

Intrinsic dynamics of PNIPAM microgels by Diffusing Wave Spectroscopy

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Thermoresponsive PNIPAM microgels are soft colloids whose size, hydration and interparticle interactions vary strongly with temperature. They therefore provide a suitable model system to study how crowding and thermal collapse affect microscopic dynamics in concentrated suspensions. We use Diffusing Wave Spectroscopy (DWS) to investigate low-crosslinked PNIPAM microgels in water without adding external tracer particles.

In this tracer-free approach, the measured decorrelation arises from the microgels themselves. The extracted mean-square displacements and viscoelastic moduli are therefore interpreted as apparent microrheological descriptors of the intrinsic microgel dynamics, rather than as conventional tracer-based bulk moduli. These quantities include contributions from microgel motion, local confinement, particle deformation, internal network fluctuations and microgel–microgel contacts.

The results indicate a slowing down of the dynamics with increasing concentration, consistent with the development of local caging in crowded soft microgel suspensions. The temperature dependence is more complex. Below and close to the PNIPAM volume-phase transition, the response is mainly governed by swelling and effective volume fraction. Above the transition, microgel collapse may reduce the effective particle volume while also promoting stronger interparticle contacts. The high-temperature behaviour is therefore interpreted as a collapsed or attractive regime, rather than as a simple fluidization process.

Tracer-free DWS provides direct access to the intrinsic dynamics of thermoresponsive microgels and highlights the competition between concentration-induced confinement and temperature-induced changes in interparticle interactions.

Keywords:

PNIPAM microgels, soft colloids, Diffusing Wave Spectroscopy (DWS), intrinsic dynamics, concentration-induced caging; thermoresponsive collapse.

References:

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