Supplementary Information for: Conformations and diffusion of flexibly linked colloidal chains

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Supplementary Movies

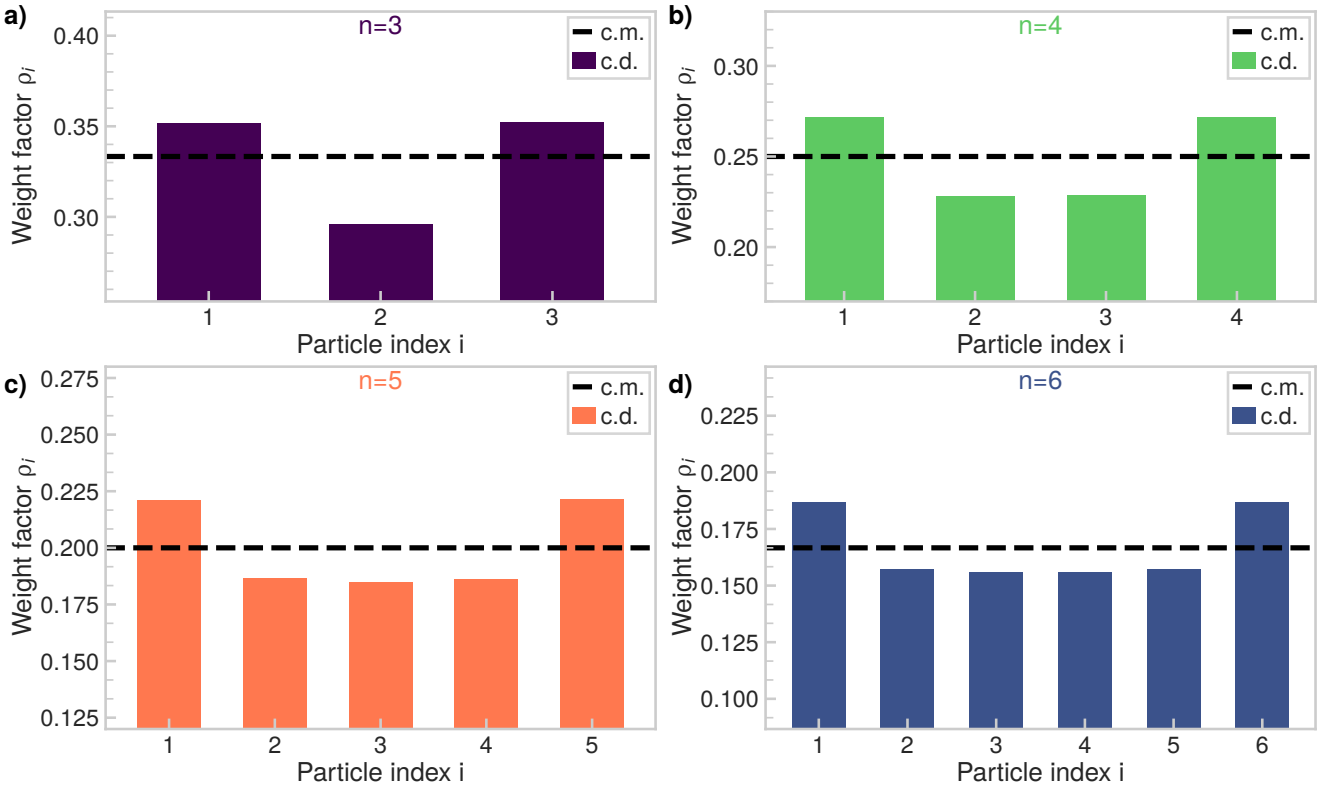
For all movies, a video without annotation is shown on the left and a video with the annotated particle positions and position of the c.m. in time is shown on the right. All videos have been sped up five times (original duration 5 min), the pixel size is indicated by a scalebar.

`MOV_S1_trimer.mp4` A flexible trimer (n=3).

`MOV_S2_tetramer.mp4` A flexible tetramer (n=4).

`MOV_S3_pentamer.mp4` A flexible pentamer (n=5).

`MOV_S4_hexamer.mp4` A flexible hexamer (n=6).



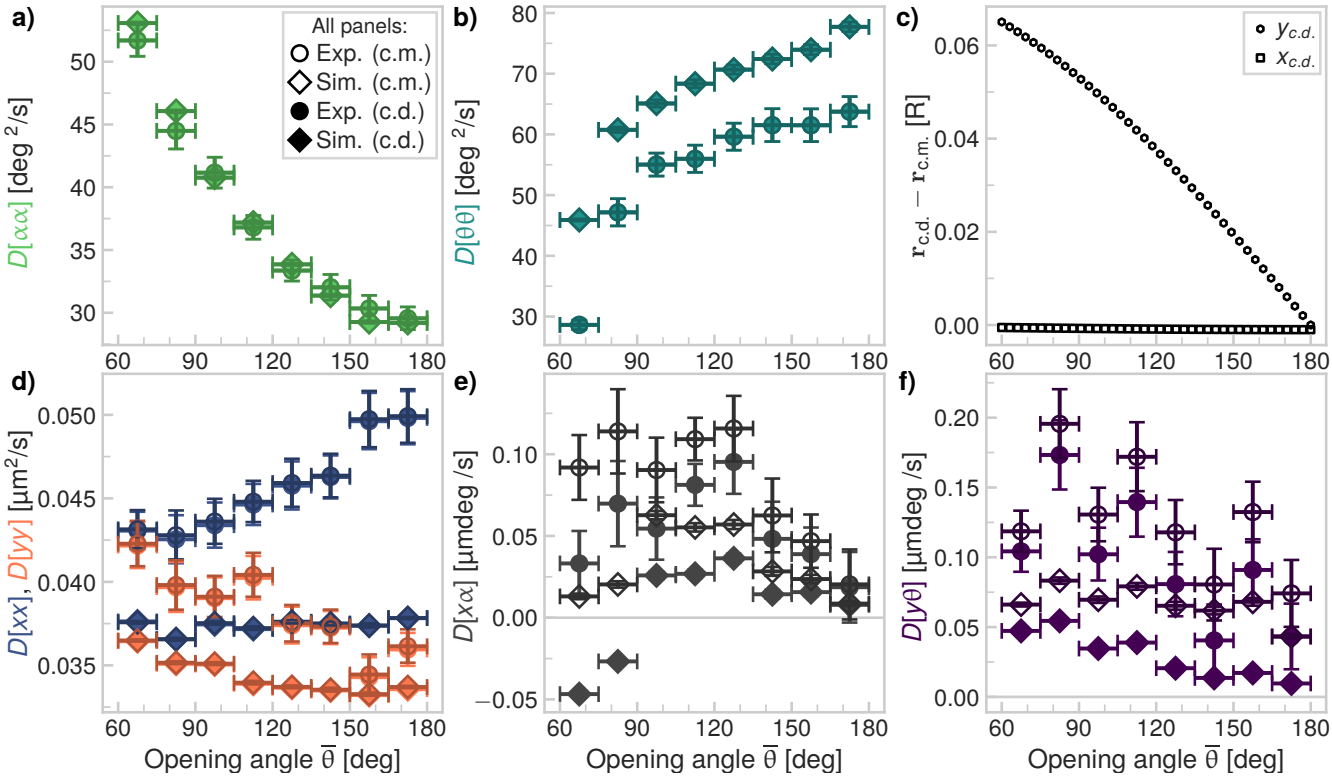
Supplementary Figure S1: **Center of diffusion (c.d.) versus center of mass (c.m.): weight factors.** Weight factors $\boldsymbol{\rho}$ for the c.m. and the c.d., for **a)** trimer (n=3) **b)** tetramer (n=4) **c)** pentamer (n=5) **d)** hexamer (n=6) chains. For the c.d., more weight is accorded to the outer particles compared to the inner particles of the chain. However, differences between the c.m. and the c.d. are small for all chain lengths.

A Effect of tracking point, bin width and lag time on the diffusivity of flexible trimers

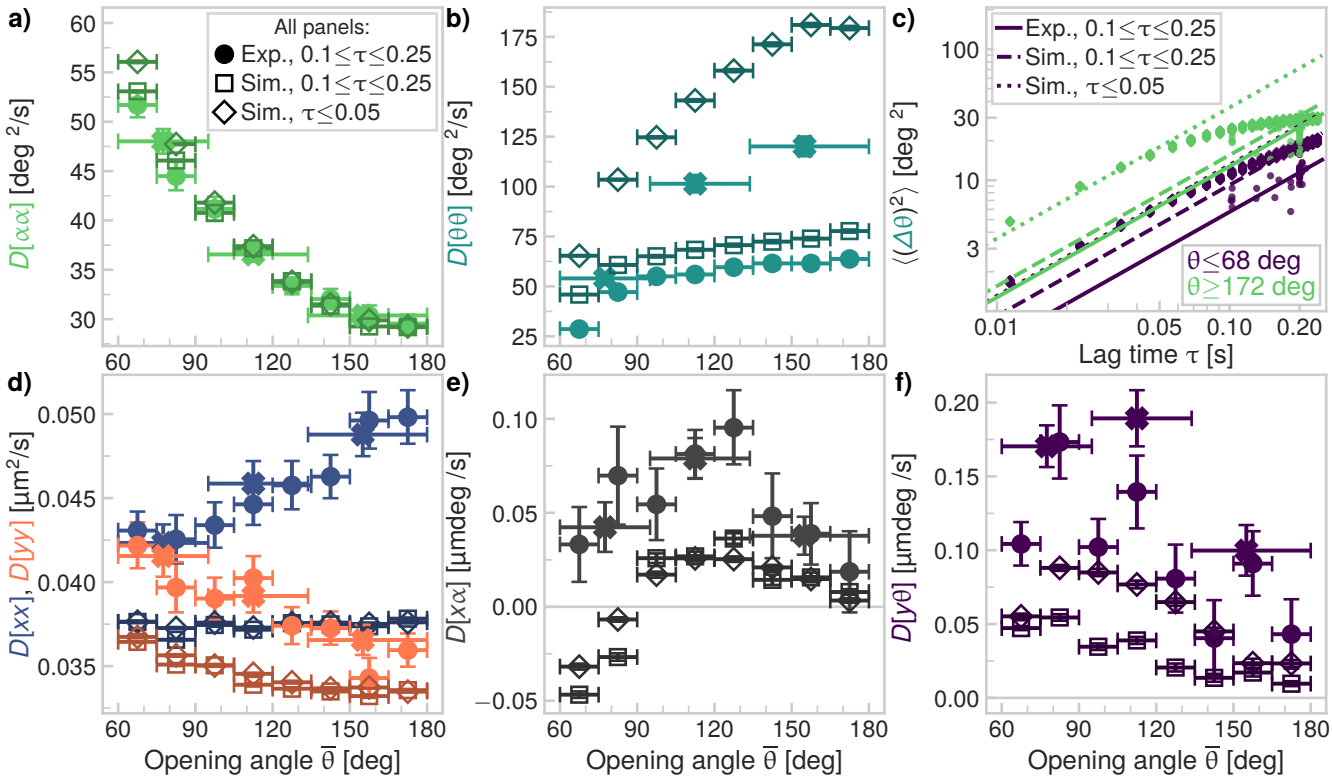
The choice of coordinate system affects the magnitude of the diffusion tensor. For all rigid objects, there exist a tracking point relative to which the diffusion elements are independent of the lag time considered, called the center of hydrodynamic stress. Although such a point doesn't exist in general for flexible objects [1], an analogous tracking point can be found where the magnitude of the diffusion tensor elements is minimal and therefore, close to the time-independent values at long lag times, called the center of diffusivity (c.d.) [2]. We compare the results of two choices of tracking points, namely, the center of mass (c.m.) of the cluster which is another common choice, and the center of diffusivity (c.d.) [2, 3].

First, as shown in Figure S1, the c.d. is very close to the c.m. for all chain lengths. A slightly larger weight is given to the outer particles for the c.d. compared to the c.m., but this has only a very small effect on the location of the c.d. Second, we compare the magnitude of the diffusion tensor of a flexible trimer relative to the c.m. as in our previous work [4] and relative to the c.d. (this work). As shown in Figure S2, the rotational (Figure S2a), flexibility (Figure S2c) and translational (Figure S2d) terms of the diffusion tensor are only slightly affected by changing the tracking point from the c.m. to the c.d. This is easily explained by the fact that the position of the c.d. only changes by approximately 6 % for the smallest opening angle compared to the c.m., as shown in Figure S2c. However, the coupling terms are lower with respect to the c.d. as shown in Figure S2e for the translation-rotation coupling term and in Figure S2f for the Brownian quasiscallop mode. The fact that these coupling terms are lower is expected, because the magnitude of the diffusion tensor is expected to be the lowest relative to the c.d., as it is closest to the long-time diffusion tensor, for which short-time correlations or memory effects are expected to vanish.

The simulations allow us to probe the diffusivity at arbitrarily high frame rates and thus arbitrarily short lag times τ, which is the time delay between the pairs of frames considered in the calculation of the mean squared displacements. There is a marked effect of lag time on the flexibility, as shown in Figure S3b. For the simulated data, we show the results for a lag time of 0.05 s (diamonds) and 0.1 to 0.25 s (squares, same lag time as experimental data). The lag



Supplementary Figure S2: **Diffusivity of flexible trimers: center of diffusion (c.d.) versus center of mass (c.m.) as tracking point.** For all panels, open points correspond to the c.m. as tracking point while filled points refer to the c.d. as tracking point. ∘ experimental data, ⋄ simulated data (both $0.1 \leq \tau \leq 0.25\,\mathrm{s}$). **a)** The rotational diffusivity does not change as function of tracking point. **b)** Also for the flexibility term, there is no influence of tracking point. **c)** The c.d. of flexible trimers is very close to the c.m.: there is only a small deviation of approximately 6 % for the smallest opening angles. The difference $\boldsymbol{r}_{\mathrm{c.d.}} - \boldsymbol{r}_{\mathrm{c.m.}}$ on the y-axis is given in terms of the particle radius R. **d)** The translational diffusivity changes only slightly with respect to a different tracking point. **e)** The effect of tracking point for rotation-translation coupling is more pronounced: values are lower when the c.d. is used as tracking point. **f)** Also for the Brownian quasiscallop mode, the values are lower when using the c.d. as tracking point instead of the c.m.



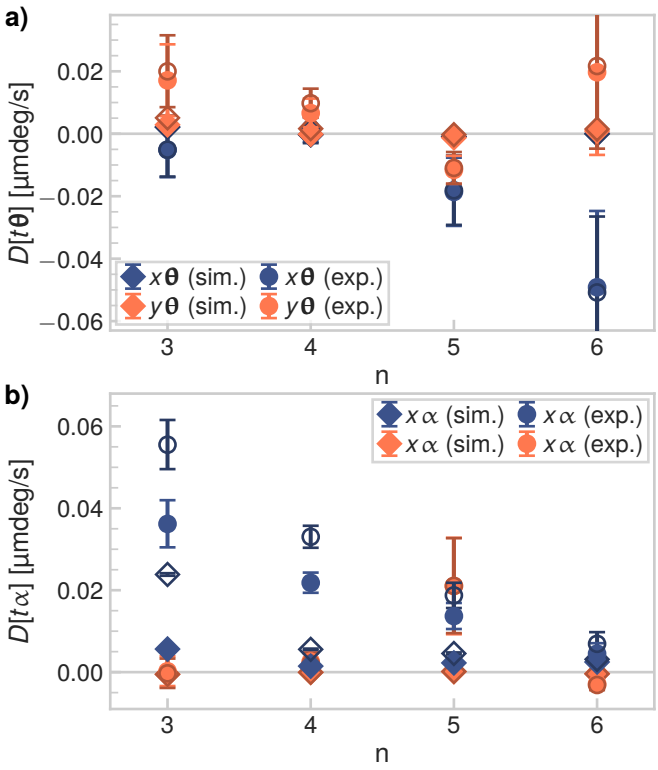
Supplementary Figure S3: **Trimer: effect of varying the bin size / lag time** Comparison between • experimental data, × experimental data with a larger bin width (both $0.1 \leq \tau \leq 0.25\,\mathrm{s}$) and simulated data: ◇ $\tau \leq 0.05\,\mathrm{s}$, □ $0.1 \leq \tau \leq 0.25\,\mathrm{s}$. **a)** The rotational diffusivities are largely unaffected by the different choices for lagtimes (except for small opening angles), the experimental data agrees with the simulated data. **b)** The flexibility is highly sensitive for the choice of lagtimes. **c)** Mean-squared angular displacement of the opening angle reveals caging effects at longer lagtimes, which are more pronounced for higher flexibilities, an effect inherent to the analysis method. **d)** The translational diffusivities are less sensitive to the choice of lagtimes. The experimental translational diffusivities are larger than the simulated ones. **e)** Translation-rotation coupling terms. **f)** Translation-flexibility coupling terms, including the Brownian quasiscallop mode $D[y\theta]$ [4], which is sensitive to the choice of lagtimes.

times of the experimental data range from 0.1 to 0.25 s, as set by the frame rate of the camera. The simulated data with longer lag times are close to the experimental data. However, when we analyze the simulated data using a shorter lag time, we find a large increase in the flexibility. This difference can easily be explained by considering the mean squared angular displacement of the opening angle in Figure S3c. Especially for the larger opening angles, we see that the mean squared displacements show a plateau at longer lag times, leading to a smaller apparent flexibility when the data is fitted using a linear model. The effect of lag time is also present in the Brownian quasiscallop mode in Figure S3e. For terms not directly related to flexibility, such as translational diffusivity in Figure S3d, rotational diffusivity in Figure S3a and translation-rotation coupling in Figure S3e, we see there is no appreciable effect of different lag times.

This plateauing for flexibility-related diffusion terms is caused by the calculation method of the shape-dependent diffusivity. That is, we consider only those pairs of frames where the shape of the particle stays within the limits of the particular opening angle bin of the first frame. Therefore, if the flexibility is high, a large percentage of frames will exceed the initial bin and these will not be considered in the analysis. The frames where the bin is not exceeded, as a result, are those in which the flexibility is lower, which leads to the apparent decrease in flexibility at longer lag times.

To solve this, larger bin widths can be used at the expense of a lower resolution in opening angle. We tested this in Figure S3b and found that indeed, the values for the flexibility were higher, while the other diffusion tensor elements were not affected (see Figure S3, crosses). In fact, by using a larger bin width, we measure the "true" short-time flexibility: the ratio between the experimental flexibility for the smaller bins (circles in Figure S3b) and the simulated flexibility for the experimental lag times (squares in Figure S3b) is equal to 0.78 ± 0.07. By using the larger bins, the ratio between the experimental flexibility and the simulated flexibility at short lag times (diamonds in Figure S3b) is also equal to 0.77 ± 0.07.

In conclusion, the diffusivity of the c.d. is very close to that relative to the c.m. Interestingly, the interplay of lag time and bin width has a critical effect on the measured short-time diffusion tensor elements related to shape changes and should be carefully considered in the analysis of experimental data.



Supplementary Figure S4: **Shape-averaged coupling terms as function of chain length.** In all panels, filled symbols are with respect to the c.d. and unfilled symbols are with respect to the c.m. **a)** The shape-averaged translation-flexibility coupling modes in the y-direction are positive for a trimer (Brownian quasiscallop mode) but average out for larger chain lengths. **b)** The shape-averaged translation-rotation coupling mode in the x-direction is positive for trimers and decreases as function of chain length.

B Shape-averaged coupling terms as function of chain length

We have calculated the shape-averaged translation-flexibility and translational-rotational coupling terms with respect to both the c.m. and the c.d., as shown in Figure S4. The shape-averaged translation-flexibility coupling modes in the y-direction are positive for a trimer, which corresponds to the Brownian quasiscallop mode [4] of the shape-dependent diffusion tensor, as shown in Figure S4a. For longer chain lengths, this coupling term is averaged out, most likely because of the negative correlation we have found between the flexibility of the two opening angles of the tetramer chain, which indicates that such coupling terms may be present for longer chain lengths as well. Because the coordinate system is not centered on the trimer segment, overall shape changes are taken into account. We find that overall, there is no average coupling between translational diffusivity in the y-direction and the overall flexibility $D[\boldsymbol{\theta\theta}]$.

On the contrary, in Figure S4b, we see that there is a positive coupling between rotational diffusivity and translational diffusivity in the x-direction, which decreases as function of chain length. This is the same coupling we have found for the shape-dependent diffusion tensor of both trimers [4] and tetramers.

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