Electronic Supplementary Material (ESI) for Soft Matter.

Homogeneous percolation versus arrested phase separation in attractively-driven nanoemulsion colloidal gels

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Electronic Supplementary Information

Given the broad gel transition for samples in the low-ϕ regime where a homogeneous percolated structure occurs, the following measurements were performed in order to assess the time stability of intermediate states of gelation. All measurements were performed on the sample with $\phi = 0.21$ to be directly comparable to SANS/USANS measurements. An aliquot of sample was loaded on the rheometer, and equilibrated at a temperature $T << T_1$. The sample was then slowly heated during an oscillatory time sweep ($\omega = 10$ rad/s, $\gamma_0 = 0.05\%$) at a very slow rate (0.2 °C/min) to various temperatures spanning the gel transition from T_1 to T_2. After reaching the final temperature, the sample was held at this temperature for a period of several hours in order to assess the time stability of the viscoelasticity. In particular, we wish to assess whether temperatures where $T_1 < T < T_2$ show equilibrated viscoelasticity that precedes the critical gel point (defined here as when G' = G").

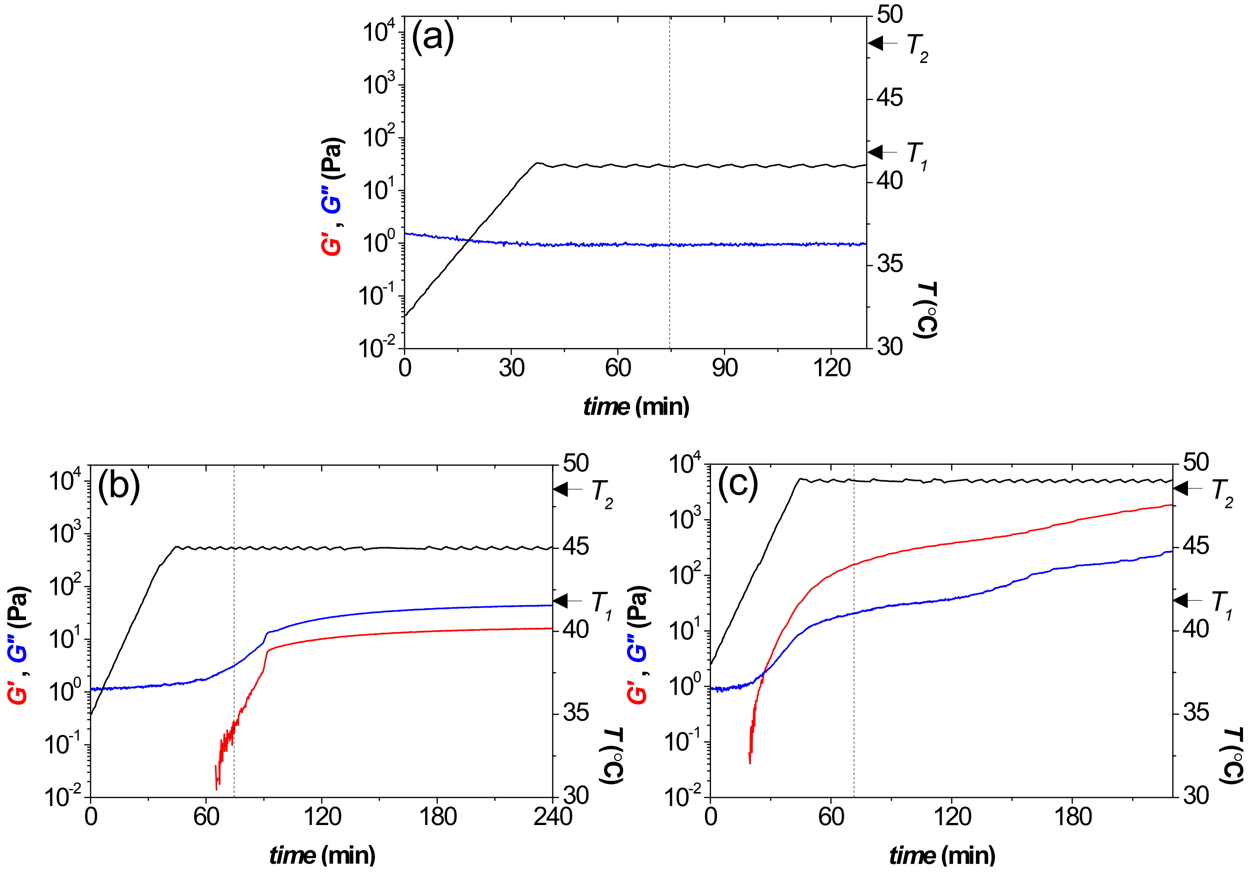

Fig. S1. Representative temperature ramps from the liquid state to temperatures (a) below T_1, (b) between T_1 and T_2, and (c) above T_3. Dotted line indicates time point where USANS measurements would begin.

These measurements were performed for final temperatures spanning the gel transition, including both $T < T_1$ and $T > T_2$, and the results are plotted in Fig. S1. For a thermal quench to $T < T_1$, the sample achieves an equilibrium viscosity in the liquid state (Fig. S1a). For a thermal quench to $T_1 < T < T_2$, the sample begins to build significant viscoelasticity approximately 30 minutes after thermal equilibration, but this viscoelasticity plateaus at long times at a point below the critical gel point (Fig. S1b). Finally, for a thermal quench to $T > T_2$, viscoelasticity begins to build during the temperature ramp (shortly after the temperature crosses T_2), and gels prior to thermal equilibration. However, once temperature is equilibrated, the moduli continue to increase by nearly an order of magnitude over the course of several hours. This slow increase could be due to a number of factors – it may be due to aging of the gel, although it could be due to slow evaporation of the sample over time (we have found that the solvent trap on the cone-plate geometry begins to exhibit insufficient wetting after approximately two hours).

We thus conclude that the fluid achieves a highly stable state for all $T < T_2$. Above T_2, slow (though significant) aging of the gel possibly occurs over a period of hours, although this may be due to sample evaporation in the rheometer (as opposed to the USANS samples which are sealed). We note that, in all cases where $T < T_2$, the sample fully equilibrates at its final state within 30 minutes of when the measurement would begin. Given that the USANS measurements last approximately 5 hours for each temperature, we thus presume that the microstructure (at least for length scales probed by USANS) is approximately unchanged over the course of measurement at a single fixed temperature. This is even the case for $T > T_2$, since our USANS data show that the microstructure is essentially unchanged for the final three temperatures above T_2 (representing 15 hours of measurement).