

Confinement induced splay to bend transition of colloidal rods

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We study the nematic phase of rodlike *fd*-virus particles confined to channels with wedge-structured walls. Using laser scanning confocal microscopy we observe a splay-to-bend transition at the single particle level as a function of the wedge opening angle. Lattice Boltzmann simulations reveal the underlying origin of the transition and its dependence on **nematic elasticity and wedge geometry**. Our combined work provides a simple method to obtain the splay-to-bend elasticity ratios and offers a way to control the position of defects through the confining boundary conditions.

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Packing and confinement problems emerge in fields ranging from biology to engineering. In biological systems the organization of the cell is determined, among other things, by the packing of fibril-like particles (actin filaments, DNA) [1, 2]. An example of the subtlety of packing phenomena is the plethora of liquid crystalline phases that can be found in arrangements of anisotropic particles by increasing concentration [3, 4]. Confinement of liquid crystals adds to the complexity, since the interactions of the particles with the walls may lead to structures that compete with those formed in the bulk [5, 6]. Many of the next generation liquid crystal display devices exploit this interplay by using structured or patterned surfaces as an essential element of their design [7, 8]. Very recently, the ordering at sawtoothed structures has been studied theoretically within a Landau-De Gennes framework [9, 10], with a focus on the wetting behaviour. In this Letter, in a combined experimental and theoretical effort, we show the rich phenomenology that emerges when confining a nematic liquid crystal to a microfluidic channel with a wedge structured wall. We seek to disentangle how the **wedge geometry and elasticity of the *fd*-virus' nematic phase** determine the adopted deformation in the wedge. **We introduce a new method for estimating elastic constants suitable to colloidal and biological systems, as an alternative to previous methods using magnetic fields [11] or light scattering [12]**. Specifically, we determine the transition from a splay to a bend director field, with increasing wedge angle.

We use the *fd*-virus, which is an excellent model liquid crystal system for both static and dynamic behaviour [13–16]. The virus' contour length and diameter are 0.88 μm and 6.6 nm, respectively. These dimensions allow for the 3D determination of the position and orientation of individual particles by means of laser scanning confocal microscopy (LSCM). Thus we obtain detailed mechanistic insights on a single particle level of the director field. Moreover, due to the relatively large size of the particles,

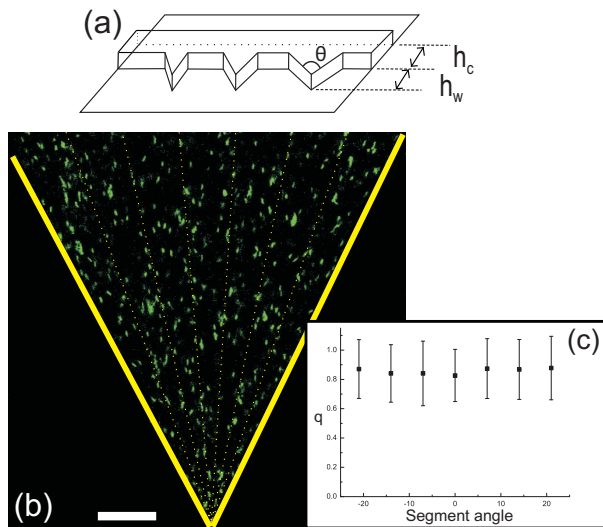


Figure 1: (a) Geometry of the microfluidic channel. (b) Microscopy picture of the nematic phase in the splay deformation, obtained by overlaying 7 LSCM images. Only the fluorescent *fd*-virus particles are visible. Scale bar is 10 μm . See supplementary material for movie. (c) Plot of order parameter versus segment angle for the movie corresponding to the image in (b). The segments are indicated in (b) by the overlaid dashed lines.

we can study effects of wall structures that are, when translated to the scale of thermotropic liquid crystals, very small and inaccessible.

The particles were grown following standard protocols [17] and dispersed in 20 mM tris buffer at pH 8.15 with 100 mM NaCl and 15% EtOH. The ethanol was added to prevent the growth of bacteria. The virus concentration was 24 mg/ml, which is in the nematic phase. Of the particles 1% was fluorescently labeled with Alexa-488 NHS ester. The labeled particles were imaged by means of confocal microscopy using a Zeiss LSM 5 Exciter, 63x 1.4 NA oil-immersion objective. Microfluidic

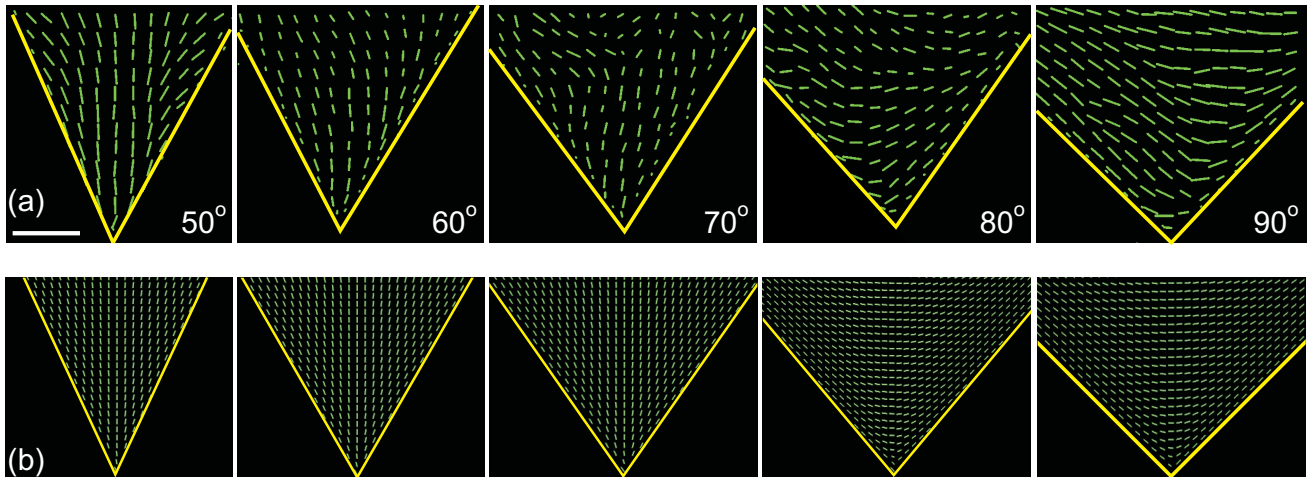


Figure 2: Director field in the wedge for varying wedge angle $\theta = 50^\circ - 90^\circ$: (a) Director fields from experiments, calculated by averaging over 10 images. Scale bar is $50\mu\text{m}$. (b) Director field from lattice Boltzmann simulations. In both cases the transition from a splay to a bend configuration occurs between $70 - 80^\circ$.

channels were constructed from UV glue (NOA 81) and bound to glass coverslips as described in the soft lithography protocols [18], which guaranteed sealing over the course of the experiment. One of the walls was structured with wedges with a range of opening angles, see fig. 1a. The radius of curvature of the tip of the wedge is smaller than $2.5\mu\text{m}$ and the walls are smooth on the colloidal lengthscale ($1\mu\text{m}$). The measurement range was $40-100^\circ$ in steps of 10° . The height of the channels was $10\mu\text{m}$, which is smaller than the cholesteric pitch [19], giving ‘pseudo 2D’ confinement. This was confirmed by three dimensional LSCM scans. Due to the thin samples polarization microscopy was not possible. The width of the channels is characterized by h_c and h_w (fig. 1a). We used $h_c = 500\mu\text{m}$ and $h_w = 75, 750$ and $1125\mu\text{m}$.

The structured microfluidic channels were filled by capillary action. Directly before filling the channels were plasma cleaned, which changes the hydrophilicity of the channels and offers a way to control the speed of filling. This enabled us to set the initial conditions of the experiment due to the coupling between the nematic director and flow: low filling speeds created an initial disordered configuration, while high filling speeds resulted in the rods immediately adopting metastable aligned deformations, which only slowly found equilibrium [20]. We filled the channels slowly and from a disordered configuration the equilibrium was reached within a couple of hours.

Fig. 1b displays a LSCM image of the fluorescently labeled rods in a splay deformation. The nematic deformations are clearly seen from movies in which the rods move along the director lines, see supplementary material. Tracking the particles close to the walls we verified no rods were sticking to the walls. To quantify the LSCM images we first use image analysis software to identify each rod’s position and orientation [21]. Fig. 2a shows

the experimental director fields, obtained by dividing a series of ten $202 \times 202\mu\text{m}$ LSCM images into squares of area $13.5 \times 13.5\mu\text{m}$ and then averaging the orientation of the rods in each square. The average number of rods per square is 50 rods, and the standard deviation in the orientation is 10%. The lapse time between images was 30 seconds which is longer than the typical self-diffusion time, ensuring the images are statistically independent. In addition, for splay deformations we calculated the order parameter q [3] in piece-wise segments across the wedge. We find that the order parameter is constant across the wedge, which indicates strong planar anchoring, see fig. 1c.

We observe splay deformations, accompanied by a defect in the bulk of the wedge, below 70° and bend deformations above 80° .

Clearly, the location of the splay-to-bend transition will depend on the ratios of the splay (K_1) to bend (K_3) elasticity. Starting from a simplified picture we may assume the following: In going from an opening angle of 180° , i.e. a flat wall, to an opening angle of 0° we go from a bend to a splay deformation. For the semi-flexible *fd-virus* we expect $K_3/K_1 \approx 1$, from reported values of semi-flexible liquid crystals [3, 12, 22]. Due to the underlying symmetry of the problem we would then expect the splay to bend transition to occur at 90° . Mottram also found the transition to occur at 90° by using a conformal mapping technique within the one constant approximation [23].

To elucidate our observations we performed numerical simulations taking the actual channel geometry into account. The simulations are based on the Beris-Edwards [24] model for liquid crystal hydrodynamics where the continuum equations of motion are written in terms of a tensor order parameter $Q_{\alpha\beta} = q(3n_\alpha n_\beta - \delta_{\alpha\beta})/2$. Its

largest eigenvalue gives the nematic degree of order q and the corresponding eigenvector the director field $\hat{\mathbf{n}}$. The equilibrium properties of the liquid crystal are described by the Landau-de Gennes free energy [3, 25]. This comprises a bulk term f_b and an elastic term f_{el} :

$$f_b = A_0 \left[\frac{1}{2} \left(1 - \frac{\gamma}{3} \right) Q_{\alpha\beta}^2 - \frac{\gamma}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{\gamma}{4} (Q_{\alpha\beta}^2)^2 \right], \quad (1)$$

$$f_{el} = \frac{L_1}{2} (\partial_\alpha Q_{\beta\gamma})^2 + \frac{L_2}{2} (\partial_\alpha Q_{\alpha\gamma}) (\partial_\beta Q_{\beta\gamma}) + \frac{L_3}{2} Q_{\alpha\beta} (\partial_\alpha Q_{\gamma\epsilon}) (\partial_\beta Q_{\gamma\epsilon}). \quad (2)$$

In eq. (1) γ is a measure of the rod concentration, which sets the location of the first order isotropic-nematic transition to $\gamma = 2.7$ and the nematic degree of order, and A_0 is a constant. In eq. (2) the prefactors L_n with $n = 1, 2$ or 3 are linear combinations of the Frank elastic constants, K_n [26]:

$$\begin{aligned} K_1 &= \frac{9q^2}{4} (2L_1 + L_2 - qL_3), \\ K_2 &= \frac{9q^2}{4} (2L_1 - qL_3), \\ K_3 &= \frac{9q^2}{4} (2L_1 + L_2 - 2qL_3). \end{aligned} \quad (3)$$

The anchoring of the director on the walls is modeled by using a Rapini-Papoular-like surface free energy density, $f_s = W^{uni} (Q_{\alpha\beta} - Q_{\alpha\beta}^0)^2$, where W^{uni} denotes the uniform anchoring strength and $Q_{\alpha\beta}^0 = q(3n_\alpha^0 n_\beta^0 - \delta_{\alpha\beta})/2$ corresponds to the preferred director orientation $\hat{\mathbf{n}}^0$ imposed by the walls. The equations of motion are solved using a hybrid lattice Boltzmann scheme [27]. Although we report only results in equilibrium, solving the full hydrodynamic equations was found to be an efficient way of accessing the free energy minimum.

Apart from reproducing the geometry of the microchannel, there are several conditions that need to be fulfilled in order to match the experimental conditions. First, we keep the nematic degree of order q around 0.8 to match the ordering in the experiments. Second, the starting configuration is matched by choosing an isotropic configuration in the wedge ($q = 0$), and a nematic state with a horizontal director $\hat{\mathbf{n}}$ in the channel above the wedge. Third, we take $K_3/K_1 = 1$, as discussed earlier, and consider strong planar surface anchoring that leads to perfect alignment of the rods with the surfaces, as in the experiments. Finally, we approach the experimental situation by using $\xi_N/h_w \sim 0.5/100$ and $1/100$. The nematic correlation length ξ_N sets the lengthscale for the variations in the nematic degree of order q . Experimentally, ξ_N is of order of the rod dimensions, i.e. $\sim \mu\text{m}$.

Fig. 2 compares the director field obtained in experiment and simulation, showing very close agreement. In

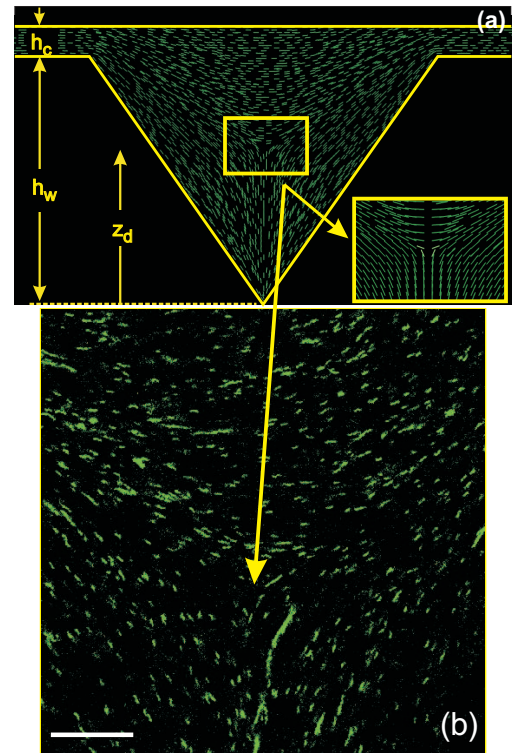


Figure 3: (a) Director field from a simulation for a wedge angle of 70° showing a defect of strength $s = -1/2$, where the splay configuration meets the bend configuration. The inset shows a zoom of the defect. (b) Microscopy picture of the corresponding defect, obtained by overlaying 5 LSCM images. Only the fluorescent *fd*-virus particles are visible. Scale bar is $10\mu\text{m}$. See supplementary material for movie.

particular, both sets of data display a splay-to-bend transition at opening angles $\sim 70^\circ$. This gives us the confidence to use the simulations to demonstrate the mechanism behind the transition, and its dependence on the details of the confinement geometry.

In the case of splay deformations, the inevitable frustration of the director field due to the horizontal configuration in the main channel leads to an $s=-1/2$ defect in the wedge. Fig. 3a shows the numerical director profile at a wedge opening angle of 70° , close to the splay to bend transition. The rods adopt a splay deformation at the tip and a bend deformation at the top of the wedge resulting in an $s=-1/2$ defect. This is indeed observed in the experiments, see fig. 3b and the accompanying movie for images of the defect at the single particle level. The presence of this defect plays an important role in determining the stable director configuration. For a full understanding of the splay-to-bend transition, the complete geometry, including the top wall bounding the micro channel, needs to be considered, as is evident from fig. 3.

Fig. 4 shows experimental and simulation results for the relative position of the defect, defined as $\tilde{h} = z_d/h_w$

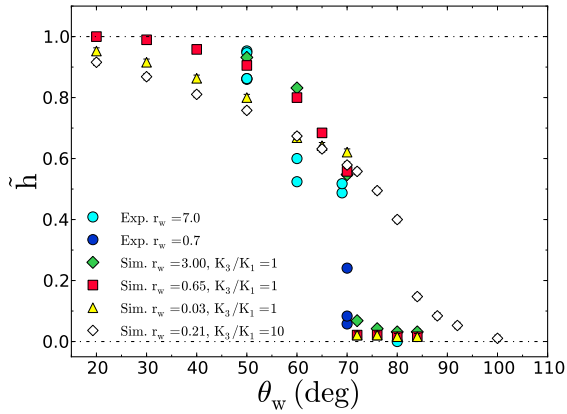


Figure 4: The relative position of the defect within the wedge $\bar{h} = z_d/h_w$ plotted as a function of the wedge angle θ_w , for varying channel geometries $r_w = h_c/h_w$. For an elasticity ratio $K_3/K_1 = 1$ the splay to bend transition takes place at the same wedge opening angle, independent of the width of the microfluidic channel above the wedge. For $K_3/K_1 = 10$, however, the transition moves to a higher opening angle.

with z_d the height of the defect with respect to the tip, plotted as a function of the opening angle θ_w . Results are presented for different values of the ratio of channel height to wedge length $r_w = h_c/h_w$. For the largest wedge heights h_w multidomains (Schlieren-texture) may be present near the top of the wedge, which is suppressed for the small h_w . For small θ_w the defect lies close to the top of the wedge, marking the boundary between the splay ordering imposed by the wedge and the horizontal nematic configuration imposed by the top channel boundary. With increasing wedge angle the splay deformation becomes less favourable, and the defect is pushed into the wedge by the dominance of the nematic order in the microchannel. This effect is more pronounced for the narrower channels for which the top wall has a stronger effect. The curves converge as the wedge angle increases indicating that the defect has moved sufficiently far down into the wedge that it no longer feels the upper surface. An abrupt transition is observed just above 70° for all values of r_w . This corresponds to the splay to bend transition: for higher wedge angles the defect is no longer present and a bend deformation is adopted. **The transition occurs when the energy of the splay configuration plus the energy of the defect becomes equal to the energy of the bend configuration. Here the transition occurs at an angle smaller than the predicted $\theta_w \sim 90^\circ$ for an infinitely large wedge.**

Fig. 4 shows that the transition is sharp and does not depend on r_w . As we encounter the bend to splay transition the main channel maintains its horizontal director field and, therefore, the location of the transition is determined mainly by the wedge. It can be shifted to much

higher opening angles, but only in the limit of very large ξ_N/h_w , where h_w is of the order of 10 rod lengths, in which case the defect becomes energetically more important.

Simulations with a higher ratio of elastic constants $K_3/K_1 = 10$, which mimics stiff rods, revealed that the defect can now persist to higher angles, and positions closer to the bottom of the wedge.

To conclude, we have used laser scanning confocal microscopy to image the director field of a colloidal liquid crystalline virus on a single particle level. Thus it was possible to directly observe the nematic ordering in a microchannel patterned with wedges of varying opening angle. The complex interplay between confinement, elasticities and surface anchoring led to a splay to bend transition mediated by a defect in the centre of the wedge. Numerical results, in quantitative agreement with the experiments, enabled us to predict the position of the defect as a function of opening angle, and elucidate its role in the change of director structure. Our experiments have relevance to novel energy saving, liquid crystal devices [28] which rely on defect motion and pinning to create bistable director configurations.

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