From Bulk to Confinement: Slowing Dynamics in Bicontinuous Microemulsions

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The influence of hard and soft confinement on simple fluids, binary mixtures, and colloidal systems continues to attract considerable attention. Confinement encompasses a wide range of situations, from soft matter in proximity to solid interfaces to crowded, fluctuating environments and porous materials. Both theoretical and experimental studies have shown that fluid properties can change significantly when the confinement length scale becomes comparable to a characteristic length of the confined liquid. In complex, nano-structured fluids, additional structure-related length scales become important.
In the past, microemulsions have been extensively studied and carefully characterized, making them ideal model systems for soft systems with fluctuating membranes. For example, in the bulk, bicontinuous microemulsions exhibit an isotropic, periodic internal structure in which interpenetrating oil and water domains are separated by a fluctuating surfactant interface, forming a sponge-like morphology.
Here, we discuss how three-dimensional confinement, as realized by the mesoporous structure of controlled pore glasses, affects the phase behavior of such microemulsions, how these effects manifest in their dynamical properties, and how they compare to the corresponding bulk behavior.
A confined bicontinuous microemulsion is studied using neutron spin echo spectroscopy, a technique uniquely suited to probing thermally activated fluctuations in soft matter. In contrast, small-angle neutron scattering provides only the time-averaged structure of the fluctuating microemulsion.
Hydrophilic and hydrophobically modified controlled pore glasses serve as confining matrices, with pore diameters ranging from 10 to 100 nm. The pore sizes are selected such that, in one case, the characteristic oil and water domain size is significantly smaller than the pore diameter, while in another case it is larger.
As a first step, the bulk microemulsion is characterized using NSE and dynamic light scattering, allowing the determination of its intrinsic collective dynamics and the undulation dynamics of the surfactant film.
Under confinement, a pronounced slowing down of the intrinsic collective dynamics is observed across all investigated pore sizes compared to the bulk. The analysis indicates that enhanced interactions with the pore walls suppress long-wavelength fluctuations in the undulation mode spectrum.
Interestingly, the chemical nature of the pore surfaces appears to play only a minor role. The undulation behavior of the surfactant film remains largely unchanged in both hydrophilic and hydrophobic confinement.

Keywords:
microemulsion, dynamics, confinement, controlled pore glass

References:

[1] M.Dahl et al. Soft Matter 2024, 20, 8692-8701