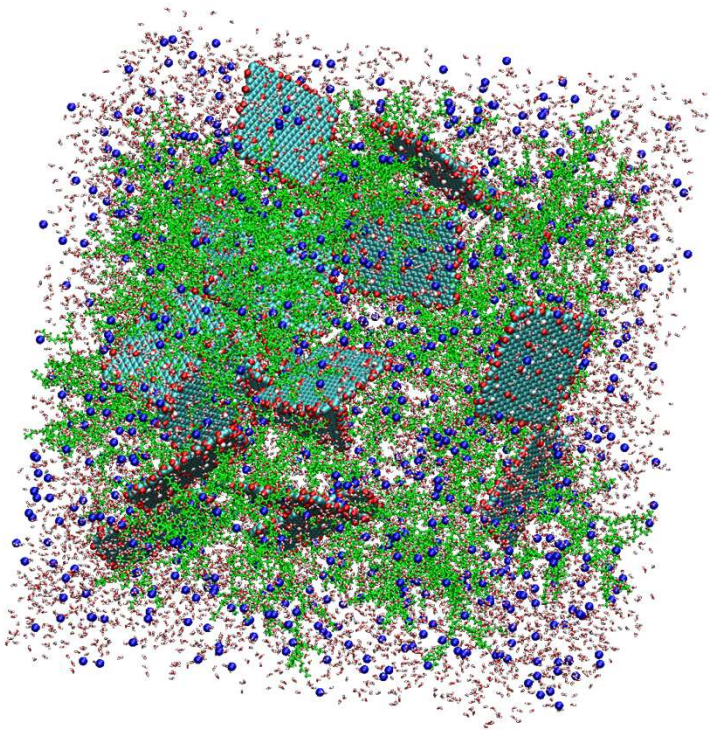
Joint EuroCC/SimEA seminar series

Polymer/graphene-based nanocomposites: a microscopic view through the magnifying glass of molecular dynamics simulations

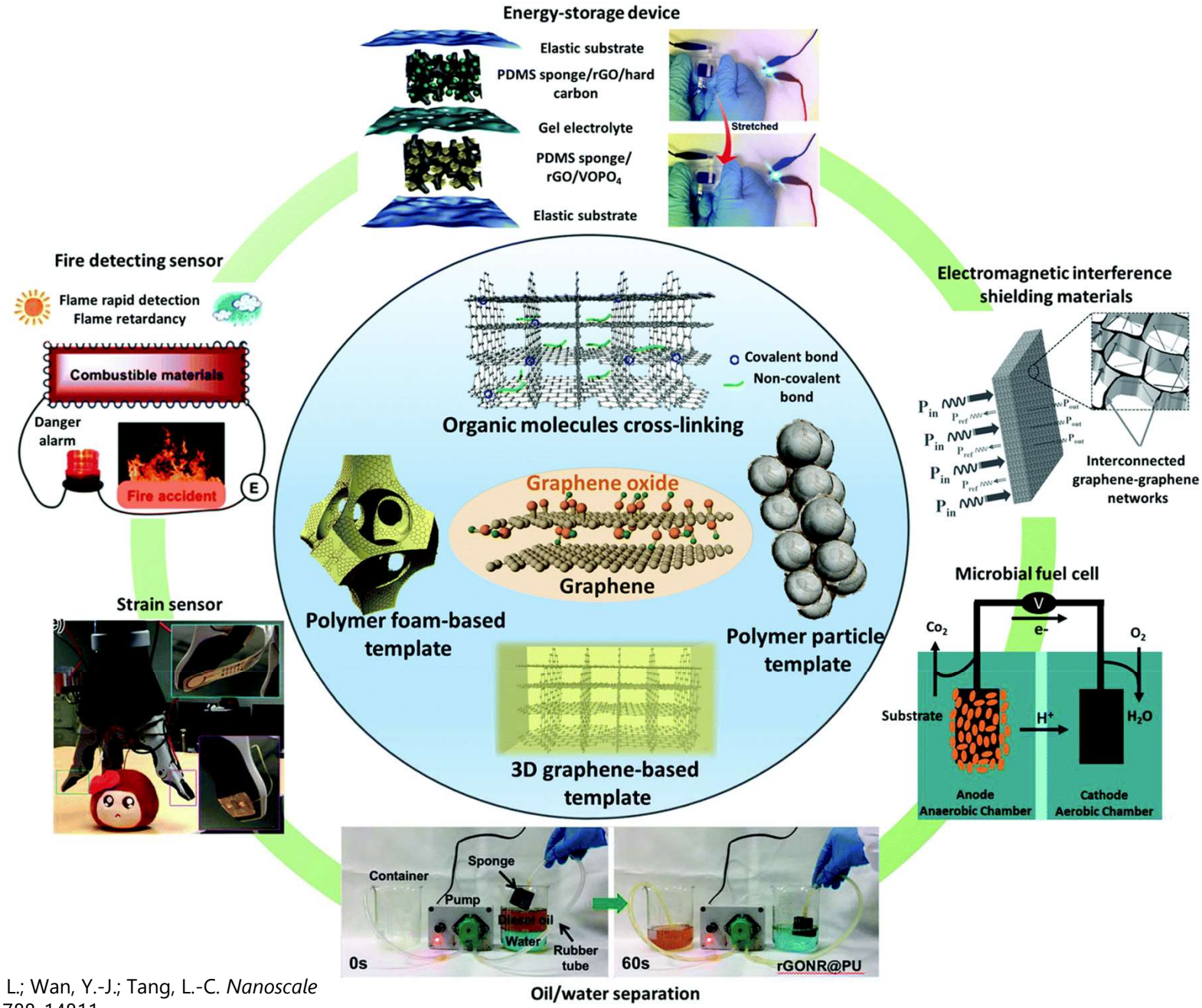


K. Karatasos

September 7, 2021

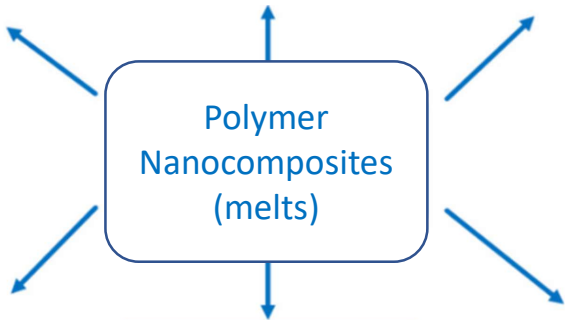
Aristotle University of Thessaloniki, Chemical Engineering Department

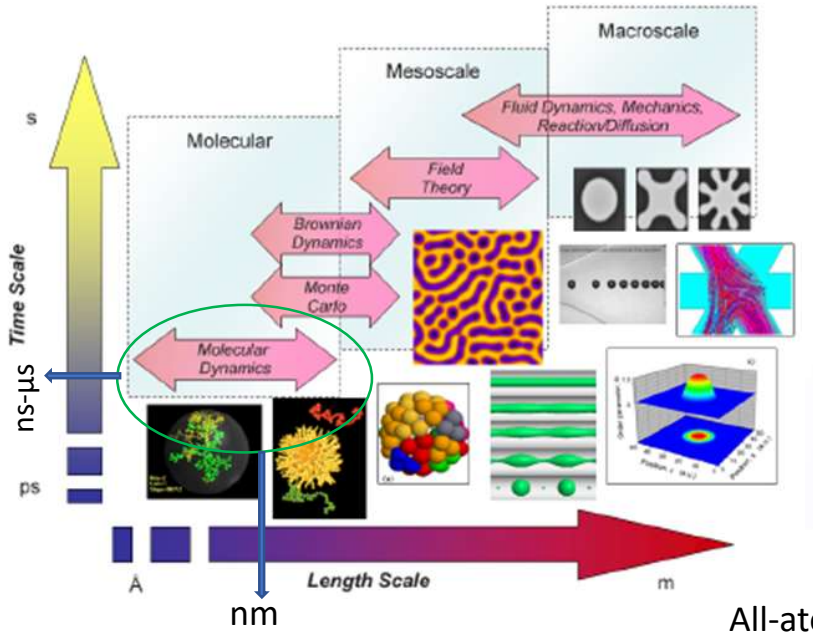
Graphene-based nanocomposites

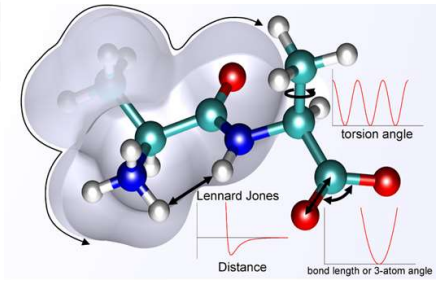


Guan, L.-Z.; Zhao, L.; Wan, Y.-J.; Tang, L.-C. *Nanoscale* **2018,** 10 (31), 14788-14811

Parameters that can affect the polymer composite properties (thermal, mechanical, electrical)



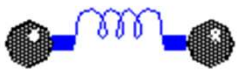




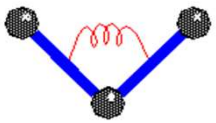
All-atom MD simulations

$$U = U_{\text{bond}} + U_{\text{angle}} + U_{\text{diheral}} + U_{\text{improper}} + U_{\text{vdw}} + U_{\text{elec}}$$

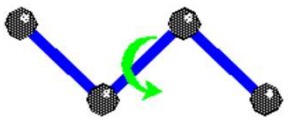
$$U_{\text{bond}} = \frac{k_b}{2}(l - l_0)^2$$



$$U_{\text{angle}} = k_\theta(\theta - \theta_0)^2$$

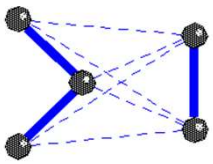


$$U_{\text{diheral}} = k_d[1 + \cos(n\varsigma - \delta)]$$



$$U_{\text{improper}} = k_\psi(\psi - \psi_0)^2$$

$$U_{\text{vdw}} = 4\varepsilon\left[\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^{6}\right]$$



$$U_{\text{elec}} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

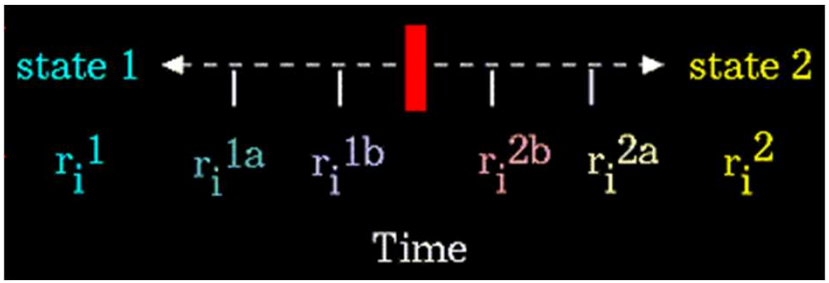
The set of parameters in the energetic components → "Forcefield"

$$m_i \frac{d^2}{dt^2}\vec{r}_i = \vec{F}_i(\bar{r})$$

$$\vec{F}_i(\bar{r}) = -\nabla_i U(\bar{r})$$

$$with\ \bar{r} = (\vec{r}_1, \cdots \vec{r}_N)$$

Trajectory



Calculation of desired properties as time and ensemble averages

Systems and parameters explored

GR/PEG: Effects of polymer size (unentangled)

- Constant (high) graphene loading
- No specific interactions

GO/PAA: Effects of filler's loading (still at the high loading limit).

- Constant polymer size (unentangled).
- Presence of specific interactions.

PAA or PS / GO or GR: Effects of the flakes' nanoroughness and the nature of the interactions

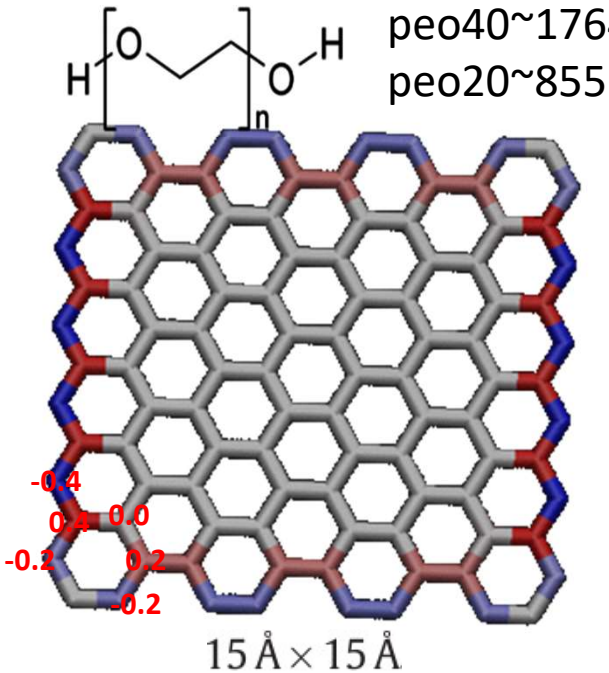
- Constant polymer size (unentangled)
- Low GR, GO loading
- Presence/absence of specific interactions

PAA/GO: Effects of the filler's size, conformations at the interface, effects in dynamics.

- Constant polymer size (unentangled)
- Low GO loading

Graphene/PEG: non specific interactions. Effects of polymer size at constant loading

System notation	Number of PEG monomers per chain	Number of PEG chains	Number of Graphene Sheets	Weight fraction of Graphene
20peo40g	40	20	20	44%
40peo20g	20	40	20	45%
20peo40	40	20		
40peo20	20	40		



peo40~1764 g/mol (below entanglement)
peo20~855 g/mol

High loading limit

	Experiment Niedzwiedz et al.	Estimation	Estimation	Experiment Niedzwiedz et al.
M_w (g/mol)	890	855.014	1764.118	2100
T_g (°C)	- 83	≃ - 80	≃ - 76	- 74
T_m(°C)	33			48

Niedzwiedz, K., et al., Macromolecules, 2008. 41: p. 4866-4872

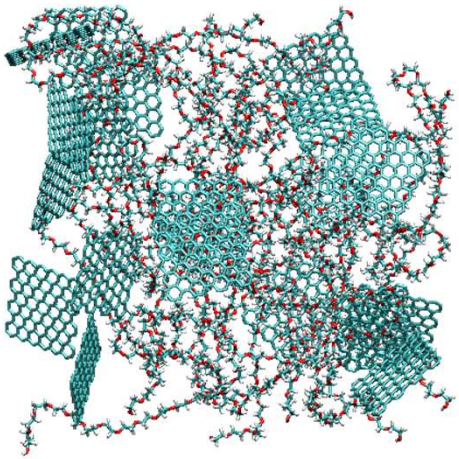
Roussou, R.-E.; Karatasos, K. *Materials & Design* **2016,** 97, 163-174

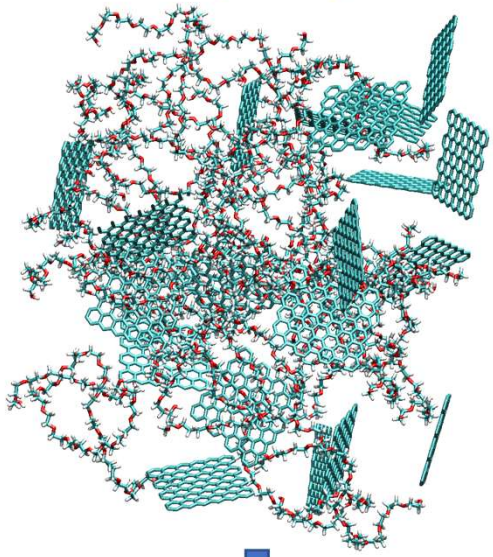
Simulation Details: composites

20peo40g

Initial Configurations

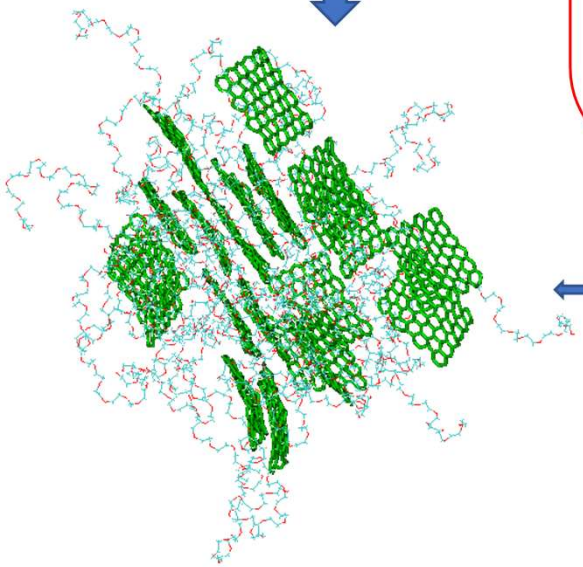
40peo20g



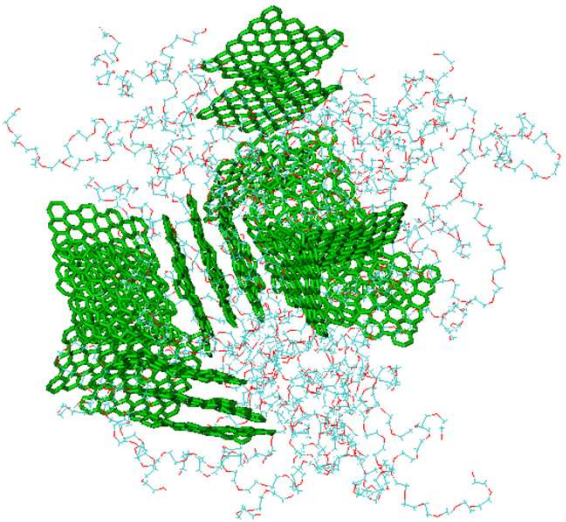


Simulation Protocol

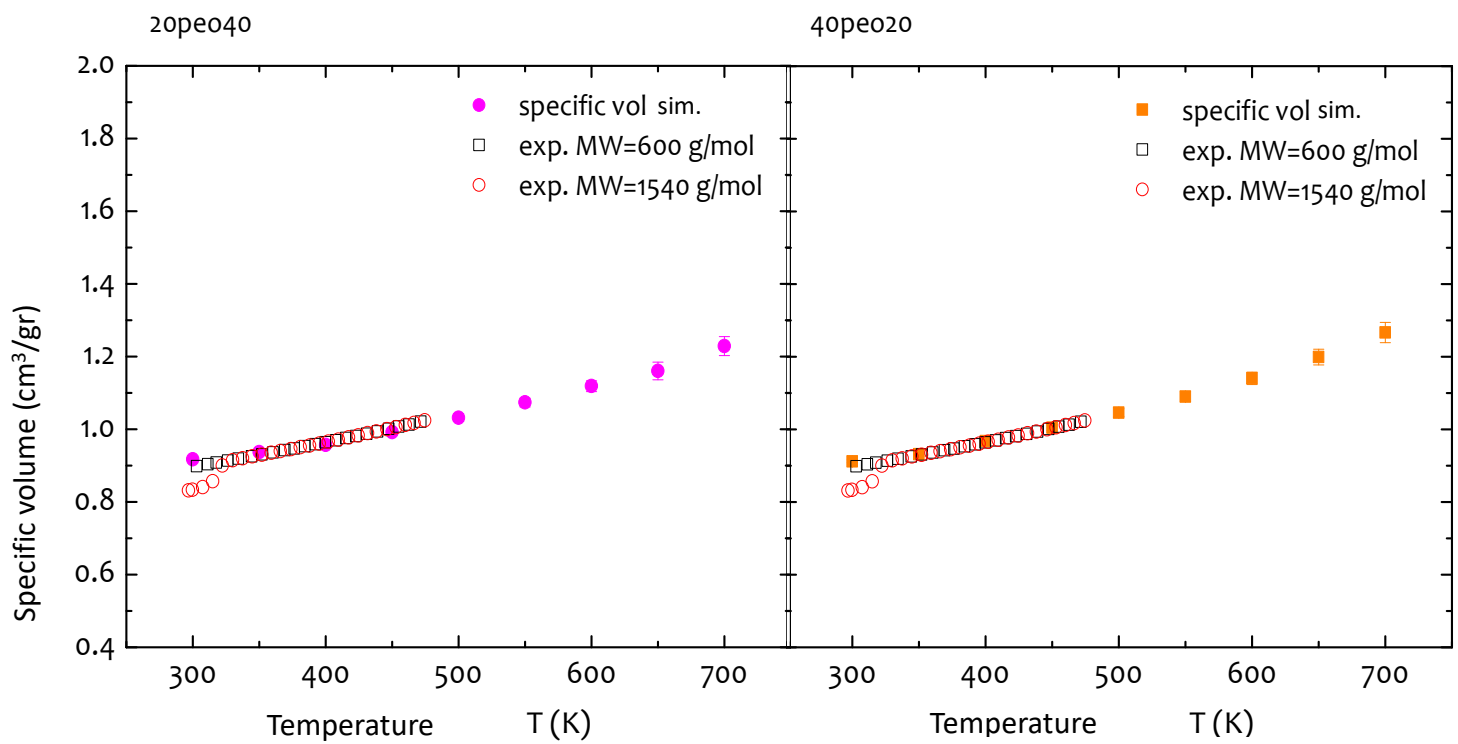
Isobaric-Isothermal Molecular Dynamics Simulations
AMBER forcefield for PEG,
Gradual heating from 300K to 700K at 50K steps (energy minimization and NPT MD 30ns to 100ns at each T, P=1bar) followed by gradual cooling at 50K steps (30 to 100ns after energy minimization, depending on T). Trajectories of 30ns to 200ns depending on T

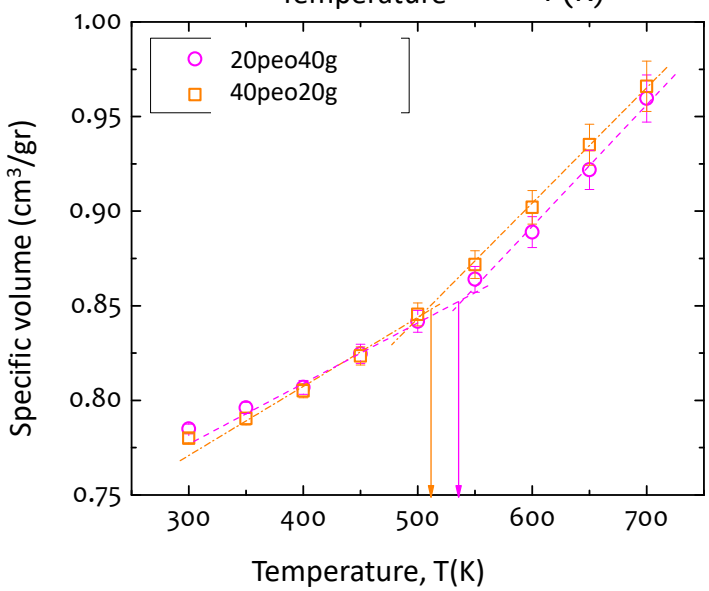


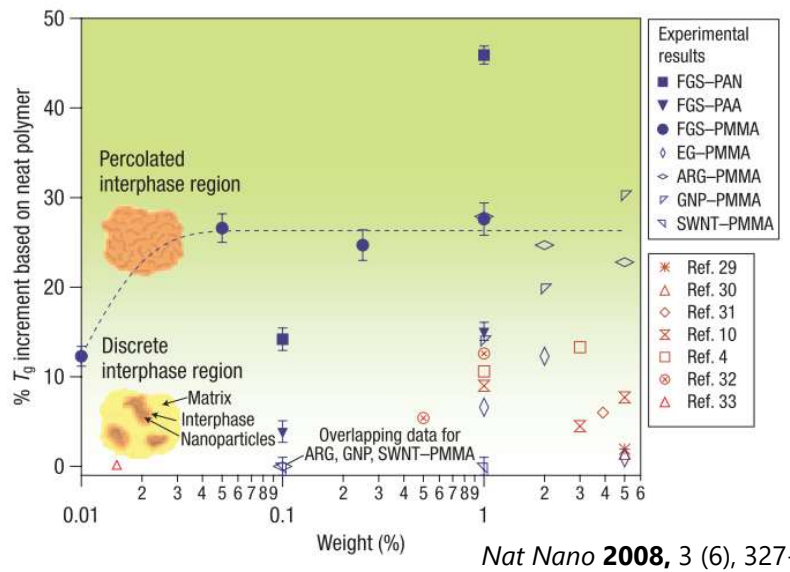
@ 600K after annealing



Thermal behavior



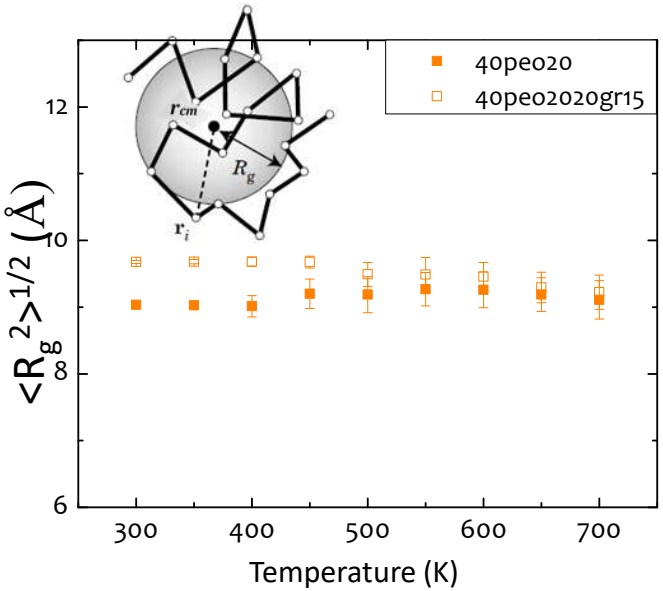


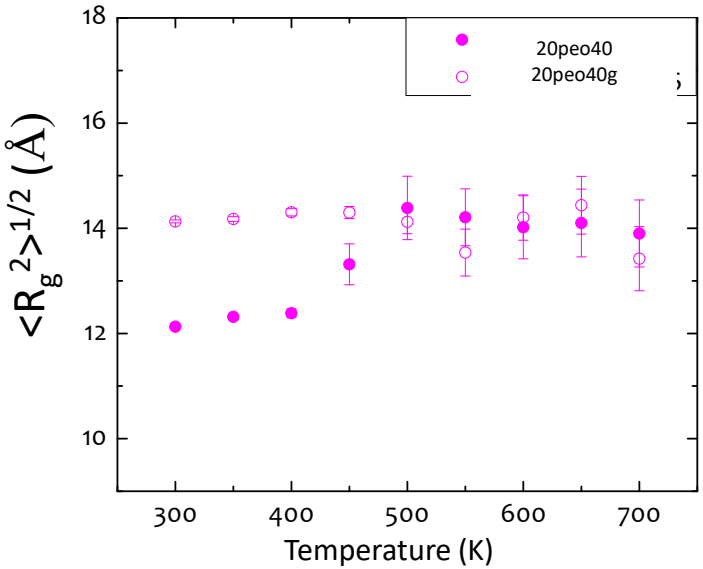


Nat Nano **2008,** 3 (6), 327-331

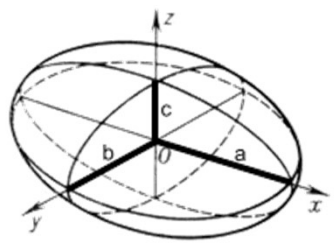
Chain conformational changes

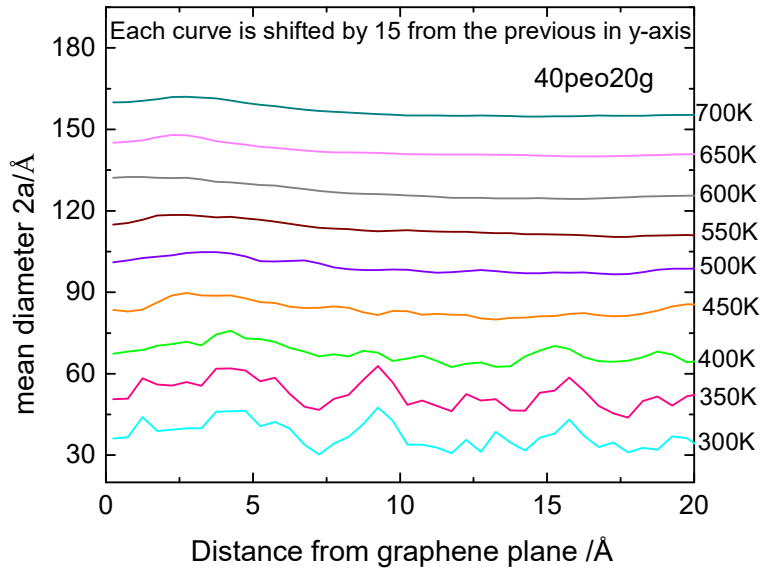
$$\langle R_g{}^2\rangle^{1/2} = \left[\frac{1}{N}\sum_{i=1}^{N}\langle(\vec{r}_i - \vec{r}_{cm})^2\rangle\right]^{1/2}$$



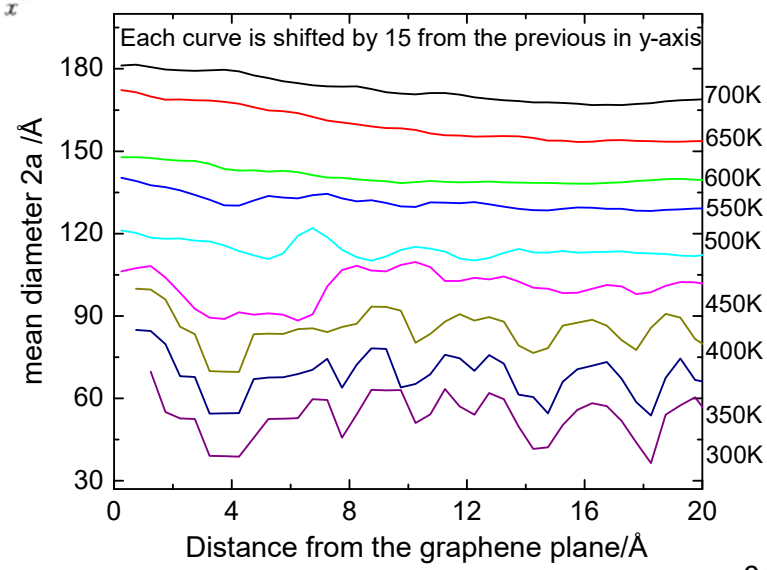


Ellipsoid of inertia for PEG chains





20peo40g

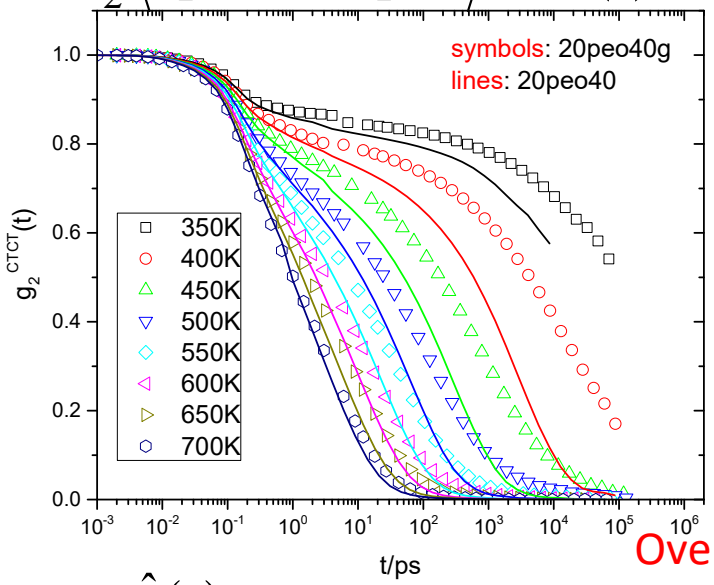


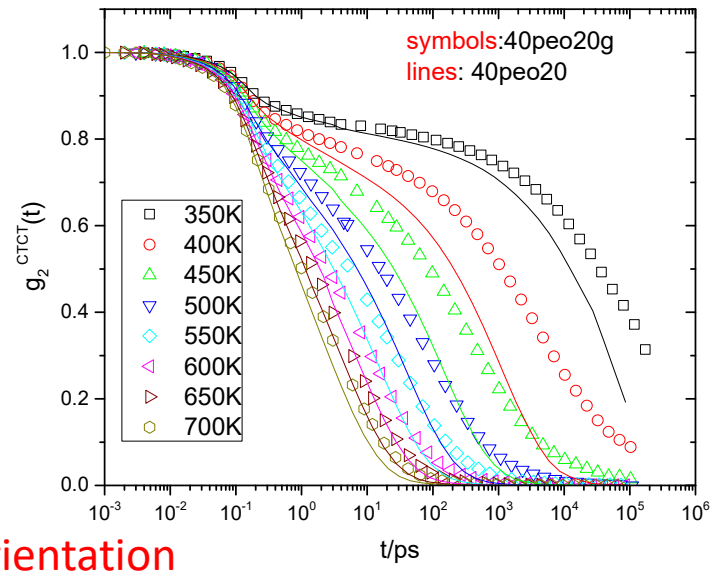
Bond reorientation and overall chain rotation of PEG polymers

C-C backbone bond reorientation

$$C(t)=\frac{1}{2}\left\langle 3\left[\hat{h}(t)\cdot\hat{h}(0)\right]^2-1\right\rangle$$

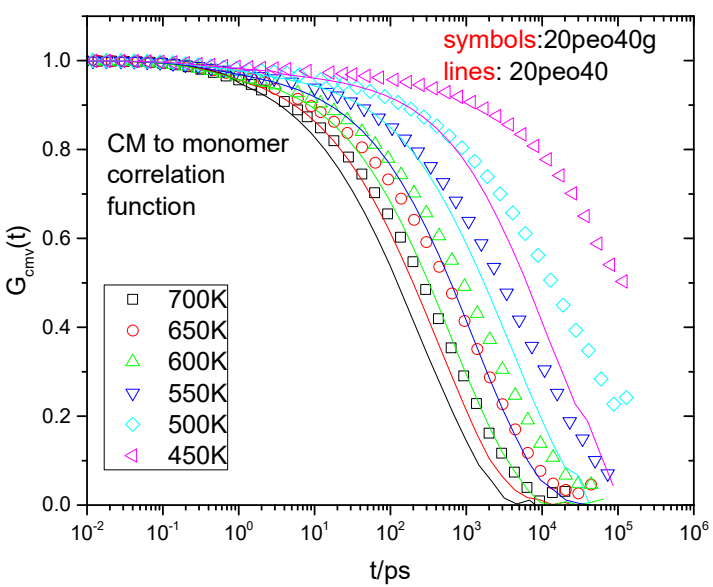
$\hat{h}(t)$: a unit vector along the studied bond

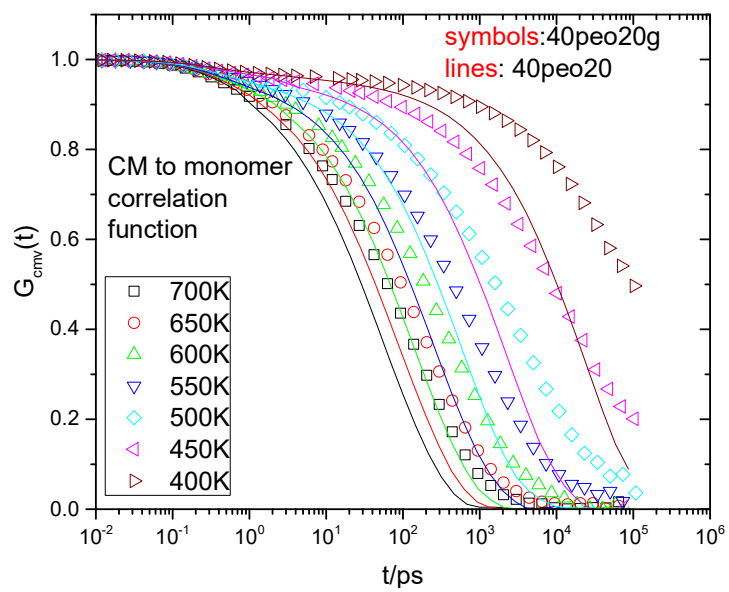




Overall chain reorientation

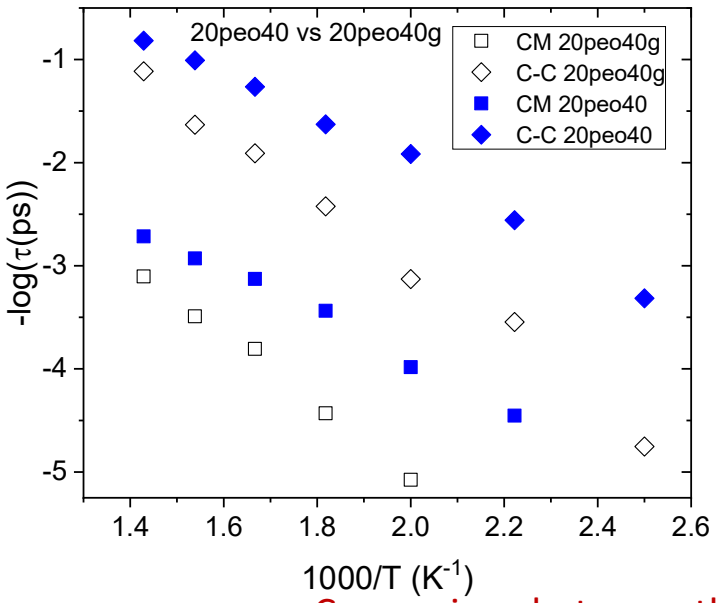
$\hat{h}(t)$: unit vector connecting the center of mass with the monomers

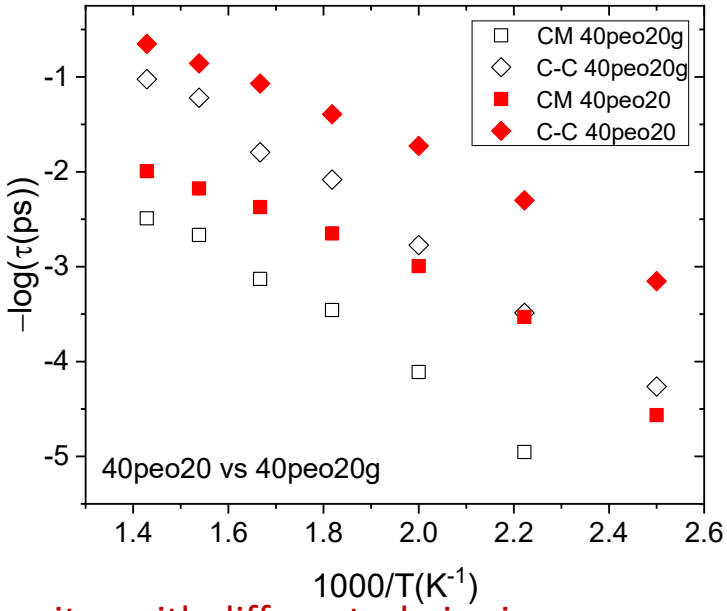




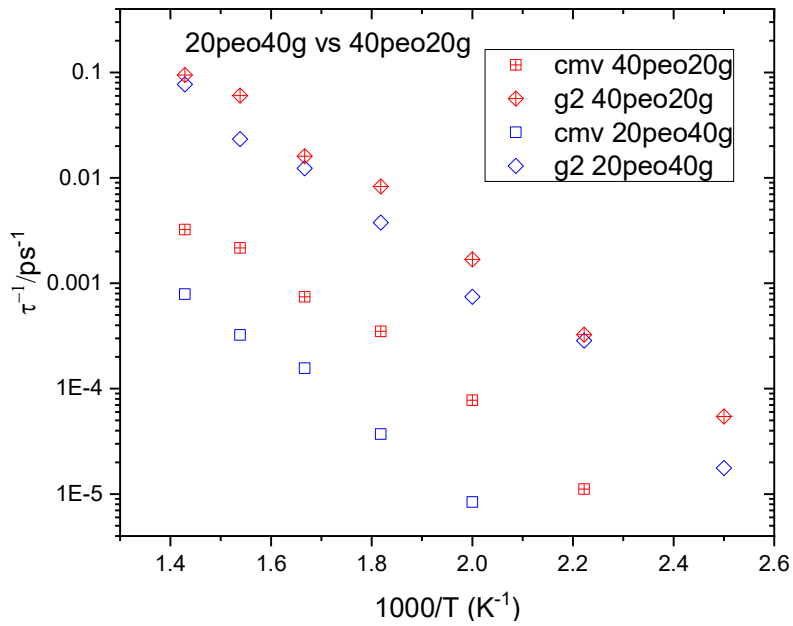
Comparison of average polymer global and local relaxation rates

Comparison between the nanocomposites and the bulk at constant chain size



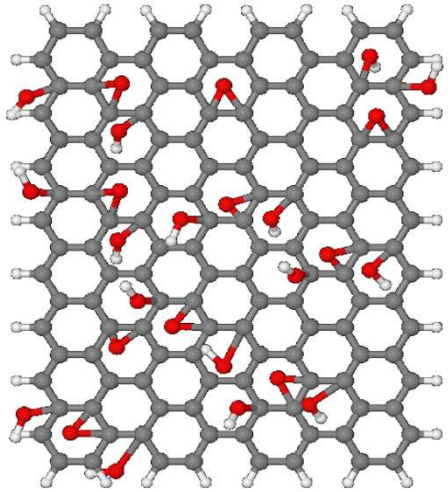


Comparison between the nanocomposites with different chain size

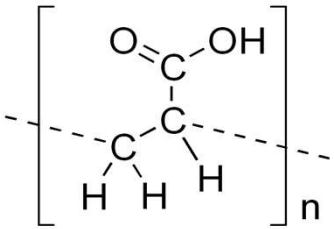


Graphene Oxide/PAA: presence of specific interactions. Effects of filler's loading

Graphene Oxide (GO)



Poly(acrylic acid) (PAA)



n=40 (atactic, below entanglement)

C to O atom ratio of 5:1 and a hydroxyl to epoxy group ratio of 3:2 approximately

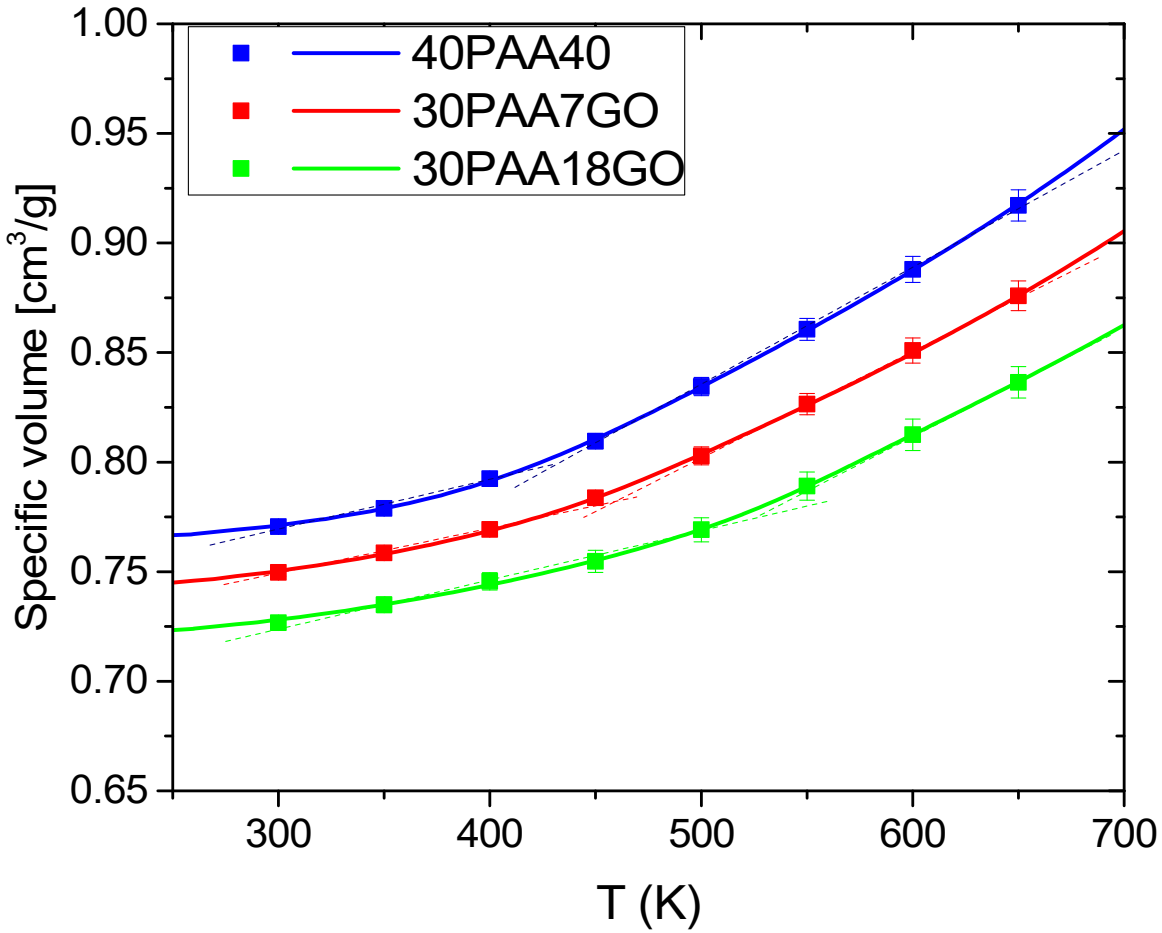
D. Stauffer et *al.*, Journal of Chemical Physics **141** (2014) (GO model details, partial charges for GO)

Systems	Number of GO sheets	Number of PAA chains	wt % in GO
30paa7GO	7	30	14.5
30paa18GO	18	30	30.3
40paa40	0	40	0

Karatasos, K.; Kritikos, G., *RSC Advances* **2016,** 6, 109267.

Karatasos, K.; Kritikos, Materials Today: Proceedings **2018** (5) 27526–27535

Thermal Behavior



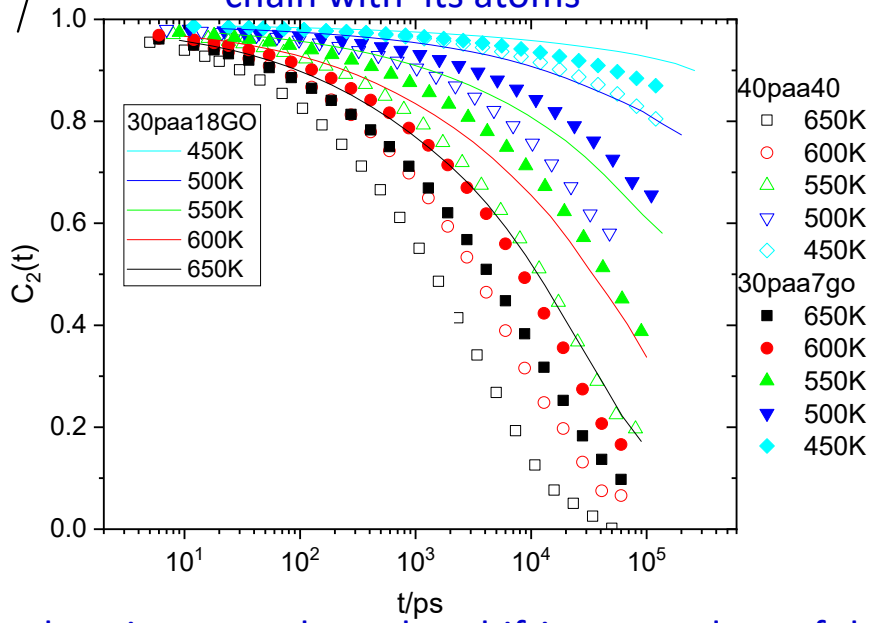
Estimated values for T_g : 412 ± 4 K for the pristine PAA, 450 ± 10 K for 30paa7GO and 545 ± 9 K for 30paa18GO

Comparison to experiment for the bulk PAA : 401 K (L. Shao *et* al, Soft Matter, 2010, **6**, 3363)

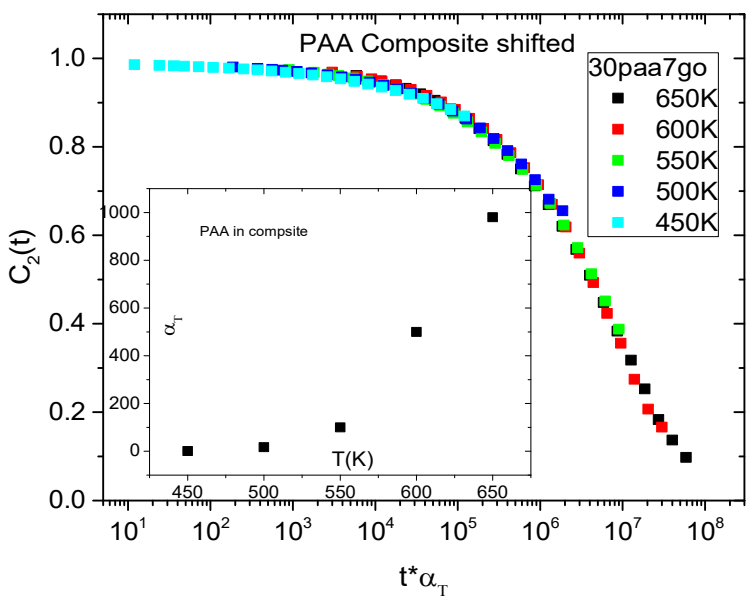
Global polymer dynamics: overall chain rotational motion

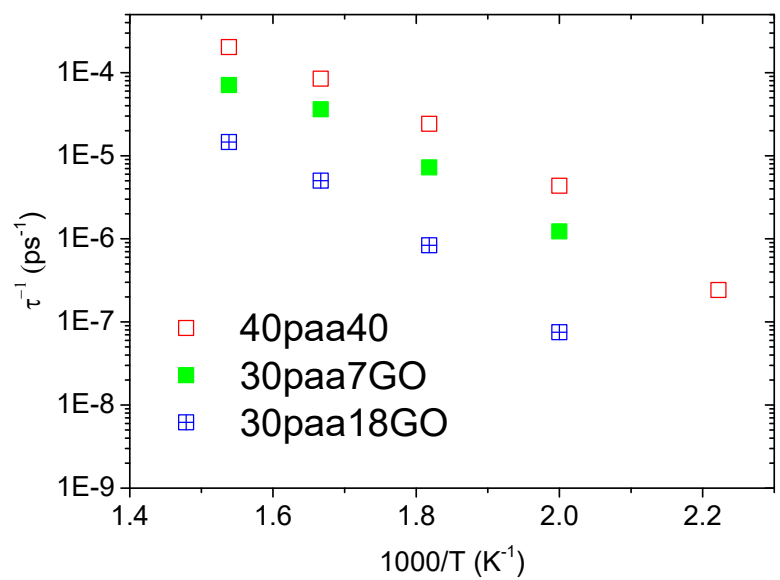
$$C_2(t) = \frac{1}{2}\left\langle 3\left[\hat{h}(t)\cdot\hat{h}(0)\right]^2 - 1\right\rangle$$

$\hat{h}(t)$ are unit vectors connecting the center of mass of a polymer chain with its atoms



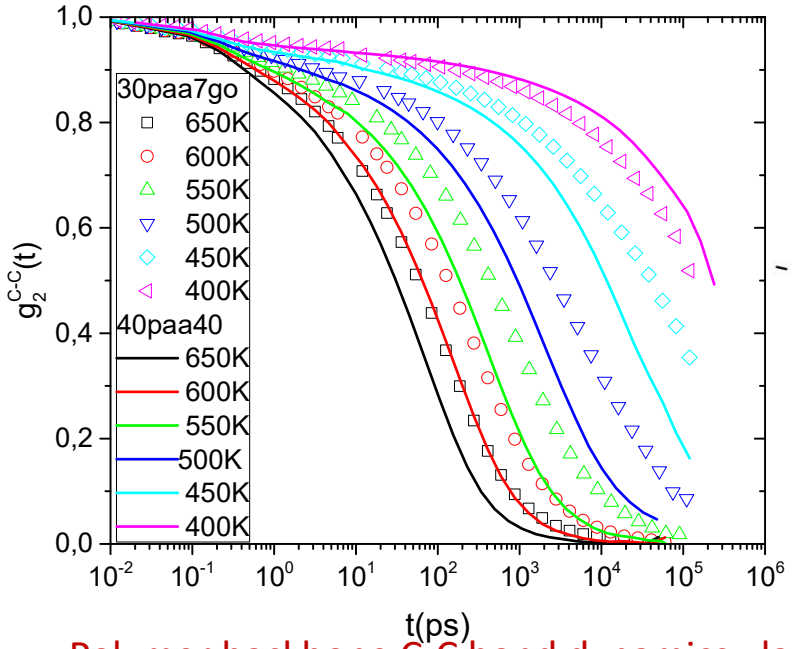
Calculation of characteristic relaxation rates through a shifting procedure of the ACFs

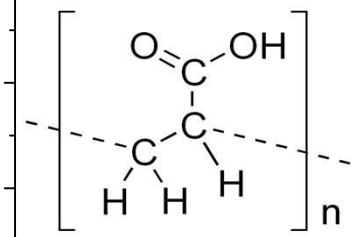




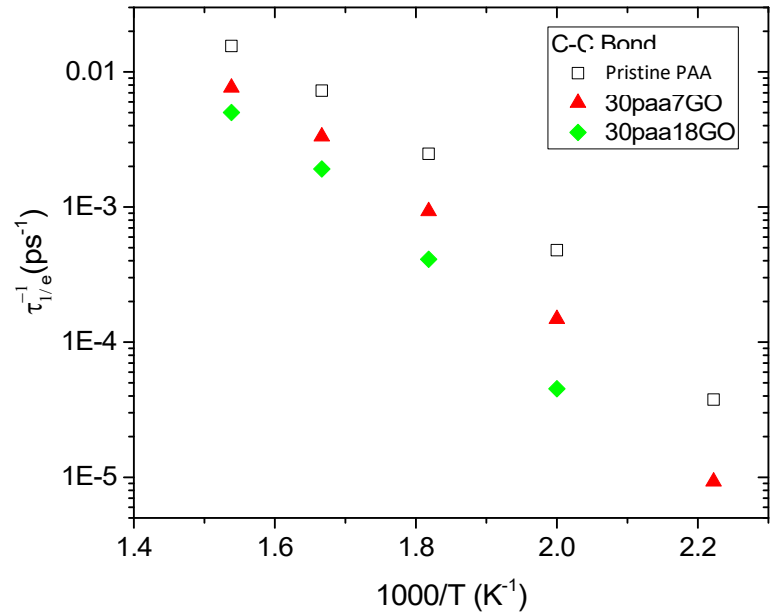
Local polymer dynamics: bond reorientational motion

Polymer backbone C-C bond dynamics: all bonds

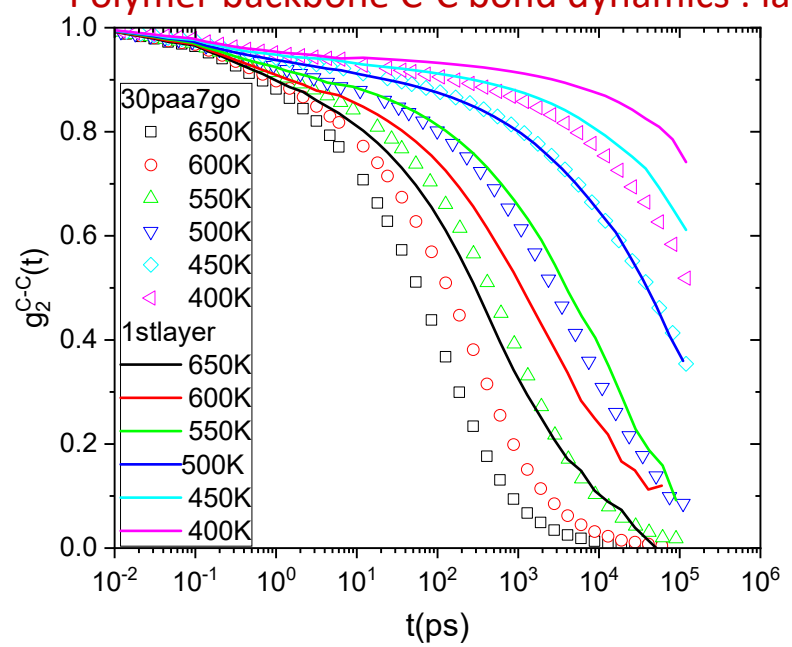


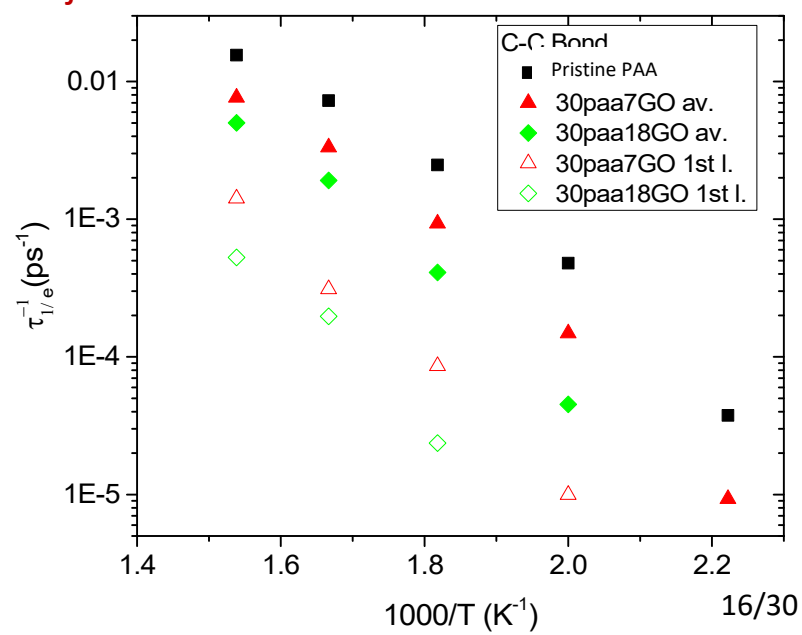


Relaxation rates $\tau_{1/e}^{-1}$: $g_2(\tau_{1/e})=e^{-1}$



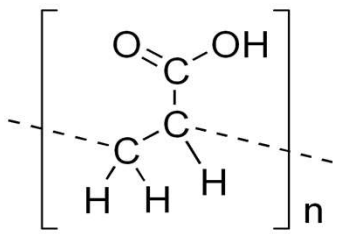
Polymer backbone C-C bond dynamics : layer of thickness 5Å adjacent to the GO flake



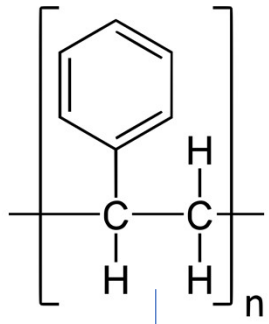


Exploring the bound layer at the polymer/filler interface

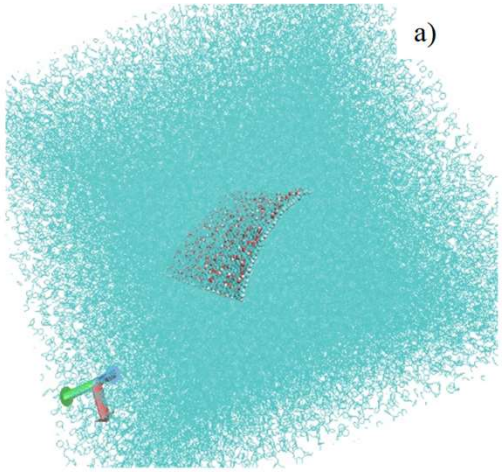
Poly(Acrylic Acid) (PAA)

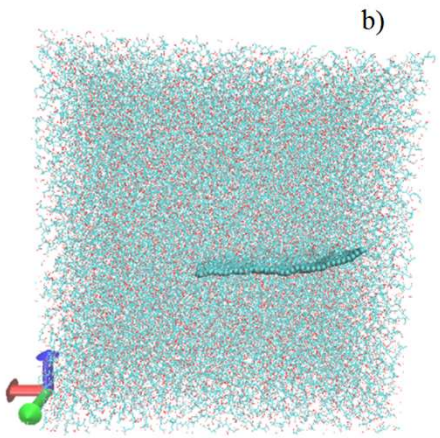


Poly(styrene) (PS)



- *Lower filler loading (wt<1%)*
- *Larger filler size (size of chain/size of filler ~14/200)*
- *Different filler's nanoroughness*
- *Presence of absence of specific interactions*





Fillers size: ~ 9x9nm^2

4 systems
PAA/GO, PAA/GP, PS/GO, PS/GP

GO: higher nanoroughness than GP

GO: H-bond interactions with PAA

GP: π-π interactions with PS

- T_g PAA: 412K (1300 chains, 40 monomers/chain, unentangled)
- T_g PS: 360K (1485 chains, 40 monomers/chain, unentangled)
- Temperature range : 100-250K above the polymer's Tg

Kritikos, G.; Rissanou, A. N.; Harmandaris, V.; Karatasos, K. Bound Layer Polymer Behavior on Graphene and Graphene Oxide Nanosheets. *Macromolecules* **2020,** 53 (15), 6190-6203

Chain adsorption/desorption dynamics

Definition of layers

0 : from 0 to 5 Å from any filler's atom (bound layer)

1 : between 5 and 15 Å from any filler's atom

Bulk: >30 Å from any filler's atom

Adsorption criterion:

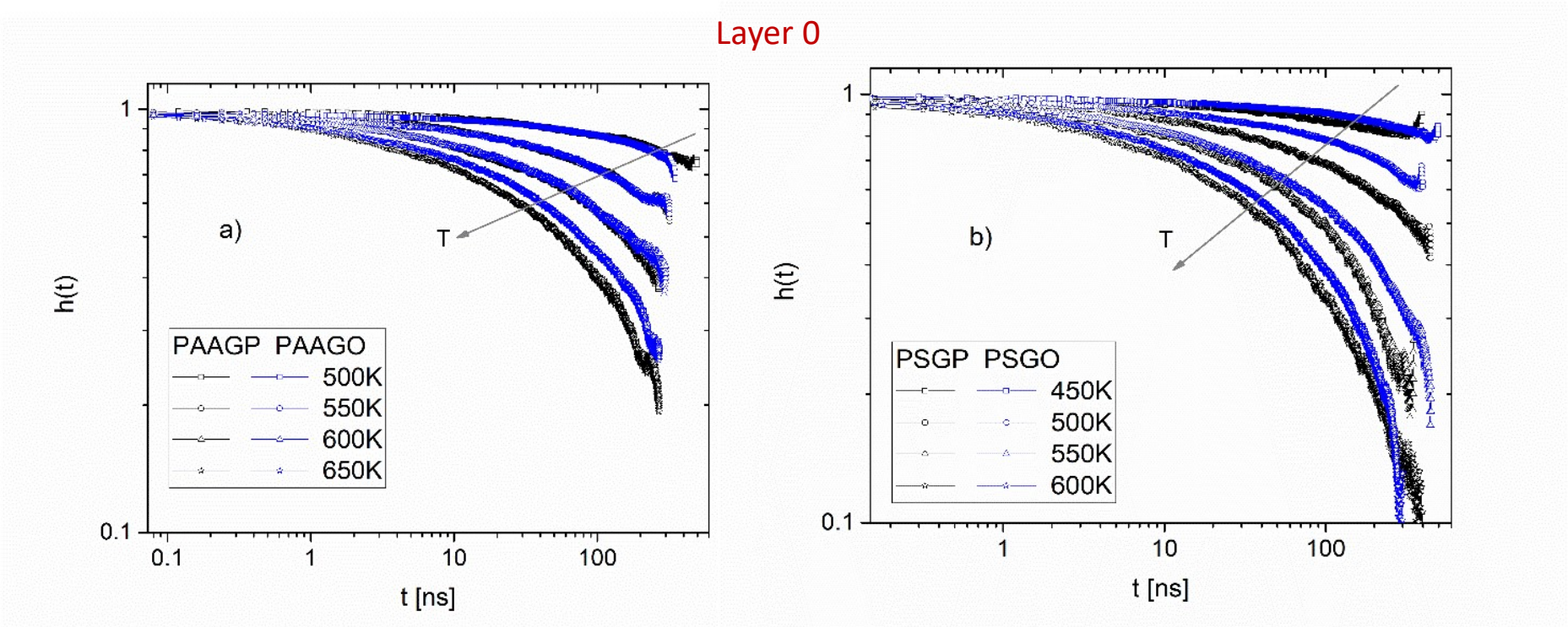
if any atom of the chain belongs to layer 0

Adsorption correlation function

$$h(t) = \frac{\langle g(t)g(0)\rangle}{\langle g^2\rangle}$$

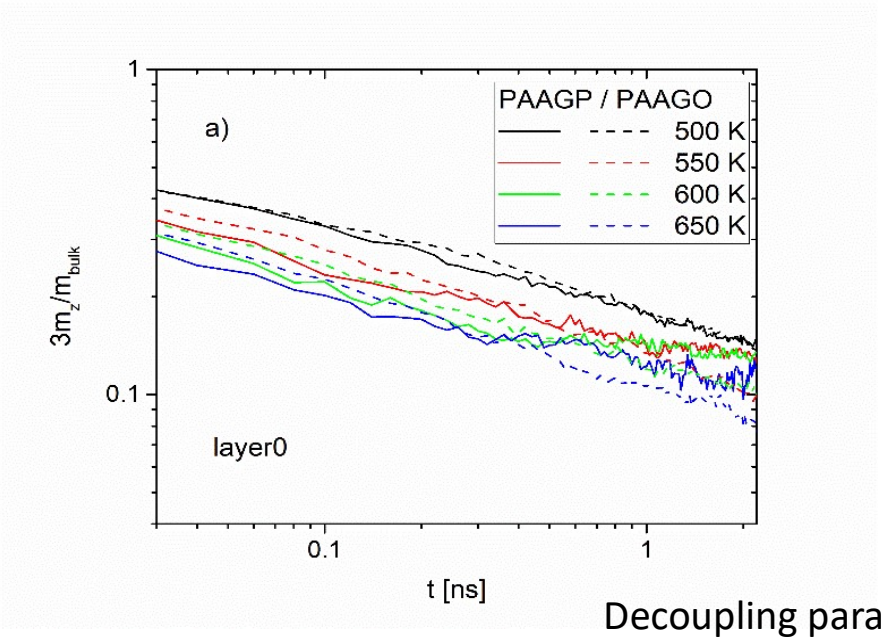
g(t) takes the value of 1, if at least one atom of the chain satisfies the adsorption criterion at time t and 0 otherwise. <> denotes statistical averaging over all chains and time origins

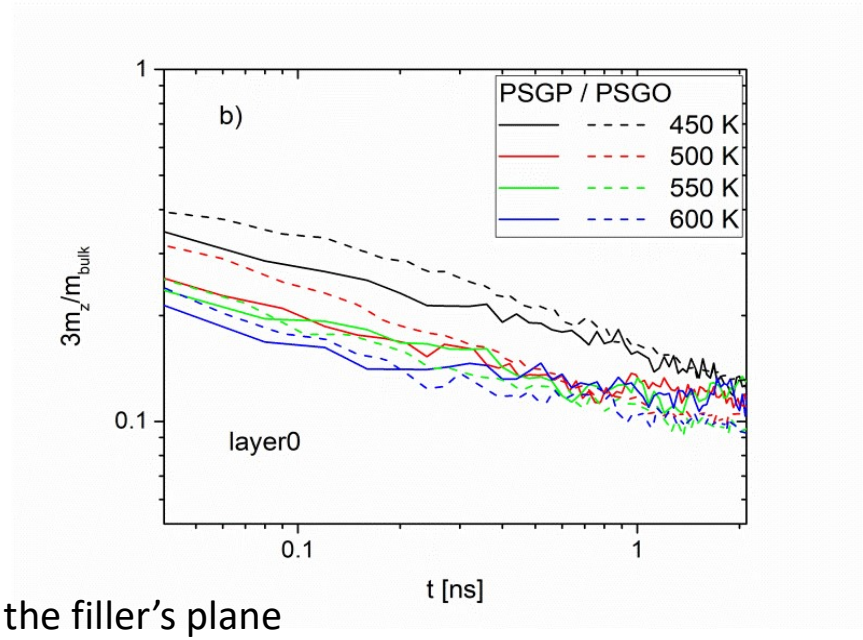
Layer 0



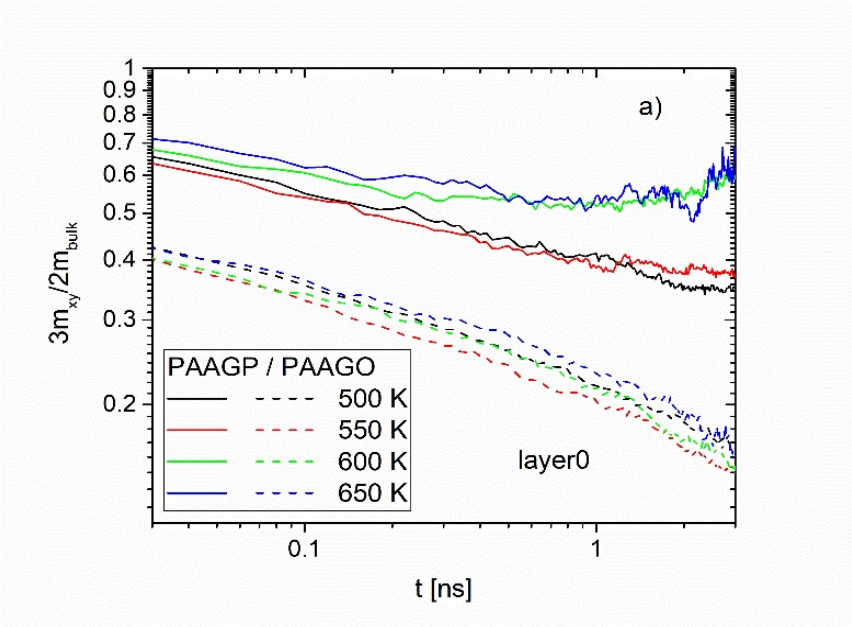
Characteristics of the dynamic decoupling of the adsorbed layer from the bulk behavior

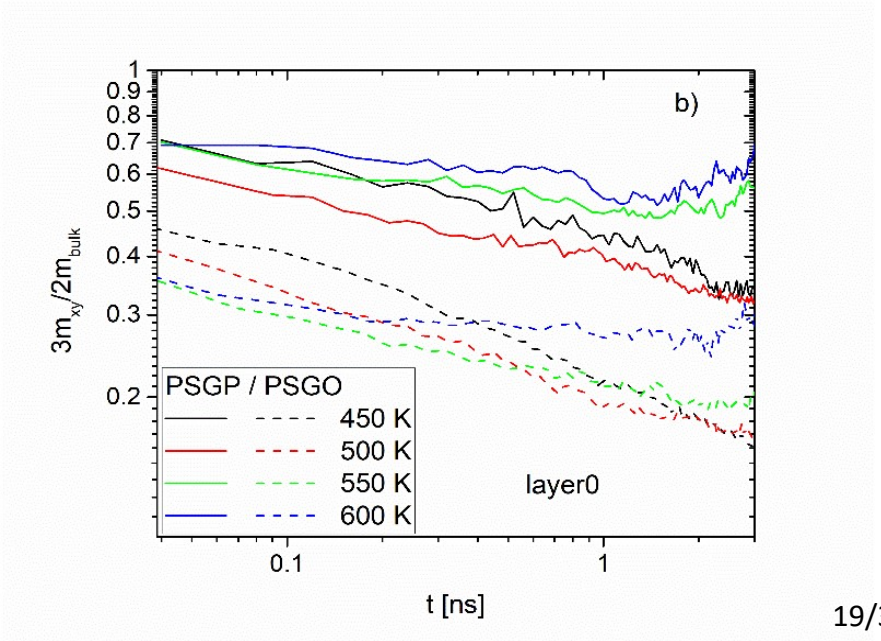
Decoupling normal to the filler's plane





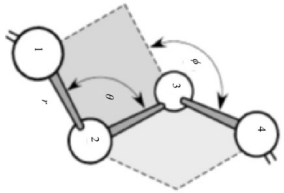
Decoupling parallel to the filler's plane





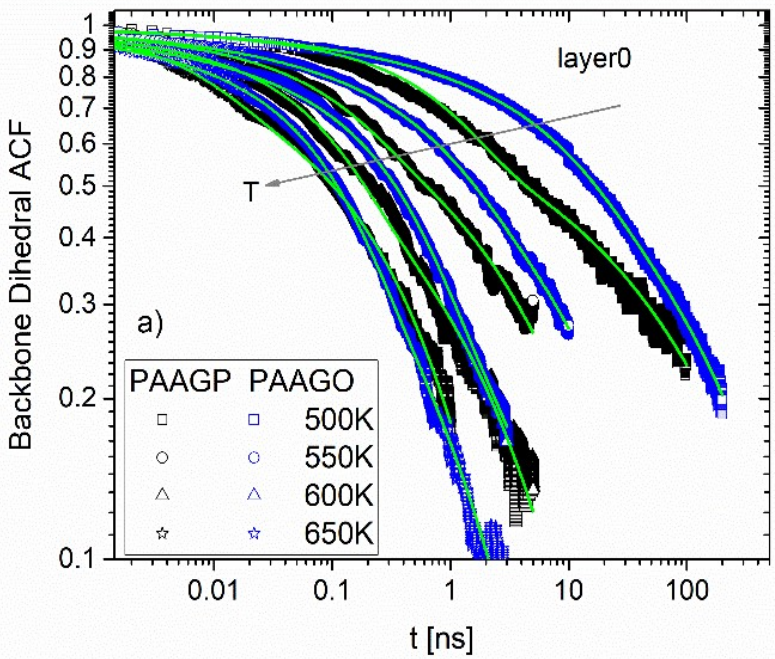
Chain conformational dynamics at the adsorption layer

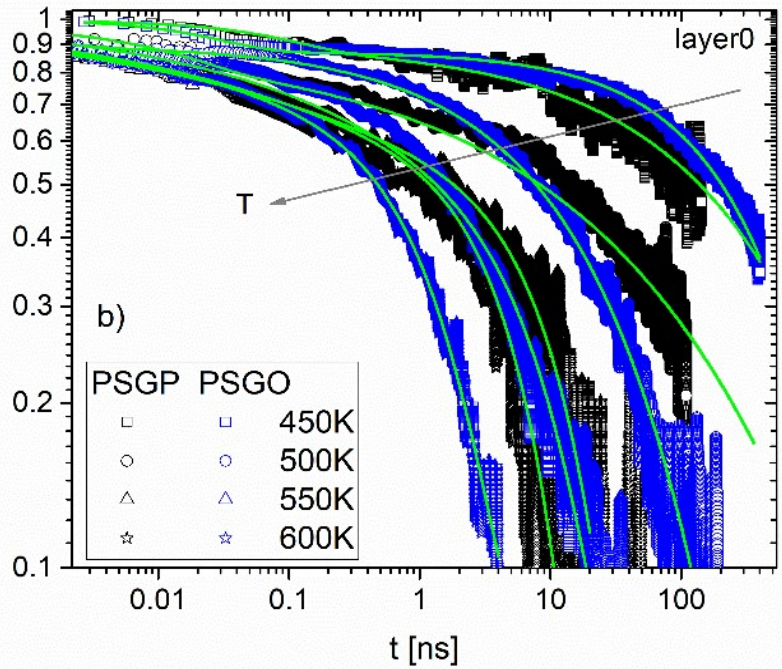
Backbone dihedral ACF



$$P(\varphi(t)) = \frac{\langle \cos\varphi(t)\cos\varphi(0)\rangle - \langle \cos\varphi(0)\rangle^2}{\langle \cos\varphi(0)\cos\varphi(0)\rangle - \langle \cos\varphi(0)\rangle^2}$$

φ(t) symbolizes a backbone dihedral angle at time *t*.

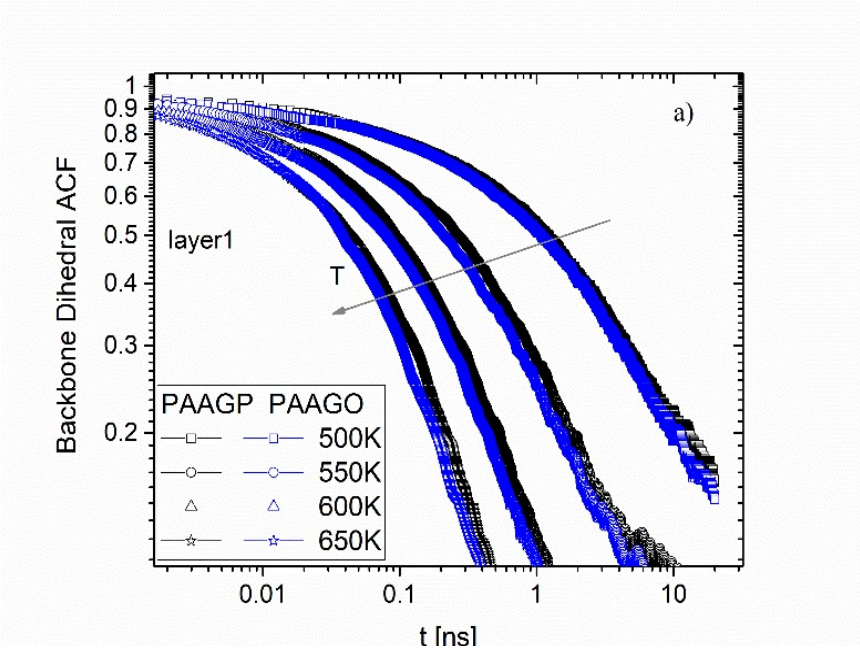


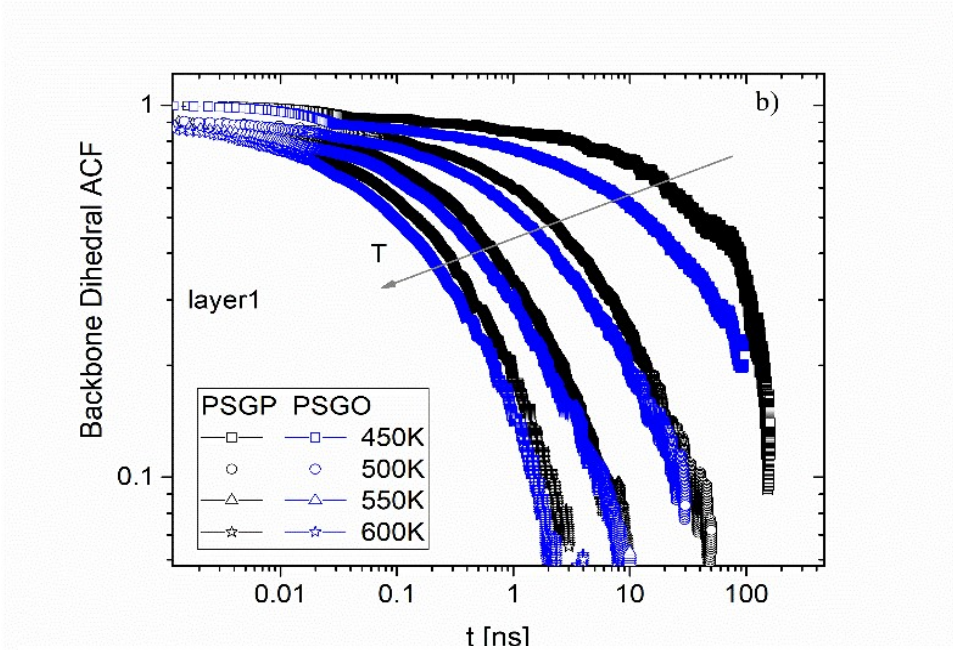


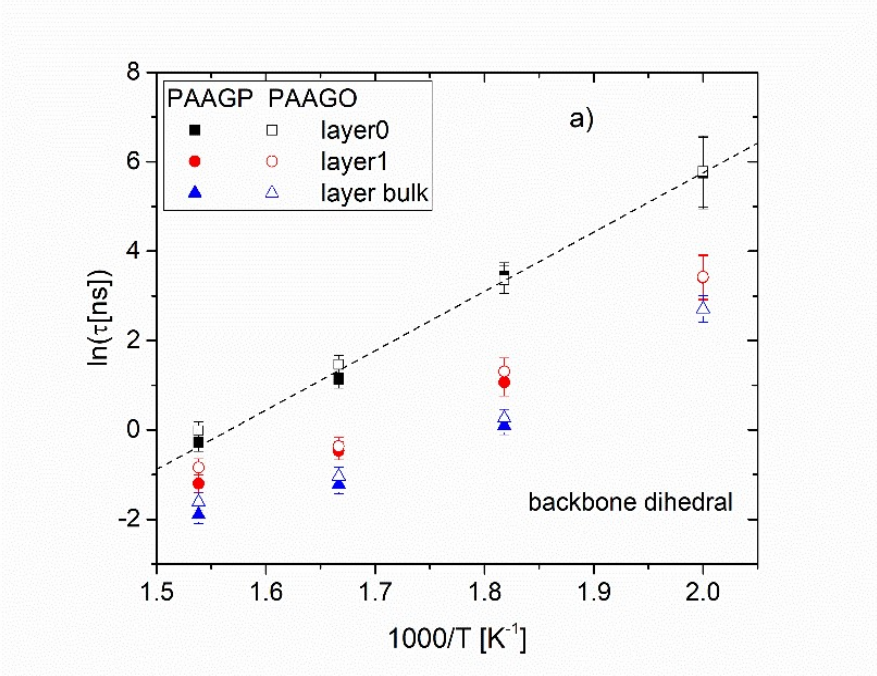
$$P(t) = a_1 \exp\left[-\frac{t}{\tau_1}\right] + (1-a_1)\exp\left[-\left(\frac{t}{\tau_2}\right)^{\beta}\right]$$

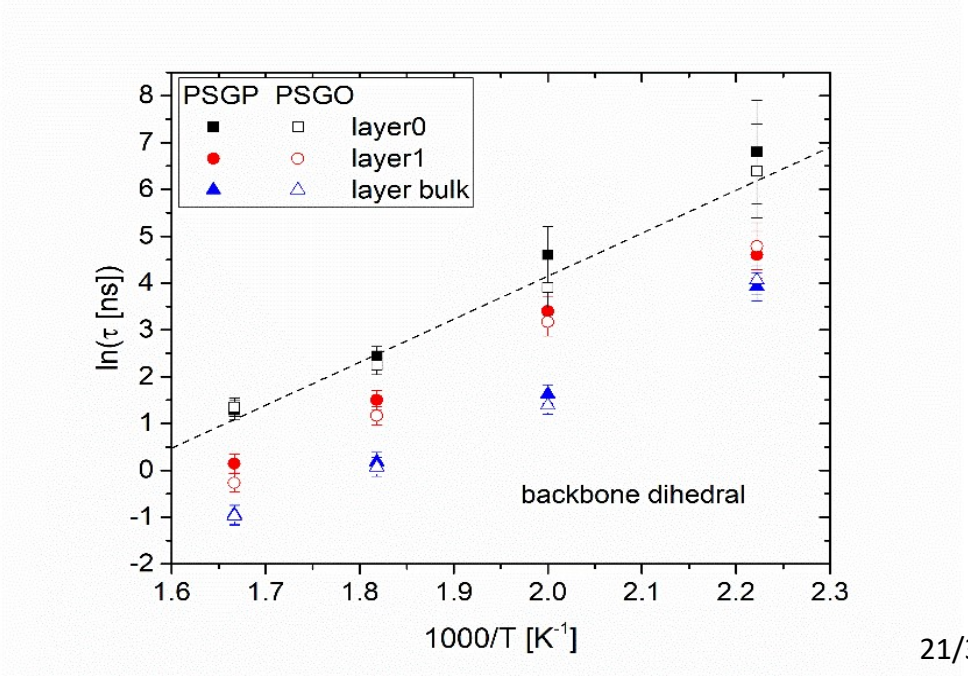
$$\tau_c = \alpha_1\tau_1 + (1-\alpha_1)\left(\frac{\tau_2}{\beta}\right)\Gamma\left(\frac{1}{\beta}\right)$$

Chain conformational dynamics adjacent to the adsorbed layer



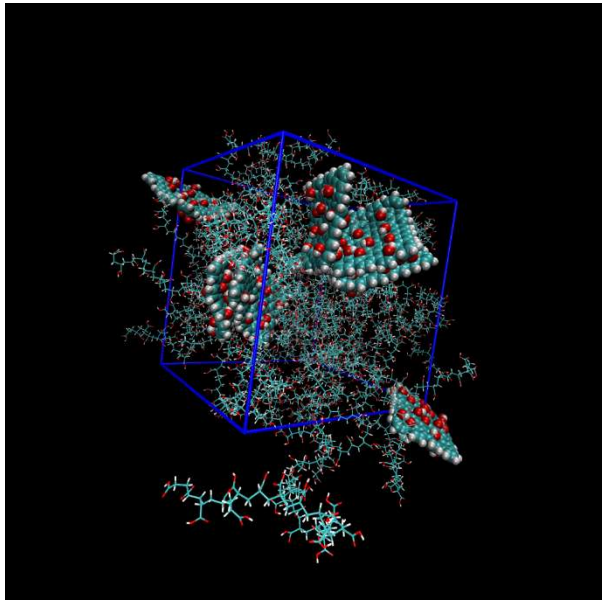






The role of the size of the nanosheet

PAAsGOhwt (small GO)

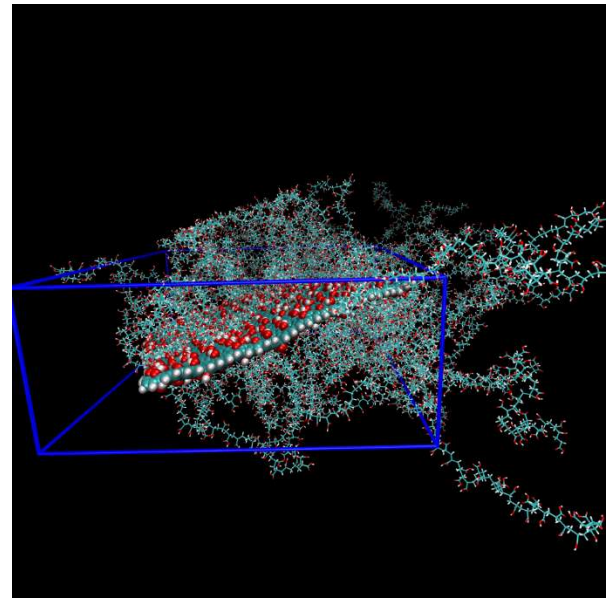


PAA/GO at constant GO loading (13.5%w)

Chain size: (40 monomers unentangled)

Temperature range: 300K-700K

PAAGOhwt (large GO)



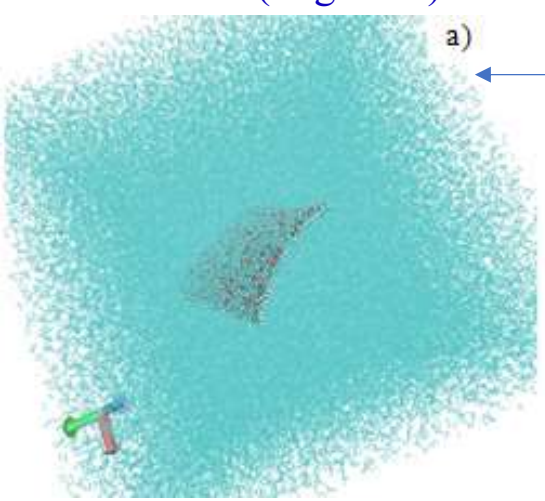
GO flake dimensions: 1.5x2nm^2

7 GO flakes, 32 PAA chains

GO flake dimensions: 9x8.4nm^2

1 GO flake, 90 PAA chains

PAAGOlwt (large GO)

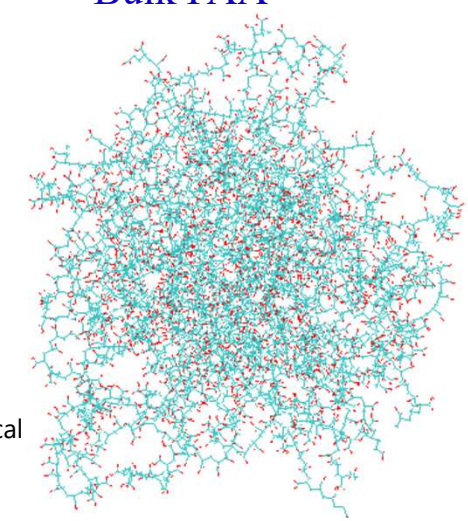


GO flake dimensions: 9x8.4nm^2

1 GO flake, 1300 PAA chains

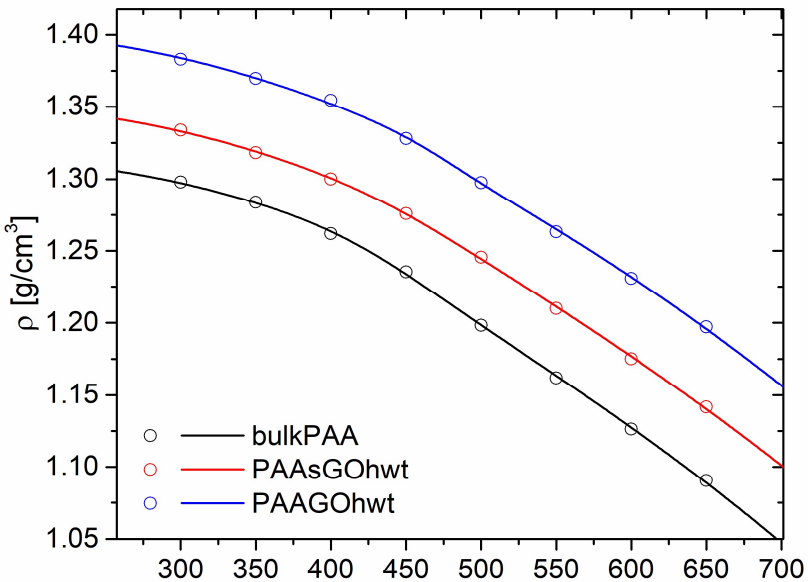
50 PAA chains

Bulk PAA



Kritikos, G.; Karatasos, K. Effect of Nanofiller Size on the Mechanical Properties of Poly(acrylic acid)/Graphene Oxide Nanocomposites. *Macromolecules* **2021,** 54 (9), 4164-4175

Effects on thermal properties



$$\frac{Pv}{kT} + \left(1 - \frac{1}{r}\right)\tilde{\rho} + ln(1 - \tilde{\rho}) + \chi\tilde{\rho}^2 = 0$$

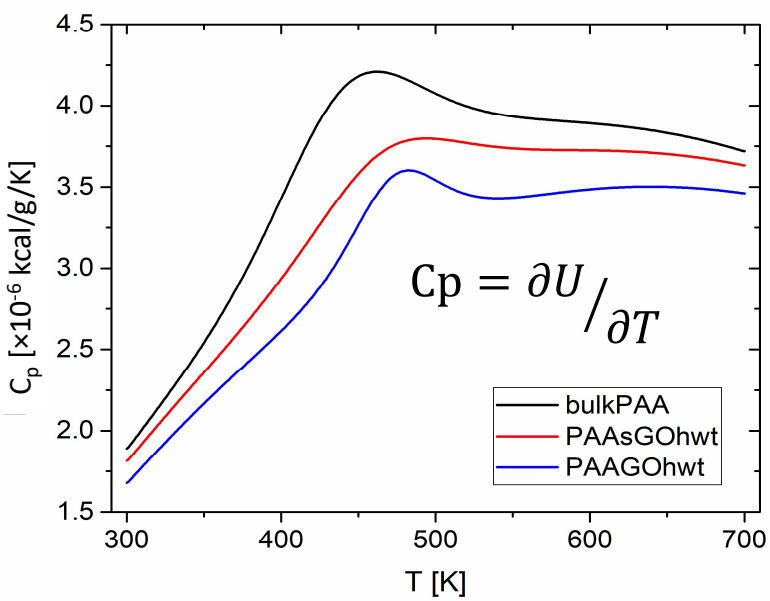
Materials Today Communications **2017,** 13 (Supplement C), 359-366

Soft Matter **2020,** 16 (29), 6902-6913

Macromolecules **2021,** 54 (9), 4164-4175

P: pressure, *v*: segmental volume at the solid state
r: the degree of polymerization, *k* : the Boltzmann's constant, $\tilde{\rho} = {}^{\rho}/_{\rho_o}$ and *ρ:* density at T , ρ_o: density at the solid state
χ: FH parameter

P=1MPa, v=22-23Å^{3,} ρ_o (bulk)≅1.31 (g/cm^3),
ρ_o(PAAsGOhwt)≅1.35 (g/cm^3)
ρ_o(PAAGOhwt)≅1.40 (g/cm^3)



T_g of PAAGOhwt (large GO) ≅ 471 K

T_g of PAAsGOhwt (small GO) ≅ 460 K

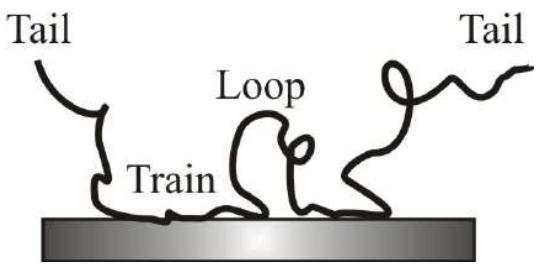
$$U = kT^*\tilde{\rho}(1 - \tilde{\rho})N_A\, r/M\, W$$

Polymer configurations: trains, loops, tails, bridges, free

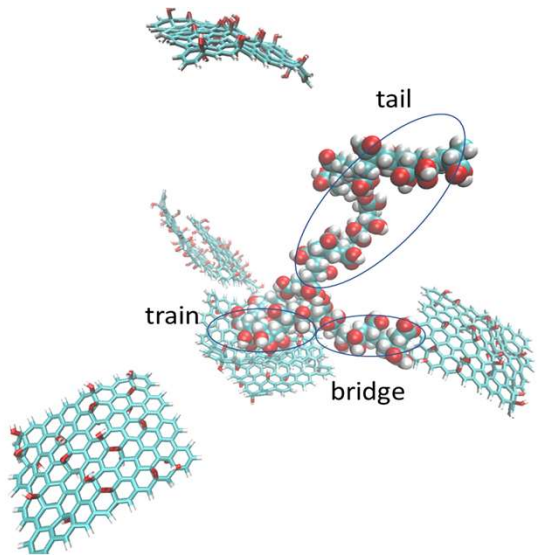
How can the size of the filler affect the bound layer dynamics?

Does the presence of neighbouring flakes affect the bound layer dynamics?

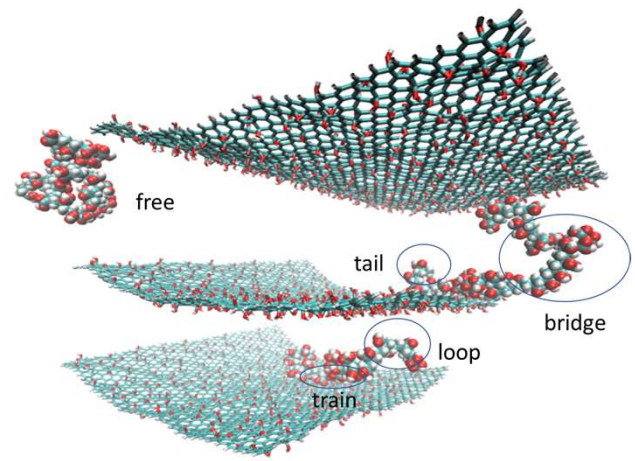
Chain conformations near an adsorbing surface



PAAsGOhwt (small GO)

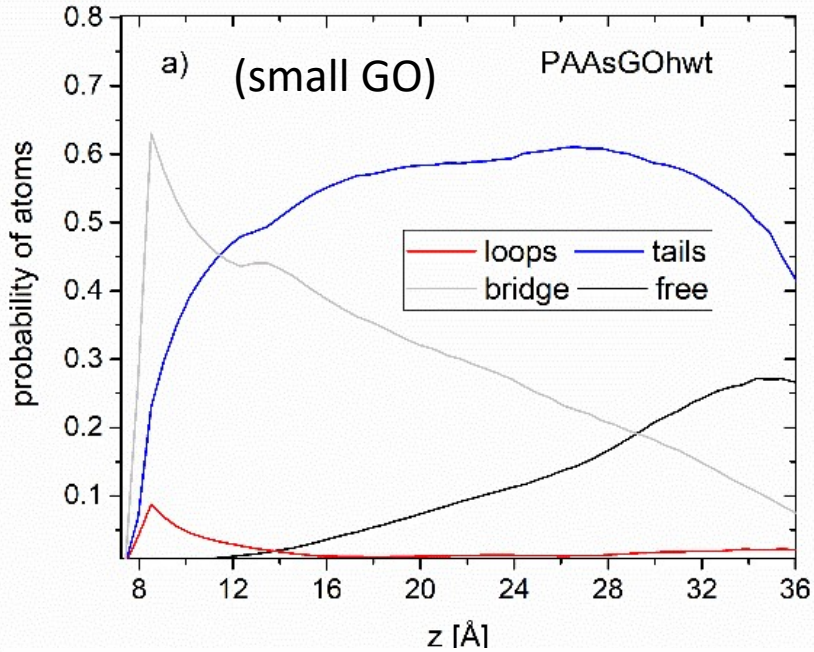


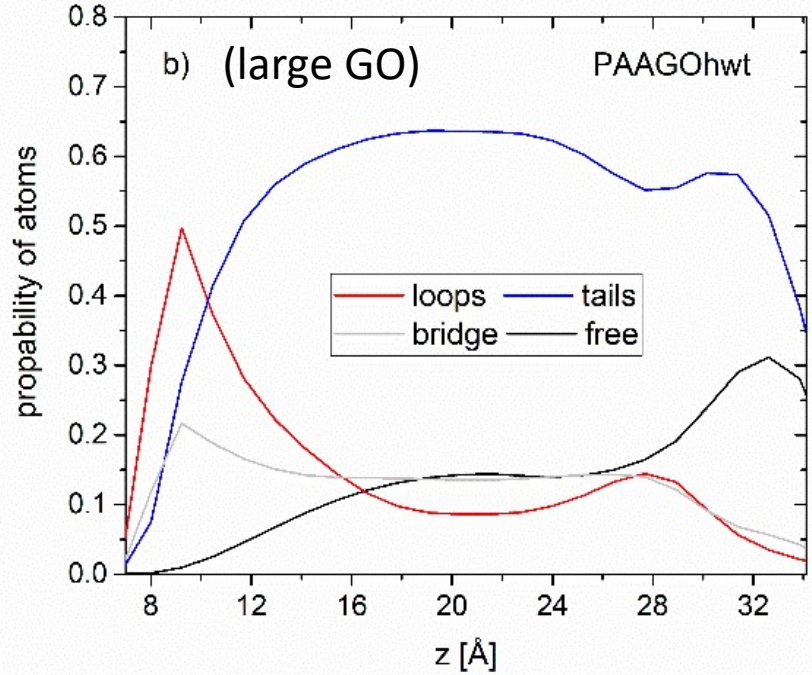
PAAGOhwt (large GO)

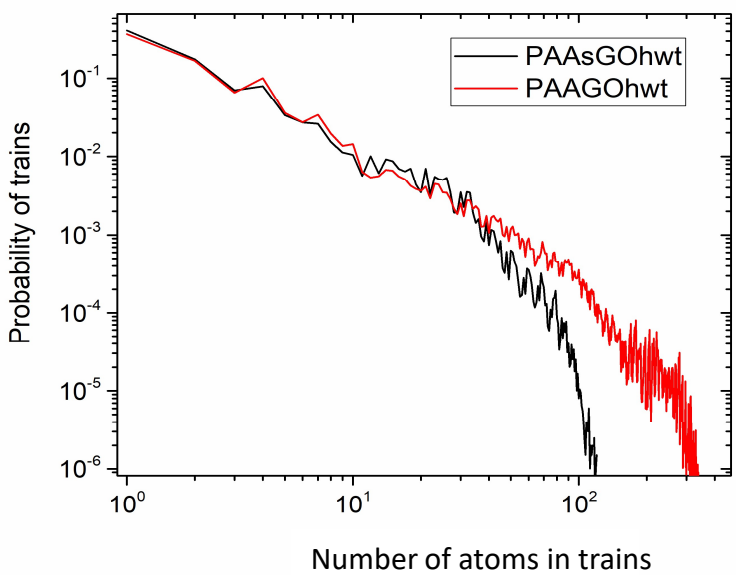


Definition: the *bound layer* includes all polymer conformations at layer 0 of the surface

Conformational probability distributions



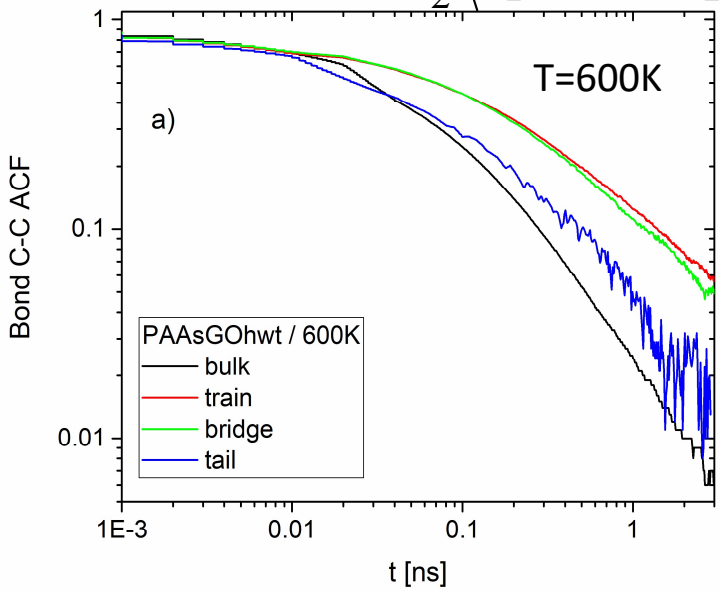


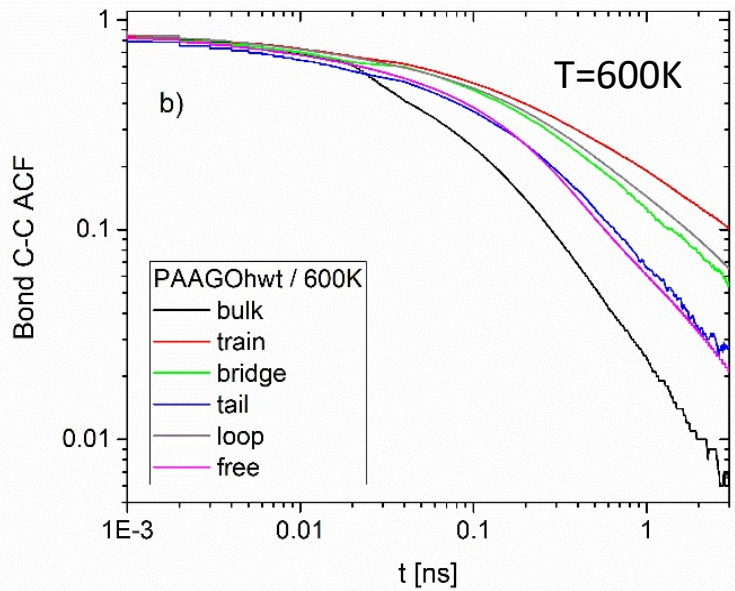


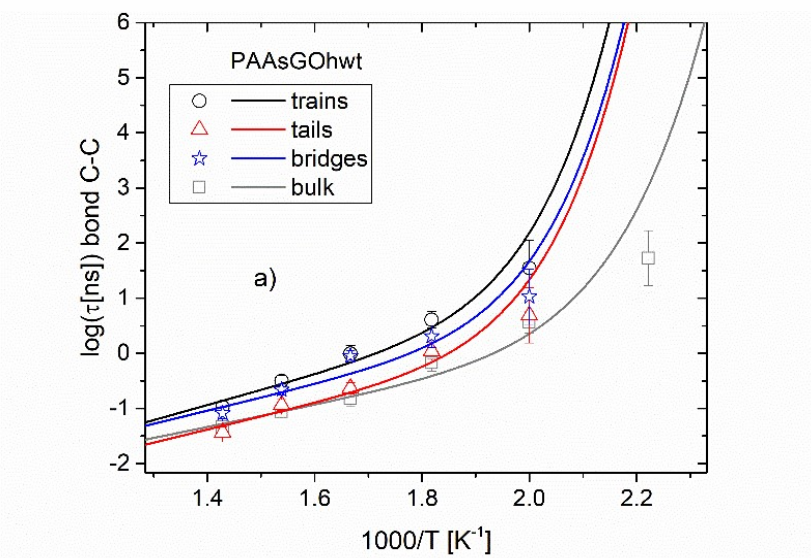
- Tail configurations with similar probability distributions
- Bridges are more frequent when the filler size is small
- Loops are more abundant in the larger size filler
- Free chain distributions are not affected by the flake size
- Longer train sequences can be formed in the larger GO system

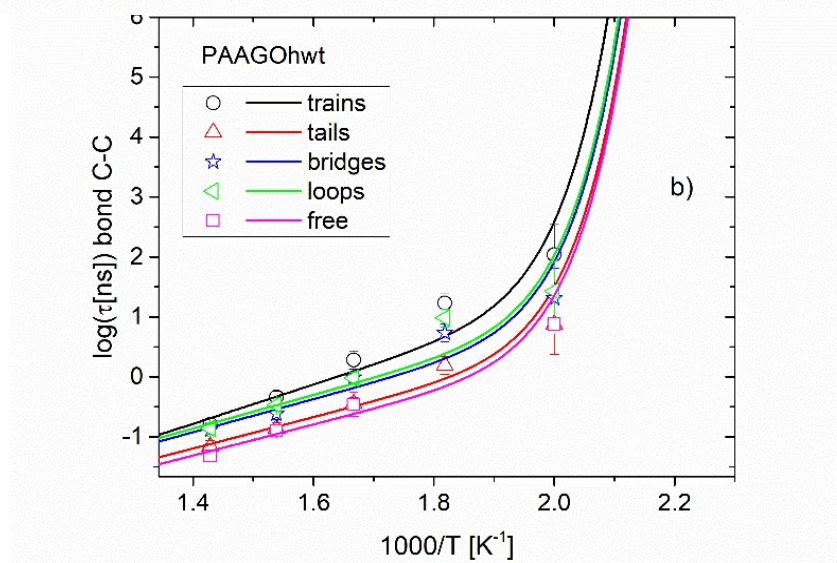
Conformational-specific local dynamics at the bound layer

Bond C-C ACF $C(t) = \frac{1}{2}\left\langle 3\left[\hat{h}(t)\cdot\hat{h}(0)\right]^2 - 1\right\rangle$ $\hat{h}(t)$: a unit vector along the studied bond









$$\tau = \tau_o exp\left(\frac{B}{T}\left[1 + exp\left(\frac{T_g - T}{\delta_g}\right)\right]\right)$$

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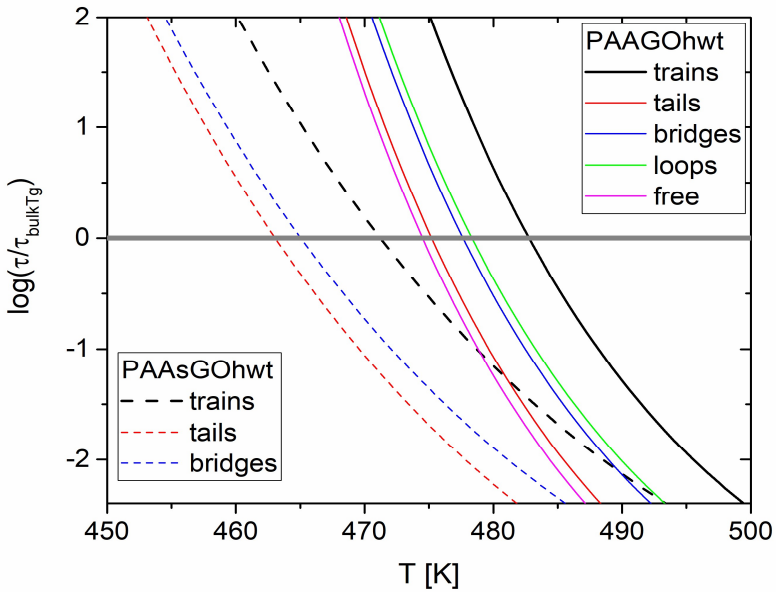
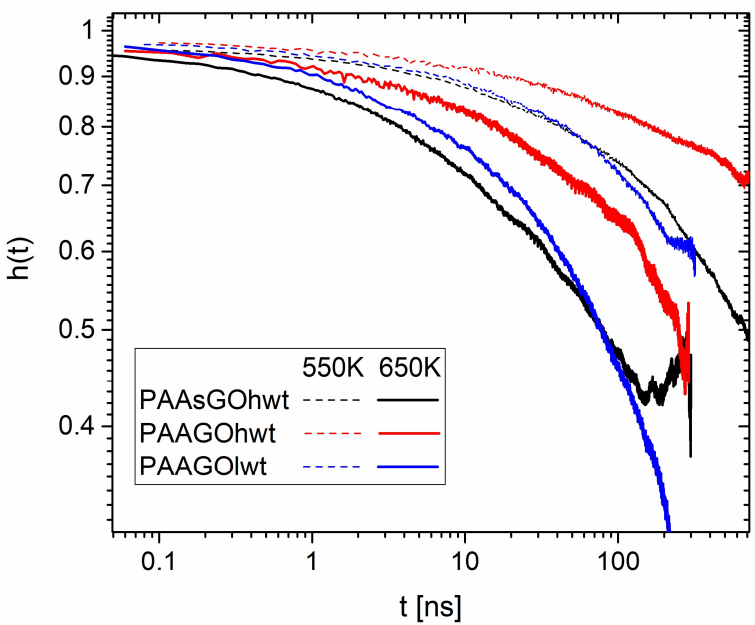
Conformational-specific local dynamics and adsorption/desorption at the bound layer



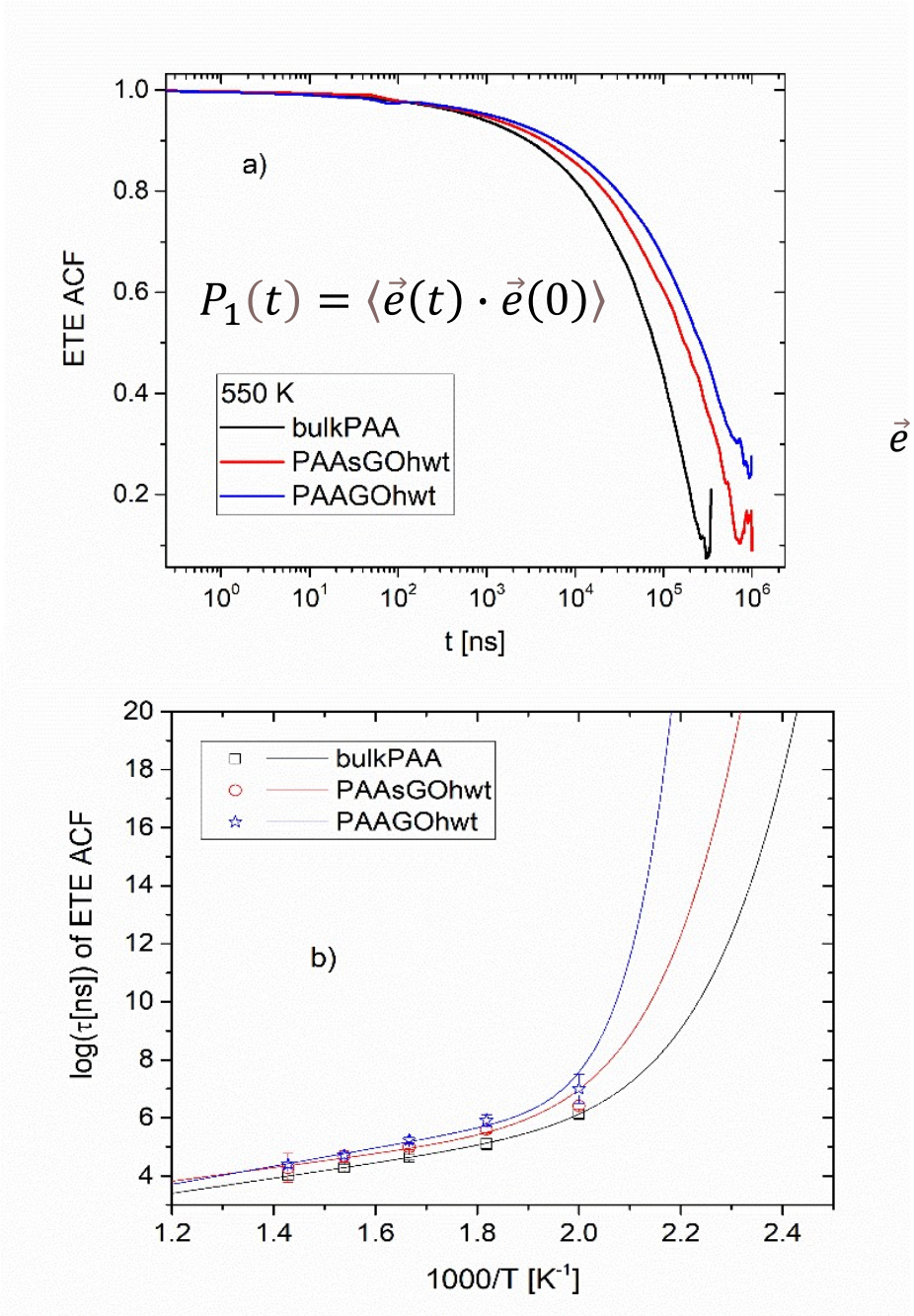
- The bulk vitrification times of the different conformations are reached at higher temperatures in the larger in size GO composite and for the slower moving configurations.



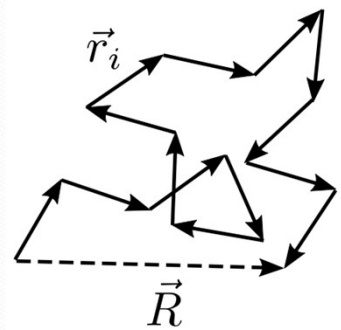
- At constant loading (red and black curves), longer desorption times in the larger GO systems

- At constant GO size (large flake, red and **blue** curves), the desorption times increase at higher loading (stronger confinement) conditions.

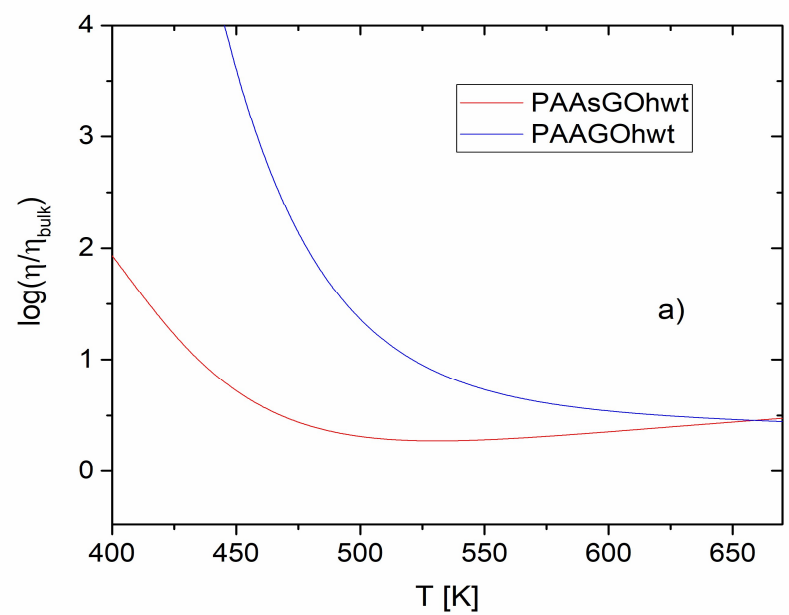
Average chain relaxation and macroscopic properties



$$P_1(t) = \langle \vec{e}(t) \cdot \vec{e}(0) \rangle$$



$\vec{e}(t)$ is a unit vector along R



Summary of the main findings (for unentangled polymer chains)

- Slower polymer dynamics close to the interface is associated with slow relaxing configurations such as trains, loops and bridges

- Larger flakes favor the formation of longer trains, more loops and longer-lived bridges. A higher filler concentration may also increase the number of bridges

- Longer polymer chains are more likely to form such configurations, and thus to exhibit slower dynamics close to the interface.

- Higher nanoroughness slows down the interfacial motion, particularly the lateral diffusivity, resulting in slower and more anisotropic motion close to the interface

- Different chain characteristics and different interactions between the polymer matrix and the interface result in a different degree of "cloaking" of the surface dynamics from the bulk. A weak "cloaking" leads to slower polymer dynamics at longer distances from the interface, affecting more the average dynamic behavior

- A higher filler concentration, apart from confining global chain motion, it also results in a higher degree of overlap between the slow relaxing layers of neighboring flakes, and thus affects strongly the average polymer dynamics. This is related to a shift of the thermal transitions to higher temperatures, and to enhanced mechanical response of the composites

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Computing Resources

AUTh High Performance Computing (HPC)