Hierarchical Approach to Flow Calculations for Polymeric Liquid Crystals

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I. Introduction

Liquid crystalline polymers (LCPs) are macromolecules that contain long, rigid or approximately rigid segments. Because of these rigid units, LCPs can display structural phase transitions between isotropic (disordered) and nematic (oriented) states. LCPs are classified as thermotropic or lyotropic depending on whether the structural transitions are induced by changes in temperature or in concentration, respectively^{1,2}. Some of these materials are known to have interesting macroscopic properties, such as high modulus in the solid phase and low viscosity in the melt or in solution. They can also display a rich phase behaviour as temperature or concentrations or both are changed, even in quiescent conditions. Non-equilibrium, macroscopic flow conditions can further complicate their phase behaviour.³

Macroscopic viscoelastic flow calculations for LCPs typically start with the derivation of macroscopic, approximate equations for quantities of interest, such as order parameters. Analytical developments towards a closed constitutive equation very often necessitate the introduction of more or less *ad hoc* closure approximations.⁴⁻⁶

The difficulty in obtaining accurate closures has motivated the use of direct simulations. These take place typically at one of two levels of description:

1. Integration of the partial differential equation (PDE) governing the temporal evolution of the orientational probability distribution function (pdf) $\psi(\underline{u}, t)$ for the orientation of the molecule, as given by the unit vector $\underline{u}$, in a coarse grained

sense, i.e. $\underline{u}$ represents the molecule by its head-to-tail connector vector. This equation is typically a non-linear Fokker-Planck (FP) equation which has to be solved in configuration space by means of suitable discretization methods. Solution techniques are basically identical to those used to integrate the accompanying macroscopic conservation equations, also expressed as PDEs. For Doi's widely used model for LCPs the FP equation for takes the form:

$$\begin{aligned} \frac{\partial \psi(\underline{u}, t)}{\partial t} = & -\frac{\partial}{\partial \underline{u}} \cdot \left[(\underline{u} \cdot \nabla \underline{v} - \underline{u} \underline{u} \underline{u} : \nabla \underline{v}) \psi(\underline{u}, t) \right] + \\ & + \frac{\partial}{\partial \underline{u}} \left\{ \tilde{D}_r(\underline{u}) \left[\frac{\partial \psi(\underline{u}, t)}{\partial \underline{u}} + \psi(\underline{u}, t) \frac{\partial}{\partial \underline{u}} \left(\frac{V_{ev}(\underline{u})}{kT} \right) \right] \right\} \end{aligned} \quad (1)$$

where $\psi(\underline{u}, t)$ is the probability that a rod-like molecule has an orientation given the by the unit vector $\underline{u}$ at time t ; $\nabla \underline{v}$ is the local velocity gradient the LCP molecule is subjected to at time t , and $\tilde{D}_r(\underline{u})$ is the orientation-dependent rotary diffusivity given by:

$$\tilde{D}_r(\underline{u}) = D_r \left[\frac{4}{\pi} \int \psi(\underline{u}') \sin(\underline{u}', \underline{u}) d\underline{u}'^2 \right]^{-2} \quad (2)$$

where D_r is the rotary diffusivity in a hypothetical isotropic solution of molecules at the given concentration and $\sin(\underline{u}', \underline{u})$ is the positive sine of the angle between the unit vectors $\underline{u}$ and $\underline{u}'$ describing the orientation of two LCP molecules⁴. $V_{ev}(\underline{u})$ is the excluded volume interaction potential, e.g. in the Onsager form:

$$V_{EV}(\underline{u}) = 2cdL^2 k_B T \int \psi(\underline{u}') \sin(\underline{u}', \underline{u}) d\underline{u}'^2 \quad (3)$$

(see Section III below). The integrals in (2) and (3) are performed over the surface of a unit sphere the radial vectors of which form the configuration (in this case, orientation) space. The operator $\frac{\partial}{\partial \underline{u}}$ is the gradient operator on this manifold:

$$\frac{\partial}{\partial \underline{u}} = r \left[(\underline{\delta} - \underline{u}\underline{u}) \cdot \underline{\nabla} \right] = \underline{\delta}_\theta \frac{\partial}{\partial \theta} + \underline{\delta}_\varphi \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \quad (4)$$

$\underline{\delta}$ the unit second order tensor and $\underline{\delta}_\theta$ and $\underline{\delta}_\varphi$ are the polar and azimuthal unit vectors in spherical coordinates⁷. A way to solve the rather complex PDE (1) is to factor and expand the pdf in the eigenfunctions of the Laplacian operator in spherical coordinates, i.e. in spherical harmonics^{3, 8}:

$$\psi(\underline{u}, t) = \sum_{\substack{l=0 \\ \text{even}}}^{\infty} \sum_{m=-l}^l b_{l,m}(t) Y_{lm}(\underline{u}) \quad (5)$$

A weak formulation of Eq. (1) is obtained by truncating the expansion at a level dictated by the desired numeral accuracy and subsequently applying a Galerkin scheme. Typically, n is of $O(10)$ and the resulting set of ordinary differential equations, although rather cumbersome, can be integrated numerically with moderate effort.

2. Integration of a large number (an ensemble) of individual trajectories $\underline{U}(t)$ for the unit vector defining the orientation of single LCP molecules^a. The evolution of individual molecules is described by means of a stochastic differential equation (SDE) for the time evolution of the Markovian process $\underline{U}(t)$. If properly constructed, the evolution of an ensemble of trajectories is in exact correspondence with the evolution of the pdf as described by (1). Integration of the SDE associated with Doi's model can be accomplished by the simple algorithm³:

$$\underline{U}_{j+1} = \frac{\underline{U}_j + \underline{f}(\underline{U}_j)\Delta t + \left(2\tilde{D}_r(\underline{U}_j)\Delta t\right)^{1/2} \underline{W}_j}{\left|\underline{U}_j + \underline{f}(\underline{U}_j)\Delta t + \left(2\tilde{D}_r(\underline{U}_j)\Delta t\right)^{1/2} \underline{W}_j\right|} \quad (6)$$

$$\underline{f}(\underline{U}) = \underline{U} \cdot \underline{\nabla}_v - \frac{\tilde{D}_r(\underline{U})}{kT} \frac{\partial V_{ev}(\underline{U})}{\partial \underline{U}} + \frac{\partial \tilde{D}_r(\underline{U})}{\partial \underline{U}}$$

where $\underline{U}_j = \underline{U}(j\Delta t)$. This algorithm guarantees that the constraint $|\underline{U}_j| = 1$ is fulfilled at all times and for all finite time steps. It does not require application of

^a $\underline{U}(t)$ is used instead of $\underline{u}(t)$ to emphasize the character of stochastic process of the former and distinguish it from the latter.

the transverse projector operator $\underline{\underline{\delta}} - \underline{\underline{U}}\underline{\underline{U}}$ nor of the transverse gradient $\frac{\partial}{\partial \underline{\underline{U}}}$.

The simplicity of this algorithm is in stark contrast with the substantial complication of the numerical schemes used to integrate (1). However, it must be borne in mind that the ensemble approach yields "noisy" results, as a consequence of the stochastic term $\underline{\underline{W}}_j$, the components of which are three random numbers sampled from a Gaussian distribution of mean zero and variance unity⁹, and as a consequence of finite ensemble size. It can therefore be computationally very expensive to obtain high accuracy solutions, since the amplitude of noise, i.e. the error bar inherent in any average quantity computed over the ensemble, decreases with the square root of the number of trajectories.

Both levels of description can be used to compute macroscopic values of an arbitrary quantity $A(\underline{\underline{u}})$:

$$\int A(\underline{\underline{u}})\psi(\underline{\underline{u}}, t_j) d\underline{\underline{u}}^2 = \frac{1}{N_T} \sum_{n=1}^{N_T} A(U_j^{(n)}) \quad (7)$$

While the ensemble approach is not suited to obtain the full pdf $\psi(\underline{\underline{u}}, t)$ with reasonable accuracy, it is however a very powerful alternative for the calculation of moments of $\psi(\underline{\underline{u}}, t)$ or of general average expressions like Eq. (7), since they can be computed satisfactorily even in configuration spaces of very high dimensionality.

Throughout the previous discussion of the two main alternatives, the velocity gradient was considered to be a given, spatially constant, at most time-varying, magnitude, i.e. the velocity gradient field was assumed to be spatially homogeneous.

Inhomogeneous flows are clearly important, since most real-life flow problems belong in this class. Over the last 15 years, both of the above techniques have started to be used to solve *inhomogeneous* flow problems in combination with computational fluid dynamics methods.¹⁰

In addition, the numerical values of the parameters appearing in (1), namely the rotary diffusivity and the strength parameter of the excluded volume interaction $V_{ev}(\underline{\underline{u}})$, are either set to values within given ranges in parametric studies, or estimated by straightforward arguments.

The present investigation is a modest attempt to advance the current state-of multi-scale approaches to flow calculations of LCPs. Only very few complex, i.e. non-

homogeneous, flow calculations for models such as Doi's have been performed up to date^{11, 12}. In some cases, the kinematics were decoupled from the molecule dynamics, i.e. although spatially non-homogeneous, the velocity field was obtained non-consistently from a simpler constitutive law, like in the work by Grosso et al.⁶, where Doi's equation was solved in given Newtonian kinematics in a large-eccentricity journal-bearing geometry. More recently, Lattice Boltzmann methods have also been used in conjunction with the LCP model of Beris and Edwards¹³⁻¹⁹.

In the first part of this work, coarse-graining is applied to obtain one of the parameters in Doi's equation from a detailed atomistic model of the liquid-crystal forming polymer poly-(*n*-propyl isocyanate) $[-\text{CO}-\text{N}(\text{C}_3\text{H}_7)]_n$ (PPIC) dissolved in toluene.

II. Atomistic-level (Level 1 and 2) description of poly-(*n*-propyl isocyanate) (PPIC)

The lowest, most detailed, level of description considered in this work is atomistic (we will refer to it as Level 1 in the following). The force field of Amber¹⁷⁻¹⁹ was used at this Level 1 to obtain the most stable polymer configuration for single chains *in vacuo* and then in solution. To this end, a single PPIC containing 40 structural repeat units $[-\text{CO}-\text{N}(\text{C}_3\text{H}_7)]$ and terminated with capping H atoms was simulated in full explicit detail both *in vacuo* and immersed in a solvent of toluene (C_7H_8) molecules also represented fully explicitly under periodic boundary conditions. In the calculations in a solvent, the number of toluene molecules was chosen so that, after subtracting the helix volume (more precisely, the volume of the Connolly surface²⁰ of the helix for a probe sphere of radius 0.38 nm, representative of a toluene molecule) from the total volume of the simulation box, the density of toluene in this remaining volume matched the experimental macroscopic value at $T = 298 \text{ K}$ ²¹.

Atom naming convention, definitions of bond lengths, bond angles and torsion angles for the helix backbone and side propyl groups were as follows:

Figure 1. Naming convention for atoms and bond lengths in PPIC backbone and side group

Figure 2. Bond angle definition for PPIC backbone and side group

Figure 3. Torsion angle definition for PPIC backbone and side groups

The simulation box was a right-angle parallelepiped of 8.1 by 1.5 by 1.5 nm. The PPIC center of mass was placed in the geometrical center of the box, the helix axis was aligned with the long dimension of the box and it was ensured in all cases that interactions with periodic copies of the central chain were absent.

Time integration was performed by means of a velocity Verlet MD algorithm²². Temperature was set at 298 K and a Nosé-Hoover thermostat²²⁻²⁴ was used to keep temperature at this set value. Electrostatic contributions to the force field were computed by considering the helix environment as a continuum with a constant value of the dielectric constant. The values of $\epsilon = 1$ and $\epsilon = 2.1$ were used, as representative of the vacuum and the nonpolar solvent.

Partial electrostatic charges were found to be important for backbone atoms, where highly polar moieties reside. Side propyl branches can be considered electrostatically neutral for all practical purposes. Starting configurations for the PPIC chain were constructed following the parameters of Lukasheva et al.²⁵, which corresponds to a left-handed Natta-Corradini 8/3 helix. Starting from this helix conformation, the system was integrated for a total run length of 12 ps.

During the run, helix conformation was monitored by following the length of the head-to-tail vector, which reacts very sensitively to conformational (torsional) changes in the polymer backbone. Side group conformation was similarly monitored by following the length the vector joining the side chain-helix attachment point with the center of the last C atom in the propyl group, i.e. the vector from backbone nitrogen atom N_i to carbon atom $C_{i,3}$. After a short transient of approx. 3.4 ps, both the helix and the side group conformations were found to reach a steady average state with low amplitude oscillations around these most probable values.

This steady state was characterized by a stable 8/3 helix, virtually undistinguishable from the starting structure (which was taken from the *in vacuo* runs) and by almost fully extended side propyl groups. The rapid convergence to a stable conformation very similar to that obtained in Refs.²⁵⁻²⁸ using the PCFF force field in the absence of solvent, and also very close to experimentally determined structures²⁹. References³⁰⁻³² suggests that rigid helical conformations are indeed a robust characteristic of PPIC chains. This is also in agreement with previous work²⁷ and with the estimated persistence length of PPIC.

Figure 4. Stick perspective representation of PPIC helix backbone in most probably conformation; 8 residues (3 helix turns) and only one propyl side group is also represented. Solvent molecules not represented. Left, helix axis contained in plane of paper. Right, helix axis perpendicular to plane of paper. Blue segments correspond to N atoms, grey to C, white to H. Observe tight winding of 8/3 helix and almost fully extended configuration of side propyl group.

Figure 5. Two views of the same fragment of the PPIC helix as in previous figure; left and right images are taken after performing a 90° rotation around the helix axis. Atoms are represented as spheres with van der Waals radii. Helix backbone is very effectively shielded from solvent molecules by side propyl groups.

The first-level calculation just described, although incorporating a single PPIC 40-mer chain, requires a significant amount of computation. Moving on to a semi-

dilute or concentrated system using Level 1 description would require consideration of a large, multi-chain system, each of them comprising (for a degree of polymerization of 40) 520 explicit atoms plus additional explicit solvent molecules, comprising 15 atoms each. This MD calculation, although feasible with the computational resources available today; would however be impossible to extend to the time scale required to observe Einsteinian rotary diffusion regime. Therefore, a direct attempt to observe typical multi-chain, cooperative behaviour and transitions in LCP's remains a major computational challenge for present-day hardware.

However, the high rigidity of the helix in PPIC makes it amenable to an alternative approach where a moderate simplification (coarse-graining) of the full atomistic detail is performed.

In this second stage, advantage was taken of the following observations collected during the MD run:

- the PPIC backbone torsion and bending angles, and bond lengths, remained virtually unchanged during the entire run, with only very small fluctuations around their most probable values. The following table summarizes the essential helix parameters. For torsional angles, mean and standard deviation of the mean are given:

$\langle \phi_i \rangle$	$\langle \psi_i \rangle$	$\langle \chi_{i,1} \rangle$	$\langle \chi_{i,2} \rangle$	n residues per turn	ρ_0 helix angle per residue	τ helix advance per residue
-161.3° ±1.3°	37.5° ±0.9°	-98.1° ±3.9°	175.8° ±5.5°	2.68	132°	.201 nm

- furthermore, changes in torsional angles in side propyl changes were also very minor (see previous table) and the last (2nd) torsional angle $\langle \chi_{i,2} \rangle$ was on average very close to *trans*.
- by performing short MD bursts branching off from the main conformational trajectory and with a force field modified in its electrostatic contribution (partial charges of the side groups set to zero), it was observed that the electrostatic contributions to the force field have a very direct effect on helix stability but none whatsoever on side propyl group conformation nor on inter-chain interactions.

Based on these observations, a simplified yet, for our purposes, faithful representation of PPIC chains was implemented (called Level 2 in the following). In the Level 2 representation:

- explicit hydrogen atoms are removed and methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) groups are described as single entities or united atoms, as is current practice in many atomistic polymer simulations.
- explicit toluene molecules were similarly represented by united atoms, namely aromatic $-\text{CH=}$, $-\text{CH}_2-$ and $-\text{CH}_3$ groups. United atom parameters were taken from the Amber united-atom force field³³ and from the work of Cross and Fung^{34, 35}.
- except for the deletion of C-H bonds as a consequence of the use of pseudoatoms, PPIC helix geometry was kept in its full detail, but bond lengths, bond angles and torsion angles were frozen at their most probable values, as collected during the MD run. This "freezing" of conformational degrees of freedom was performed for all bond lengths, all bond angles and all torsional angles in the helix, while the torsional angles $\chi_{i,1}$ and $\chi_{i,2}$ were allowed to vary.

The rationale behind this simplification is that, for the purpose of studying the interaction of helices which are known or have been shown to be very rigid, the only relevant feature of the internal structure of the helix is its rigidity. Since inter-helix interaction is mostly short-range steric (excluded-volume) and long-range electrostatics plays no role, it suffices to keep an explicit representation of those helix atoms which reside in an outermost shell. In Level 2, helices consist of a rigid core and pendant propyl groups with torsional degrees of freedom. Helices interact with one another and with the neutral toluene molecules via the short range LJ potential. This coarse-graining makes physical sense and leads to a significant saving of computational effort.

Along the polymer backbone, only two types of atoms are present: nitrogen and carbon. Hence, for a polymer consisting of n repeat units, $6n$ degrees of freedom were necessary to specify the precise conformation of its backbone. A possible set of such coordinates is the set of all Cartesian coordinates of its constituent atoms. Alternatively, the coordinates of one atom of the backbone considered as chain origin (3 d.o.f), the Euler angles defining the orientation of a bond in the backbone (3 d.o.f), $2n - 3$ torsional angles, $2n - 1$ bond lengths and $2n - 2$ bond angles, in all, $6n$ d.o.f. By employing the assumption of rigidity of the main chain the number of degrees of freedom was reduced by fixing the values of $2n - 3$ torsional angles and $2n - 2$ bond angles, i.e. a total of $4n - 5$ holonomic constraints. These constraints were imposed by a minimum triangulation scheme that ensures helix rigidity by fulfilling the following set of equalities:

$$\begin{aligned}
(\underline{r}_{C_i} - \underline{r}_{C_{i+1}})^2 - K_1 &= 0 \quad (n-1 \text{ constraints}) \\
(\underline{r}_{N_i} - \underline{r}_{N_{i+1}})^2 - K_2 &= 0 \quad (n-1 \text{ constraints}) \\
(\underline{r}_{C_i} - \underline{r}_{N_{i+1}})^2 - K_3 &= 0 \quad (n-1 \text{ constraints}) \\
(\underline{r}_{C_i} - \underline{r}_{N_{i+2}})^2 - K_4 &= 0 \quad (n-2 \text{ constraints}) \\
\text{total : } 4n - 5 \text{ constraints}
\end{aligned} \tag{8}$$

where the K 's were obtained from the single-chain MD run. Anderson's adaptation of the SHAKE algorithm²² to velocity Verlet^{22, 24} was used to satisfy (8).

Figure 6. Schematic representation of backbone constraints required to impose helix rigidity.

III. Level 3: Coarse-grained molecular description via Doi's model

The task of coarse-graining or projecting a model from a given level to another with many fewer degrees of freedom is in general non-univocal, since it depends on the specific aspects of the material which are of interest at the coarse-grained level. In the present framework of Doi's LCP model, the entire atomistically detailed representations of PPIC (Levels 1 and 2) need to be reduced to the two scalar parameters appearing in the constitutive equation to be used for viscoelastic flow calculations, namely:

1. The strength parameter appearing in the excluded volume interaction potential $V_{ev}(\underline{u})$. Determining the interchain interaction from Level 1 and 2 MD runs is probably at the limit of feasibility today, even when resorting to major

computational capabilities. Thermodynamic consistency requires a careful analysis of the form of the friction matrix in the framework of GENERIC in analogy to (8.169) of Ref.³⁶, which is applicable to reptation models. Strictly speaking, thermodynamic consistency also implies that the Level 3 of description should incorporate the orientation distribution function $\psi(\underline{u}, t)$ directly and not any strength parameter. This path was however not explored in the scope of the present work. Hence, and although not strictly self-consistent, the calculation of the effective excluded-volume potential was made according to the widely used Onsager form⁴:

$$V_{EV} = V_0(\underline{u}) = 2cdL^2k_BT \int \psi(\underline{u}') \sin(\underline{u}, \underline{u}') d\underline{u}' \quad (9)$$

where d is the rod diameter, L its length and c is the number concentration of rods in solution. Values of $d = 0.79$ nm and $L = 6.8$ nm were readily extracted from Level 1 simulations. This latter value should be compared with experimental values ($\cong 200$ -300 nm) of the persistence length of PPIC in non-polar solvent solution^{25, 29, 30}.

2. the rotary diffusivity in a hypothetical isotropic solution of molecules at the given concentration, appearing in (2)

This much rougher level of description will be referred to as Level 3. Although at atomistic levels 1 and 2, the nature of the interaction between polymer helices can only be energetic, via the force field and mediated by solvent molecules as well, at Level 3, interchain interaction is of entropic nature and the explicit solvent is absent.

Regarding the second point above, the rotary diffusivity that characterizes the rotational Brownian motion of the head-to-tail vector $\underline{u}$, is illustrated in the following figure:

Figure 7. Rotational Brownian motion of LCP head-to-tail vector.

For short times, in the sense that $D_r t \ll 1$, the random motion of $\underline{u}$ can be regarded as Brownian motion of the tip of the head-to-tail vector (scaled to unity) on a two-dimensional flat surface⁴. The mean square displacement of the unit vector $\underline{u}(t)$ in a time t can be written as:

$$\left\langle (\underline{u}(t) - \underline{u}(0))^2 \right\rangle = 4D_r t \quad (10)$$

where D_r is the rotary diffusivity that appears in Eq. (2). Since the units of this rotary diffusivity are inverse time, this rotary diffusivity is frequently employed to make time dimensionless by introducing the relaxation time $\tau_r \equiv D_r^{-1}$ and $\tilde{t} \equiv t / \tau_r = t D_r$. The same factor is also employed to render the strain rate dimensionless: $\Gamma \equiv \dot{\gamma} \tau_r = \dot{\gamma} / D_r$. In most studies published to date, the actual numerical value of D_r comes either i) from an experimental measurement in solution, for example via the Miesowicz viscosity, ii) from an estimation based on geometric factors and solvent viscosity, or iii) in parametric studies, numerical values are selected from intervals often chosen because striking changes in dynamical behaviour take place within them.

In this work, however, we have followed a hierarchical route in which MD results from Levels 1 and 2 are used to compute D_r according to (10). Unlike in the atomistically detailed simulations at Levels 1 and 2, the extraction of the rotary diffusivity must be done in a multi-particle setting, i.e. on a system appreciably larger than that needed for the single-rod calculation. To this end, a large atomistically detailed, Level 2 system was prepared containing 57 identical PPIC molecules, each of them containing 40 residues and capped by terminal hydrogens. They were placed in a cubic simulation cell of 8 nm edge, together with 1824 toluene molecules, comprising a total number of 26471 pseudoatoms. Initial polymer helix configurations were generated in the absence of solvent molecules by uniformly sampling space for positioning helix origins, and uniformly sampling the unit sphere in order to define the orientation of the helix axis. When rod placements using this uniform sampling scheme led to unrealistic rod-rod overlaps, the latest trial rod was discarded and a new attempt performed. Since the rod volume fraction is not excessively high (see below), this simple procedure was more than adequate. Rod-rod overlaps were detected using the rod dimensions estimated at Level 1, namely rod length $L = 6.8$ nm and rod diameter $b = 0.79$ nm. From these values, the volume of individual PPIC molecules, considered as cylinders, was $3.33 \times 10^{-27} \text{ m}^3$, so that the volume fraction occupied by the rods was 0.37 and the numeric volumetric concentration was $c = 1.11 \times 10^{26}$. This value can be compared

with the volume concentration at which the isotropic phase is estimated to become unstable:

$$c^* = \frac{16}{\pi d L^2} = 1.39 \times 10^{-26}$$

so the system under consideration was at the boundary between semi-dilute and concentrated. In terms of c^* , the concentration of the system was $c^* = 0.79$. Once polymer molecules were placed in the simulation cell, solvent molecules were introduced one by one using a similar brute force scheme in a first stage. As the filling procedure progressed and density increased, overlaps were progressively more frequent, since, at liquid-like densities, brute force insertion of a molecule as large as toluene had a very low probability. As total system density reached 80% of the final one $\rho = 1174 \text{ kg/m}^3$, insertions of toluene molecules were complemented by a van der Waals radius staged inflation³⁷ which alleviated major overlaps. Initial structure preparation was finalized by energy relaxation via simple Metropolis Monte Carlo and by subsequently performing a full-scale equilibration MD run of 10 ps duration. An integration time step of 1.9 fs was used.

In order to extract the value of the rotary diffusivity in the isotropic phase, an isothermal production MD run was carried out to a total of 5 ns. During the production run, helix orientation and center of mass trajectories were stored periodically for all chains in the system.

Due to the high packing density, helix (rod) mobility was severely hindered. From the two plots included in the next figure (where the 1824 toluene molecules have been omitted for clarity) it is possible to judge the considerable packing density of PPIC helices in the isotropic solution:

Figure 8. Dense PPIC in toluene system. All 57 helices have been represented by semi-transparent cylinders (dots placed on the surface of cylinders) of diameter $b = 0.79$ nm and length $L = 6.8$ nm.

In the left figure, cube edge has been set to 12 nm for representation only and periodic boundary conditions have been suppressed to improve visibility. In the right figure, PPIC rods are folded back into the simulation cell by means of periodic boundary conditions, and cell edge has been set to 8.0 nm. Solvent (toluene) molecules not represented.

Although helix center of mass diffusion had not progressed beyond the rod length, i.e. $\langle (\underline{r}_{c.o.m.}(t) - \underline{r}_{c.o.m.}(0))^2 \rangle < L$. The main result of this extensive calculation is presented in the following two figures (in linear and log scales respectively), which show Einsteinian diffusive behavior of the unit head-to-tail vector at long times. Although it may seem that even longer MD runs would lead to better approximations to D_r , a key result from the GENERIC formalism of non-equilibrium thermodynamics indicates that the MD run is not only adequate, but should not be made any longer³⁶.

Figure 9. Diffusion on unit surface of the tail-to head vector, averaged over all PPIC polymer rods in the system.

The value of the rotary diffusivity obtained from a least squares fit of the long-time behaviour of $\langle (\underline{u}(t) - \underline{u}(0))^2 \rangle$ turns out to be $D_r = 12.7 \times 10^5 (\pm 3.1) \text{ s}^{-1}$.

IV. Viscoelastic flow calculations using CONNFFESSIT for Doi's constitutive equation

At this stage, all parameters required to perform complex viscoelastic flow calculations using CONNFFESSIT³⁸ are available. These parameters are the rotary diffusivity, the temperature and the geometric parameters of the rods (length and diameter). Furthermore, the use of CONNFFESSIT makes it possible to use either an average rotary diffusivity (averaged over the instantaneous molecular orientation distribution) or to apply an orientation-dependent rotary diffusivity.

CONNFFESSIT was used to perform a viscoelastic flow calculation in a complex geometry, namely a 3:1 (ratio of tube radii) or 9:1 (ratio of tube cross sectional areas) axisymmetrical contraction. The calculation was 3D and did not exploit the axial symmetry^b. The objective of the calculation in the contraction geometry, was to solve the equations of mass and momentum conservation for the incompressible and isothermal flow of the PPIC solution in toluene, whose rheological behavior is described by Doi's model. The conservation equations for mass and momentum to be solved are:

$$\begin{aligned} \rho \frac{\partial \underline{v}}{\partial t} + \rho \underline{v} \cdot \underline{\nabla} \underline{v} + \underline{\nabla} p - \underline{\nabla} \cdot \underline{\tau}_p + \eta_s \left(\underline{\nabla} \underline{v} + (\underline{\nabla} \underline{v})^T \right) &= 0 \\ \underline{\nabla} \cdot \underline{v} &= 0 \end{aligned} \quad (11)$$

The stress is seen to contain a Newtonian contribution, due to the toluene solvent, and a non-Newtonian contribution $\underline{\tau}_p$ arising from the presence of polymer molecules, PPIC rigid helices or rods in the present case.

Unlike in purely macroscopic formulations¹⁰, in CONNFFESSIT the polymer contribution to the rheological behavior of the complex fluid is obtained as a function of the local, instantaneous velocity gradient and of the instantaneous configurations of the members (coarse-grained molecules) of ensembles of unit vectors which obey the dynamics (6). In addition, a rule for the calculation of the stress is required, which for Doi's model consists of a Brownian contribution and an excluded volume contribution which can be written in terms of the configurational probability distribution function⁴:

^b the reason for performing what is essentially a 2D calculation in a 3D setting is that for higher values of the strain rate, three dimensional behaviour can emerge even if the initial and boundary conditions are axisymmetric, due to out-of-plane attractors for $\underline{u}$.

$$\underline{\tau}_{=p} = \underline{\tau}_{=p}^B + \underline{\tau}_{=p}^{EV} \quad \left\{ \begin{array}{l} \underline{\tau}_{=p}^B = -\frac{ck_B T}{2} \int \left(\underline{uu} - \frac{1}{3} \underline{\delta} \right) \frac{\partial}{\partial \underline{u}} \cdot \frac{\partial \psi}{\partial \underline{u}} d^2 u \\ \underline{\tau}_{=p}^{EV} = -\frac{ck_B T}{2} \int \left(\underline{uu} - \frac{1}{3} \underline{\delta} \right) \frac{\partial}{\partial \underline{u}} \cdot \psi \frac{\partial}{\partial \underline{u}} \left(\frac{V_{EV}}{k_B T} \right) d^2 u \end{array} \right. \quad (12)$$

In Eq. (12) the integral operation $\int \dots d^2 u$ is equivalent to $\int \dots \sin \theta d\theta d\varphi$ with integration ranges $0 < \theta \leq \pi, 0 < \varphi \leq 2\pi$ ⁷.

The basic idea of CONNFFESSIT is to use a discretization method, such as finite elements, to solve the mass and momentum conservation equations while the polymer contribution to the stress is obtained by averaging the individual contributions of a great many molecules and not from a constitutive equation³⁸⁻⁴². These molecules are entrained by the fluid much as it happens in real flow situations. In addition to their macroscopic degrees of freedom (spatial coordinates), they possess internal degrees of freedom, those of $\underline{u}$, the time evolution of which is governed by the stochastic differential equation (6).

The integration domain for the conservation equations and the stochastic version of the constitutive equation was the 3:1 axisymmetric contraction flow. The flow in this geometry is essentially axisymmetric Poiseuille flow far away upstream and downstream from the contraction, but has a significant extensional component close to the contraction itself. At high values of the strain rate, off-plane attractors for the director lead to loss of axial symmetry. Although the calculations to be presented were performed in a full 3D fashion, this regime was not explored in the present work. The domain was discretized by means of 17453 vertices in 91834 tetrahedra. The resulting mesh is shown in the following figure.

Figure 10. Finite Element mesh for the 3:1 axisymmetric contraction. The mesh contains 17453 vertices and 91834 tetrahedra. Dimensions in 10^{-5} m.

The mesh is refined around the abrupt contraction, as can be observed in the cutaway 3D view of the mesh above.

Figure 11. Refinement of the Finite Element mesh close to the contraction. The view on the left is a transversal section at $z = 0.15$. The section on the right contains the symmetry axis. Dimensions in 10^{-5} m.

In spite of this local refinement, the mesh is still relatively coarse compared with some of the meshes used in macroscopic calculations. Our relatively large element size is dictated primarily by available computational resources. It is also important to keep in mind that, to the best of our knowledge, this is the first time a 3D CONFFESSIT calculation is performed (3D Brownian Configuration Fields⁴³⁻⁴⁵ had been already done by Ramírez and Laso³⁹). Although conceptually identical to 2D calculations, complex flow 3D problems are computationally at the edge of feasibility with present day hardware. To give an idea of the size of the numerical task at hand, the integration domain contained a total of 67108864 (2^{26}) "molecules", i.e. $\underline{U}$ processes, uniformly distributed over the 91834 tetrahedra in which the domain was partitioned. This high number of individual trajectories was required in order to keep the statistical uncertainty in the calculation of the polymer contribution to the stress acceptably low. This is a particularly important concern in Doi's model, since the finite size of the ensemble has a "noise" effect on the determination of the instantaneous value of the rotary diffusivity according to Eq. (2) and of the stresses³.

Initial director vectors for the PPIC rods ("molecules") were chosen to be isotropically distributed in the wide part of the contraction flow and homeotropically distributed in the narrow part of the channel. Boundary conditions at the inlet were parabolic velocity profile and isotropic director distribution at all locations. The inlet flowrate was set at $1.94 \cdot 10^{-13} \text{ m}^3/\text{s}$ (193 pl/s). The characteristic

dimensions of the contraction and the flowrate were chosen as typical of those used in recently developed devices for fluid transport using nanoelectromechanical actuators⁴⁶. Instead of a reference time based on the rotary diffusivity, an apparatus-related reference time scale was defined as the transit time through the domain for a molecule along the centerline and with a constant velocity set at the average inlet value, which leads to $t_{ref} = 1.81 \cdot 10^7$ s. Calculation times and shear rates were made dimensionless using t_{ref} . The inlet radius was taken as the reference length L_{ref} . The dimensionless rotary diffusivity was then $D_r = 0.23$ (all variables in the following are understood to be dimensionless, except where units appear explicitly). Finally a mapping from the Onsager expression for the excluded volume to the Maier-Saupe excluded volume function (see below) based on a simple fit of the integral of the force acting on the atomistic (Level 2) PPIC rods to the Maier-Saupe potential for a perfect parallel alignment, which resulted in a dimensionless Maier-Saupe interaction potential of $U = 14.5 \frac{4}{3} cdL^2 = 7.21$

Selected individual particle trajectories are shown in the next figure. Each individual curve corresponds to the projection of the three-dimensional trajectory of one of the 2^{26} molecules on the plane defined by the symmetry axis and the starting point of the trajectory on the inflow (leftmost) boundary. The effect of statistical noise on the resulting velocity field is clearly seen as wiggles in what should otherwise be smooth trajectories.

This effect is however magnified in the upper figure by the use of different scale factors in the axial and radial axes. In the lower part of the figure a different set of trajectories is depicted and both axes are identically scaled so that the length-width aspect ratio is the real one. In the upper part of the figure it can also be observed that some particle trajectories cross the symmetry axis of the domain and also present loops.

Both of these effects are a consequence of the projection of 3D trajectories on the plane of the figure (although the calculation is fully 3D and does not exploit the symmetry of the domain, in this figure, axes are shown as those of cylindrical coordinates r and z).

Figure 12. Representative individual particle trajectories. Lines are projections of 3D trajectories on the plane defined by the symmetry axis of the domain and the starting point of the trajectory. Loops and axis crossings appear for some trajectories as a consequence of the planar projection.

The field of the velocity modulus $V = \sqrt{v_1^2 + v_2^2 + v_3^2}$ and the pressure field are presented as a shaded surface plots in the next two figures. In both figures, two snapshots at two different times have been overlapped so that the magnitude of fluctuations due to finite ensemble size can be appreciated. Spatial fluctuations at fixed time are visible as differences in shades of gray either at the upper or at the lower half of the plot.

Figure 13. Field of velocity modulus ($V = \sqrt{v_1^2 + v_2^2 + v_3^2}$) represented as shaded surface plot.

Upper and lower halves correspond to two different times $t = 25$ and $t = 30$, both at steady state, in order to show the magnitude of spatial and temporal fluctuations in the velocity field. Molecule trajectories from previous figure have been overlaid.

Figure 14. Pressure (p) field represented as shaded surface plot. Upper and lower halves correspond to two different times $t = 25$ and $t = 30$, both at steady state, in order to show the magnitude of spatial and temporal fluctuations in the pressure field.

Temporal fluctuations are responsible for differences in shading between upper and lower parts of the plot (which correspond to two different times).

Finally, the director field at $t = 10$ is represented as an arrow plot in the next figure. In order to make the visualization of the full 3D field of director vectors as clear as possible, first azimuthal averaging over the entire $[0, 2\pi]$ range was performed in order to obtain a 2D field, which was then smoothed by projection, using a coarse two-dimensional mesh based on quadrangles: if the functional space for $\underline{u} = \langle \underline{U} \rangle$ is denoted F_U , find $\underline{u} \in F_U$ such that for all $\underline{s} \in F_U$ we have:

$$\left(\underline{s}, \underline{u} - \frac{1}{N_t} \sum_{j=1}^{N_t} \underline{U}_j \right) = 0$$

where N_t is the number of trajectories used to build the azimuthal average, and the parentheses imply multiplication by the test function $\underline{s}$ and integration over the domain. For the approximation space F_U discontinuous bilinear polynomials (Q_1) were used. The initially isotropic orientational distribution evolves in the course of the flow development. At $t = 10$ it has given rise to a complex spatial organization in which axially oriented domains seem to be dominant. An in-depth analysis of the dynamic evolution of textures and domains is currently being pursued but will not be dealt with here since the purpose of the present work is to illustrate the scale crossing methodology only and not to investigate texture evolution.

Figure 15. Director field represented at $t = 10$. The area represented is a close-up of the zone around the contraction.

V. Level 4: Orientational distribution function for Doi's model via reduced order modelling

Although powerful and of general validity, the CONNFFESSIT approach applied in the previous section is very computationally intensive, especially for 3D problems. A radically different approach to the calculation of the orientational probability distribution function $\psi(\underline{u}, t)$ will be employed here.

It serves as an independent cross check, and also as the last and most macroscopic level (Level 4) in the hierarchical chain of description of liquid crystal polymers under flow. It is worth recalling that starting from a very detailed, atomistic model of individual polymeric helical chains for PPIC, here we reach the level of description of configurational distribution functions; i.e. even the concept of a highly simplified, coarse-grained stochastic model based on head-to-tail helix vector $\underline{u}$ is superseded by that of a distribution of orientations of such molecules.

The discretization methodology to be applied here is based on a weak formulation of the conservation and constitutive equations, but employs the concept of model reduction⁴⁷. Its basis has been described in detail^{47, 48} and applied to homogeneous flows, i.e. to predicting the evolution of $\psi(\underline{u}, t)$ in a given, spatially uniform velocity gradient field. The key idea behind the reduction method is the use of a

reduced set of basis functions with wide support , such that they constitute the optimal choice for representing the solution at the desired level of detail

It operates extracting automatically, and in a way completely transparent for the user, the most relevant information of the unknown solution for constructing the functional approximation to the macroscopic fields from the information just extracted. The new shape functions (the most characteristic functions related to the model solution) have a large support, i.e. they are defined in the whole domain in an appropriate manner (see below). Thus, the number of degrees of freedom involved in the solution of the Fokker-Planck equation is very significantly reduced. The construction of those new approximation functions is done with an 'a priori' approach, which combines a basis reduction (using the Karhunen-Loève decomposition) with a basis enrichment based on the use of some Krylov subspaces⁴⁹⁻⁵¹.

In order to show the capabilities of the reduction method, we have taken the kinematic results (velocity and velocity gradient fields) of the viscoelastic flow calculation obtained by means of CONNFFESSIT along a selected streamline. Therefore, in the following, the flow kinematics and the microstructure evolution are fully uncoupled, i.e. the PPIC molecules, described by means of $\underline{u}$ in Level 3 and by means of $\psi(\underline{u}, t)$ at the present Level 4, will evolve in a known velocity field which is time and, implicitly, spatially dependent, the known dependence being given by the Lagrangian history of flow along a streamline selected from the solutions to the viscoelastic flow problem computed in Section IV. To this end, the velocity gradient history entering the FP equation along a streamline that starts at $r = 0.025$ (which corresponds to the uppermost or lowermost streamlines plotted in the figures in Section IV) was extracted in the following way: the 3D velocity field was averaged azimuthally over the entire $[0, 2\pi]$ range in order to obtain a 2D field, which was then smoothed by projection, in the same way as it was done for the director field. This reason for doing this projection was that although the calculation was entirely 3D in Cartesian coordinates, all fields remained, except for fluctuations, essentially axisymmetric. Hence, the statistical noise in the solution can be greatly reduced by averaging. For this reason, in the remainder of this Section, the variables r and z will appear in labels, subindices, etc. But it should be kept in mind that the calculation was not performed under the assumption of axial symmetry. Only after projection and smoothing were the variables r and z introduced.

The evolution of the velocity gradient, given by its shear and extensional components along the streamline, is shown in the following two figures, for shear and for extension respectively.

In both of these figures, the origin of time is assigned to the instant when the trajectory reaches the surface that separates the wide and the narrow parts of the domain, i.e. when it reaches $z = 0.15$. Thus, negative times correspond to flow in the wide cylindrical part of the domain, positive times to flow in the narrow part. Hence, the flow along this streamline contains both shear and elongational components in varying proportions. Roughly speaking, there is no appreciable shear until the streamline reaches the narrow portion of the contraction, whereupon shear reaches an almost constant value.

Figure 16. Temporal evolution of the shear component of the velocity gradient along a streamline entering the domain at $y = 0.025$. Negative times correspond to flow in the wide cylindrical part of the domain; positive times to flow in the narrow part (see text).

Elongation however is mostly confined to the part of the flow where the cross section drops abruptly. There is no appreciable extensional component far from this region. Notice also the rather noisy curves for both components of the strain rate tensor.

Figure 17. Temporal evolution of the elongational component of the velocity gradient along a streamline entering the domain at $y = 0.025$. Negative times correspond to flow in the wide cylindrical part of the domain; positive times to flow in the narrow part (see text).

The rate of strain tensor to be used as the input in the calculation of the evolution of $\psi(\underline{u}, t)$ will therefore have the form:

$$\underline{\dot{\gamma}} = \begin{pmatrix} -\frac{1}{2}\dot{\epsilon}_{zz}(t) & 0 & \dot{\gamma}_{rz}(t) \\ 0 & -\frac{1}{2}\dot{\epsilon}_{zz}(t) & 0 \\ \dot{\gamma}_{rz}(t) & 0 & \dot{\epsilon}_{zz}(t) \end{pmatrix} \quad (13)$$

where the time dependences come from the CONNFFESSIT calculation as tabular data and are represented in the two previous figures (r, z labels are used because azimuthal averaging has been performed; calculation and unsmoothed strain rates are of course Cartesian 3D).

V.1. Discretization of the Fokker-Planck equation

In order to solve Eq. (1) for given $\underline{\nabla}\underline{v}$, a natural discretization of this problem defined on the unit surface is based on the use of the spherical polar and azimuthal angles (φ, θ) :

$$\underline{u} = \begin{pmatrix} \cos \varphi \cos \theta \\ \sin \varphi \cos \theta \\ \sin \theta \end{pmatrix} \quad (14)$$

where both angular coordinates are defined in: $\varphi, \theta \in [0, 2\pi[\times [0, \pi]$. However singularities are encountered at the ends of the θ definition interval, because of the

term $\frac{D_r}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2}$ in the polar expression of the Fokker-Planck equation. Moreover,

this kind of discretization requires an explicit imposition of the periodicity condition. Thus, it was chosen to work in Cartesian coordinates, where the surface of the unit sphere is approximated by a set of planar triangular facets. The nodal coordinates of the vertices of these triangles are given by:

$$\underline{u}_i = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} \quad (15)$$

which satisfy $\sqrt{x_i^2 + y_i^2 + z_i^2} = 1$, and where the natural periodicity is implicitly verified.

Integrating Eq. (1) along the streamlines where the kinematics history, that is $\underline{v}(t)$, is known, that equation can be rewritten in the following form that only involves the conformation (orientation) coordinates and time:

$$\frac{\partial \psi}{\partial t} + E_0(\underline{u})\psi + \underline{E}_1^T(\underline{u}) \frac{\partial \psi}{\partial \underline{u}} - D_r \frac{\partial^2 \psi}{\partial \underline{u}^2} + H_0(\underline{u}, \underline{S})\psi + \underline{H}_1^T(\underline{u}, \underline{S}) \frac{\partial \psi}{\partial \underline{u}} = 0 \quad (16)$$

where $\psi(t, \underline{u}) = \psi(\underline{x}(t), t, \underline{u})$ and $\underline{x}(t) = \underline{x}(t=0) + \int_0^t \underline{v}(t') dt'$. The two scalar

functions $E_0(\underline{u})$, $H_0(\underline{u}, \underline{S})$ as well as the two vector fields $\underline{E}_1(\underline{u})$, $\underline{H}_1(\underline{u}, \underline{S})$ can be easily deduced from the equation (1). We denote by Ω the domain in configuration space where equation (16) is defined, namely the two dimensional manifold spanned by the unit orientation vector $\underline{u}$, i.e. the surface of the unit sphere.

First, the problem is formulated in the Finite Element framework using a weighting function ψ^* :

$$\begin{aligned} \int_{\Omega} \psi^* \frac{\partial \psi}{\partial t} d\underline{u} + \int_{\Omega} \psi^* E_0(\underline{u}) \psi d\underline{u} + \int_{\Omega} \psi^* \underline{E}_1^T(\underline{u}) \frac{\partial \psi}{\partial \underline{u}} d\underline{u} \\ - \int_{\Omega} \psi^* D_r \frac{\partial^2 \psi}{\partial \underline{u}^2} d\underline{u} + \int_{\Omega} \psi^* H_0(\underline{u}, \underline{S}) \psi d\underline{u} + \int_{\Omega} \psi^* \underline{H}_1^T(\underline{u}, \underline{S}) \frac{\partial \psi}{\partial \underline{u}} d\underline{u} = 0 \end{aligned} \quad (17)$$

The computational domain Ω (in configuration space) is partitioned into a collection of non-overlapping finite elements (triangular facets covering the surface of the unit sphere). A linear and continuous interpolation of the distribution function is then built in each triangle, from which:

$$\psi^e(\underline{u}) = \sum_{i=1}^3 N_i(\underline{u}) \psi_i^e$$

and $\psi^{e*}(\underline{u}) = \sum_{i=1}^3 N_i(\underline{u}) \psi_i^{e*}$ where ψ_i^e and ψ_i^{e*} are the values at node i of ψ

and ψ^* respectively, and $N_i(\underline{u})$ is the associated shape function which takes a unit value at the node i vanishing at the other nodal positions.

Integrating equation (17) by parts and taking into account that the configuration space for $\underline{u}$ is unbounded, we obtain:

$$\begin{aligned} \int_{\Omega} \psi^* \frac{\partial \psi}{\partial t} d\underline{u} + \int_{\Omega} \psi^* E_0(\underline{u}) \psi d\underline{u} + \int_{\Omega} \psi^* \underline{E}_1^T(\underline{u}) \frac{\partial \psi}{\partial \underline{u}} d\underline{u} \\ + \int_{\Omega} \left(\frac{\partial \psi^*}{\partial \underline{u}} \right)^T D_r \frac{\partial \psi}{\partial \underline{u}} d\underline{u} + \int_{\Omega} \psi^* H_0(\underline{u}, \underline{S}) \psi d\underline{u} + \int_{\Omega} \psi^* \underline{H}_1^T(\underline{u}, \underline{S}) \frac{\partial \psi}{\partial \underline{u}} d\underline{u} = 0 \end{aligned}$$

Due to the advection-diffusion character of that equation, an appropriate stabilization of the Finite Element scheme is needed to avoid numerical instabilities induced by the convection term. Stabilization is achieved by using a SUPG formulation, which modifies the weighting functions related to the advection term $\overline{\psi^*}$ as described later. The stabilized variational formulation results in:

$$\begin{aligned} & \int_{\Omega} \psi^* \frac{\partial \psi}{\partial t} d\underline{u} + \int_{\Omega} \psi^* E_0(\underline{u}) \psi d\underline{u} + \int_{\Omega} \bar{\psi}^* \underline{E}_1^T(\underline{u}) \frac{\partial \psi}{\partial \underline{u}} d\underline{u} \\ & + \int_{\Omega} \left(\frac{\partial \psi^*}{\partial \underline{u}} \right)^T Dr \frac{\partial \psi}{\partial \underline{u}} d\underline{u} + \int_{\Omega} \psi^* H_0(\underline{u}, \underline{\underline{S}}) \psi d\underline{u} + \int_{\Omega} \bar{\psi}^* \underline{H}_1^T(\underline{u}, \underline{\underline{S}}) \frac{\partial \psi}{\partial \underline{u}} d\underline{u} = 0 \end{aligned}$$

where in each element $\bar{\psi}^{e*}(\underline{u}) = \sum_{i=1}^3 \bar{N}_i(\underline{u}) \psi_i^{e*}$ with $\bar{N}_i(\underline{u}) = N_i(\underline{u}) + \frac{\beta h}{2} \frac{\partial N_i(\underline{u})}{\partial \underline{u}}$

where h is the characteristic element size and β is the upwinding parameter given by

$$\beta = \coth(Pe) - \frac{1}{Pe}$$

where the Peclet number Pe is given by

$$Pe = \frac{\max(\|\underline{E}_1(\underline{u})\|, \|\underline{H}_1(\underline{u}, \underline{\underline{S}})\|) h}{2D_r}$$

In order to construct $E_0(\underline{u})$ and $H_0(\underline{u}, \underline{\underline{S}})$ the differential operators must be projected on the plane tangent to the unit sphere. The required gradient projection is as follows: if we consider a triangular facet defined by its three vertices: (x_1, y_1, z_1) , (x_2, y_2, z_2) , (x_3, y_3, z_3) reference coordinates (ξ, η) can be defined using an isoparametric geometrical interpolation:

$$\begin{aligned} x &= \sum_{i=1}^3 N_i(\xi, \eta) x_i \\ y &= \sum_{i=1}^3 N_i(\xi, \eta) y_i \\ z &= \sum_{i=1}^3 N_i(\xi, \eta) z_i \end{aligned}$$

We denote by $\underline{e}_1$ and $\underline{e}_2$ two vectors defined in the plane containing the triangle, which can be expressed as:

$$\underline{e}_1 = \begin{pmatrix} \frac{\partial x}{\partial \xi} \\ \frac{\partial y}{\partial \xi} \\ \frac{\partial z}{\partial \xi} \end{pmatrix} = \begin{pmatrix} \frac{\partial \left(\sum_{i=1}^3 N_i x_i \right)}{\partial \xi} \\ \frac{\partial \left(\sum_{i=1}^3 N_i y_i \right)}{\partial \xi} \\ \frac{\partial \left(\sum_{i=1}^3 N_i z_i \right)}{\partial \xi} \end{pmatrix} \quad \underline{e}_2 = \begin{pmatrix} \frac{\partial x}{\partial \eta} \\ \frac{\partial y}{\partial \eta} \\ \frac{\partial z}{\partial \eta} \end{pmatrix} = \begin{pmatrix} \frac{\partial \left(\sum_{i=1}^3 N_i x_i \right)}{\partial \eta} \\ \frac{\partial \left(\sum_{i=1}^3 N_i y_i \right)}{\partial \eta} \\ \frac{\partial \left(\sum_{i=1}^3 N_i z_i \right)}{\partial \eta} \end{pmatrix}$$

The relation between the gradient in the Cartesian coordinates and the one expressed on the manifold tangent to the unit sphere is given by⁵²:

$$\begin{pmatrix} \frac{\partial \psi^e}{\partial x} \\ \frac{\partial \psi^e}{\partial y} \\ \frac{\partial \psi^e}{\partial z} \end{pmatrix} = (\underline{e}_1 \quad \underline{e}_2) \begin{pmatrix} \underline{e}_1^T \underline{e}_1 & \underline{e}_1^T \underline{e}_2 \\ \underline{e}_2^T \underline{e}_1 & \underline{e}_2^T \underline{e}_2 \end{pmatrix}^{-1} \begin{pmatrix} \frac{\partial \psi^e}{\partial \xi} \\ \frac{\partial \psi^e}{\partial \eta} \end{pmatrix}$$

where

$$\psi^e = \sum_{i=1}^3 N_i(\xi, \eta) \psi_i^e$$

and the matrix $\begin{pmatrix} \underline{e}_1^T \underline{e}_1 & \underline{e}_1^T \underline{e}_2 \\ \underline{e}_2^T \underline{e}_1 & \underline{e}_2^T \underline{e}_2 \end{pmatrix}$ contains the elements of the metric tensor $\underline{\underline{g}}$

corresponding to a given triangular facet. Note that the required properties of differentiability, symmetry, non-singularity and positive-definiteness are satisfied by construction in Cartesian coordinates.

As it is usual in the FEM framework, after numerical integration and assembling of element contributions the following non-linear system is obtained:

$$\underline{\underline{M}} \underline{\dot{\psi}} + (\underline{\underline{G}} + \underline{\underline{H}}(\underline{\psi})) \underline{\psi} = 0$$

The non-linearity follows from the dependence of the nematic potential on the average of the distribution function itself on the unit sphere. When one uses an explicit time discretization technique, the non-linear system can be linearized by considering the nematic potential calculated at the previous time step.

V.2. Model Reduction

In this section the ideas described by Ammar et al.⁴⁷ are applied to the discrete problem resulting from the discretization of the Fokker-Planck equation that governs the evolution of the configuration distribution.

We consider that the probability distribution have been accurately described in the time interval $[0, t_\alpha]$. We assume that at time $t_\beta > t_\alpha$ the reduced approximation basis is given by $\underline{\underline{B}}^{(n)}$. The i, j -component of $\underline{\underline{B}}$ represents the value at node i of the j -th eigenvector ($j \in [1, r^{(n)}]$). Moreover, at certain times $t_p, p \in [1, \dots, P], t_p = t_\alpha$, the solution is assumed properly computed and defined by the reduced vectors $\underline{a}_p^{(n)}$. Knowing $\underline{a}_p^{(n)}$, the finite element description of ψ at time t_p results: $\underline{\psi}_p = \underline{\underline{B}}^{(n)} \underline{a}_p^{(n)}$. We can assume that the first approximation basis $\underline{\underline{B}}^{(0)}$ contains a single vector that corresponds to the initial probability distribution $\underline{\psi}_0$.

Now, we can compute the evolution of ψ in $[t_\alpha, t_\beta]$ solving the explicit system:

$$\underline{\psi}_{t+\Delta t} = \underline{\underline{M}}^{-1} \left(\underline{\underline{M}} - \Delta t \left(\underline{\underline{G}} + \underline{\underline{H}}(\underline{\psi}_t) \right) \right) \underline{\psi}_t$$

that can be written in the reduced approximation basis as:

$$(\underline{\underline{B}}^{(n)})^T \underline{\underline{B}}^{(n)} \underline{a}_{t+\Delta t}^{(n)} = (\underline{\underline{B}}^{(n)})^T \underline{\underline{M}}^{-1} \left(\underline{\underline{M}} - \Delta t \left(\underline{\underline{G}} + \underline{\underline{H}}(\underline{\underline{B}}^{(n)} \underline{a}_t^{(n)}) \right) \right) \underline{\underline{B}}^{(n)} \underline{a}_t^{(n)}$$

which results in:

$$\underline{a}_{t+\Delta t}^{(n)} = \left((\underline{\underline{B}}^{(n)})^T \underline{\underline{B}}^{(n)} \right)^{-1} (\underline{\underline{B}}^{(n)})^T \underline{\underline{M}}^{-1} \left(\underline{\underline{M}} - \Delta t \left(\underline{\underline{G}} + \underline{\underline{H}}(\underline{\underline{B}}^{(n)} \underline{a}_t^{(n)}) \right) \right) \underline{\underline{B}}^{(n)} \underline{a}_t^{(n)} \quad (18)$$

In order to conclude about the solution accuracy at time t_β we compute the residual according to:

$$\underline{R}_\beta = \underline{\underline{B}}^{(n)} \underline{a}_{t_\beta+\Delta t}^{(n)} - \underline{\underline{M}}^{-1} \left(\underline{\underline{M}} - \Delta t \left(\underline{\underline{G}} + \underline{\underline{H}}(\underline{\underline{B}}^{(n)} \underline{a}_{t_\beta}^{(n)}) \right) \right) \underline{\underline{B}}^{(n)} \underline{a}_{t_\beta}^{(n)}$$

If $\|\underline{R}_\beta\| < \varepsilon$, we can put $t_\alpha = t_\beta$ and continue the solution of the evolution problem in the reduced approximation basis $\underline{\underline{B}}^{(n)}$ for $t \geq t_\alpha$. When $\|\underline{R}_\beta\| > \varepsilon$ we need to look for a smaller time t_β ($t_\alpha + \frac{t_\beta - t_\alpha}{2} = t_\beta$) such that $\|\underline{R}_\beta\| < \varepsilon$ after a new solution of the evolution problem in $[t_\alpha, t_\beta]$. If the residual criterion is still

unsatisfied when $t_\beta - t_\alpha$ becomes smaller than the time step Δt , then we set $t_{p+1} = t_\alpha$ and proceed to an enrichment of the approximation basis.

The new reduced approximation basis $\underline{\underline{B}}^{(n+1)}$ is defined by adding to the significant information extracted from $\underline{a}_p^{(n)}$, $\forall p$ ($p \leq P+1$), some Krylov subspaces. The construction of $\underline{\underline{B}}^{(n+1)}$ proceeds as follows:

We define the matrix $\underline{\underline{Q}}$ containing the reduced vectors $\underline{a}_p^{(n)}$, $\forall p \leq \alpha$ and we solve the eigenvalue problem defined by:

$$\underline{\underline{Q}}\underline{\underline{Q}}^T \underline{\phi} = \mu \underline{\phi}$$

whose solution results in $r^{(n)}$ couples $(\underline{\phi}_k, \mu_k)$, where we assume that $\mu_1 \geq \mu_2 \cdots \geq \mu_{r^{(n)}}$. We select the $\tilde{r}^{(n+1)}$ eigenvectors $\underline{\phi}_k$ related to the eigenvalues verifying $\mu_k > 10^{-8} \mu_1$, and these eigenvectors define the matrix $\underline{\underline{V}}$ of $(r^{(n)} \times \tilde{r}^{(n+1)})$. Now we can write

$$\underline{\underline{\tilde{B}}}^{(n+1)} = (\underline{\underline{B}}^{(n)} \underline{\underline{V}})$$

Obviously, the change in the reduced approximation basis implies a change in the expression of the reduced vectors $\underline{a}_p^{(n)}$, $\forall p$. For this purpose we can write

$$\underline{\underline{\tilde{B}}}^{(n+1)} \underline{\tilde{a}}_p^{(n+1)} = \underline{\underline{B}}^{(n)} \underline{a}_p^{(n)}$$

from which it results

$$(\underline{\underline{\tilde{B}}}^{(n+1)})^T \underline{\underline{\tilde{B}}}^{(n+1)} \underline{\tilde{a}}_p^{(n+1)} = (\underline{\underline{\tilde{B}}}^{(n+1)})^T \underline{\underline{B}}^{(n)} \underline{a}_p^{(n)}$$

or

$$\underline{\tilde{a}}_p^{(n+1)} = \left((\underline{\underline{\tilde{B}}}^{(n+1)})^T \underline{\underline{\tilde{B}}}^{(n+1)} \right)^{-1} (\underline{\underline{\tilde{B}}}^{(n+1)})^T \underline{\underline{B}}^{(n)} \underline{a}_p^{(n)}, \forall p$$

Now, we can add to $\underline{\underline{\tilde{B}}}^{(n+1)}$ a number N_{new} ($N_{new} = 3$ in the present work) of Krylov subspaces defined at time t_β :

$$\underline{\underline{B}}^{(n+1)} = (\underline{\underline{\tilde{B}}}^{(n+1)}, \underline{R}_\beta, \underline{\underline{K}} \underline{R}_\beta, \underline{\underline{K}}^2 \underline{R}_\beta)$$

where the matrix $\underline{\underline{K}}$ is defined by:

$$\underline{\underline{K}} = \frac{1}{\Delta t} \underline{\underline{M}} + \left(\underline{\underline{G}} + \underline{\underline{H}} (\underline{\underline{B}}^{(n)} \underline{a}_t^{(n)}) \right)$$

The introduction of the Krylov's subspaces implies a new change in the expression of the reduced vectors $\tilde{\underline{a}}_p^{(n+1)}$. For this purpose we add to those N_{new} new vectors components that are assumed initially null because the new approximation functions just introduced operate only for $t > t_p$. Thus we can write:

$$\left(\tilde{\underline{a}}_p^{(n+1)}\right)^T = \left(\left(\underline{a}_p^{(n)}\right)^T, 0, 0, 0\right); \forall p$$

The algorithm just presented can be summarized in pseudocode as follows:

$$t = t_\alpha = 0 ,$$

$$t_\beta = t_\alpha + \tau \quad (\tau \gg \Delta t; t_\beta \leq T)$$

While $t_\alpha < T$

While $t_\beta - t_\alpha > \Delta t$

Compute the evolution of the reduced variables in $[t_\alpha, t_\beta]$

Update the matrix H at each iteration

If $\left\|\underline{R}(t = t_\beta)\right\| < 0.001$ *then:*

$$\delta = t_\beta - t_\alpha$$

$$t_\alpha = t_\beta$$

$$t_\beta = t_\alpha + 2\delta$$

If $\left\|\underline{R}(t = t_\beta)\right\| > 0.001$ *then:*

$$\delta = t_\beta - t_\alpha$$

$$t_\alpha = t_\alpha$$

$$t_\beta = t_\alpha + \frac{\delta}{2}$$

Karhunen-Loève expansion in $[0, t_\alpha]$

Basis enrichment using Krylov's subspaces related to the residual at t_β

$$t_\beta = t_\alpha + \tau$$

V.3. *Orientational distribution function and order parameter along a streamline*

The reduction scheme just presented was applied to obtain the dynamic evolution of $\psi(\underline{u}, t)$ along a streamline starting at $r = 0.025$. In accordance with the boundary conditions imposed in the CONNFESSIT calculation, the initial orientational distribution was set to isotropic on the unit sphere:

$\psi(\underline{u}, t = 0) = (1/4\pi)\delta(|\underline{u}| - 1)$. Instead of the Onsager form for the interaction potential, Eq. (9) the Maier-Saupe form⁵³ was assumed:

$$V_{EV}(\underline{u}) = -\frac{3}{2}Uk_B T(\underline{uu} : \underline{\underline{S}}) \quad (19)$$

where U is a dimensionless interaction potential and the second order traceless symmetric orientation tensor $\underline{\underline{S}}$ is defined by:

$$\underline{\underline{S}} = \langle \underline{uu} \rangle - \frac{1}{3}\delta_{\underline{\underline{S}}} \quad (20)$$

where the averaging $\langle \rangle$ is done with the instantaneous value of the orientational distribution function:

$$\langle \underline{uu} \rangle = \int (\underline{uu})\psi(\underline{u}, t) d\underline{u} \quad (21)$$

A scalar orientational order parameter S associated with the second order tensor $\underline{\underline{S}}$ is defined by:

$$S = \sqrt{\frac{3}{2}\underline{\underline{S}} : \underline{\underline{S}}} \quad (22)$$

S is a useful measure of the average degree of orientation, since it takes the value 0 in the isotropic phase, the value of 1 in a situation where all rods are perfectly aligned and intermediate values in the nematic phase. In addition, in this Section a constant value of the rotary diffusivity D_r was employed. The use of (19) instead of (3) for the excluded volume interaction, and of constant D_r instead of (2) for the rotary diffusivity represent two simplifications, so that no perfect agreement can be expected between the results obtained by integrating (1) along a streamline by model reduction and the CONNFESSIT results. The simplifications however are not so drastic as to make the comparison meaningless, as will be seen below. A more sophisticated treatment by reduction, in which the more general forms for the excluded volume interaction and for the rotary diffusivity are used is also possible and constitutes work in progress. From a numerical point of view, this can be done using a fixed point strategy in the framework of an explicit algorithm.

For the calculation by model reduction, a mesh of 2560 nodes on the unit sphere was used. It is important to emphasize that this size of the mesh is also the size of the sparse linear system that would have to be solved at each iteration when using a semi-implicit finite element technique, in contrast with the dense but very small size of the system to be solved when using model reduction. This is a very attractive feature of model reduction and is of course a consequence of the use of very few characteristic functions (typically, a few tens) in order to represent the whole temporal evolution of the distribution function when using model reduction. In this

particular calculation, the number of significant functions used is approximately 20 (according to the criterion of 10^{-7} for the ratio between the contributions of the least significant and the most significant one)

The evolution of $\psi(\underline{u}, t)$ along the selected streamline is presented in the following figures as a sequence of snapshots of a colour surface plot on the unit sphere.

Figure 18. Surface plot of $\psi(\underline{u}, t)$ at $t = -10.0$.

Figure 19. Surface plot of $\psi(\underline{u}, t)$ at $t = -5.0$.

Figure 20. Surface plot of $\psi(\underline{u}, t)$ at $t = -0.9$.

Figure 21. Surface plot of $\psi(\underline{u}, t)$ at $t = -0.35$.

Figure 22. Surface plot of $\psi(\underline{u}, t)$ at $t = 0.0$.

Figure 23. Surface plot of $\psi(\underline{u}, t)$ at $t = 0.7$.

Figure 24. Surface plot of $\psi(\underline{u}, t)$ at $t = 10.0$.

This series of snapshots nicely shows how starting from an isotropic distribution, $\psi(\underline{u}, t)$ becomes sharply peaked along the flow direction (z). In the next figure, the orientational order parameter is presented as a function of time.

Figure 25. Scalar order parameter as a function of time.

Starting from the initial isotropic state, and due almost exclusively to shear flow close to the tube wall, S rapidly climbs from 0 to about 0.8 and stays at that level until the streamline approaches the sudden contraction (which happens at $t = 0$). At that point, the velocity field departs from pure shear and develops an appreciable extensional component, the competition of the two deformation mechanisms initially leads to a decrease in order and then to a sequence of oscillations before settling on a final value of around 0.7 in the narrow part of the domain.

Figure 26. The scalar order parameter as a function of time. The extensional and shear components of the velocity gradient as a function of time have also been included. The abscissa axes of the three plots are properly scaled, so that the vertical dashed lines join simultaneous values of S , $\dot{\gamma}$ and $\dot{\epsilon}$.

The evolution of $\psi(\underline{u}, t)$ and of the scalar order parameter along the streamline closely follow the history of the strain rate tensor, as can be seen in the previous figure. A note of caution is however necessary: although a sharp peak in the extensional component of the rate of strain at the contraction ($t = 0$) is a physically correct feature of the flow field, the sharp oscillations around the peak are very

probably an artifact caused by insufficient mesh resolution and statistically noise in the CONNFFESSIT calculation, imposed by available computational resources. Hence, the oscillations of the order parameter around $t = 0$ must to some extent be attributed to this artifact. Besides, the simplifications in rotary diffusivity and in excluded volume made in the reduced model, make this figure of qualitative value only.

VI. Conclusions

Starting from an atomistically detailed description of the LC-forming poly-(*n*-propyl isocyanate) PPIC, a sequence of coarse-graining steps have been performed in order to obtain a macroscopic description of a PPIC solution in toluene which can be employed in viscoelastic flow calculations. The two first levels of description reside at the atomistic level and differ only in a computationally convenient reduction of the number of degrees of freedom through the introduction of holonomic constraints. The jump to the Level 3 description represents a major reduction in the detail of the description, so that the $O(10^5)$ degrees of freedom in Level 1 are reduced to only two mesoscopic parameters describing the rotary diffusivity of PPIC helices (considered as rigid rods) and the entropic excluded volume interaction between rods via purely geometric parameters and not in a fully thermodynamically consistent way.

These parameters are then used in the framework of Doi's model for LCP's to perform a complex viscoelastic flow calculation in a three dimensional 3:1 (9:1 cross section area ratio) cylindrical contraction using CONNFFESSIT.

Finally, the use of a model reduction technique was demonstrated by integrating the Fokker-Planck equation, which controls the dynamic evolution of $\psi(\underline{u}, t)$, along a streamline for which the history of the strain rate had been calculated with CONNFFESSIT.

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