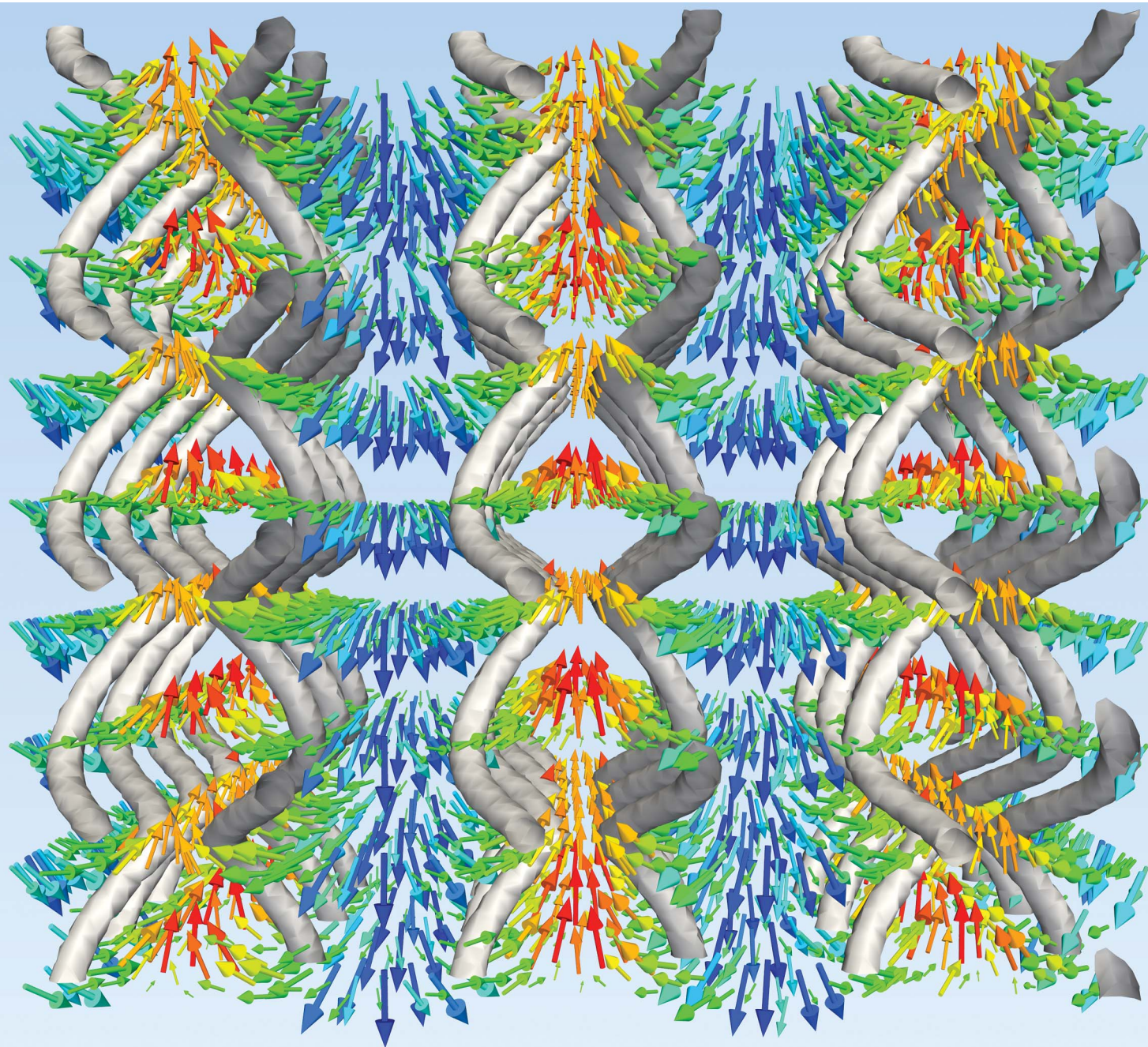


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Rheology of cubic blue phases

Cite this: *Soft Matter*, 2013, **9**, 10243Oliver Henrich,^{*ab} Kevin Stratford,^a Peter V. Coveney,^b Michael E. Cates^c and Davide Marenduzzo^c

We study the behaviour of cubic blue phases under shear flow via lattice Boltzmann simulations. We focus on the two experimentally observed phases, Blue Phase I (BPI) and Blue Phase II (BPII). The disclination network of Blue Phase II continuously breaks and reforms under steady shear, leading to an oscillatory stress response in time. At larger shear rates, the structure breaks up into the Grandjean texture with a cholesteric helix lying along the flow gradient direction. Blue Phase I leads to a very different response. Here, oscillations are only possible for intermediate shear rates; very slow flow causes a transition of the initially ordered structure into an amorphous network with an apparent yield stress. Larger shear rates lead to another amorphous state with a different structure of the defect network. At even larger flow rates the same break-up into the Grandjean texture as for Blue Phase II is observed. At the highest imposed flow rates both cubic blue phases adopt a flow-aligned nematic state. Our results provide the first theoretical investigation of sheared blue phases in large systems, and are relevant for the understanding of the bulk rheology of these materials.

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1 Introduction

Cholesterics are liquid crystals in which the local nematic director field shows a spontaneous twist in thermodynamic equilibrium.¹ The simplest manifestation is the standard cholesteric phase where the director precesses around a single helical axis of fixed orientation. For highly chiral systems, however, the preferred configuration close to the isotropic boundary features a twist around two perpendicular axes, as opposed to just one axis in the regular cholesteric state, and the corresponding deformation is referred to as “double-twist cylinder”. As it is topologically impossible to cover continuous 3D space with double-twist cylinders, defects arise. The resulting disclination lines (at which the nematic director is undefined) organise into a variety of regular periodic lattices, giving rise to the so-called cubic blue phases (BPs).^{2,3} There are two experimentally observed cubic blue phases, BPI and BPII (a third, BPIII, is thought to be amorphous⁴).

BPs were long considered as purely of academic interest due to their very narrow range of stability. This view has changed since the creation of polymer-stabilised and other thermally stabilised BPs,^{5,6} which has opened up the possibility of novel applications. During the last few years considerable progress has been achieved regarding the behaviour of BPs in confined geometries,^{7–9} under external fields,^{10–14} and in the presence of

colloidal particles.¹⁵ The kinetics of BP domain growth have been recently addressed.¹⁶ However, our understanding of their dynamical behaviour under flow remains very limited. The aim of this work is to address this issue by studying, for the first time, the response of large BP samples to a shear flow.

The flow response in cholesterics is both strongly non-Newtonian and highly anisotropic. For example, if a standard cholesteric phase is subjected to a Poiseuille flow along its helical axis, small pressure differences drive the flow mainly through “permeation”, as first investigated by Helfrich.¹⁷ In the permeation mode the liquid crystal flows while leaving the director field virtually unchanged, which leads to high dissipation and large viscosities. Early experiments with cholesteric liquid crystals showed that a flow can also give rise to conformational transitions.¹⁸ Marenduzzo *et al.*^{19,20} simulated shear and Poiseuille flows in cholesteric liquid crystals in the permeation mode, and showed the importance of the boundary conditions in determining the apparent viscosity of the fluid. They also found that a strong secondary flow appears. Rey^{21,22} theoretically studied the shear in cholesterics oriented with the helix along the vorticity axis and found that, at low Ericksen numbers, travelling twist waves appear which lead to the rotation of the cholesteric helix. Under higher forcing, the helix uncoils, creating a flow-induced nematic phase. However, this result was derived under the assumption that the molecules rotate only in the flow-gradient plane whilst the orientation of the cholesteric helix remained unchanged. Rey also studied cholesterics subjected to both steady flow and low frequency small amplitude oscillatory shear for different helix orientations.^{23,24} He found that splay/bend/twist deformations were excited when the helix was aligned along the flow direction;

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splay/bend deformation occurred when the helix was aligned along the velocity gradient, but only twist deformations appeared when the helix was aligned along the vorticity axis.

Dupuis *et al.*²⁵ performed the first numerical investigation of BP rheology in a Poiseuille flow, starting from equilibrium structures of BPI and BPII and a periodic array of doubly twisted cylinders. Under small forcing, the network opposed the flow, giving rise to a significant increase in apparent viscosity. Upon increasing the forcing they found clear evidence of shear thinning. In the crossover region they predicted a novel oscillatory regime where the network continuously breaks and reforms as portions of the disclinations in the centre of the channel move to neighbouring cells and relink with the parts of the network left behind by the flow. The viscosity still decreases with forcing (the system shear thins) but much less than for cholesterics in the permeation mode, which is in agreement with experiments.^{26,27}

Our work differs from these earlier studies as it addresses homogeneous shear flows, and focuses on the flow-induced reconstruction and nonequilibrium transition between different blue phase networks, which appear at intermediate or high shear. Our simulations employ Lees-Edwards boundary conditions, which are naturally suited to address these regimes, and bulk as opposed to the boundary-dominated flow. Our simulations are conducted on a large scale and are parallel, so that we can study significantly larger systems than previously possible, and our results can in principle be compared with bulk rheology experiments.

Our paper is organised as follows. In Section II, we describe the method we use and review the hydrodynamic equations of motion which we aim to solve. In Section III, we report our numerical results, separating them into subsections referring to Blue Phase I and Blue Phase II, and corresponding to low, intermediate, and high shear. Finally, we draw conclusions in Section IV.

2 Model and methods

Our approach is based on the well-established Beris-Edwards model for studying hydrodynamics of cholesteric liquid crystals,²⁸ which describes the ordered state in terms of a traceless, symmetric tensor order parameter $\mathbf{Q}(\mathbf{r})$. In the uniaxial approximation, the order parameter is given by $Q_{\alpha\beta} = q_s \left(\hat{n}_\alpha \hat{n}_\beta - \frac{1}{3} \delta_{\alpha\beta} \right)$ with \hat{n} being the director field and q_s being the amplitude of nematic order. More generally, the largest eigenvalue of \mathbf{Q} , $0 \leq q_s \leq \frac{2}{3}$, characterises the local degree of orientational order. The thermodynamic properties of the liquid crystal are determined by a free energy \mathcal{F} , the density f which consists of a bulk contribution part f_b and a gradient part f_g , as follows,

$$\begin{aligned} f_b &= \frac{A_0}{2} \left(1 - \frac{\gamma}{3} \right) Q_{\alpha\beta}^2 - \frac{A_0 \gamma}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{A_0 \gamma}{4} (Q_{\alpha\beta}^2)^2, \\ f_g &= \frac{K}{2} (\varepsilon_{\alpha\gamma\delta} \partial_\gamma Q_{\delta\beta} + 2q_0 Q_{\alpha\beta})^2 + \frac{K}{2} (\partial_\beta Q_{\alpha\beta})^2. \end{aligned} \quad (1)$$

The first term contains a bulk-free energy constant A_0 and the temperature-related parameter γ which controls the magnitude of order. The second part quantifies the cost of elastic distortions, which is proportional to the elastic constant K ; for simplicity we work on the one-elastic constant approximation.¹ The wavevector q_0 is equal to $2\pi/p_0$, where p_0 is the cholesteric pitch. The actual periodicity of the BP structure, p , does not need to be equal to p_0 . Indeed, the “redshift” $r = p/p_0$ is adjusted during the equilibration phase of the simulation to optimise the free energy density before shearing begins, this is done by following the procedure previously described in ref. 29.

A thermodynamic state is specified by two dimensionless quantities: the reduced temperature

$$\tau = \frac{27(1 - \gamma/3)}{\gamma}, \quad (2)$$

which vanishes at the spinodal point of a nematic state ($q_0 = 0$), and the reduced chirality

$$\kappa = \sqrt{\frac{108Kq_0^2}{A_0\gamma}}, \quad (3)$$

which measures the ratio of gradient to bulk free energy.

The dynamical evolution of the order parameter is given by the equation

$$(\partial_t + v_\alpha \partial_\alpha) \mathbf{Q} - \mathbf{S}(\mathbf{W}, \mathbf{Q}) = \Gamma \mathbf{H}. \quad (4)$$

The first term on the left hand side of eqn (4) is a material derivative, which describes the rate of change of a quantity advected by the flow. The second term accounts for the rate of change due to local velocity gradients $W_{\alpha\beta} = \partial_\beta v_\alpha$, and is explicitly given by²⁸

$$\begin{aligned} \mathbf{S}(\mathbf{W}, \mathbf{Q}) &= (\xi \mathbf{A} + \mathcal{Q}) \left(\mathbf{Q} + \frac{\mathbf{I}}{3} \right) + \left(\mathbf{Q} + \frac{\mathbf{I}}{3} \right) (\xi \mathbf{A} - \mathcal{Q}) \\ &\quad - 2\xi \left(\mathbf{Q} + \frac{\mathbf{I}}{3} \right) \text{Tr}(\mathbf{Q}\mathbf{W}), \end{aligned} \quad (5)$$

where Tr denotes the tensorial trace, while $\mathbf{A} = (\mathbf{W} + \mathbf{W}^T)/2$ and $\mathcal{Q} = (\mathbf{W} - \mathbf{W}^T)/2$ are the symmetric and antisymmetric parts of the velocity gradient, respectively. ξ is a constant depending on the molecular details of the liquid crystal. Flow alignment occurs if $\xi \cos 2\theta = (3q_s)/(2 + q_s)$ has a real solution for θ , the so-called Leslie angle; we select this case by setting $\xi = 0.7$ in our simulations. \mathbf{H} is the molecular field, which is a functional derivative of \mathcal{F} that preserves the tracelessness of \mathbf{Q} :

$$\mathbf{H} = -\frac{\delta \mathcal{F}}{\delta \mathbf{Q}} + \frac{\mathbf{I}}{3} \text{Tr} \left(\frac{\delta \mathcal{F}}{\delta \mathbf{Q}} \right). \quad (6)$$

The rotational diffusion constant Γ in eqn (4) is proportional to the inverse of the rotational viscosity $\gamma_1 = 2q_s^2/\Gamma$.¹

The time evolution of the fluid density and velocity are respectively governed by the continuity equation $\partial_t \rho = -\partial_\alpha (\rho v_\alpha)$, and the following Navier-Stokes equation:

$$\partial_t v_\alpha + \rho v_\beta \partial_\beta v_\alpha = \partial_\beta \Pi_{\alpha\beta} + \eta \partial_\beta [\partial_\alpha v_\beta + \partial_\beta v_\alpha]. \quad (7)$$

This emerges from the Chapman–Enskog expansion of the lattice Boltzmann (LB) equations that we solve numerically. A further term $\eta \left(1 + 3 \frac{\partial P_0}{\partial \rho}\right) \partial_\mu v_\mu \delta_{\alpha\beta}$ that formally appears in this expansion is negligible under the slow flows considered here for which the fluid motion is almost incompressible.³⁰ η is an isotropic background viscosity which is set to $\eta = 0.6666$ in LB units (these are discussed below, see ref. 4 and 16). The thermodynamic stress tensor reads explicitly

$$\begin{aligned} \Pi_{\alpha\beta} = & P_0 \delta_{\alpha\beta} - \xi H_{\alpha\gamma} \left(Q_{\gamma\beta} + \frac{1}{3} \delta_{\gamma\beta} \right) \\ & - \xi \left(Q_{\alpha\gamma} + \frac{1}{3} \delta_{\alpha\gamma} \right) H_{\gamma\beta} + Q_{\alpha\gamma} H_{\gamma\beta} - H_{\alpha\gamma} Q_{\gamma\beta} \\ & + 2\xi \left(Q_{\alpha\beta} + \frac{1}{3} \delta_{\alpha\beta} \right) Q_{\gamma\nu} H_{\gamma\nu} - \partial_\alpha Q_{\gamma\nu} \frac{\delta F}{\delta \partial_\beta Q_{\gamma\nu}} \end{aligned} \quad (8)$$

and is responsible for strong non-Newtonian flow effects. In the isotropic state $\mathbf{Q} \equiv 0$ and eqn (8) reduces to the scalar pressure as would appear in eqn (7) for a Newtonian fluid.

We next define a dimensionless number that describes the deformation of the director field under flow. This so-called Ericksen number is given by

$$Er = \frac{\eta v l}{K} \quad (9)$$

with η and K being defined previously, and v and l being a typical velocity and length scale. In the present work $l = p_0/2 = \pi/q_0$ was used as this is the approximate size of the BP unit cell. Likewise, v was taken to be the velocity difference across one unit cell, *i.e.* $v = \dot{\gamma}l$. The elastic constants were $K = 0.02$ (BPII) and $K = 0.04$ (BPI), respectively.

The system of coupled partial differential eqn (4) and (7) is solved by means of a hybrid method³¹ which uses a combination of lattice Boltzmann and finite difference schemes. (This is in contrast with some earlier methods using solely LB.^{30,32}) The Navier–Stokes equation is solved *via* the lattice Boltzmann approach, using a standard three-dimensional model with 19 discrete velocities (D3Q19). A regular lattice with spacing $\Delta x = \Delta y = \Delta z = 1$ is used and the time step is $\Delta t = 1$ in lattice units. Coupling to the thermodynamic sector is *via* a local body force computed as the divergence of the thermodynamic stress eqn (8); the resulting velocity field is used in the computation of the time evolution of \mathbf{Q} *via* a standard finite difference method using the same grid and the same time step as for the LB. The system is periodic in all three coordinate directions. Sliding boundary conditions, or Lees–Edwards planes,³³ are explicitly implemented in both hydrodynamic and thermodynamic sectors to impose shear on the system. The same method with Lees–Edwards planes has been used successfully to study binary mixtures, particle suspensions,^{34,35} emulsions³⁶ and smectic liquid crystals.³⁷ A more detailed discussion of our use of Lees–Edwards boundary conditions can be found in the Appendix.

In the following we report results of simulations of the bulk flow behaviour of the cubic Blue Phases BPI and BPII. Typical runtimes for the system size $L_x \times L_y \times L_z = 128^3$ on 512 processes were in the range of 18 to 24 hours. The timestep and

lattice spacing in lattice Boltzmann units (LBU) can be mapped approximately to ~ 1 ns and ~ 10 nm in SI units, respectively. The LB unit of stress is equal to about 10^8 Pa. Further details about the conversion from LBU to SI units can be found elsewhere.^{4,16} In what follows, x , y and z denote respectively the velocity, velocity gradient and vorticity direction; Π_{xy} is therefore the shear stress.

3 Results and discussion

For typical simulations reported in this work, we chose as initial conditions thermodynamic states that are well inside the equilibrium region of the individual blue phase, and far away from the cholesteric–isotropic transition. Thus, the temperature and chirality were $\tau = -0.5$, and $\kappa = 1.0$ in the case of BPI and $\tau = -0.5$, and $\kappa = 2.0$ for BPII, respectively. For these parameters the total free energy density f remained always negative at all flow rates simulated. Since by eqn (1) $f = 0$ for an isotropic phase with $\mathbf{Q} \equiv 0$, this means that our system, which is never far from equilibrium locally even under flow, always remains in a liquid crystalline state. We also performed selected simulations on metastable states at higher and lower temperatures, and at different chiralities, but did not find any significant differences in the general flow behaviour from that described below. The only quantitative difference we found was that for thermodynamic states that are closer to the phase boundary than the one we focused on (and describe below), the critical shear rate at which the disclination network broke up into chiral nematic states was lower. This is expected as these states have on average higher free energy densities and smaller order parameters than those we focus on in what follows, and cannot therefore withstand the same external forces before breaking down.

As usual in BP simulation studies,^{4,16} we initialised our runs with analytical solutions that minimise the free energy functional eqn (1) in the high-chirality limit and equilibrated these configuration for 5000 LB timesteps before we started the shear flow. During the equilibration sequence the optimal redshift r was calculated and applied at every timestep. After equilibration the redshift was kept constant throughout the rest of the simulation with shear flow (as it is no longer justified to optimise the free energy in a nonequilibrium scenario). We chose a pitch length of 32 LBU for BPII and 64 LBU in the case of BPI, and we considered in both cases 4 unit cells along each coordinate direction, for a total of 64 unit cells in our simulation box. Runs with higher resolution confirmed that this choice was adequate to track all kinematic details of the blue phase networks in shear flow. This includes reconstruction of the unit cell not accessible in simulation with only few cells.²⁵

A simple shear flow was imposed by means of the Lees–Edwards boundary conditions with the top (bottom) part of the system flowing in the positive (negative) x -direction and the velocity gradient along the y -direction. The shear rates were varied over more than three orders of magnitude from about $\dot{\gamma} = 2.44 \times 10^{-6}$ to 3.75×10^{-3} LBU. For clarity we classify various flow regimes, namely three in the case of Blue Phase II and five in the case of Blue Phase I. These regimes comprise

those with periodically recurring conformations and oscillatory stress response (PRC), amorphous networks (AN), as well as those featuring the Grandjean texture (GJ) which may be partly frustrated (FGJ) and a flow-aligned nematic state (FN). GJ and FN occur in both blue phases as steady states regardless of the initial state.

These regimes are characterised by the following approximate flow rates:

Name	$\dot{\gamma}$	Er
BPI-1 (AN)	$\leq 1.95 \times 10^{-5}$	≤ 0.17
BPI-2 (PRC)	3.91×10^{-5} to 2.34×10^{-4}	0.33–2
BPI-3 (AN)	3.13×10^{-4} to 4.69×10^{-4}	2.67...4
BPI-4 (GJ, FGJ)	5.47×10^{-4} to 1.88×10^{-3}	4.67–16
BPI-5 (FN)	$\geq 2.5 \times 10^{-3}$	≥ 21.33
BPII-1 (PRC)	$\leq 3.91 \times 10^{-4}$	≤ 3.33
BPII-2 (GJ)	4.69 to 1.25×10^{-3}	4–10.67
BPII-3 (FN)	$\geq 1.88 \times 10^{-3}$	≥ 16

As is standard^{16,38} disclination lines are represented by plotting an isosurface of the scalar order parameter q_s . Typical choices are $q_s = 0.17$ for BPI and $q_s = 0.15$ for BPII. (Note that q_s is small but non-zero at the disclination core. The director is undefined there because the largest and second largest eigenvalues of \mathbf{Q} coincide.)

3.1 Blue Phase II

We start our discussion with BPII as its flow behaviour is somewhat simpler than that of BPI. BPII has simple cubic symmetry and the disclination lines intersect and form a characteristic network of nodes. Ahead of the more detailed discussion we provide first a general overview of the flow behaviour at all applied shear rates.

Fig. 1 shows a flow curve, defined as time averages of the shear stress $\bar{\Pi}_{xy}$ as a function of shear rate $\dot{\gamma}$. Time averages

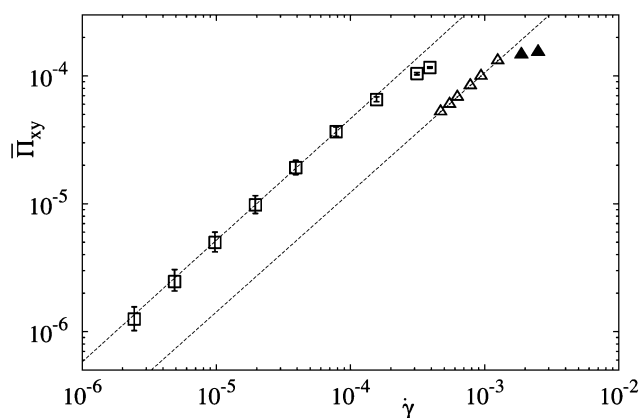


Fig. 1 Flowcurve $\bar{\Pi}_{xy}(\dot{\gamma})$ of BPII. The open squares show the average shear stress in the regime with periodically recurring conformations, whereas the error bars indicate the maximum and minimum stresses that occur during one cycle. Above a critical flow rate the network breaks up into the Grandjean texture (open triangles) or a flow-aligned nematic state at even higher flow rates (solid triangles). The two dashed lines represent fits to the data with $\bar{\Pi}_{xy}(\dot{\gamma}) \propto \dot{\gamma}^{0.95}$ (left) and $\bar{\Pi}_{xy}(\dot{\gamma}) \propto \dot{\gamma}^{0.94}$ (right), respectively.

were taken as an average over one stress cycle in the steady state. Where no oscillations occurred we used the final value at the end of the run. For the lowest up to intermediate shear rates, the regime we refer to as BPII-1, a power law fit $\bar{\Pi}_{xy} = a\dot{\gamma}^b$ with $a = 0.30$, and $b = 0.95$ describes the data to a very good approximation. This holds true even in the regime BPII-2, where the network breaks up and the liquid crystal adopts a Grandjean structure with the helical axis oriented along the flow gradient direction (y). Here, the coefficients of the power law fit are $a = 0.68$ and $b = 0.94$. Hence, for the range of shear rates which we have explored here, the degree of shear-thinning is remarkably small in BPII.

Fig. 2 shows the ratio between the apparent viscosity, defined as $\eta_{app} = \langle \Pi_{xy} \rangle / \dot{\gamma} + \eta$, and the background viscosity η over the total strain. A numerical value of $\eta_{app}/\eta = 1$ corresponds to a fully Newtonian flow, without any additional stress contribution from the liquid crystal. The top picture shows data for the regime BPII-1, where the periodic break-up and reconnecting of the network in shear flow causes sinusoidal oscillations in η_{app} . As noted in the Appendix, the absence of a permeation mode at very low shear rates may be due to our choice of boundary

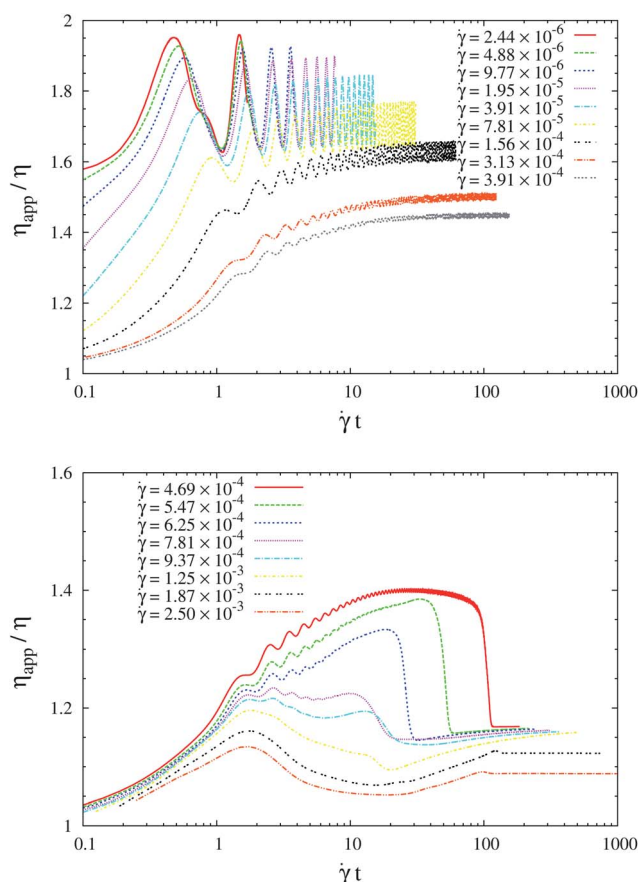


Fig. 2 Apparent viscosity $\eta_{app} = \Pi_{xy}/\dot{\gamma} + \eta$ of BPII versus strain $\gamma = \dot{\gamma}t$ normalised to the background viscosity η . The pictures show the regimes BPII-1 (periodically recurring conformations, top), BPII-2 (Grandjean texture, bottom) and BPII-3 (flow-aligned nematic, bottom). The value $\eta_{app}/\eta = 1$ corresponds to the Newtonian flow without any additional contribution from the liquid crystal, i.e. totally shear-thinned state.

conditions. We refer the reader to the Appendix for a detailed discussion.

We observe another configuration, lying between those with periodically recurring conformations and the flow-aligned nematic state at shear rates $4.67 \times 10^{-4} \lesssim \dot{\gamma} \lesssim 1.25 \times 10^{-3}$ ($4 \lesssim Er \lesssim 10.67$). In this interval the network breaks up completely into a simple cholesteric liquid crystal, and oscillations in the stress signal are absent. The helical axis lies along the flow gradient direction (the so-called Grandjean texture¹) and the liquid crystal is flowing in “nematic planes” with the director predominantly oriented in the flow-vorticity plane and having only a small angle with the flow direction. The picture at the bottom of Fig. 2 shows data for this regime, which we refer to as BPII-2. The curves for the two largest flow rates are for BPII-3, the flow-aligned nematic state. We will address these regimes in Section 3.3, as they are common to both cubic blue phases BPI and BPII.

The travelling helical wave which was identified in ref. 21 and 22 when shearing a cholesteric helix along the vorticity axis turns out to be in a metastable flow state as it features larger free energies, higher stresses and dissipation due to the tumbling motion of the director field, which are completely absent in the Grandjean texture. For even higher shear rates the system undergoes a transition to a flow-aligned nematic state.

In the next sections we investigate the BPII-1 flow regime in more detail by looking at the kinetics of the disclination network.

3.1.1 Regime BPII-1: low and intermediate shear rates.

Fig. 3 shows the disclination network in a shear flow as it undergoes homogeneous shearing in the BPII-1 flow regime. The disclination lines break up and reconnect further downstream, forming a periodically recurring pattern. The period needed for a pattern to break up and reform along the flow direction is $\tau_F = 1/\dot{\gamma}$.

The general appearance of the flowing network is, apart from the homogeneous distortion, very close to that of the quiescent blue phase at equilibrium. This holds for all shear rates in the BPII-1 regime.

Interestingly, while being displaced with the flow the entire network moves along the vorticity direction (z) as well. A similar behaviour has been recently observed for blue phases in shear flow in confined geometries.³⁸ In contrast to the stick-slip motion that has been reported there, in this case the movement is steady. The vorticity motion occurs in such a way that the positions of breakup and reconnection point in the network, visible in Fig. 3, are slightly offset and allow the network to travel along the z -direction. The periodicity of the motion along the vorticity direction is $\tau_V = 6\tau_F$, *i.e.* it takes a displacement of six unit cells along x (the flow direction) for the network to move one unit cell along z (the vorticity direction).

Fig. 4 shows the disclination network in the middle of a breakup-reconnection cycle, with superimposed velocity vectors. The plot shows the secondary velocity components, obtained by projecting the velocity onto a plane perpendicular to the flow direction. This gets rid of the dominating velocity component along the flow, v_x , and allows visualisation of the patterns in the two much smaller components v_y and v_z . The

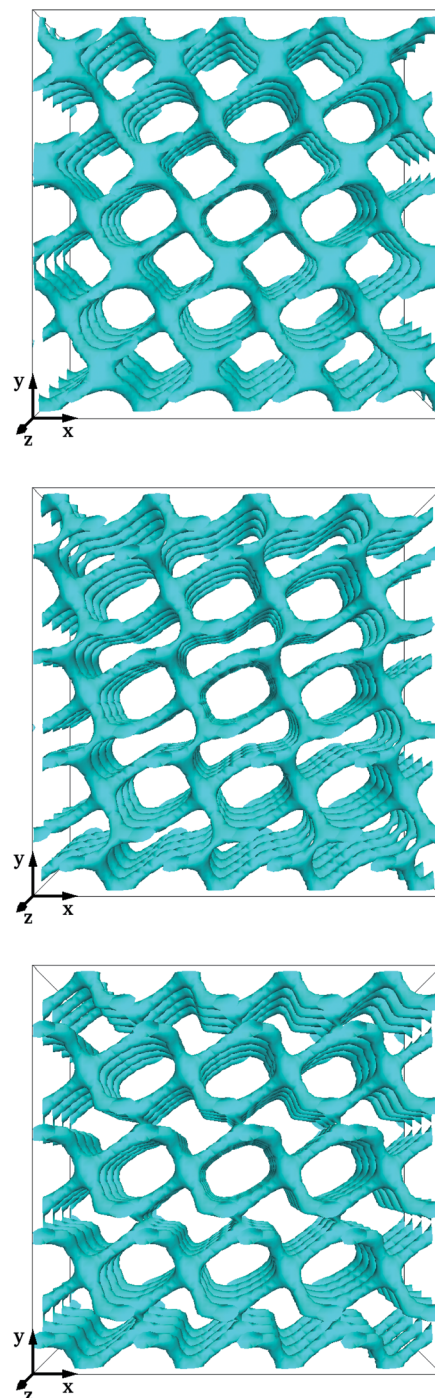


Fig. 3 Disclination network of BPII in shear flow: The pictures show a typical sequence of snapshots in the steady state at $\dot{\gamma} = 1.56 \times 10^{-4}$ and time steps $t = 1.60, 1.64$, and 1.65×10^5 . The velocity gradient is oriented along the vertical direction (y), whereas the horizontal direction (x) is the flow direction. Lees–Edwards boundary conditions have been imposed in such a way that the network moves to the right in the upper half and to the left in the lower half of the picture.

magnitude of the secondary components is typically in the range of a few percent of the primary flow component for the shear rates and system sizes simulated here.

Characteristic bands are visible in Fig. 4, which are oriented along the vorticity direction. The direction of the

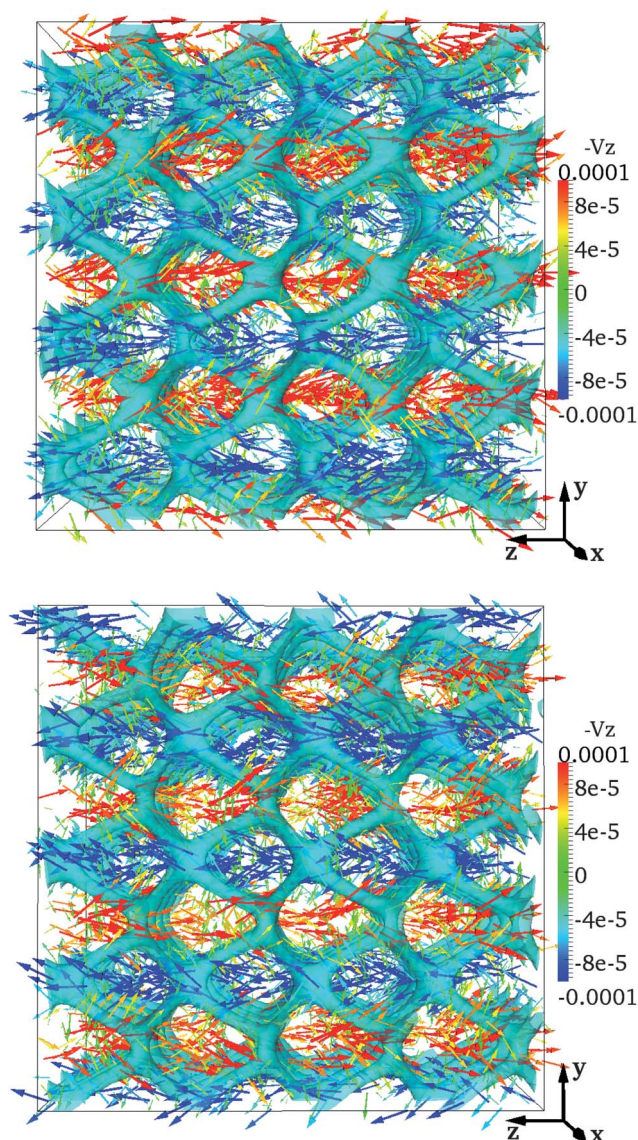


Fig. 4 Velocity patterns and disclination network in BPII for positive (left) and negative (right) helicity of the underlying cholesteric helix: The pictures show velocity vectors ($0, v_y, v_z$). The view is along the x -direction. This means the velocity \mathbf{v} has been projected onto a plane perpendicular to the flow direction. The vertical and horizontal directions are the gradient and vorticity direction, respectively. The colour code gives the magnitude and sign of the component in the vorticity direction. The snapshot shows a typical frame during a periodically recurring sequence. The network on the left with right-handed helicity ($q_0 > 0$ in eqn (1)) travels rightwards, whereas the one on the right, with reversed helicity, moves leftward. The periodicity of the motion along the vorticity direction is six times longer than the time it takes for the network to reconnect along the flow direction.

flow in each of the bands depends on the helicity of the underlying cholesteric liquid crystal (*i.e.* on the sign of q_0 in eqn (1)), and the velocity patterns for left-handed and right-handed BPs are the mirror images of one another. Further quantitative evidence for a direct link between the sense of motion and the helicity can be gained by time-averaging over individual cycles.

Table 1 in the Appendix gives minima, maxima, averages and standard deviations of the velocity components. All

values for the two runs with inverted helicity are identical apart from a change of sign of the z -components. There is only a slight imbalance in the magnitude between the maximum and the minimum velocities along the z -direction. Therefore the averaged flow along the vorticity direction is very small, and much smaller than the local flow velocity. This suggests that the flow of the network along the vorticity direction is permeative. This claim is further supported by the characteristic velocity bands in the secondary flow, as shown in Fig. 4. The secondary flow in the vorticity direction clearly takes place in positive and negative z -directions, whereas the movement of the network as a whole is only in one direction.

3.2 Blue Phase I

BPI has body-centred cubic symmetry and, unlike BPII, the disclination lines characterising its equilibrium structure are well separated and do not intersect. (The quiescent state resembles the first frame in Fig. 9 below.) We believe that this topological difference is responsible for most of the differences between BPI and BPII regarding their rheological response. We present again key aspects in an overview before we address specific features in more detail.

Fig. 5 shows the flow curve of BPI for the same range of shear rates as in Fig. 1 and Fig. 6 depicts the apparent viscosity ratio η_{app}/η as a function of the total strain.

For intermediate (but not too low) shear rates ($3.91 \times 10^{-5} \leq \dot{\gamma} \leq 2.34 \times 10^{-4}$; $0.33 \leq Er \leq 2$), we once more find regular oscillations in the network morphology and in the stress response *versus* time. We label this regime BPI-2. The centre picture of Fig. 6 shows the corresponding data for the apparent viscosity ratio *versus* strain.

The BPI-2 regime now does not persist to arbitrarily low shear, there the oscillations become irregular and seemingly chaotic, and after a few cycles the disclination pattern becomes amorphous. For these low shear rates ($2.4 \times 10^{-6} \leq \dot{\gamma} \leq 1.95 \times 10^{-4}$; $0.02 \leq Er \leq 0.17$) the flow curve in Fig. 5 develops a horizontal yield stress branch. We refer to this flow regime as BPI-1.

The BPI-2 regime is also unstable if the shear is increased *above* a critical value, which is in the range of Ericksen numbers $Er \approx O(1)$. We labeled this regime ($3.13 \times 10^{-4} \leq \dot{\gamma} \leq 4.69 \times 10^{-4}$; $2.67 \leq Er \leq 4$) as BPI-3. It is characterised by the balance between viscous and elastic forces. This has an influence on the stability of the disclination network as it seems to become increasingly sensitive to small perturbations in the flow field which couple back to the order parameter dynamics and *vice versa*. This phenomenon forms a possible route towards an instance of “rheochaos”.^{39,40}

Finally, for shear rates such that $5.47 \times 10^{-4} \leq \dot{\gamma} \leq 1.88 \times 10^{-3}$ ($4.67 \leq Er \leq 16$) and before the break-up into a flow-aligned nematic occurs (BPI-5, $2.5 \times 10^{-3} \leq \dot{\gamma}$; $21.33 \leq Er$) we observe the same cholesteric Grandjean configuration with the helical axis along the gradient direction as for BPII-2. For clarity we refer to this regime as BPI-4. It will be discussed in Section 3.3.

Table 1 Minima, maxima and standard deviation of time-averaged velocity components for BPI ($\tau = -0.5$, $\kappa = 1.0$) and BPII ($\tau = -0.5$, $\kappa = 2.0$) in a steady shear flow. All velocity values are given in 10^{-5} lattice units. The last six columns refer to the secondary flow. The transient dynamics prior to regular oscillations or network break-up have not been included into the averages. The regimes comprise the formation of an amorphous network (AN, BPI-1), periodically recurring conformations with the oscillatory stress response (PRC, BPI-2 and BPII-1), amorphous networks at Ericksen numbers $Er \approx O(1)$ (AN, BPI-3), the Grandjean texture that may be frustrated (GJ and FGJ, BPII-2 and BPI-4), and a flow-aligned nematic state (FN, BPI-5 and BPII-3). Bold figures indicate the mean minima and maxima in v_z and the standard deviation of the runs with inverted helicity

	$\dot{\gamma}$	Er	q_0	$\bar{v}_{x,\min} \times 10^5$	$\bar{v}_{x,\max}$	$\bar{v}_{x,\text{std}}$	$\bar{v}_{y,\min}$	$\bar{v}_{y,\max}$	$\bar{v}_{y,\text{std}}$	$\bar{v}_{z,\min}$	$\bar{v}_{z,\max}$	$\bar{v}_{z,\text{std}}$
BPI												
BPI-1 (AN)	0.24	0.02	0.1388	-17.7	16.7	3.7	-3.6	3.6	3.5	-3.9	3.1	2.8
BPI-1 (AN)	0.49	0.04	0.1388	-33.4	32.0	4.3	-3.0	3.1	3.2	-3.7	2.5	3.1
BPI-1 (AN)	0.98	0.08	0.1388	-64.4	63.6	4.7	-3.6	3.4	4.8	-5.3	-4.2	4.4
BPI-1 (AN)	1.95	0.17	0.1388	-126.2	127.0	6.8	-3.8	4.8	6.7	-5.2	5.1	6.2
BPI-2 (PRC)	3.91	0.33	0.1388	-248.6	248.3	2.8	-5.4	5.6	5.1	-3.8	4.6	3.9
BPI-2 (PRC)	7.81	0.67	0.1388	-497.5	496.4	5.2	-8.5	8.0	8.4	-5.9	7.8	6.8
BPI-2 (PRC)	15.63	1.33	0.1388	-995.0	993.0	8.7	-13.1	13.8	13.2	-13.0	15.6	11.2
BPI-2 (PRC)	15.63	1.33	-0.1388	-995.0	993.0	8.7	-13.1	13.8	13.2	-15.6	13.0	11.2
BPI-2 (PRC)	23.44	2.00	0.1388	-1492.2	1485.5	9.6	-4.8	3.7	12.3	-5.7	4.6	14.8
BPI-3 (AN)	31.25	2.67	0.1388	-1990.6	1983.2	17.6	-4.5	6.3	13.3	-8.3	10.0	15.9
BPI-3 (AN)	46.87	4.00	0.1388	-2988.2	2985.5	42.4	-10.5	12.3	28.4	-15.5	15.2	26.8
BPI-4 (GJ)	54.69	4.67	0.1388	-3475.1	3473.4	—	—	—	—	-8.9	8.8	—
BPI-4 (FGJ)	62.50	5.33	0.1388	-4101.7	4122.7	—	—	—	—	-29.6	20.0	—
BPI-4 (FGJ)	78.13	6.01	0.1388	-5140.0	5092.3	—	—	—	—	-35.8	24.6	—
BPI-4 (GJ)	93.75	8.00	0.1388	-5955.4	5946.1	—	—	—	—	-15.5	15.1	—
BPI-4 (GJ)	125.0	10.67	0.1388	-7935.0	7933.7	—	—	—	—	-21.3	20.1	—
BPI-4 (GJ)	187.5	16.00	0.1388	-11901.7	11901.7	—	—	—	—	-32.8	29.1	—
BPI-5 (FN)	250.0	21.33	0.1388	-15875.0	15875.0	—	—	—	—	-0.2	-0.1	—
BPI-5 (FN)	375.0	32.00	0.1388	-23812.5	23812.5	—	—	—	—	-0.3	0.1	—
BPII												
BPII-1 (PRC)	0.24	0.02	0.1963	-7.8	7.7	0.1	-0.2	0.2	0.1	-0.3	0.3	0.2
BPII-1 (PRC)	0.49	0.04	0.1963	-15.5	15.4	0.2	-0.3	0.4	0.2	-0.5	0.4	0.2
BPII-1 (PRC)	0.98	0.08	0.1963	-31.0	30.8	0.3	-0.6	0.6	0.4	-0.9	0.8	0.4
BPII-1 (PRC)	1.95	0.17	0.1963	-62.0	61.6	0.6	-1.2	1.2	0.8	-1.8	1.6	0.8
BPII-1 (PRC)	3.91	0.33	0.1963	-123.9	123.3	1.2	-2.1	2.1	1.6	-3.4	3.0	1.5
BPII-1 (PRC)	7.81	0.67	0.1963	-247.5	246.8	2.0	-3.8	3.8	3.0	-6.5	5.5	2.6
BPII-1 (PRC)	15.63	1.33	0.1963	-494.3	493.7	2.5	-5.5	-5.5	4.0	-10.9	8.7	3.9
BPII-1 (PRC)	15.63	1.33	-0.1963	-494.3	493.7	2.5	-5.5	5.5	4.0	-8.7	10.9	3.9
BPII-1 (PRC)	31.25	2.67	0.1963	-987.5	987.1	3.5	-6.9	6.9	5.1	-17.7	13.1	5.0
BPII-1 (PRC)	39.06	3.33	0.1963	1233.9	1233.6	3.7	-6.9	6.9	5.1	-20.0	14.5	5.2
BPII-2 (GJ)	46.87	4.00	0.1963	-1479.8	1477.0	—	—	—	—	-10.0	9.6	—
BPII-2 (GJ)	54.69	4.67	0.1963	-1720.5	1720.8	—	—	—	—	-11.5	11.2	—
BPII-2 (GJ)	62.5	5.33	0.1963	-1966.7	1966.2	—	—	—	—	-13.3	12.7	—
BPII-2 (GJ)	78.13	6.01	0.1963	-2458.3	2457.8	—	—	—	—	-16.9	15.7	—
BPII-2 (GJ)	93.75	8.00	0.1963	-2949.7	2949.7	—	—	—	—	-20.3	18.4	—
BPII-2 (GJ)	125.0	10.67	0.1963	-3932.8	3932.8	—	—	—	—	-26.6	22.4	—
BPII-3 (FN)	187.5	16.00	0.1963	-5906.2	5906.2	—	—	—	—	-0.6	0.4	—
BPII-3 (FN)	250.0	21.33	0.1963	-7874.9	7874.9	—	—	—	—	-0.5	0.3	—

3.2.1 Regime BPI-1: low shear rates. The rheological response of BPI at low shear rates, $\dot{\gamma} \leq 1.95 \times 10^{-5}$ ($Er \leq 0.33$), is strikingly different from that of BPII and appears to show a yield stress. An explanation for this behaviour can be found by looking more closely at the average shear stress (where the background viscosity contribution has been subtracted) and free energy density as a function of time, as shown in Fig. 7. When the quiescent and equilibrated BPI network begins to flow the shear stress increases steeply and goes through a maximum. Shortly after it goes negative to become positive again later on, forming a complete cycle. The amplitude of the excursions in these stress oscillations and the presence of a part of the period where the thermodynamic contribution to the stress is negative suggest that the BPI network is subject to large

forces. Seemingly, these eventually cause the flow-induced collapse to an amorphous network state with an apparent yield stress. We should underscore that this low shear regime might depend on our choice of boundary conditions. In practice they are equivalent to having infinitely distant walls to which the network is anchored. See the Appendix for a full discussion of our boundary conditions.

To gain further insight into the flow-induced deformation, and eventual breakdown, of BPI, it is instructive to follow the dynamics of the network under a slow flow, this is depicted in Fig. 9. Three different stages can be distinguished. Just after the onset of the shear flow, the disclination lines in BPI get more and more squeezed together, and this is incompatible with the defect topology in this phase. Consequently, the network adopts

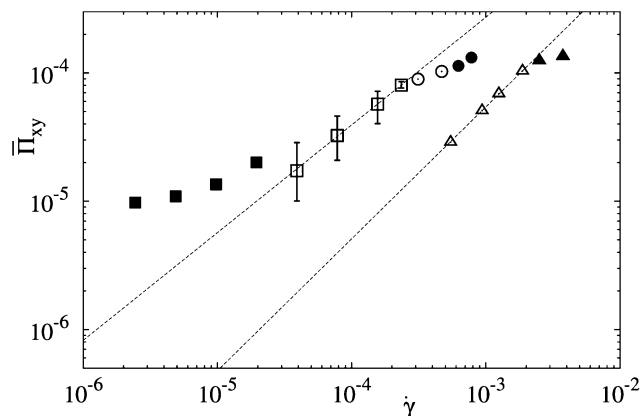


Fig. 5 Flow curve $\bar{\Pi}_{xy}(\dot{\gamma})$. Depending on the configuration in steady shear flow five different regimes can be distinguished: the amorphous BP network with apparent yield stress (BPI-1, solid squares), the steady flow with periodically recurring patterns (BPI-2, open squares), break-up of the disclination network into an amorphous state at $Er \approx O(1)$ (BPI-3, open circles), the cholesteric helix with the axis in the gradient direction, also referred to as Grandjean texture, as well as frustrated metastable Grandjean-like states that can transform into the regular Grandjean texture upon increasing the flow rate (BPI-4, open triangles and solid circles), and flow-aligned nematic state (BPI-5, solid triangles). The error bars represent the minimum and maximum shear stress during one cycle in the regime BPI-2. The two dashed lines show fits to the data in the regime BPI-2 with $\bar{\Pi}_{xy}(\dot{\gamma}) \propto \dot{\gamma}^{0.84}$ (left) and in the regime BPI-4 with $\bar{\Pi}_{xy}(\dot{\gamma}) \propto \dot{\gamma}^{1.02}$ (right), respectively.

a flow-induced conformation which consists of intertwined helices that stretch during the shear transformation. This helical conformation that emerges already at a strain $\gamma \approx 1$ is shown in Fig. 9 (top row). At this point the original BPI has already been significantly deformed. Shortly afterwards regular oscillations set up temporarily, where the disclinations form double helices which tilt and realign under the shear.

This mode of flow proves to be unstable, as after a few cycles distortions appear which lead to further destabilisation, presumably in view of the large stress fluctuations discussed above. Finally, the system loses order and transforms into an amorphous network state with almost constant stress in the range of $\Pi_{xy} \approx 1\text{--}2 \times 10^{-5}$ LBU. If the shear is stopped, this flow-induced amorphous state remains arrested and metastable, and cannot find its way back to the original BPI structure.

3.2.2 Regime BPI-2: intermediate shear rates. Adjacent to regime BPI-1 ($\dot{\gamma} \lesssim 1.95 \times 10^{-5}$; $Er \lesssim 0.33$) but at slightly larger shear rates ($3.91 \times 10^{-5} \lesssim \dot{\gamma} \lesssim 2.34 \times 10^{-4}$; $0.67 \lesssim Er \lesssim 2$) lies another region where the network flows with periodically recurring conformations (Fig. 10). We refer to this region as BPI-2. The transition between BPI-1 and BPI-2 is clear when looking at Fig. 8 which shows the shear stress *versus* the total strain. A qualitative difference between these two is the absence of the large stress fluctuations in BPI-2 that occur during the early cycles in regime BPI-1. (Recall that for even lower $\dot{\gamma}$ the thermodynamic shear stress becomes temporarily negative (Fig. 7), which caused destabilisation of the periodic network and led to the amorphous configuration in the steady state of BPI-1.) Hence, an explanation for the existence of the regular BPI-2 oscillations could be that compared to the large oscillations

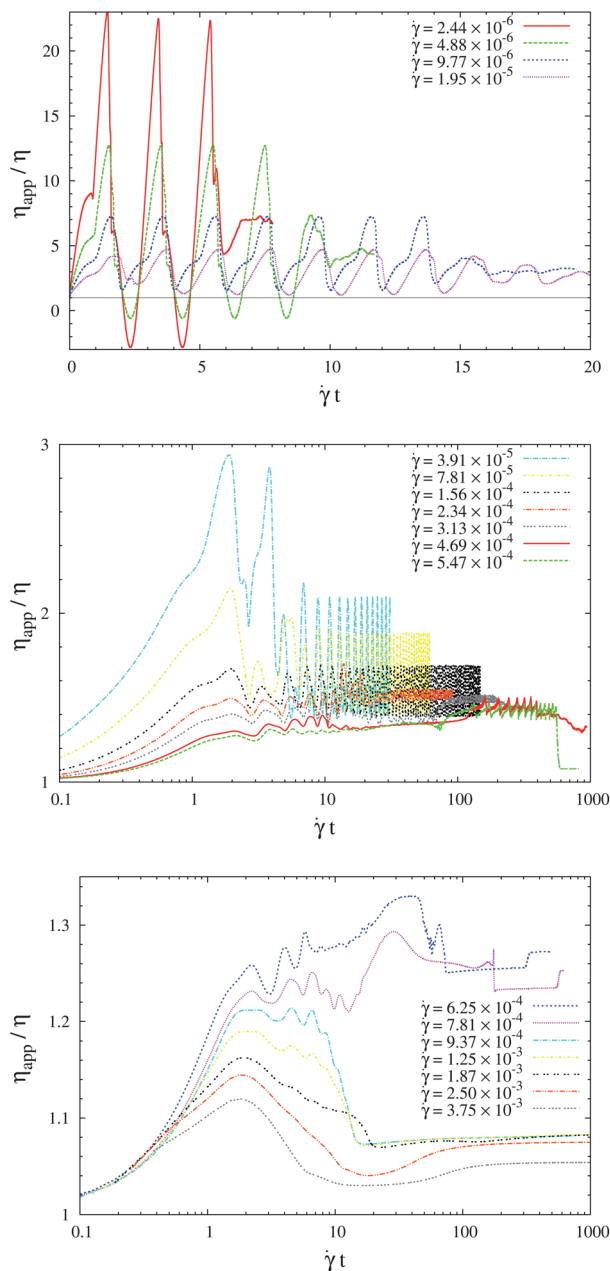


Fig. 6 Apparent viscosity $\eta_{app} = \langle \Pi_{xy} \rangle / \dot{\gamma} + \eta$ of BPI *versus* strain normalised to the background viscosity η : The top picture shows regime BPI-1 (amorphous network) where the BP network transforms into an amorphous network featuring a yield stress. The centre picture shows regimes BPI-2 (periodically recurring conformations) and BPI-3 (amorphous network), whereas the picture at the bottom depicts data of the (partly frustrated) Grandjean texture in regime BPI-4 and the flow-aligned nematic state, labelled BPI-5 in this context. Note that the η_{app}/η is sometimes negative for the lowest flow rates as the (negative) contribution of the elastic forces of the network dominates the total stress.

found transiently in the BPI-1 regime these oscillations are now fast enough to bypass or suppress large stress fluctuations, which leads to different topological reconnections and order structure and eventually to stabilisation of the flow.

Fig. 10 shows snapshots of the periodically recurring BPI in a steady shear flow. In contrast to BPI-1 at these shear rates, BPI-2 does not resemble so much the equilibrium configuration

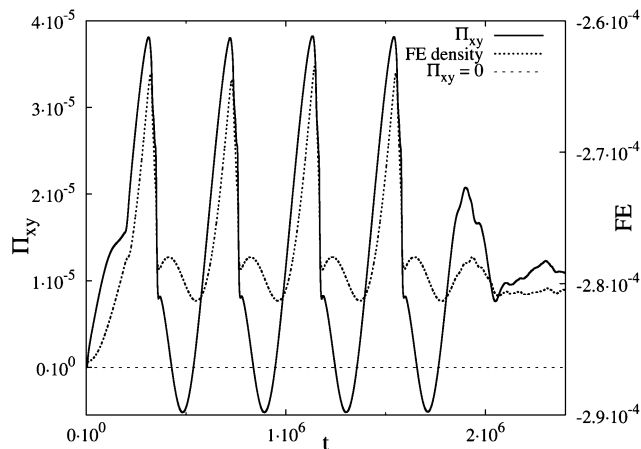


Fig. 7 Average thermodynamic shear stress and free energy density of BPI at a shear rate $\dot{\gamma} = 4.88 \times 10^{-5}$, $Er = 0.08$; the negative branch in the stress is related to a local maximum and a following local minimum in the average free energy density. This creates unstable conditions that lead to reconstruction of the defect lattice into an amorphous network state which seemingly features a yield stress.

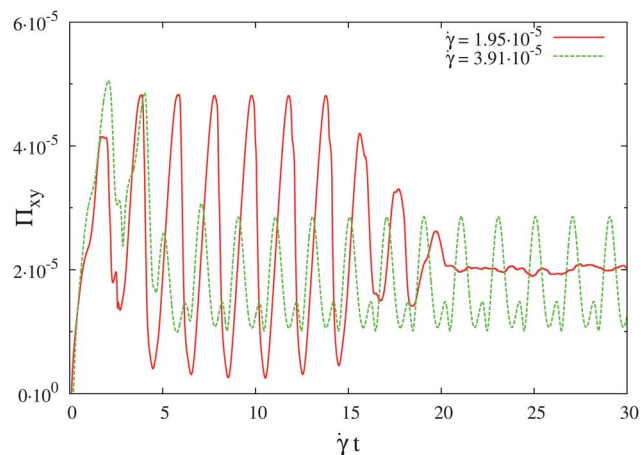


Fig. 8 Thermodynamic shear stress Π_{xy} versus strain near the transition between regimes BPI-1 and BPI-2. The shear rates are $\dot{\gamma} = 1.95 \times 10^{-5}$ (red solid) and $\dot{\gamma} = 3.91 \times 10^{-5}$ (green dashed). Compared to lower shear rates in BPI-1 where the stress goes negative (Fig. 7) the stress is positive throughout, but exhibits very large fluctuations during one cycle, which are absent in regime BPI-2 at higher shear rates than shown here.

undergoing a homogeneous topology-conserving transformation. It features intricate, flow-induced conformations consisting of well-separated undulating disclination lines similar to those intertwined helices in Fig. 9 at early times.

If the shearing is switched off in regime BPI-2 at some point during an oscillation, the flow-induced configuration cannot revert to a quiescent BPI. Instead the network is trapped in a metastable state with helicoidal intertwined disclinations similar to those in the bottom left picture of Fig. 9 or those in the top left picture of Fig. 12. However, the orientation of the helical axis is now always along the vorticity (z -) direction.

Fig. 11 depicts a snapshot of the secondary velocity components v_y and v_z of BPI at the same time steps as in Fig. 10. The emerging pattern is similar to that of BP11 shown in Fig. 4. There

is also separation into fluctuating bands which are oriented along the vorticity direction. The secondary velocity component v_z changes sign upon changing from positive to negative helicity and *vice versa*. The recurrence period is different from the one we observe in BP11. If we refer again to τ_F as the time interval between two consecutive reconnecting events of the network in the flow direction, then $\tau_F = 2/\dot{\gamma}$. A full reconnection in the vorticity direction takes place after the time $\tau_V = 4\tau_F$. We believe that the reason for these differences is also directly linked to the different topology of the defect network. The details of this mechanism will be addressed in future work.

3.2.3 Regime BPI-3: high shear rates. At higher flow rates, $3.125 \times 10^{-4} \leq \dot{\gamma} \leq 4.688 \times 10^{-4}$ ($2.67 \leq Er \leq 4$) we observe break-up of the periodically recurring disclination network in regime BPI-2 and the formation of another amorphous network. A sequence of snapshots of this is shown in Fig. 12. At first the disclination lines take the form of a regular, staggered array of helices with the helical axis lying along the flow direction. However, this mode of flow proves to be equally unstable as the regular formations dissolve into an irregular state with helicoidal disclination lines of varying appearance. The morphology is different from the amorphous network of regime BPI-1 (cf. Fig. 9) where the disclination lines are well separated but do not have a clear orientation with respect to the flow.

Interestingly, the critical Ericksen number for this observed break-up is in the range of $Er \approx 2-4$. This is a regime where viscous forces have a similar magnitude to elastic forces and where the nonlinear coupling between order and flow can cause small deviations to grow quickly over time. This suggests that the BPI-3 regime constitutes an instance of “rheochaos”^{39,40} as mentioned previously.

3.3 Transition to the cholesteric helix and flow-aligned nematic state

At shear rates beyond the regimes BPI-3 and BP11-2, but below the transition to a flow-aligned nematic state at still higher shear rates, we found another regime where both blue phases adopt the same configuration in steady shear flow, independent of their initial state. The director field of this configuration, also known as Grandjean texture, is shown in Fig. 13. It consists of a simple cholesteric helix with the helical axis oriented along the gradient direction (y). While the liquid crystal is flowing the director field is stationary and retains its relative orientation so that the depicted state is translational invariant in the flow-vorticity plane and quasi-one-dimensional. There is a small Leslie-type angle with respect to the flow-vorticity plane. In contrast to the other metastable flow states there is no tumbling motion of the director. This leads to lower shear stress and lower dissipation compared to other states such as the travelling helical wave.^{21,22}

The Grandjean configuration does not always emerge perfectly. Fig. 14 shows a time sequence of a frustrated state that undergoes a buckling transition. Initially the layers happen to be along a diagonal direction. Because the diagonal state does not have the equilibrium layer spacing the conformation buckles which reduces its free energy. Due to the periodic

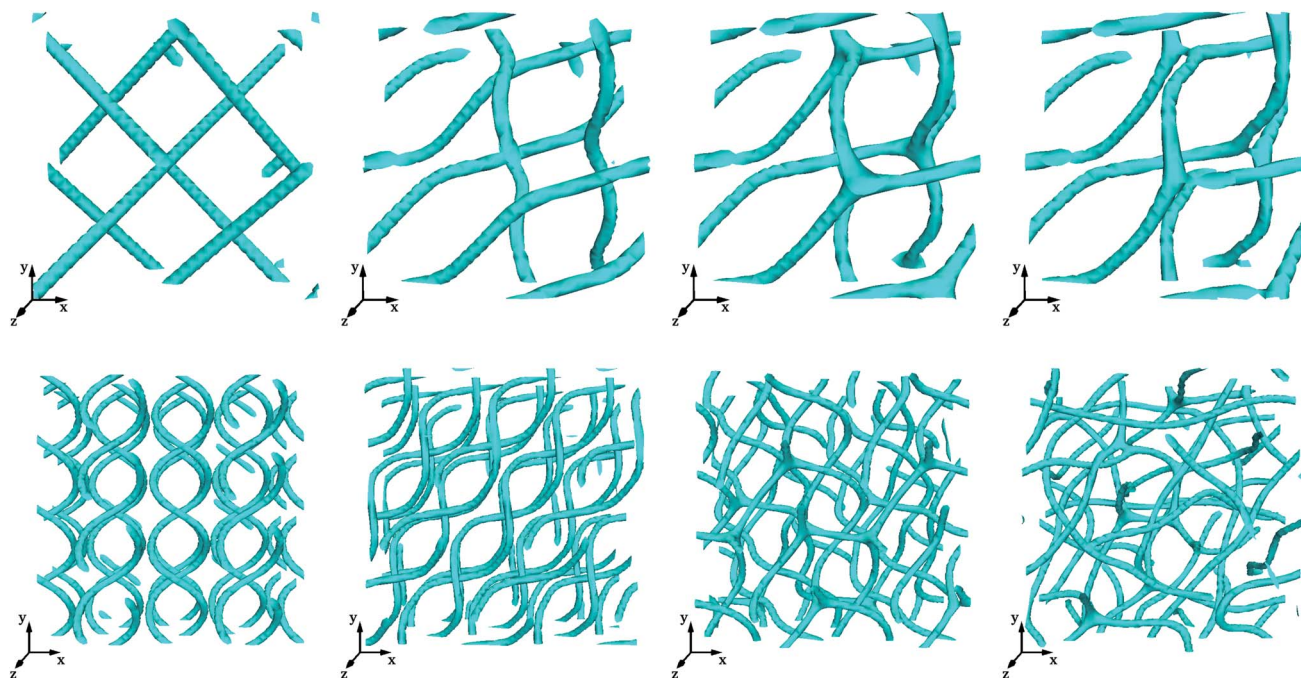


Fig. 9 Snapshots of the BPI disclination network at $\dot{\gamma} = 4.88 \times 10^{-6}$. Depicted is the transition from the quiescent state to flow-induced, intertwined helices that undergo a recurring structural transformation. The top row shows a section of one unit cell for early times $t = 1 \times 10^4$, 1.8×10^5 , 2.0×10^5 and 2.1×10^5 . The bottom pictures on the far left, centre left and centre right show the situation at later time steps $t = 1.65$, 1.8 and 2.0×10^6 , which the system passes for several cycles before it ends up in an amorphous state (bottom row far right, at a time step $t = 2.4 \times 10^6$).

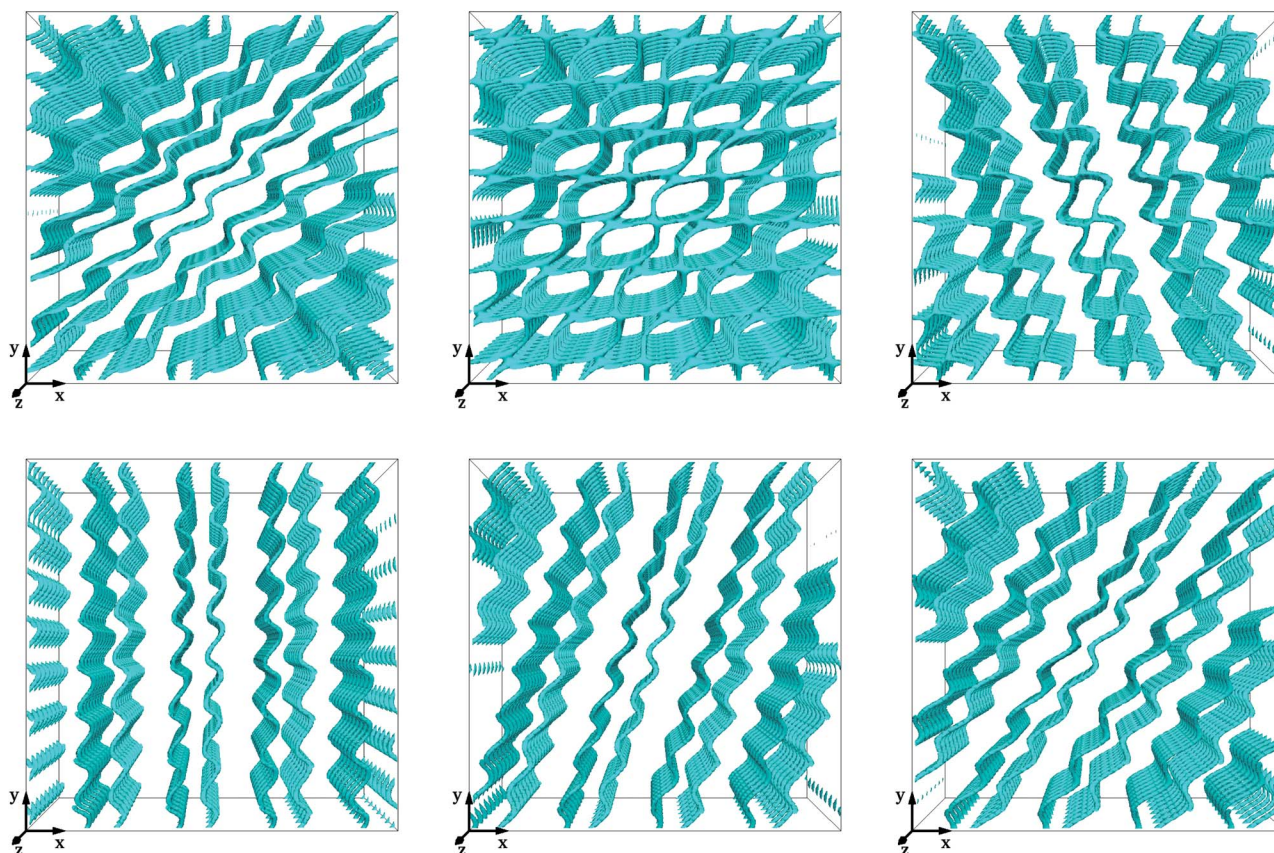


Fig. 10 Disclination network of BPI in regime BPI-2 (intermediate flow rates). The sequence shows a typical cycle of shear-induced transformations in the steady state at $\dot{\gamma} = 1.56 \times 10^{-4}$ and time steps $t = 3.64$, 3.66 , 3.68 , 3.70 , 3.72 , and 3.74×10^5 in the flow-gradient plane. During every cycle the network also is displaced along the vorticity direction just as BP11 in regime BP11-1, but at a different rate.

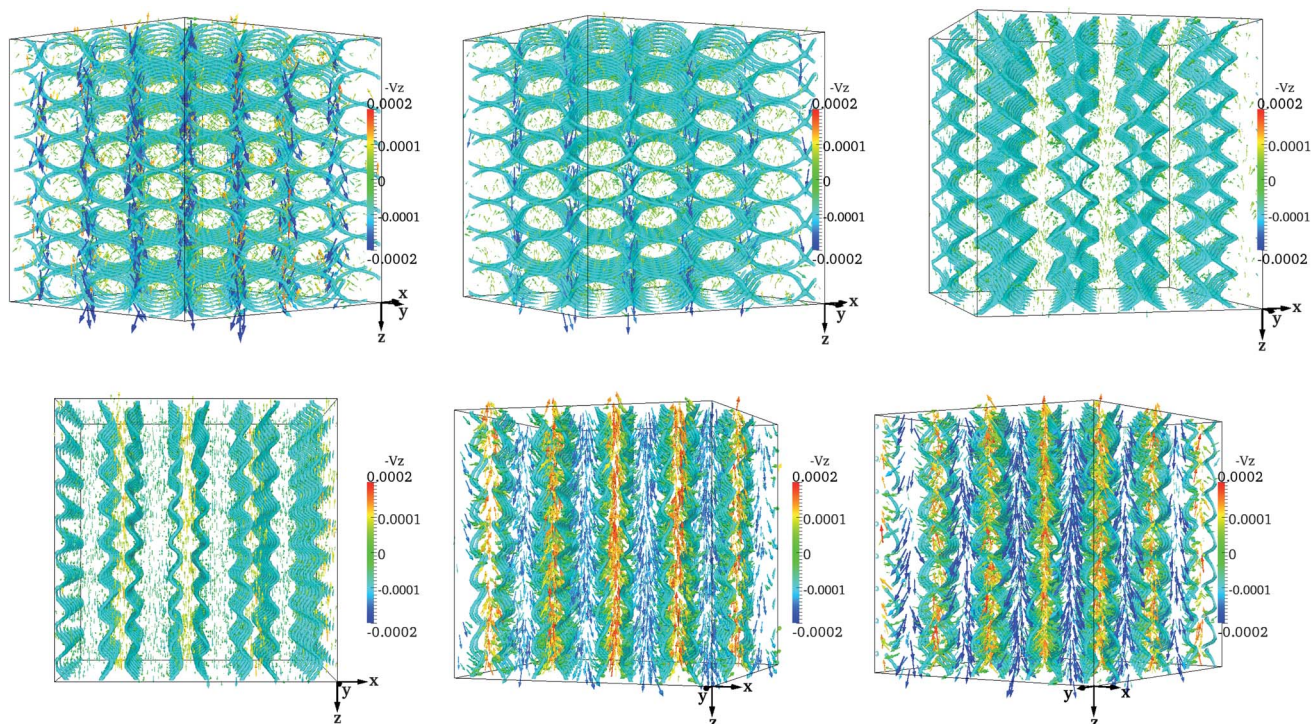


Fig. 11 Velocity patterns in BPI for positive helicity. The pictures show a snapshot of the periodically recurring patterns in the secondary velocity components (v_y , v_z) at $\dot{\gamma} = 1.56 \times 10^{-4}$ and time steps $t = 3.64, 3.66, 3.68, 3.70, 3.72$, and 3.74×10^5 , i.e. for the same shear rate and time steps as in Fig. 10. The colour code gives the magnitude and sign of the z -component. For negative helicity the sense of motion of the network and the secondary velocity components is inverted just as in Fig. 4. Note that the viewing direction has been changed along an orbit in the xy -plane to give a clearer view on the velocity pattern.

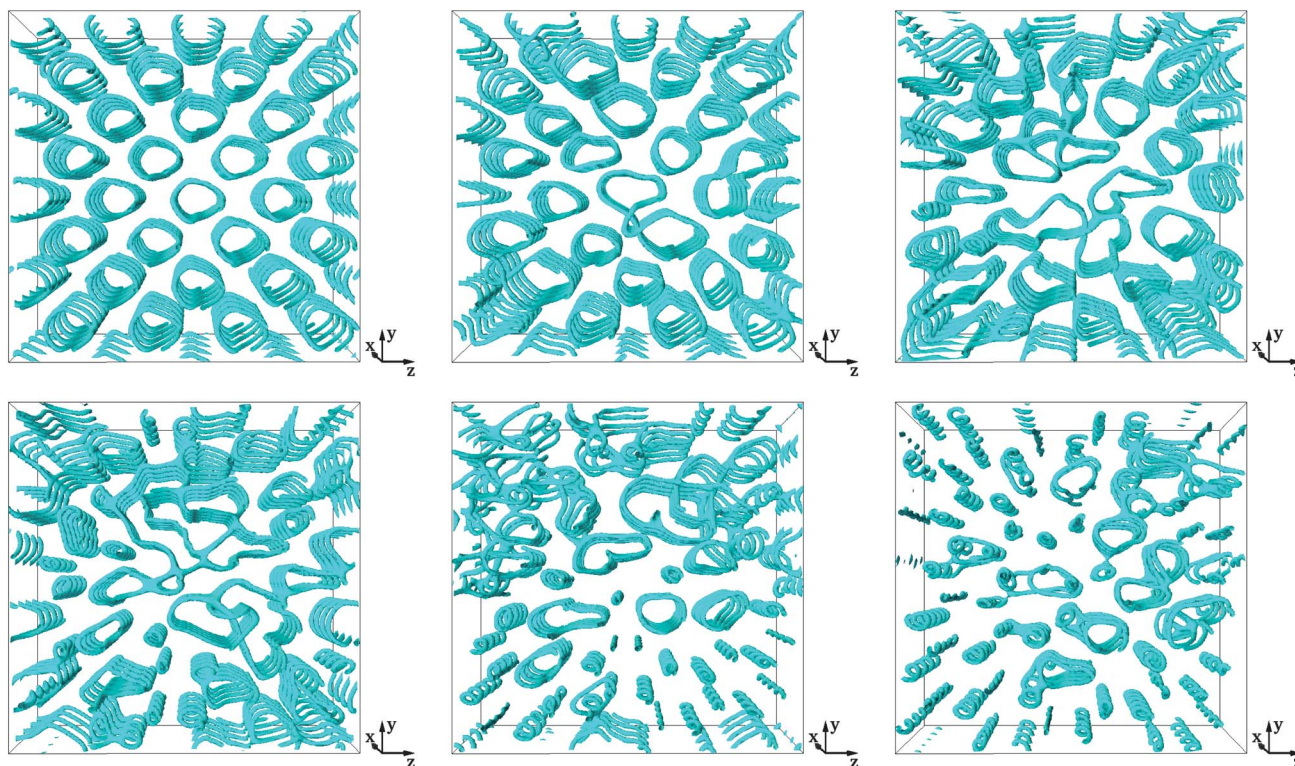


Fig. 12 Disclination network of BPI in regime BPI-2 (high flow rates). The sequence shows the break-up of the initially ordered state into an amorphous network at $\dot{\gamma} = 3.125 \times 10^{-4}$ and time steps $t = 6.0, 6.75, 7.0, 7.25 \times 10^5, 1.0$, and 1.2×10^6 in the vorticity–gradient plane. During every cycle the network also is displaced along the vorticity direction.

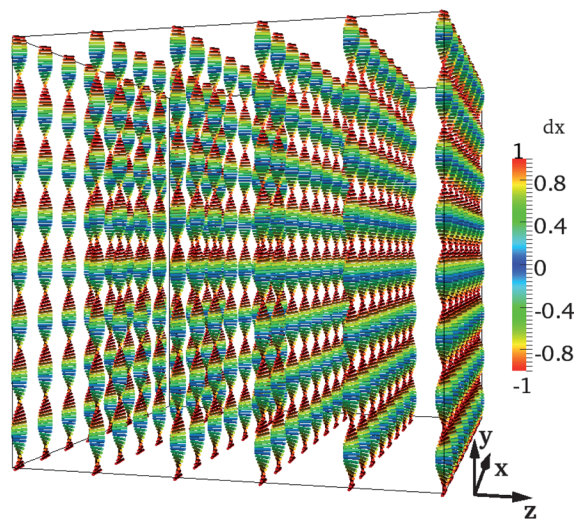


Fig. 13 Flow induced cholesteric state or Grandjean texture in regimes BPI-4 and BPII-2. The orientation of the helix is along the gradient direction. The director field is quasi-static during the flow, which occurs in "nematic layers". Colour coding indicates the x -component of the director field (see the colour bar on the right). For clarity only selected sites are shown along the y -direction. The structure is translationally invariant along the other two directions.

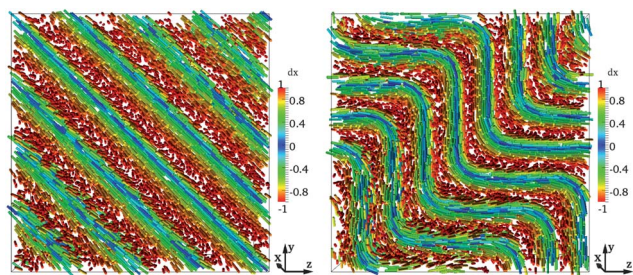


Fig. 14 Director field of BPI-4 at high shear rates. The pictures show a frustrated Grandjean configuration that formed layers along a diagonal direction. The colour code gives the magnitude of the x -component in the flow direction.

boundary conditions and their interlocking effect on the configuration this state cannot transform into a perfect Grandjean texture. However, the tilt angle of the layers with respect to the flow-vorticity (xz) plane decreases significantly if the strain rate is increased. Interestingly, the frustration can occur for any flow rates in regime BPI-4, as shown in Fig. 5, a consequence of the shearing geometry and the relative orientation of the initial state.

4 Conclusions

In summary, our work constitutes the first large scale simulation of bulk flow behaviour of cubic BPs in simple shear flow.

We were able to characterise the rheology of cubic BPs, and identified three different flow regimes for BPII and five different ones for BPI. These include some steady states that BPI and BPII have in common such as the Grandjean texture and the flow-aligned nematic state at high shear rates. Below an Ericksen number of $Er \approx 3$, BPII exhibits weak shear-thinning and obeys

a power-law flow curve with the exponent close to unity. The BPII disclination network breaks up and reconnects in the flow, which leads to a periodically recurring dependence of the shear stress. The flow-induced conformation looks generally very similar to the quiescent network at equilibrium. While being homogeneously transformed due to the shear flow the disclination network moves steadily in the vorticity direction apparently by a permeation mechanism. The sense of motion is directly linked to the helicity of the underlying cholesteric phase.

At larger Ericksen numbers, $4 \leq Er \leq 10$, the flowing BPII network breaks up into a simple cholesteric helix with the helical axis along the gradient direction, also referred to as Grandjean texture. The travelling helical wave, predicted theoretically in ref. 21 and 22 under the assumption that the director is restricted to the flow-gradient plane, turns out to be a metastable state of flow with a higher free energy. It may also transform into the Grandjean texture, the steady state with the lowest shear stress in this range of shear rates. Still larger flow rates break this residual cholesteric order and leave a standard flow-aligned nematic state, at the highest shear rate studied.

Interestingly, BPI shows a flow behaviour that is very different from that of BPII. This is a direct consequence of the topological differences between their disclination networks. Below an Ericksen number of $Er \sim 0.3$, the BPI network cannot both flow and retain a regular appearance. It eventually reorganises into an amorphous network that features yield-stress behaviour. The apparent reason is that shortly after the onset of the shearing very large stress fluctuations occur. At the lowest shear rates the thermodynamic contribution to the shear stress becomes temporarily negative during each cycle. These fluctuations seem to destabilise the network and eventually trigger the transition into an amorphous state with a residual yield stress.

At slightly larger Ericksen numbers $0.4 \leq Er \leq 2$, BPI kinematically bypasses the large stress fluctuations and flows with periodically recurring flow-induced conformations. These conformations entail regularly arranged helical disclinations which rotate due to the shear. The flow-induced conformations in this regime are not topologically connected to the quiescent state. After switching off the shear flow no regular BPI network reforms. Instead the network is trapped in a metastable state with helicoidal intertwined disclinations.

At even larger Ericksen numbers $2 \leq Er \leq 4$ the behaviour of BPI is again different. At first, it exhibits regular helicoidal disclination lines oriented along the flow direction. After a short time these become irregular and an amorphous network emerges, which has a different appearance from that observed at the lowest flow rates. We believe that at these flow rates, where neither viscous nor elastic forces clearly dominate, the coupling between order and flow makes any ordered conformation very sensitive towards irregular disturbances caused by small fluctuations. It is tempting to interpret the unsteady oscillations observed in this regime as an instance of deterministic rheological chaos.^{40,41}

Just as in the case of BPII, the BPI network breaks up at larger Ericksen numbers. First, at $5 \leq Er \leq 16$, it forms a cholesteric

helix along the flow gradient direction, the Grandjean texture. Finally, at $Er \geq 21$ (BPI) and $Er \geq 16$ (BPII) the configuration is a flow-aligned nematic state. Although experimental evidence to support our results is currently not available, we hope this work will inspire such experiments, and believe it can shed some light on the flow properties of complex liquid-crystalline phases.

Appendix

Table 1 lists the parameters chosen for our runs (values of the reduced temperature and reduced chirality are given in the caption), together with the minima, maxima, and standard deviations of the velocity field in the three directions (discussed further in the main text). The first column also describes what flow regime each simulation leads to in the steady state.

In all our runs we used Lees–Edwards boundary conditions (LEBCs).³³ This is the sheared equivalent of periodic boundary conditions, for both the velocity and the order parameter field. On crossing a Lees–Edwards boundary a Galilean transformation is applied with a velocity increment which is fixed in time (and limited in size by the low Mach number constraint of LB). An appropriate transformation of LB distributions which propagate across a boundary must be applied at each time step, and an appropriate adjustment to the tensor of velocity gradients $W_{\alpha\beta}$ is required to compute cross-plane gradients of the velocity field used in the update of \mathbf{Q} according to eqn (4). In both cases interpolation of the relevant quantities is required to cope with the relative displacement of neighbouring lattice sites separated by a sliding plane (the displacement may be a fraction of a lattice unit at any given time step).³⁷ It is worth mentioning that apart from the Galilean transformation LEBCs do not impose any further constraint. This means that the order parameter field is free to follow its own kinetic pathway at the Lees–Edwards plane. The use of multiple sliding planes equally spaced in a single system allows the overall shear rate to be maintained indefinitely as the system becomes larger in the velocity gradient direction (in contrast to the use of solid walls to impose shear). While extremely useful to simulate bulk flow, we note that these boundary conditions impose macroscopic distortion of the network. They do not allow for a free-standing network sustained stationary by permeation along the flow direction. Such a state is however forbidden for large system sizes since the local permeation rate would have to increase indefinitely with the sample thickness. The boundary condition is equivalent to infinitely distant walls along the xy -plane where the liquid crystal is anchored, not unlike the situation found in a rheometer with no-slip boundary conditions at the walls. In practice, permeation flows are only restricted to very low flow rates, and are unstable for intermediate and fast flows,²⁵ where the response of the network depends less on the details of the boundary conditions used at the wall. With free boundary conditions that do not impose macroscopic distortion and for very low flow velocity, permeative flows might instead allow for some slip of the BPI network as in cholesterics sheared along their axis.^{19,20} However, as mentioned above, a triply periodic structure cannot be maintained stationary in a large system without infinite permeation rate.

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References

- 1 P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 2nd edn, 1993.
- 2 S. S. H. Grebel and R. M. Hornreich, *Phys. Rev. A*, 1984, **30**, 3264.
- 3 D. C. Wright and N. D. Mermin, *Rev. Mod. Phys.*, 1989, **61**, 385.
- 4 O. Henrich, K. Stratford, D. Marenduzzo and M. E. Cates, *Phys. Rev. Lett.*, 2011, **106**, 107801.
- 5 H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang and T. Kajiyama, *Nat. Mater.*, 2002, **1**, 64–68.
- 6 H. J. Coles and M. N. Pivnenko, *Nature*, 2005, **436**, 997–1000.
- 7 J. Fukuda and S. Zumer, *Phys. Rev. Lett.*, 2010, **104**, 017801.
- 8 J. Fukuda and S. Zumer, *Liq. Cryst.*, 2010, **37**, 875–885.
- 9 M. Ravnik, G. Alexander, J. Yeomans and S. Zumer, *Soft Matter*, 2011, **7**, 10144–10150.
- 10 G. P. Alexander and D. Marenduzzo, *EPL*, 2008, **81**, 66004.
- 11 J. Fukuda, M. Yoneya and H. Yokoyama, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2009, **80**, 031706.
- 12 O. Henrich, D. Marenduzzo, K. Stratford and M. E. Cates, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2010, **81**, 031706.
- 13 F. Castles, S. M. Morris, E. M. Terentjev and H. J. Coles, *Phys. Rev. Lett.*, 2010, **104**, 157801.
- 14 A. Tiribocchi, G. Gonnella, D. Marenduzzo and E. Orlandini, *Soft Matter*, 2011, **7**, 3295.
- 15 M. Ravnik, G. Alexander, J. Yeomans and S. Zumer, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 5188–5192.
- 16 O. Henrich, K. Stratford, D. Marenduzzo and M. E. Cates, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 13212–13215.
- 17 W. Helfrich, *Phys. Rev. Lett.*, 1969, **23**, 372.
- 18 M. J. Press and A. S. Arrot, *J. Phys.*, 1978, **39**, 750–759.
- 19 D. Marenduzzo, E. Orlandini and J. M. Yeomans, *Phys. Rev. Lett.*, 2004, **92**, 188301.
- 20 D. Marenduzzo, E. Orlandini and J. M. Yeomans, *J. Chem. Phys.*, 2006, **124**, 204906.
- 21 A. D. Rey, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1996, **53**, 4198–4201.
- 22 A. D. Rey, *J. Non-Newtonian Fluid Mech.*, 1996, **64**, 207–227.
- 23 A. D. Rey, *J. Rheol.*, 2000, **44**, 855.
- 24 A. D. Rey, *J. Rheol.*, 2002, **46**, 225.
- 25 A. Dupuis, D. Marenduzzo, E. Orlandini and J. M. Yeomans, *Phys. Rev. Lett.*, 2005, **95**, 097801.
- 26 M. Zapotocky, L. Ramos, T. Lubensky and D. Weitz, *Science*, 1999, **283**, 209.

- 27 L. Ramos, M. Zapotocky, T. C. Lubensky and D. A. Weitz, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2002, **66**, 031711.
- 28 A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems*, Oxford University Press, 1994.
- 29 G. P. Alexander and J. M. Yeomans, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, **74**, 061706.
- 30 C. Denniston, E. Orlandini and J. M. Yeomans, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2001, **63**, 056702.
- 31 D. Marenduzzo, E. Orlandini, M. E. Cates and J. M. Yeomans, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 031921.
- 32 C. Denniston, D. Marenduzzo, E. Orlandini and J. M. Yeomans, *Philos. Trans. R. Soc., A*, 2004, **362**, 1745.
- 33 A. J. Wagner and I. Pagonabarraga, *J. Stat. Phys.*, 2002, **107**, 521–537.
- 34 R. M. MacMeccan, J. R. Clausen, G. P. Neitzel and C. K. Aidun, *J. Fluid Mech.*, 2009, **618**, 13–39.
- 35 C. K. Aidun and J. R. Clausen, *Annu. Rev. Fluid Mech.*, 2010, **42**, 439–472.
- 36 S. Frijters, F. Gunther and J. Harting, *Soft Matter*, 2012, **8**, 6542–6556.
- 37 O. Henrich, K. Stratford, D. Marenduzzo, P. V. Coveney and M. E. Cates, *Soft Matter*, 2012, **8**, 3817–3831.
- 38 O. Henrich, K. Stratford, D. Marenduzzo, P. V. Coveney and M. E. Cates, *J. Phys.: Condens. Matter*, 2012, **24**, 284127.
- 39 B. Chakrabarti, M. Das, C. Dasgupta, S. Ramaswamy and A. K. Sood, *Phys. Rev. Lett.*, 2004, **92**, 055501.
- 40 M. E. Cates, D. A. Head and A. Ajdari, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2002, **66**, 025202.
- 41 S. M. Fielding and P. D. Olmsted, *Phys. Rev. Lett.*, 2004, **92**, 084502.