

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 [1]. 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 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 (monodisperse) nanocolloidal gels subjected to *in situ* shear, which provide information about the spatial character of nanometer-scale particle rearrangements associated with nonlinear rheology and yielding of the gels and the dynamical recovery of the gels following cessation of shear [2]. One focus will be on gels subjected to *in situ* oscillatory strain, which causes periodic echoes in the x-ray speckle pattern, thereby creating peaks in the intensity autocorrelation function. An example is shown in the Figure. The peak amplitudes become 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. Another focus will be recent

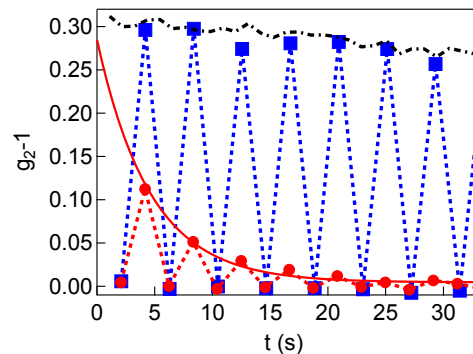


FIG. 1. Shear echoes in the XPCS intensity autocorrelation function measured on a concentrated nanocolloidal gel during application of oscillatory strain with amplitudes $\gamma = 4\%$ (blue squares) and 12% (red circles) at $q = 0.18 \text{ nm}^{-1}$. The oscillation period was 4.14 s . The dashed red and blue lines are guides to the eye. The echoes peak at $\gamma = 4\%$ decay at the same rate as the intensity autocorrelation of the quiescent gel (dash-dotted black line), indicating that shear plays no role in decorrelation for this strain amplitude. The peaks at $\gamma = 12\%$ decay rapidly with the number of cycles of shear separating x-ray images, revealing significant irreversible rearrangement in the gel. The solid red line is the result of a fit of an exponential decay to the echo peaks at $\gamma = 12\%$.

studies of gels formed from the synthetic clay Lapointe that are undergoing aging. Here, we observe that the aging can be transiently reversed (i.e., “rejuvenated”) or accelerated (i.e., “over-aged”) by shear of the appropriate frequency and amplitude.

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