Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Size effects on rotational particle diffusion in complex fluids as probed by Magnetic Particle Nanorheology

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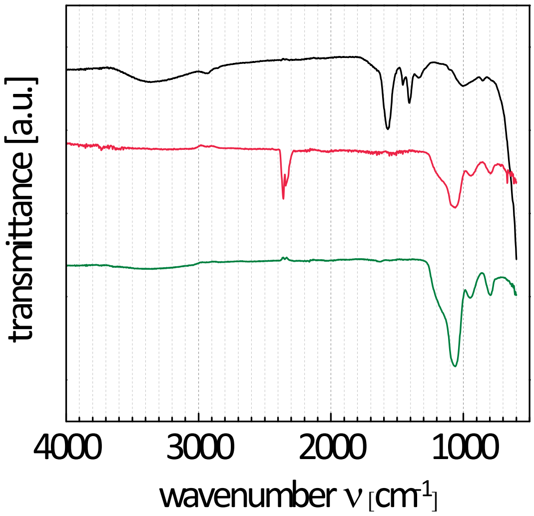
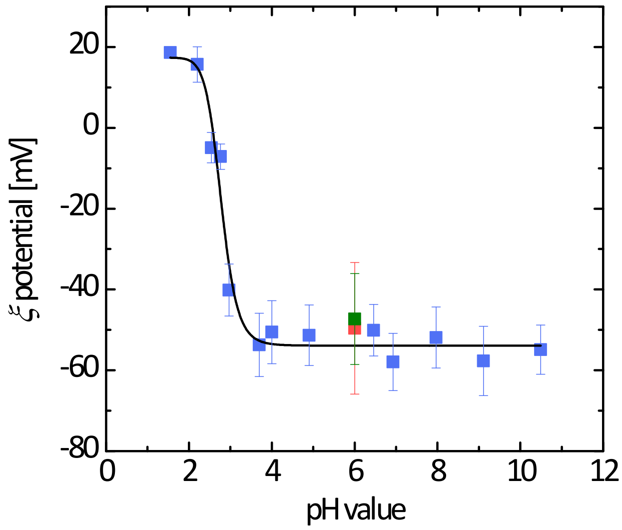
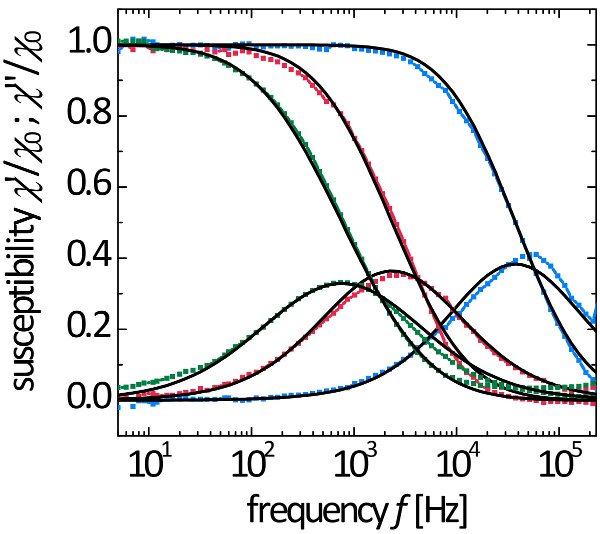


SI-Fig. 1. IR spectra of probe particles CF_12 (black), CF@SiO_2_29 (red) and b) CF@SiO_2_42 (green).

The IR spectrum of the CF_12 particles shows a broadened peak at ∼3350 cm^{-1} indicating residues of water. The CH_2 stretch band of the PAA, at 2900 cm^{-1} is only weakly observable in a broadened band.[1,2] At 1571 cm^{-1} - 1407 cm^{-1} the stretch modes of COO^- are clearly visible.[3] For the silica coated particles, the dominant bands at 1200 cm^{-1}(Si-O-Si stretching, longitudinal-optical), 1060 cm^{-1} (Si-O-Si stretching, transverse-optical), 951 cm^{-1} (Si-OH stretching) and 798 cm^{-1} (Si-O bending) are assigned to the vibration modes of silica. [4,5] The bands at 2359 cm^{-1} and 2343 cm^{-1} are connected to the asymmetric stretching mode of gas phase CO_2 from the atmosphere and are neglected.[6,7] An important band is found close to 600 cm^{-1} for all particle batches, belonging to the Me-O modes in ferrite nanoparticles.[1]



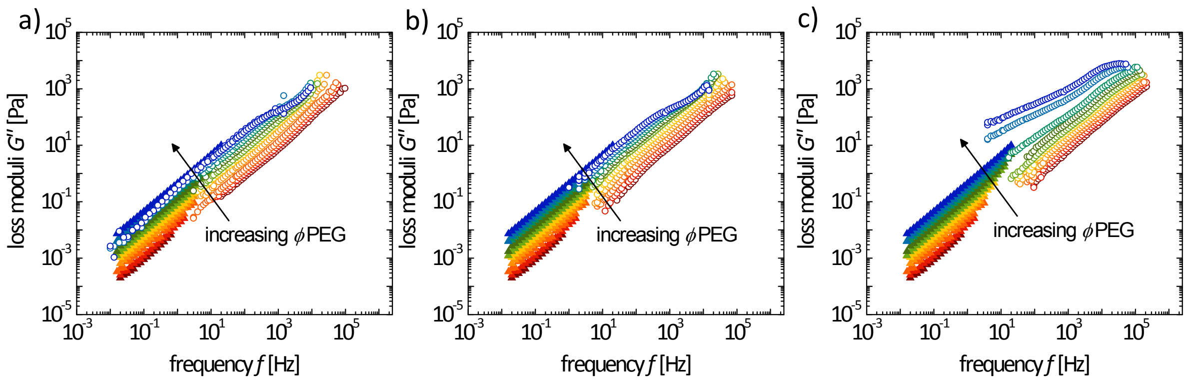
SI-Fig. 2. ζ potential measurements in dependence on pH value for probe particles CF_12 (blue), CF@SiO_2_29 (red) and b) CF@SiO_2_42 (green). The black line is a guide to the eye.



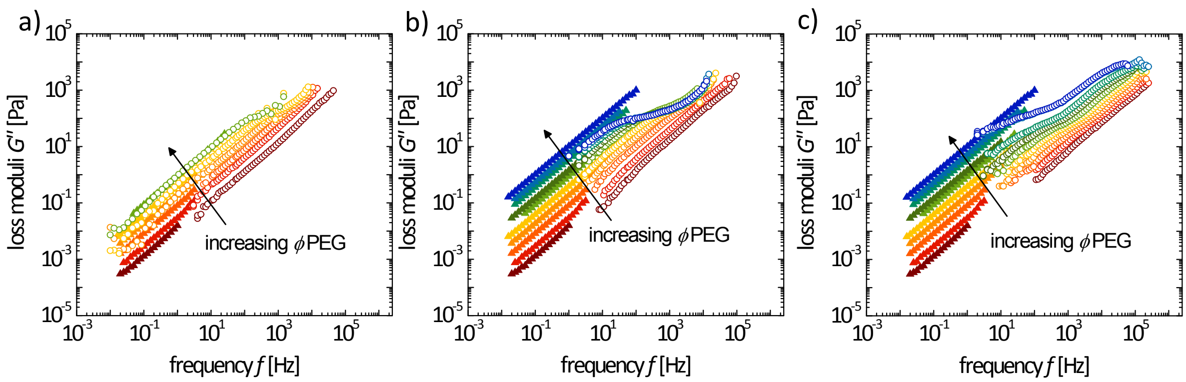
SI-Fig. 3. ACS spectra of probe particles CF_12 (blue), CF@SiO_2_29 (red) and b) CF@SiO_2_42 (green) fitted using a single Debye relaxation process including a particle size distribution (black lines).

SI-Tab. 1. Summary of critical concentrations ϕ_ξ ($\xi = r_h$) and ϕ_a ($a = r_h$) for different probe particles.

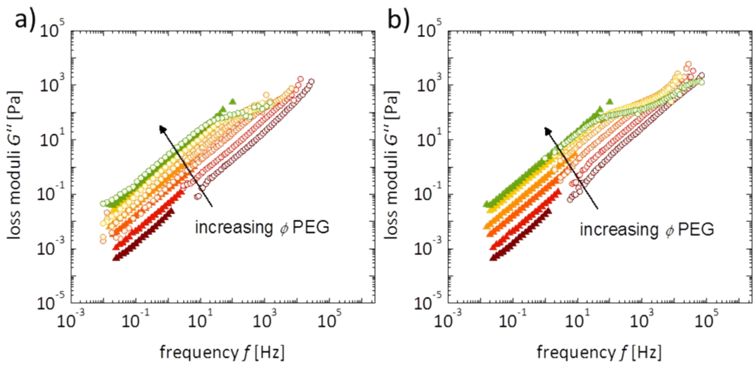
Probes	ϕ_ξ [v%]	ϕ_a [v%]
CF_12	4.5	21.9
CF@SiO_2_29	1.4	7.0
CF@SiO_2_42	0.9	4.3



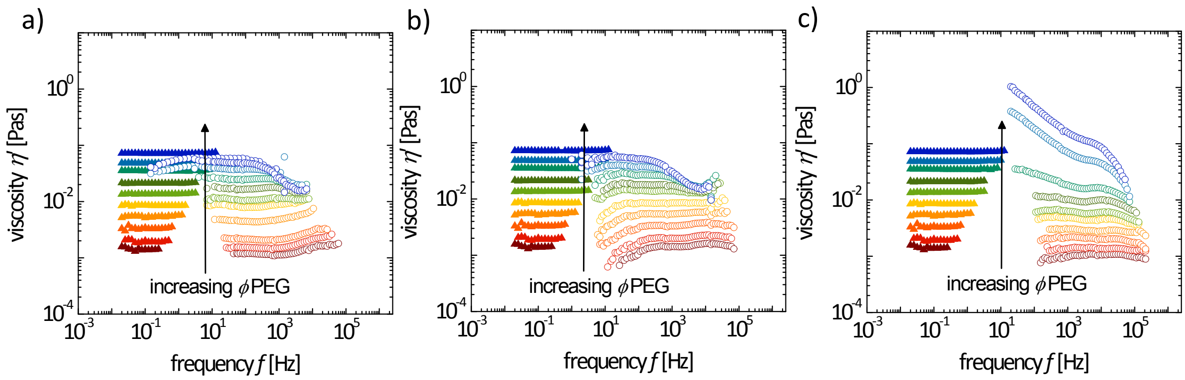
SI-Fig. 4. Loss moduli determined by macrorheology (full symbols) and nanorheology (empty symbols) in dependence on frequency *f* for PEG 4k aqueous solutions for probe particles a) CF@SiO_2_42, b) CF@SiO_2_29 and c) CF_12. The volume concentration is varied between 1.8 m% - 42.0 m% (dark red: ϕ = 1.8 v%; red: ϕ = 4.5 v%; orange: ϕ = 9.0 v%; light orange: ϕ = 13.5 v%, yellow: ϕ = 18.1 v%, light green: ϕ = 22.8 v%; olive green: ϕ = 27.5 v%; turquoise: ϕ = 32.3 v%; light blue: ϕ = 37.2 v%; blue: ϕ = 42.0 v%).



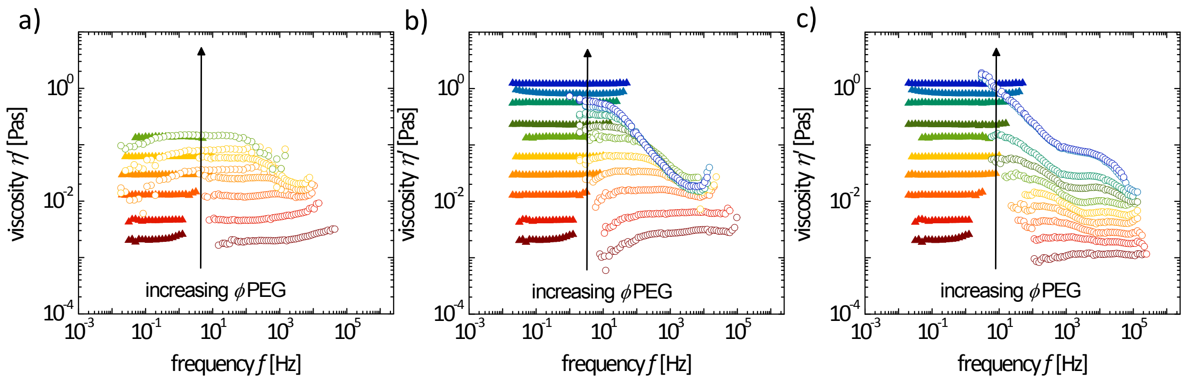
SI-Fig. 5. Loss moduli determined by macrorheology (full symbols) and nanorheology (empty symbols) in dependence on frequency *f* for PEG 20k aqueous solutions for probe particles a) CF@SiO_2_42, b) CF@SiO_2_29 and c) CF_12. The volume concentration is varied between 1.8 m% - 37.2 m% (dark red: ϕ = 1.8 v%; red: ϕ = 4.5 v%; orange: ϕ = 9.0 v%; light orange: ϕ = 13.5 v%, yellow: ϕ = 18.1 v%, light green: ϕ = 22.8 v%; olive green: ϕ = 27.5 v%; turquoise: ϕ = 32.3 v%; light blue: ϕ = 35.2 v%; blue: ϕ = 37.2 v%).



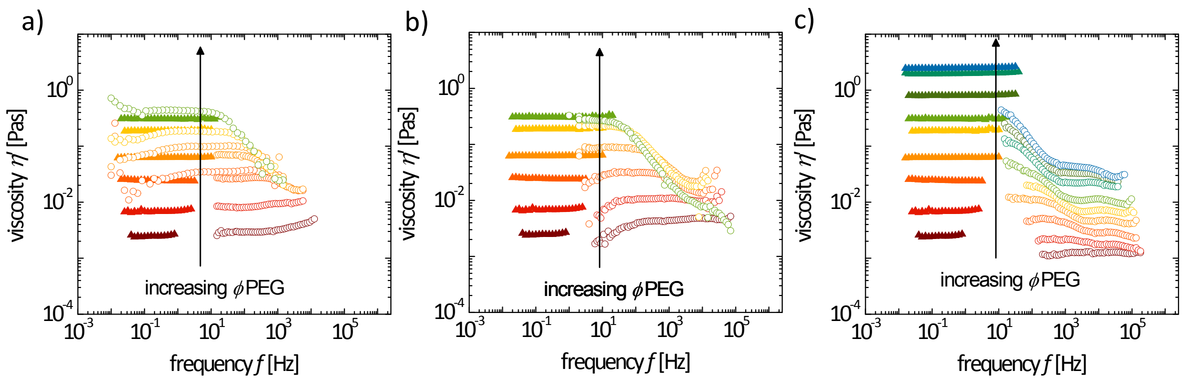
SI-Fig. 6. Loss moduli determined by macrorheology (full symbols) and nanorheology (empty symbols) in dependence on frequency *f* for PEG 35k aqueous solutions for probe particles a) CF@SiO_2_42, b) CF@SiO_2_29. The volume concentration is varied between 1.8 - 35.2 v% (dark red: ϕ = 1.8 v%; red: ϕ = 4.5 v%; orange: ϕ = 9.0 v%; light orange: ϕ = 13.5 v%, yellow: ϕ = 18.1 v%, light green: ϕ = 22.8 v%; olive green: ϕ = 27.5 v%; turquoise: ϕ = 32.3 v%; light blue: ϕ = 35.2 v%).



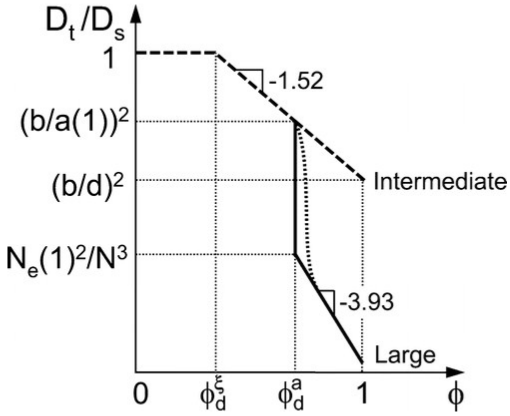
SI-Fig. 7. Viscosity determined by macrorheology (full symbols) and nanorheology (empty symbols) in dependence on frequency *f* for PEG 4k aqueous solutions for probe particles a) CF@SiO_2_42, b) CF@SiO_2_29 and c) CF_12. The volume concentration is varied between 1.8 m% - 42.0 m% (dark red: ϕ = 1.8 v%; red: ϕ = 4.5 v%; orange: ϕ = 9.0 v%; light orange: ϕ = 13.5 v%, yellow: ϕ = 18.1 v%, light green: ϕ = 22.8 v%; olive green: ϕ = 27.5 v%; turquoise: ϕ = 32.3 v%; light blue: ϕ = 37.2 v%; blue: ϕ = 42.0 v%).



SI-Fig. 8. Viscosity determined by macrorheology (full symbols) and nanorheology (empty symbols) in dependence on frequency *f* for PEG 20k aqueous solutions for probe particles a) CF@SiO_2_42, b) CF@SiO_2_29 and c) CF_12. The volume concentration is varied between 1.8 m% - 37.2 m% (dark red: ϕ = 1.8 v%; red: ϕ = 4.5 v%; orange: ϕ = 9.0 v%; light orange: ϕ = 13.5 v%, yellow: ϕ = 18.1 v%, light green: ϕ = 22.8 v%; olive green: ϕ = 27.5 v%; turquoise: ϕ = 32.3 v%; light blue: ϕ = 35.2 v%; blue: ϕ = 37.2 v%).



SI-Fig. 9. Viscosity determined by macrorheology (full symbols) and nanorheology (empty symbols) in dependence on frequency *f* for PEG 35k aqueous solutions for probe particles a) CF@SiO_2_2, b) CF@SiO_2_1 and c) CF. The volume concentration is varied between 1.8 - 35.2 v% (dark red: ϕ = 1.8 v%; red: ϕ = 4.5 v%; orange: ϕ = 9.0 v%; light orange: ϕ = 13.5 v%, yellow: ϕ = 18.1 v%, light green: ϕ = 22.8 v%; olive green: ϕ = 27.5 v%; turquoise: ϕ = 32.3 v%; light blue: ϕ = 35.2 v%).



SI-Fig. 10. Concentration dependence of terminal diffusion coefficient D_t of particles in entangled athermal polymer solutions normalized by their diffusion coefficient $D_s = k_B T/(\eta_s d)$ in pure solvent. Dashed line is for intermediate size particles ($b < d < a(1)$), and solid line is for large particles ($d > a(1)$). The crossover concentrations $\varphi_d{}^\xi$ and $\varphi_d{}^a$, at which the correlation length ξ and the tube diameter *a* are on the order of particle size *d*. Dotted line corresponds to the crossover taking into account the contribution of hopping process to the particle mobility. Logarithmic scales. Reprinted with permission from L.-H. Cai, S. Panyukov and M. Rubinstein, *Macromolecules*, 2011, **44**, 7853–7863. Copyright 2011 American Chemical Society.

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