Computational study of the dynamics and thermodynamics of highly confined polyethylene

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Abstract

The study of chain diffusion in polymers is an active research field, since it is related to the glass transition. Although in simple molecules liquid mobility requires a minimum of kinetic energy, in macromolecules before the liquid to solid transition the viscosity and the relaxation times increase dramatically. Moreover it has been shown [1-5] that attractive confining walls introduce one more mechanism (in addition to the caging effect and intramolecular conformational barriers) for time scale separation of glass forming polymers. This mechanism is the slow desorption kinetics of monomers from the surface, leading to slow layer exchange dynamics on the length scale of (at least) the radius of gyration of the chains. Several experimental works [6] have supported the idea that the confined/bounded layer is immobilized above the major T_g, in such a way that finally it does not participate in the glass transition.

We present results concerning the dynamics and the structure of the adsorbed layer of polyethylene (PE) between two graphite surfaces [7]. By the use of molecular dynamics simulation we reveal the distribution of relaxation times as a function of the distance from the graphite walls at the temperature of 450 K. From the atomic-level stresses we calculate the adhesion tension. Although the gap between the two walls is comparable to the width of the adsorbed layer, we do not record the formation of 'glassy bridges'. The diffusion of polymer chains in the middle layer is not inhibited significantly by the existence of the two adsorbed layers (loops and tails). Then by modifying the Sanchez-Lacombe EoS [8] we follow accurately the temperature dependence of the free volume. Using a self consistent mean field theory we make predictions about gradients in viscosity. Also we locate and characterize the transition of the confined layer to a rigid amorphous phase.

References

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