

5 Conclusions and Outlook

An extensive simulations of highly incompatible polymers with different stiffnesses and polymers with different monomer sizes have been presented. Of special interest is to study interfacial properties in both cases and phase behavior in stiffness disparity systems.

The flexibility of semiflexible polymers covers whole range, i.e. from flexible to stiff rod. The semiflexible chains are constructed by keeping restrictions on the consecutive bond vectors of a chain. The thermodynamic quantities like interfacial tension and interfacial width have been studied. The interfacial tension increases with increase in stiffness of the semiflexible component and there is a strong tendency towards saturation. It gets saturated well below the stiffness of semiflexible chains which form nematic phase. In this range of low stiffness of semiflexible chains the simulation data agree very well with the self-consistent field (SCF) theory data of Helfand and Sapse [20] by taking account of finite length of the polymers. The intrinsic interfacial width which is calculated by considering persistence length as the lower cutoff length also agrees very well with mean field SCF theory of Helfand and Sapse [20] by taking into account the finite length of the polymers. The intrinsic interfacial width increases with the stiffness of the semiflexible polymers whereas the total interfacial width decreases. The interfacial width decreases remarkably in the isotropic-nematic interface than in isotropic-isotropic interface. To characterize the local structure of the interface, the density profile of different monomer species, distribution of chain end, distribution of center of mass of chains, orientation profiles of chains and bonds are studied as function of stiffness of the semiflexible components. As the stiffness increases the density profile becomes sharper in semiflexible side and the depth in the total density profile goes on increasing. The flexible chains in a region rich in stiff chains cost more configurational entropy than stiff chains in a flexible-rich region. Therefore, flexible chains are expelled from the stiff-rich side, leading to steeper gradients in monomer density profile. A similar effect is seen in the phase behavior of blends of stiff and flexible chains [91]. The chain ends are more in the interface and the effect increases with the increase in the stiffness of the semiflexible component. Center of mass of chains have minima at the center of the interface. Near the interface, the polymers are stretched parallel to the interface. The polymers are strongly stretched on side of semiflexible polymers and the effect increases with the stiffness of the semiflexible component. The individual bonds also orient parallel to the interface and the effect is stronger on side of semiflexible polymers. The effect increases with the stiffness of the semiflexible components. Until the semiflexible chains in a flexible-semiflexible system

are close to isotropic-nematic transition, the orientational effect tends to be small. This leads to interfacial tensions governed solely by the composition profile and so it agrees very well with that of Helfand-Sapse. In the case of flexible-highly-stiff polymer system the interfacial tensions governed not only by compositional profile and hence one has to take into account the orientational profiles also. For such a system a mean field theory beyond Helfand-Sapse is an essential.

The critical value of χ for a flexible-semiflexible polymer systems are estimated using the mean field exponents. From our results, it is seen that the mean field exponents are correct. The critical value of χ decreases with the stiffness of the semiflexible component hence the critical temperature increases.

The interfacial tension for a monomer size disparity system agrees very well in both cases namely, monomer size disparity with equal number of monomers per chain and monomer size disparity with almost equal radius of gyration of two types of chains. The interfacial width increases with the monomer size disparity. The monomer density profiles are calculated for the different species. Similarly, to the case of stiffness disparity the polymer chains prefer to orient parallel to the interface in the interface region. The chains having larger beads of unsymmetric systems orient more parallel to the interface in comparison to the symmetric system. The effect is not strong like the case of semiflexible chains close to isotropic-nematic transition. The chain ends are more at the interface and the effect is stronger for the monomer size disparity systems. The center of mass of polymers have minima at the interface.

The main conclusion of the present work is the following. The mean field theory of Helfand-Sapse is correct for the flexible-semiflexible polymer system provided semiflexible chain are far enough from isotropic-nematic transition. It can describe the monomer size disparity system also.

The effect of flexible-semiflexible diblock copolymers on the flexible-semiflexible homopolymer interfaces and polydispersity effect will be our future work in this field. Further the combination of stiffness disparity and monomer size disparity (which are studied in the present work) may help to model any polymer blends.