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The use of atomistic simulations to guide the derivation and verification of molecular theories

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Outline

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❑ TUBE-REPTATION THEORY

Computational approach that allows us to obtain the LVE properties of high-MW polymer melts starting from detailed atomistic simulations.

❑ POLYMER NANOCOMPOSITES

-Perform detailed atomistic MD simulations of the same systems in order to get direct predictions of their structural and (particularly) dynamic properties, and directly compare with the experimental data.

-Provide a detailed presentation of the theoretical model which is based on the Rouse theory suitably adapted for adsorbed polymer chains by one or both ends

Tube-reptation model

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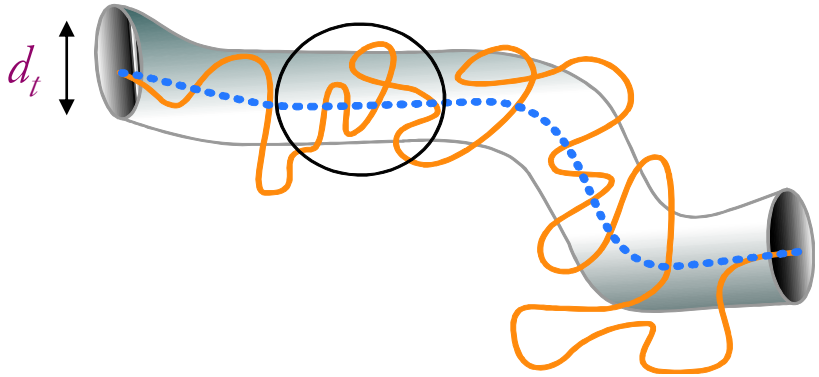
- For $M<M_c$ the Rouse model predictions are verified $\eta_0 \propto M, D_G \propto M^{-1}$
- For $M>M_c$, $\eta_0 \propto M^{3.4}, D_G \propto M^{-2.3}$
- Uncrossability of chains ⇒ topological constraints ⇒ increase of viscosity and decrease of diffusivity

❖Edwards' Tube idea:

- Surrounding chains restrict transverse polymer motion
- Each polymer is thus confined in a tube-like region.[1]

Sam Edwards, 1967

[2]



- Strength of the tube -the effective tube diameter d_t

- The axis is the shortest path connecting the two ends and obeys the topology of constraints (primitive path, PP).[1]

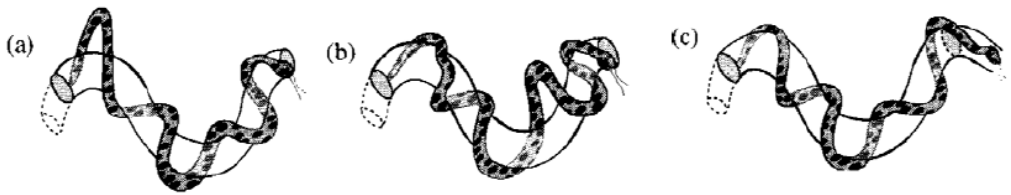
1. Edwards, *Polymer*, 9, 140 (1977).
2. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)

Tube-reptation model

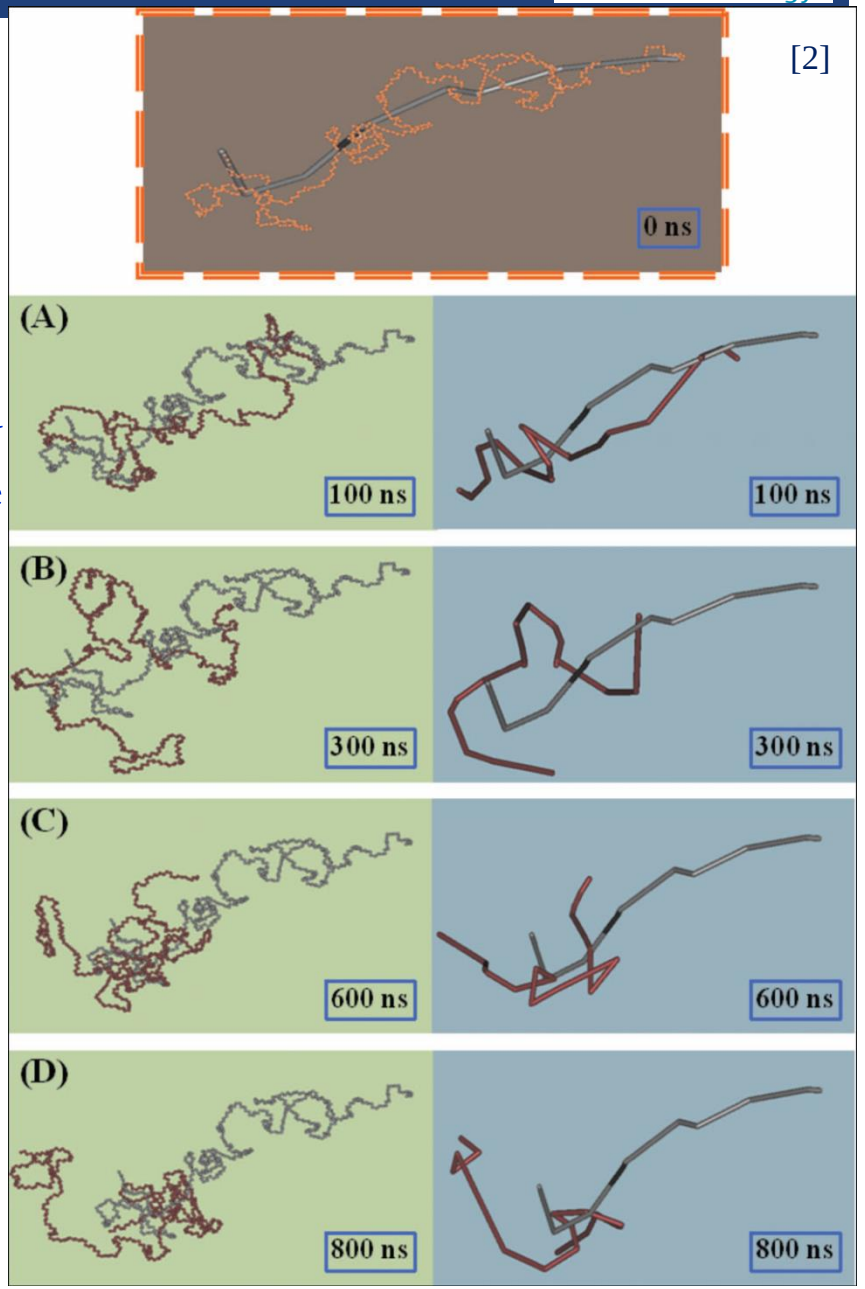
De Gennes' Reptation idea:

Pierre-Gilles de Gennes, 1971

❑ Since tangential movement is severely hindered, the chain is forced to move along the tube-*reptate*



[2]



1. de Gennes, *J. Chem. Phys.*, 55, 572 (1971).
2. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)

Tube-reptation model

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- Key ingredient: $\psi(s,t)$ defining the probability that after time *t*, a given segment s along the PP is still inside the initial (defined at *t*=0) tube.

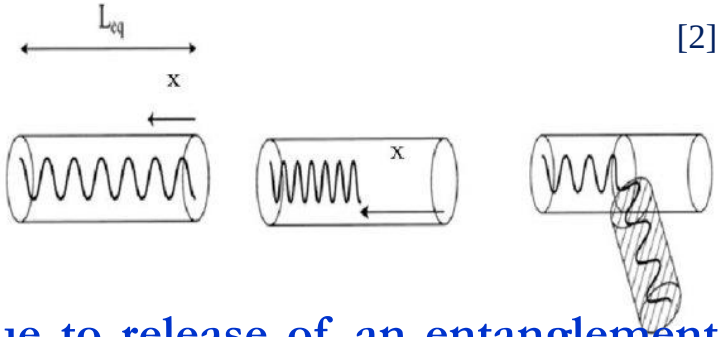
- The average probability, $\Psi(t) = \int_0^1 ds\psi(s,t)$, gives ALL Linear Viscoelastic properties:[1]

$$G(t) = G_N^0 \Psi(t) \; (t \geq \tau_e) \qquad \eta_0 = \int_0^\infty dt G(t)$$

$$G'(\omega) = \omega \int_0^\infty \sin(\omega t) G(t) dt$$

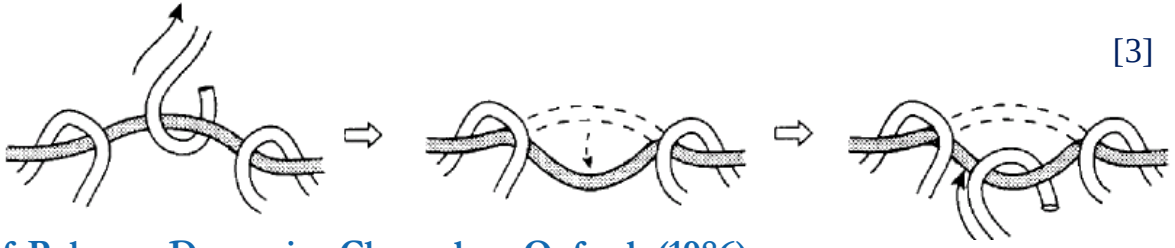
$$G''(\omega) = \omega \int_0^\infty \cos(\omega t) G(t) dt$$

- CLFs (Contour Length Fluctuations), due to the breathing motion of chain ends



[2]

- CR (Constraint Release) due to release of an entanglement from a surrounding chains



[3]

1. Doi and Edwards, The Theory of Polymer Dynamics Clarendon, Oxford, (1986).
2. Van Ruymbeke, Liu, and Bailly, *Rheology Reviews*, 53-134 (2007)
3. Watanabe, *Prog. Polym. Sci.* 24, 1253 1999.

Objectives

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- Calculate $\psi(s,t)$ for moderately entangled polyethylene systems .
- Introduce modifications to the dual constraint model and…
- …show that these modifications improve the predictions of the model for moderately entangled systems.

Objectives

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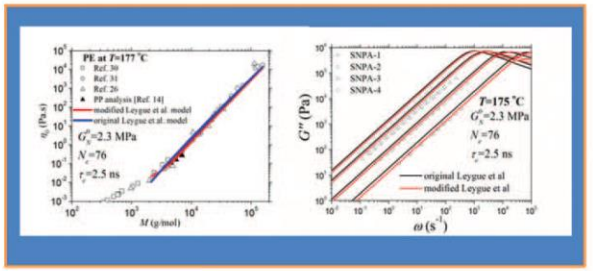
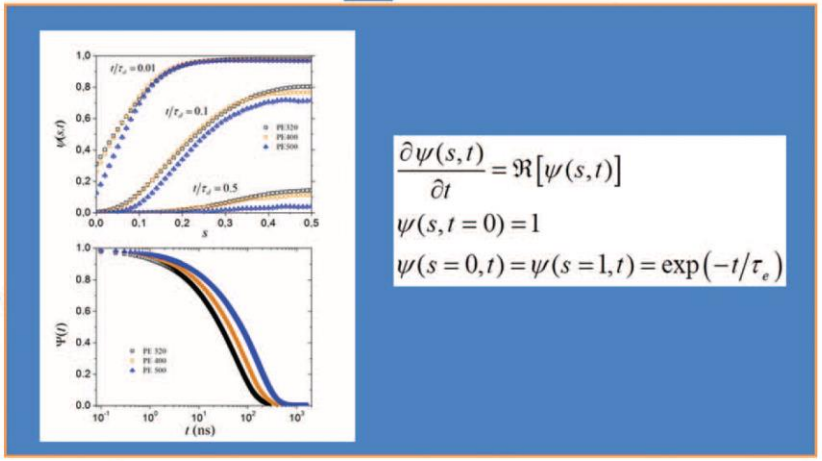
- Schematic illustration of our multi-scale methodology for predicting the linear viscoelastic properties of polymer melts starting from the molecular level.

time

Use of the tuned tube model to get the LVE data [1]

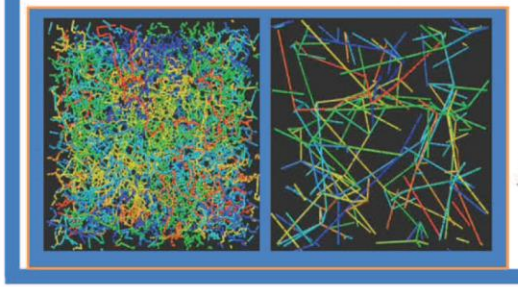




$$\frac{\partial \psi(s,t)}{\partial t} = \Re[\psi(s,t)]$$

$$\psi(s,t=0) = 1$$

$$\psi(s=0,t) = \psi(s=1,t) = \exp(-t/\tau_e)$$



Computation of $\psi(s,t)$ –Mapping to tube model

Atomistic MD simulation-Reduction to entanglement network

length

1. Edwards, *Polymer*, 9, 140 (1977).
2. PSS, and, Mavrantzas, *J. Chem. Phys.*, 140, 214903 (2014)

Methodology

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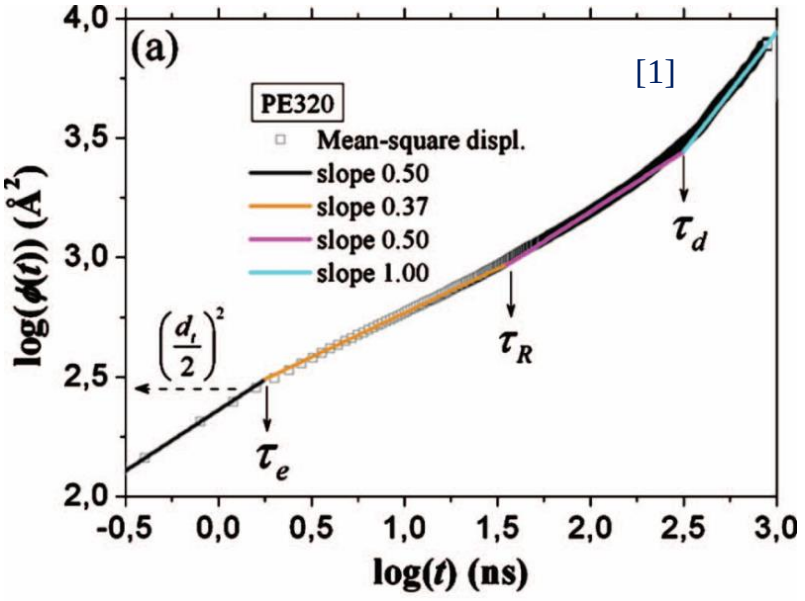
Stage 1:

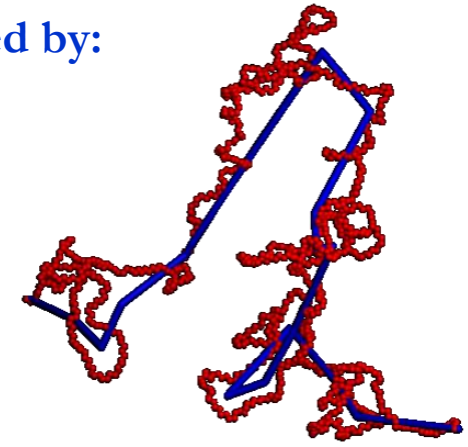
Conduct long atomistic molecular dynamics simulations on model, entangled polymeric systems (PE, cis-1,4-PB, trans-1,4-PB) ⇒ Get estimates of the tube diameter d_t, the entanglement time τ_e, and the disengagement time τ_d by analyzing on a log-log plot segmental mean square displacement (msd) versus time curves on the basis of the Doi-Edwards theory



Stage 2: Perform the topological analysis using Z1-code on the accumulated atomistic trajectories ⇒ Map atomistic data onto trajectories of PPs

Numerically, the problem of constructing Primitive Paths was solved by:

- Everaers et al.[2]
- Kröger[3] [The Z-code]
- Foteinopoulou et al.[4] [The Z1-code]
- Tzoumanekas, and Theodorou[5] [The CReTA-code]



1. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)
2. Everaers et al., *Science* 303, 823 (2004).
3. M. Kröger, *Comput. Phys. Commun*. 168, 209 2005.
4. Foteinopoulou et al., *Macromolecules* 39, 4207 2006.
5. Tzoumanekas and Theodorou, *Macromolecules* 39, 4592 (2006).

Methodology

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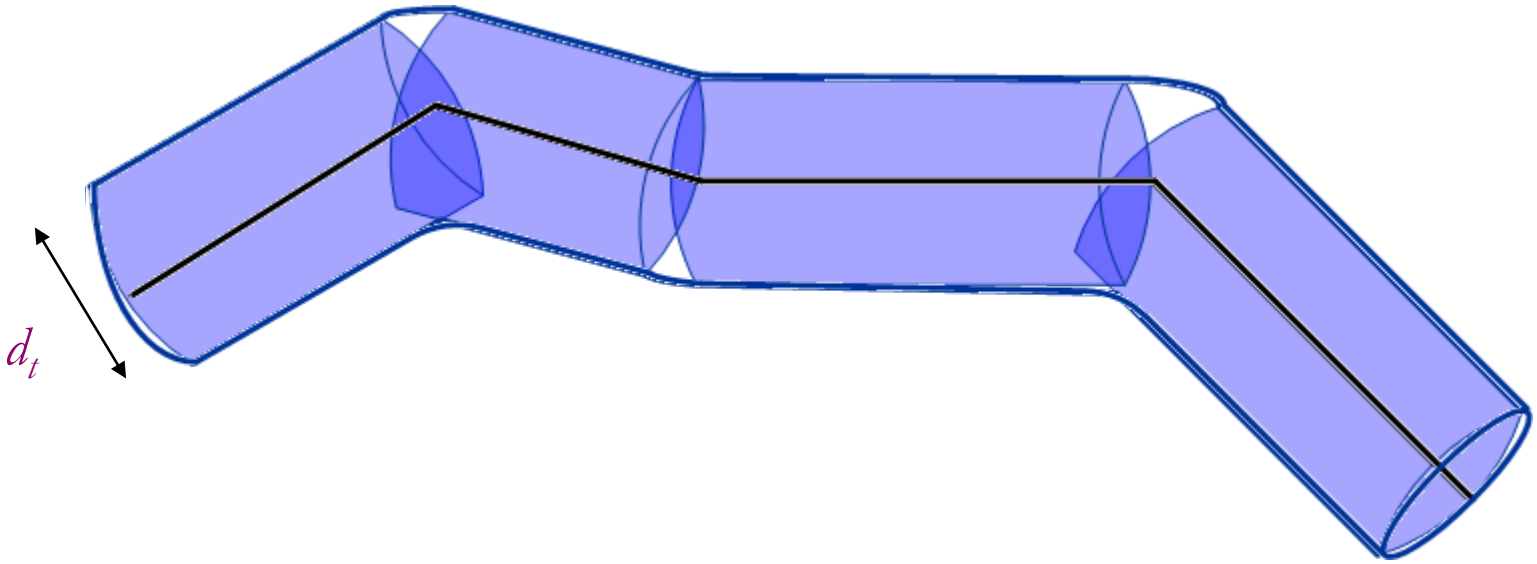
Stage 3: Calculate $\psi(s,t)$ function using the following four-step approach:[1]

(a) Geometrically construct the initial (at time t=0) tube piece-by-piece by approximating it by the space of a small cylinder around each entanglement strand along a chain having the same axis as the entanglement strand itself and a diameter equal to the estimated average tube diameter



1. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)

Methodology

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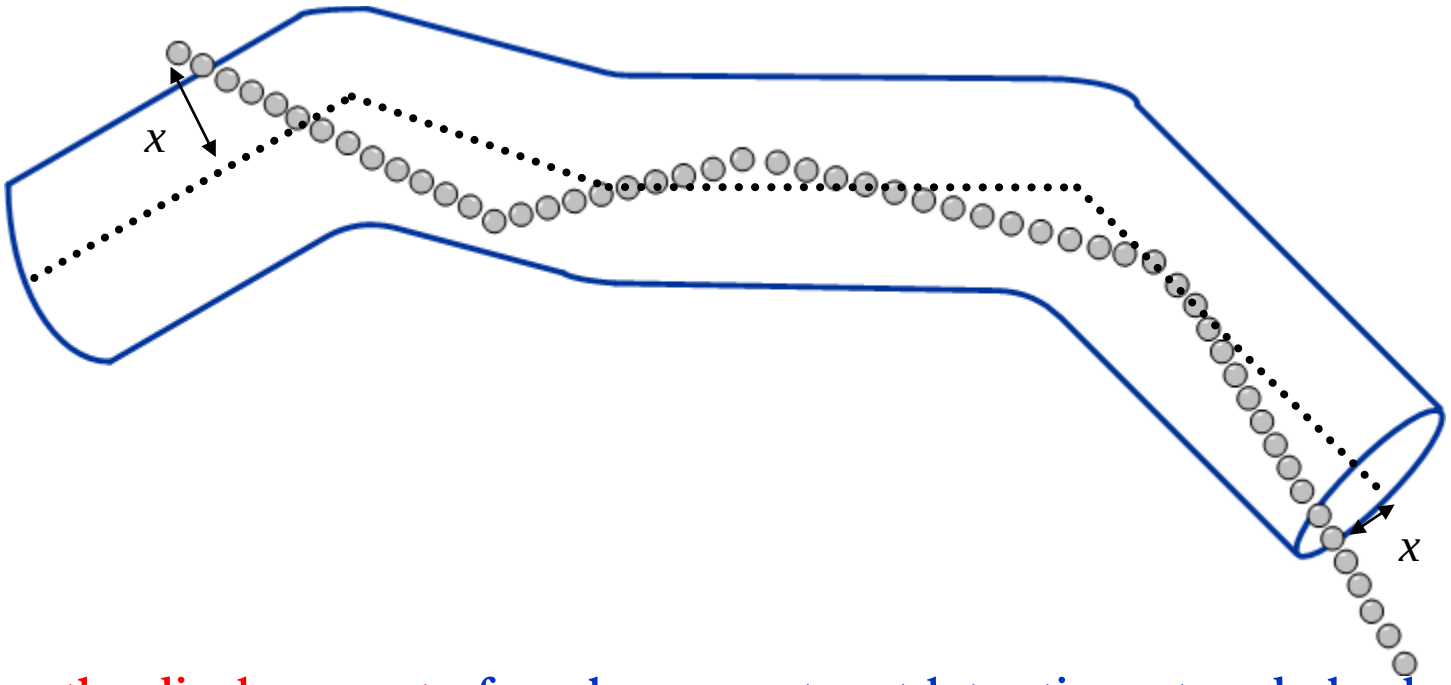
(b) Place segments s along the PP at equidistant points on the normalized [0,1] interval



(c) Monitor the displacement of each segment s at later times t and check whether it has escaped the initial tube or not: (i) if $x(s)>d_t/2$, the segment has escaped from the initial tube perpendicularly; (ii) if $x(s)<d_t/2$, we further check if the segment has escaped the tube laterally along its curvilinear axis

(d) For a given point s in the [0,1] interval, average the results for their survival probability (in the initial tube) in the course of time over all chains to calculate the function $\psi(s,t)$

1. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)

Atomistic MD simulations

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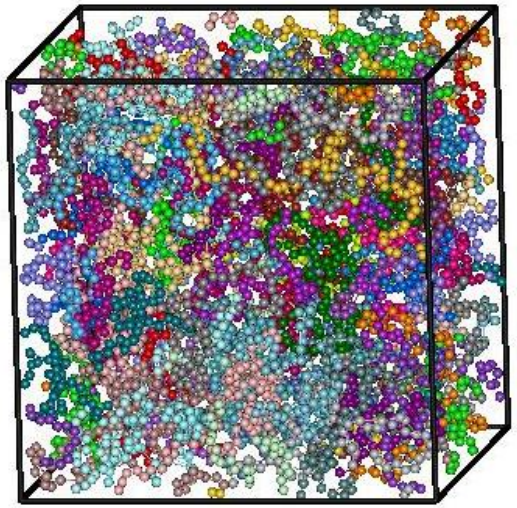
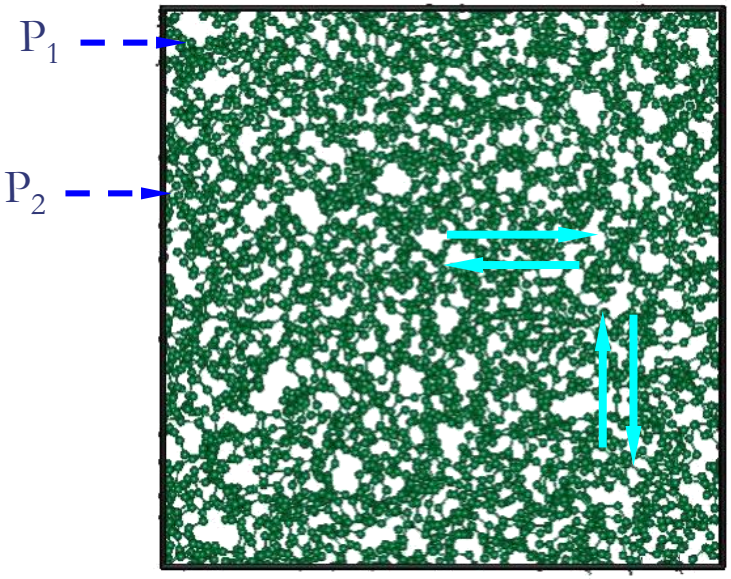
- Execution of parallel MD simulation runs using the LAMMPS code in the NPT statistical ensemble
- Monodisperse PE systems with 320, 400 and 500 carbon atoms per chain at 450 K and 1 atm.
- Total simulation time from 0.8 μs up to 2 μs





Results: Monodisperse PE systems

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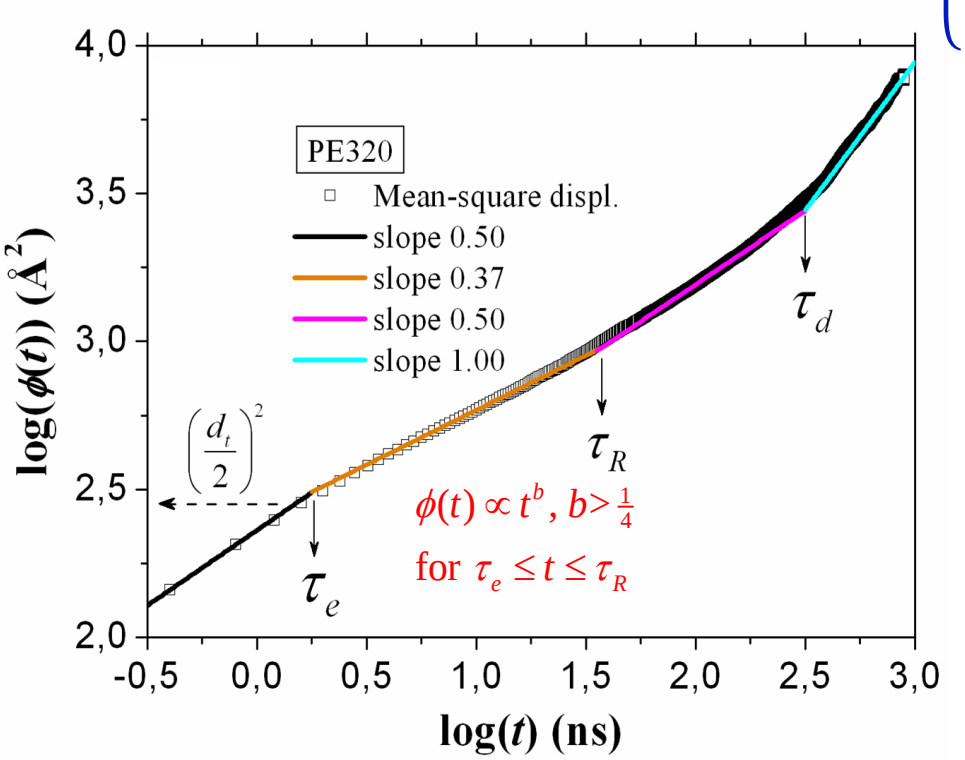
Stage 1: Estimation[1] of d_t, τ_e, and τ_d

Mean Square Displacement of Chain Segments: $\phi(t) = \frac{1}{2n+1} \sum_{i=\frac{1}{2}N-n}^{\frac{1}{2}N+n} \left\langle \left(\boldsymbol{R}(i,t) - \boldsymbol{R}(i,0) \right)^2 \right\rangle$

Predictions of Reptation Theory:[2] $\phi(t) = \begin{cases} t^{1/2}, t \le \tau_e \\ t^{1/4}, \tau_e \le t \le \tau_R \\ t^{1/2}, \tau_R \le t \le \tau_d \\ t^{1}, t > \tau_d \end{cases}$



Estimation of tube diameter[1]

The incipient point where the slope starts to deviate in the first region as $d_t = 2\sqrt{\phi(t)}$

1. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)
2. Doi and Edwards, The Theory of Polymer Dynamics Clarendon, Oxford, (1986).

Results: Monodisperse PE systems

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Stage 1: Estimation[1] of d_t, τ_e, τ_d , and the step length $a_s = \langle R^2_{ete} \rangle / \langle L \rangle$

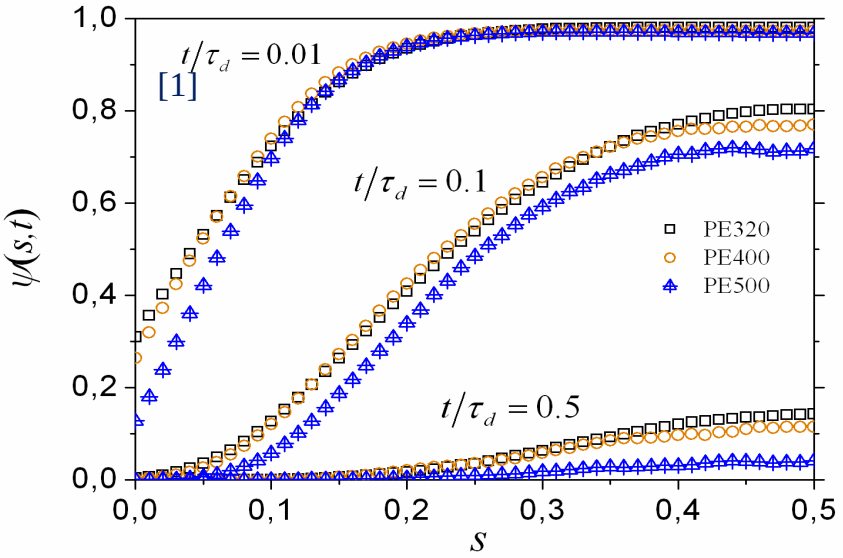
System	ρ (g/cm^3)	τ_e (ns)	τ_d (ns)	d_t (Å)	a_s (Å)
PE320 (32)	0.767	2.1±0.5	316±32	32.8±0.45	37.4±4.4
PE400 (16)	0.768	2.9±0.4	489±25	32.9±0.31	38.7±6.6
PE500 (16)	0.769	2.8±0.4	1042±46	32.4±0.85	42.5±9.3

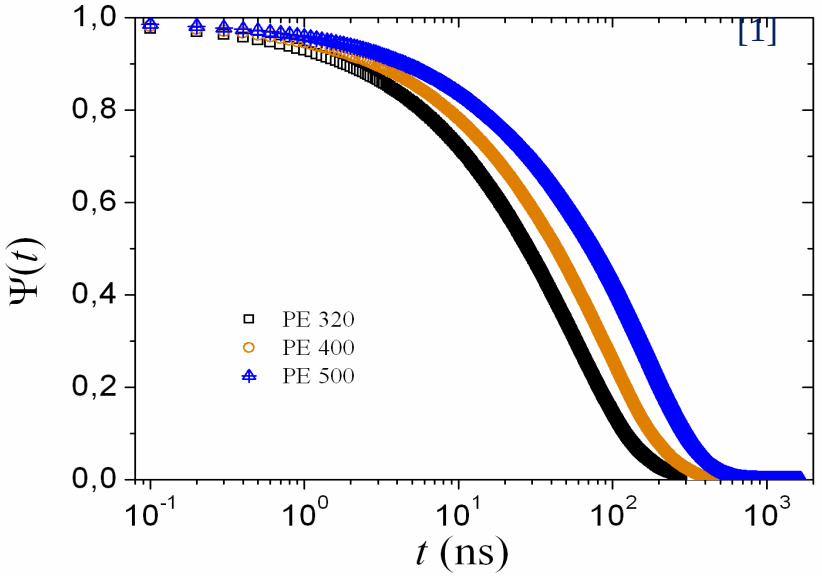
$\tau_e = 2 - 3$ ns

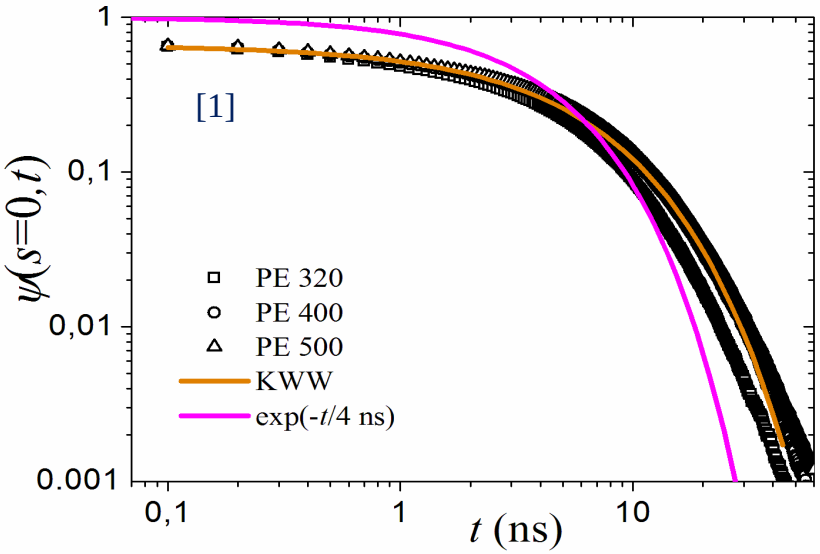
1. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)
2. Doi and Edwards, The Theory of Polymer Dynamics Clarendon, Oxford, (1986).

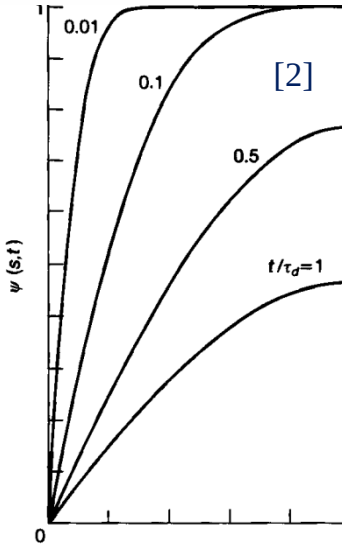
Results: Monodisperse PE systems

Stage 3: Calculate $\psi(s,t)$ function









1. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010)
2. Doi and Edwards, The Theory of Polymer Dynamics Clarendon, Oxford, (1986).

The dual-constraint model

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- Comprised of two stages:[1,2] Stage A (adding CLF) and stage B (also adding CR)

- In both a diffusion equation with a reaction-type term added is solved:

$$\frac{\partial \psi^*(s,t)}{\partial t} = \frac{1}{\pi^2 \tau_d}\frac{\partial^2 \psi^*(s,t)}{\partial s^2} - \frac{1}{\tau(s)}\psi^*(s,t) \qquad \psi^*(s = 0 \text{ or } 1, t) = 0, \forall t > 0$$

- $\tau(s)$ is given as follows:

$$\tau(s) = \begin{cases} \tau_{early}(s), & s < C_1 \\ \sqrt{\tau_{early}(s)\tau^*_{late}(s)}, & C_1 < s < C_2 \\ \tau^*_{late}(s), & s > C_2 \end{cases}$$

$$\tau_{early}(s) = \frac{9\pi^3}{16}\frac{\tau_R}{4}\left(\frac{Z}{2}s^2\right)^2$$

$$\tau^*_{late}(s) = \frac{\tau_R}{4}\exp[U^*(s)]$$

$$U^*(s) = \frac{3Z}{2}s^2$$

- The overall survival probability is then compared against the CR Rouse process of the tube and the result is used in the second stage to introduce CR

1. Pattamaprom et al., *Rheol. Acta* 39, 517 (2000)
2. Pattamaprom and Larson, *Rheol. Acta* 40, 516 (2001).

The MODIFIED dual-constraint model

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1. First change: Adding τ_e to τ_{early}

$$\frac{\partial\psi(s,t)}{\partial t} = \frac{1}{\pi^2\tau_d}\cancelto{0}{\frac{\partial^2\psi(s,t)}{\partial s^2}} - \frac{1}{\tau_{early}(s)}\psi(s,t) \Rightarrow \frac{\partial\psi(s,t)}{\partial t} \approx -\frac{1}{\tau_{early}(s)}\psi(s,t) \Rightarrow$$

$$\psi(s,t) = \exp\left[-\frac{t}{\tau_{early}(s)}\right]$$

- **However,**

$$\tau_{early}(s) = \frac{9\pi^3}{16}\frac{\tau_R}{4}\left(\frac{Z}{2}s^2\right)^2 \Rightarrow \psi(s=0,t) = 0$$

- **On the other hand,**

$$\psi(s=0,t) = \exp\left(-\frac{t}{\tau_e}\right) \Rightarrow \tau_{early}(s) = \tau_e + \frac{9\pi^3}{16}\frac{\tau_R}{4}\left(\frac{Z}{2}s^2\right)^2$$

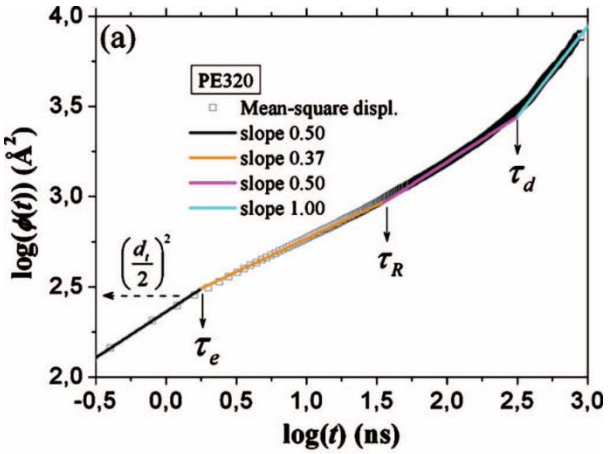
2. Second change: Modifying the exponent

Since,[1] $\phi(t) \propto t^{1/4} \Rightarrow \tau_{early}(s) \propto \left(\frac{3\pi^{3/2}}{4}Zs^2\right)^2$ (when $\tau_e \le t \le \tau_R$) then as noted

$$\phi(t) \propto t^b, b > \frac{1}{4}, \tau_e \le t \le \tau_R$$

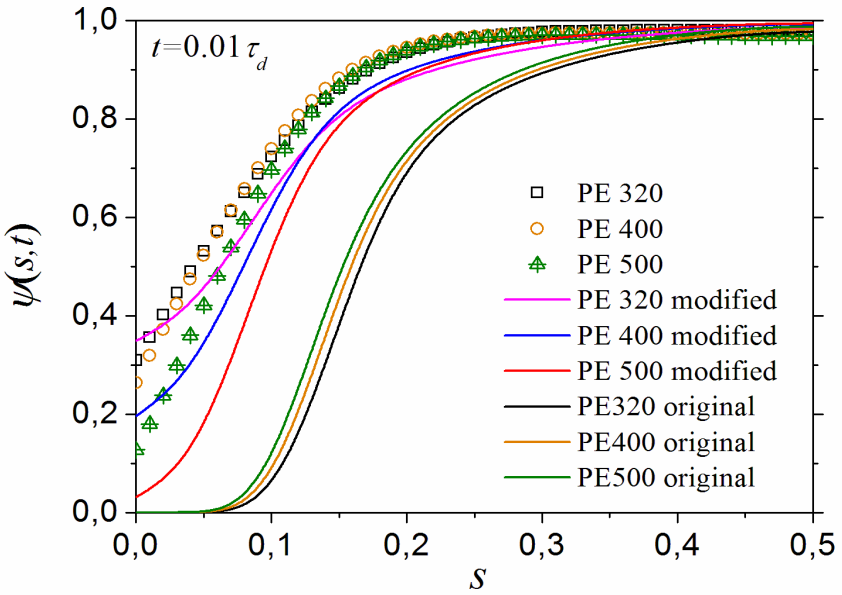
then

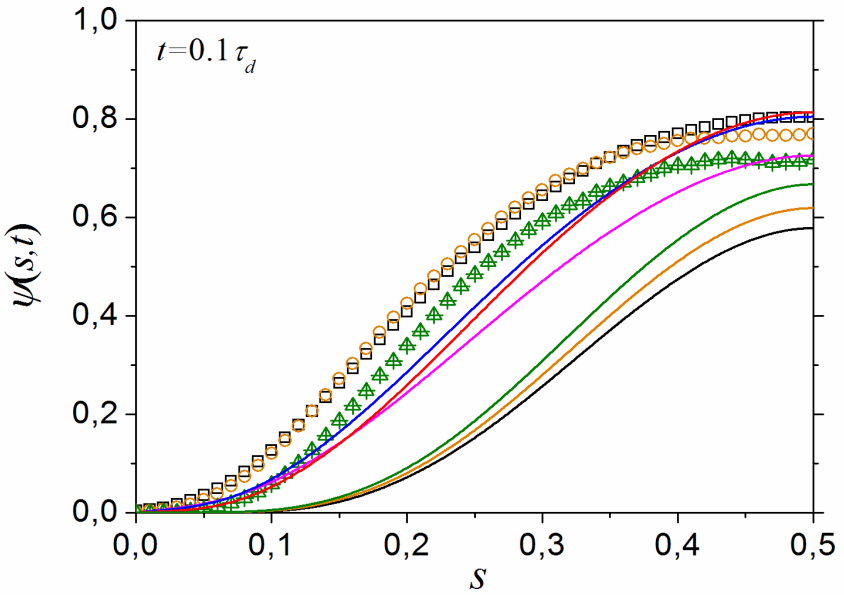
$$\tau_{early}(s) = \tau_e + \left(\frac{3\pi^{3/2}}{4}Zs^2\right)^\beta \tau_R,\ \beta = (2b)^{-1}$$



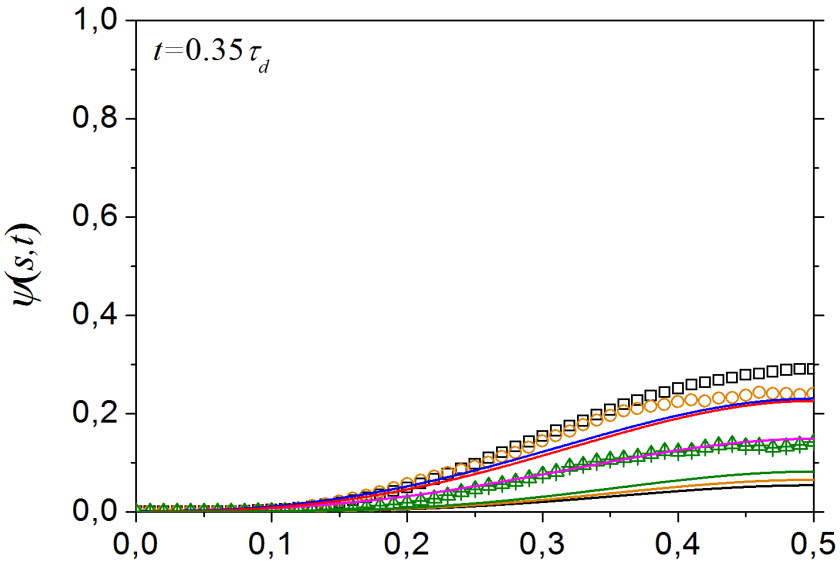
1. Milner and McLeish, *Macromolecules*, 30, 2159 (1997).

MODIFIED vs original dual-constraint model





[1]



Modified model

τ_d, τ_R
β
} from atomistic simulations

Original model

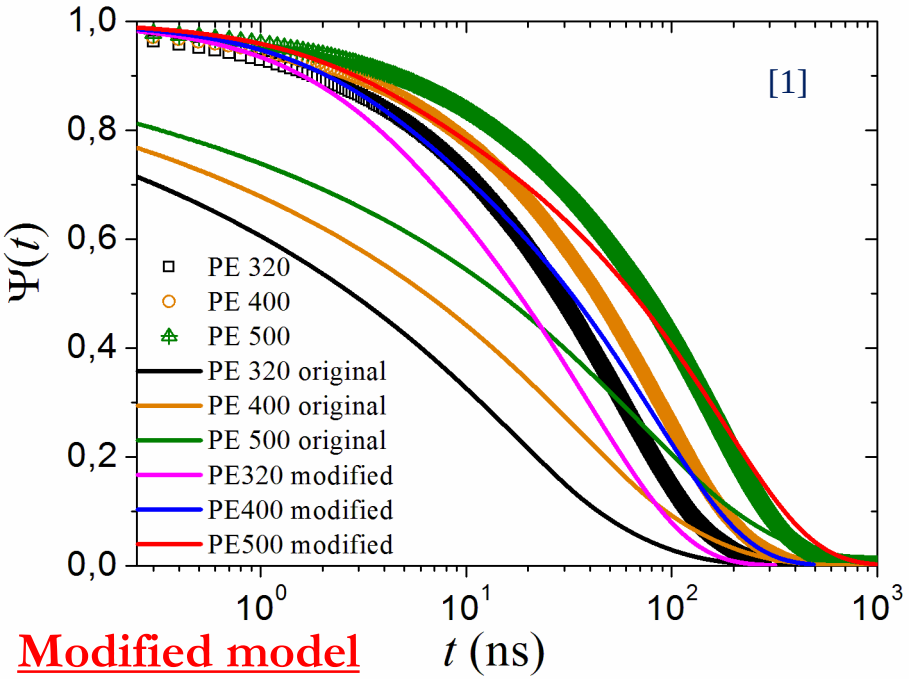
$\tau_d = 3Z^3\tau_e$

$\tau_R = Z^2\tau_e, \beta = 2$

Both: $N_e = 76$, $\tau_e = 3\ ns$ } from atomistic simulations

1. Stephanou, and Mavrantzas, *J J. Non- Newtonian Fluid Mech.* 200, 111-130 (2013).

MODIFIED vs original dual-constraint model



For Polyethylene

$G_N^0 = 2.3$ MPa [2]

$$\eta_0 = \int_0^\infty dt G(t) = G_N^0 \int_0^\infty dt \Psi(t)$$

Modified model

τ_d, τ_R
β
} from atomistic simulations

Original model

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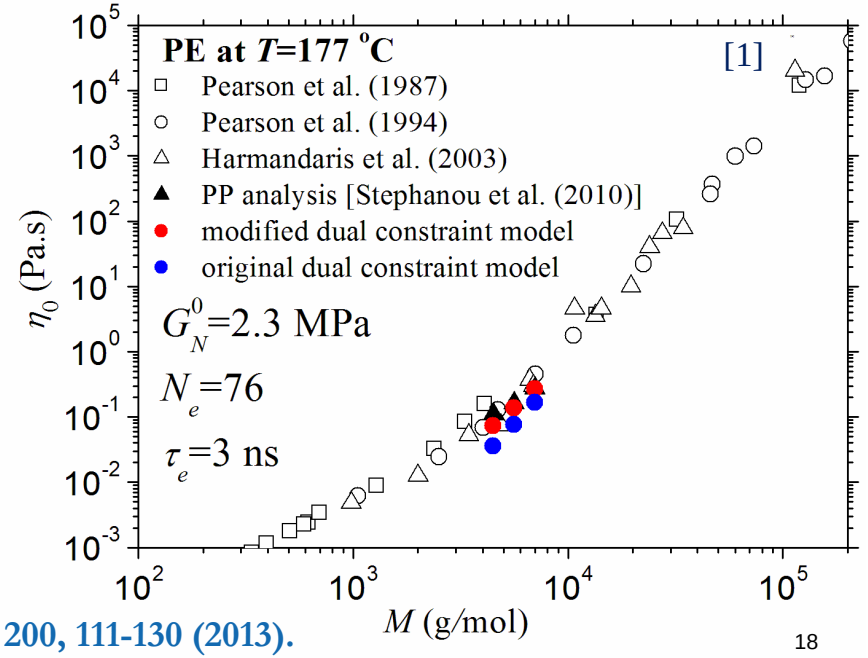


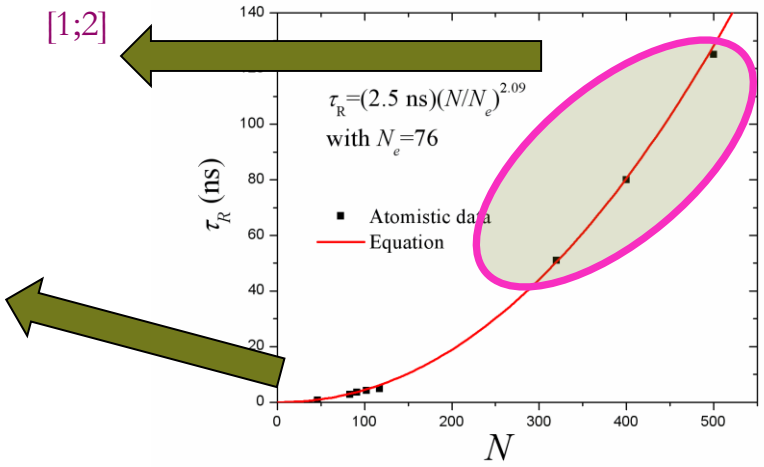
1. Stephanou, and Mavrantzas, *J. Non- Newtonian Fluid Mech.*, 200, 111-130 (2013).
2. Pearson et al., *Macromolecules* 27, 711–719 (1994).

The MODIFIED model: Generalization

1. Rouse time: From atomistic simulations $\tau_R \propto N^2$

[1;2]

[3]



We can thus safely use $\tau_R = Z^2\tau_e$

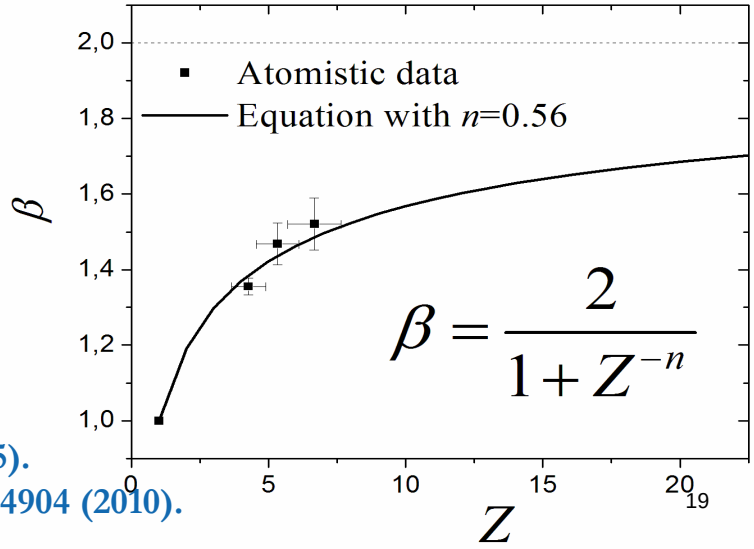
2. Reptation time: Adding also CLF corrections $\tau_d = 3Z^3\left(1 - 0.6Z^{-1/2}\right)^2\tau_e$

3. Msd parameter:

β=1 (b=1/2) for Z=1 (unentangled systems)

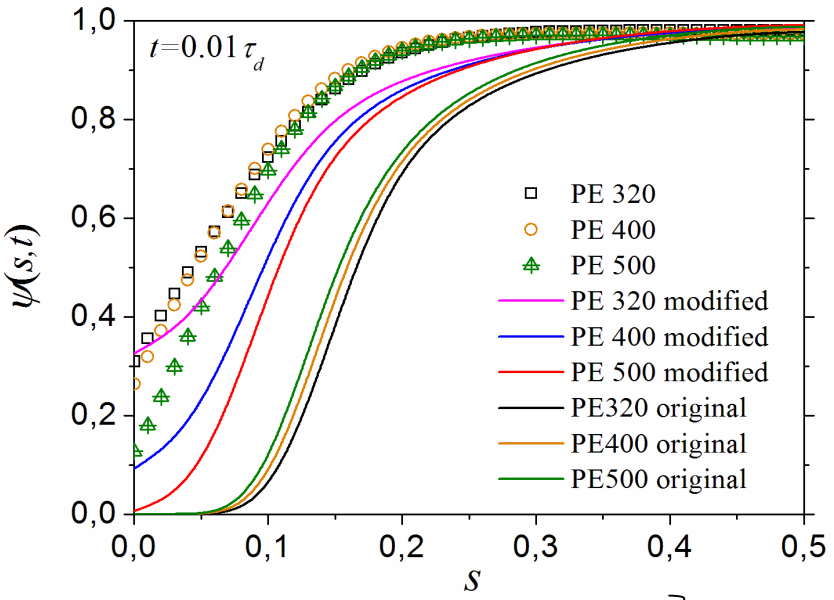
β=2 (b=1/4) for very long chains (Z>>1)

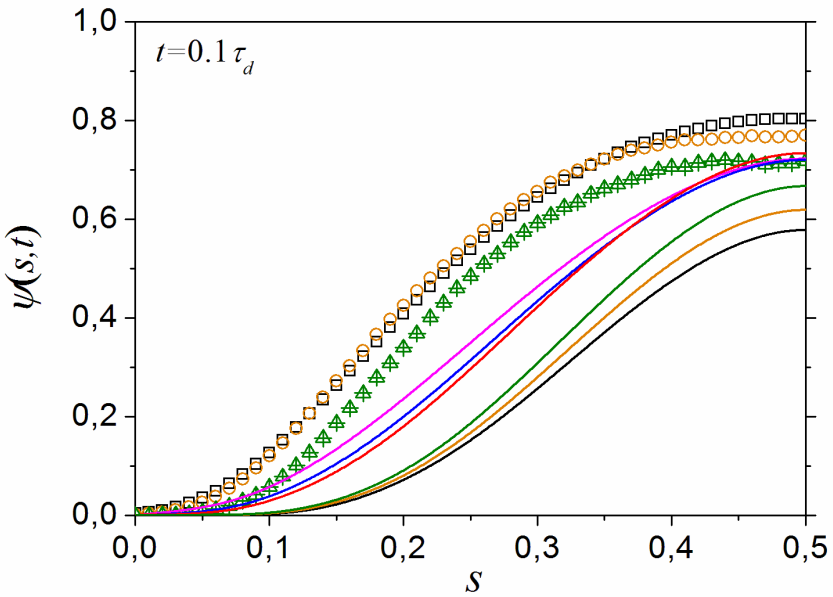
$$\beta = \frac{2}{1+Z^{-n}}, Z \geq 1$$



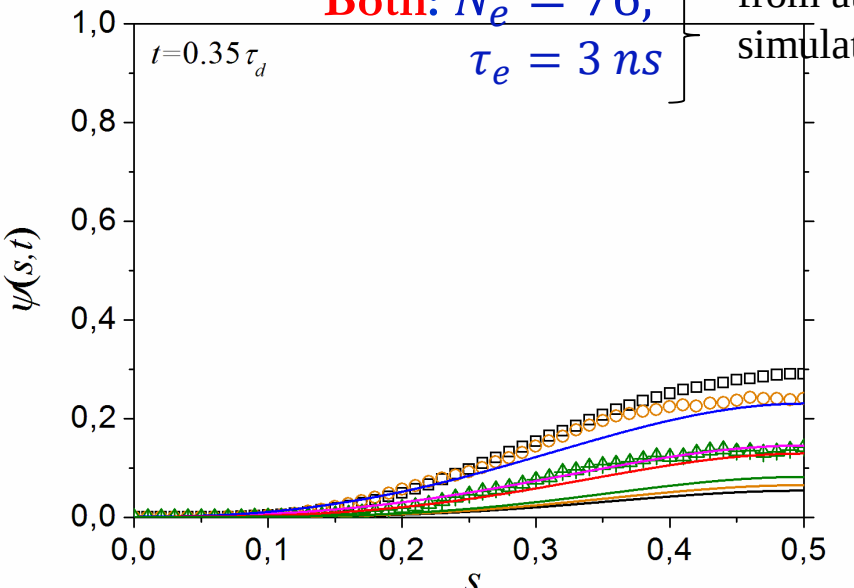
1. Karayiannis and Mavrantzas, *Macromolecules*, 38, 8583–8596 (2005).
2. PSS, Baig, Tsolou, Mavrantzas, and Kröger, *J. Chem. Phys.*, 132, 124904 (2010).
3. Harmandaris et al., *Macromolecules*, 36, 1376–1387 (2003).

MODIFIED vs original dual-constraint model





[1]



Both: $N_e = 76$, $\tau_e = 3\ ns$ from atomistic simulations

Modified model

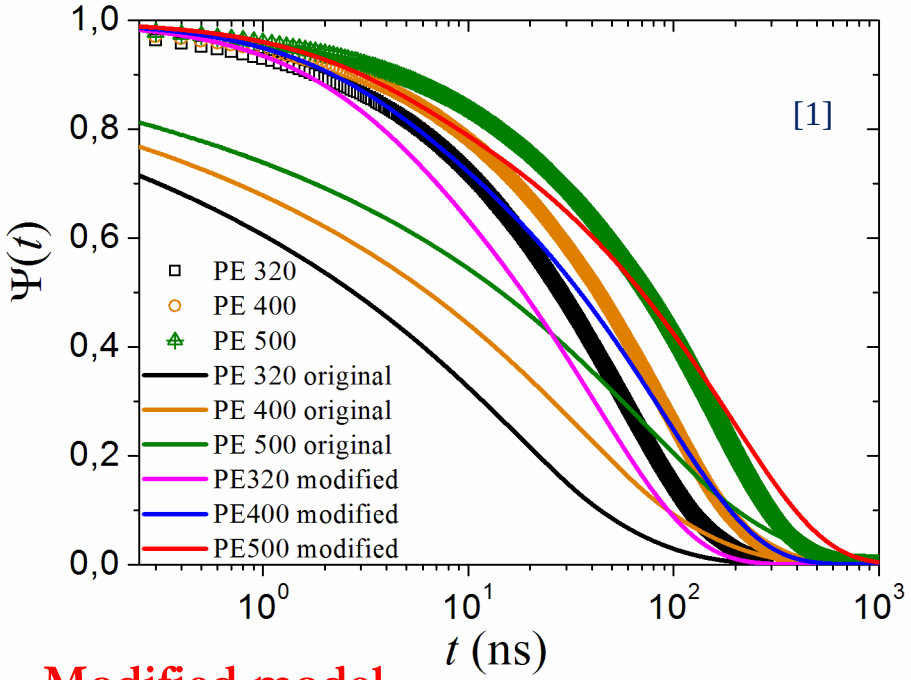
$$\tau_d = 3Z^3\left(1 - 0.6Z^{-1/2}\right)^2\tau_e,$$
$$\tau_R = Z^2\tau_e$$
$$\beta = 2/(1 + Z^{-n})$$

Original model

$$\tau_d = 3Z^3\tau_e$$
$$\tau_R = Z^2\tau_e, \beta = 2$$

1. Stephanou, and Mavrantzas, *J. Non- Newtonian Fluid Mech.*, 200, 111-130 (2013).

MODIFIED vs original dual-constraint model



For Polyethylene

$G_N^0 = 2.3$ MPa [2]

$N_e = 76$,

$\tau_e = 3\ ns$

} from atomistic simulations

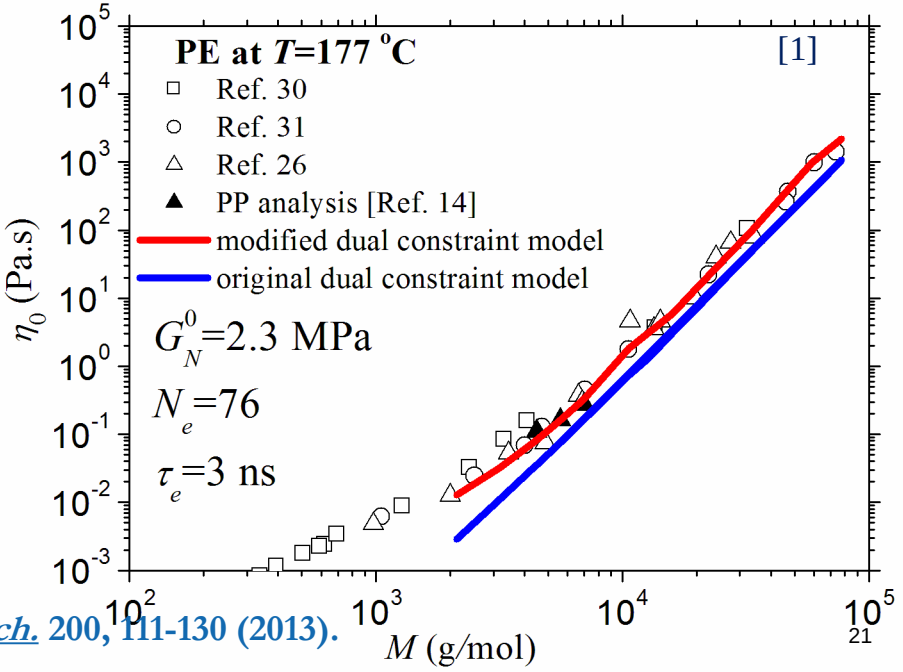
$$\eta_0 = \int_0^\infty dt G(t) = G_N^0 \int_0^\infty dt \Psi(t)$$

Modified model

$$\tau_d = 3Z^3\left(1 - 0.6Z^{-1/2}\right)^2 \tau_e,$$
$$\tau_R = Z^2\tau_e$$
$$\beta = 2/(1+Z^{-n})$$

Original model

$$\tau_d = 3Z^3\tau_e$$
$$\tau_R = Z^2\tau_e, \beta = 2$$



1. Stephanou, and Mavrantzas, *J. Non- Newtonian Fluid Mech.* 200, 111-130 (2013).
2. Pearson et al., *Macromolecules* 27, 711–719 (1994).

Outline

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❑ TUBE-REPTATION THEORY

Computational approach that allows us to obtain the LVE properties of high-MW polymer melts starting from detailed atomistic simulations.

❑ POLYMER NANOCOMPOSITES

-Perform detailed atomistic MD simulations of the same systems in order to get direct predictions of their structural and (particularly) dynamic properties, and directly compare with the experimental data.

-Provide a detailed presentation of the theoretical model which is based on the Rouse theory suitably adapted for adsorbed polymer chains by one or both ends

Introduction

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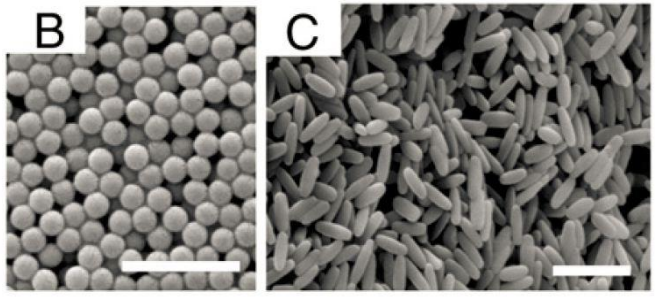
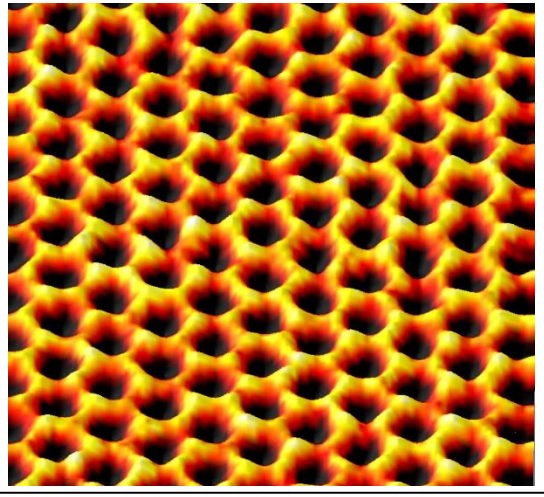
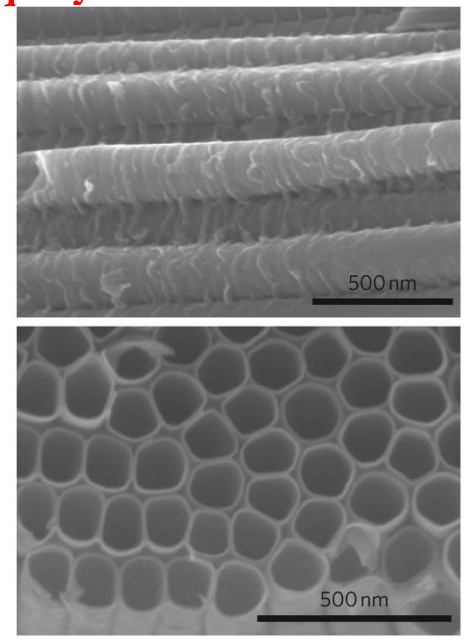
- **Polymer matrix nanocomposites (PNCs) are hybrid organic/inorganic composite materials formed by the addition of nanoparticles (NPs) to a polymer matrix**



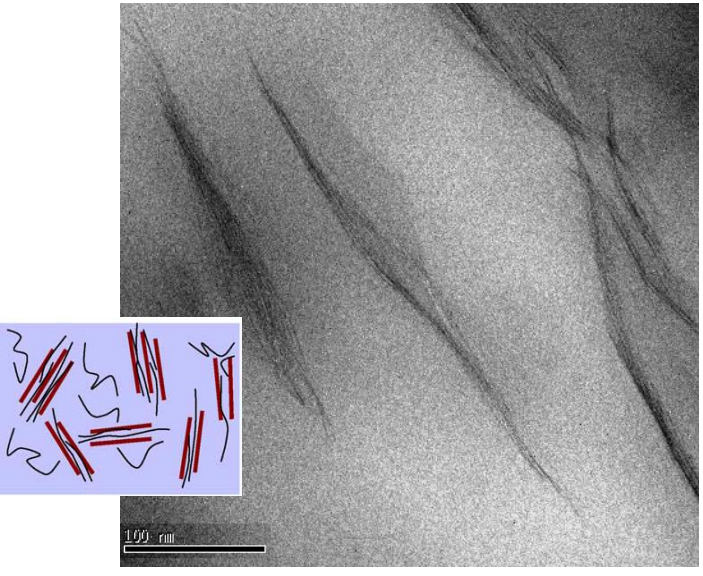
Polystyrene nanospheres (200±0.01 nm in diameter) (B) elongated nanoparticles (nanorods) ([501±43.6 nm]×[123.6±13.3 nm])
[Kolhar et al., PNAS 110, 10753-8 (2013)]



Scanning electron micrograph of graphene, showing the hexagonal structure of the single layer of carbon atoms
[http://arstechnica.com/science/2012/10/the-graphene-age-isnt-quite-here-yet/]



Scanning electron microscopy images of TiO_2 nanotube arrays
[Richter and Schmttenmaer, Nature Technology 5, 769-72 (2010)]



High resolution transmission electron micrograph (HRTEM) of a Nylon-12 layered silicate nanocomposite
[http://www.qub.ac.uk/mrg/research/polymermaterials/tmcnally.php]

Introduction

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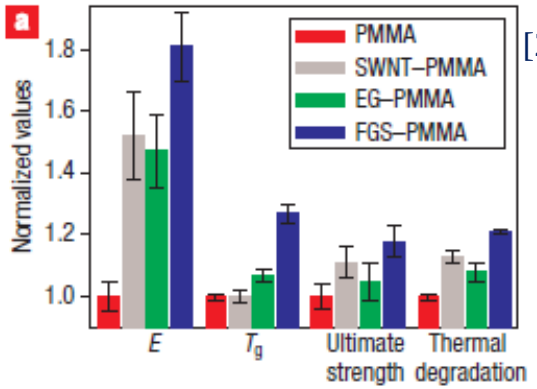
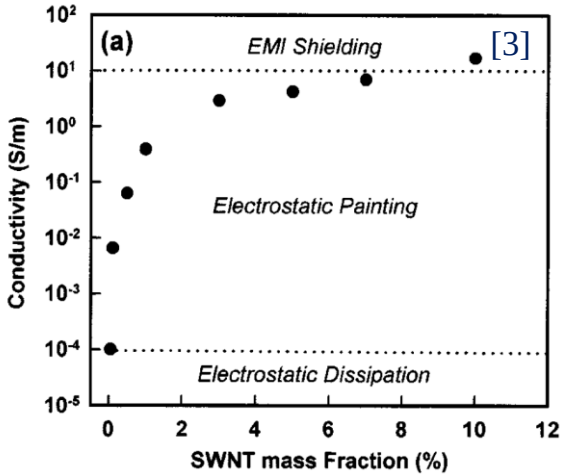
- As a result, the composite material can exhibit significantly improved properties relative to the pure polymer matrix (shear and bulk modulus, yield strength, toughness, film scratch resistance, optical properties, electrical conductivity, gas and solvent transport, among many) even at small volume fractions (loadings) of the nanoparticles.[1]

Summary of thermomechanical property improvements for 1 wt% (functionalized graphene sheets) FGS–PMMA compared to SWNT–PMMA and (Expanded graphite) EG–PMMA composites.

(All property values are normalized to the values for neat PMMA)



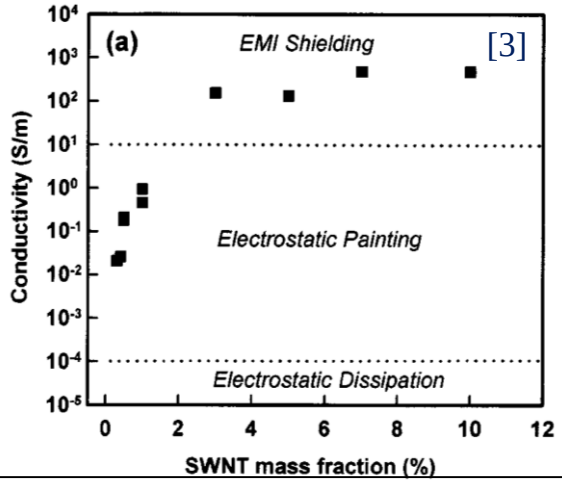
[2]



[3]

PPE-functionalized SWNTs/polystyrene

Electrical conductivity improvement of x-SWNT (Single Wall Nanotubes) as a function of the SWNT weight loading



[3]

PPE-functionalized SWNTs/polycarbonate

1. Jancar *et al.*, *Polymer*, 51, 3321-3343 (2010).
2. Ramanathan *et al.*, *Nature Nanotechnology*, 3, 327 - 331 (2008)
3. Ramasubramaniam *et al.* *Appl. Phys. Lett.*, 83, 2928 (2003).

Introduction

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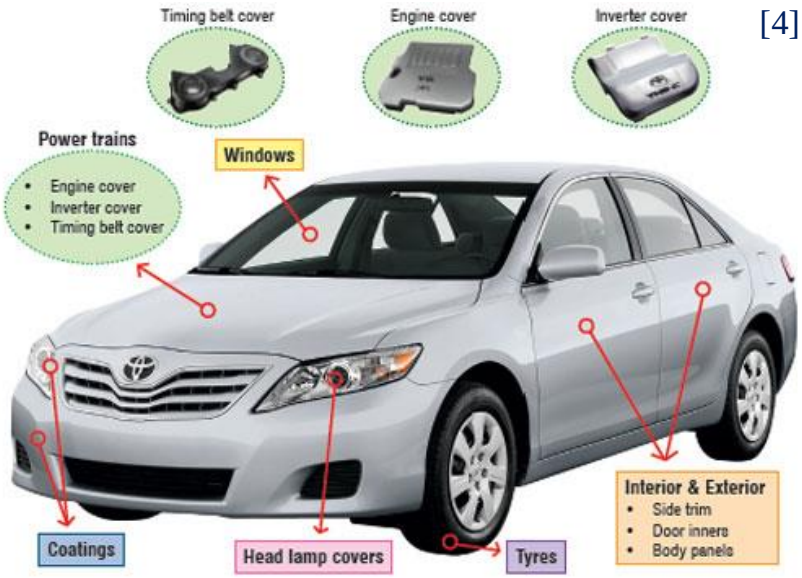
❖Recent applications:

- in solar photovoltaic devices[1,2]

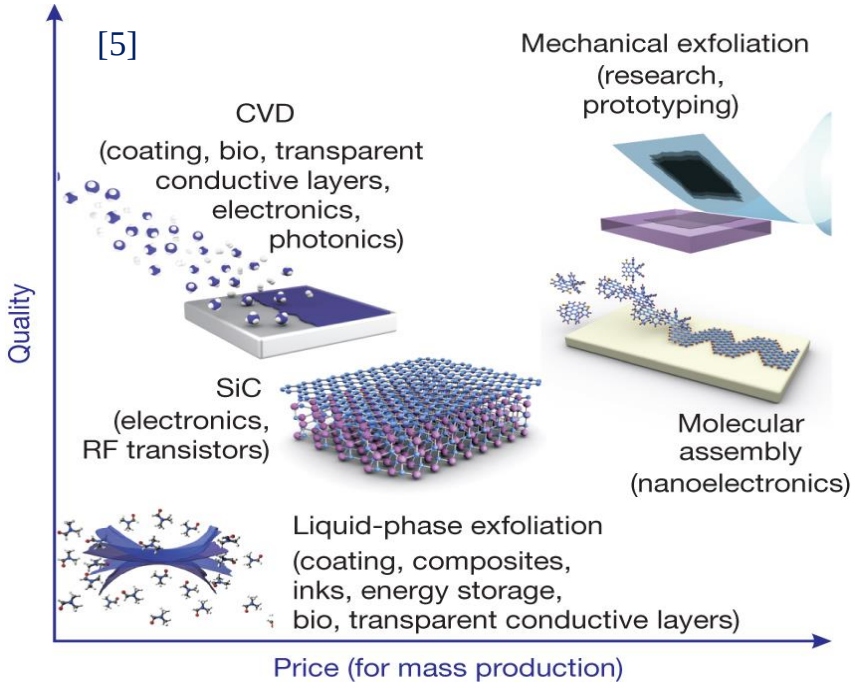
-as lightweight materials with enhanced mechanical, thermal, electrical, and barrier properties of the nanoparticles.[3]

[4]



Usage of polymer nanocomposites as car parts

[5]



There are several methods of mass-production of graphene, which allow a wide choice in terms of size, quality and price for any particular application

1. Moulé et al. *J. Phys. Chem. C*, 112, 12583–12589, (2008)
2. Jancar et al., *Polymer*, 51, 3321-3343 (2010).
3. Kumar and Krishnamoorti, Annu. Rev. Chem. Biomol. Eng. 1, 37–58 (2010)]
4. http://www.nanowerk.com/spotlight/spotid=23934.php
5. Novoselov et al. *Nature* 490,192–200 (2012).

Introduction

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- Insertion of attractive nanoparticles in a host polymer matrix leads to the formation of a dense polymer layer adsorbed around the nanoparticles, wherein chain dynamics is considerably slower compared to the bulk.[1]

- Glomann *et al.*[2] performed Neutron Spin Eco (NSE) experiments of low MW PEG-silica nanocomposites, and recorded significant chain relaxation despite that dynamics at all length scales was much slower compared to the corresponding pure polymer melt system.

- They had also proposed a theoretical model with a small number of adjustable parameters capable of describing quite well the experimental data as well as differences in the dynamics of the two types of systems studied (hydroxyl-terminated versus methoxy-terminated).

1. Baeza et al., *Nat Commun* 2016,
2. Glomann *et al.*, *Phys. Rev. Lett.*, 110, 178001 (2013); Glomann et al., *Soft Matter* ., 9, 10559(2013)

Introduction

Cyprus University of Technology

- For the hydroxyl-terminated chains they considered end-attached chains as virtual free chains with double the molecular weight, centered at the adsorbed end. Since translational motion is suppressed for this virtual chain, its center is fixed in space. They also allowed for a reduced diffusion coefficient of free (non-adsorbed) chains due to the presence of nanoparticles.

- For the more strongly adsorbed methoxy-terminated chains, on the other hand, they assumed that the full spectrum of internal chain dynamics is suppressed.

- The dynamics of free chains for both types of nanocomposites were described through the original Rouse model.

- A very attractive feature of the polymer nanocomposite systems studied by Glomann *et al.*[1] is the relatively short MW of the host PEG matrix, which renders them amenable to full atomistic MD simulation.

1. Glomann *et al.*, *Phys. Rev. Lett.*, 110, 178001 (2013); Glomann et al., *Soft Matter*., 9, 10559(2013);

Scope

Cyprus University of Technology

- Perform detailed MD simulations of the same systems using a reliable, well-validated atomistic model in order to get direct predictions of their structural and (particularly) dynamic properties, and directly compare with the experimental data.

- Provide a detailed presentation of the theoretical model which is based on the Rouse theory suitably adapted for adsorbed polymer chains by one or both ends

Rouse Theory for Free Chains

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- Chain dynamics is described via the following partial differential equation (PDE):

$$\zeta \frac{\partial \mathbf{R}(n,t)}{\partial t} = \frac{3k_BT}{b^2}\frac{\partial^2 \mathbf{R}(n,t)}{\partial n^2} + \boldsymbol{f}(n,t), n \in [0, N_{free}] \quad (1a)$$

- The random Brownian force on each bead obeys the fluctuation-dissipation theorem:

$$\langle \boldsymbol{f}(n,t)\rangle = \mathbf{0}$$
$$\langle f_\alpha(n,t) f_\beta(m,t')\rangle = 2\zeta k_BT\delta_{nm}\delta_{\alpha\beta}\delta(t-t') \quad (1b)$$

- For a free linear chain the following boundary conditions (BCs) should be used

$$\left.\frac{\partial \mathbf{R}(n,t)}{\partial n}\right|_{n=0} = \left.\frac{\partial \mathbf{R}(n,t)}{\partial n}\right|_{n=N_{free}} = 0 \quad (2)$$

- The mean-square displacement (msd) of chain segments, $\phi_{nm}(t) = \langle[\mathbf{R}(n,t) - \mathbf{R}(m,0)]^2\rangle$ is[1]

$$\phi_{nm}(t) = 6D_G + |n-m|b^2 + 4N_{free}b^2 \sum_{p=1}^{\infty} \frac{1}{(p\pi)^2} \cos\left(\frac{p\pi n}{N_{free}}\right)\cos\left(\frac{p\pi m}{N_{free}}\right)\left[1 - \exp\left(-\frac{p^2 t}{\tau_R^{free}}\right)\right] \quad (3)$$

where $\tau_R^{free}(N_{free}) = \frac{\zeta N_{free}^2 b^2}{3\pi^2 k_BT}$ is the longest relaxation time of the chain.

1. Doi, M.; Edwards, S. F., The theory of polymer dynamics. Clarendon Press: Oxford University Press (1986).

Rouse Theory for one-end-adsorbed Chains

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- For a tail (i.e., a chain segment adsorbed at the nanoparticle surface by one of its ends), the PDE is the same as for a free chain, but with the following BCs:

$$\left.\frac{\partial \mathbf{R}(n,t)}{\partial n}\right|_{n=0} = 0, \mathbf{R}(n = N_{tail}, t) = \mathbf{R}_{N_{tail}} \quad (4)$$

- The tail has the $n = 0$ bead free and the $n = N_{tail}$ bead adsorbed to the surface of the nanoparticle (at position $\mathbf{R}_{N_{tail}}$ at all times), with N_{tail} the length of the tail.

- The msd of tails is

$$\phi_{nm}(t) = |n-m|b^2 + 4N_{tail}b^2 \sum_{p=1,3,5,..}^{\infty} \frac{1}{(p\pi)^2} \cos\left(\frac{p\pi n}{2N_{tail}}\right) \cos\left(\frac{p\pi m}{2N_{tail}}\right) \left[1 - \exp\left(-\frac{p^2 t}{\tau_R^{tail}}\right)\right] \quad (5)$$

where $\tau_R^{tail}(N_{tail}) = 4\tau_R^{free}(N_{tail})$ i.e., the corresponding relaxation time of the tail is four times larger than that of the free (non-adsorbed) chain of the same molecular length.

- The expression of Glomann *et al.*[1] is identical to ours except for an extra prefactor.

- It can be shown that this result for the msd would not change if we had considered the first bead to be the adsorbed one and the last bead to be the free one.

1. Glomann *et al.*, *Phys. Rev. Lett.*, 110, 178001 (2013); Glomann et al., *Soft Matter*., 9, 10559(2013);

Rouse Theory for both-end-adsorbed Chains

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- For a loop (a polymer segment adsorbed by both of its ends onto the nanoparticle surface) , again the PDE is the same as for a free chain, but with the following BCs:

$$\mathbf{R}(n=0,t)=\mathbf{R}_0, \mathbf{R}(n=N_{loop},t)=\mathbf{R}_{N_{loop}} \quad (6)$$

where N_{loop} is the size (molecular length) of the loop.

- Then,

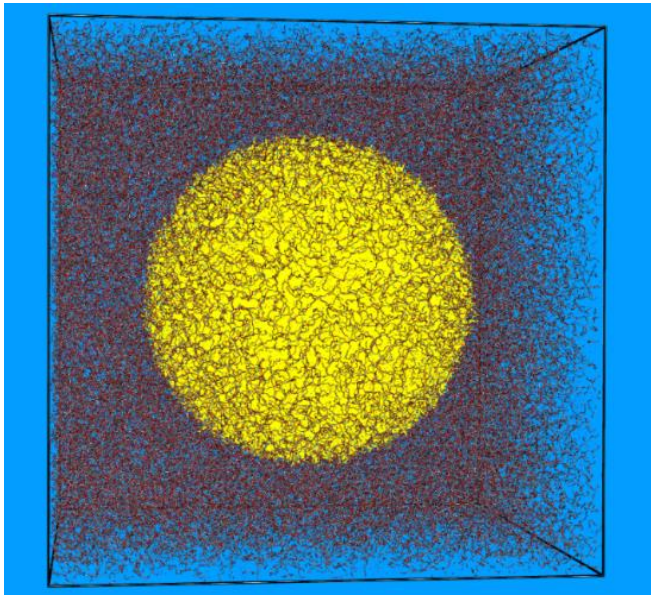
$$\begin{aligned}&\phi_{nm}(t)\\&=\left(\mathbf{R}_{N_{loop}}-\mathbf{R}_0\right)^2\left(\frac{|n-m|}{N_{loop}}\right)^2+\left(1-\frac{|n-m|}{N_{loop}}\right)|n-m|b^2\\&+4N_{loop}b^2\sum_{p=1.}^{\infty}\frac{1}{(p\pi)^2}\sin\left(\frac{p\pi n}{N_{loop}}\right)\sin\left(\frac{p\pi m}{N_{loop}}\right)\left[1-\exp\left(-\frac{p^2t}{\tau_R^{free}(N_{loop})}\right)\right]\end{aligned} \quad (7)$$

- It can be generalized to address chains that are multiply adsorbed along their backbone on the nanoparticle
- For the MD simulations reported here, $\left(\mathbf{R}_{N_{loop}}-\mathbf{R}_0\right)^2 \ll N_{loop}b^2$.

1. Glomann *et al.*, *Phys. Rev. Lett.*, 110, 178001 (2013); Glomann et al., *Soft Matter* ., 9, 10559(2013)

Molecular Model and Systems Studied

- Strictly monodisperse pure PEG melts and PEG-silica nanocomposite melts
- An additional nanocomposite melt was constructed wherein the terminal hydroxyl (H-O-) groups of the PEG chains were replaced by methoxy (CH_3-O-) ones.
- In all cases, PEG chains with 41 monomers and a spherical silica nanoparticle of radius 63.9 Å
- Long MD simulation in the *nPT* statistical ensemble at 413 K and 1 atm, same as the experimental data.[1]



System	End-functional group of PEG chains	Number of polymer chains	Number of silica nanoparticles	Silica loading (v/v %)	Total number of interacting particles
PEG	-OH	1,000	-	0.0	126,000
PEGSil-OH	-OH	1,799	1	14.98	305,887
PEGSil-CH_3	-CH_3	1,898	1	14.97	329,749

1. Glomann *et al.*, *Phys. Rev. Lett.*, 110, 178001 (2013); Glomann et al., *Soft Matter*., 9, 10559(2013)

Results

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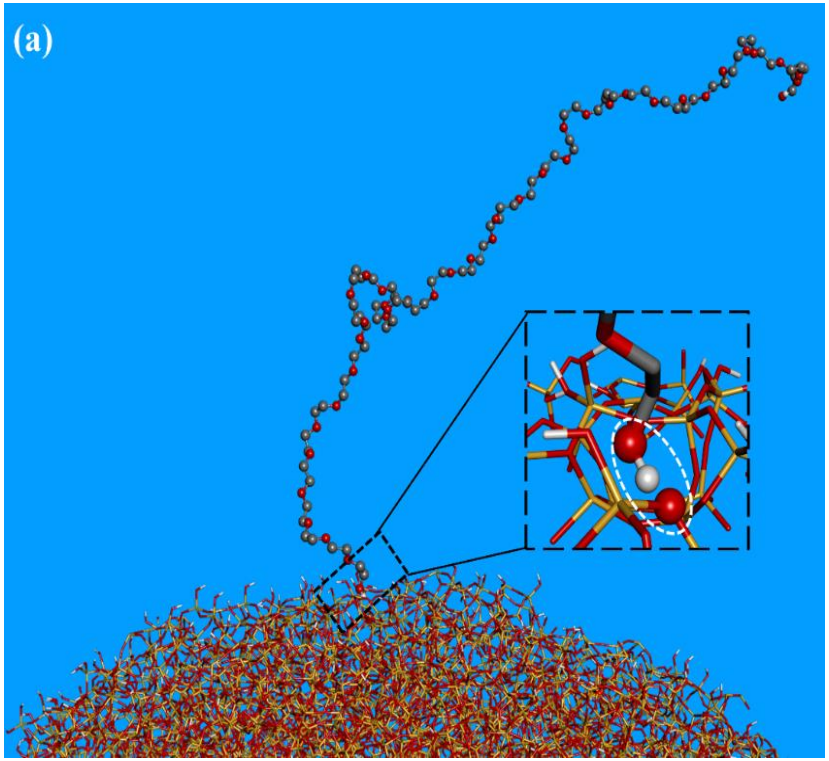
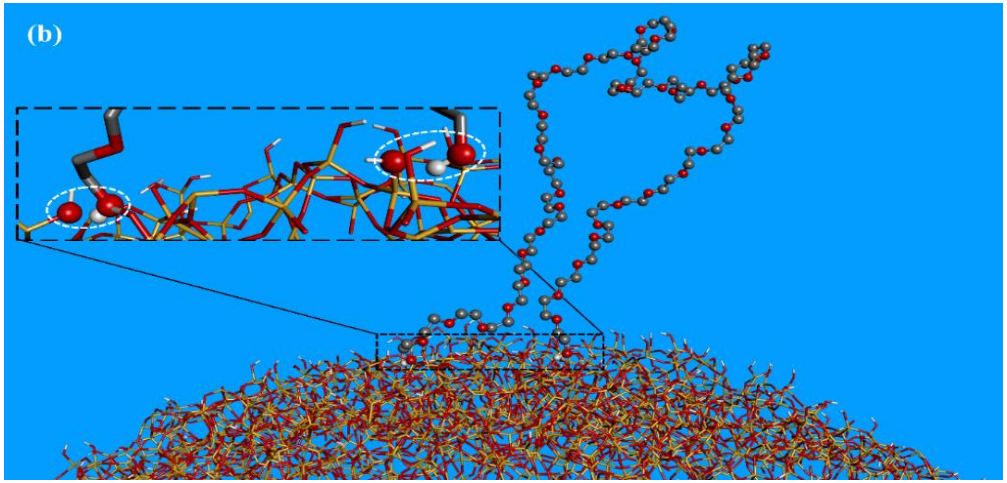
- Typical atomistic snapshots of chains on the surface of the silica nanoparticle :

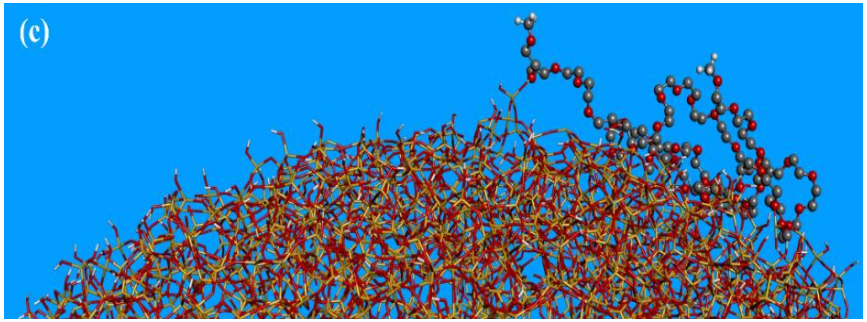
(a) and (b) PEG-OH, and

(c) PEG-CH_3 chains

(oxygen, hydrogen, and silicon atoms depicted in red, white, and yellow color, respectively).







Results

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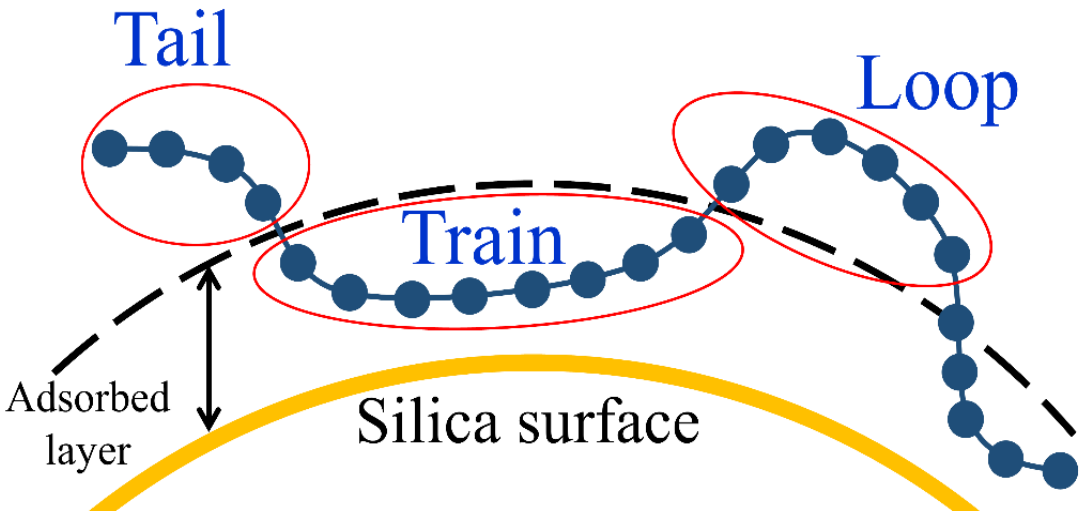
- **Trains:** monomer sequences that are adsorbed on the surface of the nanoparticle along their entire path.
- **Loops:** sequences of intermediate segments along the polymer chain connecting trains but lying outside the adsorbed layer.
- **Tails:** sequences of segments at the end of a chain lying outside the adsorbed layer, with their non-terminal monomer connected to a train.



Results

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- MD predictions for the average values of the population per adsorbed PEG chain and length of these conformations.

System	Population, v_i			Length, N_i		
	trains	loops	tails	trains	loops	tails
PEGSil-OH	1.73 ± 0.03	0.73 ± 0.03	0.76 ± 0.03	3.53 ± 0.11	13.91 ± 0.22	33.76 ± 0.58
PEGSil-CH_3	2.07 ± 0.09	1.07 ± 0.07	1.51 ± 0.04	6.67 ± 0.18	5.83 ± 0.38	14.55 ± 0.87

- The number of train and loop conformations per adsorbed PEG-CH_3 chain is larger, thus they are adsorbed on silica at several points along their contour

- The average number of tails per adsorbed PEG-CH_3 chain is larger than the corresponding number per adsorbed PEG-OH chain,

1. meaning that PEG-OH chains adsorb onto the silica nanoparticle by forming terminal hydrogen bonds, thus leaving them with only one or no free ends at all,
2. whereas PEG-CH_3 chains form hydrogen bonds along their entire contour resulting in adsorbed conformations with enhanced tail populations.

Results

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- The single-chain intermediate coherent dynamic structure factor $S(Q,t)$ is a quantity that can be accessed experimentally by state-of-art techniques, such as dynamic light scattering (DLS) and NSE.

- Then, for the single-chain dynamic structure factor

$$\frac{S(Q,t)}{S(Q,0)} = (1-a)\frac{S^{free}(Q,t)}{S^{free}(Q,0)} + a\left[C_{tail}\frac{S^{tail}(Q,t)}{S^{tail}(Q,0)} + C_{loop}\frac{S^{loop}(Q,t)}{S^{loop}(Q,0)} + C_{train}\right] \quad (8)$$

a is the fraction of adsorbed chains and $C_{tail}, C_{loop}, C_{trail}$ the fraction of adsorbed PEG chains belonging to tail, loop and tail conformation, respectively.

- MD simulation results, experimentally measured data and theoretical model predictions for $S(Q,t)/S(Q,0)$ for all systems examined are presented below.

- All parameters involved in the theoretical calculations (translational diffusion coefficient D_G, longest relaxation time of free chains of non-adsorbed PEG chains τ_R^{free}, $\langle R_{ete}^2 \rangle = N_{free} b^2$, fraction of adsorbed chains a and detailed statistics of adsorbed PEG chains) were provided **DIRECTLY** from the MD simulations.

Results

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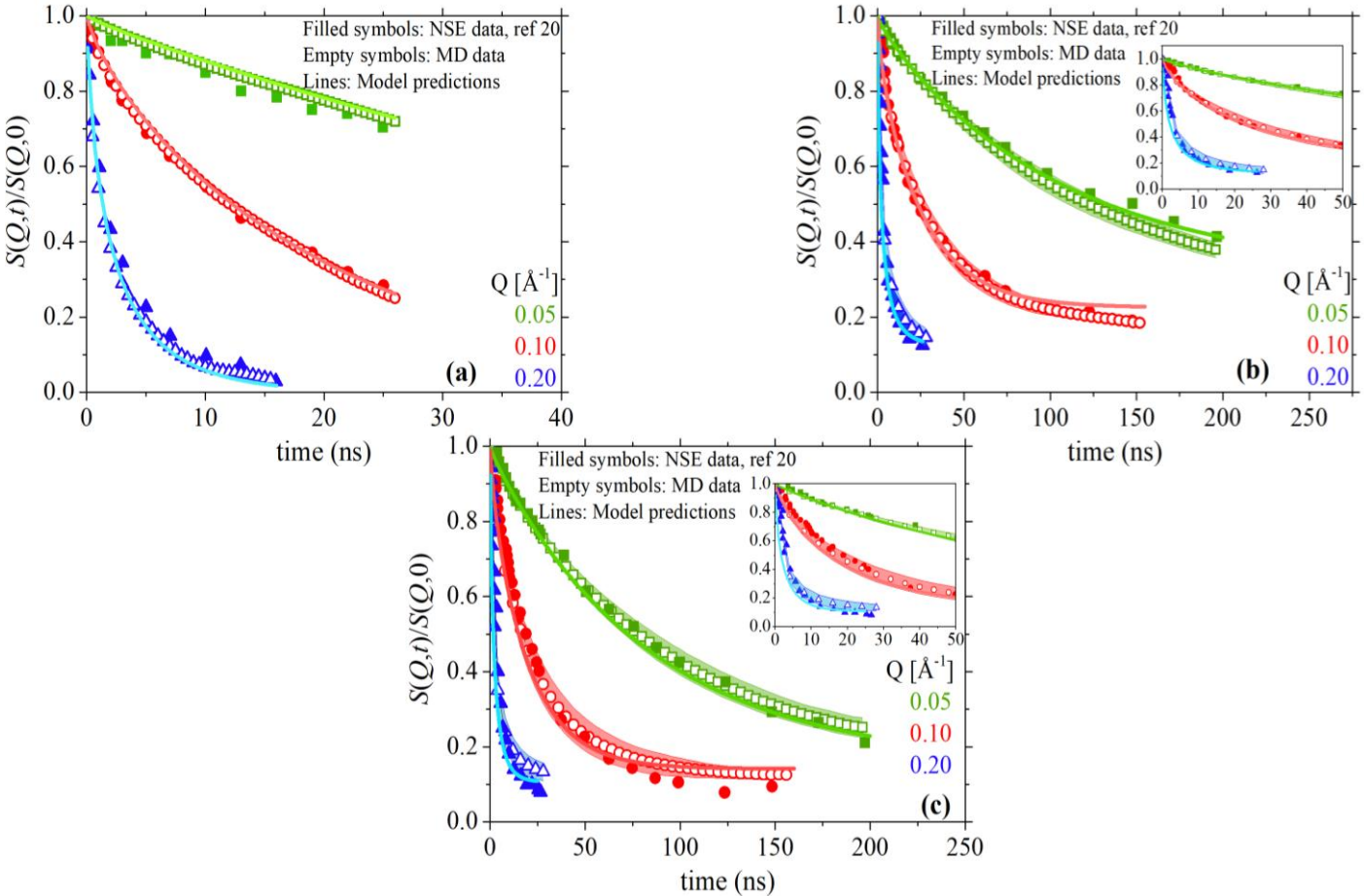
- For pure PEG melt (a): excellent agreement between MD simulation (empty symbols) and the experimentally measured ones (filled symbols), and the original Rouse model (solid lines) at all time-scales.
- For the two nanocomposites [(b) for the PEGSil-OH and (c) for PEGSil-CH_3]: again excellent agreement, both simulation result and theoretical predictions suggest different dynamical behaviors- deceleration.



Relevant Publications

Relevant publications:

1. PSS, C. Baig, G. Tsolou, V. G. Mavrantzas, and M. Kröger, J. Chem. Phys. 132, 124904 (2010).

2. C. Baig, PSS, G. Tsolou, V. G. Mavrantzas and M. Kröger, Macromolecules 43, 8239-8250 (2010).

3. PSS, C. Baig and V. G. Mavrantzas, Soft Matter 7, 380–395 (2011).

4. PSS, C. Baig, and V.G. Mavrantzas, Macromol. Theor. Simul. 20, 752–768 (2011).

5. J. Qin, S. T. Milner, PSS, and V.G. Mavrantzas, J. Rheol. 56, 707-723 (2012).

6. PSS, and V.G. Mavrantzas, J. Non- Newtonian Fluid Mech. 200, 111-130 (2013).

7. PSS and V.G. Mavrantzas, J. Chem. Phys. 140, 214903 (2014).

8. E. N. Skountzos, D. G. Tsalikis, PSS, and V. G. Mavrantzas, Macromolecules, 54, 4470–4487 (2021).

Introduction

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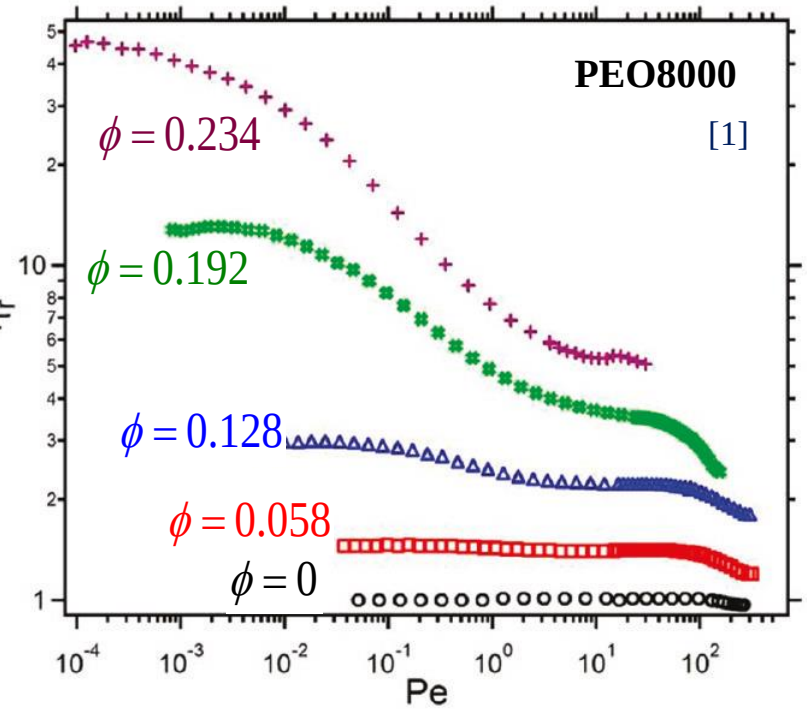
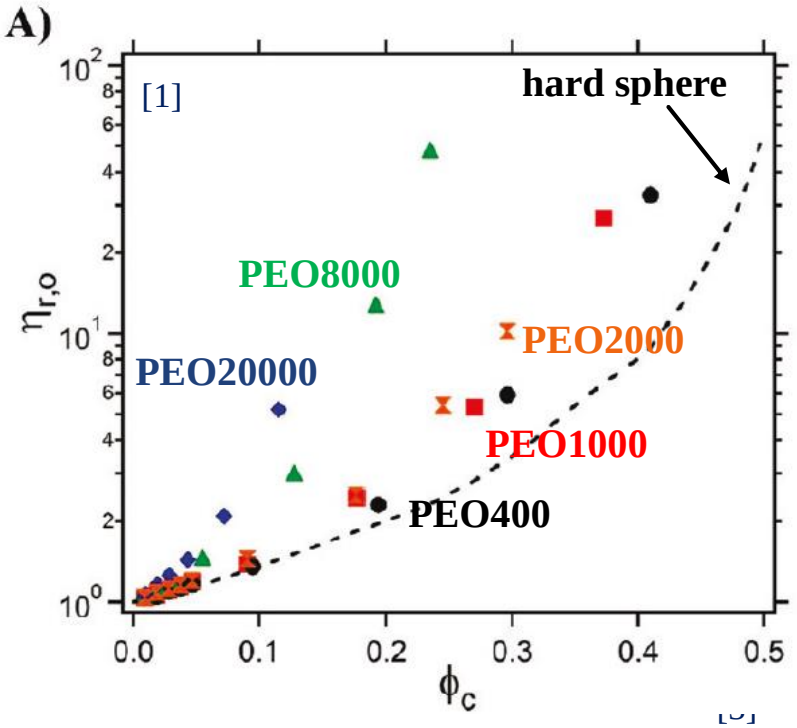
Zero shear rate relative viscosity of 44nm silica nanoparticles in PEO-X (X is polymer molecular weight) as a function of volume fractions





Relative shear viscosity of 44nm silica nanoparticles in PEO-8000 as a function of shear rate

1. Anderson and Zukoski, *Macromolecules* 42, 8370-8384 (2009).

Synopsis

- Our work reveals that the adsorbed layer around the silica nanoparticle is far from being characterized as "glassy" or "immobilized".

- The simulations also reveal that

1. hydroxyl-terminated PEG chains are adsorbed by their ends giving rise to a brush-like structure,
2. whereas methoxy-terminated ones are adsorbed equally probably along their entire contour thus resulting in better packing of adsorbed segments.

- Direct comparison of simulation and theoretical predictions with previously reported experimental data in the literature for the dynamic structure factor for the same systems reveals excellent agreement.[1]

1. Glomann *et al.*, *Phys. Rev. Lett.*, 110, 178001 (2013); Glomann et al., *Soft Matter*., 9, 10559(2013)