Supplementary information for

A facile evanescent-field imaging approach for monitoring colloidal gel evolution near a surface

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Materials. *N*-isopropylacrylamide (NIPAM) was recrystallized in a benzene/n-hexane mixture. *N,N′*-Methylenebis(acrylamide) (BIS) was recrystallized in methanol. Potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were used as received. All chemicals were purchased from Sigma-Aldrich, US as analytical reagent.

Microgel Synthesis. PNIPAM microgels were synthesized via a standard one-pot precipitation polymerization.[1] NIPAM (8.09 g), BIS (0.58 g), and SDS (0.29 g) were dissolved in 295 mL MilliQ water and put into a flask with a magnetic stirrer, a reflux condenser, and a nitrogen gas inlet. After the solution was stirred for 40 min at 70 ℃ under nitrogen, KSP (0.27 g)/5 mL MilliQ water was injected to initiate the polymerization. The reaction was maintained at 70 ℃ for 4 hours. To remove unreacted chemicals and surfactants, the dispersion was purified via filtration (0.45 μm Nylon filter membranes, Sigma-Aldrich, US) and dialysis (50 kDa MWCO, Spectra/Por Labs, CA) for 4 days. The dispersion was concentrated to 0.0554 g/mL by rotary evaporation.

Characterizations. The hydrodynamic diameter D_h of the microgels was determined by dynamic light scattering (ALV/DLS/SLS-5022F, correlator ALV5000, $\lambda = 632.8$ nm) at $c = 4.3 \times 10^{-7}$ w/w. The DLS data corresponded to the intensity autocorrelations at scattering angles from 20° to 40°, each

measurement was acquired over 300 seconds. The solution was allowed to equilibrate at least for 1 hour at each temperature before measurement.

The intrinsic viscosity $[\eta]$ of the microgel dispersions was measured through a Cannon-Ubbelohde viscometer (No. 25-B164, Cannon Instrument Co., US) at c = 2−10 mg/mL. The effective volume fraction ϕ_{eff} of the microgels was estimated by $\phi_{eff} = bcD_h^3/2.5$, where b is the proportionality constant between $[\eta]$ and D_h^3 based on the Huggins and Mead–Fuoss plots.[2-4]

The zeta potential ζ of the microgels was determined via a Zetasizer Nano (ZS90, Malvern Instruments Inc., UK) at $c = 5.5 \times 10^{-5}$ w/w. The measurement was conducted three times at set temperatures with an equilibration time ≥ 5 min. ζ is presented as the mean ± standard deviation.

The penetration depth d_p was estimated by $d_P = \lambda / [4\pi\sqrt{(n_1 \sin\theta)^2 - n_2^2}]$, where λ = 632.8 nm is the laser wavelength, θ = 70° is the incident angle, n_1 = 1.52 is the refractive index of the 70° prism, and $n_2 \approx 1.35$ is the refractive index of the dispersion at c = 0.0554 g/mL at temperatures from ~35 ℃ to 40 ℃, which was measured by an Abbe refractometer (Model 102539, 2WA-J, Shanghai, CN).

Instrumental setup. The microgel dispersion was injected into an ultrathin flow cell (200 μm inner thickness, hollow rectangular capillaries, Borosilicate Glass Co., US), placed on a homemade thermal control device (see Fig. S2) including a recirculating water bath (THX-05, Ningbo Tianheng Instrument Co., CN), two Peltier modules (TEC1-06306, Hebei I.T. (Shanghai) Co. Ltd., CN), and a PID controller with three negative temperature coefficient (NTC) sensors (PR-59, Laird Technologies Inc., US). For each measurement, the temperature was increased from room temperature (~ 25 ℃) to a set one at a rate of ~ 0.1 ℃/min. Once the set temperature is reached, the images were recorded for 10 s at t = 0 s, 300 s, 600 s, and 1200 s, respectively.

The thermal control device was equipped on an inverted Leica DM LFSA microscope with a 50× objective (N PLAN, NA = 0.5, WD = 7 mm). An evanescent field was generated by a laser beam with a wavelength of 632.8 nm at the glass/liquid interface where the penetration depth d_p is ~ 110 nm. The scattering images were captured by a sCMOS camera (Zyla 5.5, 2560 × 2160 pixels, pixel size = 6.5 μm, Andor Technology Ltd., UK) at a sampling rate of 10–50 fps. More details could be found in Fig. S2.

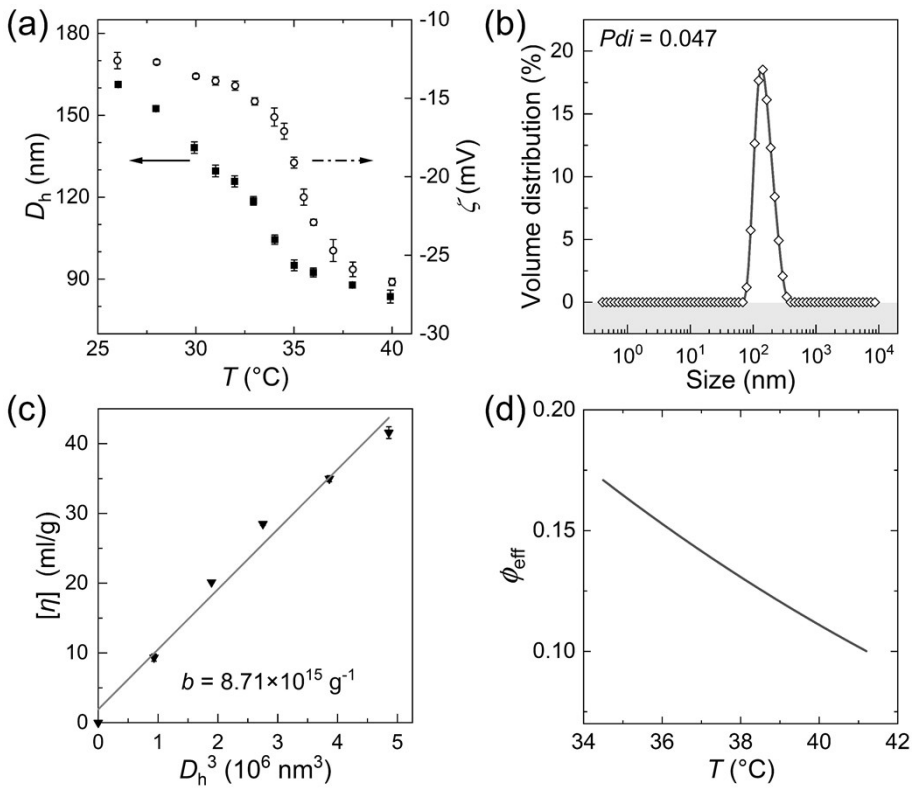

Fig. S1 (a) The hydrodynamic diameter D_h (squares) and zeta potential ζ (circles) of PNIPAM microgels as a function of temperature. (b) Typical particle size distribution of microgels at 25 ℃. The polydispersity index (Pdi) < 0.05. (c) The intrinsic viscosity [η] of microgel dispersions as a function of D_h^3. (d) The effective volume fraction ϕ_{eff} of microgels as a function of temperature.

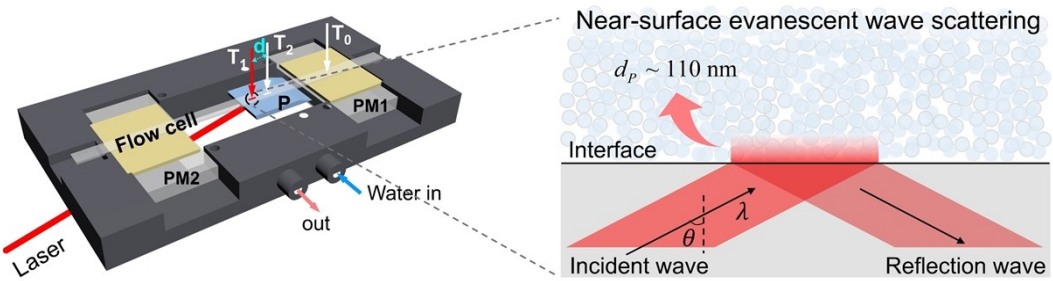

Fig. S2 Schematic of the thermal control device incorporated on a total internal reflection microscope (TIRM). P is the 70° prism, PM1 and PM2 are the Peltier modules and/or copper plates (yellow). T_0, T_1, and T_2 are temperatures at individual regions along the flow cell. d (~5 mm) is the distance between regions T_1 and T_2. At region T_1, an evanescent field is generated on the liquid/glass interface with d_P ~ 110 nm, where the scattering intensity is recorded by a sCMOS camera.

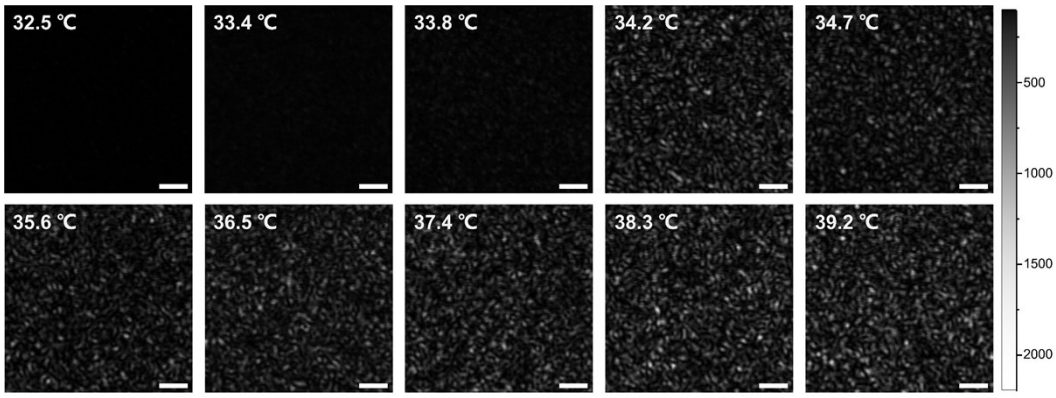

Fig. S3 Original total internal reflection microscope (TIRM) images of colloidal gels. The dynamic speckles emerge after 34 ℃, corresponding to $\phi_{eff} \sim 0.23$. Scale bars represent 5 μm. Gray scale represents the intensity.

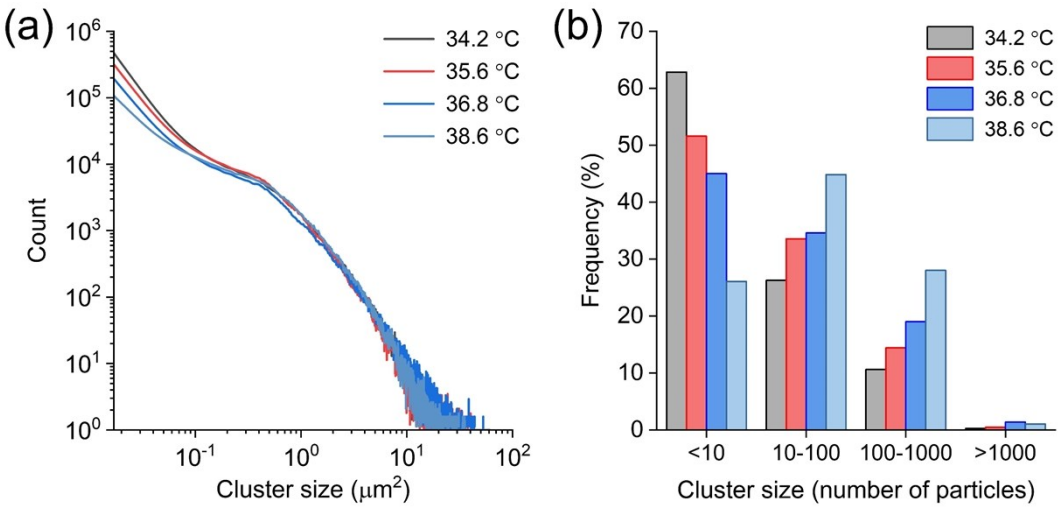

Fig. S4 Cluster size distribution in count (a) and histogram (b) at different temperatures. The clusters are 2D projections, which sizes are counted based on a sequence of binarized images after default thresholding *via ImageJ*.

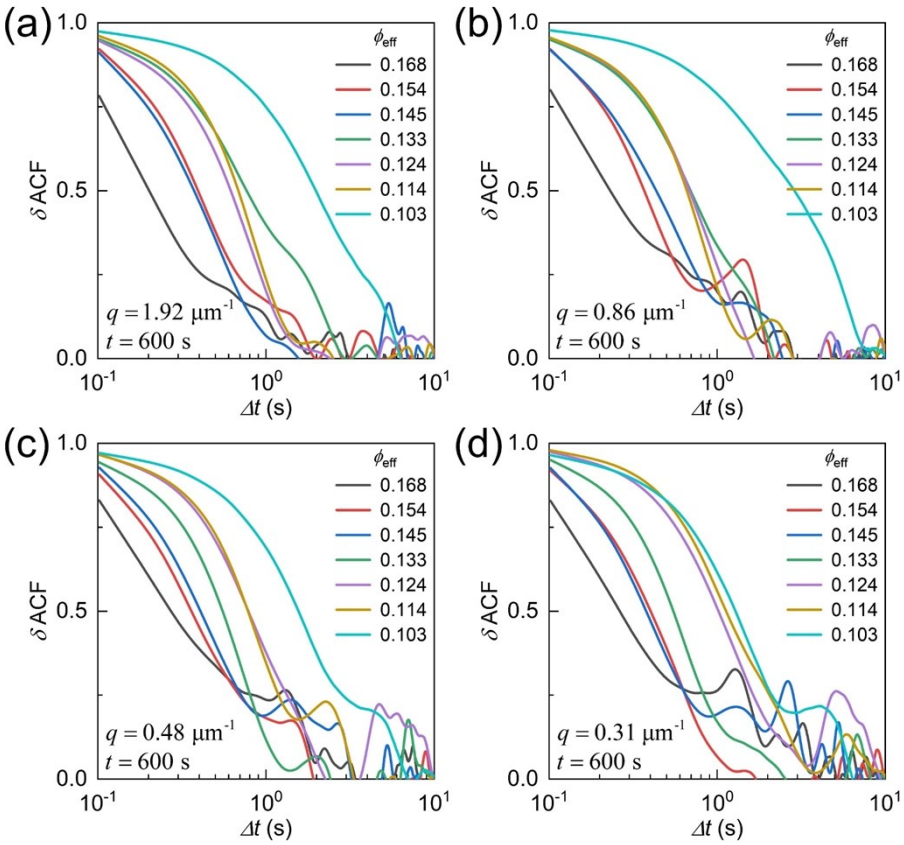

Fig. S5 Typical density-fluctuation autocorrelation functions (δACF) for ϕ_{eff} varying from 0.103 to 0.168 at various q from 0.31 μm^{-1} to 1.92 μm^{-1} (t = 600 s).

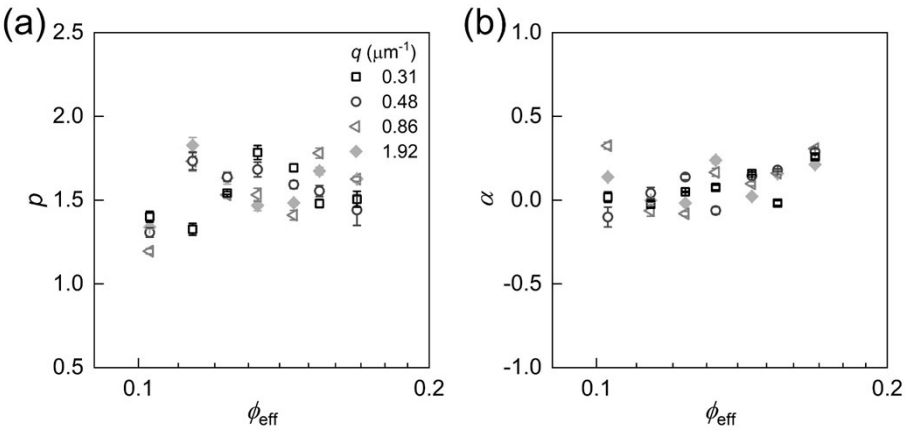

Fig. S6 Fitting parameters p and α for the compressed exponential decay functions at different ϕ_{eff} at various q from 0.31 μm^{-1} to 1.92 μm^{-1} (t = 600 s).

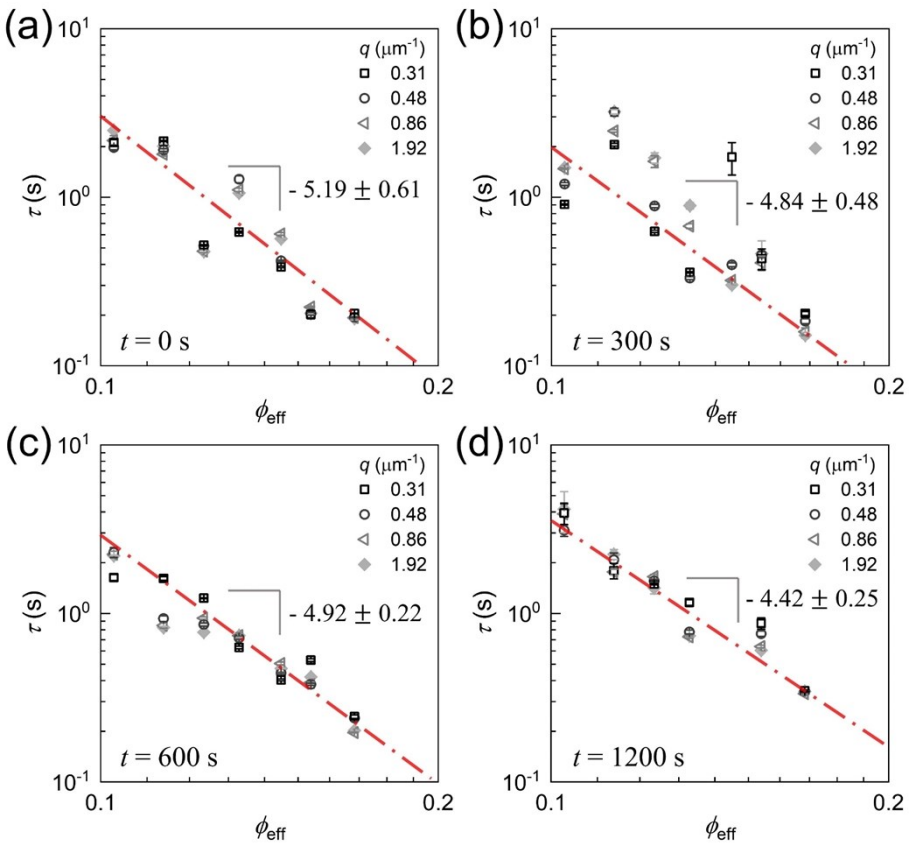

Fig. S7 Relaxation time τ as a function of ϕ_{eff} at various q from 0.31 μm^{-1} to 1.92 μm^{-1} at t = 0 s (a), 300 s (b), 600 s (c), and 1200 s (d). The dash-dotted lines represent the linear fitting.

References

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