Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information of

Dynamical heterogeneity in the gelation process of a polymer solution with a lower critical solution temperature

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1. Temperature calibration of the microrheology

1.1 Methods

The temperature of the sample T under microrheological observation differed significantly from the nominal values of the incubator T_{nominal}. The viscosity–temperature dependence of a glycerol/water mixture was measured under a rotational rheometer (ARES-RFS, TA Instruments). Viscosity of the same sample was also measured by microrheology at a series of nominal incubator temperatures. The sample temperature T is believed to be the same as T_{ARES} when the two viscosities equal each other. The temperature of microrheology was then calibrated using the temperature of ARES-G2.

1.2 Results

As shown in Figure S 1 the measured viscosities from both microrheology and macrorheology depends on the nominal temperature of the corresponding instruments linearly with different slopes. By equating the two viscosity, the nominal temperatures from the two instruments have the relation $T_{\text{micro}} = 23.6\ ℃ + 0.43\ T_{\text{macro}}$.

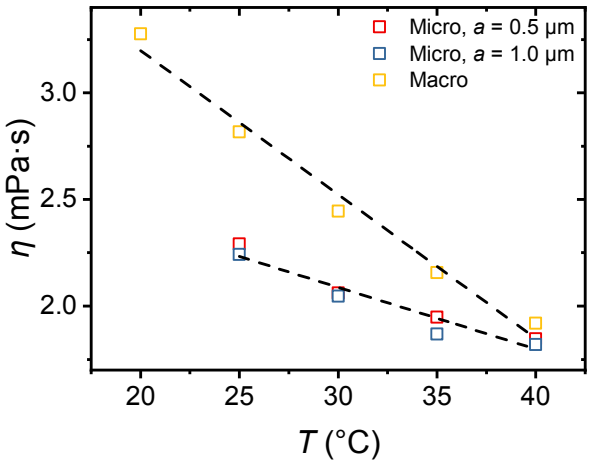

Figure S 1 Viscosities of microrheology by two sizes of probe particles (a = 0.5 μm and 1.0 μm) plotted against the nominal temperature of the incubator; Viscosity of macrorheology plotted against the rheometer temperature. Dash: linear fit.

2. Static error measurement

2.1 Methods

Synthetic hectorite (LAPONITE® XLG, BYK Rockwood Ltd.) was dried in vacuum at 50 °C for 12 hr. The dried powder of the clay was then gradually added to deionized water during stirring to ensure no large agglomeration occur. After the addition of clay, the suspension was stirred for 10 min and ultrasonicated for 5 min. NaCl solution was then added to the suspension and stirred for 5 min. The container of the suspension was then sealed with paraffin. In this experiment, the concentration of the clay c_L is 3%wt and the concentration of NaCl c_s is 1 mM. During the preparation of hectorite suspension, carboxylate-modified fluorescent polystyrene microspheres of diameter $2a$ = 0.5 μm, 1 μm and 2 μm dispersion of 2% solids content (FluoSphere®, ThermoFisher) were diluted with deionized water to particle concentration of 0.02%wt, 0.04%wt and 0.08%wt, respectively. After the hectorite is dissolved totally, the prepared microsphere dispersion was added to the solution to a final particle concentration of 0.0002% wt, 0.0004%wt and 0.0008%wt, respectively. The mixed solution was injected into a home-made glass chamber sealed with vacuum grease for microscopic observations. After 3 hours, the hectorite suspension L_3S_1 had finished the gelation, it is a colloidal hydrogel with a modulus of *ca.* 100 Pa. Therefore, probe particles are effectively immobile within the time scale and resolution of our microrheology observation. The "tracks" identified by our routines are the static error, denoted as ε^2.

The trajectories of the probe particles in the Hectorite hydrogel were recorded under a fluorescent inverted microscope (Nikon Eclipse Ti-s) with a 60x oil-immersed objective of numerical aperture (NA) of 1.40. The brightness of the probe particles was varied by adding neutral density filter to the exciting beam. The field of view (FOV) was set to be 276.48 μm × 233.28 μm approximately. The sample temperature was 30 ± 0.1 ℃. Videos were acquired at 49.65 frame per second (fps) and 0.01 ms exposure time using an sCMOS camera (Zyla, Andor) at resolution 2560px × 2160px, corresponding to the pixel size of 0.108 μm per px. Typically, around 50 in-frame

particles were tracked The trajectories of the particles were extracted by a MATLAB routine modified based on the one by Blair and Dufresne.[1]

2.2 Result

We found that the static error of the particles depends only on the brightness, as shown in Figure S 2, since the data of different sizes of probe particles collapse into one master curve when plotted this way. The data of different sizes of probe particle do not collapse into one master curve when plotted against signal-noise ratio (SNR). We therefore constructed working curves by linear fitting the data and estimate the static error according to the brightness in each experiment.

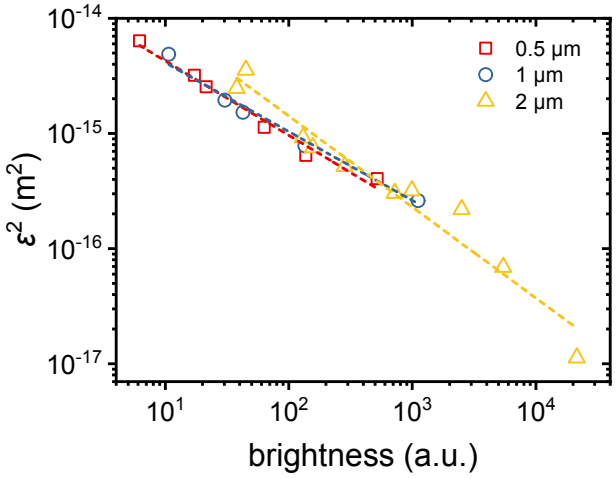

Figure S 2 Static error plotted against the brightness of the probe particles.

3. The standard error of the non-Gaussian paramete

The kurtosis g_2 of N independent and identically distributed random variables x_i, $i = 1, ..., N$ is subjected to small sample bias which lead to standard error depending on the value of N by the following relation[2]

$$\mathrm{Var}(g_2) = \frac{24N(N-2)(N-3)}{(N+1)^2(N+3)(N+5)}$$

The non-Guassian parameter $\alpha_2 = g_2/3$. The standard error of the non-Gaussian parameters was shown in Figure S 3 for two typical lag times in the form of error bars. The variation of non-

Gaussian parameter versus temperature is highly significant compared with the error bars, which means the number of samples N in the present study are generally high enough for meaninful distussion of the non-Gaussian parameteres.

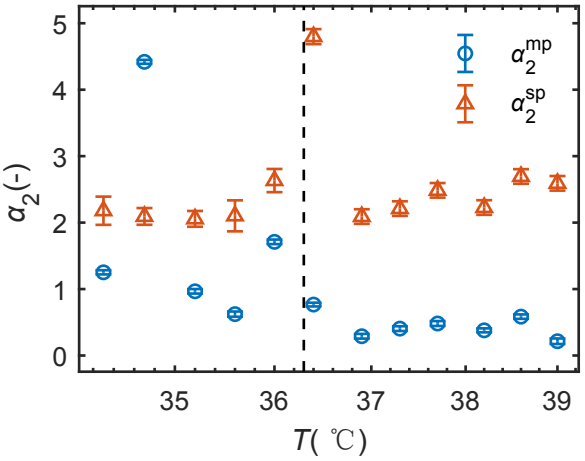

Figure S 3 Circles: multi-particle non-Gaussian parameters at Δt = 0.24 s; Triangles: single-particle non-Gaussian parameters at Δt = 14.9 s.

Reference

1. Blair, D.; Dufresne, E., The matlab particle tracking code repository. *Particle-tracking code available at* http://physics.georgetown.edu/matlab **2008**.
2. Cramér, H., *Mathematical Methods of Statistics*. Princeton University Press: 1999.