Advances in Computer Modeling of Polymer Systems

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MSU SUPERCOMPUTER: "LOMONOSOV"

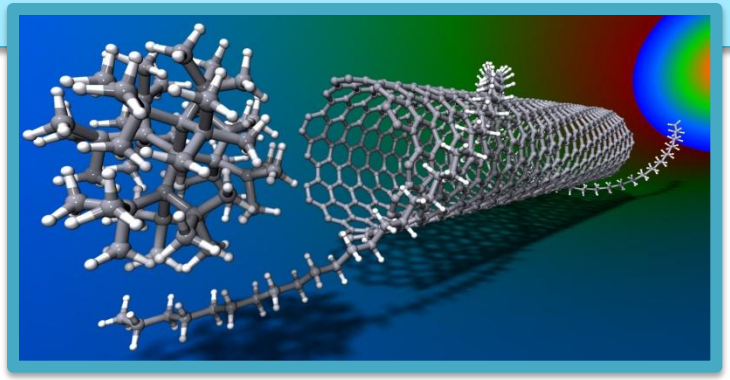
Top500 world rating - #37 (2013.XI).

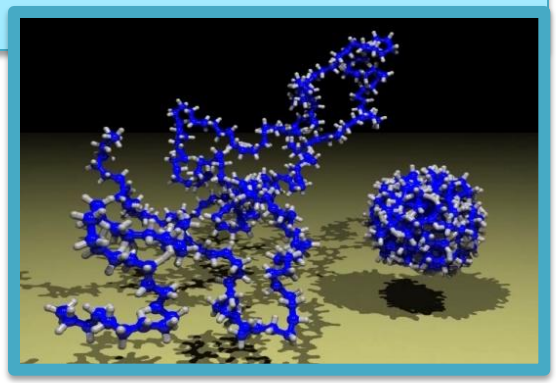
Top50 Russia rating - #1 (2014.IV).

•Peak performance	1.7 PFlops
•Linpack performance	0.9 PFlops
•Main processor types	Intel® Xeon X5570 / X5670 (12 346), NVIDIA X2070 (1 065)
•Total area (supercomputer)	252 m2
•Total equipment weight	More than 75 tons.
•Power consumption	2.6 MW

Directions of research

- Design of functional polymers
- Self-organising polymer systems
- Nanomaterials: nanocomposites, thermoplasts and thermosets
- Hydrogen energy, fuel cells
- Ultrathin nanostructured films
- Bioinspired molecular hybrids





Methods and Software

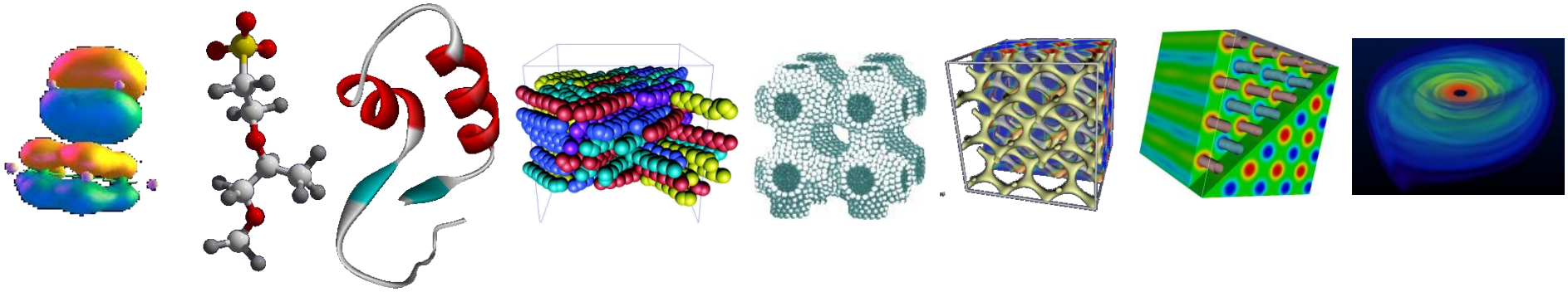
Atomistic Methods
Mesoscopic Methods
Field-Based Methods
Quantum-Chemistry Methods

Methods	Software
Classical Molecular Dynamics	LAMMPS, DL_POLY, NAMD
Reactive Molecular Dynamics	LAMMPS/ReaxFF
Dissipative Particle Dynamics (DPD)	Original code
Reaction DPD	Original code (DPDChem)
SCFT	Original code
Density Functional Theory	MesoDyn / Materials Studio
Quantum molecular dynamics	CP2k, CPMD, Quantum Espresso
Monte Carlo	Original code
RISM, MC/RISM, hybrid methods	Original code

Multiscale modeling concept

Atoms Molecules Molecular assemblies Condensed matter Composites Continuum

microscopic (1-10 nm, fs/ps) mesoscopic (10-1000 nm, ns/μs) macroscopic (~1 mm, μs/s)



Electrons ⟷ Atoms (Particles) ⟷ Particles/Fields ⟷ Fields

DFT Molecular Dynamics

Electronic state Molecular structure/motion and properties

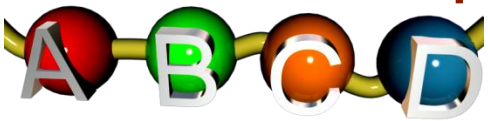
Dissipative PD (DPD)

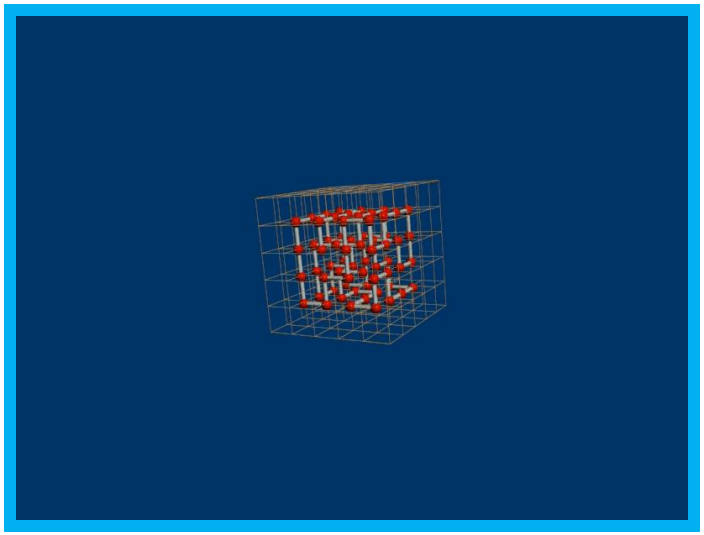
Equilibrium mesoscopic structure and properties

Finite Elements

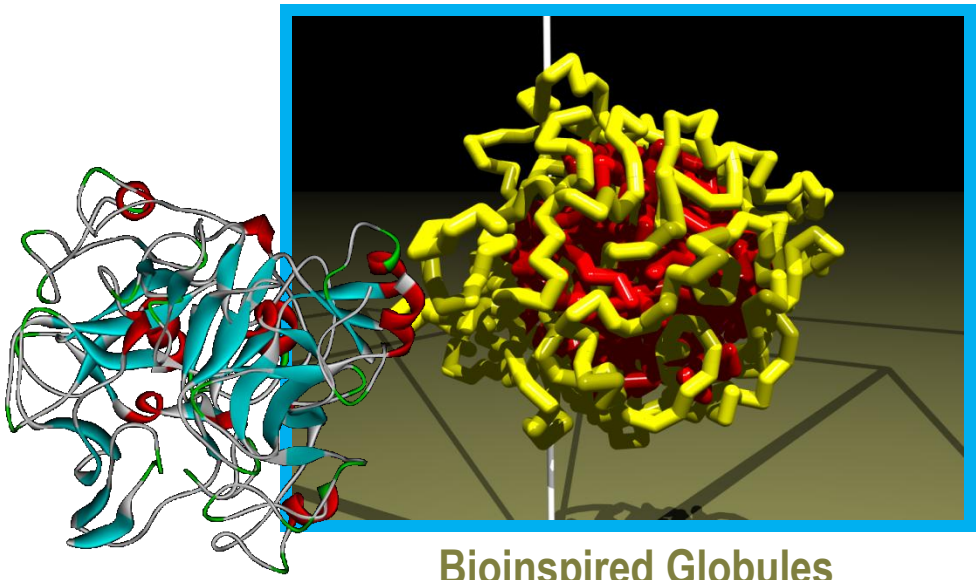
Large-scale properties

Design of functional copolymers

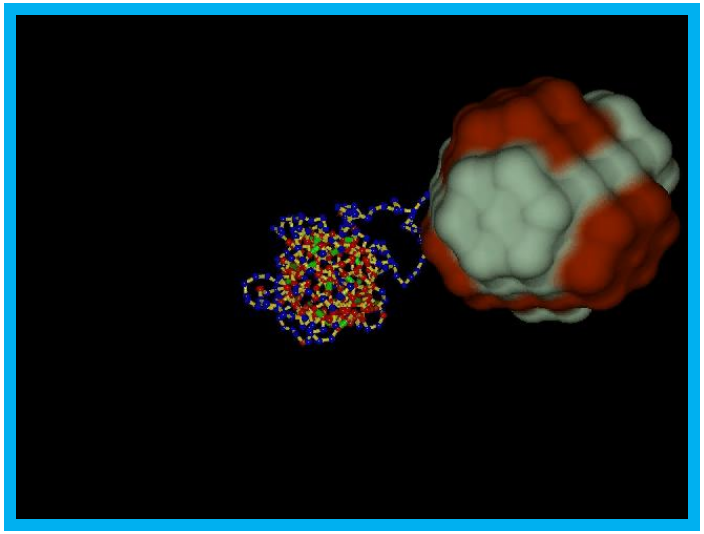




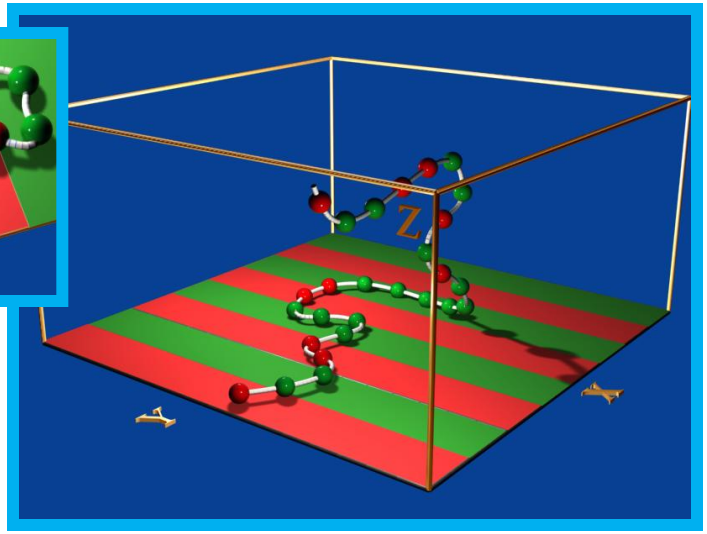
Biomimetic Design



Bioinspired Globules

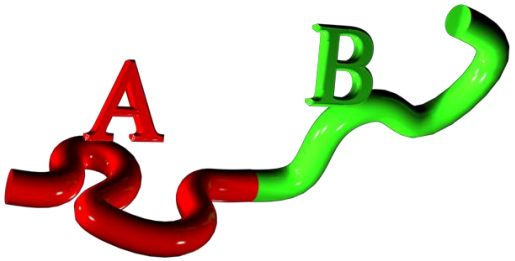


Molecular Dispenser



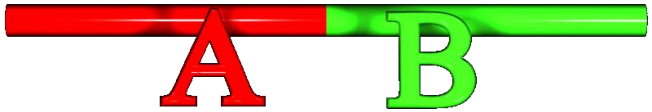
Pattern Recognition

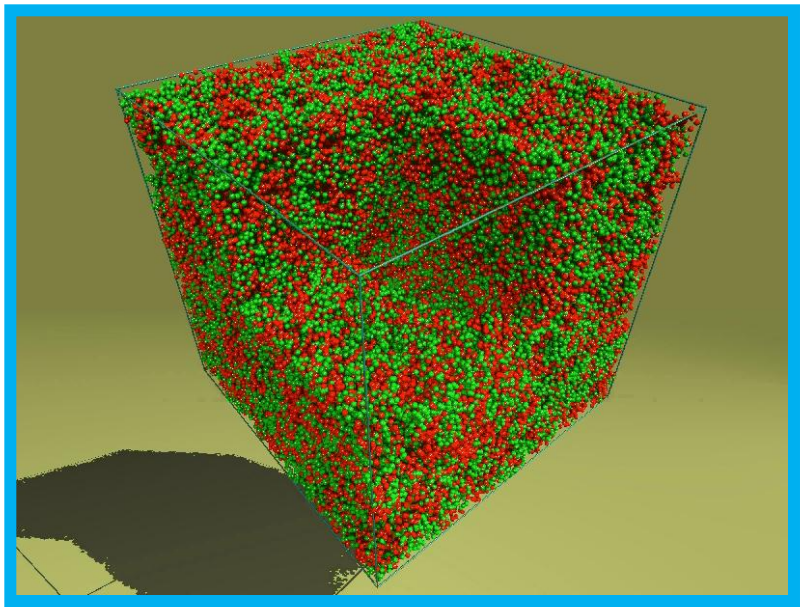
Self-organization of polymer nanostructures



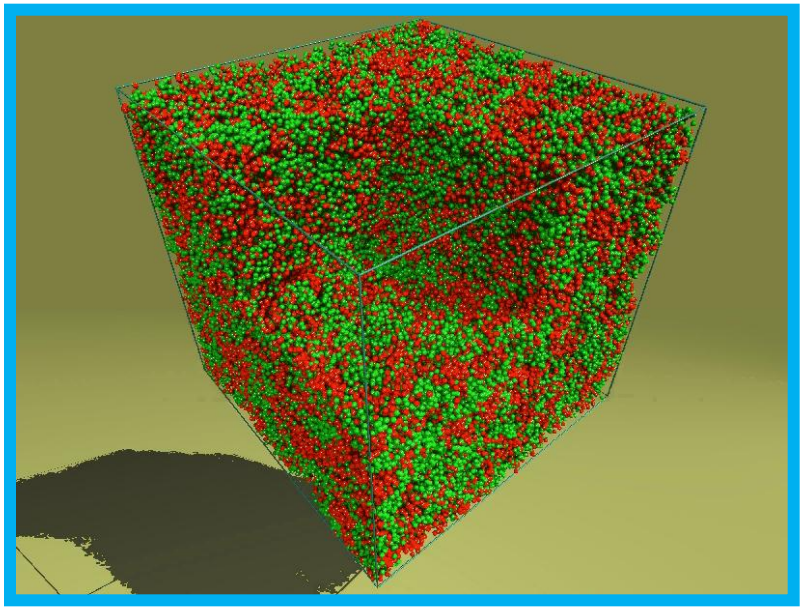
Microphase separation:
Nanostructure scale: ~10-100 nm

LAM



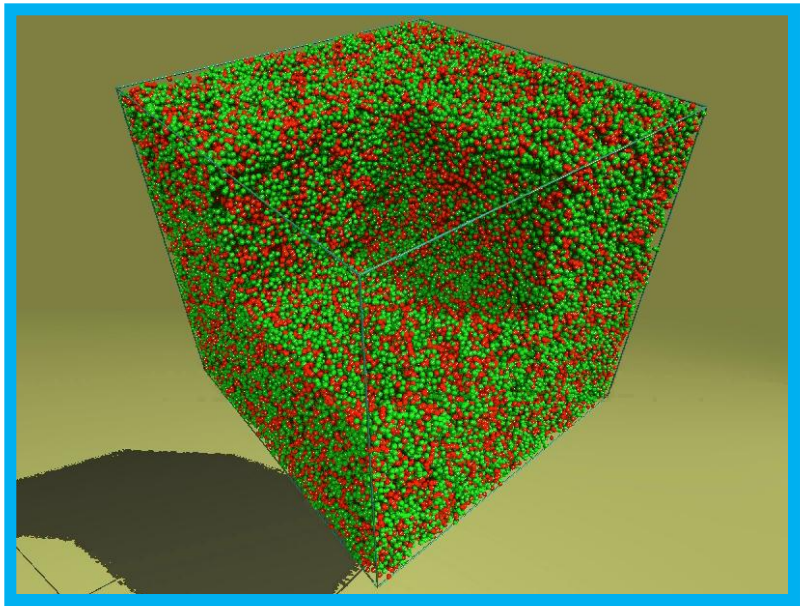


HEX



Self-organization of polymer nanostructures

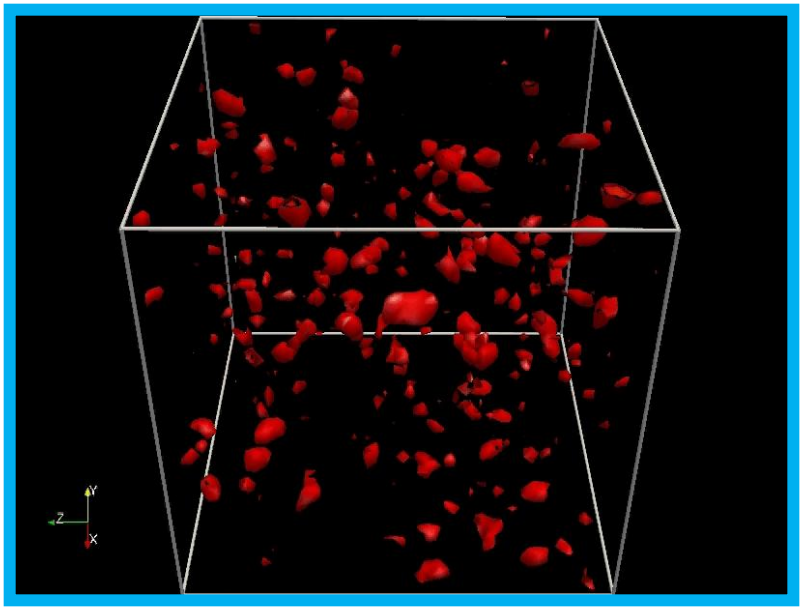
DPD



Particles

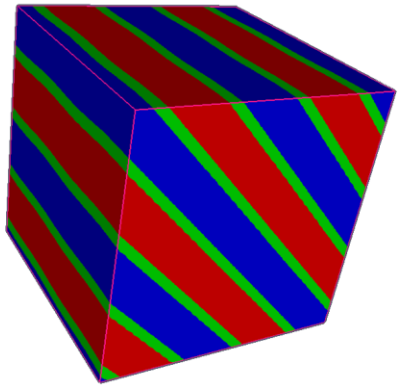
SCFT

GYR

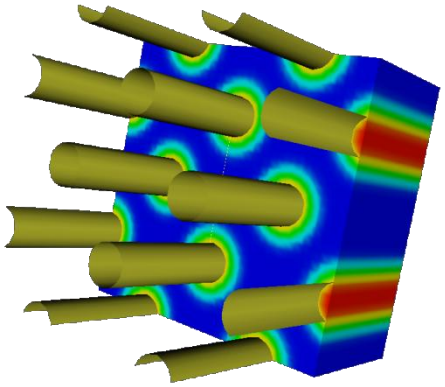


Field Representation

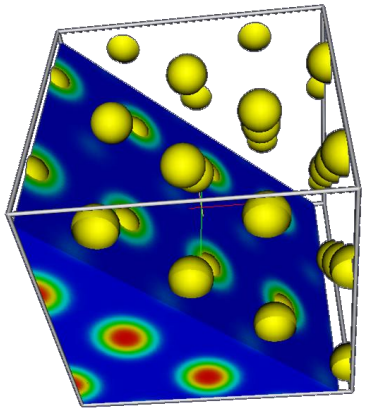
Design of polymer nanostructures



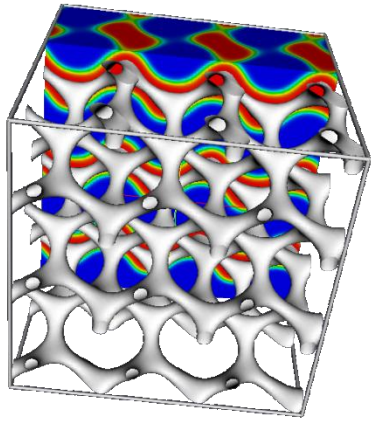
LAM



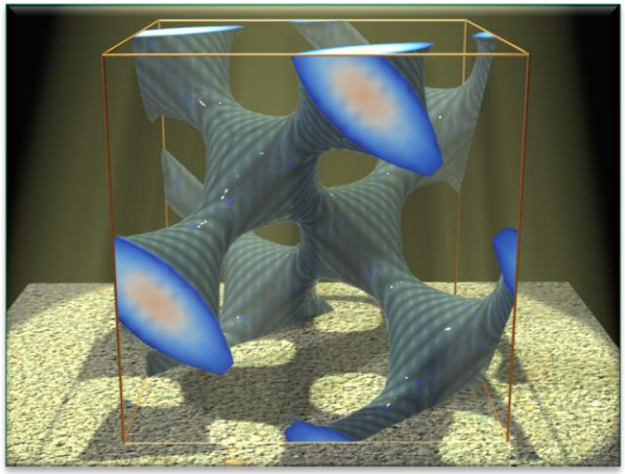
HEX

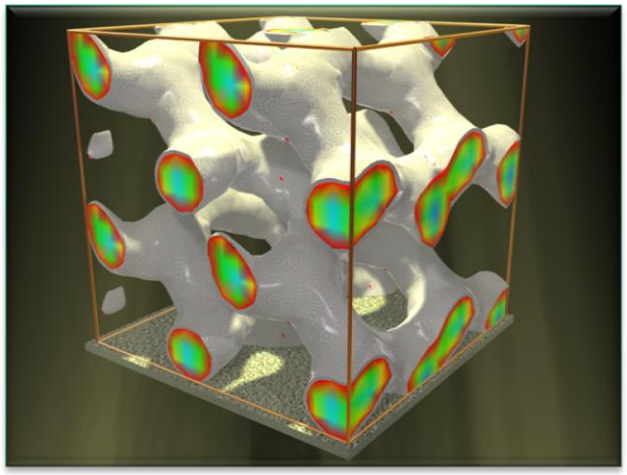


BCC



GYR

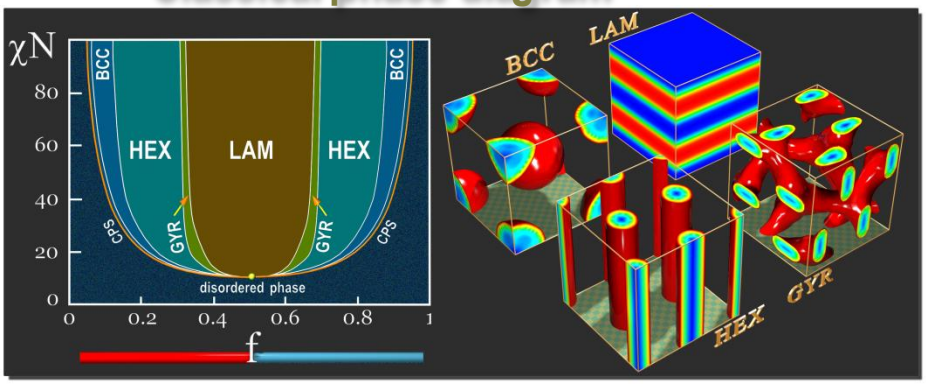




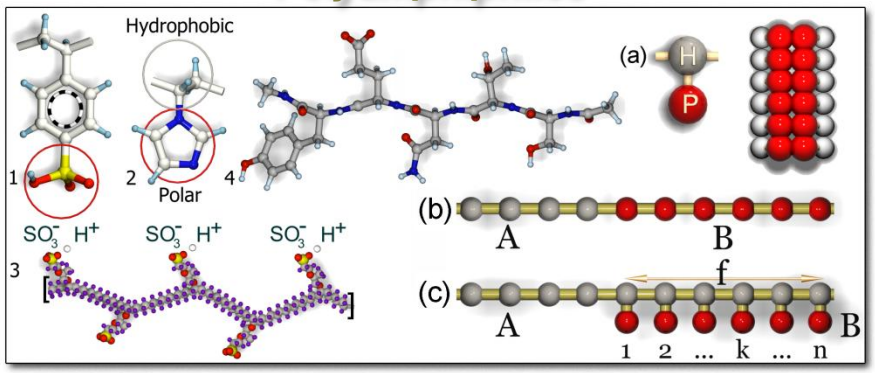
Synthetic polymers are able to self-organize in sofisticated 3D structures. This opens up opportunities for synthesis of ordered supramolecular nanostructures with controlled morphology.

Polyamphiphiles: Unusual forms of self-organization

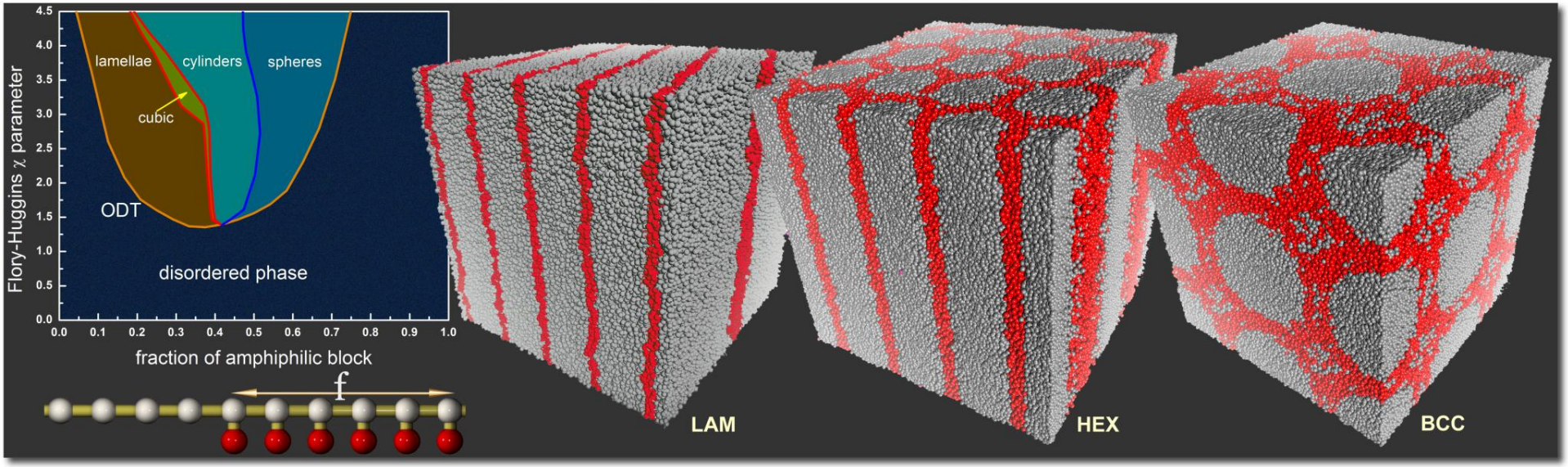
Classical phase diagram



Polyamphiphiles



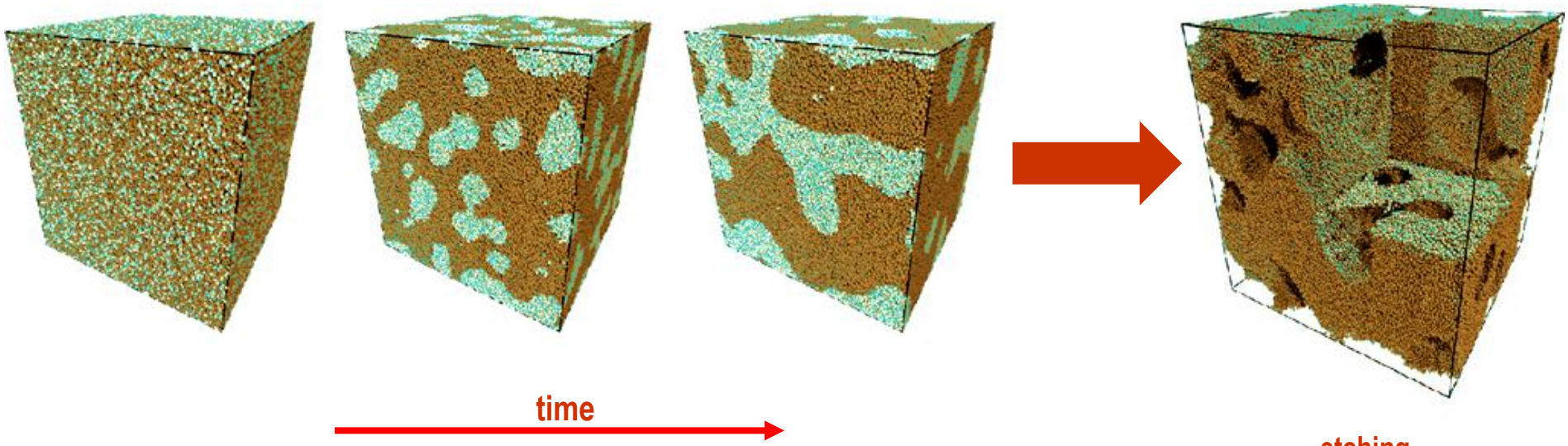
Polyamphiphiles phase diagram: Inverted mesophases



Local structure dictates global morphology

Physical Synthesis: nanostructures engineering

“Freezing spinodal decomposition"



etching

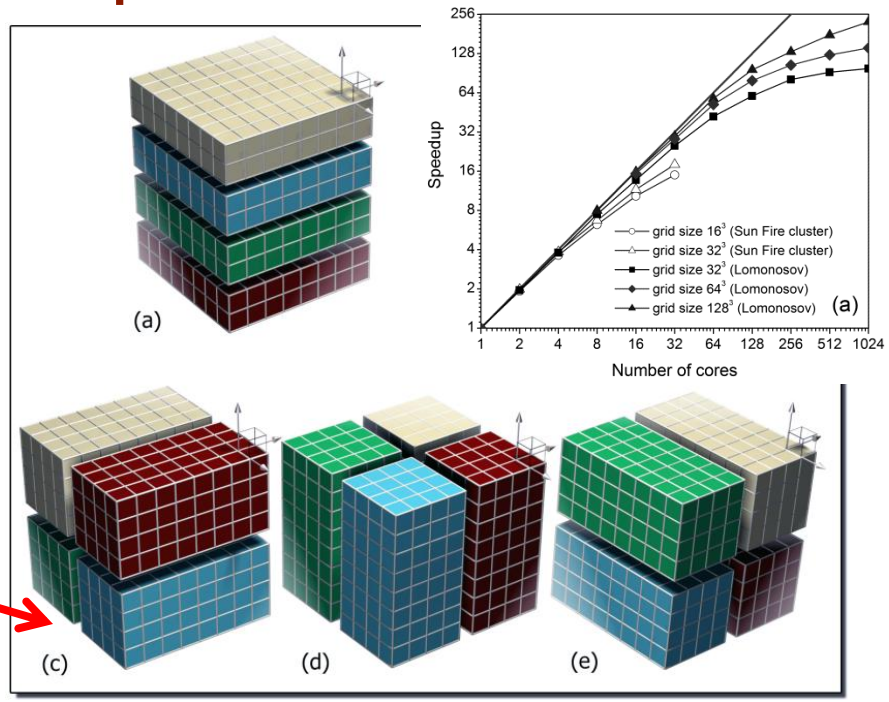
~5 nm 30-50% of pores

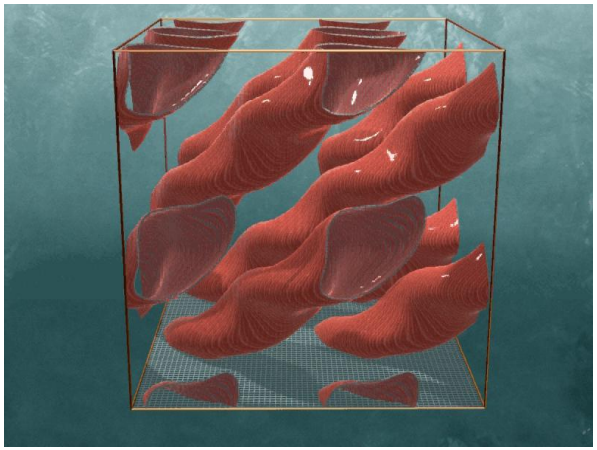
Nanoporous materials (membranes, nanofilters…)

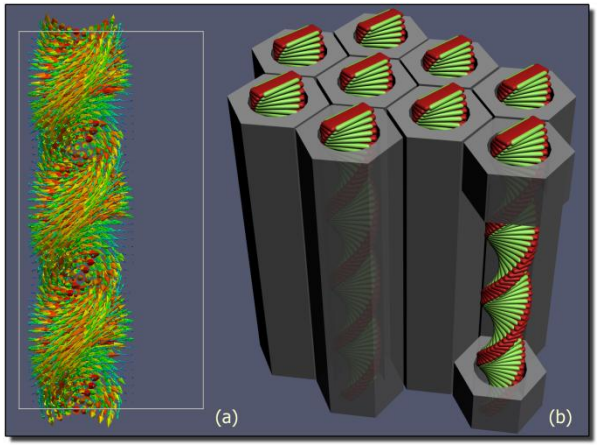
SCFT simulation: new developments and results

We have developed a parallel code for large-scale field-theoretical SCFT modeling of 3D systems on grids of the order of 1283 or more nodes. The algorithm is based on a pseudospectral method for solving the SCFT-equations and the calculation of integral operators for the matrix fields using the fast Fourier transform and 2D parallelizing ("pencil" decomposition).

For 1024 CPU acceleration >250

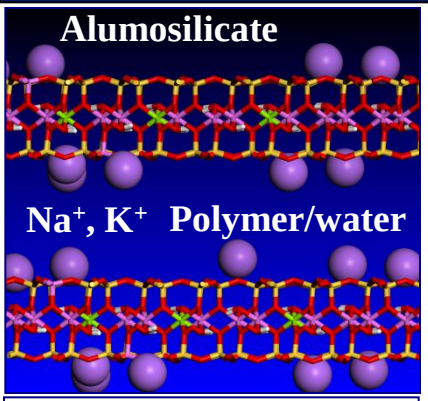


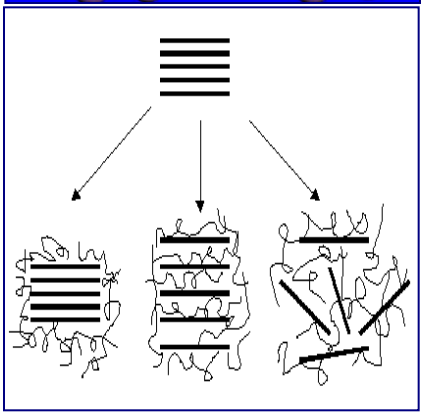


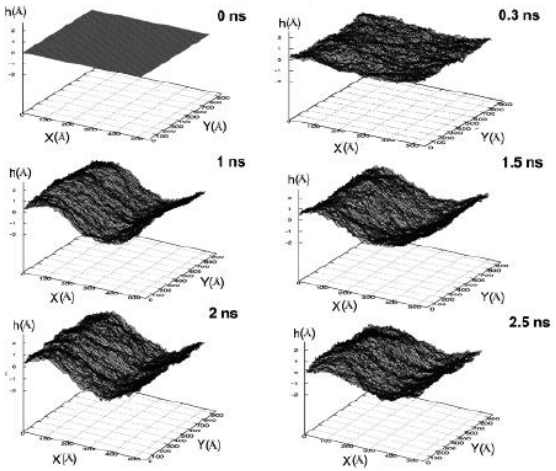


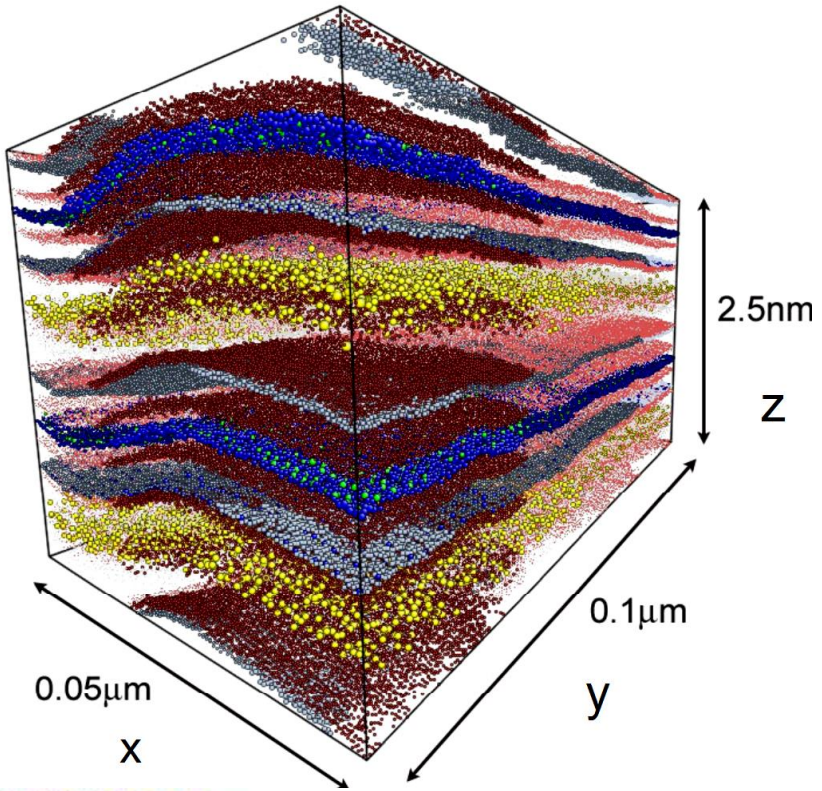
Spontaneous break of symmetry: Non-chiral objects are capable to form macroscopic chiral object!

Nanocomposites

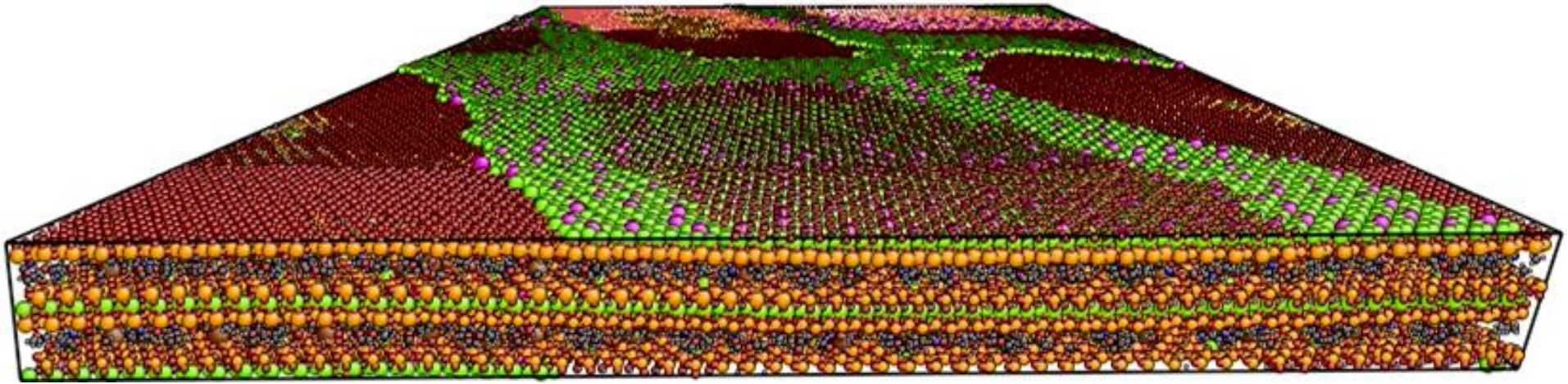






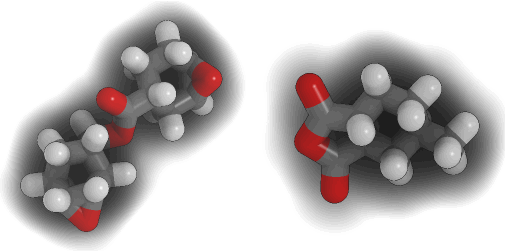


~10^6 atoms

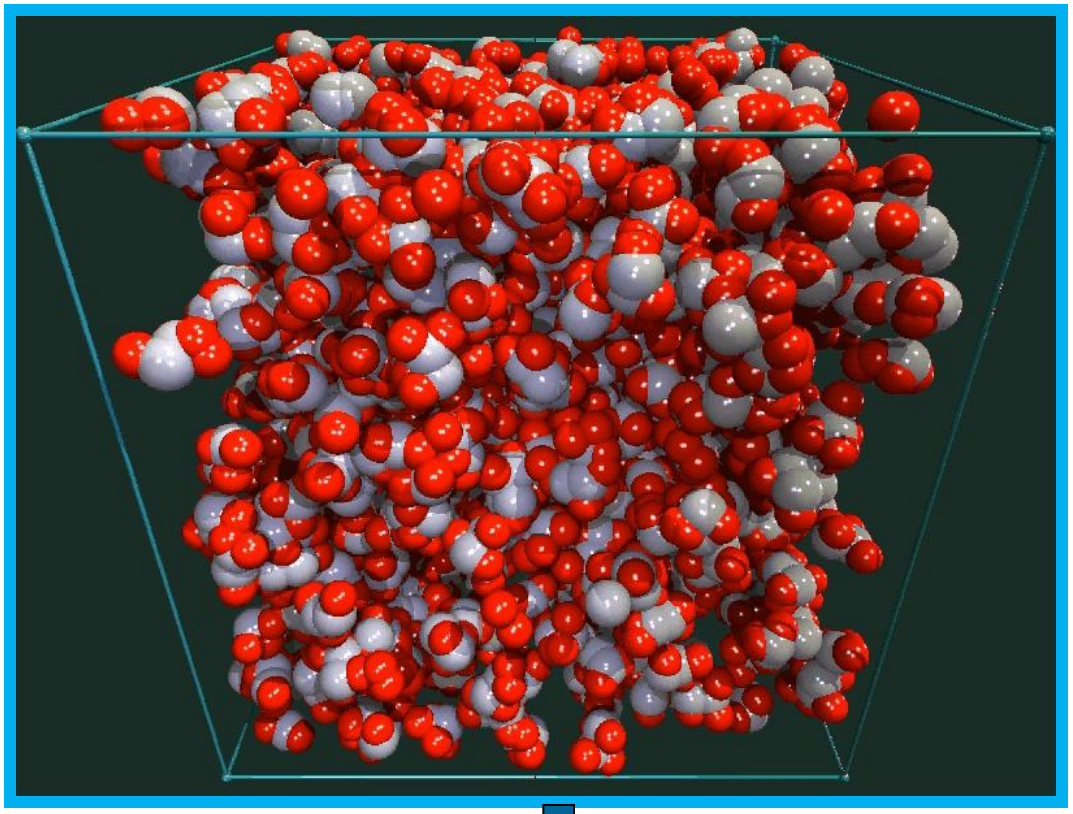


Polymerization model (chemical network)

Monomers

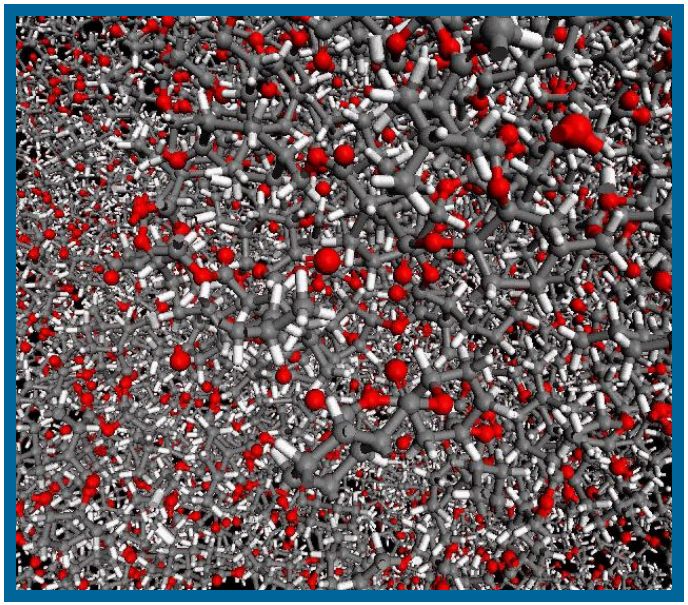


MC



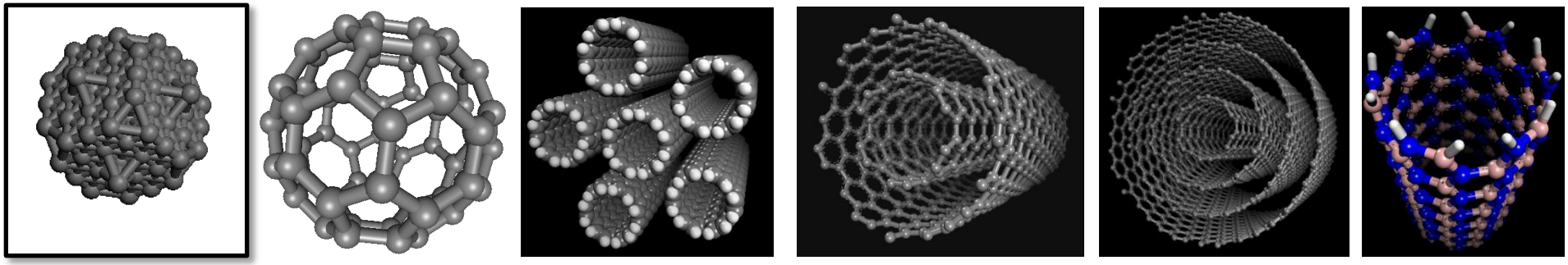
Reverse Mapping

MD

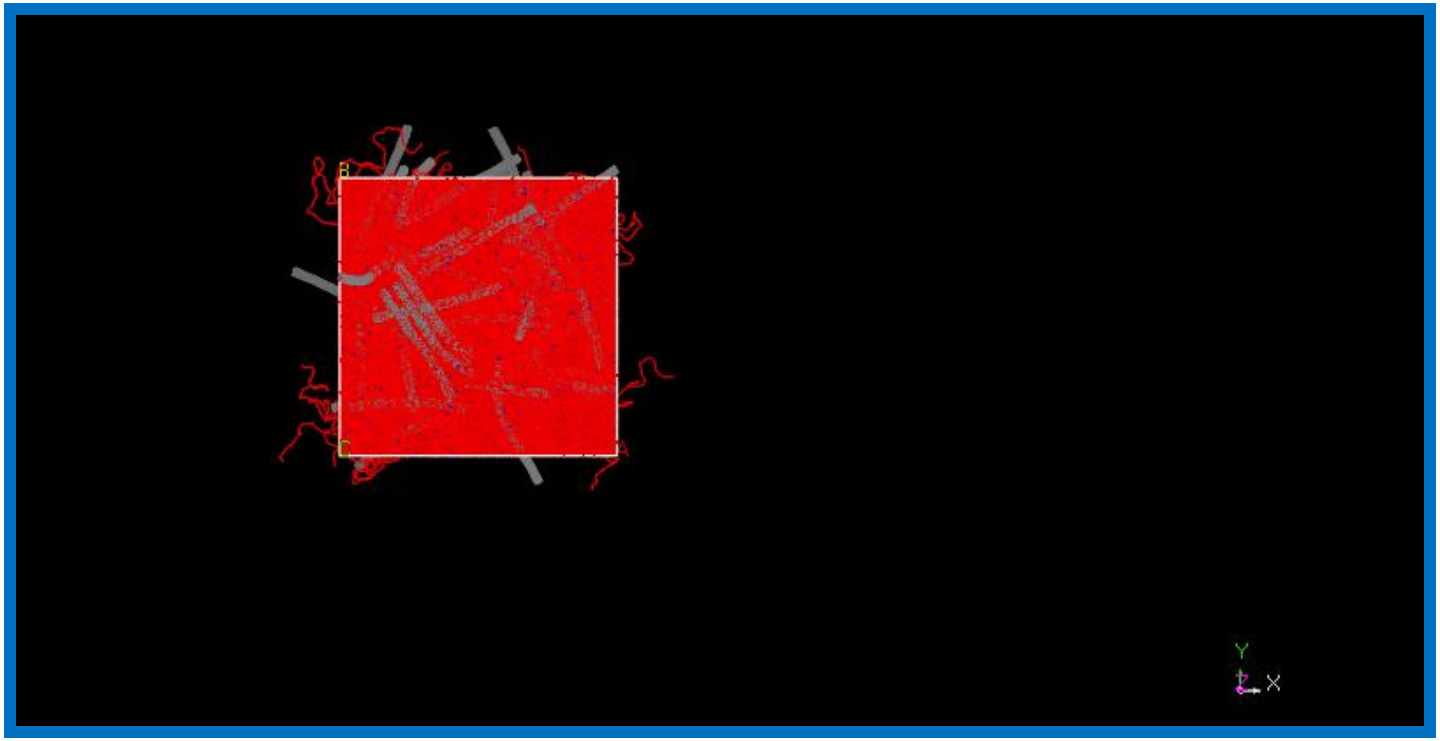


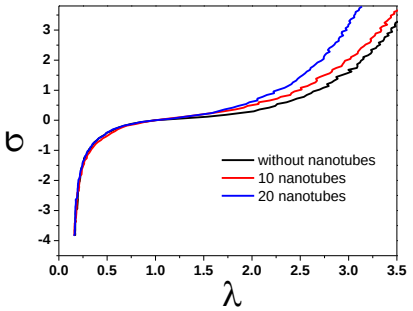
Nanocomposites: Thermosets with filler (project EU/RUS)

Different types of nanoparticles

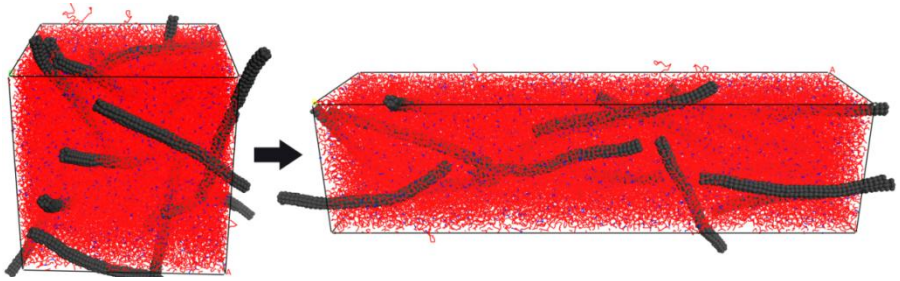


Deformation mechanics of nanocomposite material





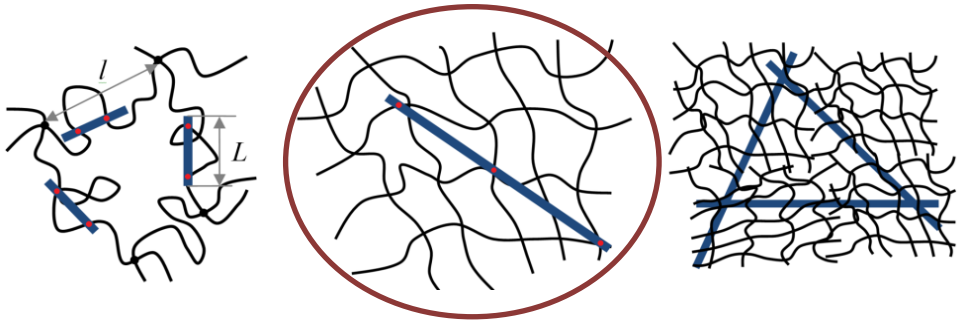
Composites with nanotubes:

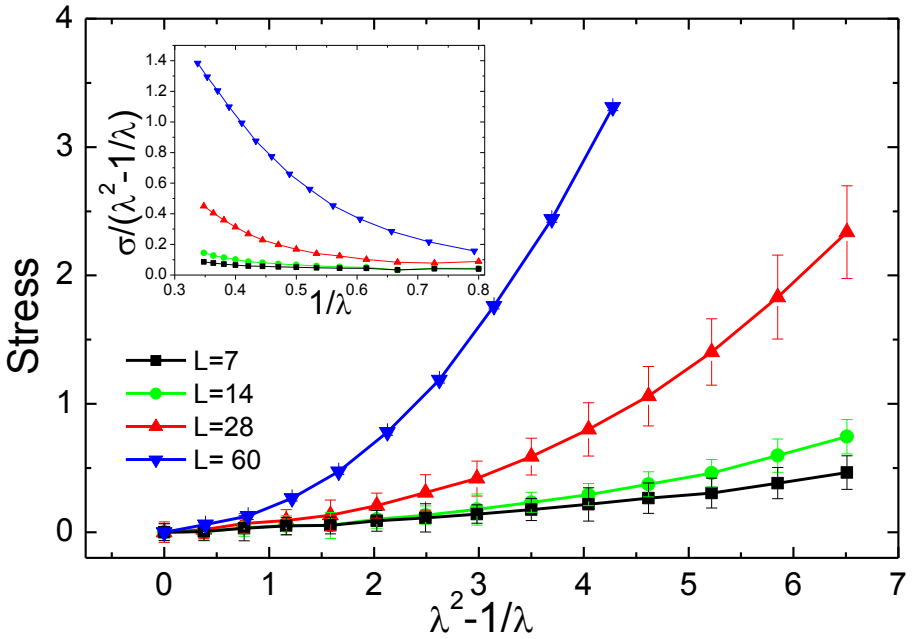


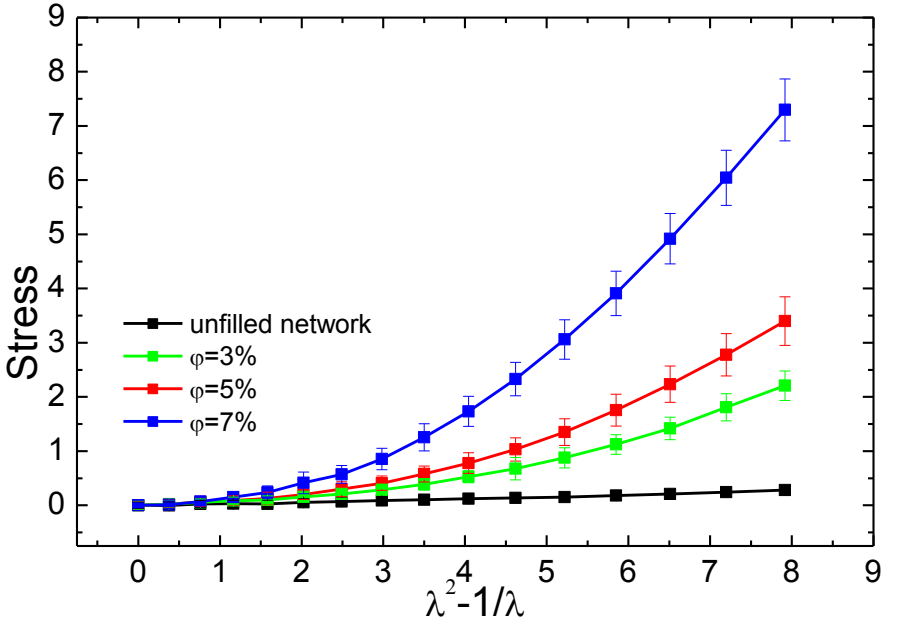
3 regimes of elastomer reinforcement:

1. *L/l ~ 1: small reinforcement*
2. *L/l > 1: main reinforcement regime*
3. *L/l >> 1: saturation after sub-network formation*

1 2 3



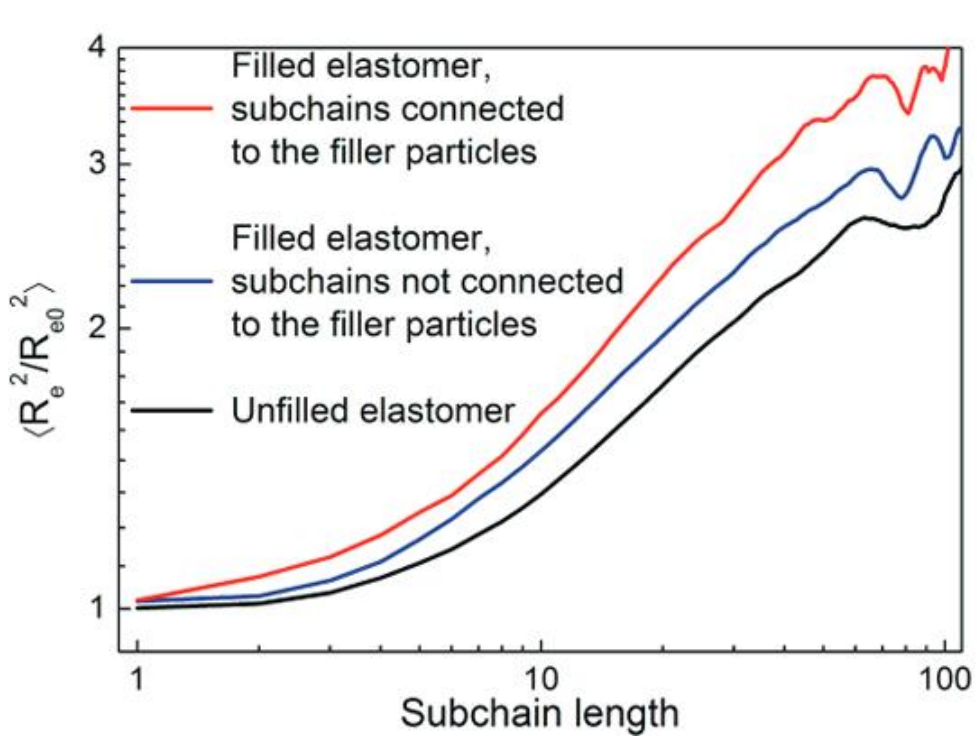


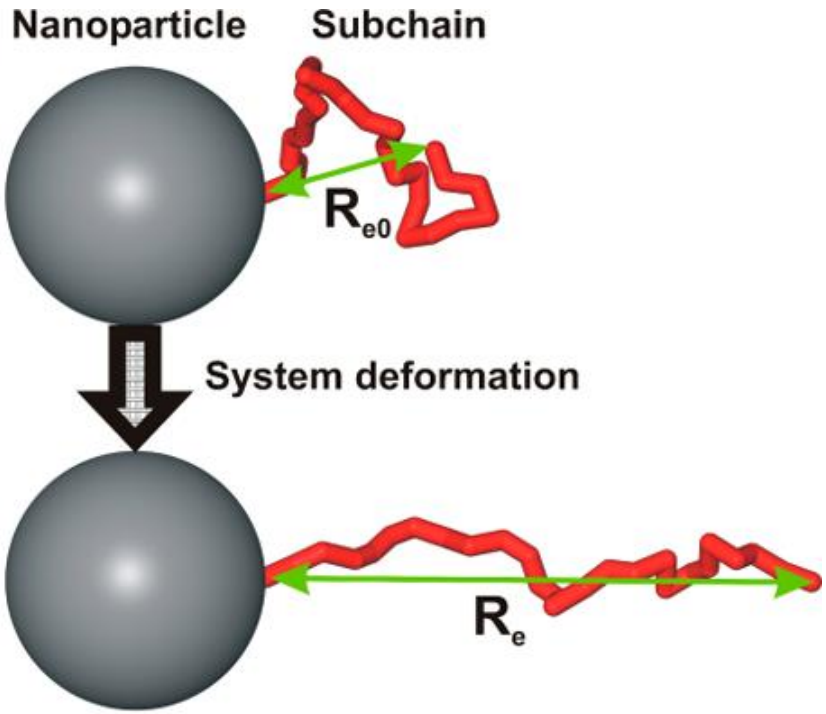


Soft Matter, 9, 4067, 2013.

Reinforcement mechanism

Presence of 2 sets of subchains: connected (adsorbed or linked) and not connected.
Subchains attached to the nanoparticles are more deformed than not attached.

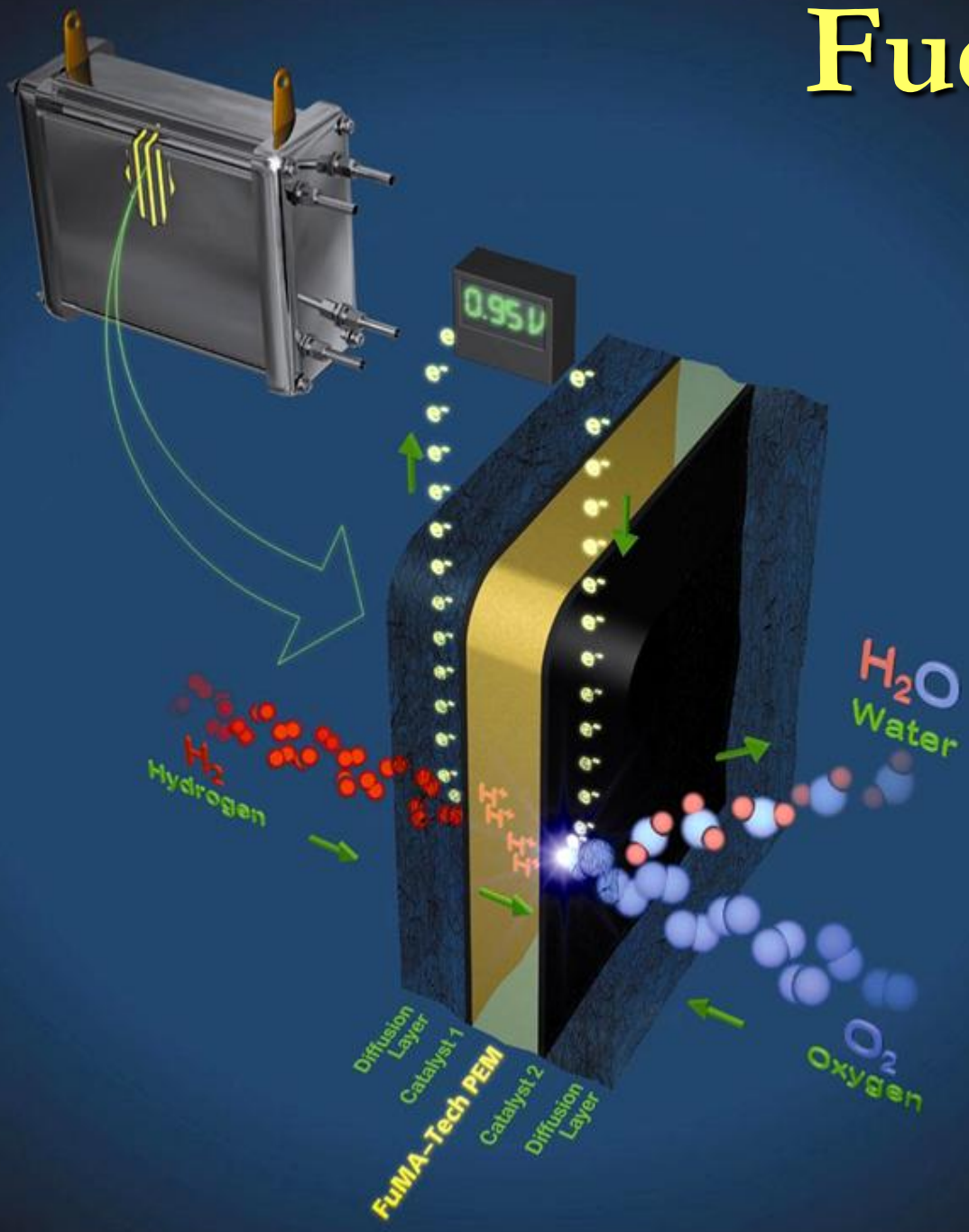




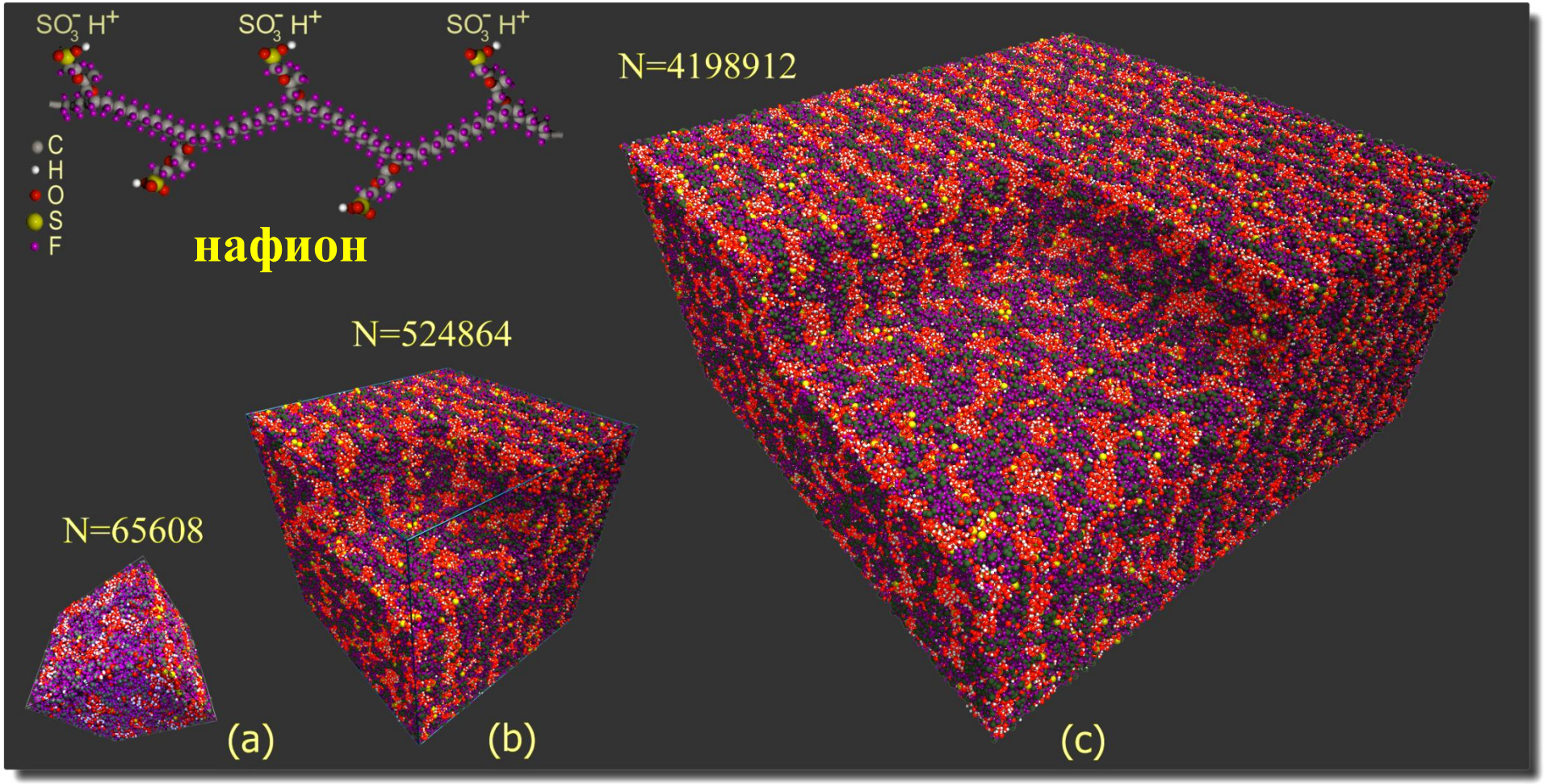
Main reinforcement mechanism: subchains which are not connected to the filler particles are deformed slightly more than in the unfilled matrix + the subchains connected (absorbed) to the filler particles are deformed significantly more.

Macromolecules, 47, 5400, 2014.

Fuel Cells


0.95V
H_2
Hydrogen
H_2O
Water
O_2
Oxygen
Diffusion Layer
Catalyst 1
FuMA-Tech PEM
Catalyst 2
Diffusion Layer

Nafion membrane: classical molecular dynamics (record large-scale modeling using LAMMPS program)

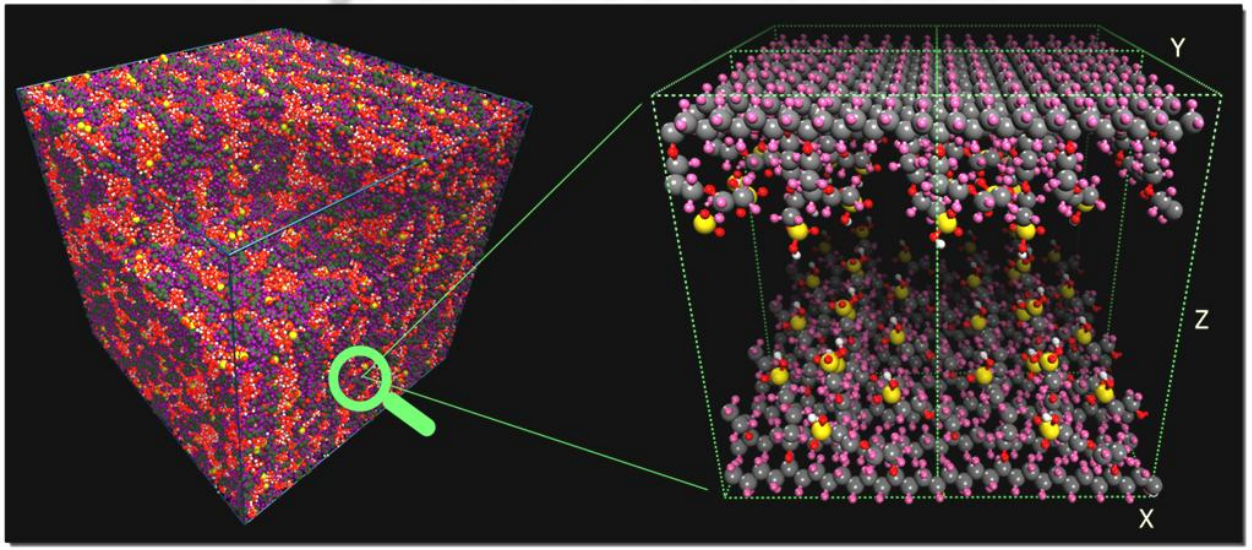


Even small water content leads to the proton conductivity

Nafion Membrane: Quantum molecular dynamics (record modeling of ion-conducting channel with the package CP2k)

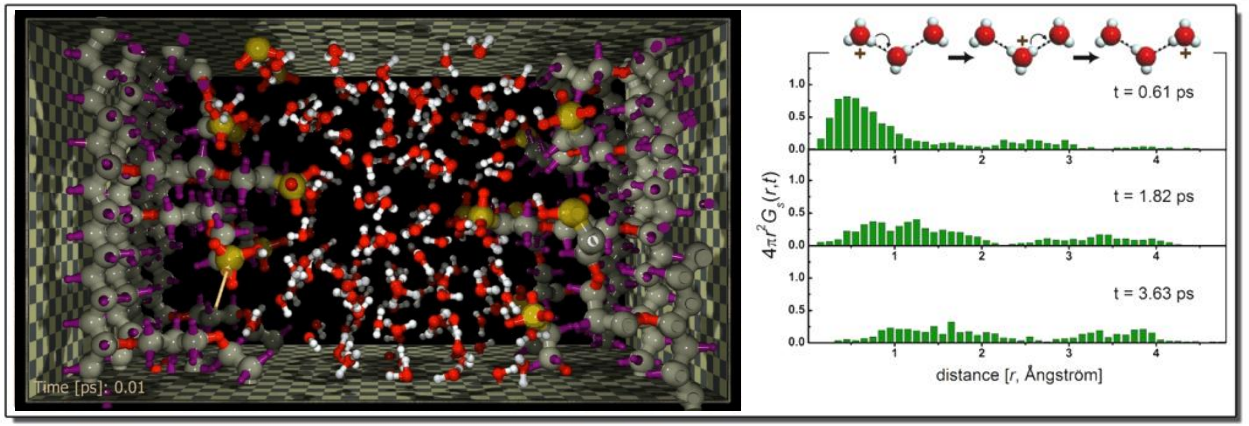
Charge transfer and Grotthus mechanism

Atomistic structure

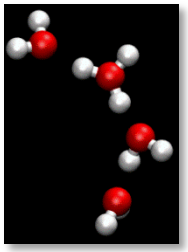


Model of channel

Quantum mol.dynamics (1200 atoms)



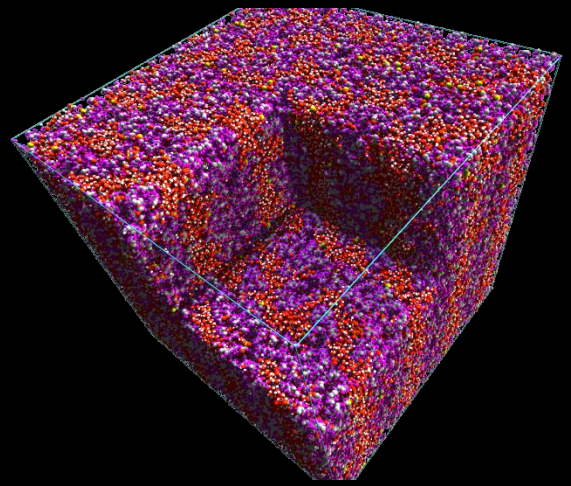
Charge transfer

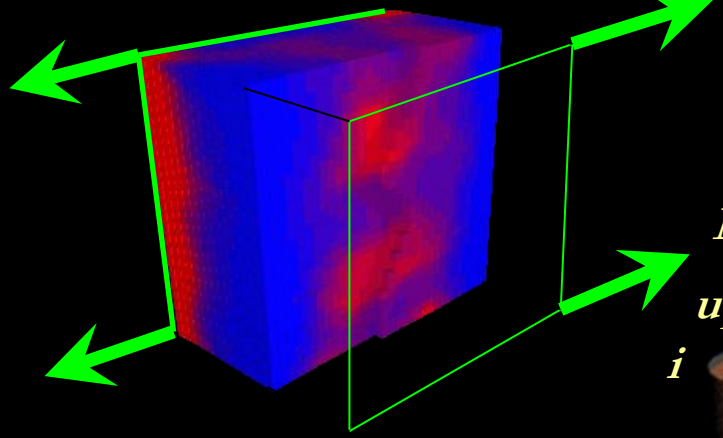


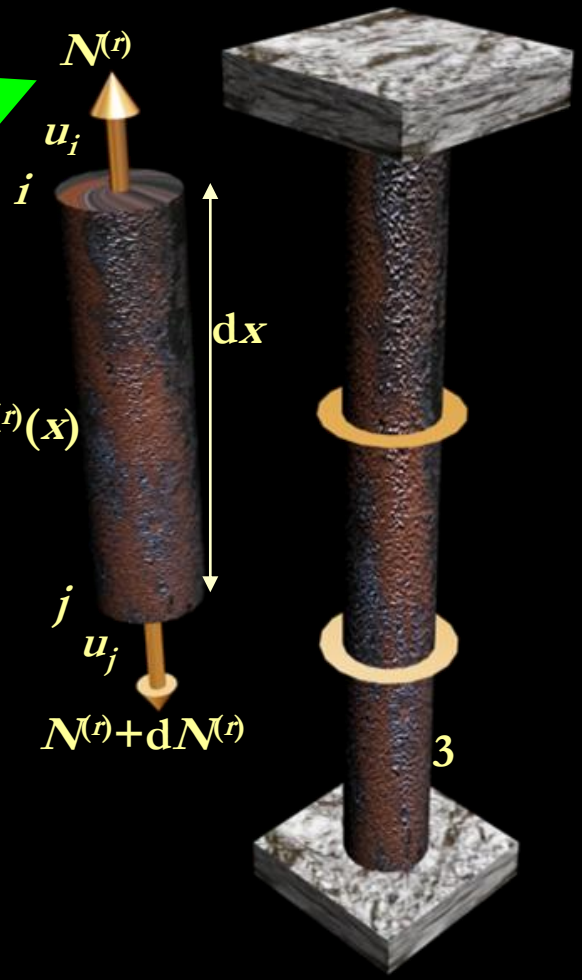
We used a hybrid approach within the framewok of the density functional theory (DFT) combining Born-Oppenheimer quantum molecular dynamics (BOMD) and Carr-Parinello method(CPMD)

The observed bimodality of Van Hove spatio-temporal correlation function $G_s(r,t)$ gives a first direct evidence of Grotthus mechanism

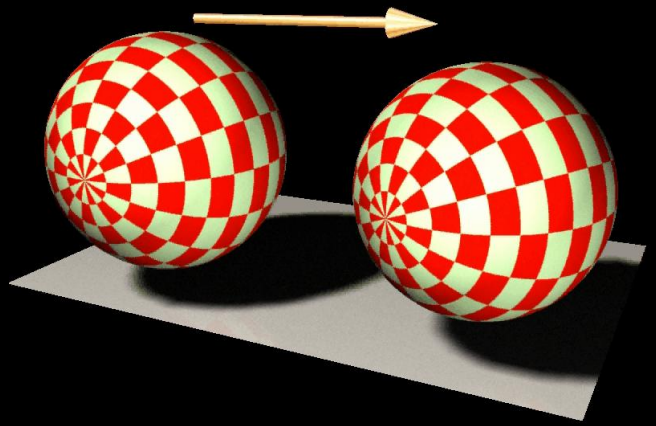
Fuel cell membrane: finite element method
(OCTA multiscale simulation software package)



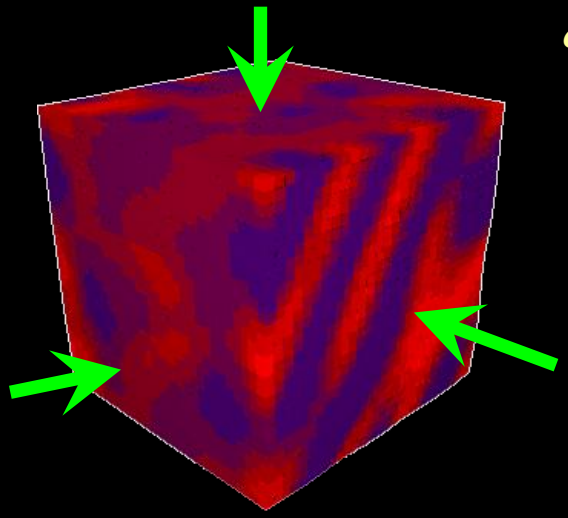




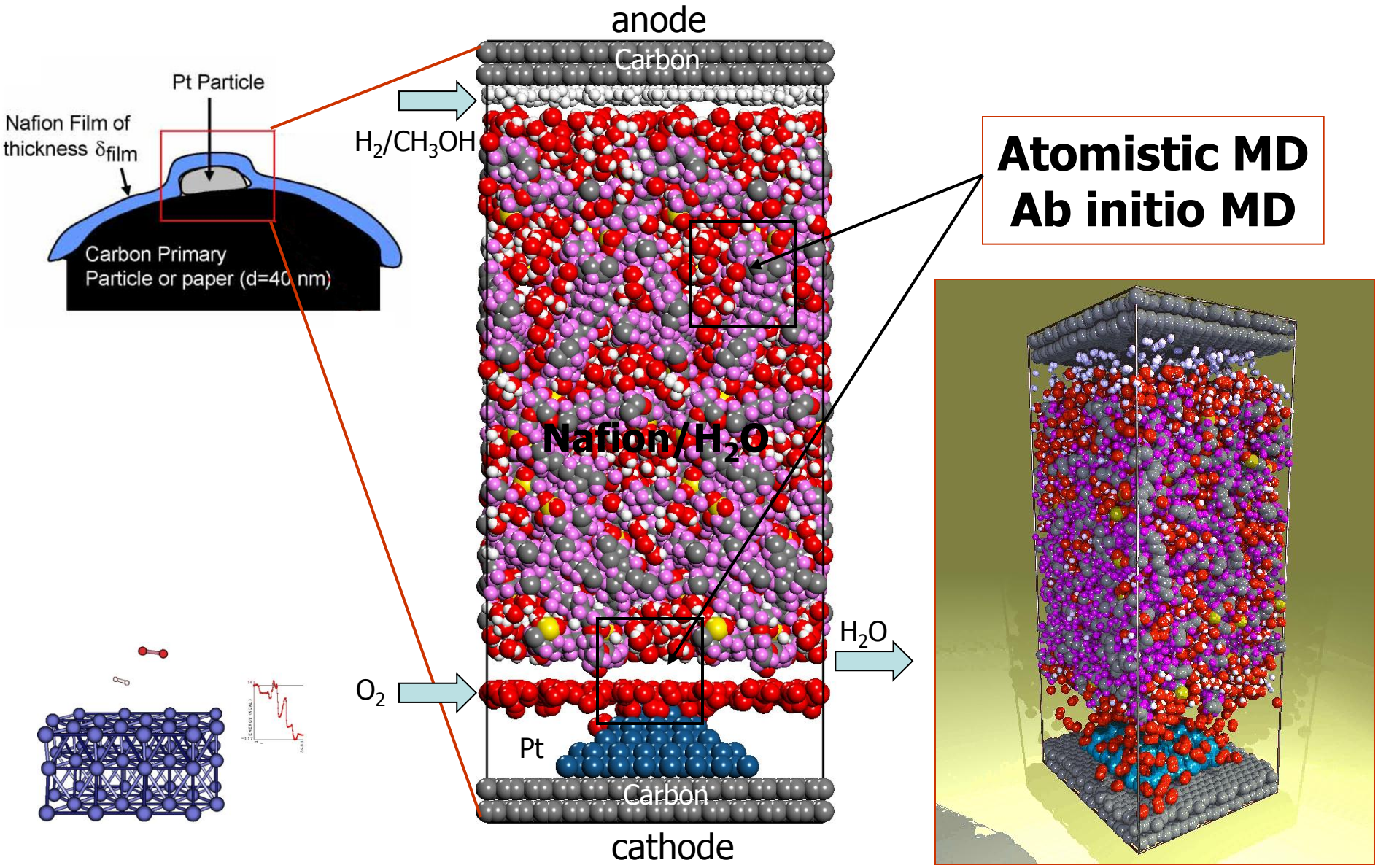
stress distribution upon deformation of the membrane



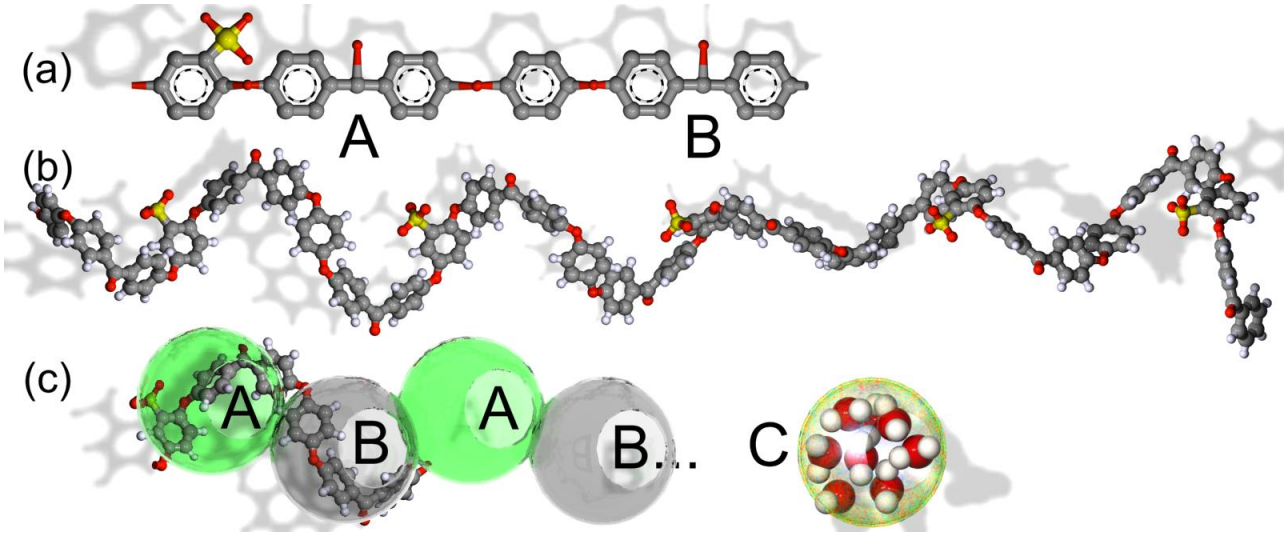
pressure

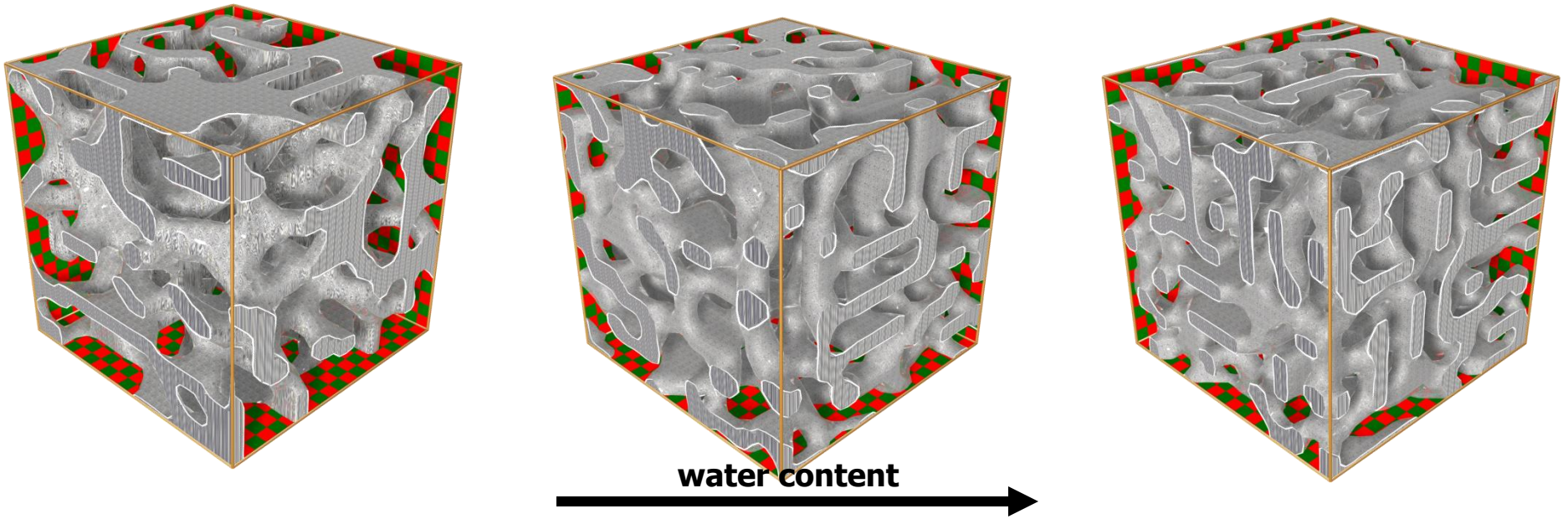


Atomistic model of the overall PEM FC,
including cathode, anode, and interfaces.

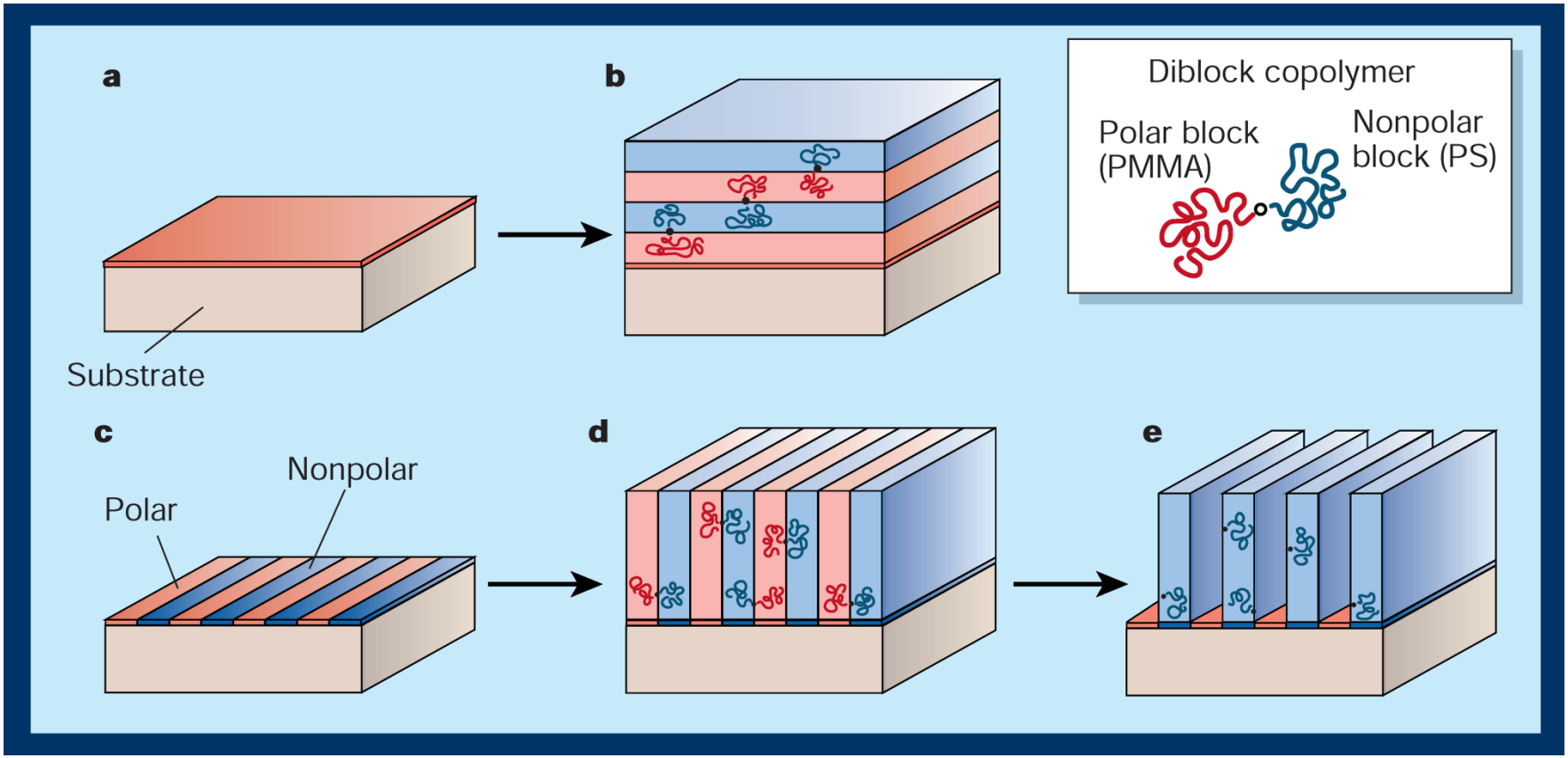


Membranes for low-temperature fuel cells based on new aromatic copolymers (mesoscopic simulation)



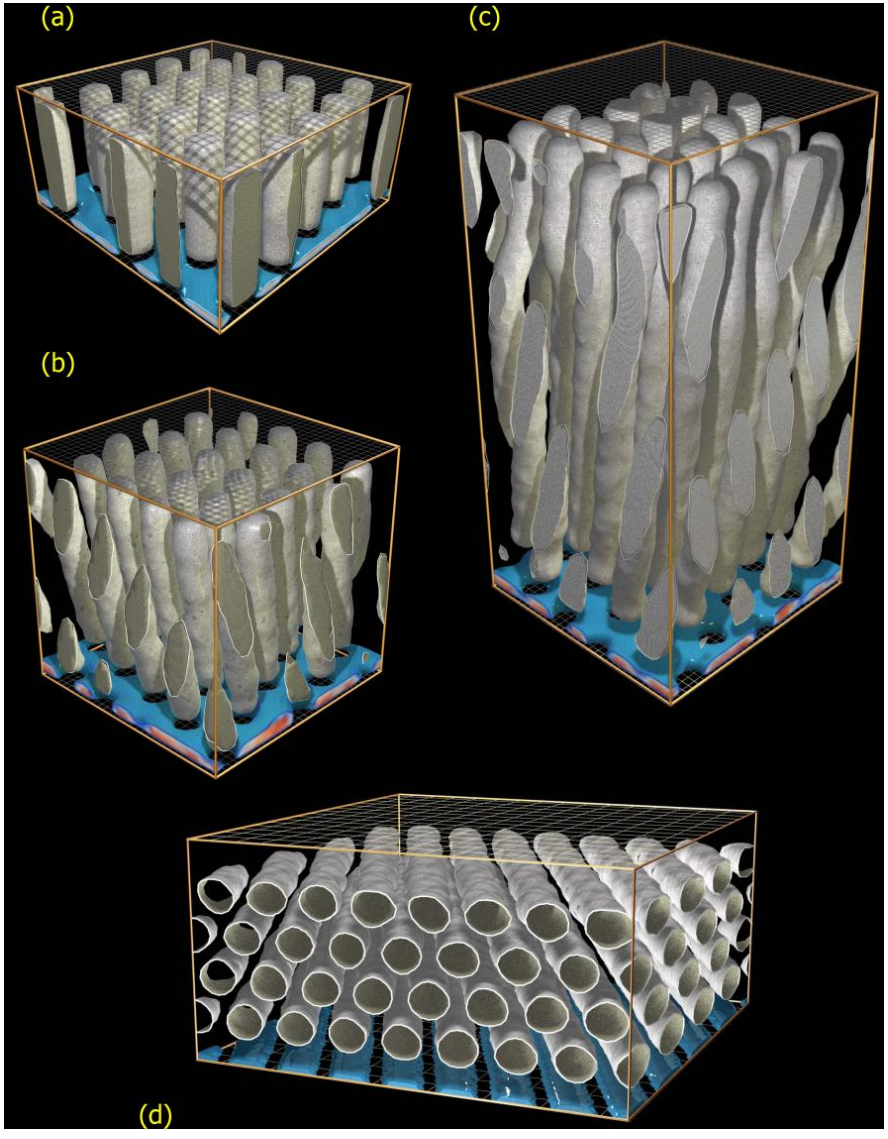


Construction of ultrathin nanostructured films

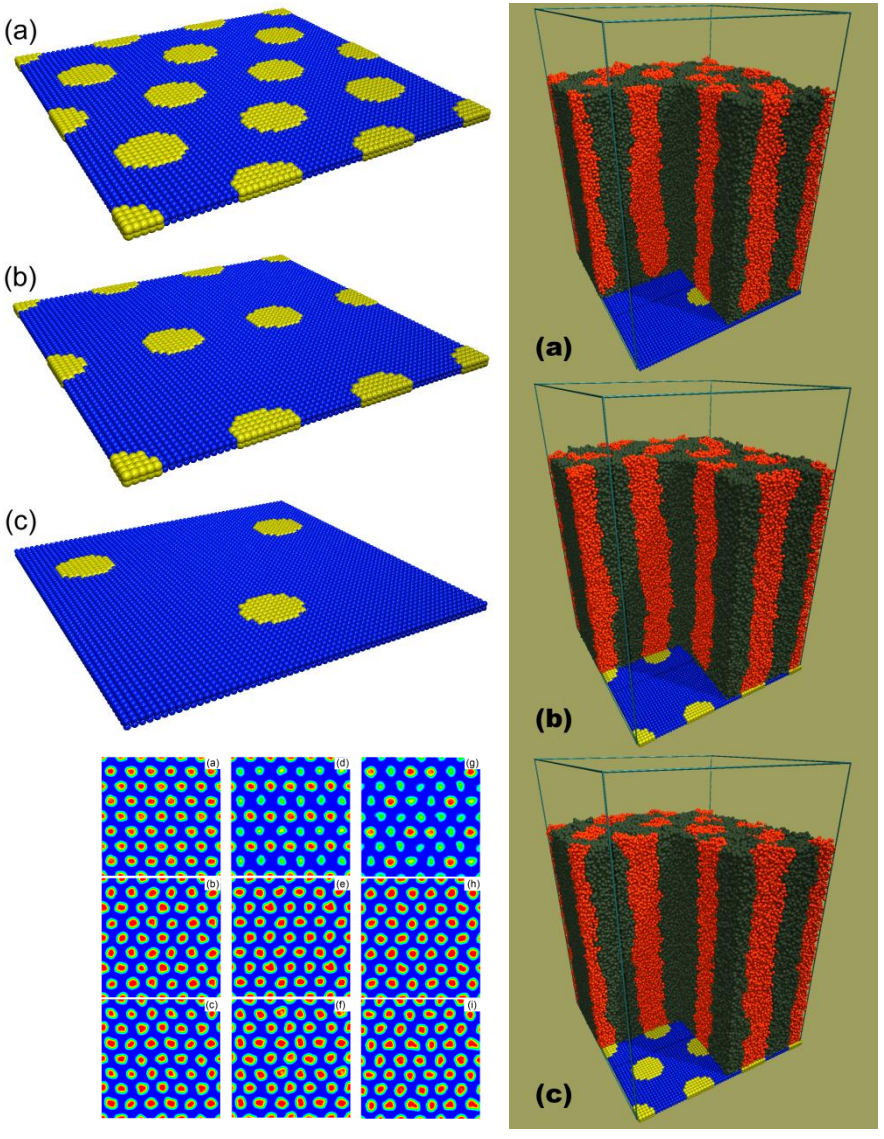


New strategies in microdomain orientation

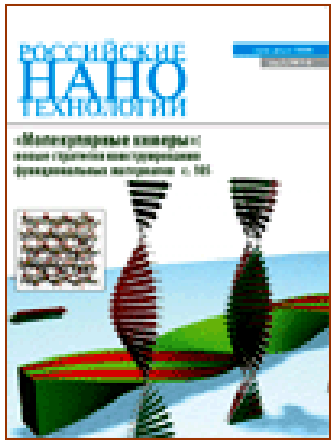
Double phase separation



Influence of orienting pattern. Effect of pattern multiplication

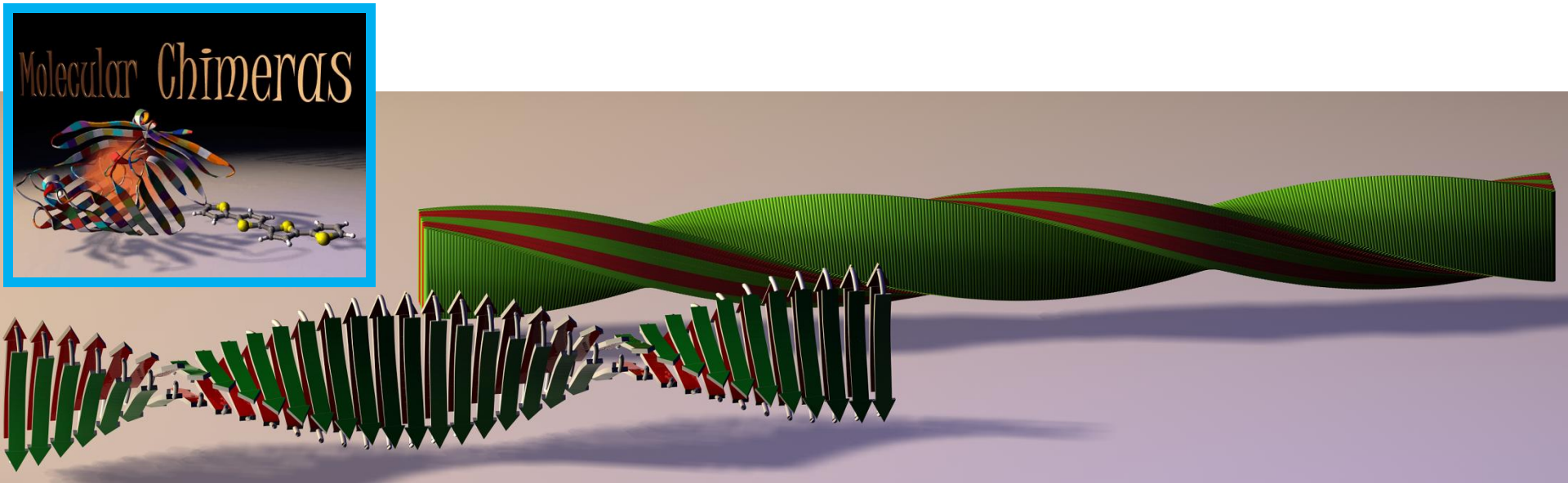


Bioinspired molecular hybrids



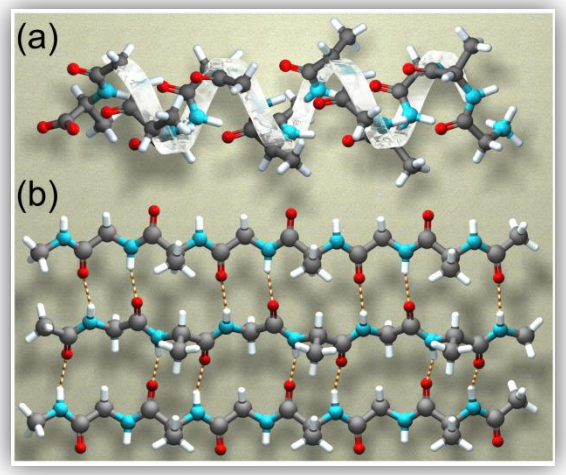
“Molecular chimeras"

… Combining functionalities of biological and synthetic worlds..



Self-organizing bioinspired nanofibers based on oligothiophene-oligopeptide “molecular chimeras"

1. Synthesis



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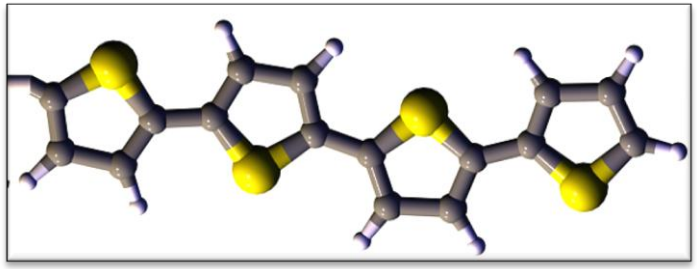

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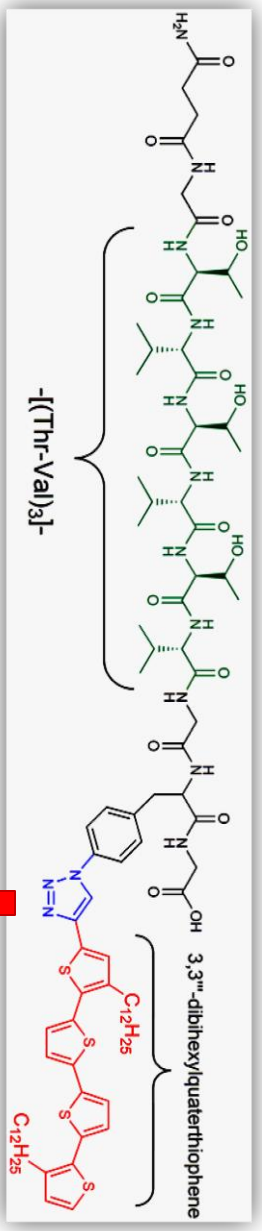
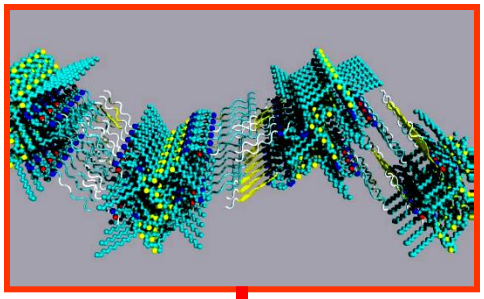
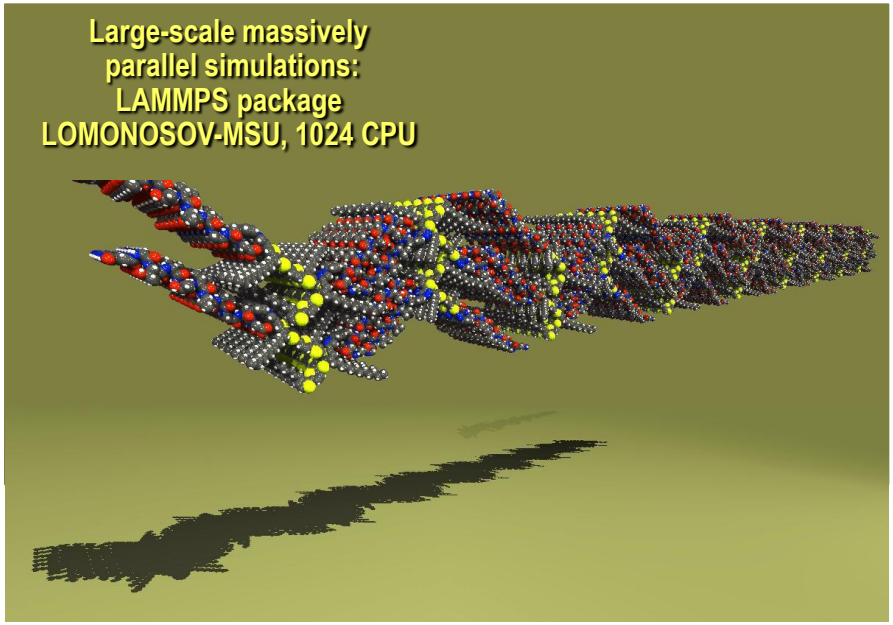


2. Self-organization

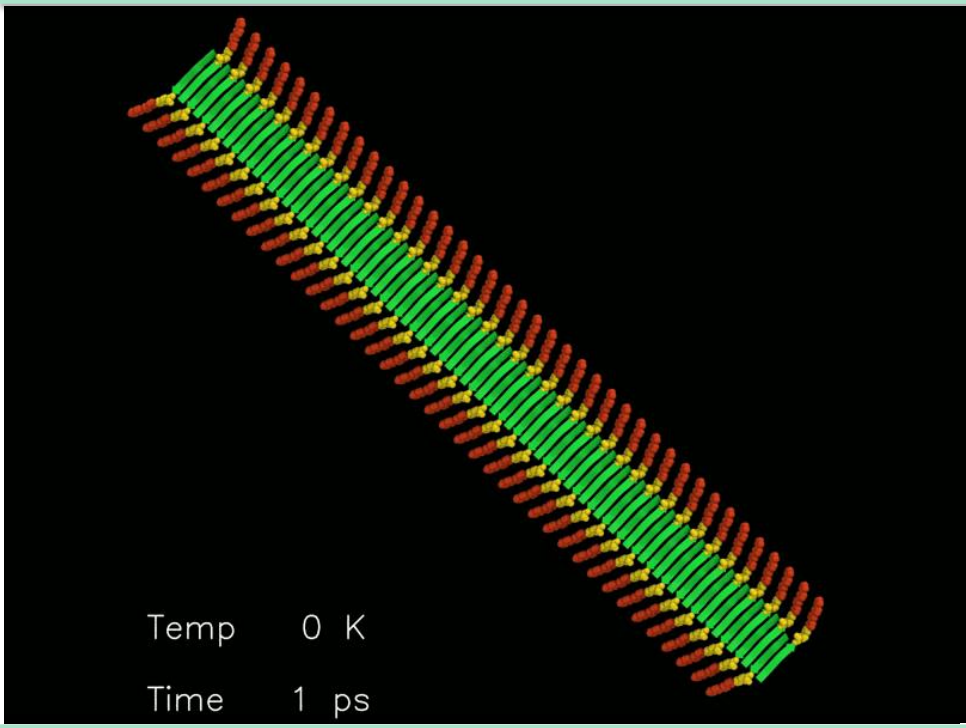


3. Simulation

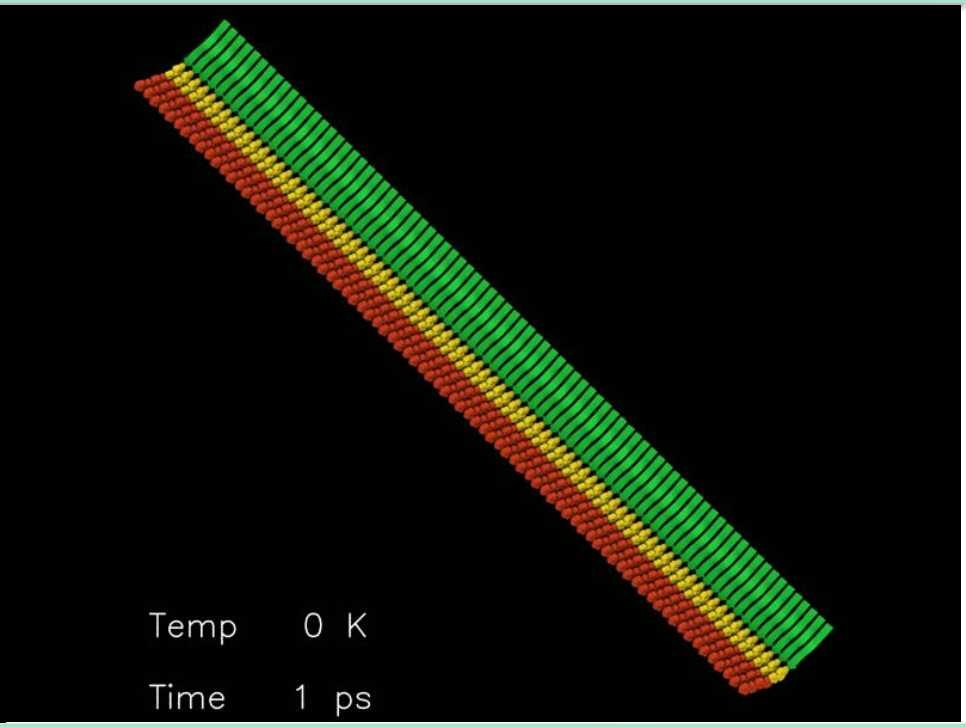


Helix-like Nanofibrils

Dependence of supramoleclar morphology in fibrils formed by thiophene-peptide diblock oligomers on the intermolecular aggregation pattern



Antiparallel arrangement of β-sheets

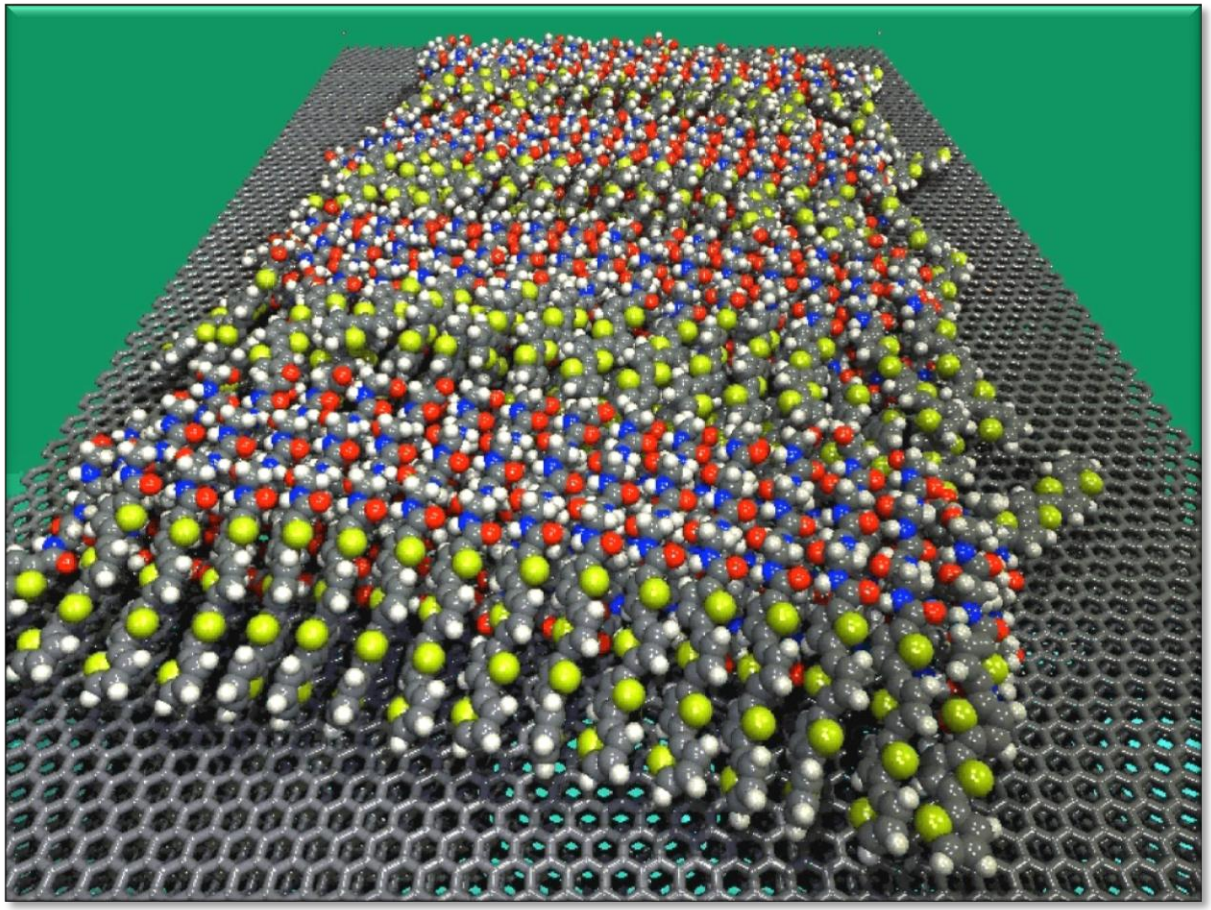


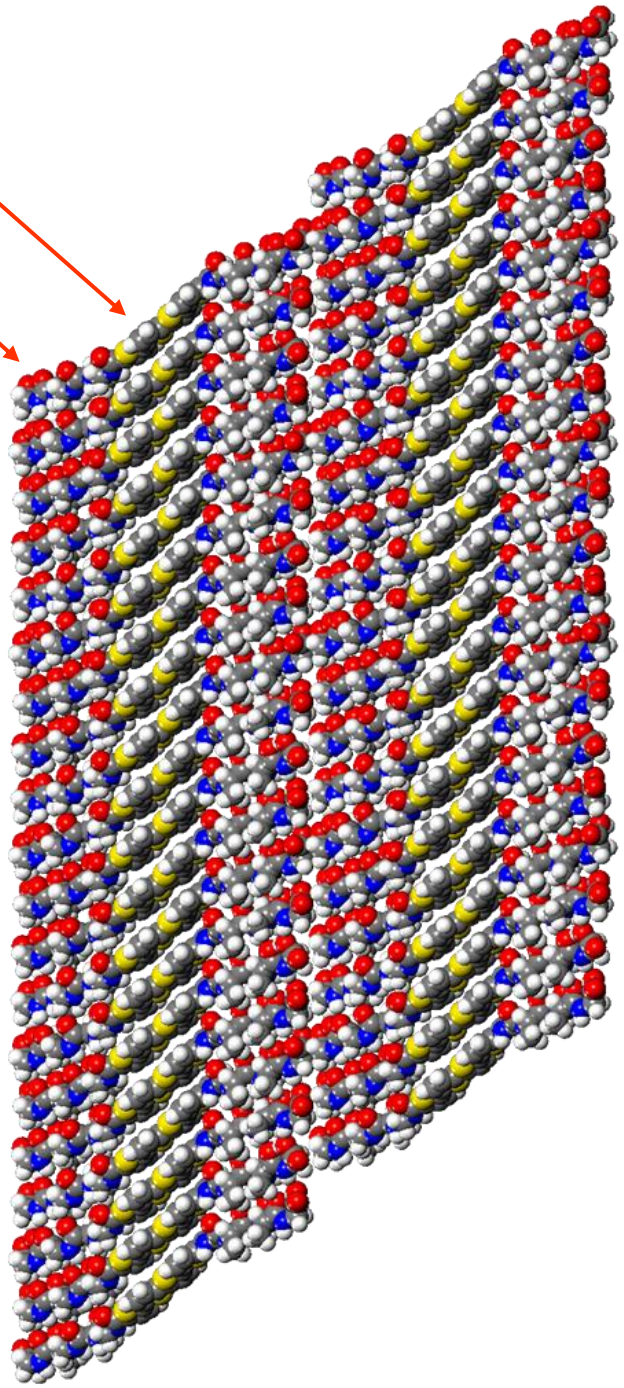
Parallel arrangement of β-sheets

Molecular self-organization on surface:
Functional layered structures

Electroconductive layer

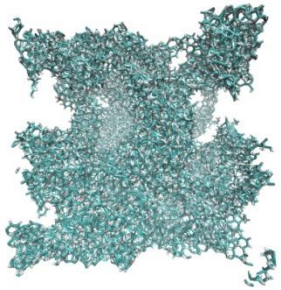
Peptide backbone



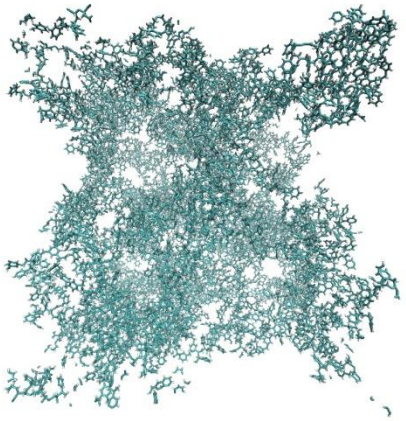


Hypercrosslinked polystyrene

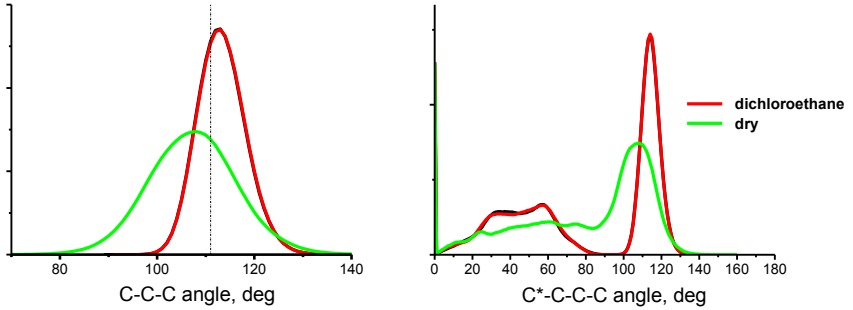
dry



1,2-dichloroethane



Bond and dehydral angles



Elastic modulus, MPa

Linker/polymer ratio *x*	CG	Atomistic
0.5	1.35±0.61	3.6±0.4
1.0	6.7±2.4	65±22

Specific surface, 10^3 m^2/g.

Linker/polymer ratio *x*	CG	Atomistic
0.5	4.6±0.2	4.2±0.2
1.0	3.4±0.2	3.3±0.2

Experimental data (V.A. Davankov, M.P.Tsurupa)
Dry hypercrosslinked PS:
inner surface up to 1000 m^2/g
pore size 2-3 nm

PS swollen in toluene:
Elastic modulus 100 -900 MPa

A. A. Lazutin, M. K. Glagolev, V. V. Vasilevskaya, A. R. Khokhlov. Hypercrosslinked polystyrene networks: an atomistic molecular dynamics simulation combined with a mapping/reverse mapping procedure. - J.Chem.Phys. 2014, v. 140, n. 13, 134903(1-8)