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Intermolecular constraints in the dynamics of semiflexible entangled polymer melts MARINA GUENZA, University of Oregon — We present a Langevin equation for the contemporary dynamics of a group of interpenetrating semiflexible entangled polymer chains. The theory explicitly accounts for the intermolecular intermonomer repulsion between a pair of chains, generated by their inability to cross each other, i.e. the phenomenon of entanglements. The "effective" potential experienced by the chains arises from the repulsion between two monomers belonging to different chains, propagating through the chain connectivity, and the dynamics of chain interdiffusion and relaxation. With time the local hard-core potential is overcome by the relative motion of the polymers and the system relaxes. The same formalism applies to both unentangled and entangled melts. Short chains do not experience entanglements, because their relaxation process is faster than the average time that is necessary for the chain to diffuse a distance comparable to the mesh size, or length between two entanglements. Finally no a priori hypothesis has to be made about the processes that drive relaxation as the formalism is simply the conventional Rouse approach, generalized to treat the motion of interacting macromolecules, whose chains cannot cross each other.

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