Mathematical and Computational Modelling of Molecular Systems

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11η Επιστημονική Διημερίδα ΙΤΕ
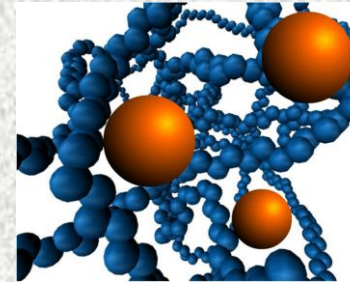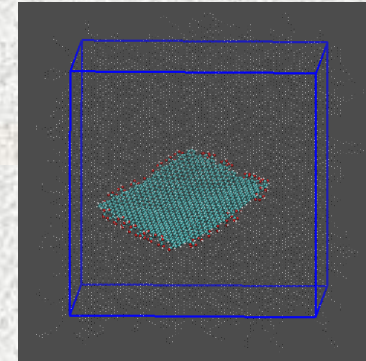*MS: Materials and Energy*
Heraklion, 13/10/17

✓ **Broad spectrum of systems, applications, length-time scales.**
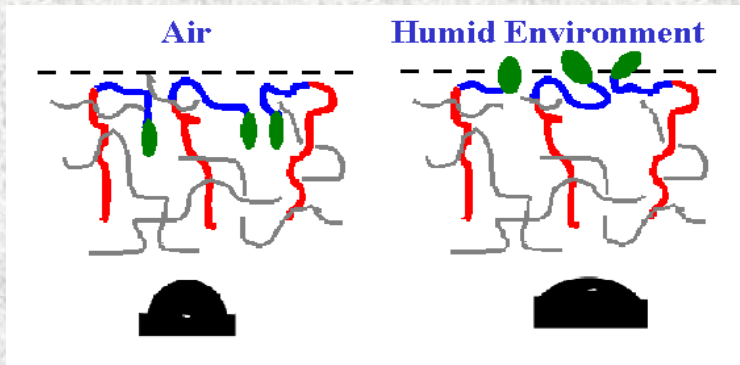
❑ <u>**Systems**</u>

  ➢ **polymers**

  ➢ **biological macromolecules** (cell membrane, DNA, lipids)

  ➢ colloids

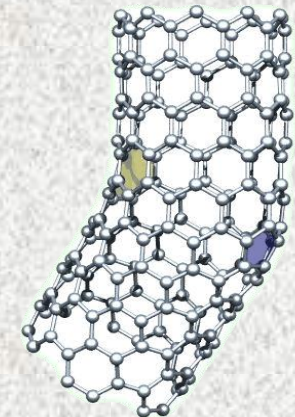 ➢ hybrid polymer **nanocomposite** systems

❑ <u>**Applications**</u>

  ➢ **Nanotechnology** (materials in nano-dimensions), **biotechnology** (drug release, … etc)

  ➢ **Clever-responsive Materials**

  ➢ **Carbon structures**

  ➢**Molecular Electronics**
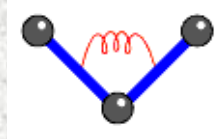
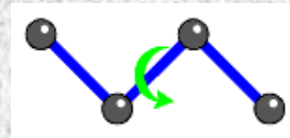# Time – Length Scales Involved in Complex Molecular Systems

❑ **Bond vibrations: ~ 10^{-15} sec**
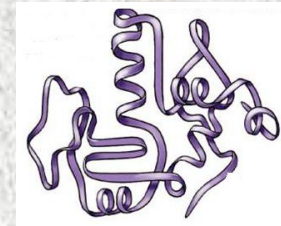

❑ **Angle rotations: ~ 10^{-13} sec**
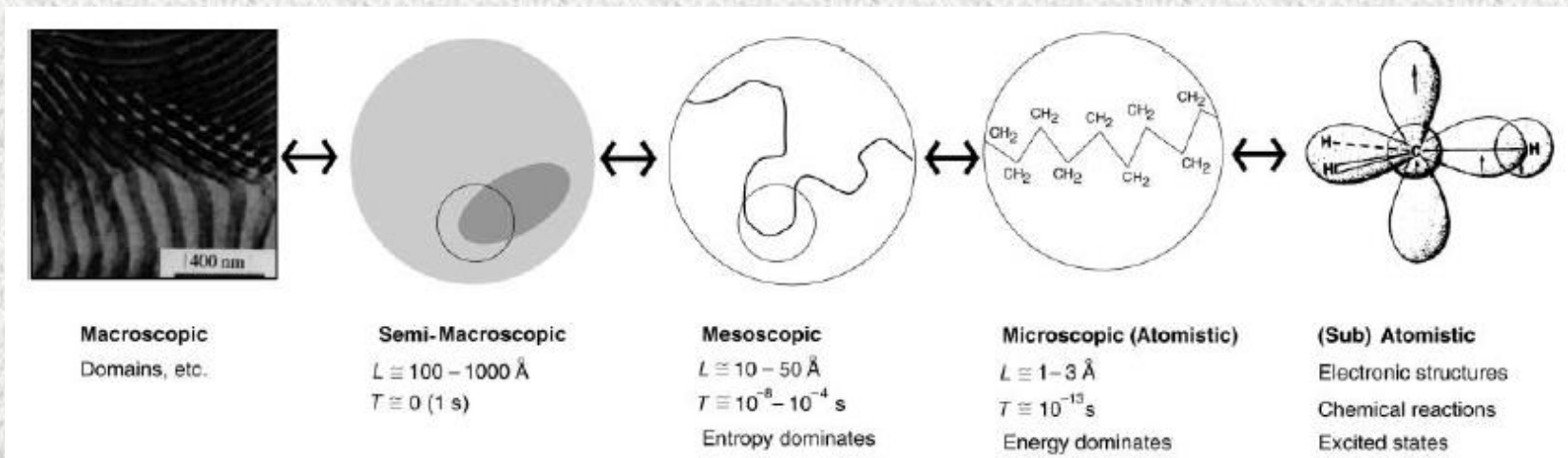

❑ **Dihedral rotations: ~ 10^{-11} sec**

❑ **Segmental relaxation: 10^{-9} - 10^{-12} sec**

❑ **Maximum relaxation time of a chain, τ_1: ~ 1 sec (in $T < T_m$)**

❑ **Polymer/solid interface characteristic relaxation times: ?**

| Macroscopic	Semi-Macroscopic	Mesoscopic	Microscopic (Atomistic)	(Sub) Atomistic
Domains, etc.	$L \cong 100 - 1000 \,\text{Å}$	$L \cong 10 - 50 \,\text{Å}$	$L \cong 1 - 3 \,\text{Å}$	Electronic structures
	$T \cong 0 \ (1\ s)$	$T \cong 10^{-8} - 10^{-4}\ s$	$T \cong 10^{-13}\ s$	Chemical reactions
		Entropy dominates	Energy dominates	Excited states

❖ **Several simulation methods that describe different length and time scales**
[K. Johnston and VH, Soft Matter, 9, 6696 (2013)]

D) description in macroscopic - continuum level

C) description in mesoscopic (coarse-grained) level

B) description in microscopic (atomistic) level

A) description in quantum level
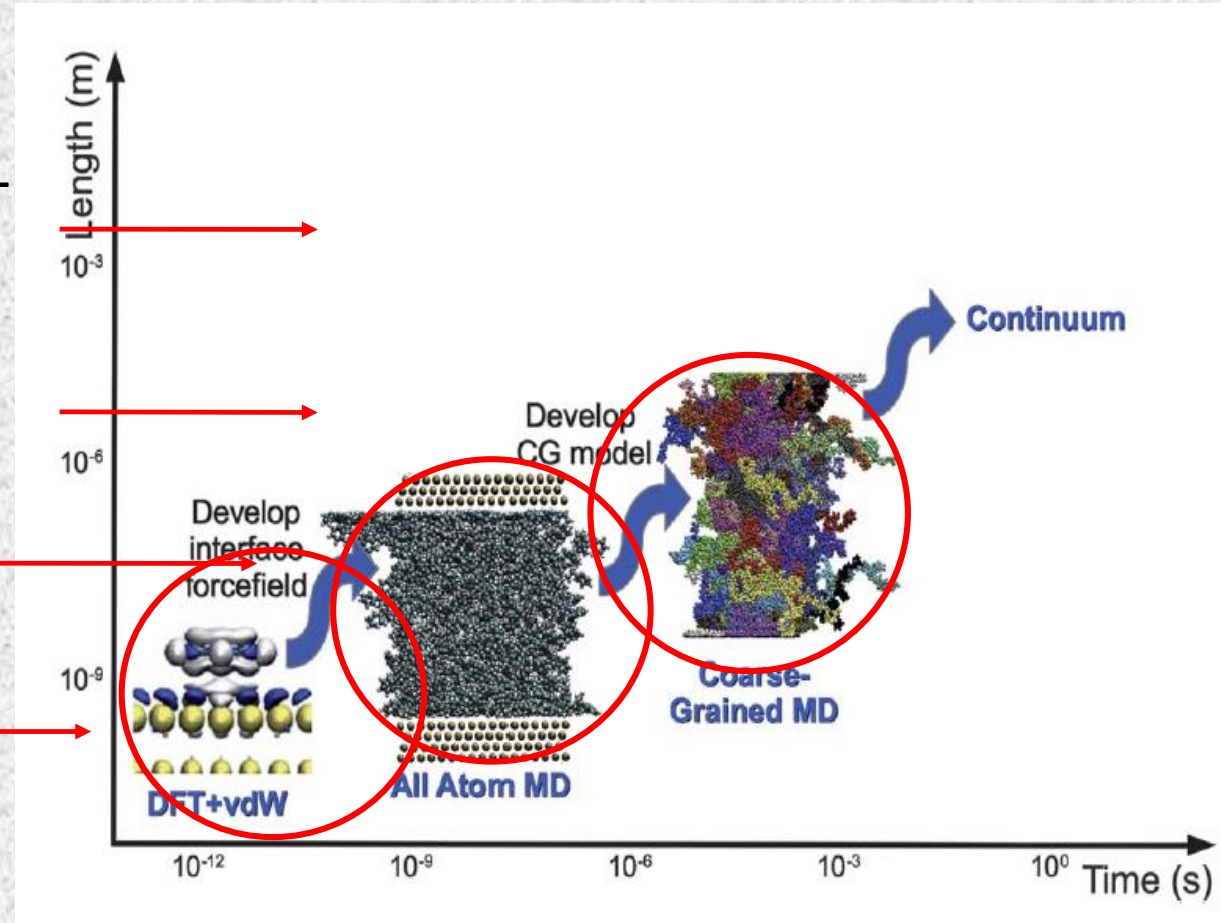
➢ **Great Challenge: Quantitative modeling of specific hybrid complex systems.**

➢ **Need: Analytical and Computational tools for rigorous "bridging" different description-simulation levels.**

# Modeling of Molecular Systems: Atomistic Molecular Dynamics

❏ **Classical mechanics**: solve classical equations of motion in phase space, Γ:=Γ(r, p).

$$r \equiv (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$
$$p \equiv (\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N)$$

$$\frac{dr_i}{dt} = M^{-1} p_i \,, \quad \frac{dp_i}{dt} = -\frac{\partial U(r)}{\partial r_i} = F_i$$

❏ **MD method**: **Numerical solution** of deterministic equations of motion

❏ **Integration time step**: dt ≈ 1fs (10^{-15} sec)

❏ **Quantum phenomena are neglected**

❏ **Time scales**: few **fs up to** ≈ 1 µs (10^{-6} sec)

❏ **Typical size (single run)**: ~ $10^5 – 10^6$ **atoms**

❏ **CPU needs (single run)**: ~ 10 – 1000 procs
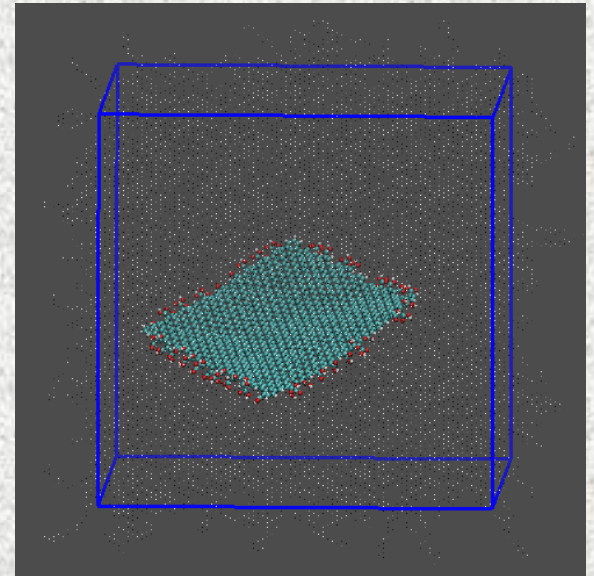
Example: Polymer Nanocomposites

[P. Bačová, et al., Macromolecules, 48, 9024 (2015); A. Rissanou et al., Macromolecules, 60, 6273 (2017); A. Power, VH, to be submitted]
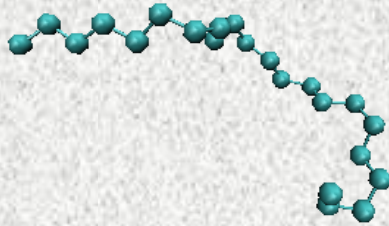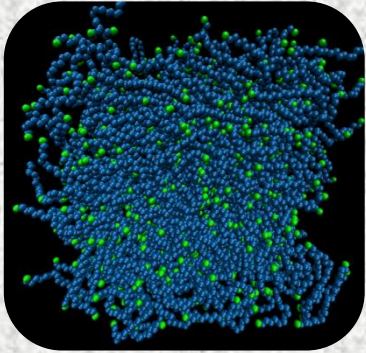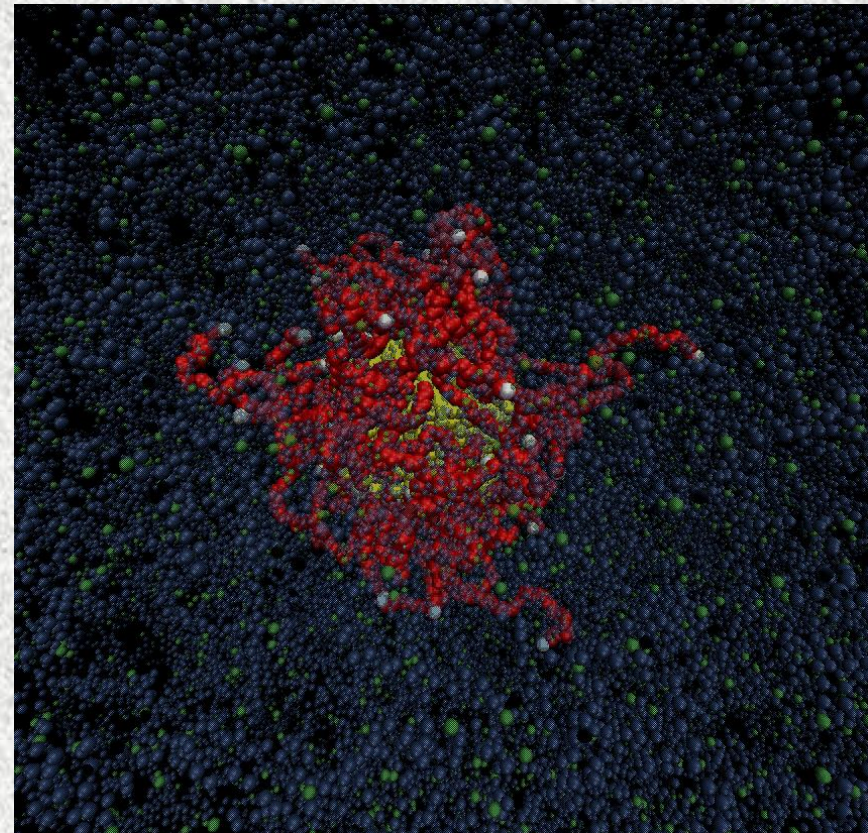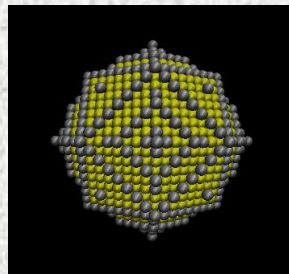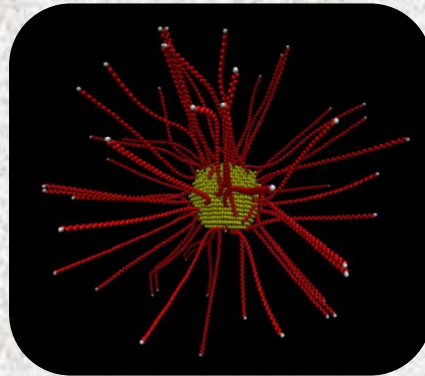

Functionalized (core/shell) Au NP:

- **Wulff construction**

- **Diameter = 5.0 nm**

- **w/w %** ~ 30

Au NP's Brushes (Hairs):

- **Polyethylene**

- **53 chains**

- **Short Brushes: 20mers**

- **Long Brushes: 62mers**

- **σ = 0.67 chains/nm^2**

Example: Nanostructured Polymer/Graphene Systems
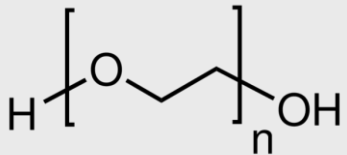
PS
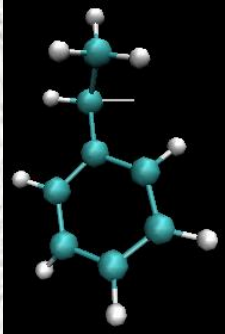
PMMA
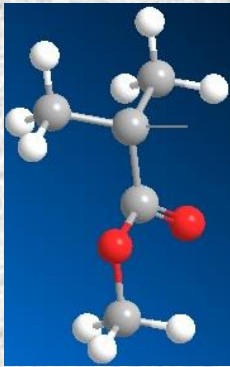
PE
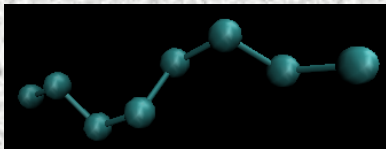
Polyethylene Oxide
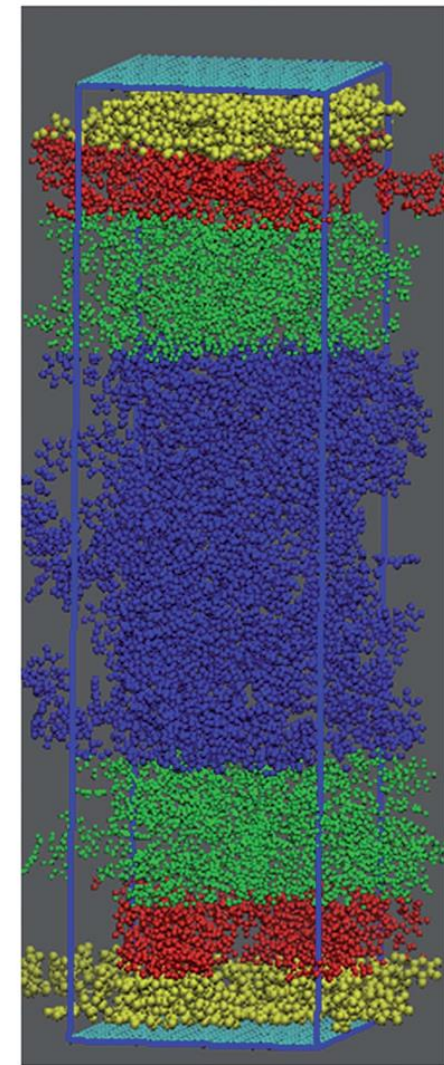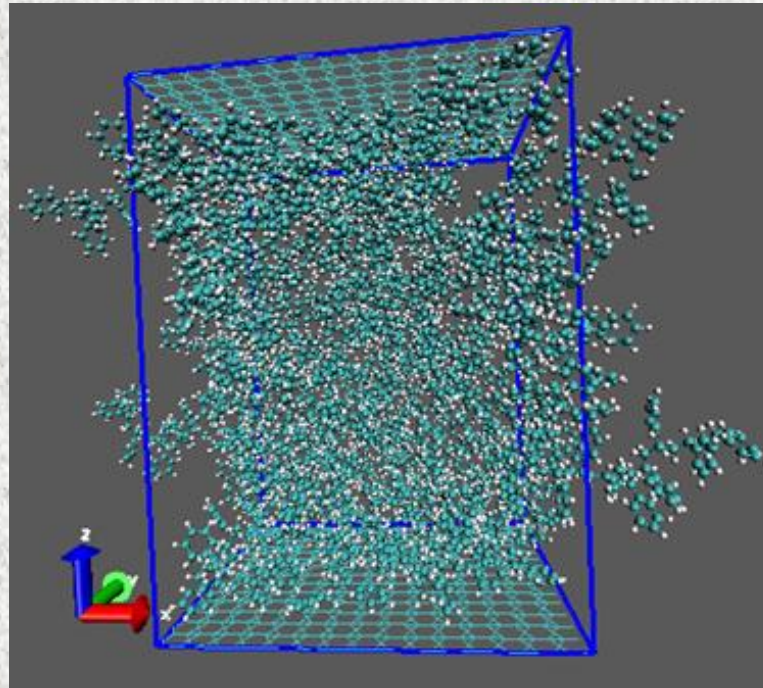
❖ **All-atom model**

❖ **Verlet algorithm, dt = 1-2 fs**

❖ **T=450-500 K.**

❖ **Short polymeric chains (10mer – 20mer)**

❖ **Loading of graphene sheets: 1-3% wt**

Confined Polymer Films – Spatial Heterogeneities

[A. Rissanou and VH, Macromolecules 48, 2761 (2015)]

❑ **Density profiles** as a function of the distance from graphene layers
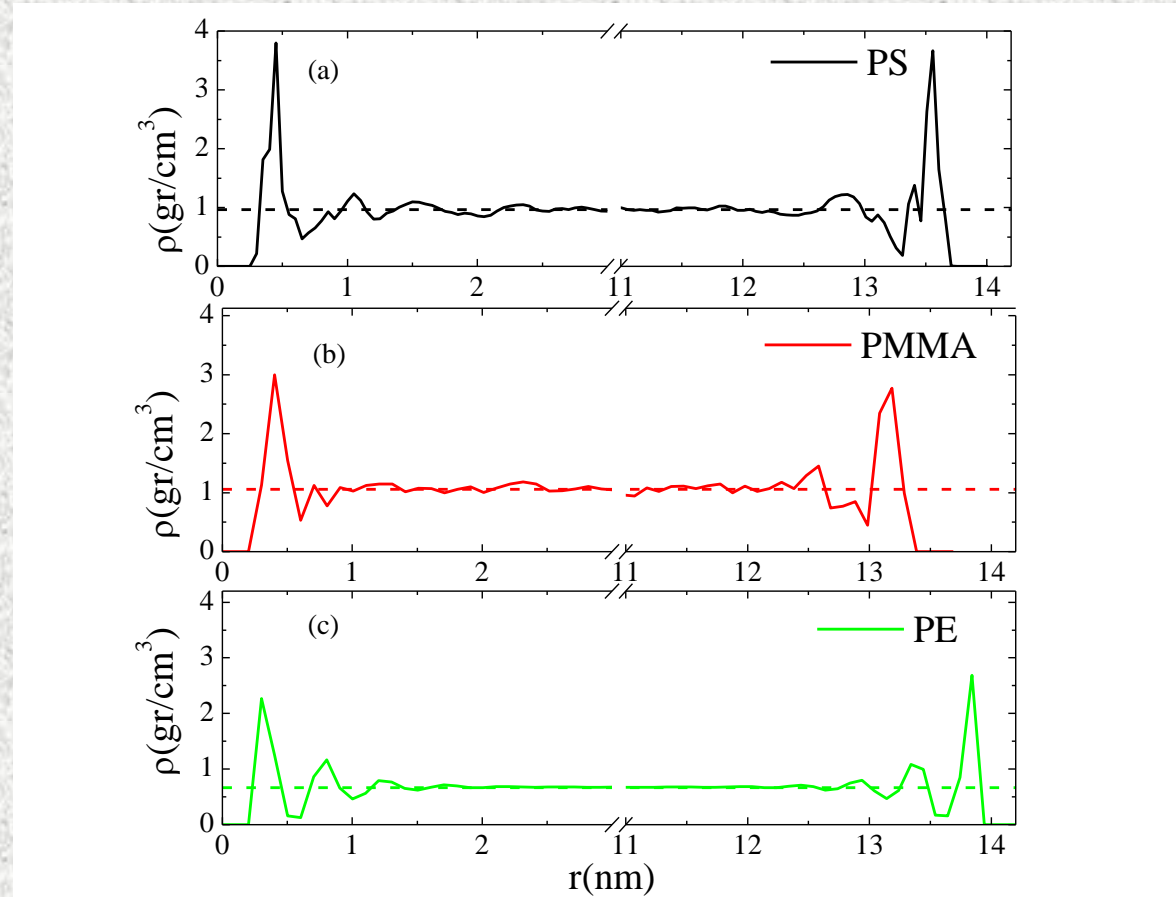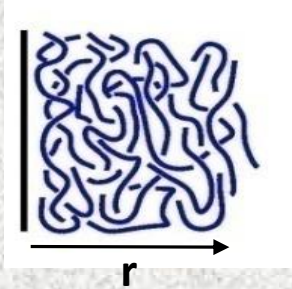
➤ **Density profiles are symmetrical with respect to the center of the film.**

➤ **All systems attain bulk density in the intermediate region between graphene layers.**

➤ **Well-ordered layered structure of PE close to graphene.**

Confined Polymer Films: Segmental Dynamics

[A. Rissanou and VH, Macromolecules 48, 2761 (2015); Soft Matter 10, 2876 (2014)]

$$P_2(t) = \frac{3}{2}\left\langle \cos^2 \theta(t) \right\rangle - \frac{1}{2}$$

r
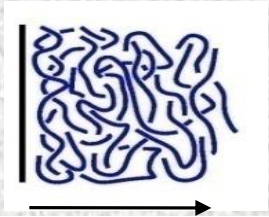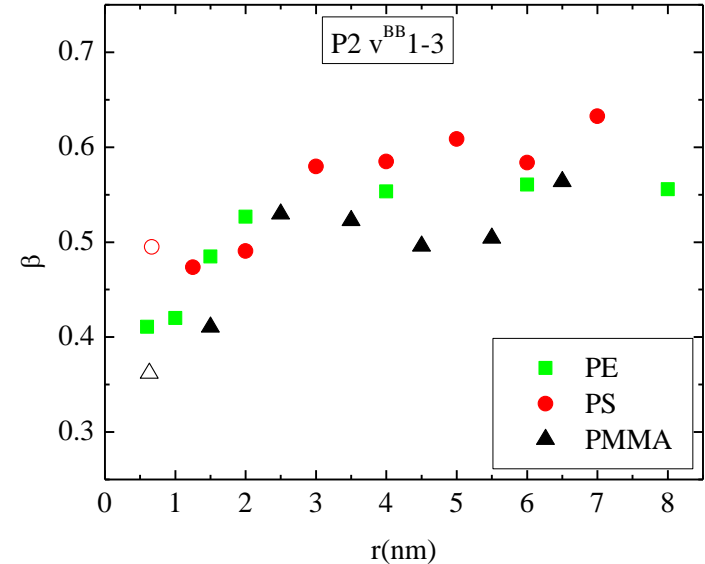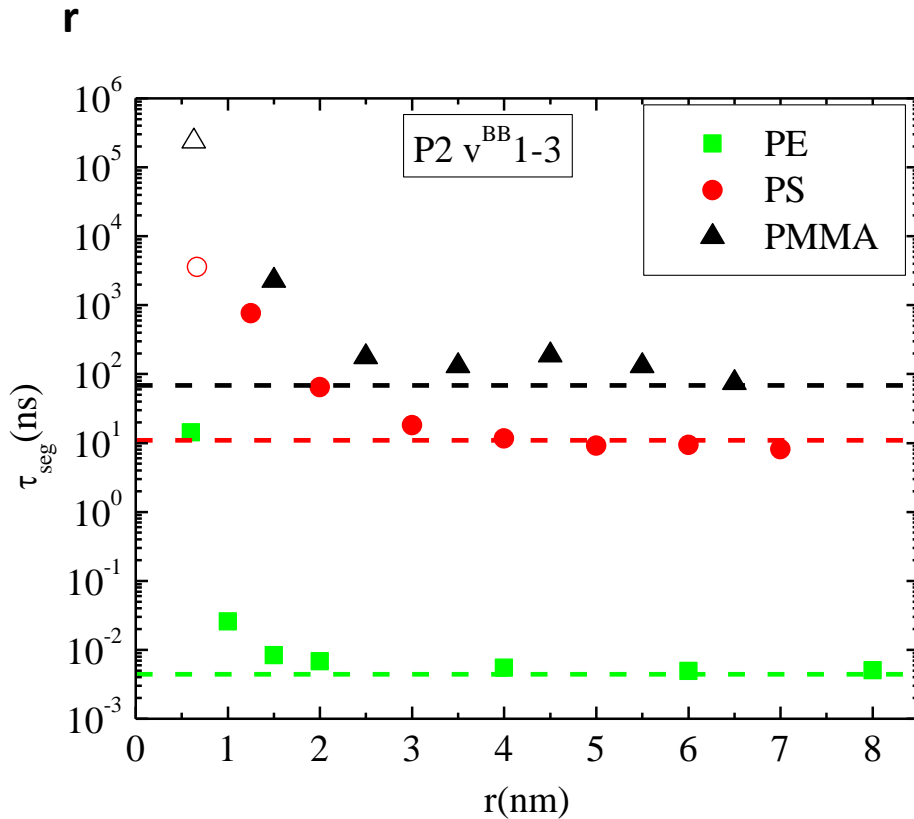
➤ **Relaxation time decreases with the distance from the graphene layer.**

➤ **Larger deviation from ideal Debye behavior close to the graphene layer.**

- ❑ **Model: All-atom model** (OPLS-AA) of PE chain adsorbed on graphene.

- ➢ **Perfect 2D single-chain polymer crystal**

❑ **Crystallization process:**

❑ **Atomistic view of melting process**

❑ **Reversible process**

❖ **Formation of a single-chain polymer crystal (time scales ~ 100ns)**

❖ **Melting: Ultra-fast dynamics of the polymer crystal (~ 100 ps)**

❖ **Melting via a transient floating phase.**
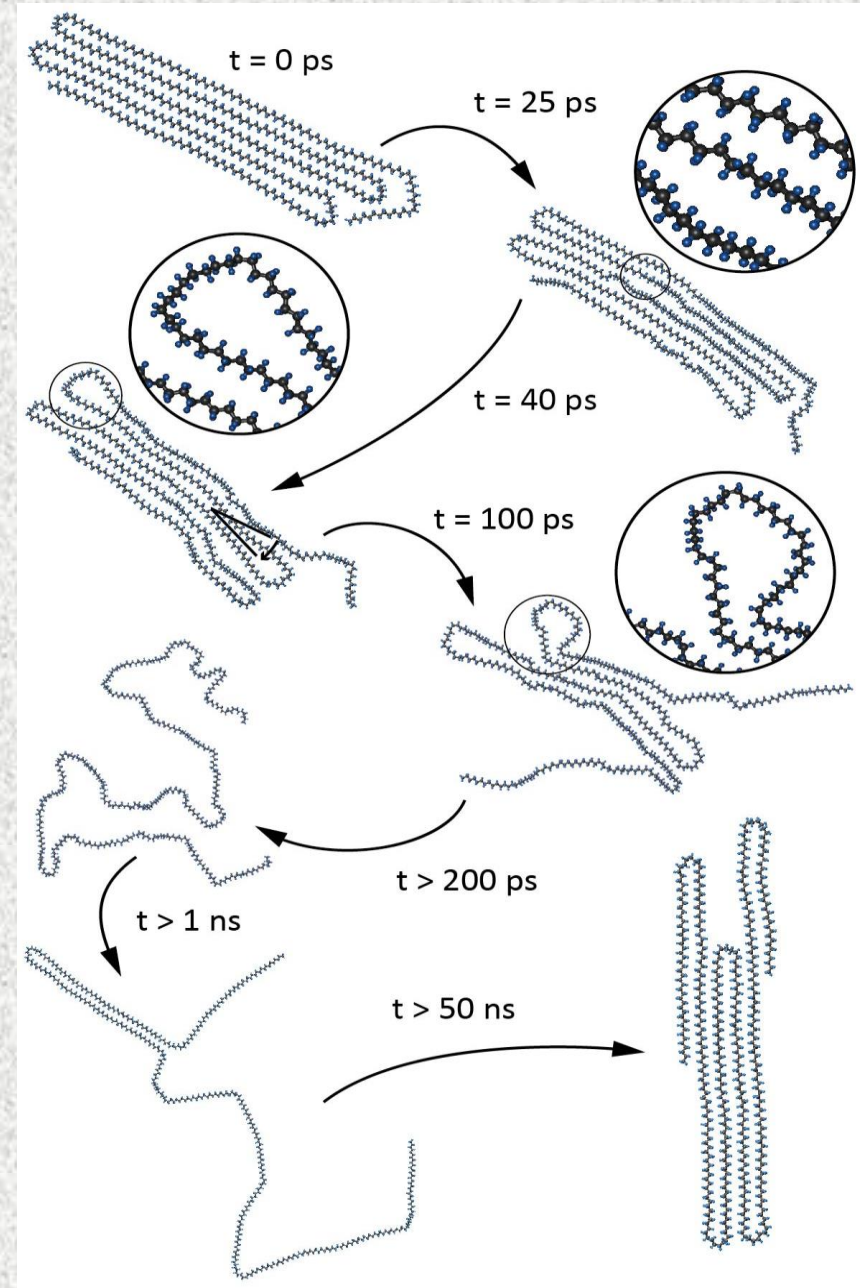
Materials for Applications in Energy: Star Polymers

[P. Bačová, et al., to be submitted; Collaboration with Dr. E. Glynos IESL/FORTH]

❑ **Model:** Mikto-arm star polymers

❑ Atomistic **polystyrene - poly(ethylene oxide)** (PS/PEO) model systems

❖ Different **nano (hetero)-structures** as a function of T, f, solvent

✓ **Single-molecule** PEO/PS star
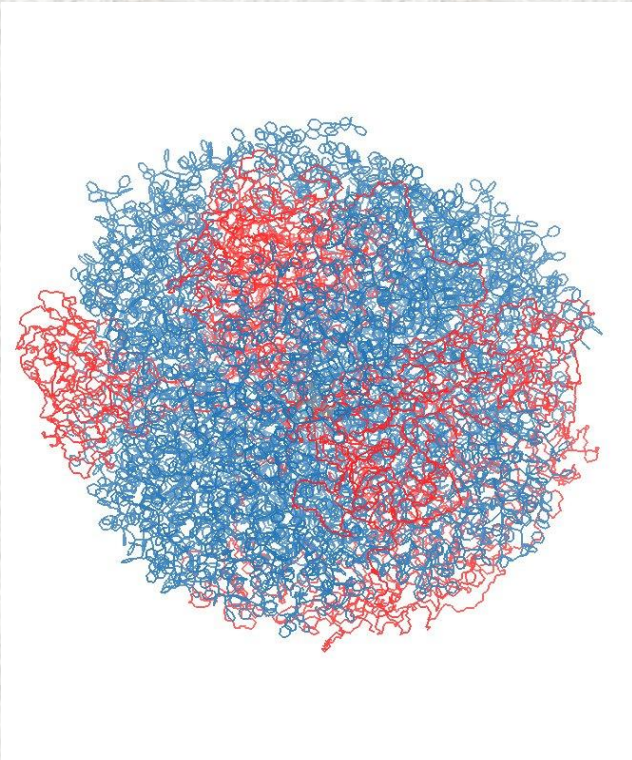
✓ PEO/PS star in PEO **solvent**
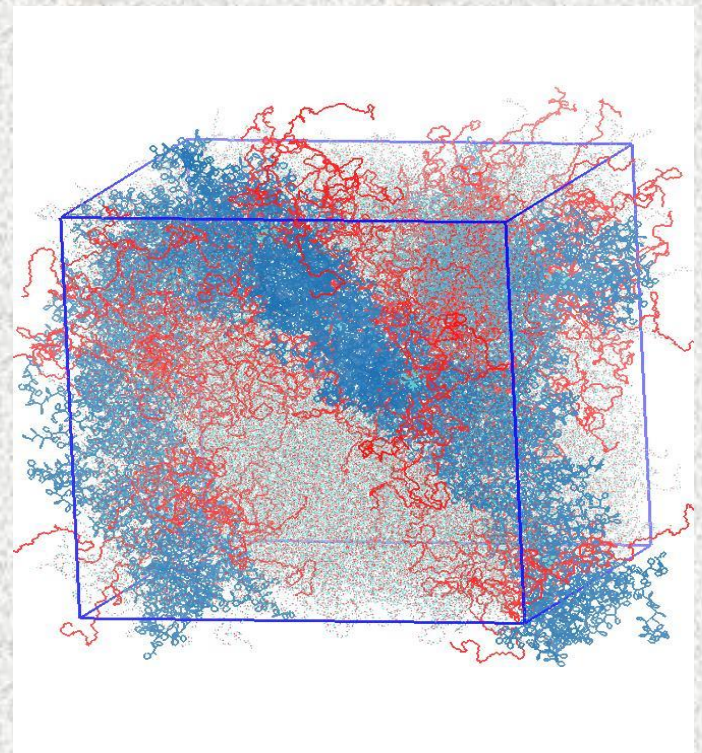
Modeling of Complex Systems: Atomistic Molecular Simulations

❑ **Atomistic molecular simulations (MD, MC) – The perfect experiment:**

➤ **Capable of quantitative predictions of the properties (structure, thermodynamics, mechanical, rheological, etc) of**

➤ **Complex multi-phase materials.**

➤ **Limits of Molecular Dynamics Atomistic Simulations (with usual computer power):**

-- **Length scales:** few Å - $O(10\text{ nm})$ -- **Time scales:** few fs - $O(1\ \mu s)$ $(10^{-15} - 10^{-6}\text{ sec})$

-- **Systems size:** $O(10^5 - 10^6\text{ atoms})$

Need:

➤ **Simulations at larger length – time scales.**

➤ **Application to molecular weights relevant to polymer processing.**

➤ **Study more complicated molecular systems – materials.**

Systematic Coarse-grained Models

[VH, et al. Macromolecules, 39, 6708 (2006); Physical Review Letters 110, 165701 (2013); V. Kalligiannaki et al, J. Chem. Phys. 143, 084105 (2015); J. Comp. Phys. 314, 355 (2016); A. Tsourtis et al. Entropy 19, 395 (2017)]

Choice of the proper CG description.

-- **Microscopic (N particles)**

$$X := \{x_1, x_2, ..., x_N\}$$
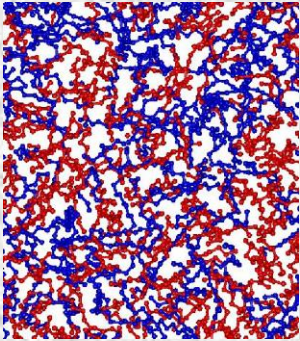
-- **Mesoscopic (M "super particles")**

$$Z := \{z_1, z_2, ..., z_M\}$$

$$Z = \xi X$$
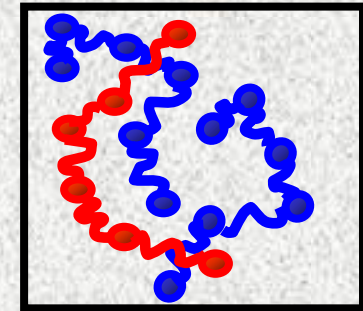
-- Usually ξ is a **linear operator**

$$z_i = \sum_{j=1}^{N} c_j x_j \qquad i = 1, 2, ..., M$$
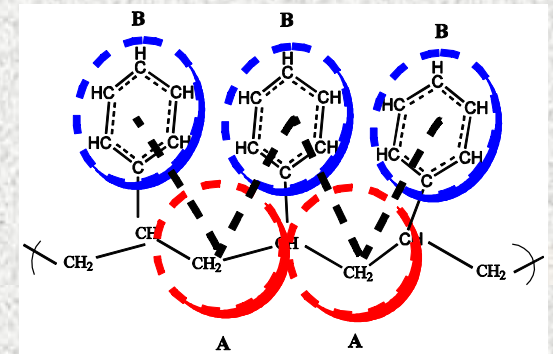
Coarse Grained Models: Effective Interaction Potential

❑ **Equations of motion in the CG scale become stochastic**

  ➢ **Langevin dynamics (through Markovian approximation):**

$z := \{z_1, z_2, ..., z_M\}$

$p := \{p_1, p_2, ..., p_M\}$

$$dz_i = M^{-1}p_i dt$$

$$dp_i = -\frac{\partial U^{CG}(z)}{\partial z_i} - \gamma M^{-1}p_i dt + \sigma dW$$

✓ $U^{CG}(z)$: **CG Interaction potential**

✓ **γ : friction σ: diffusion**

✓ **W: 3M-Brownian motion**

$\sigma\sigma^{tr} = 2\beta^{-1}\gamma$

❑ **In principle U^{CG} is a function of all CG degrees of freedom in the system (free energy, potential of mean force U^{PMF}):**

$U^{CG}(z) = U^{PMF}(z)$

➢ **CG Hamiltonian – Renormalization Group Map:**

$$U^{PMF}(z) = -\frac{1}{\beta}\log\int_{\Omega(z)} e^{-\beta U(x)}dx, \quad \Omega(z) = \{x \in \mathbb{R}^{3N} : \xi(x) = z\}$$

❑ $U^{PMF}(z)$ **is NOT possible to be calculated exactly. Various methods to be approximated:** [V. Kalligiannaki et al, J. Chem. Phys. 143, 084105 (2015); J. Comp. Phys. 314, 355 (2016); Europ. Phys. J. Special Topics, 225, 1347 (2016); A. Tsourtis et al. Entropy 19, 395 (2017)]

Confined Polymers through Hierarchical modeling

[K. Johnston and VH, J. Phys. Chem. C, 115, 1407 (2011); Soft Matter (2012); Macromolecules, 46, 5741 (2013)]

Polystyrene/Au CG model systems

❑ Molecular length: from 10mer up to 1000mer (MW=1000 – 100.000 gr/mol).

❑ Simulated times: up to ~ 1ms.
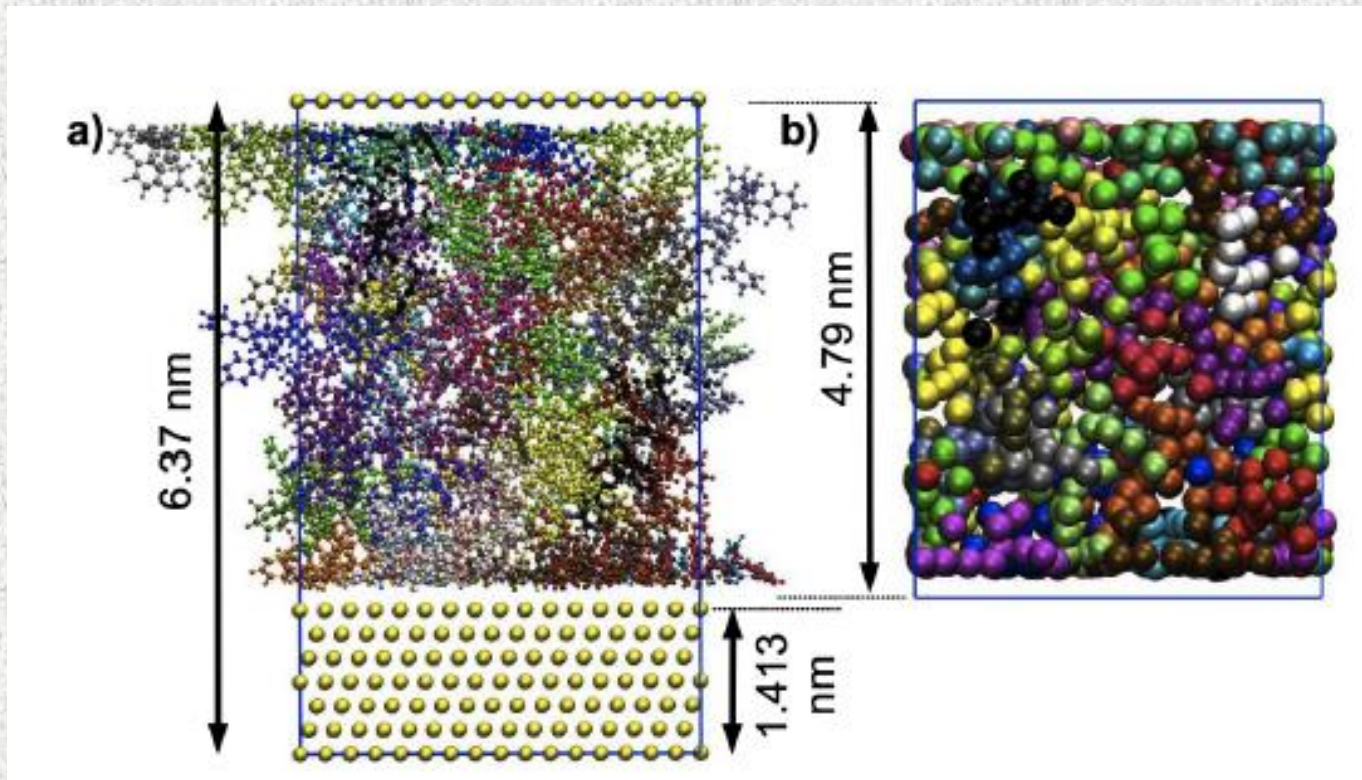
Dynamics of Bulk Polymers

[VH and K. Kremer, Macromolecules 42, 791 (2009); Soft Matter 5, 3920 (2009)]

❑ **Dynamics of polymer – Self-diffusion coefficient**
  ➢ **Crossover regime: From Rouse to reptation dynamics**

❑ **Systems up to 100.000gr/mol**

❑ **Theoretical predictions**

   -- **Rouse: D ~ M^{-1}**

   -- **Reptation: D ~ M^{-2}**

Crossover region: -- CG MD: M_e ~ 28.000-33.000 gr/mol
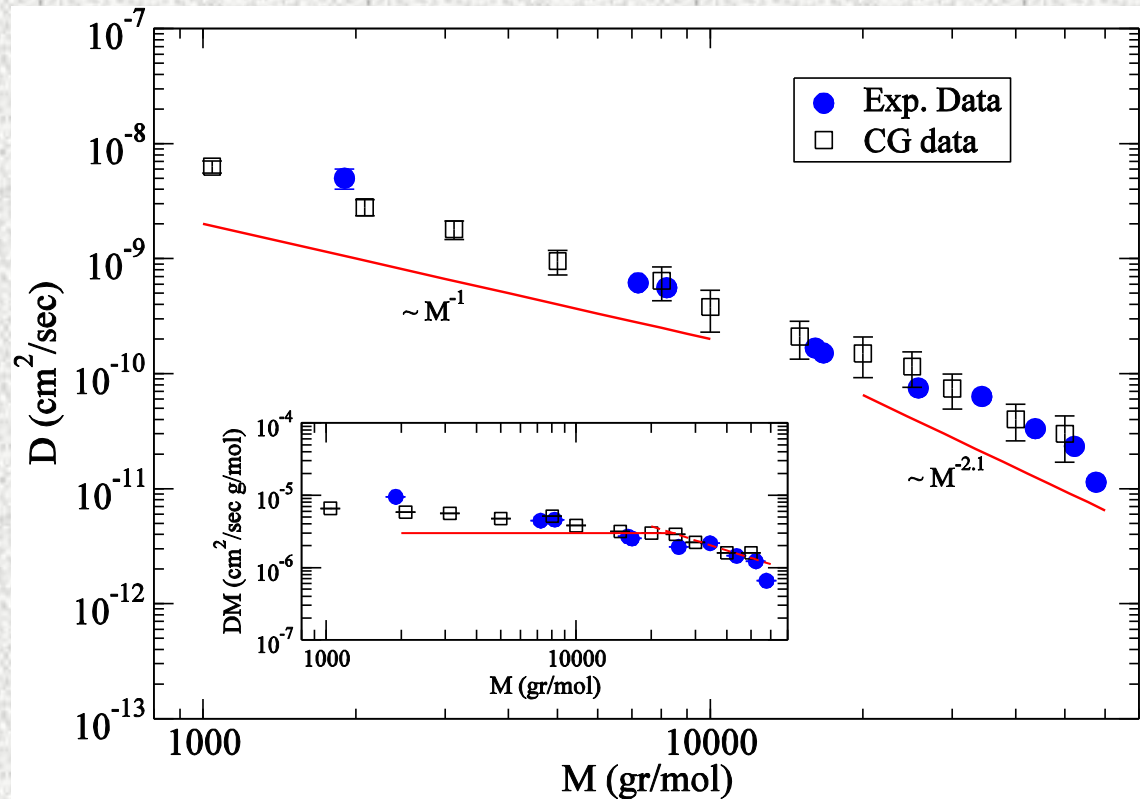   -- Exp.: M_e ~ 30.0000-35.000 gr/mol

-- Exp. Data: NMR [Sillescu et al. Makromol. Chem., 188, 2317 (1987)]

Acknowledgments

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Dr. P. Bacova

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❖ **Prof. P. Plechac** [University of Delaware, Newark, USA]

❖ **Prof. M. Katsoulakis** [University of Massachusetts, Amherst, USA]

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Thank you for your Attention!

❑ **Archimedes Center for Modeling, Analysis & Computation University of Crete**

EXTRA SLIDES

Acknowledgments

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❖ **Prof. M. Katsoulakis [University of Massachusetts, Amherst, USA]**

Conclusions

❑ **Hierarchical** systematic methods that involve coupling:

➢ **quantum** (DFT), **microscopic** (atomistic) and **mesoscopic** (coarse-grained) techniques

➢ **Length** scales: from ~ 1 Å (10^{-10} m) up to 100 nm (10^{-7} m)

➢ **Time** scales: from ~ 1 fs (10^{-15} sec) up to about 1 ms (10^{-3} sec)

❑ **Coarse-grained methods**: Rigorous dimensionality reduction approaches

❑ Equilibrium systems: several methods to **approximate** the **many-body potential of mean force**

❑ Which method to approximate the CG PMF model is **the "best" one**?

➢ All methods (IBI, FM, RE) approximate **theoretically the same PMF** for a given functional form of the CG potential.

➢ Rather similar results for **simple liquids**

➢ Numerical applications of **specific complex systems** are required

❑ **All above methods require "full" sampling of the reference system. What if we are not able to have such a sampling?**

➢ **Direct Boltzmann Inversion (DBI) based on isolated systems: Works well in many cases but neglects many-body terms [VH et al. Macromolecules 39, 6708 (2006)]**

➢ **Hierarchical cluster expansion approaches to involve many-body terms [A. Tsourtis et al. Entropy 19, 395 (2017)]**

❑ **CG models for:**

➢ **Quantitative predictions of the dynamics, of CG complex systems**

➢ **For CG systems under non-equilibrium conditions**

❖ **Semi-empirical method of CG time mapping works well only for a few cases**

❖ **New methods are required – Example: Algorithms based on path-wise tools**

➢ **Classical mechanics**: solve classical equations of motion in phase space, Γ:=Γ(r, p).

➢ **In microcanonical (NVE) ensemble**:

$$\mathbf{r} \equiv (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$
$$\mathbf{p} \equiv (\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N)$$

Liouville operator:

$$iL = \{K, H\} = \sum_{i=1}^{N} \left[\overset{g}{\mathbf{r}_i} \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \frac{\partial}{\partial \mathbf{p}_i} \right]$$

The evolution of system from time *t*=0 to time *t* is given by :

$$\Gamma(t) = \exp(iLt)\Gamma(0)$$

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \qquad \dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{F}_i$$

Hamiltonian (conserved quantity):

$$H_{NVE} = K + U(\mathbf{r}) = \sum_i \frac{\mathbf{p}_i^{2}}{2m_i} + U(\mathbf{r})$$

❑ **MD method: Numerical solution of equations of motion.**

CG Projection operator: Mori – Zwanzig Formalism

❑ **Equations of motion in the CG scale become stochastic**

$z := \{z_1, z_2, ..., z_M\}$

➤ **Langevin dynamics (through Markovian approximation):**

$p := \{p_1, p_2, ..., p_M\}$

$$dz_i = M^{-1} p_i \, dt$$

$$dp_i = -\frac{\partial U^{CG}(z)}{\partial z_i} - \gamma M^{-1} p_i \, dt + \sigma \, dW$$

✓ $U^{CG}(z)$: **CG Interaction potential**

✓ **γ : friction**   **σ: diffusion**   **-- fluctuation-dissipation relation:** $\sigma \sigma^{tr} = 2\beta^{-1}\gamma$

✓ W: **3M-dimensional Brownian motion (white noise)**

❑ **Main challenges – Computation of:**

1) **CG interaction potential,** $U^{CG}(z)$

2) **CG friction, γ**

Effective CG Interaction Potential: Equilibrium Systems

❑ **In principle U^{CG} is a function of all CG degrees of freedom in the system and of temperature (free energy, potential of mean force U^{PMF}):**

$$U^{CG}(z) = U^{PMF}(z)$$

➢ **CG Hamiltonian – Renormalization Group Map:**

$$U^{PMF}(z) = -\frac{1}{\beta} \log \int_{\Omega(z)} e^{-\beta U(x)} dx, \quad \Omega(z) = \{x \in \mathbb{R}^{3N} : \xi(x) = z\}$$

❖ **Integral is over all atomistic configurations that correspond to a specific CG (3M-dimensional one**

❑ **$U^{PMF}(z)$ is NOT possible to be calculated exactly. Typical approximation:**

$$U^{PMF}(z) = \sum_{i<j} W_2(r_{ij}) + \sum_{i<j<k} W_3(r_{ij}, r_{ik}, r_{jk})$$
$$+ \sum_{i<j<k<l} W_4(r_{ij}, r_{ik}, r_{il}, r_{jk}, r_{jl}, r_{kl}) + \dots$$

$$r_{ij} = |z_i - z_j|$$

Equilibrium CG Models: Hybrid Polymer/Solid Interfaces

❑ **Development of PMF between CG beads through DBI and IBI methods**

❑ Remember: CG superatom / Au interaction potential includes **entropic effects**.

❑ Several issues can be considered:

➢ **Position of CG beads**

➢ **Tacticity**

➢ **Effect of chain ends**
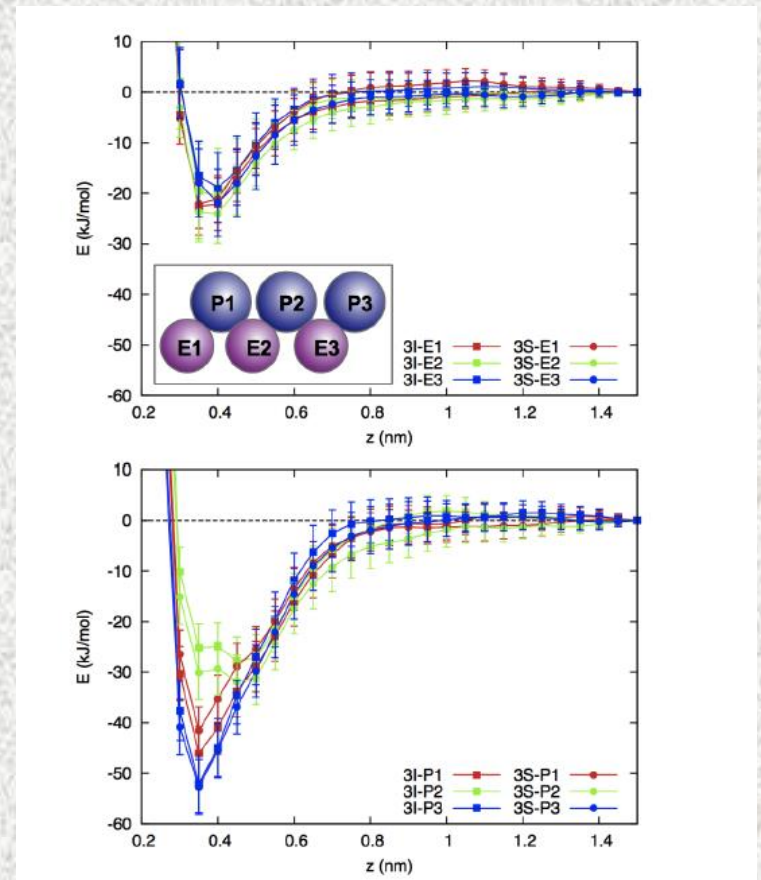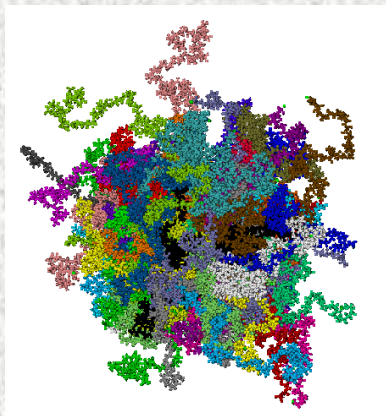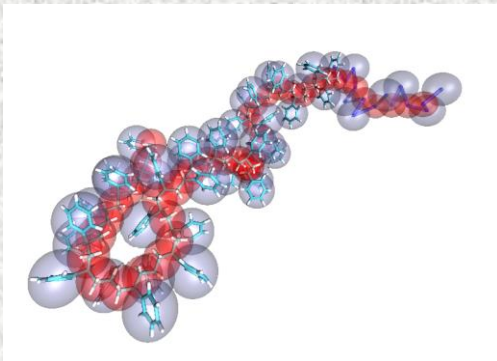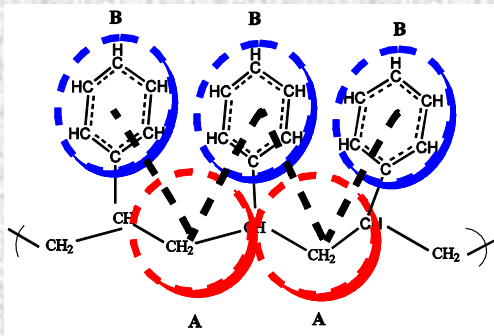
Polystyrene/Au Systems: Width of the Interface

❑ **Dependence of the interphase width on chain length using density, bond order, and conformation tensor profiles**
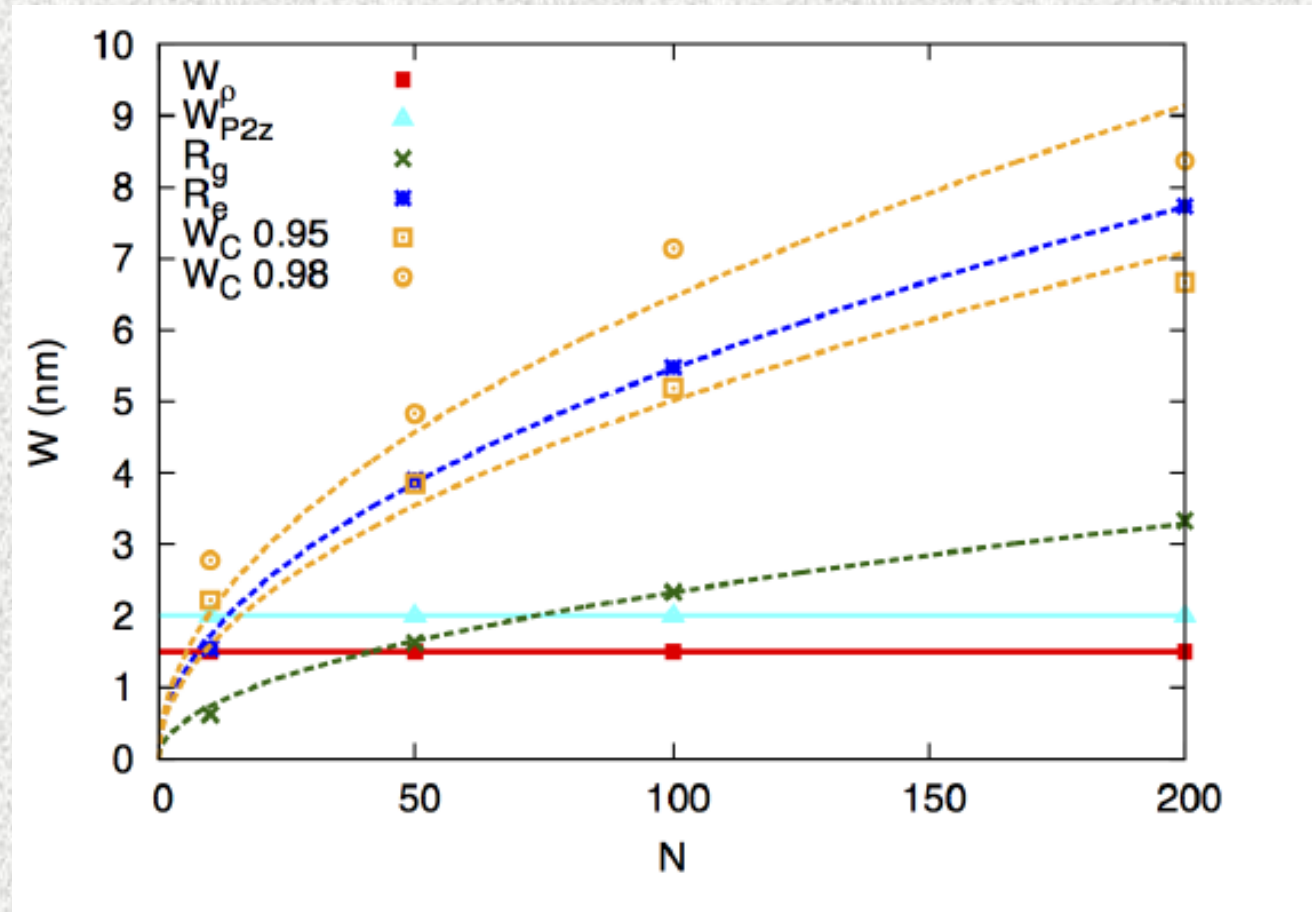
➤ **Dashed lines are fits to the data of the form:** $W \sim N^{1/2}$

- **Model: All-atom model** (OPLS-AA) of PE chain adsorbed on graphene.

- **Perfect 2D single-chain polymer crystal**

- **Crystallization process:**

Single-chain Polymer Crystal Adsorbed on Graphene

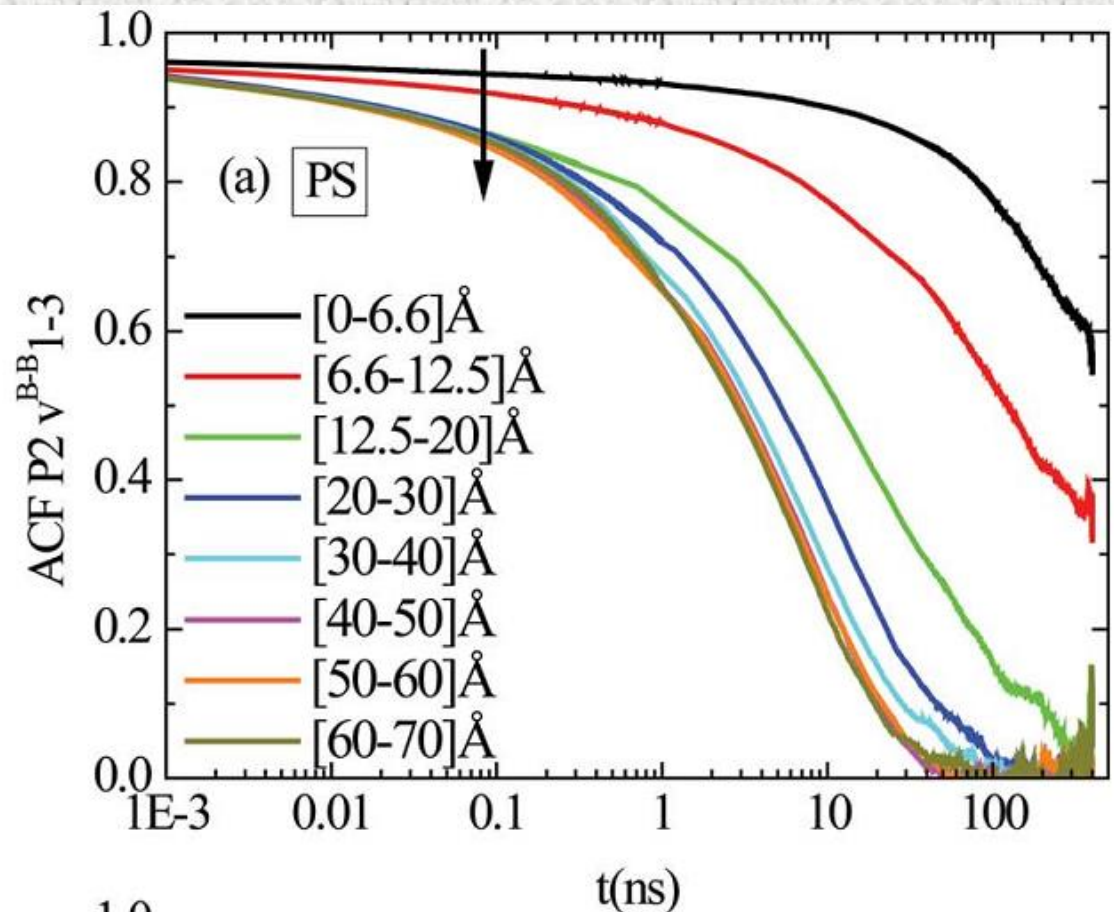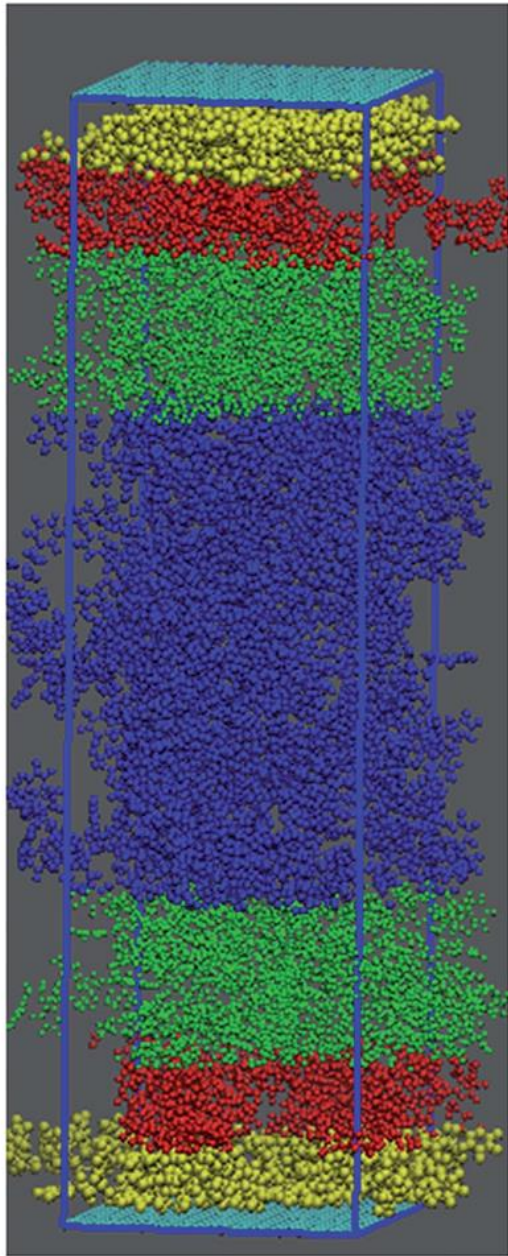❏ **Polymer configuration at** **thermal equilibrium**

❑ **Heated Graphene (T=650K): Temporal evolution of polymer conformation**
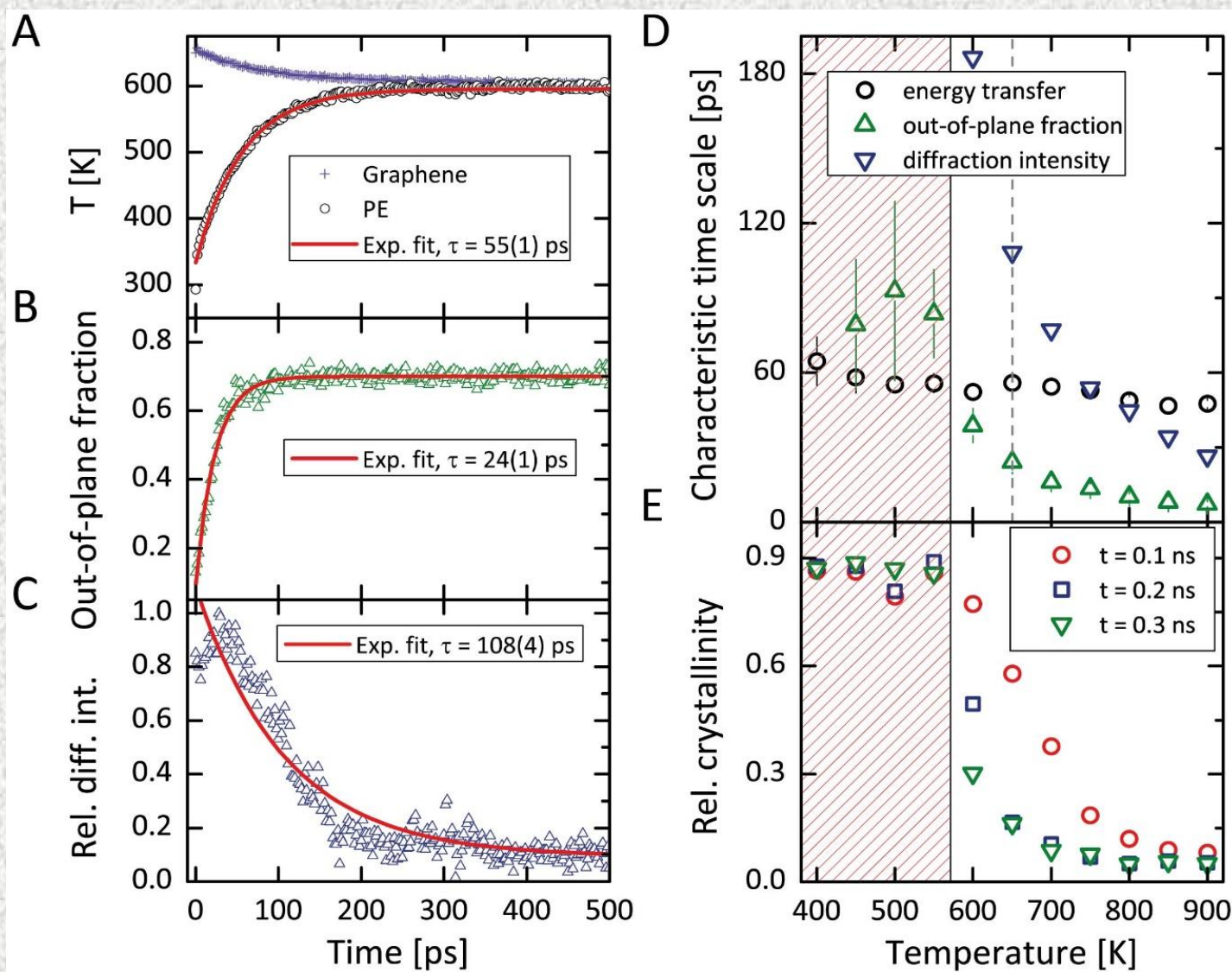
Polymer (PS) confined between Graphene: Local Dynamics

$$P_2(t) = \frac{3}{2} \langle \cos^2 \theta(t) \rangle - \frac{1}{2}$$

Regions of different mobility

Absolute segmental displacement d at time $t = 1$ ns

- d<0.5nm
- d<0.7nm
- d<0.9nm
- d>0.9nm

COOH

H
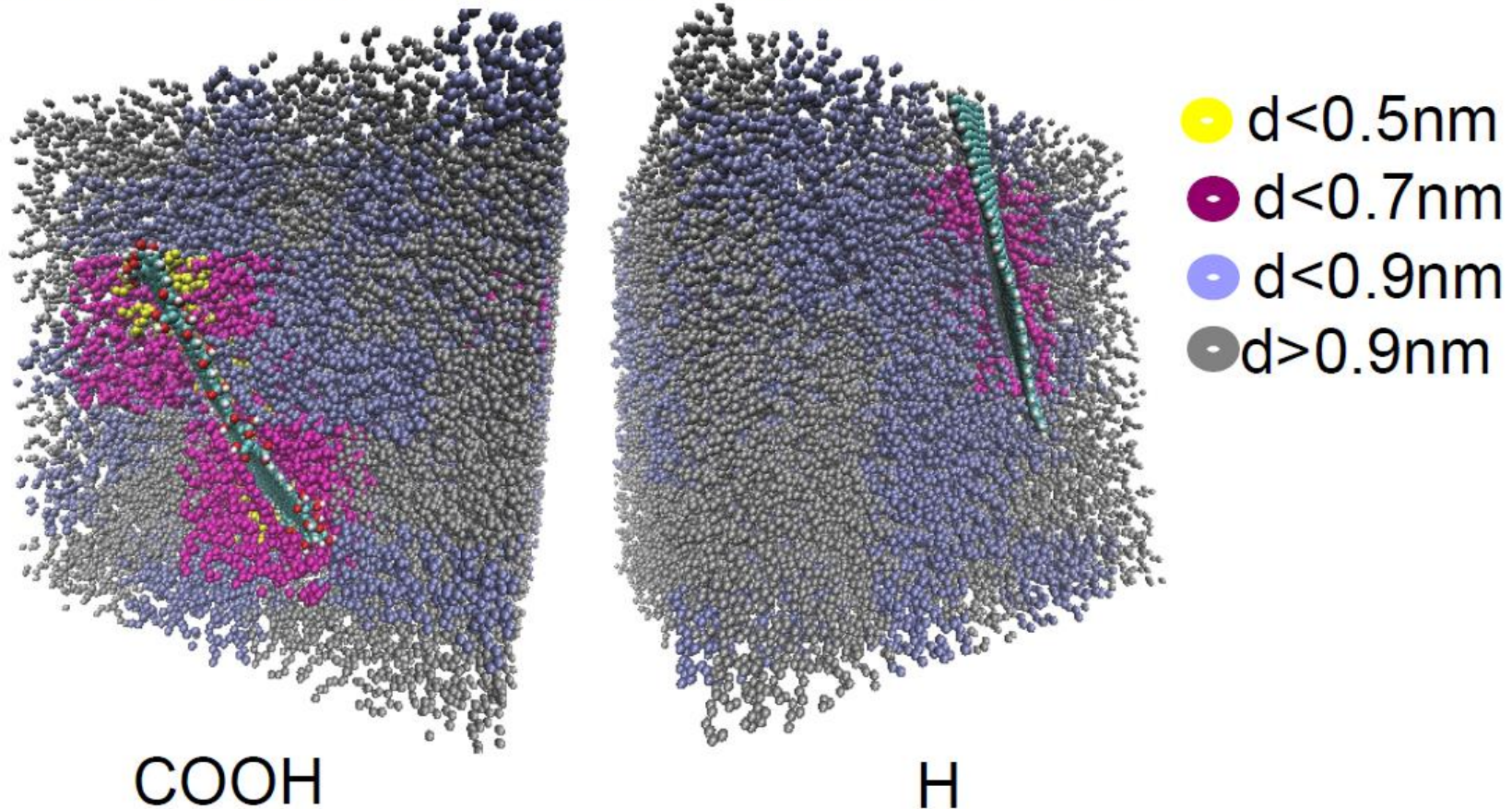
$\Rightarrow$ effect of the surface on the segmental dynamics in its vicinity
$\Rightarrow$ effect of the interaction of COOH-edges with polymer matrix

[C. Baig and VH, Macromolecules, 43, 3156 (2010)]

➢ **Non-equilibrium molecular dynamics (NEMD): modeling of systems out of equilibrium - flowing conditions.**

➢ **NEMD: Equations of motion in canonical (NVT) ensemble (Nose-Hoover)**

C. Baig et al., *J. Chem. Phys.*, 122, 11403, 2005]

$$\dot{\mathbf{q}}_i = \mathbf{p}_i \qquad \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u} - m_i \mathbf{q}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} - \frac{p_\zeta}{Q} \mathbf{p}_i$$
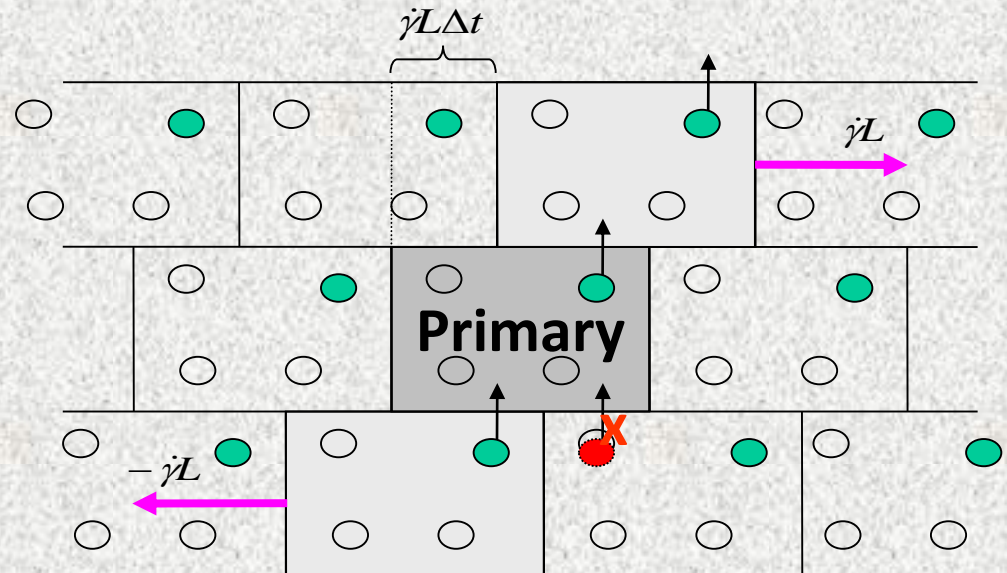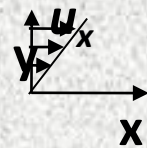
$$\dot{\zeta}_i = \frac{p_\zeta}{Q} \qquad \dot{\mathbf{p}}_\zeta = \sum_i \frac{\mathbf{p}^2_i}{m_i} - 3Nk_BT$$

Lees-Edwards Boundary Conditions

simple shear flow

$$\dot{\gamma} = \frac{\partial u_x}{\partial y}$$

$$\nabla \mathbf{u} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

➢ **CG NEMD - Remember:** CG interaction potentials are calculated as potential of mean force (they include entropy). In principle $U^{CG}(x,T)$ should be obtained **at each state point**, at each flow field.
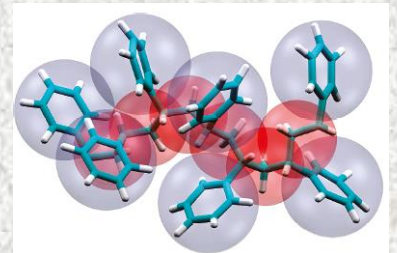

❑ **Critical question:** How well polymer systems under **non-equilibrium** (flowing) conditions can be described by **CG models developed at equilibrium**?

Method:

[C. Baig and V. Harmandaris, Macromolecules, 43, 3156 (2010)]

➡ Use of existing **equilibrium** CG polystyrene (PS) model.

➢ Direct comparison between atomistic and CG NEMD simulations for various flow fields. **Strength of flow** (Weissenberg number, W_i = 0.3 - 200)
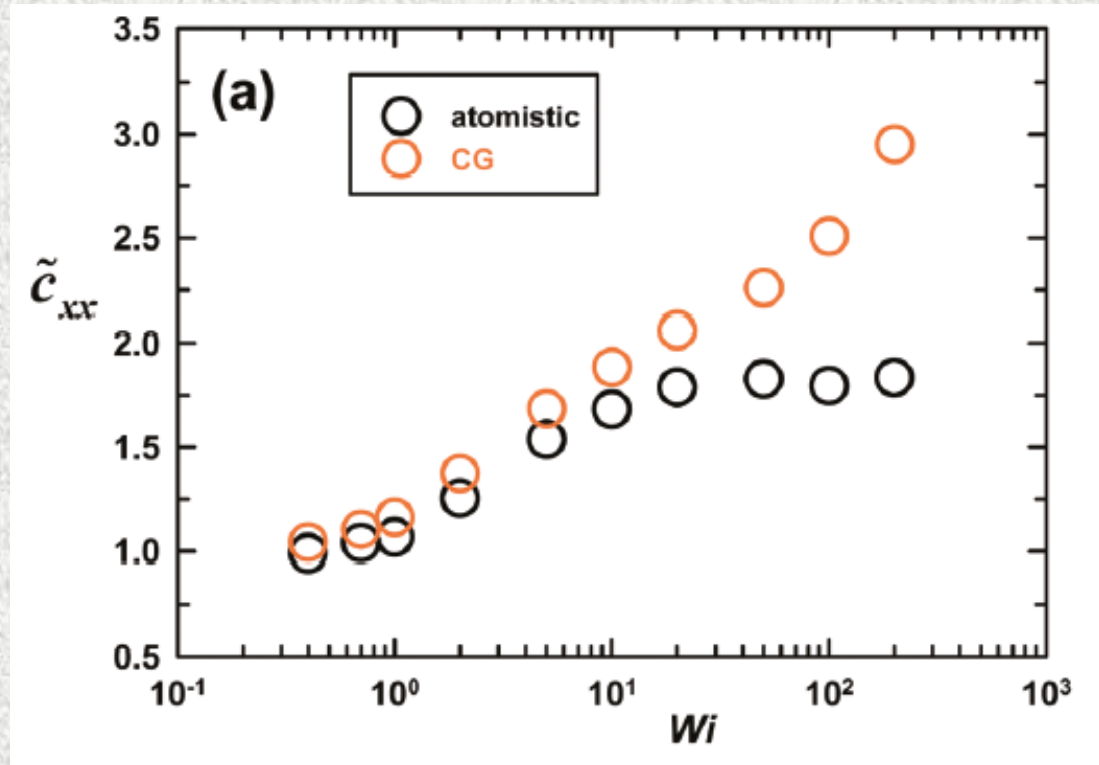
$$Wi \equiv \lambda \dot{\gamma}$$

➢ Study short atactic PS melts (M=2kDa, 20 monomers) by **both atomistic and CG NEMD simulations.**

CG Non-Equilibrium Polymers: Conformations

➤ **Properties as a function of strength of flow** (Weissenberg number) $\quad Wi \equiv \lambda \dot{\gamma}$

➤ **Conformation tensor**

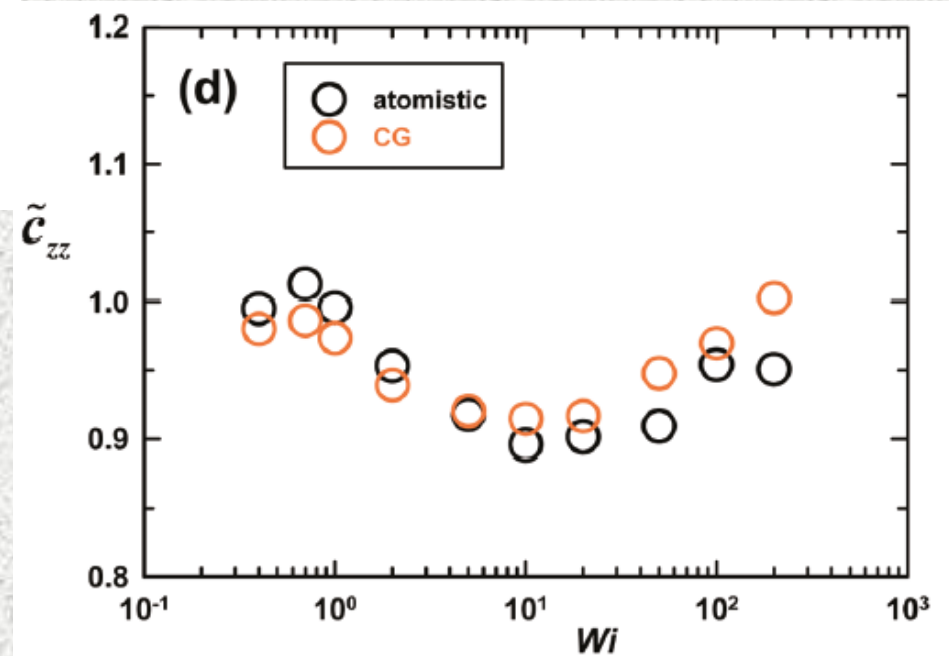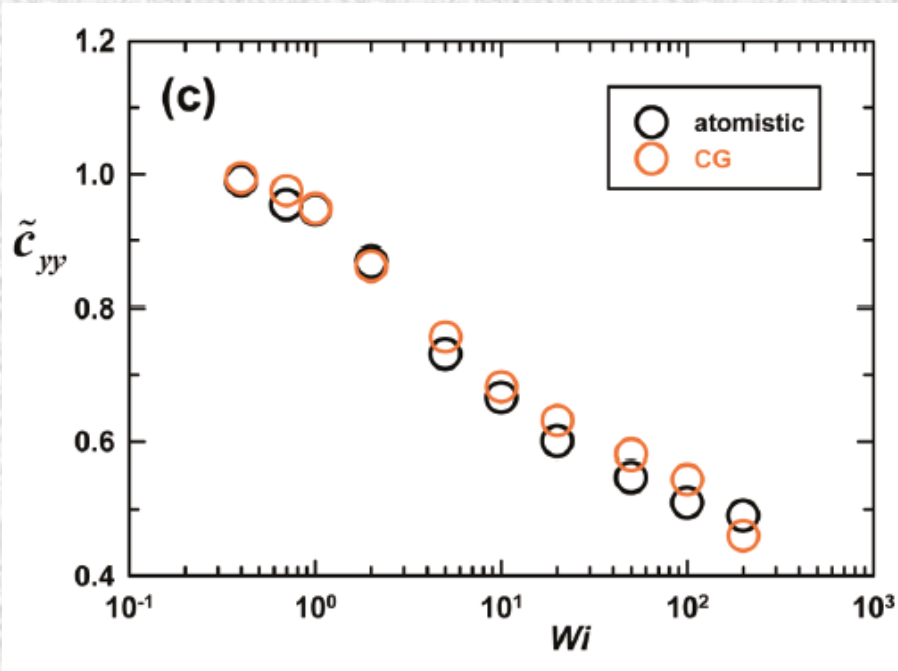$$c_{\alpha\beta} \equiv \frac{3\langle R_\alpha R_\beta \rangle}{\langle R^2 \rangle_{eq}}$$

➤ **Atomistic c$_{xx}$:** asymptotic behavior at high W_i because of (a) finite chain extensibility, (b) chain rotation during shear flow.

➤ **CG c$_{xx}$:** allows for larger maximum chain extension at high W_i because of the **softer interaction potentials**.

CG Non-Equilibrium Polymers: Conformation Tensor

➢ c_{yy}, c_{zz}: excellent agreement between atomistic and CG configurations.
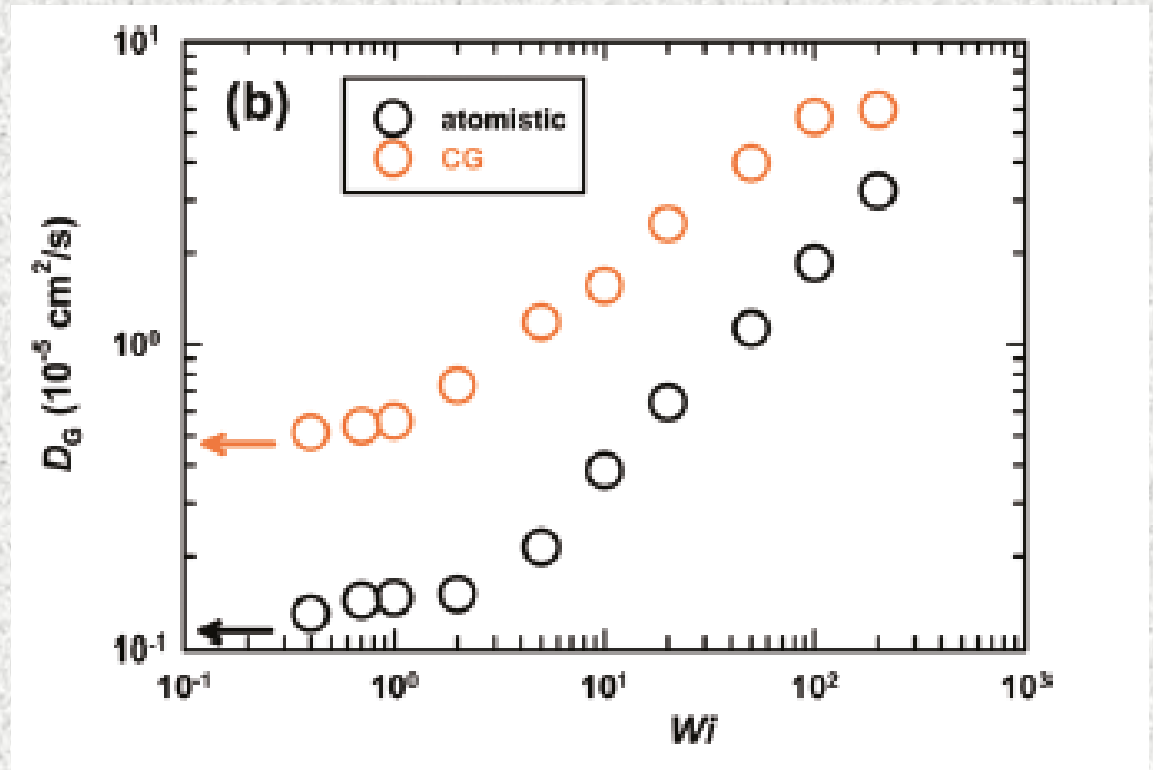
CG Non-Equilibrium Polymers: Dynamics

➢ **Is the time mapping factor similar for different flow fields?**

[C. Baig and VH, Macromolecules, 43, 3156 (2010)]

<p align="center">**Translational motion**</p>

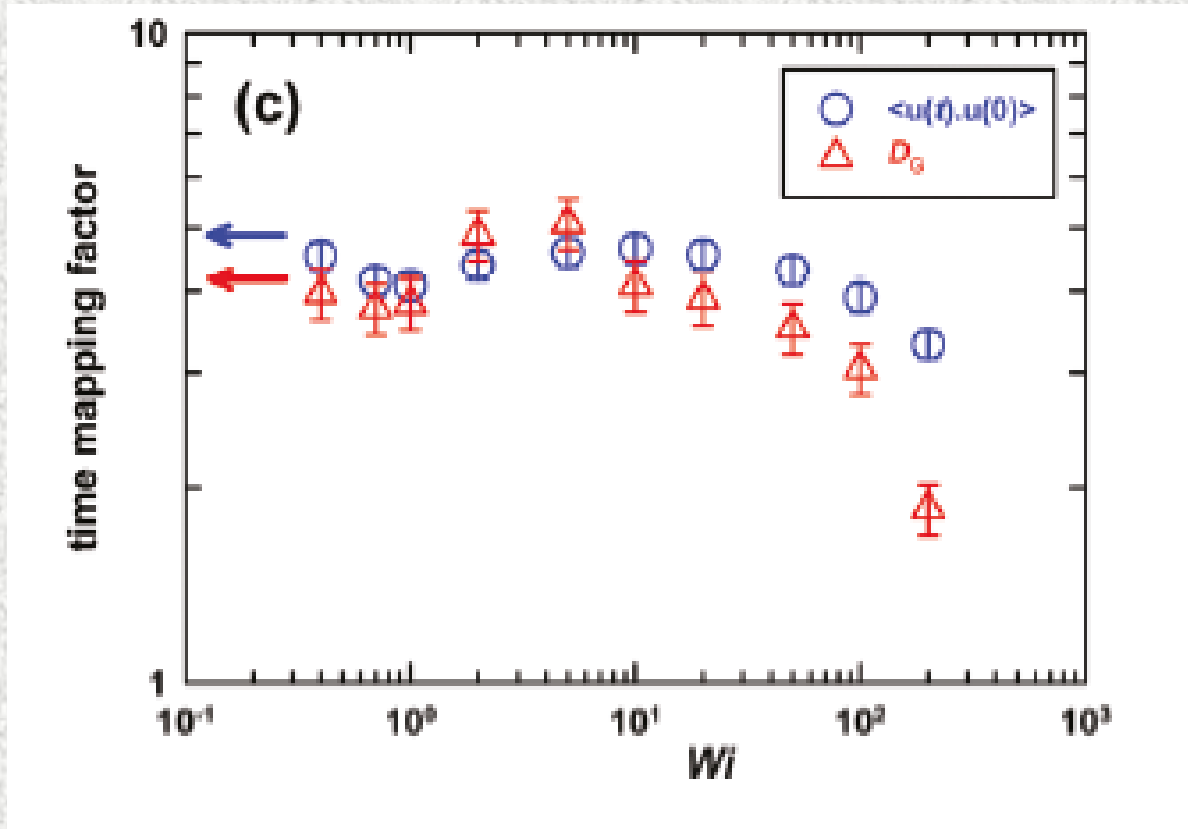➢ **Purely convective contributions from the applied strain rate are excluded.**

➢ **Very good qualitative agreement between atomistic and CG (raw) data at low and intermediate flow fields.**

CG Non-Equilibrium Polymers: Dynamics

➢ **Time mapping parameter as a function of the strength of flow.**

➢ **Strong flow fields:** smaller time mapping parameter ⮕ effective CG bead friction decreases less than the atomistic one.

Reason: CG chains become more deformed than the atomistic ones.