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The confined-to-bulk dynamics transition of polymer melts in nanoscopic pores of solid matrices with varying pore diameter

Fatkullin N., Kimmich R., Fischer E., Mattea C., Beginn U., Kroutieva M.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

The confinement of polymer melts in nanoscopic pores leads to chain dynamics significantly different from bulk behaviour. This so-called 'corset effect' occurs both above and below the critical molecular mass and induces dynamic features as predicted for reptation. The confined-to-bulk dynamics crossover is treated analytically on the basis of general thermodynamic relations connected to the fluctuation of the number of particles (Kuhn segments) in a given volume. Bulk behaviour is shown to occur only if the pore diameter complies with the limit $d_{\text{pore}} \gg (b^3/k_B T \kappa)^{1/3} R_F \approx 10 R_F$, where b is the Kuhn segment length, κ the isothermal compressibility, T the temperature, k_B the Boltzmann constant and R_F the Flory radius. For smaller pores, the confined polymer chains reptate along their own contours in tubes with an effective diameter $d \approx \sqrt{b^2 \rho_s k_B T} \approx 0.5 \text{ nm}$, where ρ_s is the number density of Kuhn segments. From the theoretical point of view, the crucial factors on which the corset effect is based are (i) impenetrable pore walls, (ii) low compressibility and (iii) the uncrossability of polymer chains.

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