



DFG

Polymer Dynamics in confinement:

Molecular Dynamics simulations of 1,4-polybutadiene at a graphite interface.

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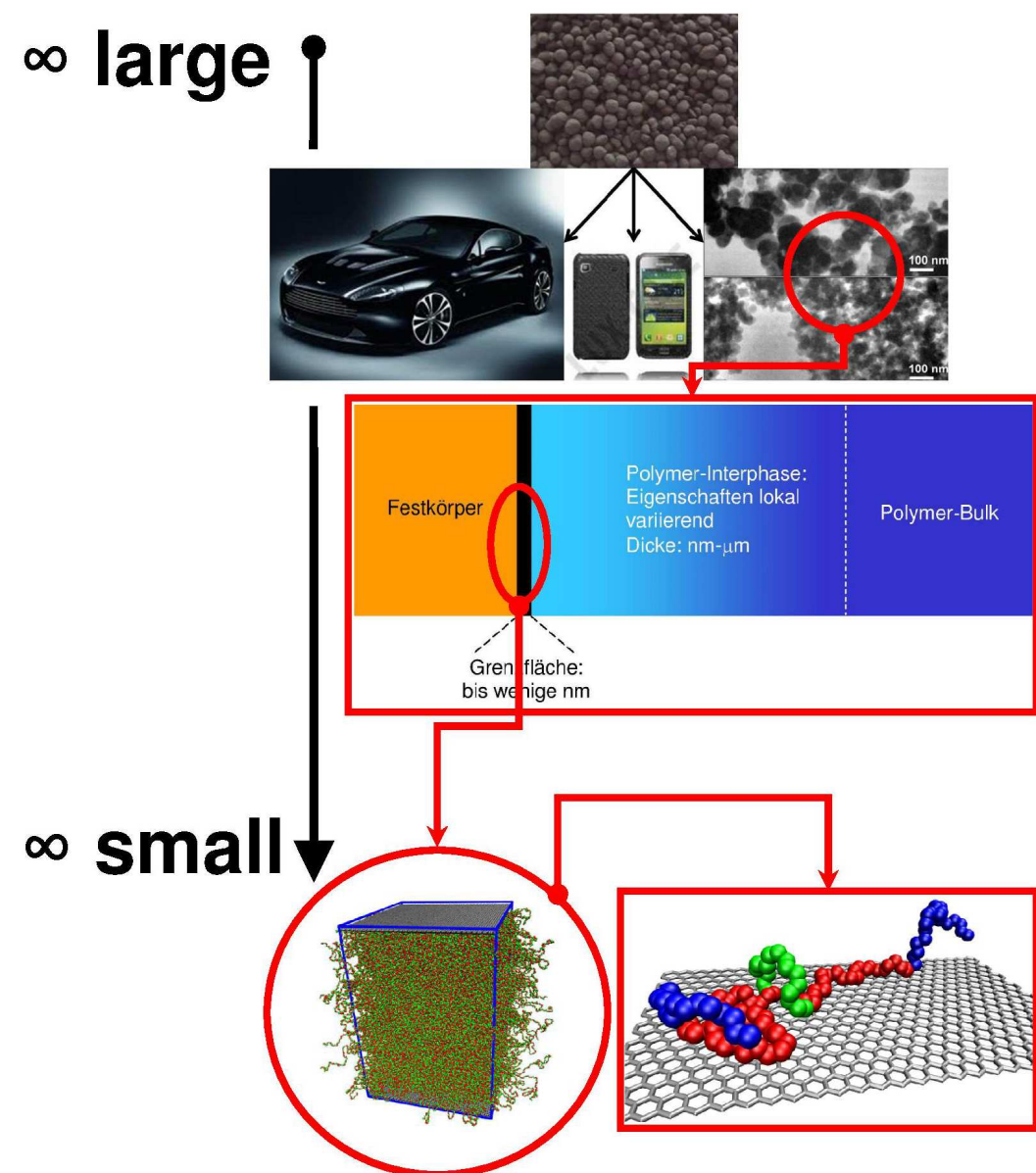
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Abstract: Polymer dynamics in confinement is both of fundamental interest concerning our understanding of the glass transition, as well as of high technological importance for the performance of composite materials. The results here presented are concerned with atomistic MD simulations of a chemically realistic model of a 1,4-polybutadiene melt (55% trans and 45% cis content in a random sequence) confined between two walls of graphite. The focus of our study is to investigate to what extent the walls are influencing structure and dynamics of the melt. The physical properties here investigated are concerned with the structure and the topology of the chains in the confined melt, but also with various experimentally accessible relaxation processes. We computed, e.g., the dielectric properties from the segmental motions, assuming that these single dipole moments relax independently and compare with dielectric experiments on similar confined polymers. This comparison provides convincing evidence that atomistic simulations are able to reproduce results in good agreement with experimental conclusions. The results presented are a key to a better understanding of the glass transition process in a confined polymer system.

Motivations



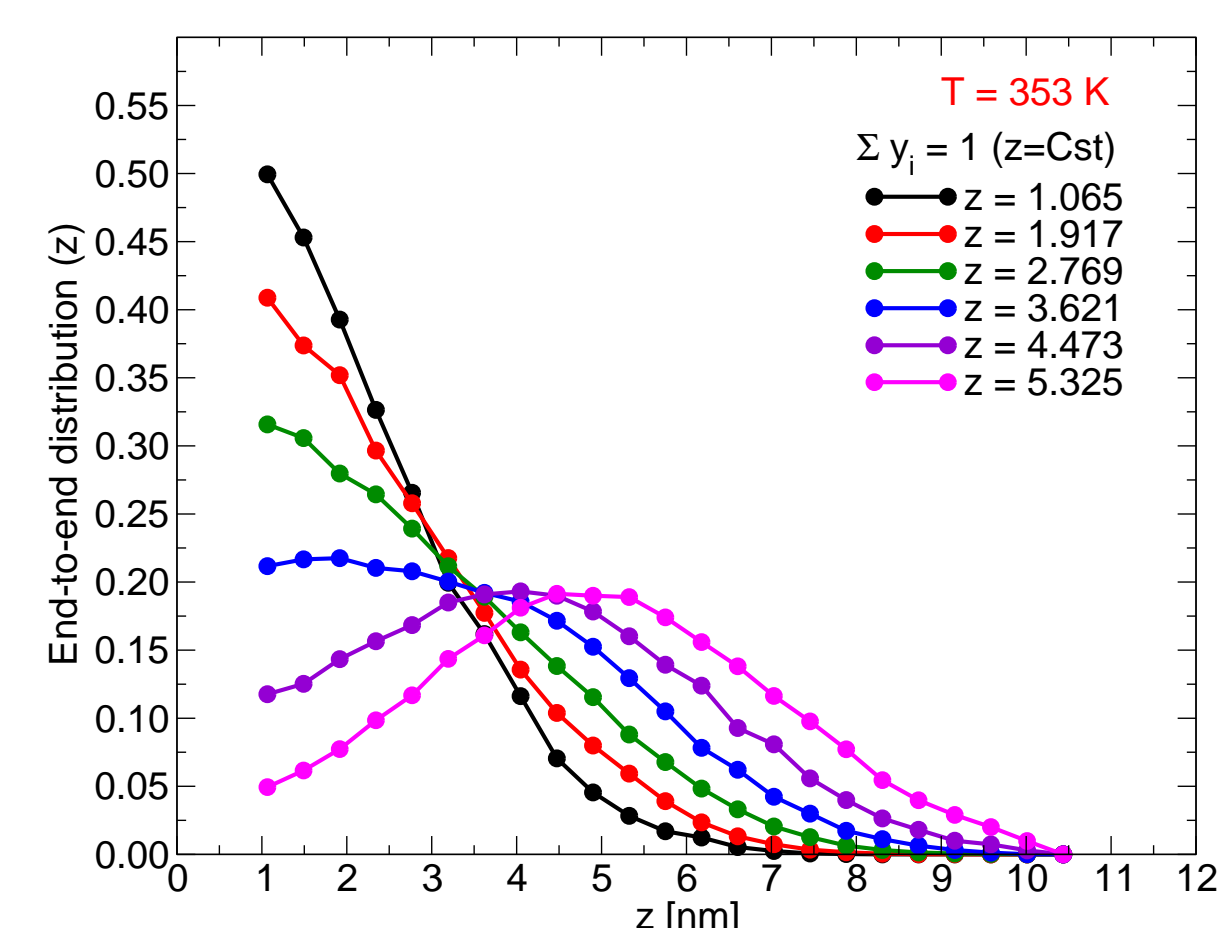
Methodology & Models

- MD simulations with Gromacs package.
- Long runs: ≥ 1 μ s.
- NVT system and PBC in x , y and z .
- 1,4-polybutadiene melt using model in [1].
- 55[%] trans and 45[%] cis content.
- Melt: chains of 116 particles.
- Glass transition: $T_g = 180$ [K].
- Size: chain nb. 720 (small) - 1440 (large).
- Walls: 3 layers (≈ 23 364 C atoms).
- T : 213 $\approx 1.2T_g$ to 353 $\approx 2T_g$ [K].

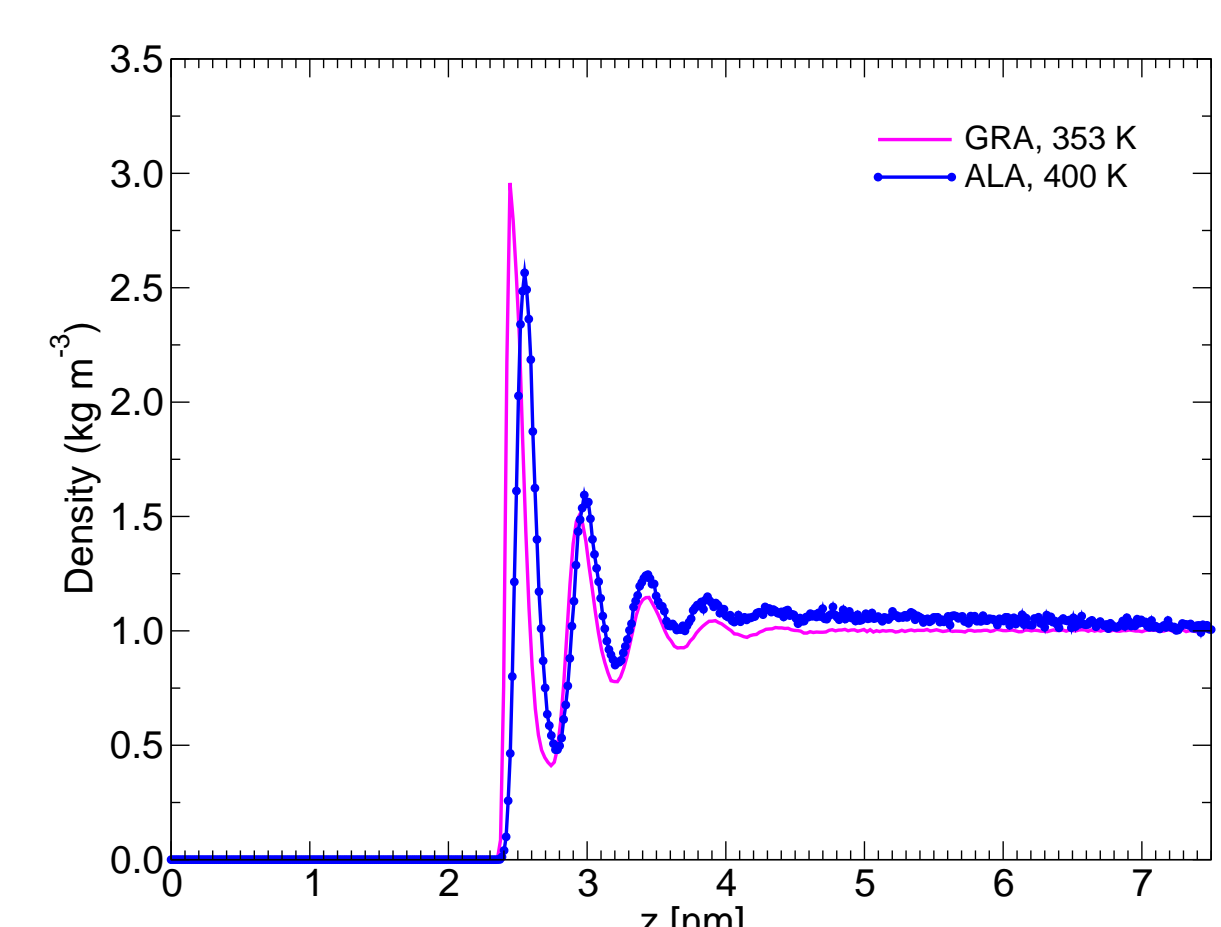
Conclusion & Outlooks

We would like to analyze the distribution of length for trains, tails, loops or end-to-end distance at the interface. In addition, investigations on the adsorption kinetics may provide a better comprehension of the specific relaxation process observed for several quantities like segmental motions. Alumina surfaces are being in preparation.

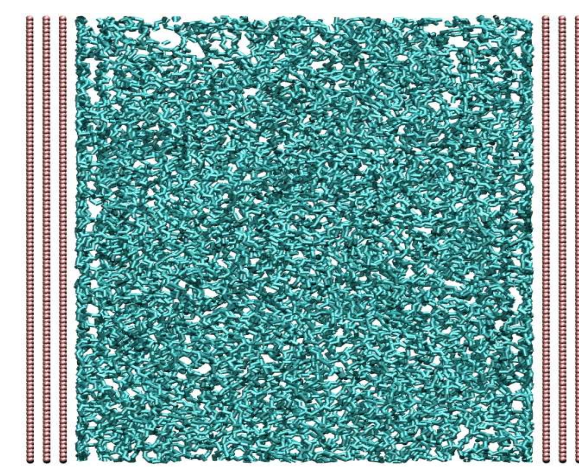
Title: probability for the chain-end position.



Title: density profiles for GRA & ALA.

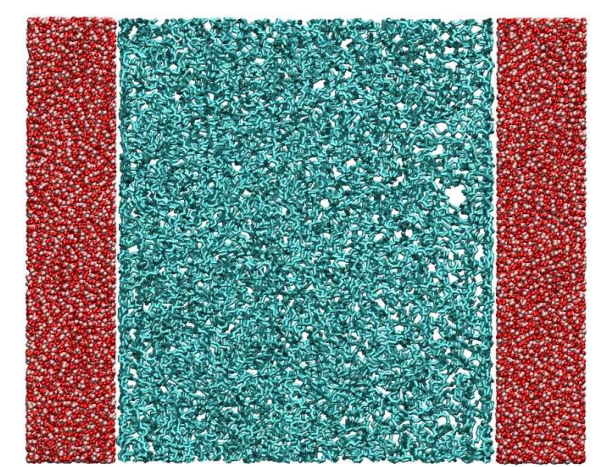


DFG Priority Program, SPP 1369 - Polymer Solid Contacts: Interfaces and Interphases.



GRAPHITE

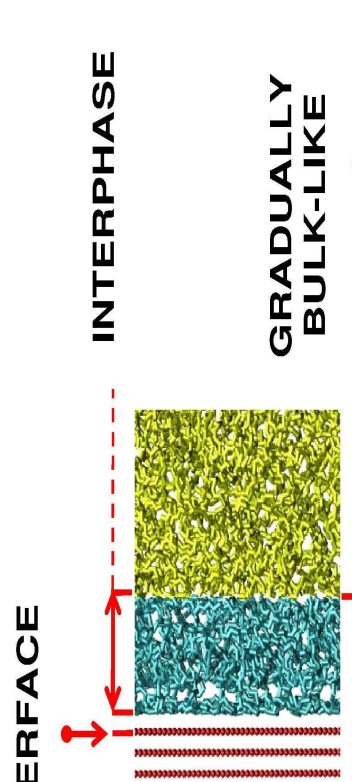
- Composite Materials: solid (nano-)particles embedded into a polymer matrix or nanopores (e.g., AAO nanopores).
- **Interphase** polymer & solid: a fitting construct to reproduce macroscopic (e.g., mechanical properties) by a 3 phase model.
- **Interphase** polymer & solid: presumably the chains adopt a different topology than in the bulk (tails, trains, loops *vs.* none-adsorbed chains).
- Simulations of polymer systems: confinement between two crystalline walls.



ALUMINA

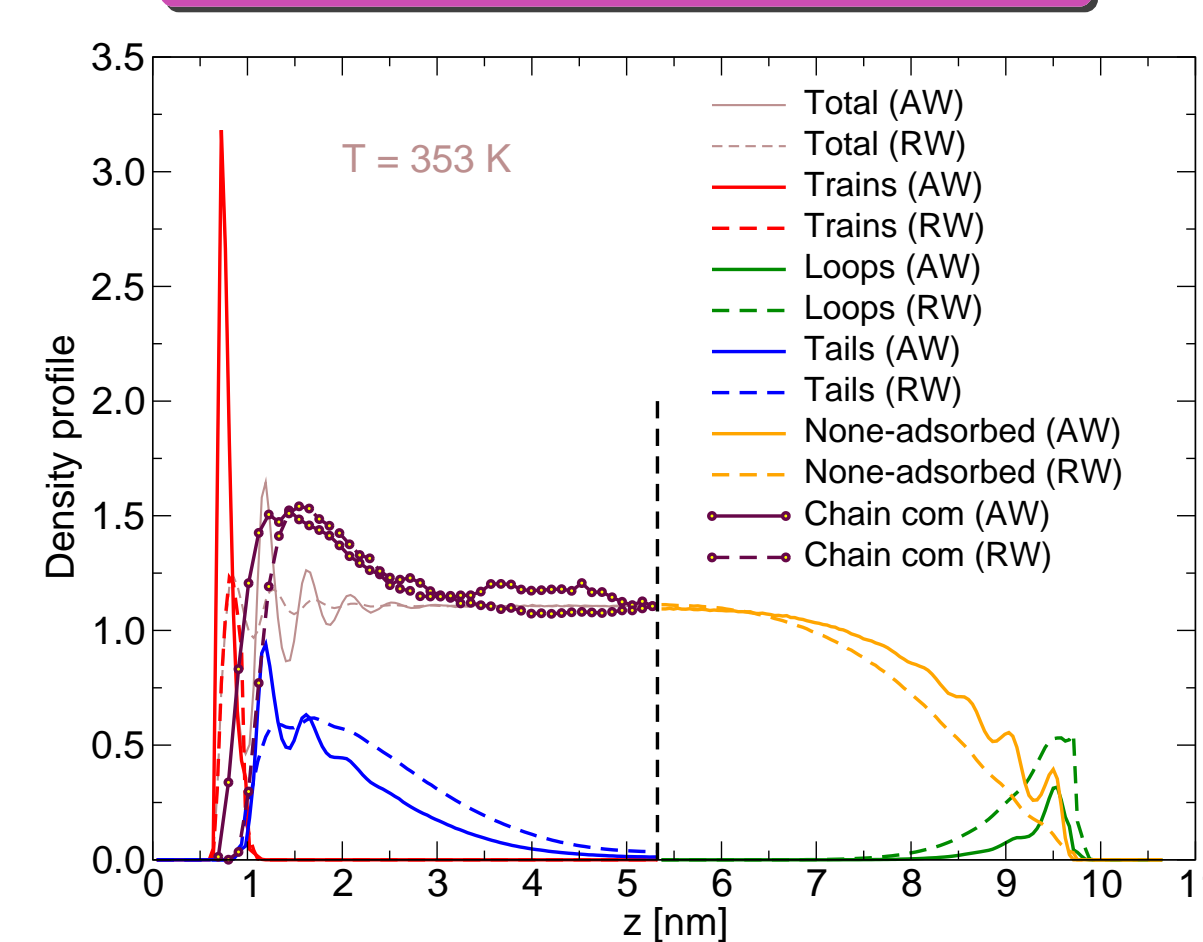
Questions

- How is the relaxation behavior modified at a solid interface?
- What is the chain topology at a solid interface?



- How a chain is adsorbed/desorbed at a solid interface?
- The dynamics and structure are not homogeneous.
- **Properties:** vary systematically as a function of the distance from the solid surface (layering).

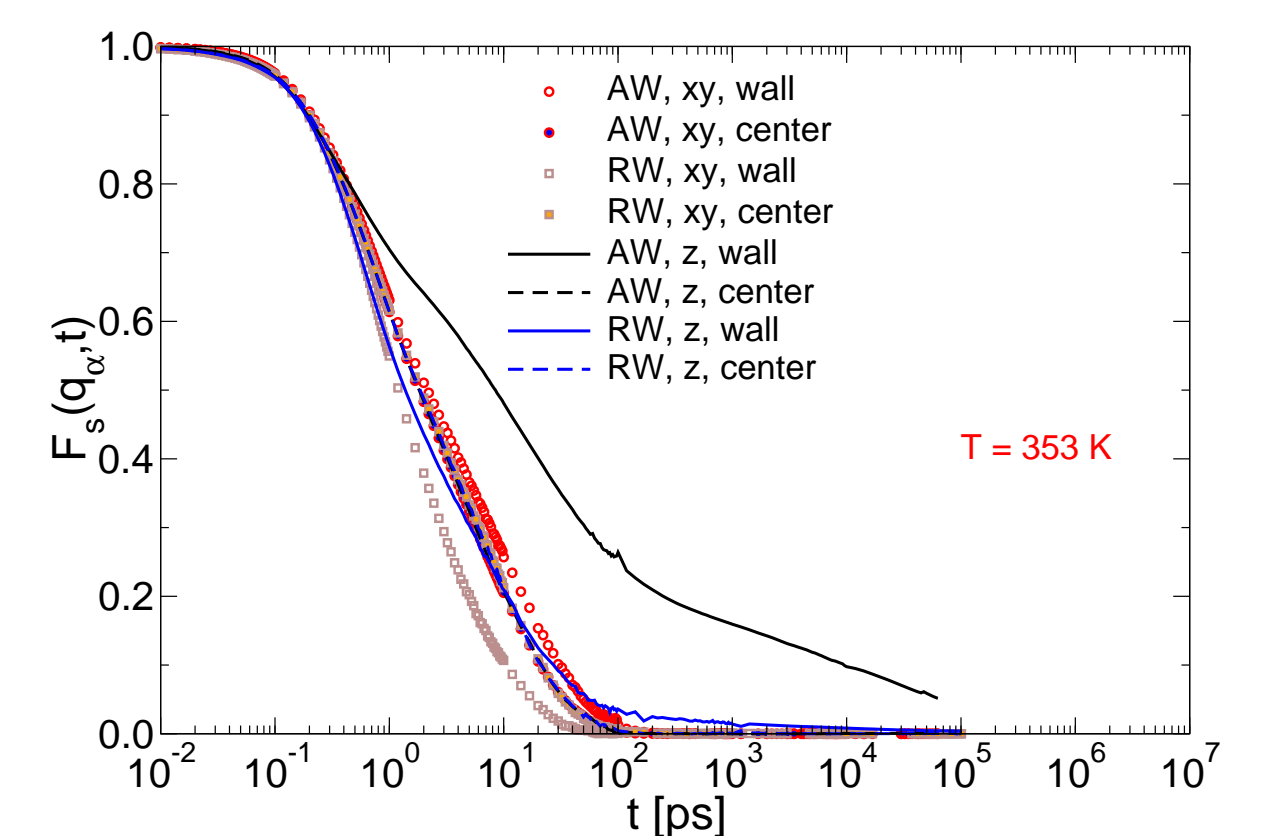
Chain topology



Keywords: AW = Attractive Walls; RW = Repulsive walls.

Comments: layering in the structure; $L \approx 2.5$ [nm]; bulk density at the center; peak (com) at ≈ 1.5 [nm] $\approx R_g$ [nm] (see Ref. [2]).

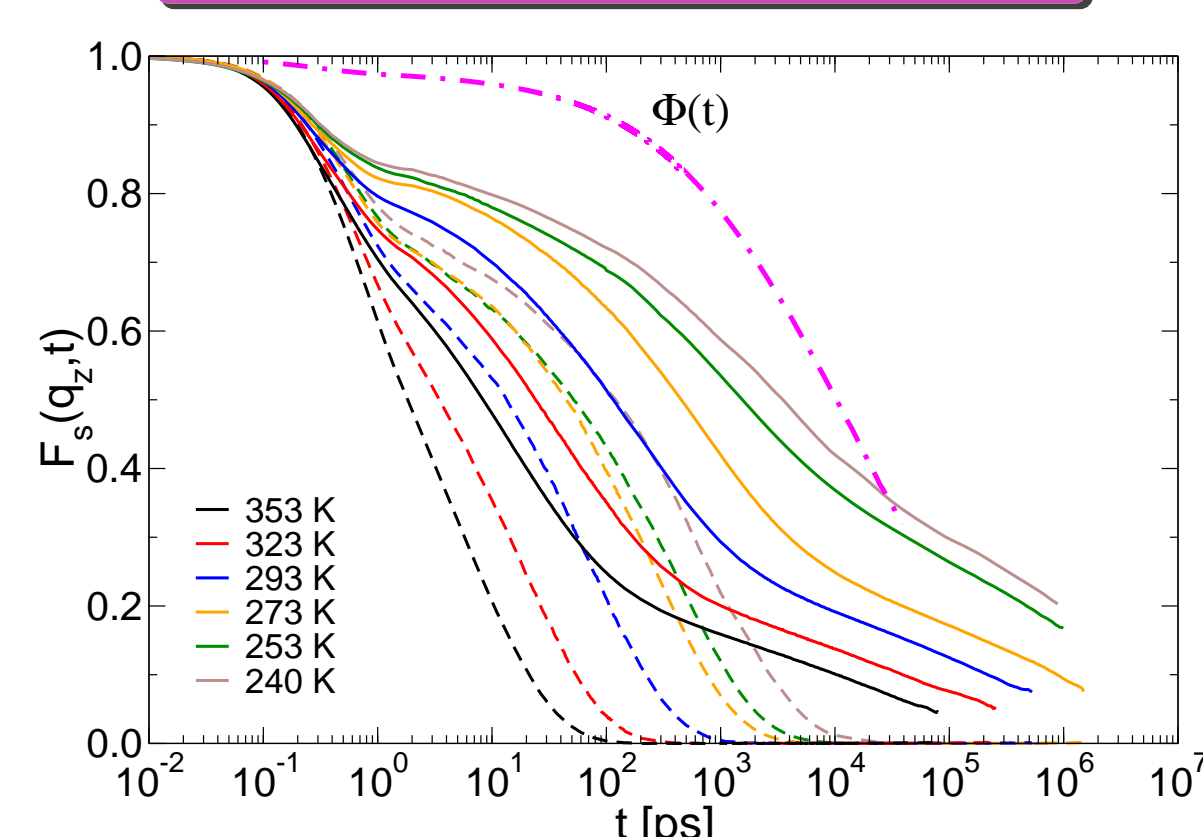
Realistic interface



Keywords: Incoherent scattering function; Full lines = Wall layer; Dashed lines = Center layer.

Comments: momentum transfer $q_a = 12$ [nm⁻¹], oriented parallel or perpendicular to the walls; three-step relaxation decay; it originates in the van der Waals interactions (realistic interface).

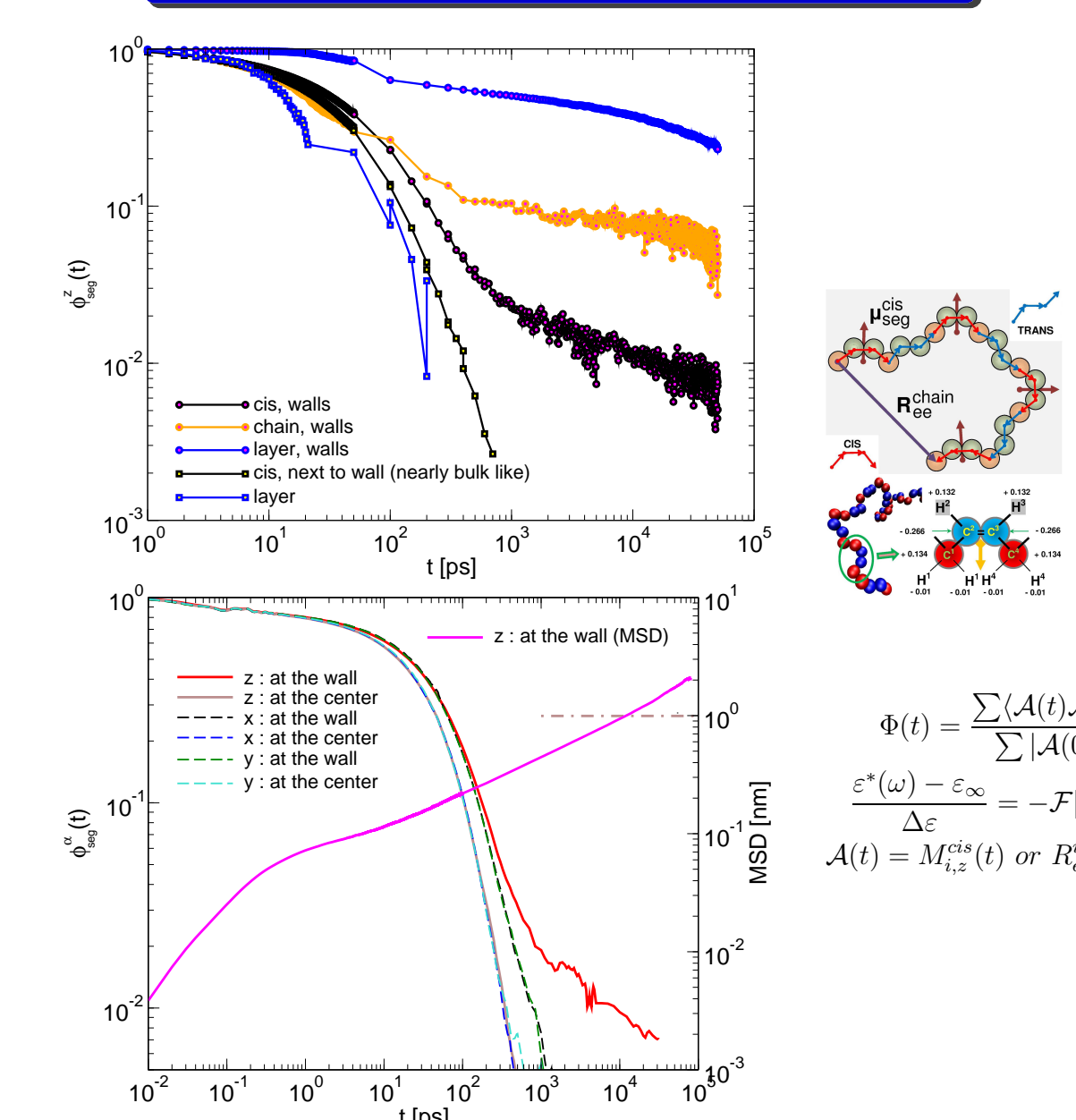
Incoherent scattering



Keywords: Incoherent scattering function; Full lines = Wall layer; Dashed lines = Center layer; Dotted magenta line = ACF ($\Phi(t)$) of monomer adsorption (see Ref. [3]).

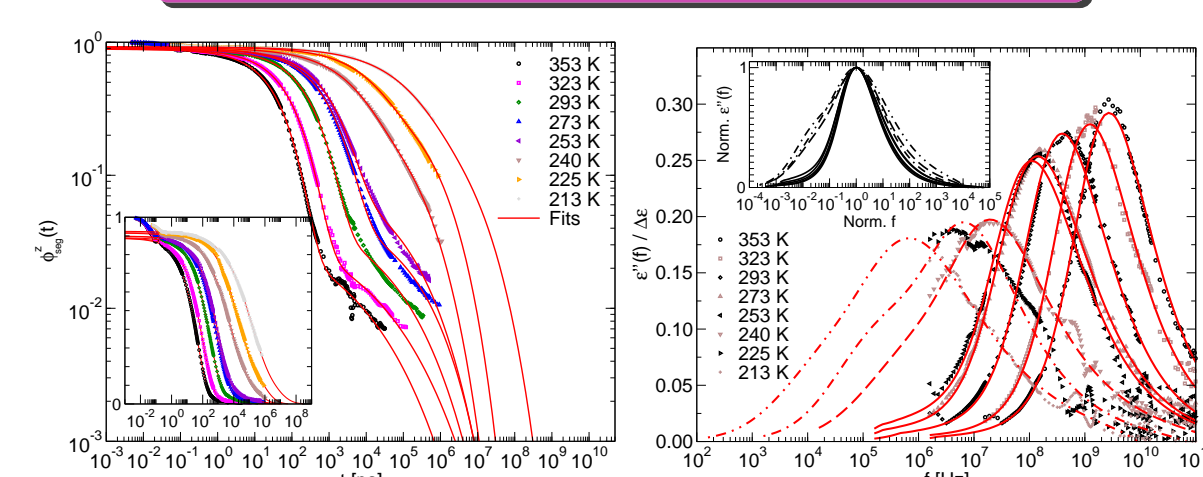
Comments: $q_a = 12$ [nm⁻¹], oriented perpendicular to the walls; three-step relaxation decay; first decay = vibrational decay; second decay = α -transition process; third decay = desorption process.

Dielectric properties



Keywords: CIS dipole moment motions = Segmental mode relaxation dynamics; End-to-end vector motions = Normal mode relaxation dynamics (see Ref. [4]); Analysis in the z direction = Influence of confinement.

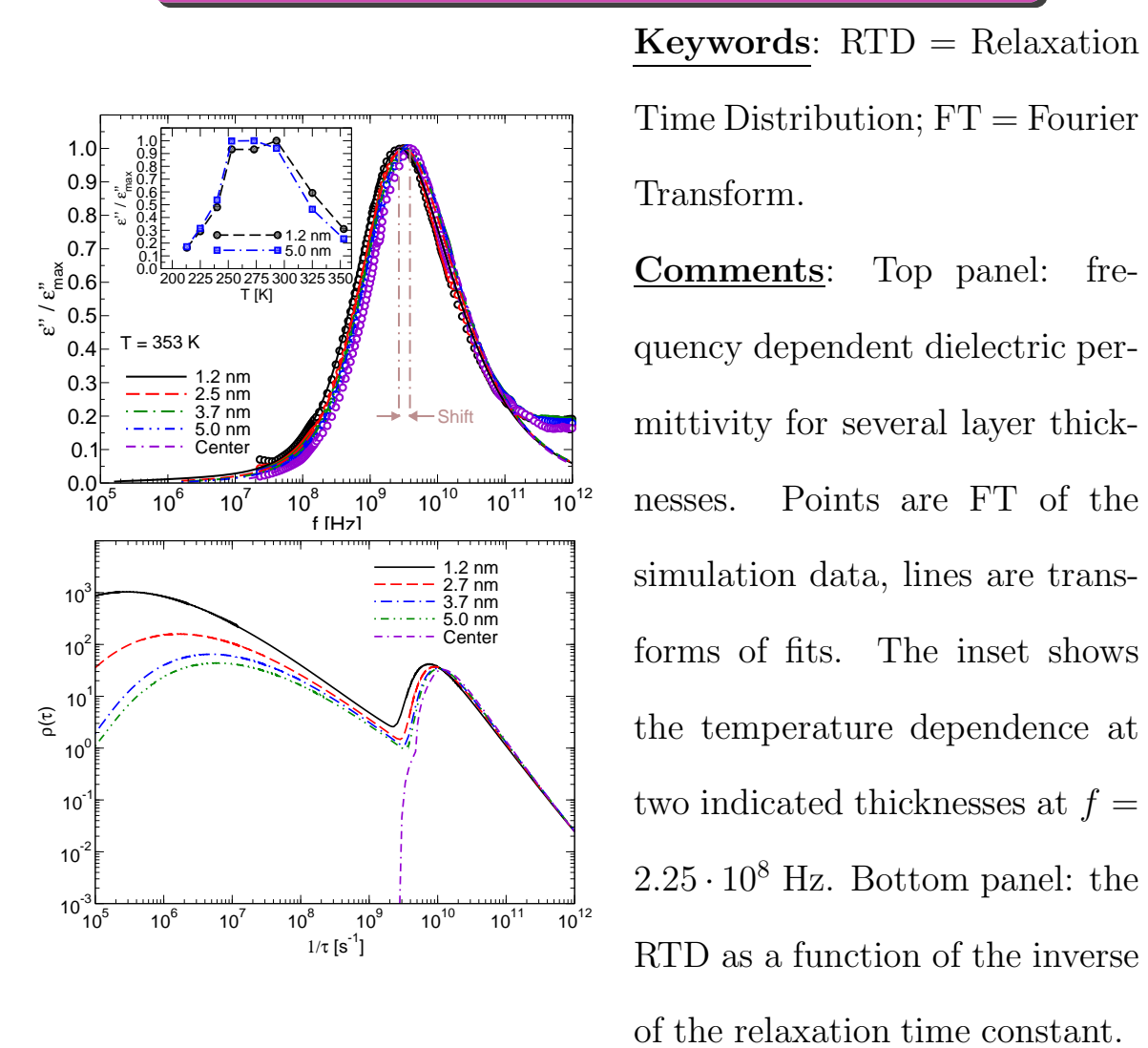
Segmental motion: T



Keywords: Time domain (left); Frequency domain (right).

Comments: left panel \rightarrow the relaxation functions were computed for a layer of width 1.2 nm next to the walls. A functional form, made of the sum of two stretched exponentials, was fitted to the data (red full lines). Right panel \rightarrow temperature dependence of the dielectric loss for the layer next to the wall. Inset: scaled representation of the same data showing a broadening of the frequency spectra at low temperatures.

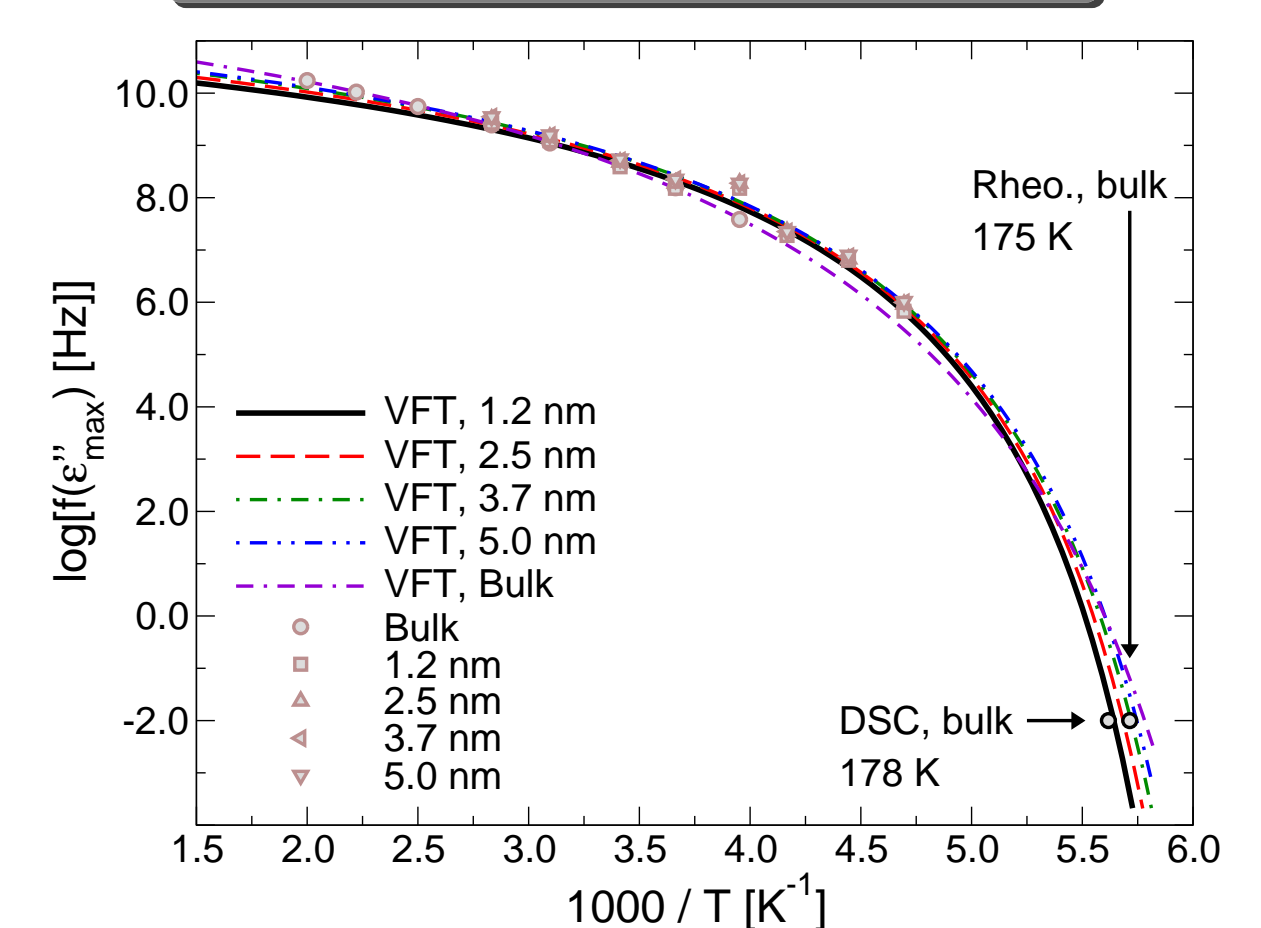
Segmental motion: z



Keywords: RTD = Relaxation Time Distribution; FT = Fourier Transform.

Comments: Top panel: frequency dependent dielectric permittivity for several layer thicknesses. Points are FT of the simulation data, lines are transforms of fits. The inset shows the temperature dependence at two indicated thicknesses at $f = 2.25 \cdot 10^8$ Hz. Bottom panel: the RTD as a function of the inverse of the relaxation time constant.

Relaxation map



Keywords: VFT fits; bulk dynamic T_g .

Comments: no T_g shift for confined polymer [7, 8], as suggested by the literature on dielectrics spectroscopy experiments [5, 6].

Some references:

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- [8] M. Solar, K. Binder and W. Paul, Advance in Dielectrics, edited by Prof. F. Kremer in Edition.

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