Soft Matter

SUPPORTING INFORMAITON

Influence of polymer flexibility on nanoparticle dynamics in semidilute solutions

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Calculation of Zero-Shear Viscosity

As discussed in the main text, the zero-shear viscosities η_0 of the polymer solutions from simulation were used as input parameters in Stokes-Einstein relation and mode-coupling theory calculations of the long-time nanoparticle diffusivity D (Figs. 4 and 5 in the main text). Estimates of η_0 were obtained from reverse nonequilibrium molecular dynamics (RNEMD) simulations[1,2] performed using HOOMD-blue with molecular dynamics[3–5] and multi-particle collision dynamics[6] accelerated on graphics processing units. Stress was imposed on the solutions by generating a momentum flux, and the shear rate $\dot{\gamma}$ was extracted from the emerging flow profile, as described in ref. 1. For the fully flexible chains ($\kappa = 0$), the linear response regime can be directly accessed in simulation to compute η_0. As the stiffness parameter κ was increased, however, the polymer relaxation slowed down significantly, making a direct measurement of η_0 computationally infeasible. Thus, we extracted η_0 by fitting our data to the Cross model,[2,7,8]

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\tau_s \dot{\gamma})^m}, \tag{S1}$$

where η_∞ is the asymptotic viscosity as $\dot{\gamma} \to \infty$, τ_s is the characteristic time for the onset of shear thinning, and m is a parameter sensitive to the degree of shear thinning ($m = 0$ for Newtonian liquids; $m \to 1$ for increasingly shear thinning fluids). The fit parameters obtained from this analysis are reported in Table S1. Uncertainties in η_0 were estimated from the error in the fits to eqn. S1. These uncertainties were propagated using standard relationships to estimate errors in other quantities calculated from η_0, such as D_{SER} reported in Fig. 4 of the main text.

The Cross model provided excellent fits to the RNEMD simulation data in each case, independent of the polymer stiffness and concentration (Fig. S1). Further, for fully flexible polymers ($\kappa = 0$), the values of η_0 extracted using eqn. S1 were found to be in excellent agreement with estimates obtained from standard linear response analysis. Analysis of η_0 reveals that it is a strong function of polymer stiffness and concentration, varying by as much as an order of magnitude over the range of conditions and parameters examined in our study (Fig. S2). These findings are consistent with our recent simulation study examining the dynamics and shear rheology of semiflexible polymers in solution using similar polymer models and computational methods;[2] we refer interested readers to this study for in-depth discussion of the influence of polymer stiffness and concentration on these solution properties.

Table S1 Parameters obtained from fitting to the Cross model

c	κ	η_0	τ_s	m
0.05	0	5.6 (1)	270 (4)	1.00 (1)
0.05	5	8.2 (2)	750 (3)	0.94 (3)
0.05	10	11.2 (4)	1900 (2)	0.81 (8)
0.05	20	14 (1)	3700 (5)	0.73 (8)
0.05	32	17 (3)	6000 (2)	0.65 (8)
0.20	0	13.4 (4)	380 (4)	1.00 (1)
0.20	5	38 (2)	1900 (2)	1.00 (1)
0.20	10	74 (4)	6300 (7)	0.95 (3)
0.20	20	130 (1)	19000 (3)	0.77 (5)
0.20	32	170 (1)	40000 (1)	0.78 (8)

Notes: Numbers is parentheses denote uncertainty in last significant digit.

References

1 F. Müller-Plathe, *Phys. Rev. E*, 1999, **59**, 4894.
2 A. Nikoubashman and M. P. Howard, *Macromolecules*, 2017, **50**, 8279–8289.
3 J. A. Anderson, C. D. Lorenz and A. Travesset, *J. Comput. Phys.*, 2008, **227**, 5342–5359.
4 J. Glaser, T. D. Nguyen, J. A. Anderson, P. Lui, F. Spiga, J. A. Millan, D. C. Morse and S. C. Glotzer, *Comput. Phys. Commun.*, 2015, **192**, 97–107.
5 M. P. Howard, J. A. Anderson, A. Nikoubashman, S. C. Glotzer and A. Z. Panagiotopoulos, *Comput. Phys. Commun.*, 2016, **203**, 45–52.

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6 M. P. Howard, A. Z. Panagiotopoulos and A. Nikoubashman, *Comput. Phys. Commun.*, 2018, **230**, 10–20.
7 D. M. Meter and R. B. Bird, *AIChE J.*, 1964, **10**, 878.
8 A. Rao, *Rheology of Fluid, Semisolid, and Solid Foods*, Springer US, 3rd edn., 2014.

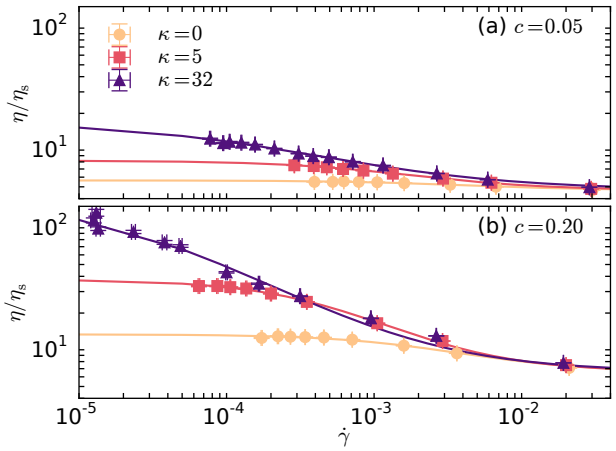

Fig. S1 Reduced viscosity η/η_s as a function of shear rate $\dot{\gamma}$ for solutions of polymers with stiffness $\kappa=0$ (◯), 5 (□), and 32 (△) at monomer concentration (a) $c=0.05$ and (b) $c=0.20$. The dynamic viscosity of the background MPCD solvent is $\eta_s\approx 4.0$. Symbols are data from RNEMD simulations, whereas solid lines are fit using the Cross model (eqn. S1)

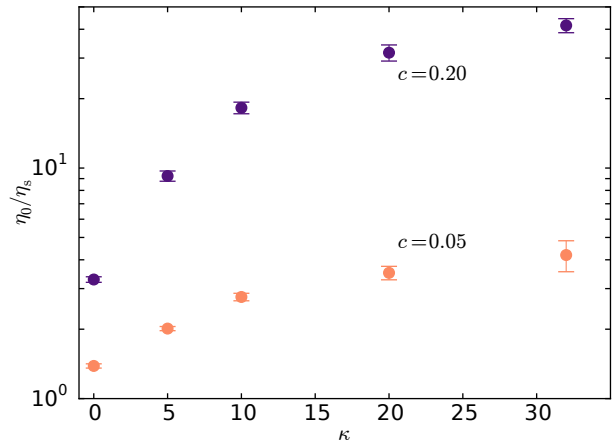

Fig. S2 Reduced zero-shear viscosity η_0/η_s as a function of chain stiffness κ for monomer concentration $c=0.05$ (orange) and $c=0.20$ (purple). The dynamic viscosity of the background MPCD solvent is $\eta_s\approx 4.0$. For each case, η_0 was estimated by fitting RNEMD simulation data to the Cross model (eqn. S1).