COHERENT X-RAY STUDIES OF THE MICROSCOPIC DYNAMICS UNDERLYING THE PHASE BEHAVIOR AND NONLINEAR RHEOLOGY OF GEL-FORMING NANOCOLLOIDAL SUSPENSIONS

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This talk will describe two related projects exploring the properties of gels formed from nanometer-scale colloids. The first involves the phase behavior and microstructural dynamics of concentrated binary mixtures of spherical colloids with a size ratio near two and with a tunable, intrinsic short-range attraction. In the absence of the attraction, the suspensions behave as well mixed, hard-sphere liquids. For sufficiently strong attraction, the suspensions undergo a gel transition. However, the fluid-gel boundary does not follow an ideal mixing law, but rather the gel state is stable at weaker interparticle attraction in the mixtures than in the corresponding monodisperse suspensions. X-ray photon correlation spectroscopy measurements reveal that, in contrast with depletion-driven gelation at larger size ratio, gel formation in the mixtures coincides with dynamic arrest of the smaller colloids while the larger colloids remain mobile. Complementary molecular dynamics simulations indicate the arrest results from microphase separation that is caused by a subtle interplay of entropic and enthalpic effects and that drives the smaller particles to form gel nuclei in the vicinity of the larger colloids.

The second part of the talk will describe coherent x-ray experiments on concentrated (monodisperse) nanocolloidal gels subjected to *in situ* large-amplitude oscillatory shear, which provide unique information about the spatial character of nanometer-scale particle rearrangements associated with nonlinear rheology and yielding of the gels. The oscillatory strain causes periodic echoes in the x-ray speckle pattern, creating peaks in the intensity autocorrelation function. The peak amplitudes are attenuated above a threshold strain, signaling the onset of irreversible particle rearrangements. The gels display strain softening well below the threshold, indicating a range of strains at which deformations are nonlinear but reversible. The peak amplitudes decay exponentially with the number of shear cycles above the threshold strain, demonstrating that all regions in the sample are equally susceptible to yielding and surprisingly that the probability of a region yielding is independent of previous shear history. The wave-vector dependence of the decay rate reveals a power-law distribution in the size of rearranging regions, suggesting a nonequilibrium critical transition at yielding.