Isotropic - Nematic Phase Behaviour in Lyotropic Solutions of Semiflexible Polymers in the Bulk and under Confinement: Density-Functional Theory tested by Molecular Dynamics

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Different Location

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LOCATION: TU Wien, Wiedner Hauptstr. 8-10, Seminar room DB gelb 7 [7th floor, yellow area]

Semiflexible polymers in solution are studied for a wide range of both contour length and persistence length as function of monomer concentration under good solvent conditions. Both density-functional theory (DFT) and Molecular Dynamics (MD) simulation methods are used, and very good agreement between both techniques is observed for rather stiff polymers. Evidence for a new mechanism of order parameter fluctuations in the nematic phase is presented, namely collective deformations of bundles of wormlike chains twisted around each other, and the typical wavelength and amplitudes of these modes are estimated. These long wavelength fluctuations cause a reduction of the order parameter in comparison with the DFT prediction. It is also found that DFT becomes unreliable for rather flexible polymers in predicting that the transition from isotropic phase to the nematic phase still exists at very high monomer concentration (which in reality does not occur). However, under conditions when DFT is accurate, it provides reliable predictions also for the width of the I-N two-phase coexistence region, which are difficult to obtain from MD in spite of the use of very large systems (up to 500,000 monomers) by means of Graphics Processing Units (GPU). For short and not very stiff chains, a pre-transitional chain stretching is found in the isotropic phase near the I-N-transition, not predicted by theories. A comparison to theoretical predictions by Khokhlov-Semenov, Odijk, as well as Chen reveals that the scaled transition densities are not simply functions of the ratio of the contour length to the persistence length only, as these theories predict, but depend on the ratio of the chain diameter to the persistence length as well. Chain properties in the nematically ordered phase are compared to those of chains confined in tubes, and the deflection length concept is tested. In addition, some consequences for the interpretation of experiments are spelled out.