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Dynamics of Polymer Melts Confined in Porous Media Probed by Computer Simulation - Influence of Corset Effect

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1. Introduction

One of the main questions of modern polymer physics concerns the long-living dynamical correlations in polymer melts appearing as a result of the uncrossability of polymer chains. It was recently observed that the confinement of polymer melts in nanoscopic pores leads to chain dynamics dramatically different from the bulk behavior already at time scales when typical segment displacements are much shorter than the pore diameter D_{pore} [1]. It was revealed that under confinement conditions polymer chains actually reptate essentially along their own contour whereas lateral displacements are strongly suppressed. The effective tube diameter under confinement conditions, $d \underset{\cdot}{\sim} 5$ Å, is one order of magnitude smaller than the diameter $d_{\mathrm{rep}} \sim 70$ Å suggested by fits of the tube reptation model to experimental data of the viscoelastic plateau. This means that under confinement conditions polymer chains actually reptate essentially along their own contour whereas lateral displacements are strongly suppressed.

The "corset effect" explicitly demonstrates that the low value of the isothermal compressibility in combination with the mutual uncrossability of polymer chains leads to dynamical correlations of chains separated from each other by distances much larger than the Flory radius. Preliminary qualitative calculations show that the terminal relaxation time should scale with the molecular mass as $\tau_1 \propto N^{13/4}$, and the self-diffusion coefficient as $D \propto N^{-9/4}$. Both results are very close to the known experimental observations $\tau_1 \propto N^{3.4}$ and $D \propto D_0 N^{-2-2.5}$.

2. Monte Carlo simulation

We use the Monte Carlo method for the simulation of model polymer melts with different density. The polymer chain represents a sequence of segments comprising n hard spheres. The move of the chain is realized according to the modified Stockmayer model [2] in a cube box with periodic boundary conditions. Our evaluations include investigations of the time dependencies of the mean squared displacement of polymer segments, the correlation function of the segment tangent vector, and the frequency dependence of the NMR spin-lattice relaxation of the bulk melt and of the melt confined in nanoscopic pores.

References

[1] N.Fatkullin, R.Kimmich, E.Fischer, C.Mattea, U.Beginn and M.Kroutieva, New Journal of Physics. – 2004.- V.6(46)
[2] A.Denisov, M.Kroutieva, N.Fatkullin, R.Kimmich, J.Chem.Phys.- 2002. - V.116, No.12. – P.5217