Kinetics and thermodynamics of solvated polymer infiltration into confinement

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We have previously introduced a one-step, room temperature method for the fabrication of high filler-fraction (> 50vol%) polymer nanocomposites through solvent-driven infiltration of polymer (SIP) into nanoparticle (NP) packings. A bilayer thin film of polystyrene (PS) and SiO_2 NPs is exposed to solvent vapor, which leads to capillary condensation of solvent in the voids of the NP packing, and subsequent plasticization and infiltration of the underlying polymer. We find that SIP is driven primarily by a competition between adsorption, solvation and confinement. After exposure to a good solvent (PS/toluene, $\chi \approx 0.3$) for a fixed period of time, the extent of polymer infiltration is strongly affected by confinement. However, at longer exposure times, systems with higher confinement reach the same final polymer volume fraction within the voids of the NP packing. This is surprising, and indicates that, while the dynamics are affected by confinement, the thermodynamic driving force for infiltration is not significantly reduced even for very strong confinement. Furthermore, we study the impact of solvent quality by using a poor solvent (PS/cyclohexane, $\chi \approx 0.5$) and the impact of polymer-NP affinity by changing the polymer to poly(2-vinylpyridine), which has H-bonding interactions with the NP surface. To unpack the dynamic scaling behavior of such systems, we develop an entropic barrier model from self-consistent field theory (SCFT) simulations of a confined, solvated polymer translocating through a narrow pore.