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Can a reduction in mass transport occur at invariant segmental time? SIMONE NAPOLITANO, MICHELE SFERRAZZA, Universite Libre de Bruxelles — The glassy dynamics of polymer melts adsorbed onto solid substrates shows a peculiar confinement effect: a severe reduction in mass transport occurs without a corresponding increase in segmental relaxation time. This phenomenon provides a "negative violation" of the Stokes-Einstein (SE) relation, not observed in bulk melts or confined water. Explaining those findings in analogy to the large drop of thermal expansion reported in polymers under 1D confinement, we considered the presence of an interfacial dead layer where tracer diffusivity assumes negligible values. To verify this hypothesis, we performed an extensive investigation of the diffusion of styrene oligomers, acting as tracers, into matrices of high molecular weight polystyrene, irreversibly adsorbed onto aluminum oxide. We demonstrate that the reduced interfacial diffusion is due to larger residence times of the tracers inside the dead layer, t_{DL}. In particular, we show that t_{DL} is directly proportional to the amount of irreversibly adsorbed monomers, a quantity limiting the available space for diffusion. We thus discuss of a dynamic dead layer evolving within the adsorbed layer, and of its role on the dynamics of glassy polymers under confinement and the "negative violation" the SE relation.

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