Toward a quantitative study of confined polymers by dissipative particle dynamics simulations

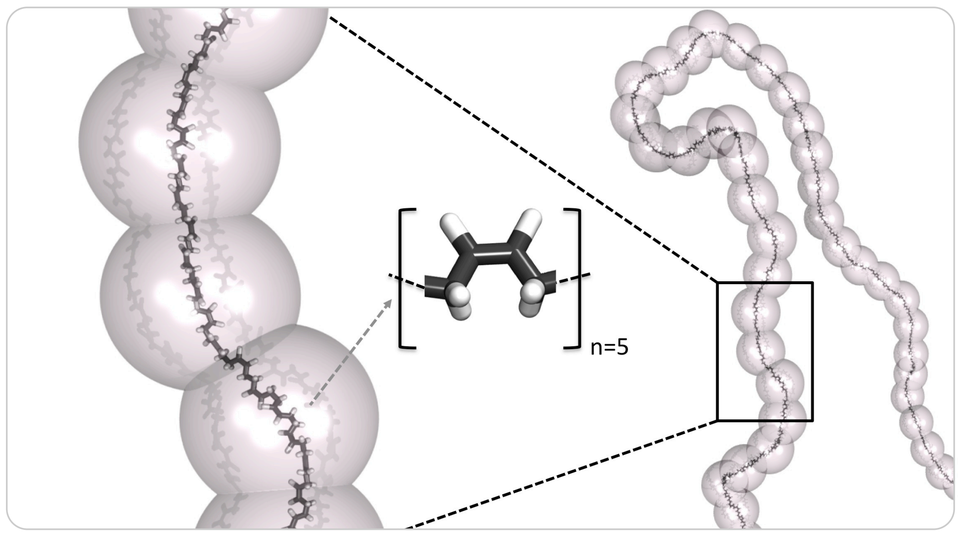
G. Maurel[†‡], B. Schnell[†], F. Goujon[‡], M. Couty[†] and P. Malfreyt[‡]

[†] Manufacture Française des Pneumatiques MICHELIN, Centre de Ladoux, 23 place des Carmes, 63000 Clermont-Ferrand, France
[‡] Institut de Chimie de Clermont-Ferrand, ICCF, UMR CNRS 6296, Université Blaise Pascal, 63177 Aubière Cedex, France

Institut de Chimie de Clermont-Ferrand

Filled elastomers systems are extensively used in the rubber industry, not only for the reinforcement of the polymer matrix but also to reduce the cost of the final product. Nevertheless, an accurate description of mechanisms that are associated to this reinforcement is still missing.

A way of considering the polymer-filler interaction is to use current simulation tools to study the motions of such a system. However, polymeric systems have various kind of motions and a multiscale approach is required to sample the largest length and time scales. Microscopic simulations using atomistic models (Molecular Dynamics) are used to perform the calculation of potentials of mean force. These potentials can be used to describe polymer-filler interaction at a mesoscopic scale using the Dissipative Particle Dynamics (DPD).



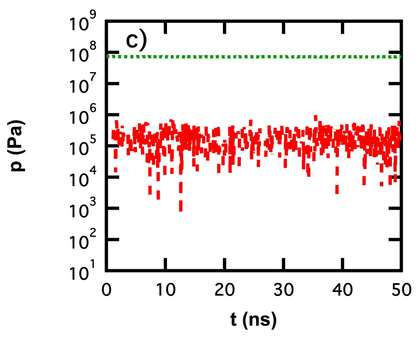
Methodology

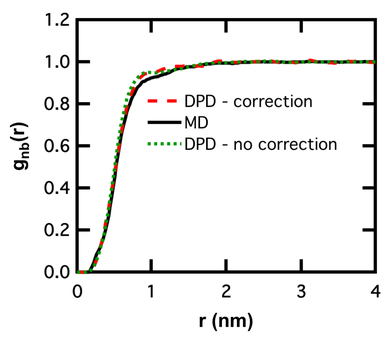
A united atom system of *cis*-polybutadiene (*cis*-PB) is initially equilibrated with Molecular Dynamics (MD) simulations. The system from the MD simulation is coarse-grained and the first interaction potentials are obtained by inverting the different radial distributions functions (RDFs). The Iterative Boltzmann Inversion method (IBI) [1] is then performed to reproduce targeted RDFs.

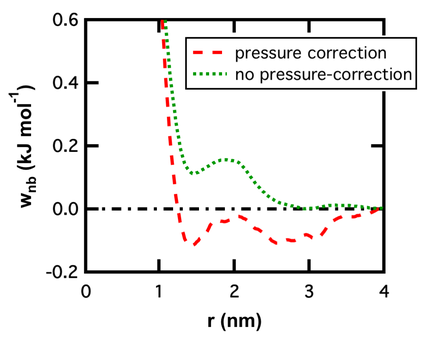
$$\omega_0(r) = -k_B T \ln\left(g^{MD}(r)\right) \qquad \omega_{i+1}(r) = \omega_i(r) + k_B T \ln\left(\frac{g_i(r)}{g^{MD}(r)}\right)$$

Finally, a correction is applied to final potentials to correct the pressure of the system. This pressure-correction allows *constant*-NpT simulations of the CG system [2].

$$\omega(r) = \omega(r) - A\left(1 - \frac{r}{r_c}\right)$$

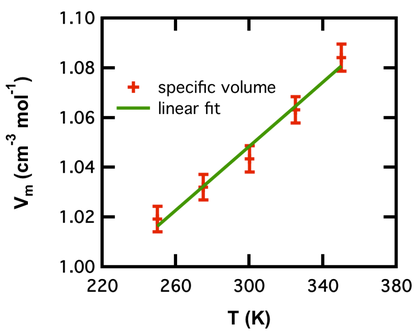


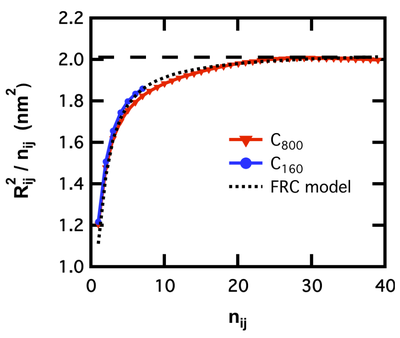


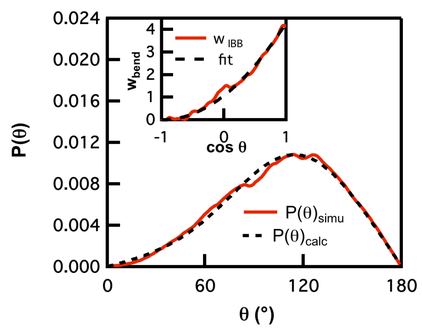


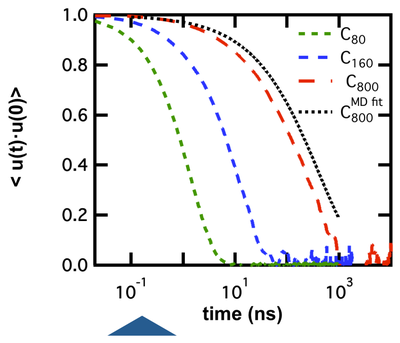
Pressure and non-bonded pair distribution function in a bulk cis-PB before and after the pressure correction.

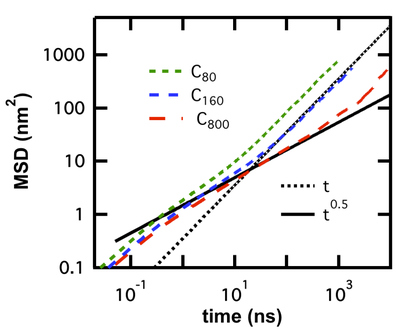
Results

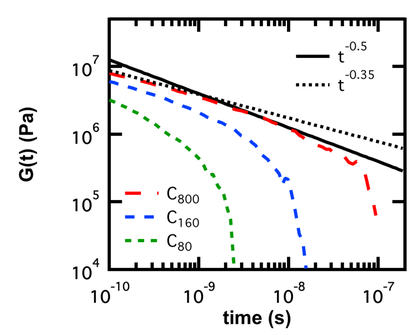








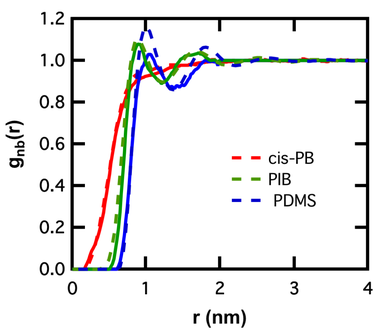


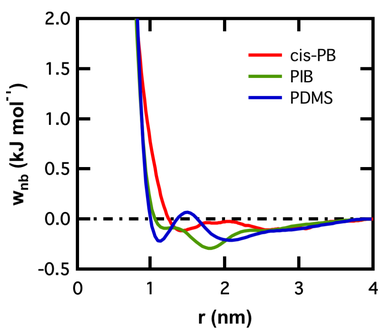


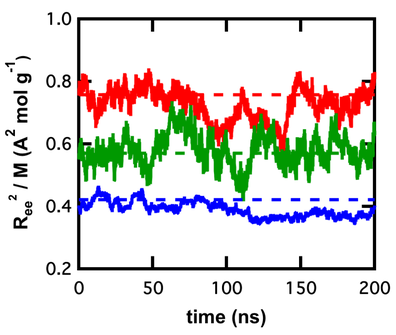
Chains are too short (C_{800} = 10.8 kg/mol) to exhibit a plateau modulus, but a characteristic slowdown with the molecular mass is shown.

Both static structure and dynamical behavior are in good agreement with literature data [3] and MD results. The methodology is then carried out on polydimethylsiloxane (PDMS) and polyisobutylene (PIB).

Chains follow the Freely Rotating Chain (FRC) model. Angular distribution is governed by the angular potential.



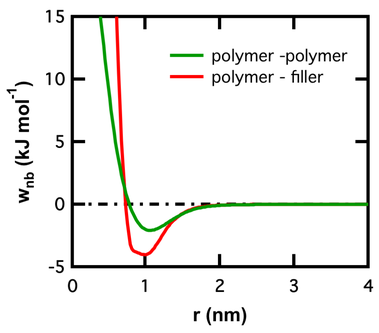




Quantitative approach that allows to distinguish several kind of polymer microstructures. The resulting static bulk properties are well reproduced.

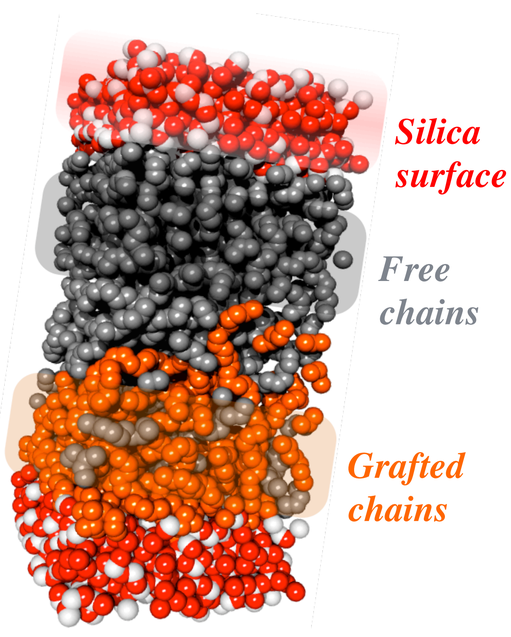
On going

The multiscale approach allows a fast exploration of the configurations while preserving structural properties.
This method is currently applied to a polymer-filler system in order to predict some properties and compare with a *bulk* polymer system.

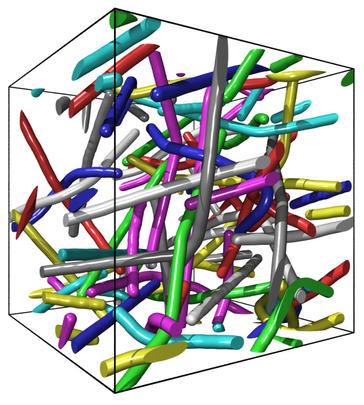


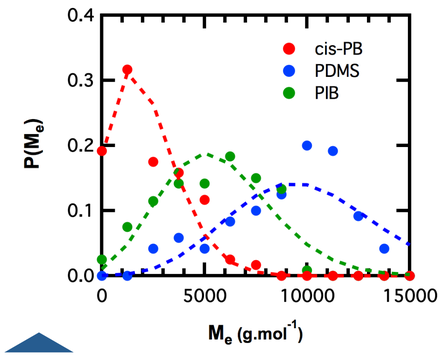
Interaction potentials for the polymer-filler system.

Two planar silica fillers confining polymer chains, grafted or not to the surface.



Primitive path analysis toward viscoelastic properties.





Entanglements distribution in several bulk systems.

Prospects :
- Optimization of the Primitive Path Analysis.
- Entanglements distribution in confined system.
- Out of equilibrium and mechanical properties.

References :

1 – Reith, D, Pütz M, Müller-Plathe F, *J. Comput. Chem.*, **2003**, 24, 1624-1636.
2 – Maurel G, Schnell B, Goujon F, Couty M, Malfreyt P, *J. Chem. Theor. Comput.*, **2012**, 8, 4570-4579.
3 – Fetters LJ, Lohse DJ, Richter D, Witten T, Zirkel A, *Macromolecules,* **1994**, *27*, 4639-4647.