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AND LIQUID CRYSTALLINE POLYMERS**

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ORAL CONTRIBUTIONS

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Computer simulation of large flexible liquid crystal molecules

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The techniques necessary for the simulation of high molar mass liquid crystals are no different to those used for low molar mass molecules. However, even relatively simple models, such as those in which single site potentials are used to model the mesogenic units and the flexible chains linking the mesogens are modelled by a string of Lennard-Jones atoms, are computationally expensive to simulate. This is partially due to the fact that, whilst the liquid crystal units are modelled at the coarse grained molecular level, the chains are modelled using atomic like potentials. To be able to simulate high molar mass, flexible liquid crystalline molecules, we require models which are computationally cheaper, but retain the essential physics of the molecules.

We highlight some preliminary results for a new model for the study of flexible, high molar mass liquid crystals, based on the bond fluctuation model which has proved to be an extremely useful model for studying polymeric systems.

The model consists of flexible chains in which the subunits are designated as either mesogenic or alkyl units, with appropriate interactions between these. In this model, the chains are modelled at the same level of detail as the mesogenic units. The phase diagram for a low molar mass system composed solely of monomers exhibits nematic and smectic A phases, in addition to an isotropic phase at high temperature.

Main chain liquid crystal polymers can easily be constructed without changing the density by joining a number of these monomers together by their terminal flexible chains. Simulations using such models indicate that the nematic phase is destabilised with respect to the smectic A phase on changing the topology of the molecules at fixed density.

Computer simulations of the dendritic molecules with the aid of configurational biased Monte Carlo

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We have developed a variant of the configurational bias Monte Carlo approach that is suitable for simulations of highly branched macromolecules.

The main targets are dendritic and elastomeric polyatomics, including ones with "internal" or "external" mesogenic groups.

The efficiency of the method described is tested using single-molecule and bulk systems of dendritic molecules of different generations.

Protein adsorption on a hydrophobic graphite surface

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We report our recent results about the adsorption of some protein fragments on a flat graphite surface. Using atomistic simulations for both the proteins and the surface, we first carry out direct energy minimizations in an effective dielectric medium, considering different orientations of the fragments close to the surface. Afterwards, we perform long Molecular Dynamics simulation (1-2 ns) of selected optimized geometries in the same medium, and finally we optimize a large number of the instantaneous snapshots in search of the absolute energy minima. We propose that this procedure yields both the initial and the final adsorption stage on a bare surface, allowing for possible rearrangements and denaturation. Short MD runs are also carried out explicitly including a very large number of water molecules to study the system hydration in both adsorption stages.

We consider two albumin fragments with different hydrophobicity patterns, and a fibronectin type I module (Protein Data Bank entries 1AO6 and 1FBR). These globular proteins of the human serum have a wholly different secondary structure, since albumin contains only α -helices, while the selected fibronectin module is made up of β -sheets (both molecules also comprise random strands, of course).

Our results indicate that the initial adsorption takes place with significant conformational rearrangements close to the surface. This feature is particularly noticeable in the albumin fragments, which lose their α -helical structure at the interface, though otherwise preserving the secondary structure and the globular shape. Conversely, the fibronectin fragment undergoes minor changes upon the initial adsorption. In the long MD runs, the fragments show much larger rearrangements and an almost complete denaturation in order to maximize the surface covering. In this way, in spite of a greater intramolecular strain they achieve a much larger interaction energy. Interestingly, we also find that the surface may induce partially ordered arrangements.

Finally, the hydration pattern shows significant changes upon adsorption. In fact, the large molecular rearrangements expose all the residues to water, thus enhancing their solvation. Accordingly, the protein fragments optimize both the interaction energy with the surface and their hydration energy.

Molecular Simulation of the Glass Transition in PMMA of Different Tacticities

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Poly(methyl methacrylate), PMMA, has the special feature of exhibiting different glass transition temperatures, T_g s, according to the tacticity of its chain. Actually this difference can be interpreted only in changes in molecular characteristics. Consequently, molecular modeling offers an ideal tool to understand, from the probing of the molecular interactions, the reasons that give rise to such a difference, and accordingly, to better understand the tricky problem of glass transition.

The difference in the T_g s between the two PMMA configurations has been accurately simulated using molecular dynamics simulation in the bulk. Variations in the non-bond energy, intra-diade angles, and in the local dynamics, are reported.

An energetic analysis shows that the non-bond energy and the bending angle energy associated to the intradiad backbone angle, principally contribute to the energetic difference between the two PMMA configurations. These two energetic contributions actually result from the substitution of the hydrogen atom attached to the chiral carbon atom in the PMA repeat unit by a methyl group, giving the PMMA. Such a substitution also implies a variation in the local dynamics.

To reveal local motions, correlation times are computed: flexibilities of the backbone and the side-chain are thus looked at. At a specific temperature, both configurations display different backbone and side chain flexibilities, but at $T + T_g$, only a difference in the side-chain mobility is observed. Considering the mode coupling theory, cooperativity can be revealed. A coupling is thus clearly observed between the side-chain and the backbone. Moreover, this coupling is different according to the chain tacticity. Such a behavior tends to explain the difference in the T_g s between the two configurations in PMMA.

Molecular modeling is thus used as a tool to probe the molecular interactions, and to guide the understanding of the glass transition, that is still a striky and conceptually unresolved thermal transition.

Entropic sampling of simple polymer models within Wang-Landau algorithm.

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A new Monte Carlo simulation technique proposed by Wang and Landau (WL) in [1] is applied to sampling of 3-dimensional lattice and continuous models of polymer chains. Density of states obtained by homogeneous (unconditional) random walk is compared with the result of entropic sampling (ES) [2-4] within WL-algorithm. While homogeneous sampling gives reliable results typically in the range of 4-5 orders of magnitude the WL entropic sampling yields them in the range of 20-30 orders and even larger. A combination of homogeneous and WL-sampling provides reliable data for events with probabilities down to $1.E-35$.

For the lattice model we consider both the athermal case (self-avoiding walks, SAWs) and the thermal case when an energy is attributed to each contact between nonbonded monomers in a self-avoiding walk. For short chains the simulation results are checked by comparison with the exact data. In WL-calculations for chain lengths up to $N=300$ the scaling relation for SAWs [5,6] is well reproduced. In the thermal case distribution over the number of contacts is obtained in the N -range up to $N=100$ and the canonical averages - internal energy, heat capacity, excess canonical entropy, mean square end-to-end distance – are calculated as a result in a wide temperature range.

The continuous model is studied in the athermal case. By sorting conformations of a continuous phantom freely joined N -bonded chain with a unit bond length over a stochastic variable – the minimum distance between nonbonded beads - we determine probability distribution for the N -bonded chain with hard sphere monomers over its diameter a in the complete diameter range, $0 < a < 2$, within a single ES run. This distribution provides us with excess specific entropy for a set of diameters a in this range. Calculations were made for chain lengths up to $N=100$ and results were extrapolated to N tending to infinity for a in the range $0 < a < 1.25$.

[1] F.Wang, D.P.Landau, Phys.Rev.Lett. 86, 2050 (2001).

[2] B.A.Berg, T.Neuhaus, Phys.Rev.Lett. 68, 9 (1992).

[3] J.Lee, Phys.Rev.Lett. 71, 211 (1993).

[4] Y.Iba, Int.J.Modern Phys. C 12, 623 (2001).

[5] P.G. de Gennes, Scaling Concepts in Polymer Science, Cornell University Press, Itaca & London (1979).

[6] J.Douglas, C.M.Guttman, A.Mah, T.Ishinabe, Phys.Rev. E 55, 738 (1997).