Supplementary Material

Microrheology of nematic and smectic liquid crystals of hard rods by dynamic Monte Carlo simulations

Fabián A. García Daza[1], Antonio M. Puertas[2], Alejandro Cuetos[3], and Alessandro Patti[1,4]

[1]Department of Chemical Engineering, The University of Manchester, Manchester M13 9PL, UK
[2]Department of Chemistry and Physics, University of Almería, 04120, Almería, Spain
[3]Department of Physical, Chemical and Natural Systems, Pablo de Olavide University, 41013, Sevilla, Spain
[4]Department of Applied Physics, University of Granada, Fuente Nueva s/n, 18071 Granada, Spain

S1. Details of the Spherical Tracers and Bath of Hard Spherocylinders Systems

We present the details of the systems studied in this paper, consisting of $N_r = 1400$ rod-like particles with length-to-diameter ratio $L^* \equiv L/\sigma = 5$ and 1 spherical tracer with diameter d_t. For comparison, we report d_t, the bath volume fraction $\phi = N_r v_r / V$ with v_r the single rod volume, elementary time steps $\delta t_{\mathrm{MC},t}$ and $\delta t_{\mathrm{MC},r}$ in units of τ, maximum displacements $\delta r_{\parallel}$, $\delta r_{\perp}$, δr in units of σ, maximum rotations $\delta\varphi$, and acceptance rates $\mathcal{A}_t$ and $\mathcal{A}_r$.

Table S1: Details of the tracer-rods systems studied in this work. The diameter d_t, MC time step $\delta t_{\mathrm{MC},t}$, maximum displacement δr of the tracer particle are presented with the acceptance rates $\mathcal{A}_t$ and $\mathcal{A}_r$ of the tracer and rods, respectively. In all the simulations the time step of the hard rods has been set to $\delta t_{\mathrm{MC},r}/\tau = 10^{-2}$, which fixes the maximum parallel, perpendicular and angular displacements of the rods to $\delta r_{\parallel}/\sigma = 2.99 \cdot 10^{-2}$, $\delta r_{\perp}/\sigma = 2.67 \cdot 10^{-2}$, and $\delta\varphi/\mathrm{rad} = 1.10 \cdot 10^{-2}$, respectively.

Isotropic phase, $\phi = 0.35$				
d_t/σ	$\delta t_{\mathrm{MC},t}/\tau$	$\delta r/\sigma$	$\mathcal{A}_t$	$\mathcal{A}_r$
0.5	$8.41 \cdot 10^{-3}$	$5.97 \cdot 10^{-2}$	0.927	0.780
1	$8.59 \cdot 10^{-3}$	$4.27 \cdot 10^{-2}$	0.908	0.780
2	$9.15 \cdot 10^{-3}$	$3.12 \cdot 10^{-2}$	0.853	0.780
4	$1.10 \cdot 10^{-2}$	$2.42 \cdot 10^{-2}$	0.712	0.781
6	$1.43 \cdot 10^{-2}$	$2.23 \cdot 10^{-2}$	0.550	0.784
8	$2.35 \cdot 10^{-2}$	$2.51 \cdot 10^{-2}$	0.334	0.785
Nematic phase, $\phi = 0.45$				
d_t/σ	$\delta t_{\mathrm{MC},t}/\tau$	$\delta r/\sigma$	$\mathcal{A}_t$	$\mathcal{A}_r$
1	$7.89 \cdot 10^{-3}$	$4.09 \cdot 10^{-2}$	0.859	0.678
2	$8.83 \cdot 10^{-3}$	$3.07 \cdot 10^{-2}$	0.769	0.679
3	$1.03 \cdot 10^{-2}$	$2.71 \cdot 10^{-2}$	0.658	0.679
Smectic phase, $\phi = 0.51$				
d_t/σ	$\delta t_{\mathrm{MC},t}/\tau$	$\delta r/\sigma$	$\mathcal{A}_t$	$\mathcal{A}_r$
1	$7.92 \cdot 10^{-3}$	$4.12 \cdot 10^{-2}$	0.838	0.663
2	$9.29 \cdot 10^{-3}$	$3.16 \cdot 10^{-2}$	0.714	0.663
3	$1.11 \cdot 10^{-2}$	$2.79 \cdot 10^{-2}$	0.596	0.663

S2. Comparison between the Fourier and Compliance Approaches to Calculate the Viscoelastic Moduli of a Bath of Hard Rods in Isotropic Phase

Along with Fourier-based methods, compliance approaches are an appropriate choice (see comment on [Soft Matter, 14, 8666, 2018] and reply on [Soft Matter, 14, 8671, 2018] as well as references therein) for calculating the viscoelastic properties of soft matter systems. Essentially, the frequency-dependent complex modulus, $G^*(\omega)$ can be computed by transforming the time dependent material's compliance, $J(t)$, which is defined as

$$J(t) = \left(\frac{\pi a}{k_\mathrm{B}T}\right)\langle\Delta r_t^2(t)\rangle, \tag{S1}$$

where a is the tracer radius, k_B the Boltzmann's constant, T the absolute temperature, and $\langle\Delta r_t^2(t)\rangle$ the tracer mean-squared displacement (MSD). Following the work of Evans *et al.* [1], the relationship between $J(t)$ and $G^*(\omega)$ reads

$$\frac{i\omega}{G^*(\omega)} = \left(1 - e^{-1\omega t_1}\right)\frac{J(t_1)}{t_1} + 6De^{-i\omega t_{N_t}} + \sum_{k=2}^{N_t}\frac{J_k - J_{k-1}}{t_k - t_{k-1}}\left(e^{-i\omega t_{k-1}} - e^{-i\omega t_k}\right), \tag{S2}$$

where N_t refers to the number of time points where the MSD was calculated, J_k indicates the value of $J(t)$ at time t_k, and $D \sim \eta^{-1}$ is related to the inverse of the system's steady-state viscosity. By using Eq. S2, it is possible to calculate the elastic, $G'(\omega)$, and viscous, $G''(\omega)$, moduli from $G^*(\omega) = G'(\omega) + iG''(\omega)$.

In Fig. S1, we compare G'' and G' by employing Fourier transformation approach by Mason [2], as reported in the manuscript (see Eqs. 14-16), and the compliance-based method [1]. In both cases, we calculated the MSD of a spherical tracer of diameter 1σ and 8σ embedded in an bath of hard spherocylinders in isotropic phase.

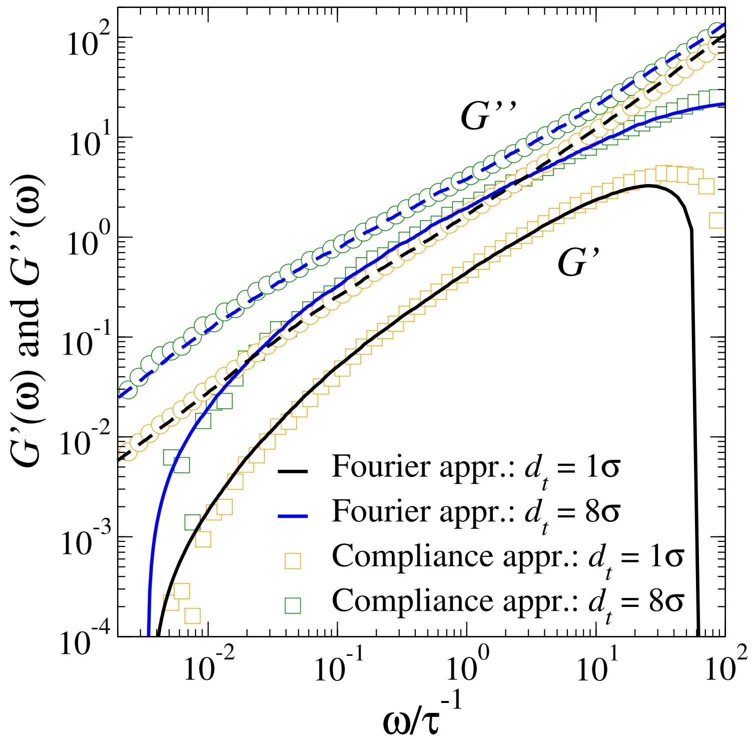

Figure S1: (colour on-line) Viscous $G''(\omega)$ (empty circles, dashed lines) and elastic $G'(\omega)$ (empty squares, solid lines) moduli as obtained with the compliance-based method by Evans [1] (symbols) and the Fourier-transform method by Mason [2] (lines) for an isotropic bath of hard rods incorporating a spherical tracer of size 1σ (orange symbols, black curves) and 8σ (green symbols, blue curves).

S3. Viscous and Elastic Moduli of a Bath of Hard Rods in Isotropic, Nematic, and Smectic Phases

Viscous (G'') and elastic (G') moduli for a tracer with different diameters immersed in a bath of hard rods in isotropic (I), nematic (N), and smectic (Sm) phases. The rods are modelled as hard spherocylinders with aspect ratio $L^* = 5$ and form I, N, and Sm phases with volume fractions $\phi = 0.35$, 0.45, and 0.51, respectively. The tracers are hard spheres whose diameter ranges between 0.5σ and 8σ. Figures S2, S3, and S4 depict, respectively, G' and G'' for systems in I, N and Sm phases and different sizes of the tracer.

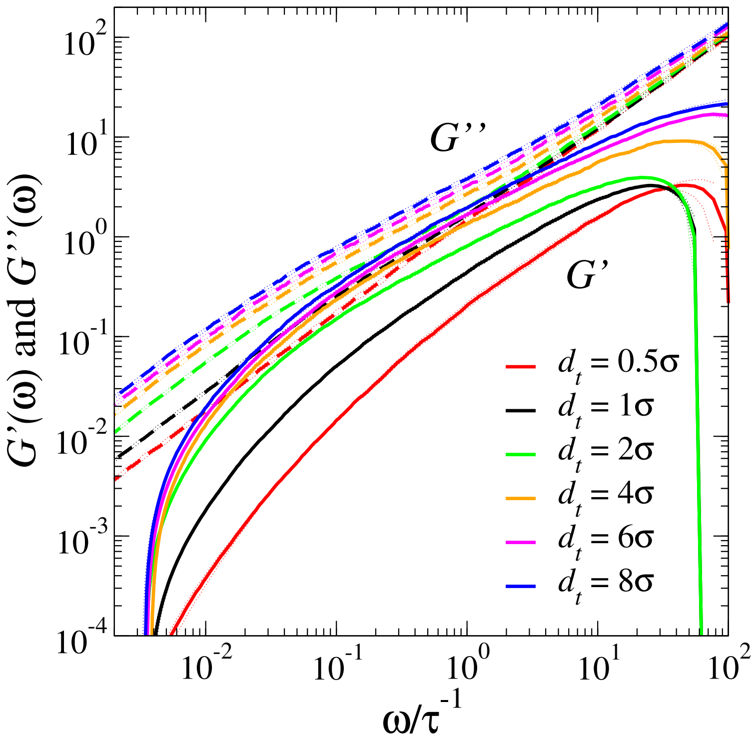

Figure S2: (colour on-line) Viscous (G'', dashed lines) and elastic (G', solid lines) moduli of a bath of hard rods forming an I phase containing a tracer particle with size 0.5σ, 1σ, 2σ, 4σ, 6σ, and 8σ represented by red, black, green, orange, magenta, and blue curves, respectively. Calculated errors are delimited by the dotted lines.

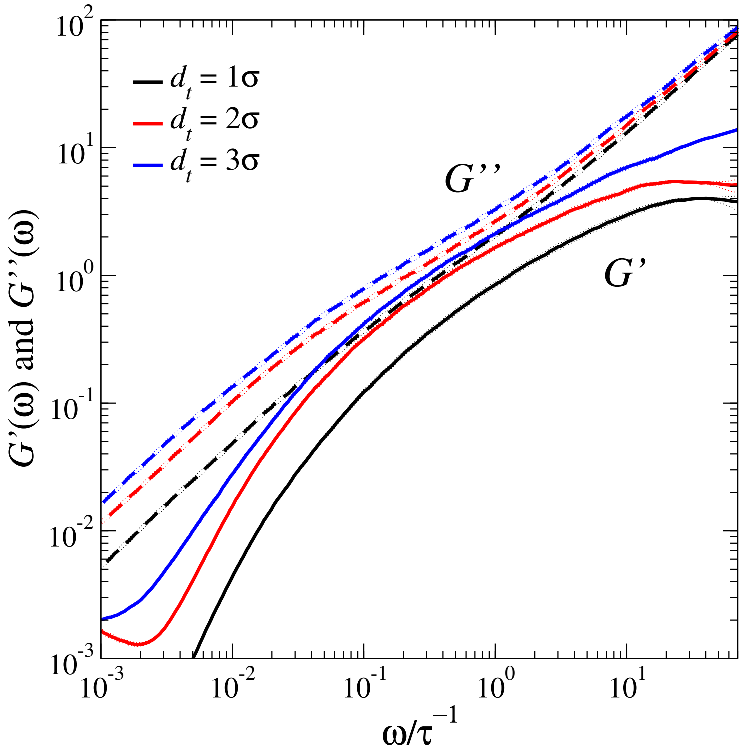

Figure S3: (colour on-line) Viscous (G'', dashed lines) and elastic (G', solid lines) moduli of a bath of hard spherocylinders in the N phase with tracer diameters 1σ, 2σ and 3σ represented by black, red, and blue solid curves, respectively. Calculated errors are delimited by the dotted lines.

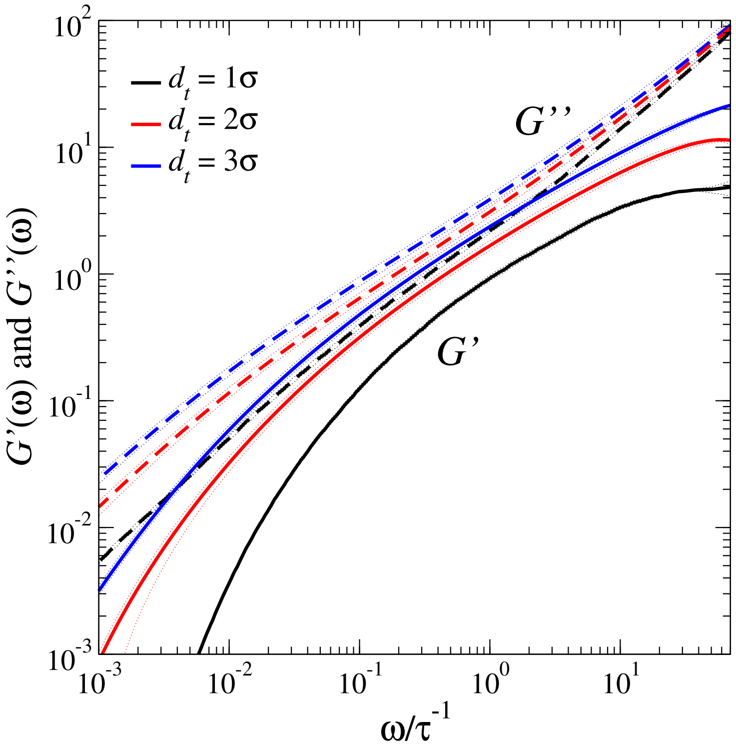

Figure S4: (colour on-line) Viscous (G'', dashed lines) and elastic (G', solid lines) moduli of a bath of hard spherocylinders in the Sm phase with tracer diameters 1σ, 2σ and 3σ represented by black, red, and blue solid curves, respectively. Calculated errors are delimited by the dotted lines.

S4. Mean Square Displacement of a Spherical Tracer in a Bath of Hard Rods in Isotropic Phase

Figure S5 shows the mean square displacement (MSD) of a tracer particle immersed in a bath of hard rods with length-to-diameter ratio $L^* = 5$ in isotropic phase at a volume fraction $\phi = 0.35$. The tracer particle is a hard sphere with a diameter that ranges from 0.5σ to 8σ. The MSD from the position of the tracer is defined as

$$\mathrm{MSD} \equiv \left\langle \Delta \mathbf{r}_{t,d}^2(t) \right\rangle = \left\langle (\mathbf{r}_{t,d}(t) - \mathbf{r}_{t,d}(0))^2 \right\rangle, \tag{S3}$$

where $\mathbf{r}_{t,d}(t)$ refers to the position of the tracer particle at time t, the brackets represent the averages over uncorrelated trajectories, and d is the dimensionality of the tracer's displacements. The case $d = 3$ corresponds to 3D displacements thus representing the total mean square displacement ($\mathrm{MSD}_{\mathrm{tot}}$).

Similarly, the values $d = 2$, and 1 represent particle displacements in two and one dimensions, respectively.

To calculate MSD_{tot}, we have simulated 4000 independent trajectories for the dynamics of the bath and tracer particles.

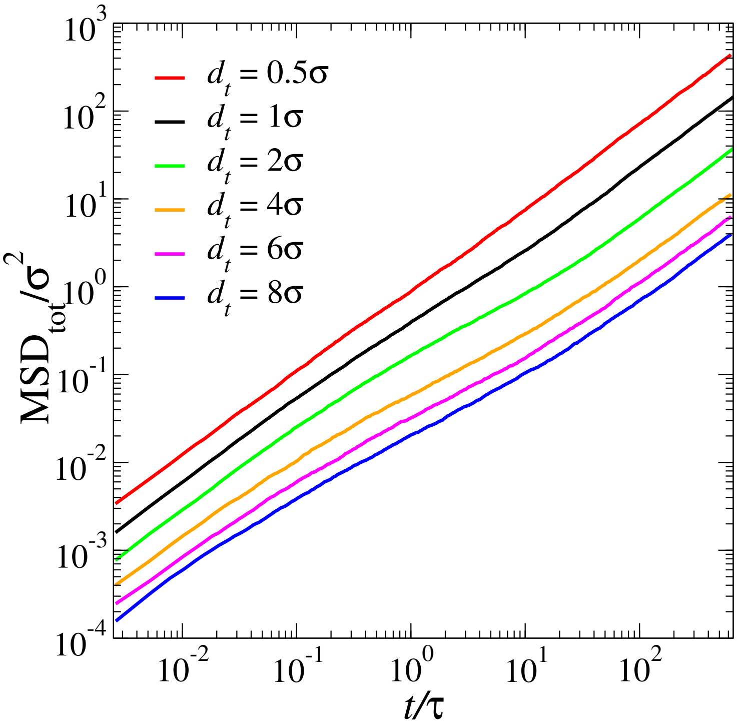

Figure S5: (colour on-line) MSD_{tot} calculated by computer simulations of a hard spherical tracer freely diffusing in a bath of hard rods. The sizes of both tracer and rod particles are $0.5\sigma - 8\sigma$ and $L^* = 5$, respectively. The bath is in an isotropic phase with $\phi = 0.35$.

S5. Effective Viscosity from DMC simulations and a Semi-Empirical Model

According to Kalwarczyk *et al.* [3, 4], the effective viscosity on tracer size in a polymer matrix can be described by a semi-empirical equation of the type:

$$\eta_{\text{MR}} = \eta_s \exp\left[\left(\frac{R_{\text{eff}}}{\xi}\right)^a\right], \tag{S4}$$

where $R_{\text{eff}}^{-2} = R_h^{-2} + (d_t/2)^{-2}$ is the effective radius of the tracer, being R_h the hydrodynamic radius of the matrix elements and $d_t/2$ the hydrodynamic radius of the particle. In the equation above, ξ refers to the mean free distance between those elements, and a is an exponent of order one. The radius of gyration of the rods (in the transverse direction) is $R_h \approx (\sigma/2)\sqrt{1/4 + (L^* + 1)^2/3}$ and in our case corresponds to $R_h|_{L^*=5} \approx 1.75\sigma$, ξ is obtained from the first neighbour peak of the rod-rod pair distribution function, located at $\sigma + \xi = 1.32\sigma$, and the exponent $a = 0.56$, which is indeed of order 1, is a fitting parameter. Figure S6 shows the rods' radial distribution function obtained from MC simulations.

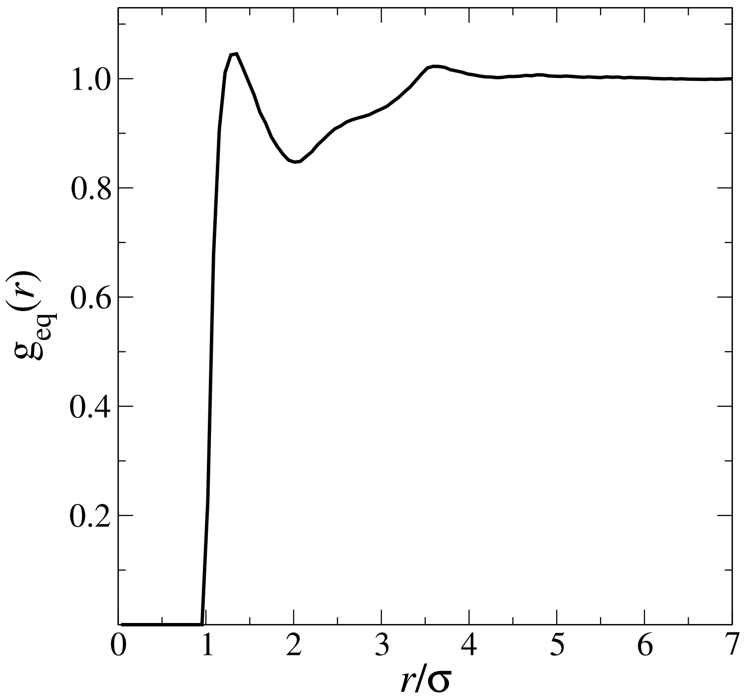

Figure S6: (colour on-line) Rod-rod radial distribution function $g_{\mathrm{eq}}(r)$ calculated by Monte Carlo simulations in a system of hard-rods with $L^* = 5$ in isotropic phase at a volume fraction $\phi = 0.35$.

S6. Loss Tangent in Nematic and Smectic Phases for Different Tracer Sizes

In Fig. S7 we present the loss tangent $\mathcal{R} \equiv G''/G'$ calculated in the three spatial coordinates for a bath of hard rods in N and Sm phases, and spherical tracers whose diameter ranges from 1σ up to 3σ.

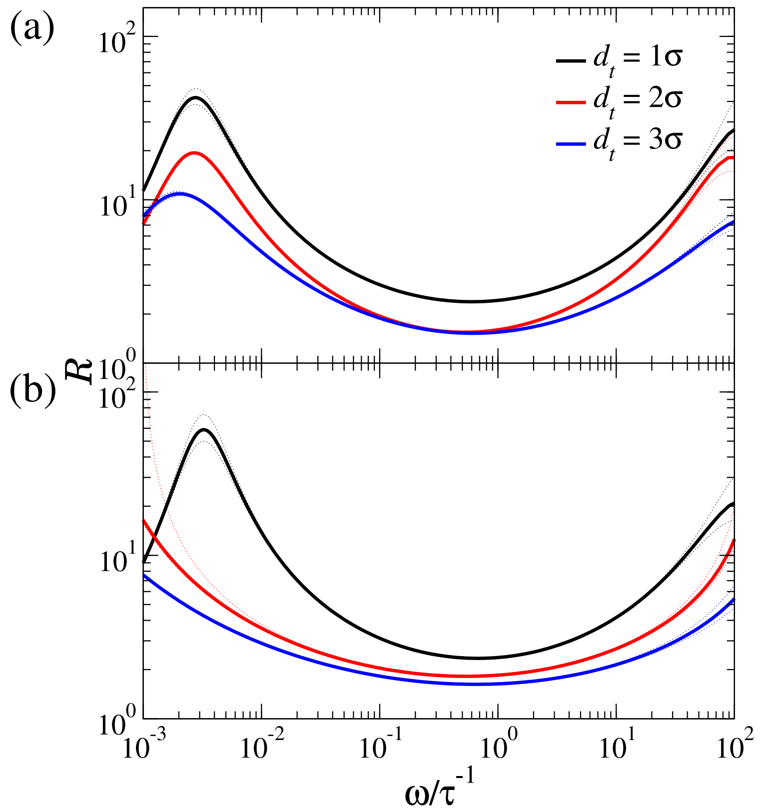

Figure S7: (colour on-line) Loss tangent, $\mathcal{R} \equiv G''/G'$, of a bath of hard spherocylinders in the N (top panel) and Sm (bottom panel) phases with tracer particle diameters 1σ, 2σ, and 3σ represented by black, red, and blue curves, respectively. Calculated errors are delimited by the dotted lines.

S7. Directional Viscous and Elastic Moduli of a Bath of Rods in Nematic and Smectic Phases

On the basis of the work of Hasnain and Donald [5], in a nematic or smectic phase, the complex moduli parallel and perpendicular to the nematic director can be written as:

$$|G_d^*(\omega)| = \frac{d\, k_\mathrm{B} T}{3\pi\,(d_t/2)\,\langle \Delta r_{t,d}^2(1/\omega)\rangle \Gamma\left[1+\alpha_d\,(\omega)\right]}, \tag{S5}$$

where d indicates the space dimension. In our case, $d = 1$ if $|G_d^*|$ is calculated along the nematic director (indicated with $\parallel$ subscript), and $d = 2$ if it is calculated in planes perpendicular to the nematic director (marked with $\perp$ subscript), resulting into $\langle \Delta r_{t,\parallel}^2(1/\omega)\rangle$ and $\langle \Delta r_{t,\perp}^2(1/\omega)\rangle$, with local exponents $\alpha_{\parallel}(\omega)$ and $\alpha_{\perp}(\omega)$, respectively. $\Delta r^2_{t,\parallel}$, and $\Delta r^2_{t,\perp}$, refer, respectively, to the tracer's MSDs parallel and perpendicular to the nematic director. The directional viscous ($G''_d = |G^*_d| \sin(\pi\alpha_d(\omega)/2)$) and elastic ($G'_d = |G^*_d| \cos(\pi\alpha_d(\omega)/2)$) moduli are shown in Figs. S8 and Fig. S9 for the N and Sm phases, respectively.

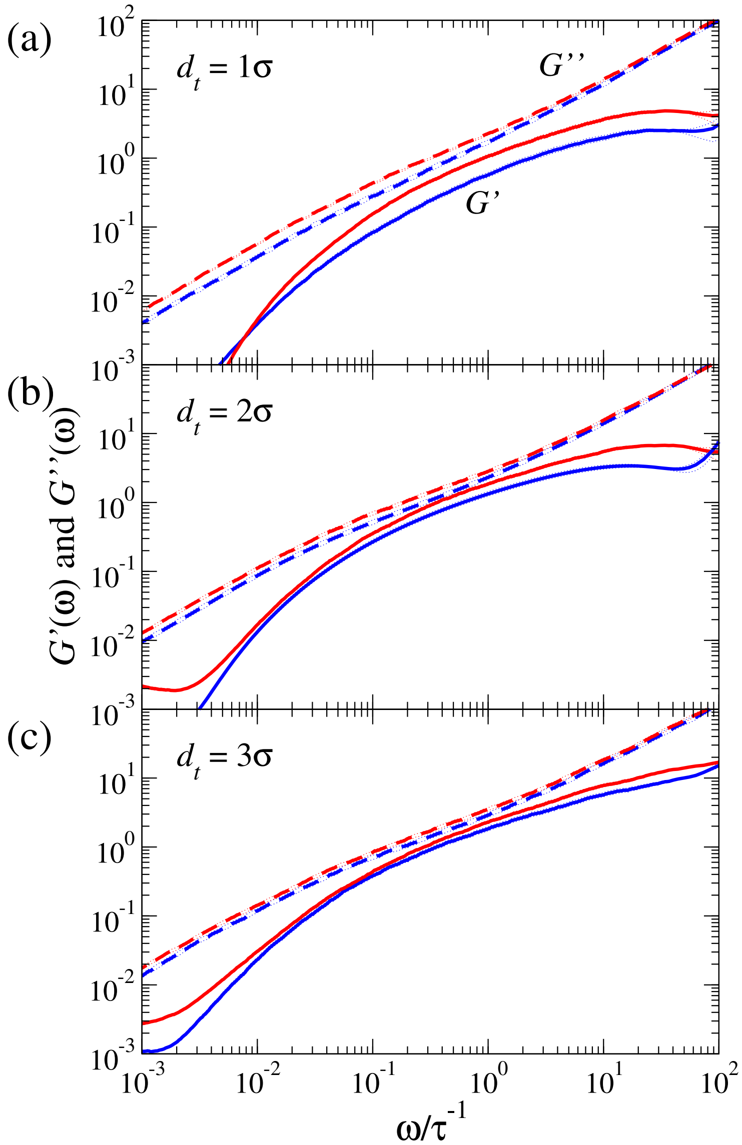

Figure S8: (colour on-line) Viscous (G'', dashed lines) and elastic (G', solid lines) moduli of a bath of hard spherocylinders in the N phase in the parallel (blue curves) and perpendicular (red curves) directions to the nematic director for tracer diameters (a) 1σ, (b) 2σ, and (c) 3σ. Calculated errors are delimited by the dotted lines.

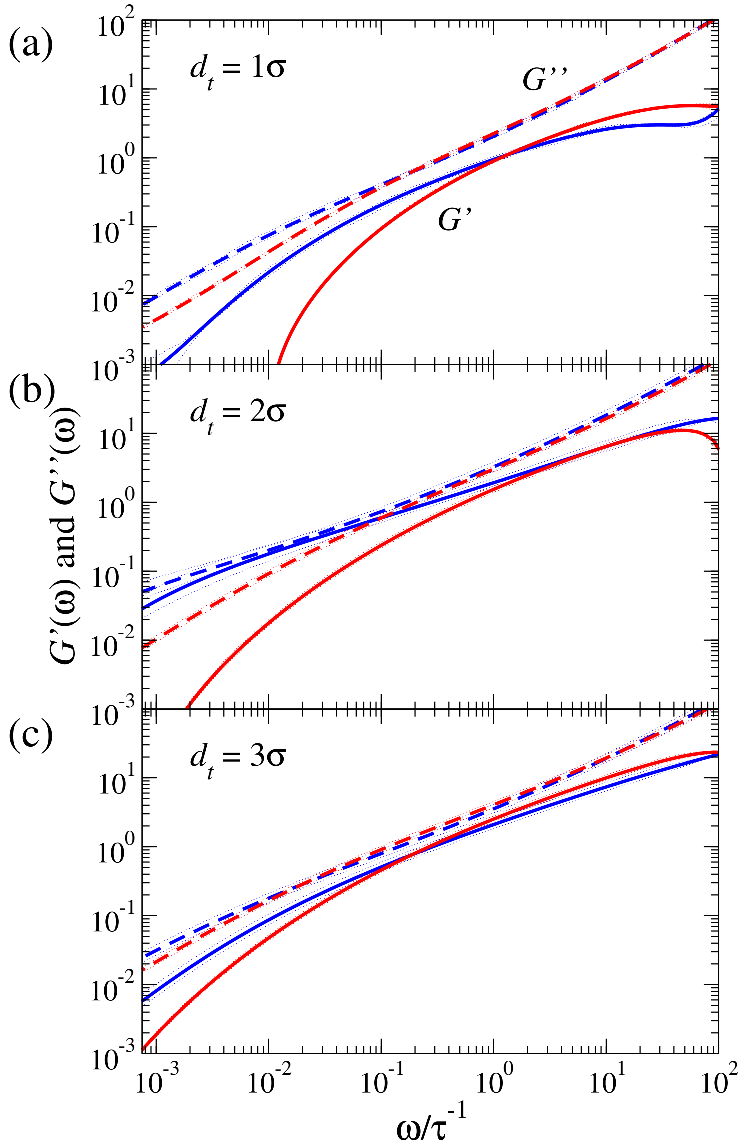

Figure S9: (colour on-line) Viscous (G'', dashed lines) and elastic (G', solid lines) moduli of a bath of hard spherocylinders in the Sm phase in the parallel (blue curves) and perpendicular (red curves) directions to the nematic director for tracer diameters (a) 1σ, (b) 2σ, and (c) 3σ. Calculated errors are delimited by the dotted lines.

S8. Mean Square Displacement of a Spherical Tracer in a Bath of Hard Rods in Smectic Phase

The MSD of a tracer particle with varying size in a bath of hard rods in smectic phase is shown in Fig. S10. While the rods are modelled as hard spherocylinders with aspect ratio $L^* = 5$, the tracer particle is represented by a hard sphere with diameter 1σ, 2σ, and 3σ. The host system is in a smectic phase at a volume fraction $\phi = 0.51$. The MSD of the tracer is calculated from Eq. S3. While the value $d = 3$ represents the total mean square displacement (MSD_{tot}), the cases where $d = 2$ and $d = 1$ are used to indicate the MSDs perpendicular ($\text{MSD}_{\perp}$) and parallel ($\text{MSD}_{\parallel}$) to the nematic director, respectively. At least 1000 trajectories have been computed to simulate the motion of bath and tracer particles.

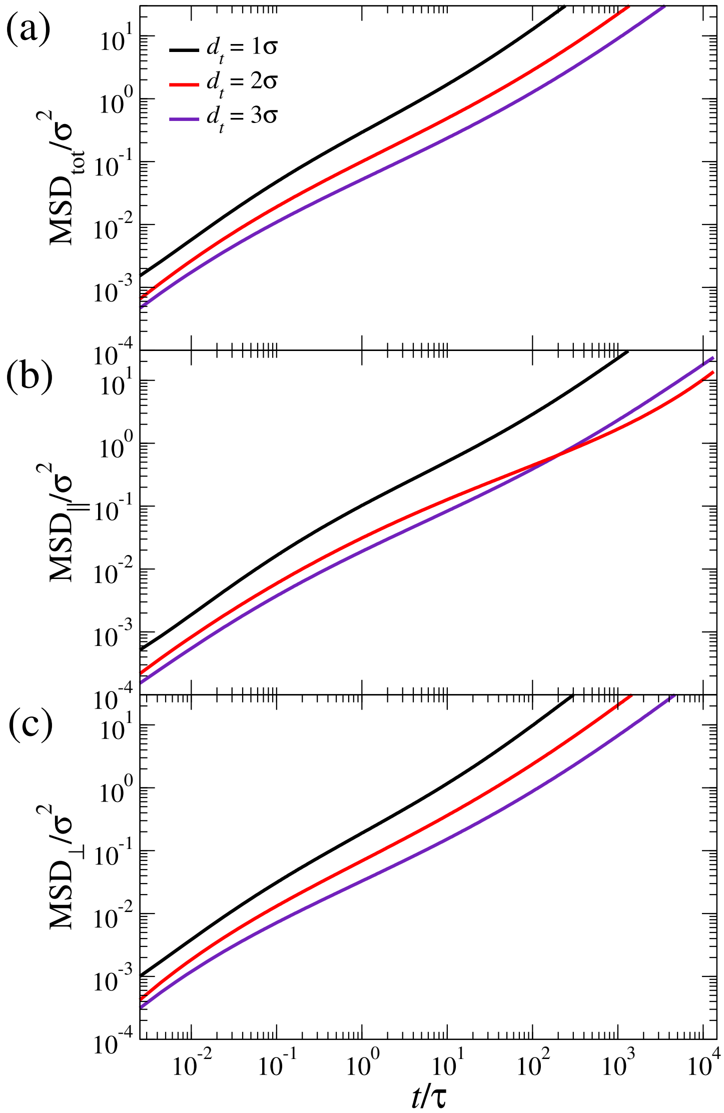

Figure S10: (colour on-line) From top to bottom: total, parallel and perpendicular MSDs of a hard spherical tracer diffusing in a bath of hard rods in smectic phase at a volume fraction $\phi = 0.51$. The rods have a fixed length-to-diameter ratio $L^* = 5$, and the diameter of the tracer particle varies between 1σ, 2σ, and 3σ represented by the black, red and blue solid lines, respectively.

S9. Trajectories of a Spherical Tracer in a Bath of Rods in Smectic Phase

Figure S11 shows typical trajectories, from DMC simulations, of spherical tracers with different sizes parallel to the nematic director, $r_{t,\parallel}(t)$. Tracers are immersed in a bath or hard rods (with $L^* = 5$) in the Sm phase.

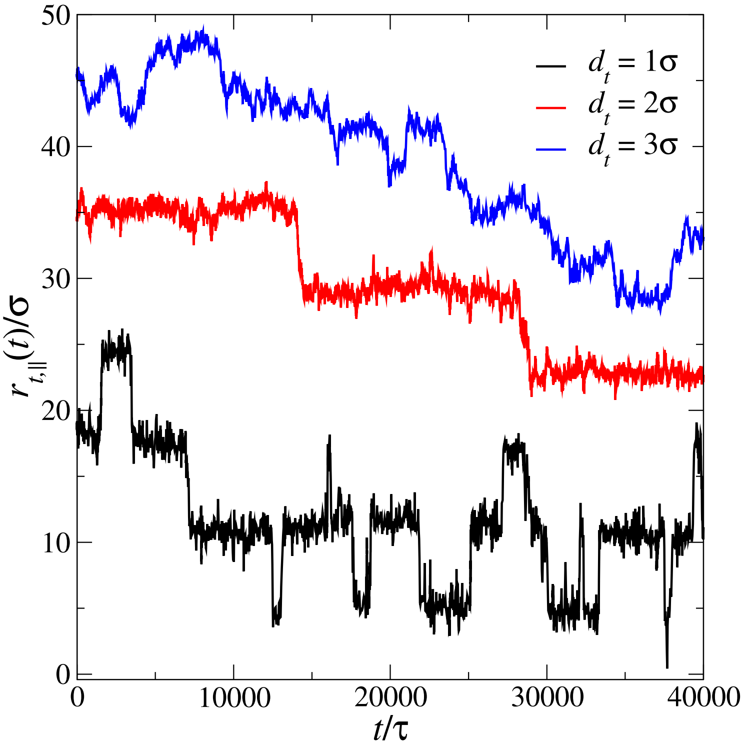

Figure S11: (colour on-line) Typical trajectories of tracers with sizes 1σ, 2σ, and 3σ represented by black, red, and blue solid lines, respectively, along the nematic director in a bath of hard spherocylinders in the Sm phase.

References

[1] R. M. L. Evans, Manlio Tassieri, Dietmar Auhl, and Thomas A. Waigh. Direct conversion of rheological compliance measurements into storage and loss moduli. *Phys. Rev. E*, 80:012501, 2009.

[2] Thomas G. Mason. Estimating the viscoelastic moduli of complex fluids using the generalized Stokes–Einstein equation. *Rheol. Acta*, 39(4):371–378, 2000.

[3] Tomasz Kalwarczyk, Natalia Ziębacz, Anna Bielejewska, Ewa Zaboklicka, Kaloian Koynov, Jędrzej Szymański, Agnieszka Wilk, Adam Patkowski, Jacek Gapiński, Hans-Jürgen Butt, and Robert Hołyst. Comparative analysis of viscosity of complex liquids and cytoplasm of mammalian cells at the nanoscale. *Nano Lett.*, 11(5):2157–2163, 2011.

[4] Tomasz Kalwarczyk, Krzysztof Sozanski, Anna Ochab-Marcinek, Jędrzej Szymański, Marcin Tabaka, Sen Hou, and Robert Hołyst. Motion of nanoprobes in complex liquids within the framework of the length-scale dependent viscosity model. *Adv. Colloid Interface Sci.*, 223:55–63, 2015.

[5] I. A. Hasnain and A. M. Donald. Microrheological characterization of anisotropic materials. *Phys. Rev. E*, 73:031901, 2006.