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Kayaking and wagging of liquid crystals under shear: Comparing director and mesogen motions

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Abstract – Rod-like colloids in dense solutions perform collective orientational motions under shear flow. The periodic tumbling motions of the director, *i.e.* the average orientation of the rods, are commonly characterized as kayaking, wagging and flow-aligning, in order of increasing shear rate. Our event-driven Brownian dynamics simulations of rigid spherocylinders reproduce these three distinct director motions, but also clearly show, for the first time, that the individual mesogens are kayaking at all shear rates. The synchrony of the mesogens's motions gradually decreases with increasing shear rate, which at a critical shear rate causes a transition of the apparent collective motion from kayaking to wagging. The rods's persistent kayaking also explains the continuity of the tumbling period at this transition and the smooth change from wagging to flow-aligning observed at higher shear rates.

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A single rod-like colloidal particle suspended in a linearly sheared solvent will tend to align its long axis with the flow direction. Because of the slightly different shear velocities at the two ends of a rod, a symmetric rod will regularly flip between the two degenerate flow-aligned states. This periodic motion of exchanging the two ends of a rod is named after Jeffery, who described this motion theoretically in 1922 [1]. Rods in a dense quiescent solution will frequently collide with their neighbours, and as a result tend to align in a nematic liquid-crystalline phase [2]. This ordering strongly affects the rods's abilities to trace out their individual Jeffery orbits under shear, and consequently forces them to perform their orientational motions collectively. The complex phase behaviour of the paths traced by the director, *i.e.* the average orientation of the rods, has fascinated theoreticians and experimentalists for several decades. While their studies have focused on the motion of the director, in the simulation studies presented here the emphasis shifts to the motion of the individual rods.

The macroscopic hydrodynamic theory for nematics by Ericksen [3,4], and its extension with Frank elastic stresses [5] by Leslie [6,7], predicts flow-induced director tumbling under favourable conditions. Hess [8] and Doi [9] approach tumbling nematics from the microscopic point of view, by combining a Smoluchowski equation for the evolution of the orientational distribution function (ODF) with a mean field approximation for rod-rod interactions, to derive an equation of motion for the order parameter tensor. Series expansions of the ODF have enabled Marrucci and Maffettone [10,11] and Larson and Öttinger [12,13] to analyse the Doi-Hess theory numerically. Kuzuu and Doi [14,15] derived relations between the microscopic particle properties and the macroscopic Leslie-Ericksen coefficients. Based on these studies, a general picture has emerged in which the director may follow various distinct periodic paths depending on the applied shear rate, the aspect ratio of the rods, their volume fraction and the degree of orientational ordering [2]. For low shear rates $\dot{\gamma}$, the director performs a “tumbling” or “kayaking” motion with the director rotating slowly when it is nearly flow-aligned and rapidly when at an angle to the flow direction, as illustrated in fig. 1. At intermediate shear rates the director switches to a “wagging” motion around the flow-aligned state, by

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Fig. 1: (Colour on-line) The evolution of the director orientation $\hat{n}$ as a function of shear strain, in the kayaking (top, $Pe_r = 0.5$) and wagging (bottom, $Pe_r = 2.0$) regime, with t denoting the time relative to one particular flow-aligned state. Plotted are the components of the director along the flow direction (dashed), the velocity gradient direction (solid) and the vorticity direction (dotted), as well as the orientational order parameter (P_2 , dash-dotted). Note that the curves in both plots have the same periodicity in the strain because the tumbling period is inversely proportional to the shear rate $\dot{\gamma}$.

oscillating up and down in the flow plane, see fig. 1. Here, we are interested in the mechanism behind this transition and the motions of individual rods in the wagging phase. The speculation by Marrucci and Maffettone [10], that individual rods quickly rotate over 180 degrees to rejoin the lingering majority of rods, still awaits a direct confirmation after 20 years. The wagging motion becomes suppressed with increasing shear rate, until the director adopts a stationary orientation at a small angle with respect to the flow direction. The interested reader is referred to the aforementioned literature for further details, to Dhont and Briels for a discussion on the assumptions underlying the Doi-Hess theory [16], and to Kröger and Hess [17,18] and Forest *et al.* [19,20] for numerically determined director orbits and phase diagrams.

A clue on the motion of individual rods is provided by the tumbling period scaling inversely proportional with the shear rate, $P \sim \dot{\gamma}^{-1}$, where ODF simulations by Kröger and Sellers [21] and by Archer and Larson [22] indicate that the proportionality constant is a function of the mesogen aspect ratio and the degree of orientational ordering. Oscillatory behaviour in agreement with theory has been observed in optical and rheological experiments on polymer liquid crystals under shear [23–26]. Experiments on an *fd*-virus solution [27] yield $P \sim \dot{\gamma}^{-1.1}$, where the slightly deviant exponent is attributed to the semi-flexibility of the *fd*-virus. The absence in these experiments of a discontinuity in the tumbling period near the kayaking to wagging transition is remarkable, since it suggests that the rods's motions are hardly affected by the transition.

Fig. 2: (Colour on-line) Probability distributions of the rods's orientation angles θ relative to the flow direction, during two consecutive kayaking periods at $Pe_r = 0.5$. Note that the nine distributions are not equidistant in time: the rods are approximately parallel to the flow direction, as in curves marked 1, 5 and 9, for the largest part of the tumbling period, while the tumbling events proceed relatively quickly; see also fig. 1. The gradual decrease in the peak heights of the three flow-aligned curves results from the occasional extraneous tumbling of single rods, as shown in fig. 3.

Particle-based computer simulations are potentially very useful towards elucidating the motions of individual rods, but have long been impeded by excessive computational demands. Hence, Yamene *et al.* [28,29] limit their simulations to semi-dilute isotropic systems, Ding and Yang [30,31] eliminate the third dimension and the rods's translational degrees of freedom, while Mori *et al.* [32,33] use Gay-Berne particles with a very low aspect ratio. We have recently developed an event-driven Brownian dynamics (BD) algorithm capable of simulating highly elongated hard spherocylinders. For rods modelled after the *fd*-virus, *i.e.* spherocylinders of effective diameter $D = 14.8$ nm and length $L = 880$ nm in an implicit solvent of viscosity 10^{-3} Pa/s and temperature 300 K, we find a tumbling period $P \sim 4.2 \frac{L}{D} \varphi \dot{\gamma}^{-1}$ for a range of volume fractions φ and, notably, for shear rates covering both the kayaking and the wagging regime [34,35]. These periods are in good quantitative agreement with the experiments on the *fd*-virus, confirming that the simulations yield an accurate representation of a real system. An inverse proportionality of P with $\dot{\gamma}$ is also observed for attractive rods in the recent multi-particle collision dynamics simulations by Ripoll *et al.* [36]. Here we present results for the *fd*-like rods, with an aspect ratio $L/D = 60$, dissolved in the aforementioned liquid at a scaled volume fraction $\frac{L}{D} \varphi = 4.5$.

The angular distributions of rod orientations, measured relative to the flow direction, are shown in fig. 2 for nine instances during two consecutive kayaking periods. The applied shear rate corresponds to a Peclet number

Fig. 3: (Colour on-line) The rods's end-to-end vectors $\hat{\mathbf{u}}_i$ plotted as dots on a unit sphere, with the solid line starting in the origin of every sphere representing the director $\hat{\mathbf{n}}$. The flow direction runs horizontally, from left to right, and the velocity gradient direction vertically, from bottom to top. Plots A to D show consecutive stages of one kayaking period at $Pe_r = 0.5$, with the snapshots taken at the instances marked by arrows in fig. 1 and roughly corresponding to curves 1, 2, 4 and 5 of fig. 2. The few rods diametrically opposite to the director have tumbled once more or once less than the majority; note that the director is insensitive to the sign of the end-to-end vector. A movie is available at <http://cbp.tnw.utwente.nl/Downloads>.

Fig. 4: (Colour on-line) Unit spheres showing the end-to-end vectors of the rods at four instances, marked in fig. 1, during a wagging period at $Pe_r = 2.0$. The rods (depicted as points) are still tumbling periodically, though less organized than in the kayaking motion of fig. 3. But the director (thick solid lines) clearly does not follow the mesogens anymore and now performs a periodic wagging motion instead. Movies showing the motions of all rods and of five random rods are available at <http://cbp.tnw.utwente.nl/Downloads>.

of $Pe_r = \dot{\gamma}/D_r = 0.5$, where $D_r = 23.5 \text{ s}^{-1}$ is the rotational diffusion coefficient of a single rod in a quiescent solvent. A particular flow-aligned configuration, which also defines time $t = 0$, has been used to remove the ambiguity of the rods's end-to-end vectors $\hat{\mathbf{u}}_i$, by selecting initial directions pointing in the flow direction $\hat{\mathbf{e}}_x$, *i.e.* $\hat{\mathbf{u}}_i(0) \cdot \hat{\mathbf{e}}_x > 0$. Hence, the angular distribution at $t = 0$ consists of a single peak centered around zero. When the rods tumble, their orientation angles steadily increase and the peak travels smoothly to higher values. The distribution broadens during every kayaking event but narrows down again when the next flow-aligned state (they are located at multiples of 180 degrees) is reached. The director follows this motion faithfully, as can be seen in fig. 3 where the rods's end-to-end vectors are plotted as dots on a sphere along with a thick line representing the director, and thus performs the kayaking motion depicted in fig. 1.

An altogether different situation is encountered at the higher shear rates of the wagging regime, illustrated here by simulations at $Pe_r = 2.0$. From the end-to-end vectors plotted on the unit sphere, see fig. 4, it is clear that the rods are still performing their kayaking motion, but this time much less synchronized than at low shear rates

in the kayaking regime. The orientational distribution becomes very wide during this tumbling event, see fig. 4F, and a significant number of rods have already made the transition to the next flow-aligned state when the majority of rods has barely left the original flow-aligned state. The angular distribution functions in fig. 5 now have peaks only near the flow-aligned orientations, at multiples of 180 degrees, which are linked by broad shoulders during tumbling events and separated by sparse regions inbetween tumbling events. A peak no longer slides from one flow aligned state to the next, as it does in the kayaking regime of fig. 2, but rather a peak diminishes by losing rods to the next peak and grows by gaining rods from its left neighbour. Since at any time the majority of rods is in a nearly flow-aligned state, while the order tensor by definition does not distinguish between the two flow-aligned states, it becomes essentially impossible for the director to follow the tumbling motion of the rods. All that remains for the director is a small amplitude wagging motion, see fig. 1, reflecting the modest deviations of the peak positions from the aligned states. Starting with the $t = 0$ flow-aligned state, the director follows the initial shift of the peak by rotating clockwise, but this

Fig. 5: (Colour on-line) Angular distributions of rods's end-to-end vectors during two consecutive wagging periods at $Pe_r = 2.0$. The motion of the rods is less synchronized than in the kayaking motion of fig. 2, as can be glanced from the wide and double-peaked distributions in the mid-period distributions marked 2 and 4. At each tumbling event a significant fraction of the rods remains trapped in their original orientation, thereby causing a steady decline of the peak heights. The fraction of rods that have tumbled more than twice during $2P$, see inset, is about 2.5% for both the kayaking and the wagging motions.

motion does not persist because the tumbling of the rods is insufficiently collective to “drag” the director along. Instead, the director remains near the dwindling original peak at $\sim 10^\circ$ and only starts to be affected by the growing opposite peak at $\sim 150^\circ$ once a large fraction of the rods has reached this second peak. In the calculation of the director, this vanguard of rods is treated identical to an equally large group of rods at $\sim -30^\circ$, and consequently the director will start to turn counter-clockwise when the majority of rods has tumbled to the second peak, thus reaching the situation depicted in fig. 4G. The continued shift of the second peak to the flow-aligned state at 180° , and the slight reverse shift of the first peak to 0° , together account for the final clockwise rotation of the director back to zero degrees. Note that the splitting of the angular distribution into two peaks is already discernible in the kayaking motion of fig. 2 for the half-period curves 3 and 7, but there the effect is still too small to deflect the director from its kayaking motion. The splitting-up becomes more pronounced with increasing shear rates, until at the kayaking-wagging transition the director no longer follows the tumbling motions of the rods. Direct visualisations of the motions of individual rods, using the Visual Molecular Dynamics (VMD) package [37], fully support these observations. Visualisations of the entire system show no signs of domain formation, neither in the kayaking nor in the wagging regime, but domain formation may contribute to $P \propto \dot{\gamma}^{-1}$ scaling behaviour in larger systems [2].

With further increases of the shear rate, the kayaking motion of the rods becomes ever less synchronous and

the distribution of end-to-end vectors over the unit sphere becomes very broad with modest peaks near the flow-aligned states. Hence, the wagging motion of the director decreases in amplitude, and at sufficiently high shear rates the director effectively adopts a nearly stationary orientation corresponding to the most probable rod orientation (of the now virtually stationary angular distribution), which is at a small angle relative to the flow direction. The rods, however, are still tumbling.

In summary, simulations of highly elongated spherocylinders in a shear flow clearly illustrate that the kayaking to wagging transition of the director orbit with increasing shear rate does not reflect a change in the motions of the individual mesogens, and thus confirm a long-standing conjecture by Marrucci and Maffettone [10]. Individual rods remain kayaking at all shear rates while the decreasing collectiveness of this motion finally prevents the director from following this motion faithfully at high shear rates. The first signs of the decreasing synchrony of the rods's motions with increasing shear rate, are detectable well below the wagging transition. The rods perform identical motions in the kayaking, wagging and flow-aligning regimes, and the smoothly diminishing synchrony forms an integral part of the power law relating their period to the shear rate. The director, on the other hand, is forced to follow the tumbling period of the rods but undergoes an artificial transition from kayaking to wagging due to its inability to follow the rods's motions —this explains why the director's period remains continuous despite the drastic change of its orbit.

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