self-assembly in soft matter systems

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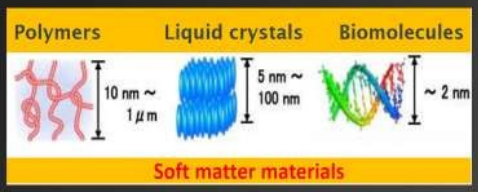
INTRODUCTION



- The macroscopic behavior and functionality of soft nanostructured materials is dictated by chain self-assembly at nano- or meso-scale.

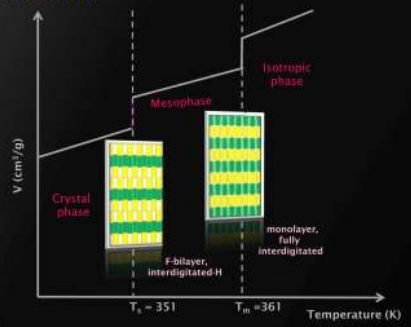
OBJECTIVE

- In this work, apart from MD simulations, **novel atomistic MC algorithms** incorporating conventional (End-mer Rotation, Flip, Reptation, Chain Pivot) and advanced moves (End-Bridging, Generalized Reptation, Concerted Rotation) are designed and implemented in order to predict:

1. the phase behavior of semifluorinated alkanes (SFAs),
2. secondary structure in simple homo-polypeptides, and
3. chain packing and conformation as a function of temperature in polythiophene (nPT) semiconductors.

1. Semifluorinated Alkanes

- Semifluorinated alkanes (SFAs, $F(CF_2)_m(CH_2)_nH$, FmHn) find important biological applications.[1,2]
- **F12H12** (perfluorododecyldodecane) is reported to undergo **two** first-order, pressure-dependent **phase transitions**.[3]



- MD and MC simulations were carried out in the NPT ensemble with the use of a united-atom model.[4]
- In most cases, a cubic simulation cell was used containing 750 chains. But we also ran two simulations using: (a) a rectangular cell , (b) a cubic super-cell (6000 chains).
- The MC code performance was improved by almost one order of magnitude by multithreading on **NVIDIA graphics processing units (GPUs)**.[4]

System	CPU time (s)	GPU-time (s)	Speedup
750-chain	0.662	0.054	12.22
6000-chain	13.84	0.62	22.43

TABLE 1: Data refer to MC simulations with the 750-chain and the 6000-chain **F12H12** systems at T = 390 K and P = 100 atm.

- A spontaneous phase transition from a liquid isotropic phase with randomly distributed chains to a layered smectic-like phase is observed below a certain temperature that is strongly pressure-dependent.

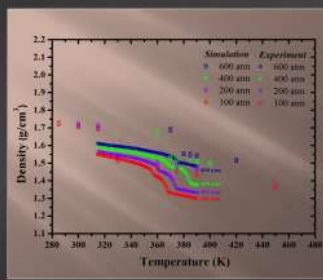


FIGURE 1: Dependence of *simulated density on temperature* at different pressures between 100 and 600 atm from the MD simulations *and comparison with experimental data.*[7] Simulation data are represented by pentagons and experimental data by squares.

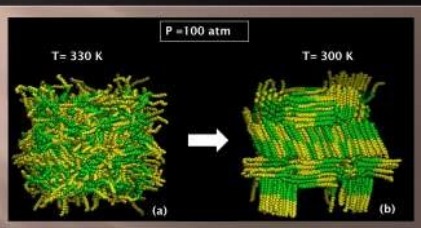


FIGURE 2: *Atomistic snapshots from* the simulations with the 750-chain F12H12 system. With yellow color we have marked the perfluorinated segment in each chain and with green the hydrogenated segment.

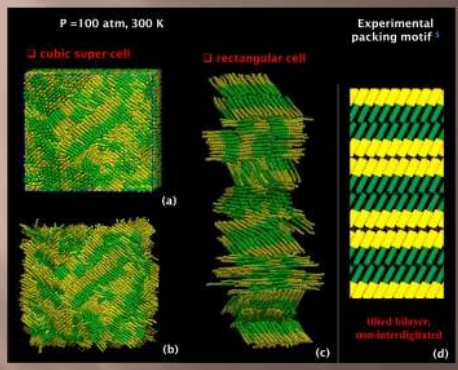


FIGURE 3: Atomistic snapshots from the MD simulations with the 6000-chain F12H12 system in wrapped (a) and unwrapped (b) coordinates, and in a rectangular cell (c), at T = 300 K and P = 100 atm. Part (d) illustrates the simulated lamellae packing (similar to the low temperature phase proposed by Russell *et al.*). With yellow color we have marked the perfluorinated segment in each chain and with green the hydrogenated one.

- Chains in the self-assembled phases are aligned and tilted with respect to the lamellar surface, exhibiting no interdigitation.

ONGOING SIMULATIONS

2. Homo-polypeptides

- **Peptides** are emerging as a new class of materials for important applications in biomedical and tissue engineering.
- **Alanine (Ala, $C_3H_7NO_2$)** is the most helix-stabilizing amino acid residue with the highest propensity for the formation of **a-helices**.[6]
- **MD and MC simulations were carried for different systems of L-Ala(n). We employed the explicit-atom AMBER94 force field.**

- A phase transition occurs from an amorphous coil conformation to an a-helix arrangement at 303 K.

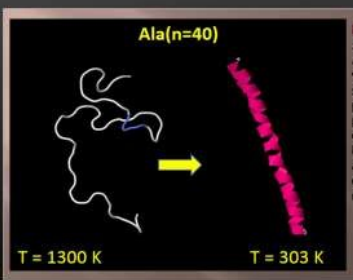
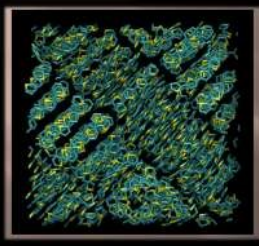


FIGURE 4: *Atomistic snapshots of L-Ala(40)* from vacuum MC simulations. White, purple, violet and pink colors correspond to coil, bend, π-helix and a-helix conformations, respectively.

- Simulations with longer chains both in vacuum and in melt are currently underway.

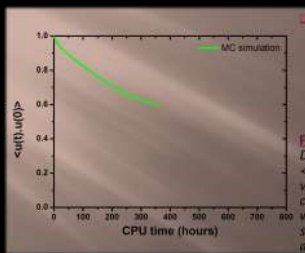
3. Polythiophenes

- **Polythiophenes (nPT, $(C_4H_2S)n$)** are active elements in (opto)electronic devices: light-emitting diodes (OLED), field effect transistors (FETs), and solar cells.
- Unsubstituted oligothiophenes pack into a herringbone arrangement, whereas long chains prefer the π-stacked packing.[7,8]
- MD and MC gradual cooling runs were carried out for nPT systems, with n=4-40. We used the explicit-atom Dreiding force field.



- Self-assembly of 4PT at 500 K.

FIGURE 5: *Atomistic snap shot* in wrapped coordinates *from the simulations with the 240 chain-4PT system, at T = 500K and P = 1atm.* With yellow color we have marked the sulfur atom and with cyan the carbon atoms. Hydrogen atoms have been omitted for clarity.



- The rate with which $\langle u(t)\cdot u(0)\rangle$ drops to zero provides a measure of the efficiency of the method to equilibrate the 20PT system.

FIGURE 6: *Decay of the ACF* $\langle u(t)\cdot u(0)\rangle$ *of the unit vector directed along the chain end-to-end vector with CPU time for the 20PT system at 1100K and 1 atm.*

- The fast equilibration of longer-chain nPT systems demands, apart from the incorporation of the end-bridging move in the MC algorithm, a MPI parallel implementation (work currently in progress).

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