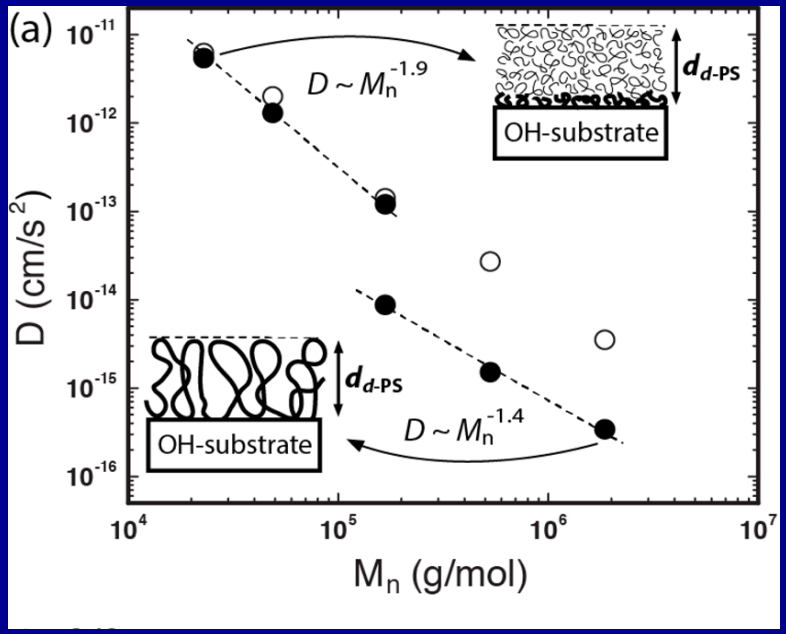
Proximity to surface impacts diffusion



Reduced diffusion coefficient dependence on distance of chain from SWCNT surface
Karatrantos et al, Macromol 2012



Experimental diffusion coefficient near flat substrate surface
Choi et al, Macromol 2017

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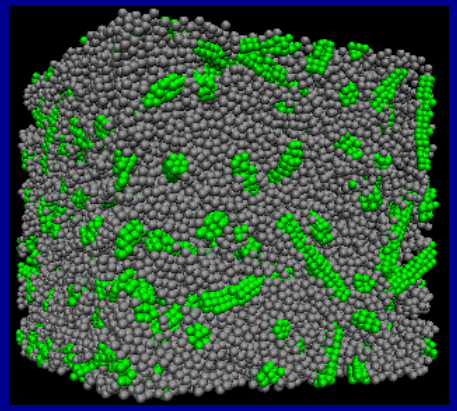
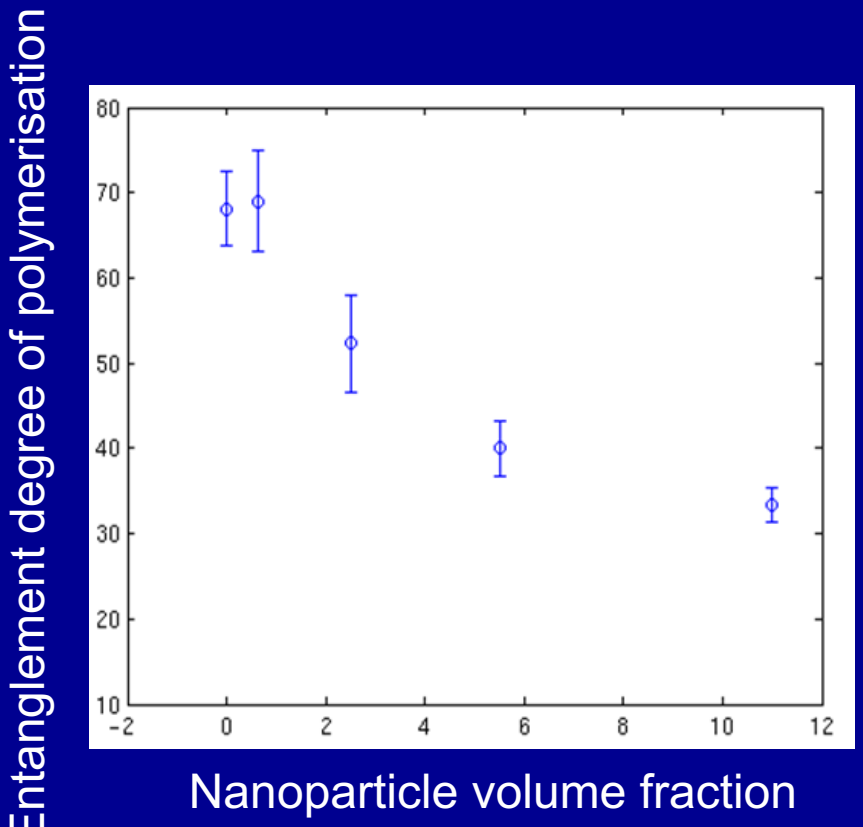
Concentrated well-entangled SWCNT nanocomposites: dissipative particle dynamics

- Soft potential replaces LJ potential

$$U(r) = \frac{\alpha}{2}\left(\sigma - r\right)^2$$

- increases time step





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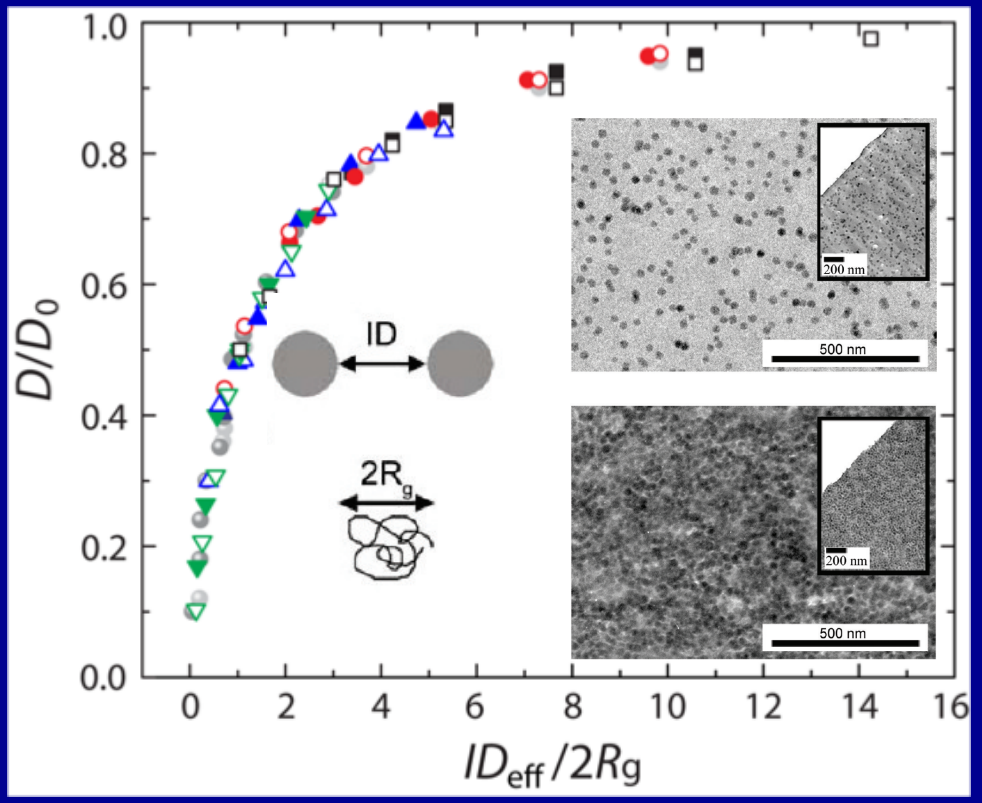
Dynamics in polymer/silica nanocomposites

- Observed ‘Master Curve’ of polymer dynamics in presence of spherical nanoparticles
  - Well dispersed up to 50% nanoparticle
  - Reduced diffusion coefficient vs interparticle distance scaled with radius gyration



Macromolecules, 2011, *Soft Matter*, 2012, *Macromolecules*, 2013, *ACS Macro Letters*, 2013, *Macromolecules*, 2014

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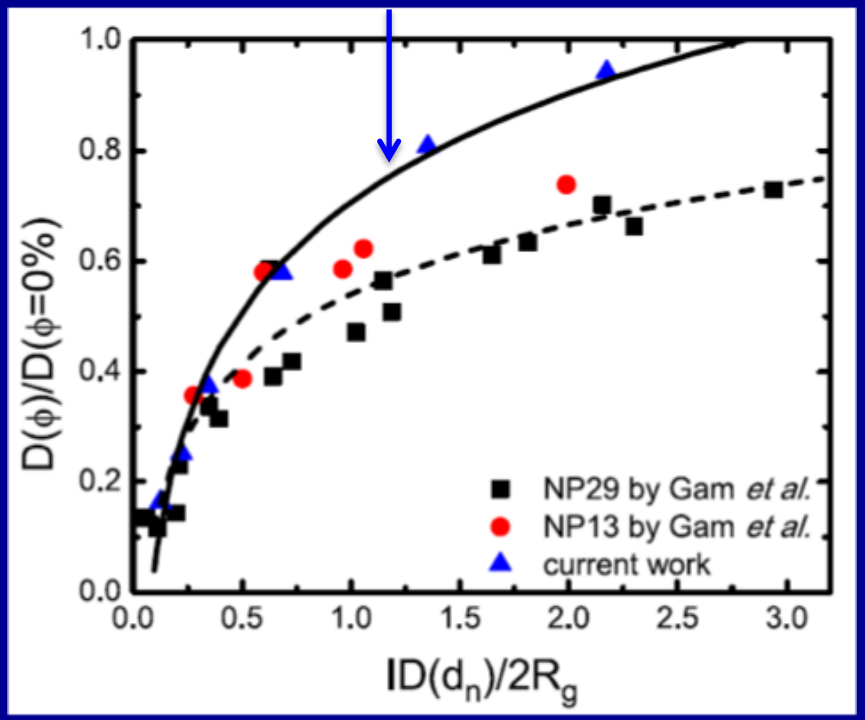
Physical mechanism?

- MD simulations by Liu *et* al of unentangled polymers does not reproduce collapse
- Is explanation related to entangled polymer dynamics?

MD results



From Liu *et al*, Soft Matter 2014

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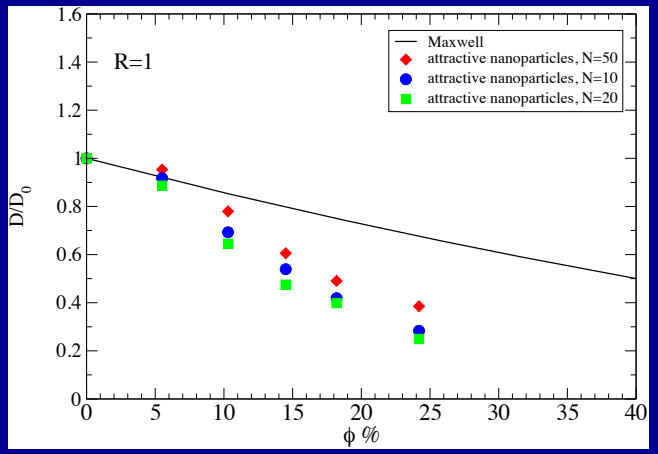
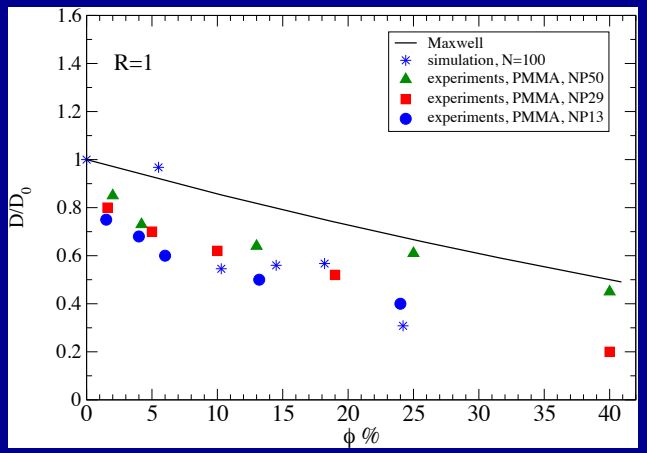
Molecular Dynamics of spherical nanoparticle/ polymer mixtures: diffusion

- For unentangled polymers:
  - At 5% diffusion obeys Maxwell geometric model for diffusion
  - Above 5% diffusion is more strongly affected than geometric model predicts



- For weakly entangled (< 2 entanglements) polymers
  - Similar behaviour at 5%
  - Above 5% trend similar to the experimental data for more entangled chains



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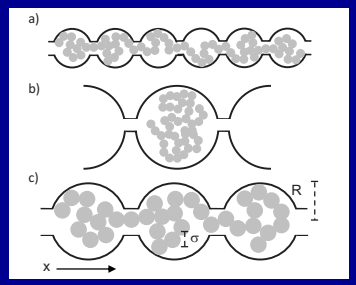
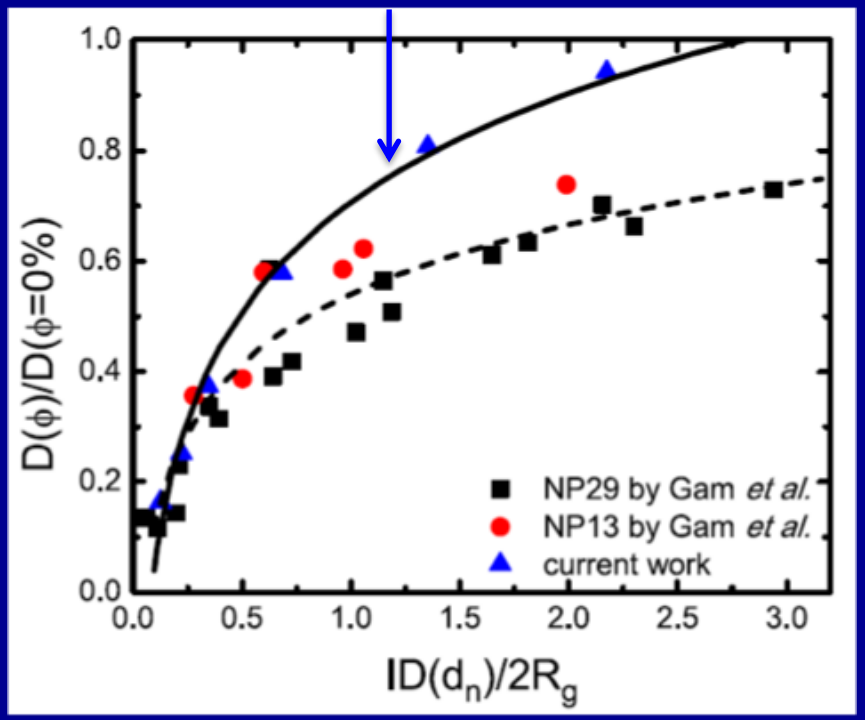
A very coarse – grained model of polymer dynamics

- Develop a simple simulation in which obstacles are regularly spaced walls with holes
- Inspired by Muthukumar work on single chain translocation through pores



from Saltzmann and Muthukumar,
J Chem Phys, 2009, 131, 214903

MD results



From Liu *et al*, Soft Matter 2014

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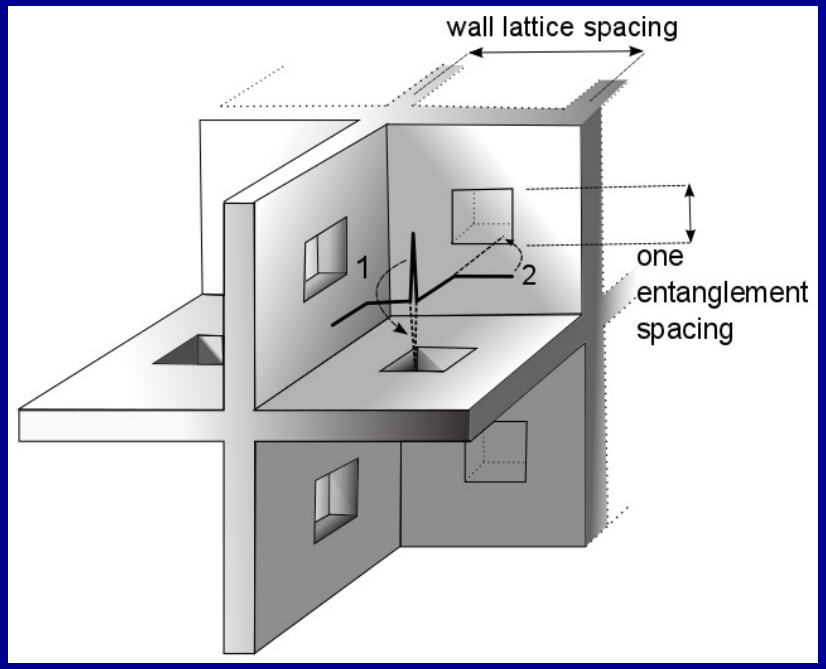
Are dynamics controlled by the presence a very few small ”pores”? Monte Carlo modelling of chain diffusion in a constrained environment



- Dynamics in nanocomposites complicated by complex structure
  - Wide range of lengthscales associated with distances between particles
- Consider motion through uniformly sized chambers with holes
  - Geometry of constraints well defined
- Reptation from the Evans-Edwards MC model

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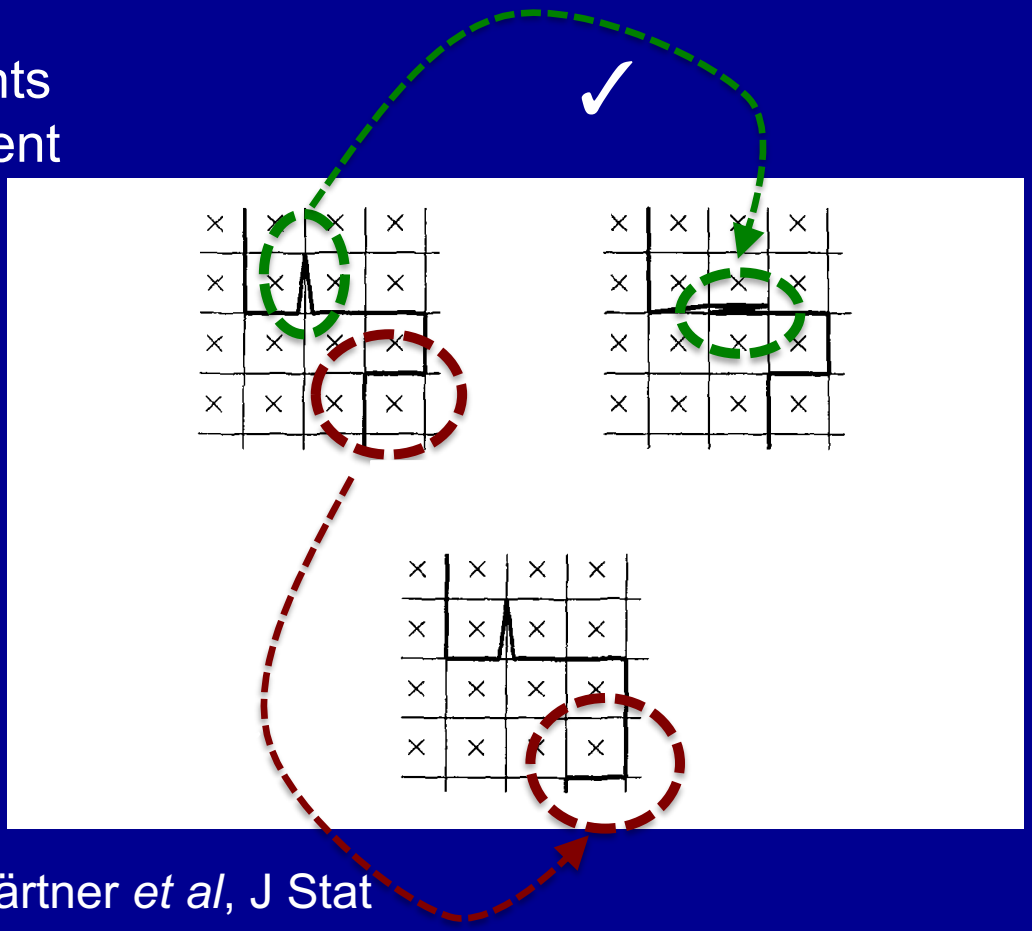
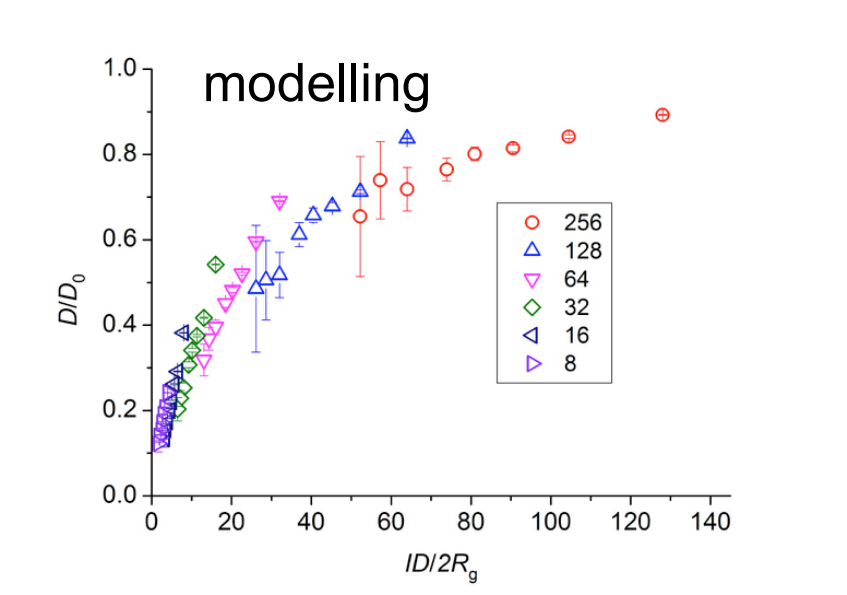
The Evans – Edwards Monte Carlo model for reptation

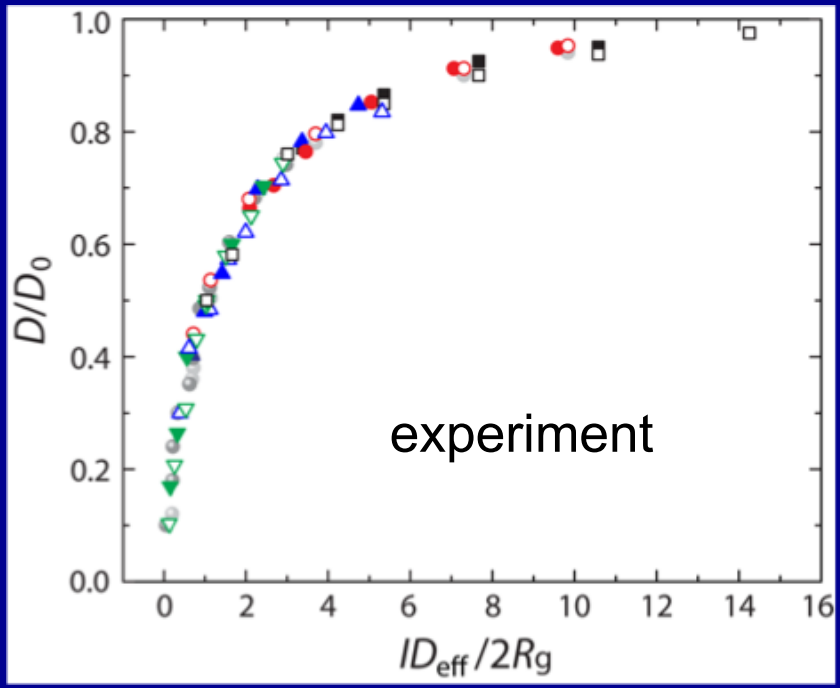
- Highly coarse-grained
  - Each segment represents an entanglement segment
- Motion occurs by
  - End segments
  - Hairpins



Taken from Baumgärtner *et al*, J Stat Phys, 1998, 90, 1375

A Master Curve?





Collapse onto a single curve almost observed

Difference due to regular vs dispersed structures?

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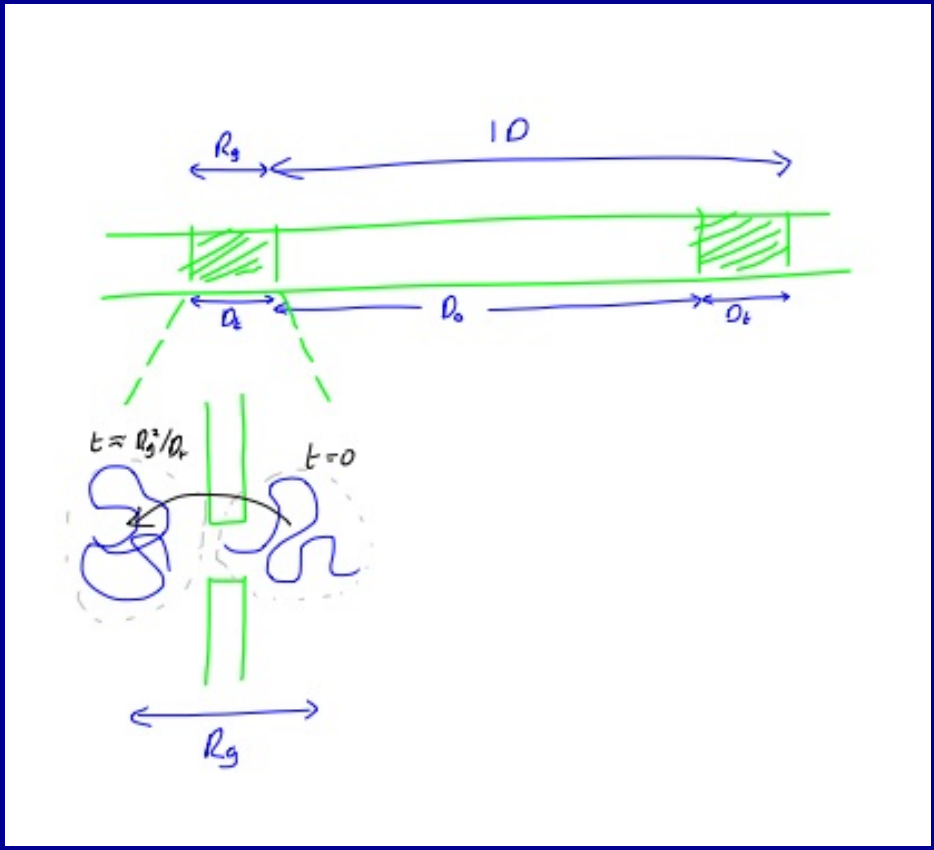
The constraint diffusion coefficient



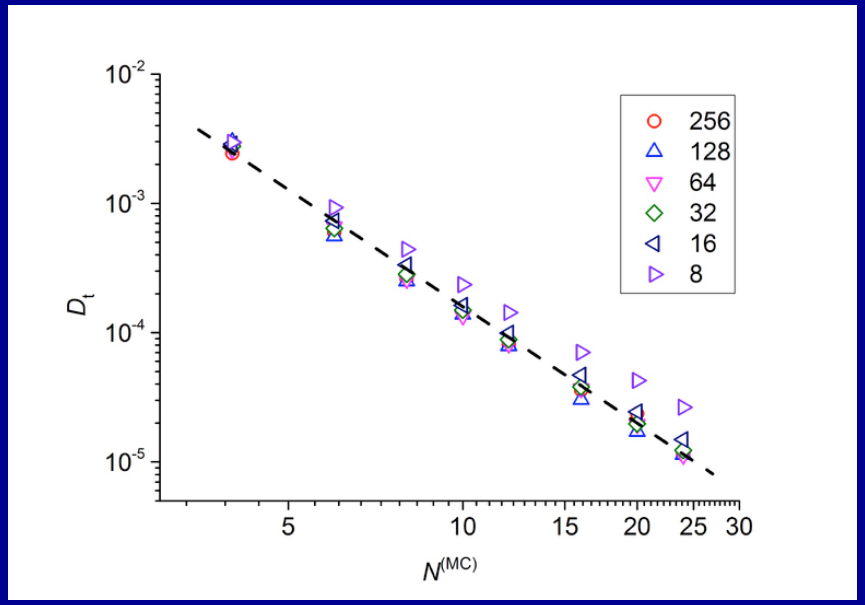
The constraint has an effective width equal to R_g

- once the chain has escaped through hole it has diffused ~ R_g

Assume that we can treat as a 1D problem

$$\frac{1}{D} = \frac{f}{D_t} + \frac{1-f}{D_0}; \quad f = \frac{R_g}{ID}$$

The constraint diffusion coefficient



- Overall diffusion due to two processes
  - Diffusion within chambers, D_0
  - Diffusion between chambers, through holes, D_t
- D_t scales with chain size as N^{-3}
  - Suggests physical mechanism
- D_0 scales with chain size as N^{-2}

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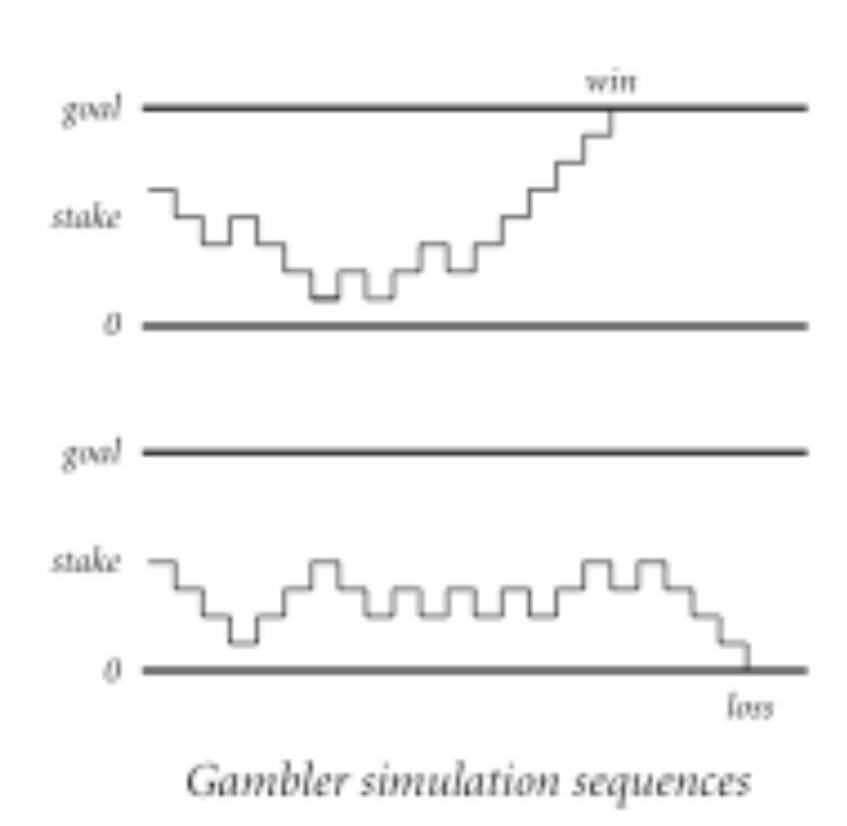
The Classic ruin problem: an explanation for scaling?



Gambler simulation sequences

- Each turn player wins or loses one dollar with equal probability
- Given an initial stake *z* dollars, and a goal *a* dollars
  - probability of win

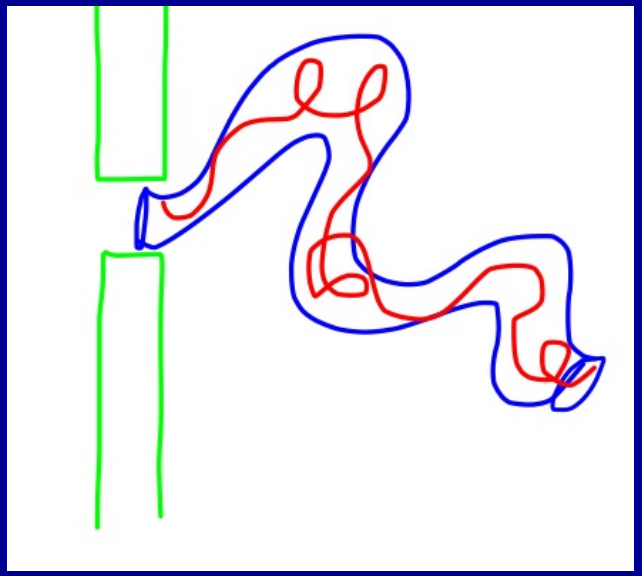
$$p(win) = \frac{z}{a}$$

  - average duration given win

$$\langle duration \rangle = \frac{1}{2}\left(a^2 - z^2\right)\tau_0$$

time for each turn

Gambler's ruin and reptation



- Reptation is a series of random walks along the tube
  - equal probability of walking one entanglement in either direction along tube
- Combine physics with statistics of gambler's ruin:

$$D_t = \frac{R_g^2}{\langle \text{duration of escape} \rangle} \approx \left(\frac{1}{N^{(\text{MC})}} \right)^3$$

Scaling observed from MC simulations

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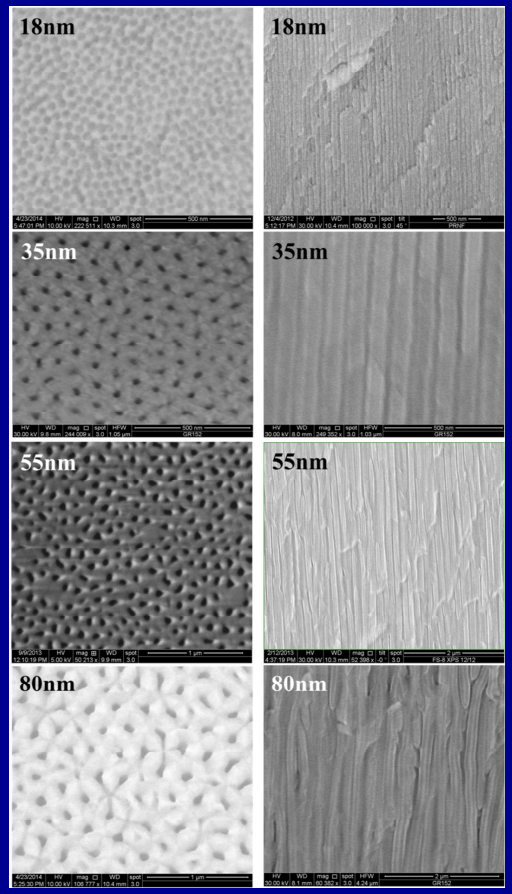
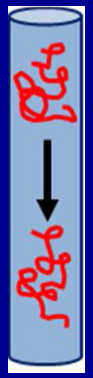
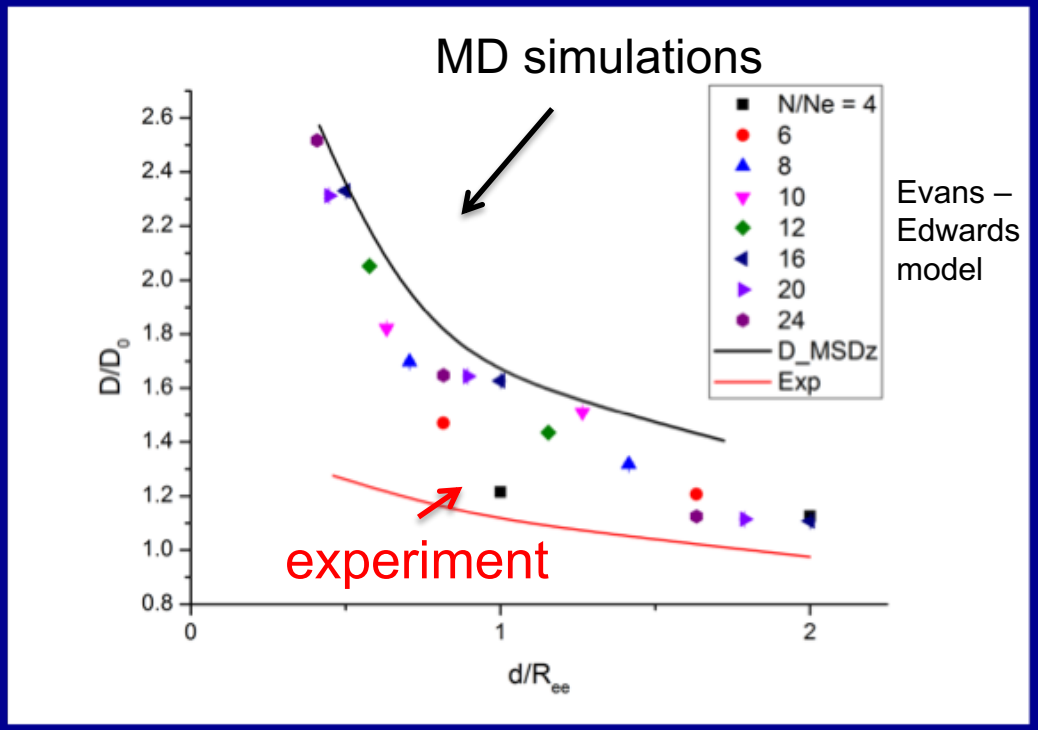
Diffusion in cylindrical confinement







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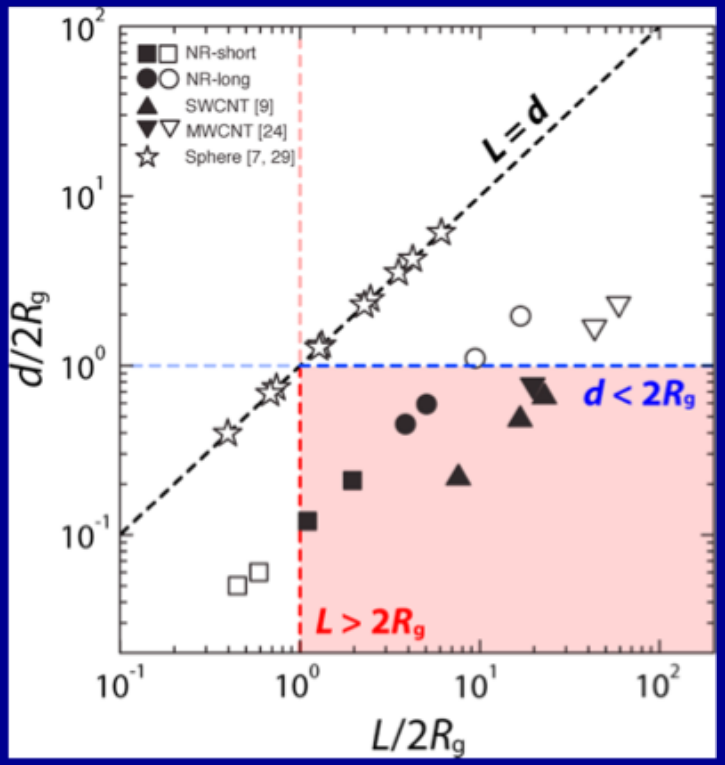
Towards a universal picture for both spherical and rod-like nanoparticles

- A minimum is observed when two geometric characteristics are met:

  $d < 2R_g$ and $L > 2R_g$



Choi *et al*, ACS Macro Lett. 2014

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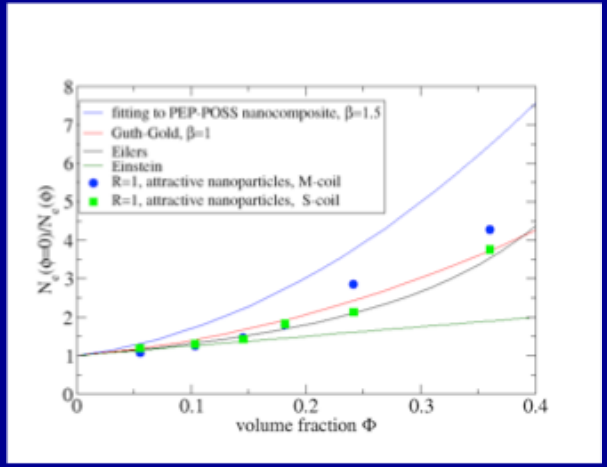
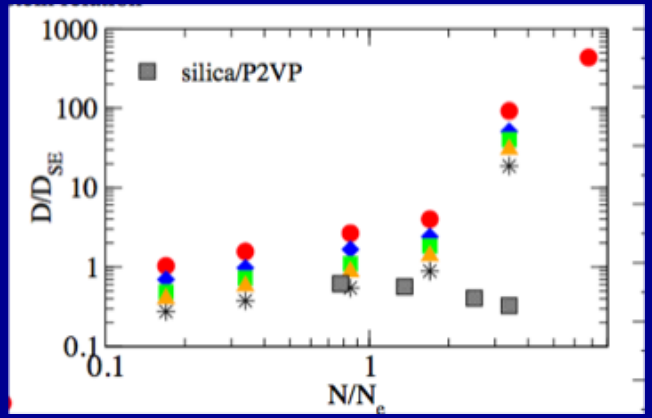
Successes and open questions

- Mesoscale models demonstrate how decoupling between diffusion and viscosity can be rationalised
- Structure predictions can help elucidate nature of surface interacrtions
- What is the molecular mechanism for a minimum in the diffusion coefficient in SWCNT/polymer mixtures?
- How should entanglements be defined in polymer/nanoparticle matrices?





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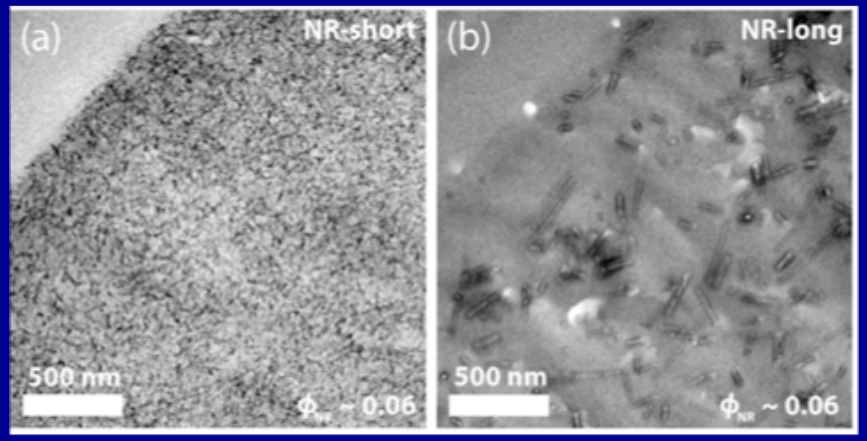
The role of nanoparticle aspect ratio

- SWCNT have very large aspect ratio: L/D >> 1
- Silica nanoparticle have aspect ratio: L/D = 1
- Is behavior difference due to aspect ratio?
  - Test by synthesizing ‘intermediate’ aspect ratio nanoparticles



Phenyl capped TiO_2 rod-like nanoparticles in polystyrene

Phenyl capped SiO_2 rod-like nanoparticles in polystyrene

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