

COUPLING EFFECTS IN EQUILIBRIUM AND NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATION OF POLYMER MELTS

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The motion in concentrated polymer systems is described by the Rouse or reptation models, which both assume that the relaxation of each polymer is essentially independent of the other polymers. In Rouse theory the only effect of surrounding chains is a random isotropic Brownian force. Reptation theory assumes that each polymer slithers through a tube made of other polymers, again independently of each other. However, various experiments have shown that there is certain cooperativity in the orientational relaxation which is called coupling effects. In our simulations, we calculate orientation self- and cross-correlation functions to quantify this coupling effect for original monomer and for coarse-grained blobs. We investigate this effect in binary blend of unentangled and weakly entangled chains in wide range of density and chain stiffness by using simple bead-spring model of polymer melt. We found that the coupling effects are very significant and increase over time. A universal time-dependent coupling parameter for monodisperse and bidisperse melts was introduced, and was consistent with the results in the experiments and other simulations. Based on this universal coupling parameter, we can predict self- and cross-correlation orientation functions in binary blends by using relaxation functions in monodisperse melt of each component. This coupling parameter is also introduced for different level of coarse-graining. The coupling decreases with increasing the coarse-graining number. We also investigated the coupling effects in the system with soft potential in which the polymer chains were allowed to cross each other. Similar behaviour was observed. However the coupling index was smaller than the original hard system at longer time, which can possibly be related to entanglements. We also investigated the coupling effect in shear of binary blends and monodisperse melts and found that the short component was oriented by coupling with long component in binary blends even if the shear rate is smaller than the inverse of the longest relaxation time of the short component.