Oligomer/polymer blend phase diagram and surface concentration profiles for squalane/polybutadiene: experimental measurements and predictions from SAFT-γ Mie and molecular dynamics simulations

Supporting Information

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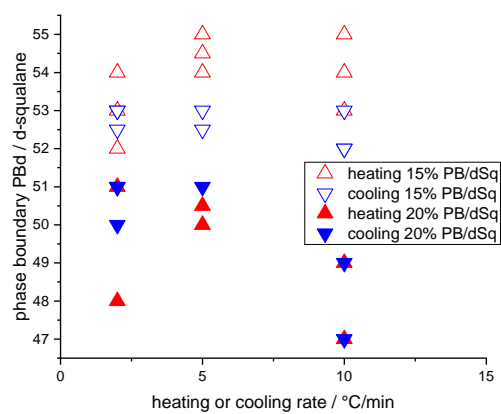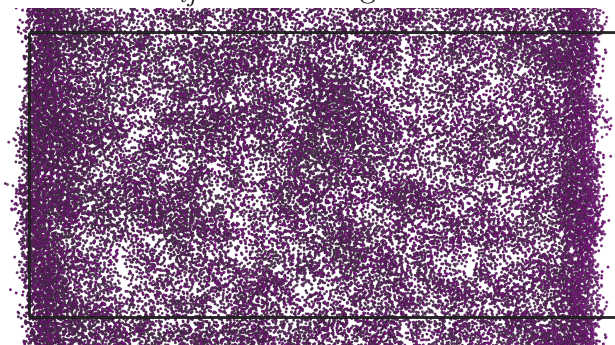
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Figure 1: Phase boundaries obtained for PB/d-sq using different heating and cooling rates.

a) Miscible conditions with $k_{ij} = 0$ showing surface enrichment by oligomers.

b) Immiscibility condition with $k_{ij} = +0.02$ showing the formation of a wetting layer and a large droplet of squalane after 360 ns of simulation time (the droplet forms after 100 ns of simulation time from an initial homogenously mixed system).
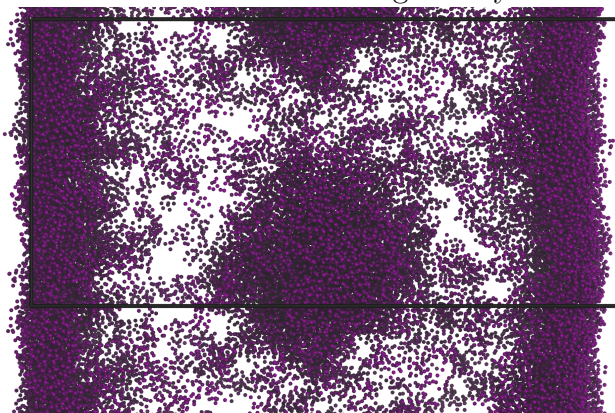
c) Immiscibility condition with $k_{ij} = +0.02$: equilibrated system after 1.367 μs of simulation time.
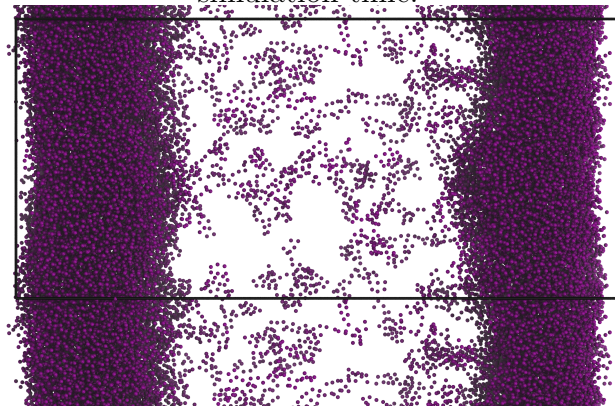

Figure 2: Molecular dynamics snapshots from a 102k bead system at 450 K with 40 w/w% oligomer. Squalane beads are shown in palatinate purple, PB polymer beads are not shown for clarity. The black box represents the explicitly modelled unit cell.
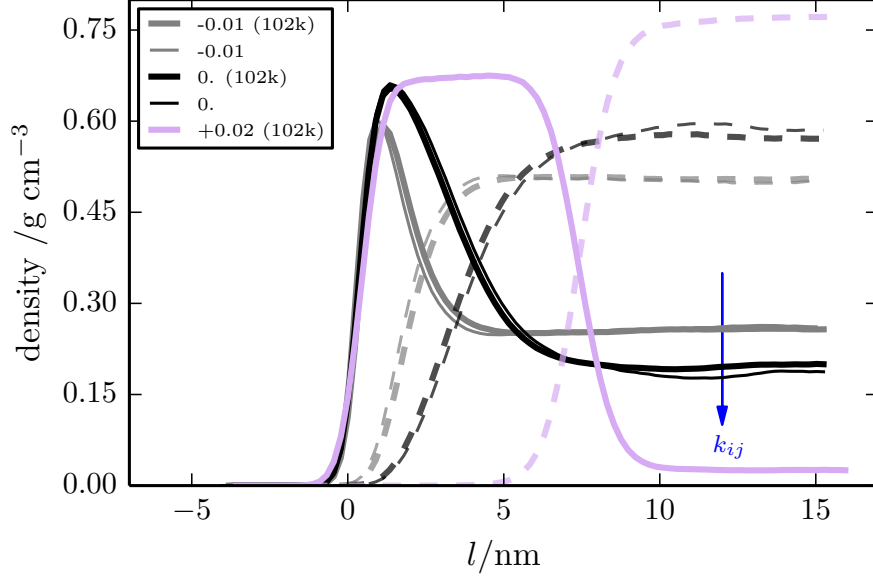
Figure 3: Squalane and polymer surface density profiles obtained by CGMD at 450 K for systems with differing unlike interaction parameter k_{ij}, ranging from attractive ($k_{ij} = -0.01$) to repulsive ($k_{ij} = +0.02$). Results are shown for a $25k$ bead system and a $102k$ bead system. The partial density of oligomers is shown by bold lines and the partial density of polymers shown by dashed lines. Surface enrichment varies from a small concentration increase at the surface to a pure squalane surface layer. An initial constant global squalane concentration of 40% was used for each simulation.
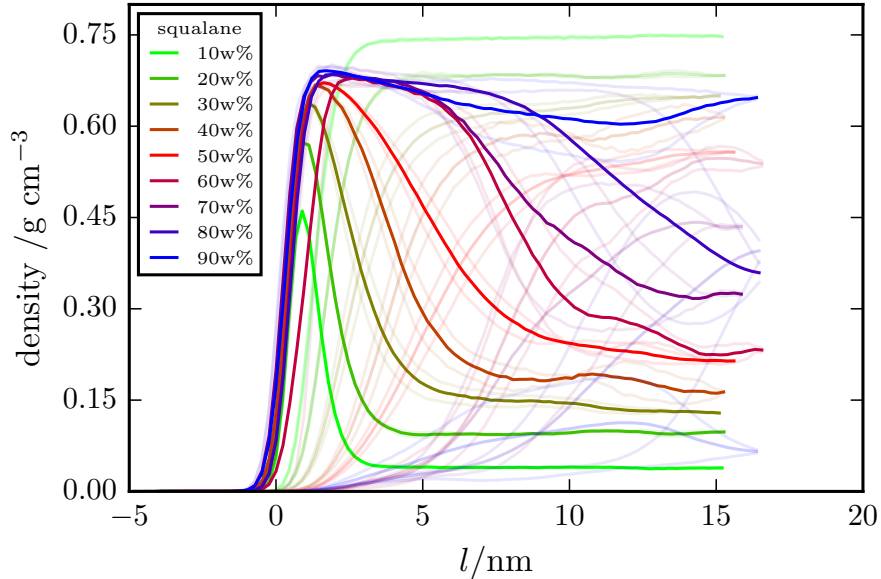

Figure 4: CGMD squalane surface profiles of a compatible system ($k_{ij} = 0.0$) at several compositions. Lines of strong colour represent squalane concentrations, half-transparent lines represent polybutadiene concentrations. Concentration profiles are obtained from averaging both surfaces. The individual surface profiles are plotted in transparent lines.
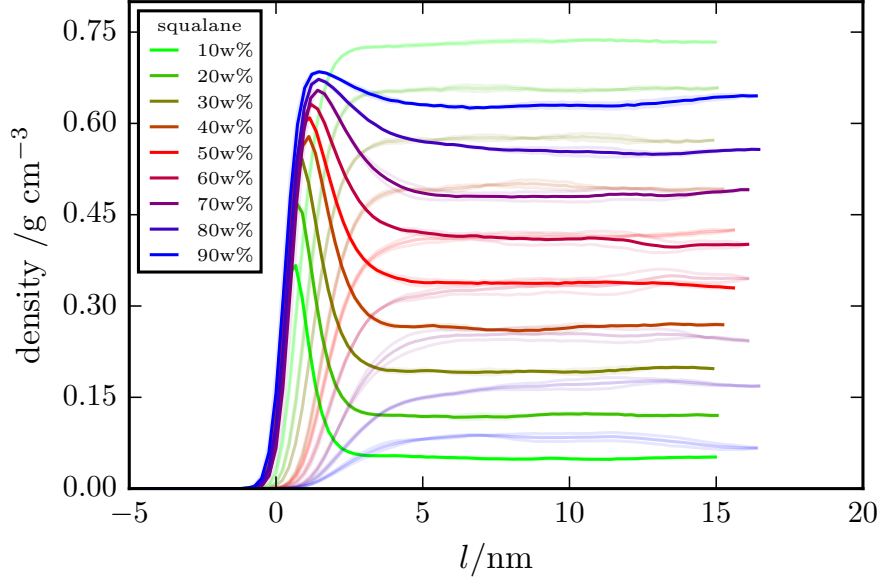
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Figure 5: CGMD squalane surface profiles of a compatible system ($k_{ij} = -0.00165$) at several compositions. Lines of strong colour represent squalane concentrations, half-transparent lines represent polybutadiene concentrations. Concentration profiles are obtained from averaging both surfaces. The individual surface profiles are plotted in transparent lines.
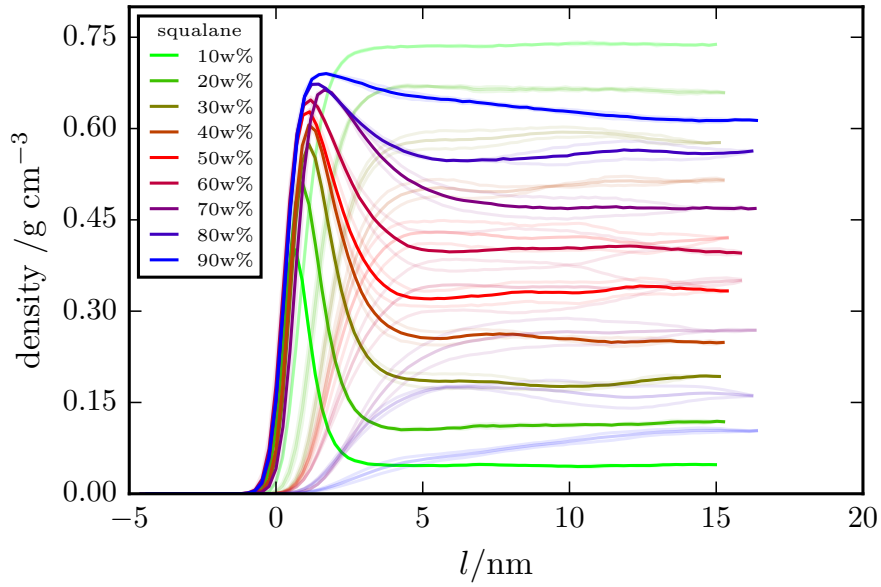

Figure 6: CGMD squalane surface profiles of a compatible system ($k_{ij} = -0.01$) at several compositions. Lines of strong colour represent squalane concentrations, half-transparent lines represent polybutadiene concentrations. Concentration profiles are obtained from averaging both surfaces. The individual surface profiles are plotted in transparent lines.