Equilibrium gels of low-valence DNA nanostars: a colloidal model for strong glass formers

Electronic Supplementary Information

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Intermediate scattering functions measured for the sample at $c_2 = 21.3\ mg/ml$

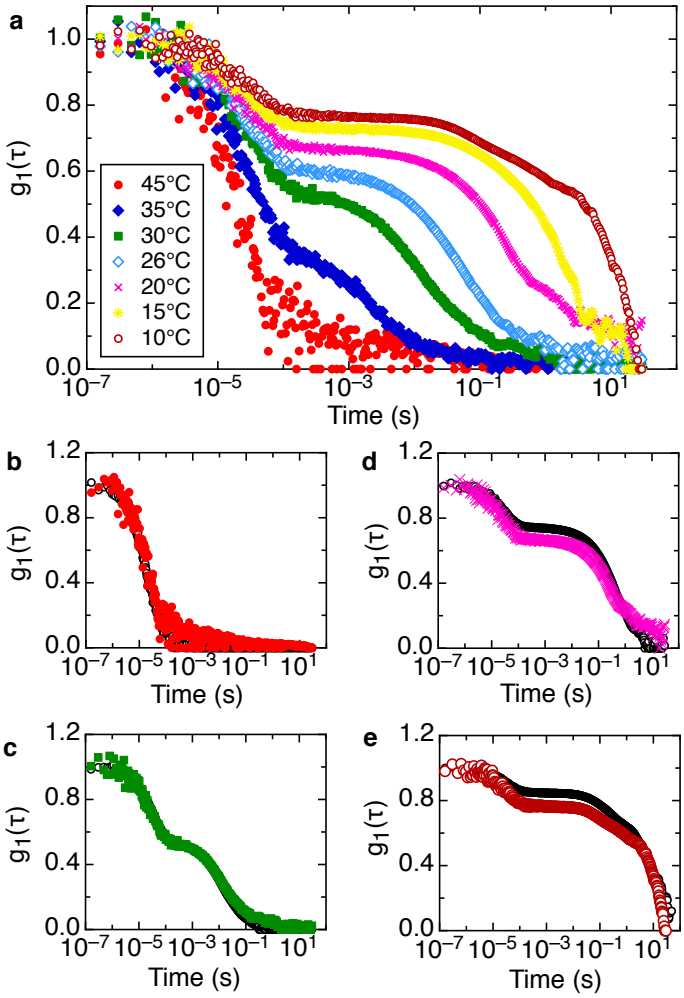

FIG. S1: (a) Intermediate scattering functions $g_1(\tau)$ *vs.* time τ measured along the dashed line of Fig. 1-b of the main text at $q = 22.3\mu\text{m}^{-1}$ at c_2. Temperatures are as listed in the legend. (b)-(e) comparison between $g_1(\tau)$ measured at the equal T in the sample at c_1 (colored dots) and c_2 (black dots). As visible, the correlation functions are basically identical, except a small variation in the contrast. Measurements at c_2 are noisier because of the smaller scattered intensity (Fig. 2 of the main text). $g_1(\tau)$ measured at 10 ^oC with both concentrations exhibit a feature at $\tau \approx 5$ s. A similar feature appears, to a lesser degree, also at the other temperatures, and it is probably an experimental artefact.

Scattered intensity vs. scattering vector

We measured the dependence of the scattered intensity on q at various T in both the c_1 and c_2 samples (red and green symbols in Fig. S2, respectively). Our intensity vs. q data suffer of a significant uncertainty due to the constraint of working with small volume samples. Being the sample contained in a small cylindrical tube, even small errors in making the center of the sample coincide with the center of the rotating arm result in an incorrect consideration of the scattering volume, which always needs to be taken into account as a normalizing factor for the measured intensity. Moreover, the measurements also suffer for unwanted collection of stray light, leading to an additional uncertainty that is more relevant with the dense system here considered where the scattered intensity is small - than with the critical system studied previously - where the critical behavior provided a significant scattering signal. Despite these problems, the observed $I(q)$ dependence appears not to be significantly affected by changing T nor to show features that would indicate the development of correlated structures on the mesoscale. This is particularly evident when compared to the $I(q)$ measured for the critical sample (black symbols, data from Ref. [1]) at $T = 28\ ^oC$, far enough from the critical point not to yield detectable q dependence and at $T = 26\ ^oC$, where instead the critical concentration fluctuations lead to a quite recognizable increment of the scattered intensity at low angles.

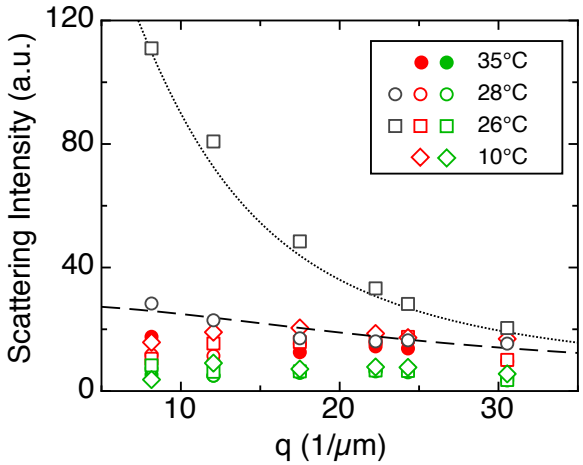

FIG. S2: Total scattered intensity measured at four different scattering angles, and at the temperatures listed in the legend. Red symbols: c_1. Green symbols: c_2. Black symbols: c^*. The two lines are obtained as best fit to the data with an Ornstein-Zernike type equation to the critical behavior (critical data are from Ref. [1]).

Viscosity

An important quantifier of the dynamical arrest undergone by the system is the T dependence of its viscosity η. One of the samples prepared at c_1 gave us the opportunity of exploring viscosity through the presence of micro-sized impurities which were introduced in the process of PAGE purification of the DNA single strands. Before being sedimented by centrifugation and thus eliminated from the sample, these large particles gave rise to a third decay in the correlation functions clearly detectable at all T. Since the decay times of the first two relaxation processes match the ones discussed in the main text and reported in Fig. 3-a, the additional relaxation time τ_P can be associated with the diffusional dynamics of the impurities and used as a convenient probe of η [2]. We find that τ_P depends on T very strongly and it reaches values larger than 10 s, the limit of our experimental observation time, when $T \approx 20°$C. The size R_0 of these contaminants was determined at $T = 55°$C, a T higher than the onset of NS clustering, where η can be assumed to be equal to the

viscosity of water η_w. Via the Stokes-Einstein relation we determined $R_0 = 0.34\mu m$. We made the assumption that R_0 is constant at all T and used $\tau_P(T)$ to determine $\eta(T)$ as seen by a micron-sized probe. Despite the ingenuous approach, the results we obtained are encouraging since the behavior of η that we determined is consistent with the establishment of a spanning network held by DNA bonds. The resulting values for the viscosity of the system are shown in Fig. S3, where three regimes can be distinguished. At high T, where DNA NS are weakly interacting, η remain similar to η_w. However, as T drops below 40^oC, where NS cluster and the network starts developing, η grows quite markedly, increasing of more than 4 order of magnitudes. At low T, where the equilibrium network structure is established, η shows an Arrhenius T dependence, with an activation enthalpy consistent with the one found for τ_s (dashed line). This appears to be a general feature of transient networks, in which both viscosity and relaxation time depend on the same microscopic bond breaking mechanism [3]. We note that the Arrhenius T dependence of η and τ_s is also analogous to what found in strong glass-formers liquids [4].

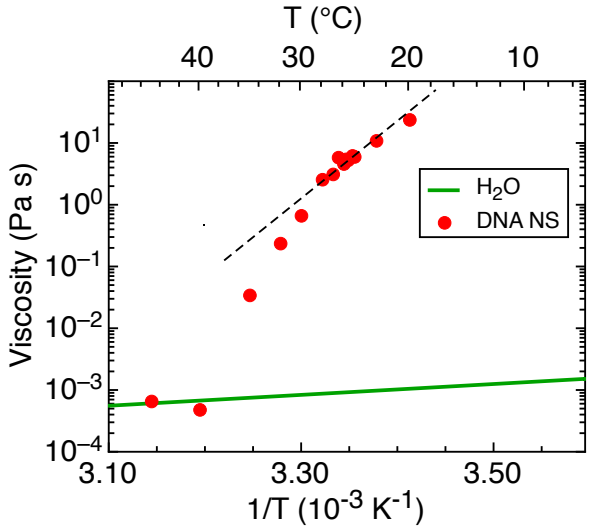

FIG. S3: Temperature dependence of the viscosity η as extracted from the diffusion coefficient of microparticles (filled red dots) within a sample of concentration c_1. The green line indicates the viscosity of water η_w. The dotted line has the same slope (i.e. the same ΔH) as the one in Fig. 3-b of the main text.

[1] Biffi, S. *et al.* Phase behavior and critical activated dynamics of limited-valence DNA nanostars *Proc. Nat. Acad. Sci.* **110**, 15633-15637 (2013).
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