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Abstract

Main-chain liquid crystalline polymers (LCPs) are used to produce strong fibers due to their ability to form highly-ordered orientational states. For sufficiently long chains it is known that loss of entropy in such highly-ordered states is partly recovered by the formation of so-called hairpins or kinks. The presence of hairpins not only modifies the microstructure of LCPs, but it has also been conjectured that hairpins influence their macroscopic mechanical behavior. In this paper the influence of hairpins on the rheological properties of concentrated solutions of LCPs is studied.

Keywords: Rouse model, LCP, hairpins, stress tensor

1   Introduction

The ability of liquid crystalline polymers (LCPs) to form highly-ordered orientational states with extraordinary mechanical properties explains why LCPs are industrially used to produce strong fibres and are the subject of numerous studies in academic circles. LCPs, as all high-molecular weight polymers, show many characteristic timescales in their relaxation behavior where short respectively large timescales are to be associated with relaxation of small respectively large parts of the chain. The largest relaxation time is related to the relaxation of the chain as a whole and dominates its macroscopic behavior. This fact justifies the success of approaches in which only the longest relaxation time is taken into account [1]. For isotropic solutions of flexible polymers, therefore, theories based on rather coarse representations of the chain microstructure adequately describe the relaxation behavior of these systems. Examples of such theories are the Rouse- and Zimm models of unentangled polymer liquids and the reptation model of entangled polymer liquids. The situation with solutions of LCPs, however, is much more complicated due to the fact that the persistence length of the chains is not negligible compared to their contour length. The persistence length is the distance along the chain over which orientational correlations persist. This leads to an anisotropic equilibrium state and a dependence of the distribution function on the nematic order parameter. Moreover, there exist several different classes of LCPs having a different chain microstructure such as main-chain and side-chain LCPs. Nevertheless, it is very useful to develop simplified models of LCP solution dynamics that only depend on a few microstructural parameters and allow one to study the effect of these parameters on the macroscopic properties of the LCP solutions in detail.

One of the most studied model of this type is the Doi rigid-rod model [2], [3], [4], [5]. The rigid-rod model, as its name suggests, neglects flexibility altogether and is applicable to LCPs for which the persistence length is of the same order as the chain length. In general, however, LCPs of sufficient length (molecular weight) are semi-flexible and hence form an intermediate case between that of rigid rods and completely flexible polymers. Consequently, models for semi-flexible LCPs were developed starting from both extremes. Either by extending the applicability of models for

flexible polymers [1] or by relaxing the rigid constraint in the rigid-rod model by introducing the so-called slightly bending rod model [6], [7], [8].

For sufficiently long main-chain LCPs in highly-ordered orientational states it was de Gennes [9] who suggested that the loss of entropy would be partly recovered by the formation of so-called hairpins or kinks. The aim of the current work is to adopt the model of the Rouse-chain to describe the influence of hairpins on the rheological properties of solutions of highly-ordered semi-flexible LCPs in simple types of flow.

In the papers of the other authors the formation and dynamics of hairpins is also discussed [10].

2 Rouse-like model with hairpins

2.1 Microscopic model

In this section we will describe our model for a solution of main-chain LCPs containing hairpins. Each polymer chain is modeled as a sequence of $N + 1$ rigid rods, which we will call nematogens or beads, connected by N flexible springs (see fig. 1). In reality main-chain LCPs are semi-flexible and will have some persistence length. This is reflected in the model via the parameter l - the length of each of the beads. The springs connecting the rods reflect the partial flexibility of the chains. These springs are usually called "entropy springs", because of the nature of their elasticity. This elasticity is due to configurational entropy and not to stretching of chemical bonds. In thermal equilibrium at a given temperature and pressure a flexible chain segment tends to have a specific average end-to-end distance, an equilibrium property. If the segment is now distorted, then due to thermal motion it will evolve back to this equilibrium state. This means that if the end-to-end distance of the segment is increased beyond its equilibrium value, then it will tend to shrink back. The nematogens, joined to the ends of such a flexible segment will therefore experience a force acting on them. This force is modeled by these "entropy springs".
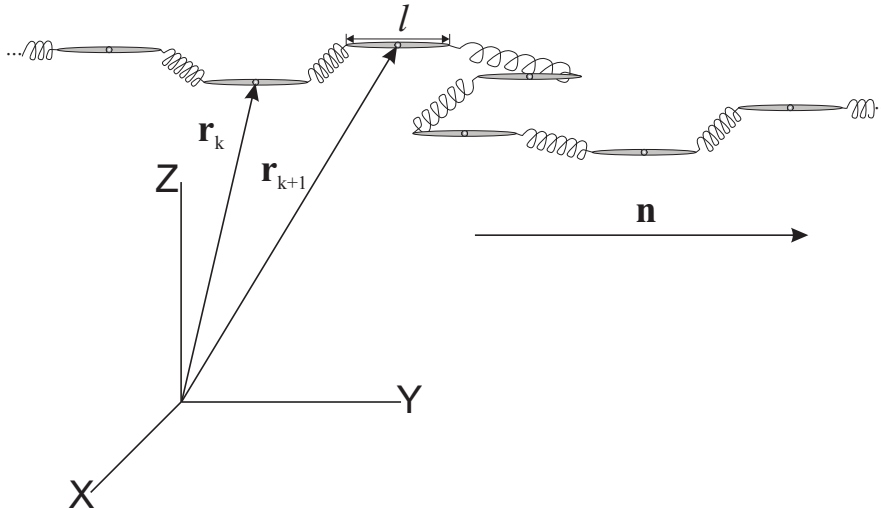

Figure 1: The chain of nematogens when strong nematic ordering takes place. $\mathbf{n}$ - director, $\mathbf{r}_k$ - vector of center mass position for k-th nematogen, l - the length of the nematogen

The above model is not only capable of describing main-chain LCPs where rigid and flexible segments actually form an alternating sequence along the chain, but also LCPs that have a more uniform structure in which the semi-flexibility manifests itself via a resistance to bending (worm-like chain behavior). In the rest of this paper we will assume that the beads are highly aligned by the nematic interaction in a given direction referred to as nematic director $\mathbf{n}$ and hence that the orientation of the individual beads will only slightly deviate from this direction. This assumption is valid in a so-called monodomain nematic phase. Hairpins in this model are described as flipped configurations of nematogens (see fig. 2, b, c). As nematogens have a so-called fore-aft or head-tail symmetry, the nematic interaction energy does not distinguish between a nematogen oriented along $\mathbf{u}$ or along $-\mathbf{u}$. It is clear however that the elastic energy associated with hairpin configurations (see fig. 2, b, c) is larger than that associated with a normal configuration (see fig. 2, a). Finally, we will assume that the chains are unentangled with one another. In that case it suffices to restrict the description to the behavior of a single chain.

We are interested in the behavior on timescales of the order of the relaxation time for a whole chain configuration. This timescale is much greater then the timescale associated with the orientation relaxation of single beads. The angular variables $\mathbf{u}$ are therefore socalled fast variables

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and in the further analysis of the model we discard intermediate configurations of the nematogen between the hairpin and the normal state. The potential energy of a polymer chain consists of two parts, an elastic and a nematic contribution.

$$U = U_{elastic} + U_{nematic} \tag{1}$$

The nematic interaction will be considered in the usual mean field way. The minimum of the nematic energy, taken to be zero, is when a bead is oriented along the director. This means that the expansion of the nematic potential energy in small deviations of the bead orientation $\delta\mathbf{u}$ from the director $\mathbf{n}$ should be quadratic in $\delta\mathbf{u}$. So

$$U_{nematic} \approx \frac{H_0|\delta\mathbf{u}|^2}{2} \tag{2}$$

For small deviations it holds that $\delta\mathbf{u} \perp \mathbf{n}$. The coefficient H_0 acts as the strength of the nematic field. This result can easily be derived from the fact that the orientations of the nematogens only slightly deviate from the director and by taking the nematic interaction to be of the Maier-Saupe form. The elastic energy of a polymer chain is given by

$$U_{elastic} = \frac{1}{2}k_0 \sum_{m=1}^{N-1} |\mathbf{b}(m)|^2 \tag{3}$$

where k_0 is the stiffness of the springs and $\mathbf{b}(m)$ is the vector connecting the end of m-th bead to the beginning of the $(m+1)$-th bead. This connector vector can be expressed in terms of the unit orientation vectors $\mathbf{u}(m)$ and $\mathbf{u}(m+1)$ of the m-th and $(m+1)$-th bead, respectively, via

$$\mathbf{b}(m) = \mathbf{r}(m+1) - \mathbf{r}(m) - \frac{1}{2}l(\mathbf{u}(m+1) + \mathbf{u}(m)) \tag{4}$$

In a strong nematic field $\frac{1}{2}(\mathbf{u}(m+1) + \mathbf{u}(m))$ will take up only three values.

$$\frac{1}{2}(\mathbf{u}(m+1) + \mathbf{u}(m)) = \left\{ \begin{array}{ll} \mathbf{u}, & case\ a \\ 0, & case\ b \\ -\mathbf{u}, & case\ c \end{array} \right. \tag{5}$$

with $\mathbf{u} \approx \mathbf{n}$. The corresponding configurations of the beads are shown in figure 2. In that figure the normal configuration corresponds to case a), the single hairpin to case b) and the "double-hairpin" to case c). To further simplify the model we will assume that case c) does not occur. The argument for this choice is that, if the density of the hairpins is low, the probability for a double hairpin to occur is much smaller than that of a single hairpin. We therefore assume

$$\frac{1}{2}(\mathbf{u}(m+1) + \mathbf{u}(m)) = \left\{ \begin{array}{ll} \mathbf{u}, & case\ a \\ 0, & case\ b \end{array} \right. \tag{6}$$

Figure 2: Three types of possible configurations of the neighboring nematogens. a). $\frac{1}{2}(\mathbf{u}(m+1) + \mathbf{u}(m)) = \mathbf{n}$; b). $\frac{1}{2}(\mathbf{u}(m+1) + \mathbf{u}(m)) = \vec{0}$; c). $\frac{1}{2}(\mathbf{u}(m+1) + \mathbf{u}(m)) = -\mathbf{n}$.

In view of expression (6) it is convenient to introduce a new stochastic variable s, that can only have two values and indicates the presence or absence of a hairpin, i.e.

$$s = \left\{ \begin{array}{ll} 1, & case\ a \\ 0, & case\ b \end{array} \right. \tag{7}$$

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Let's further introduce $\Delta\mathbf{r}(m) = \mathbf{r}(m+1) - \mathbf{r}(m)$. Then (4) becomes

$$\mathbf{b}(m, s(m)) = \Delta\mathbf{r}(m) - ls(m)\mathbf{u}(m) \tag{8}$$

The distribution function for this variable s will be taken to be a Gibbs distribution. This is justified by the assumption that $\mathbf{u}$ is a fast variable, because on the timescale in which the orientation of the beads equilibrates, the center of mass positions of the beads almost will not change. Therefore the following derivation is valid if the angular relaxation times of the beads are much smaller then the longest conformational relaxation time of the chain as a whole, the so-called (longest) Rouse time. If we now denote the energy to form a hairpin by E_h, then the expression for the distribution function of s becomes

$$w(s) = \begin{cases} \frac{1}{1+\exp(-\frac{E_h}{T})}, & s = 1 \\ \frac{\exp(-\frac{E_h}{T})}{1+\exp(-\frac{E_h}{T})}, & s = 0 \end{cases} \tag{9}$$

To simplify the notation we will write w_s instead of $w(s)$. The hairpin energy follows from the difference between the elastic energy of a spring in the presence of a hairpin and a spring in a normal configuration. From (3) we easily obtain

$$\begin{aligned} E_h &= \frac{k_0}{2}\left(|\mathbf{b}(m, s=0)|^2 - |\mathbf{b}(m, s=1)|^2\right) \\ &= k_0 l\left(\Delta\mathbf{r}(m) \cdot \mathbf{u}(m)\right) - \frac{k_0 l^2}{2} \end{aligned} \tag{10}$$

This result shows that in general the energy of a hairpin depends on the vector that connects the centers of mass of the neighboring nematogens that are involved in the hairpin. Such a dependence will introduce a nonlinearity into the stochastic formulation of the problem in terms of a Langevin equation (see next section). This is why we will treat E_h, instead, in a self-consistent way, i.e. we will consider E_h to be a constant that follows from the consistency condition

$$E_h = k_0 l\langle\Delta\mathbf{r}(m) \cdot \mathbf{u}(m)\rangle - \frac{k_0 l^2}{2} \tag{11}$$

If hairpins are only built into the polymer at the stage of polymerization, i.e. when the flow is not strong enough to create new hairpins or destroy existing ones, then E_h is the difference in chemical interaction energy between the hairpin state and the normal configuration. T in expression (9) will then be given by the temperature at which polymerization takes place. By combining (2), (3), (8) with $\mathbf{u}(m) = \mathbf{n}(m) + \delta\mathbf{u}(m)$ the expression for the total potential energy of a single chain can be written as

$$U = \sum_{m=1}^{N}\left[\frac{H_0}{2}|\delta\mathbf{u}(m)|^2 + \frac{k_0}{2}\left(\Delta\mathbf{r}(m) - ls(m)\mathbf{n}(m) - ls(m)\delta\mathbf{u}(m)\right)^2\right] \tag{12}$$

From this potential energy we can calculate the Helmholtz free energy per chain, via

$$F = -T\ln\left(\int\prod_{m=1}^{N}d\mathbf{u}(m)\exp\left(-\frac{U}{T}\right)\right) \tag{13}$$

If we now substitute (12) into (13) and use the result that $\exp(\sum_m a_m) = \prod_m \exp(a_m)$ we obtain

$$F = -T\sum_{m=1}^{N}\ln\int d\mathbf{u}(m)\exp\left(-\frac{1}{T}\left(\frac{H_0}{2}|\delta\mathbf{u}(m)|^2 + \frac{k_0}{2}\left(\Delta\mathbf{r}(m) - ls(m)\mathbf{n}(m) - ls(m)\delta\mathbf{u}(m)\right)^2\right)\right) \tag{14}$$

The integral should be taken over the unit sphere, as $\mathbf{u}(m)$ is a unit vector. However, in the limit of strong nematic order, the integration over the unit sphere can be replaced by an integration

over the two-dimensional vector $\delta\mathbf{u}$ that lies in the tangent plane orthogonal to $\mathbf{n}$. Of course for large $\delta\mathbf{u}$ this tangent plane deviates considerably from the unit sphere, but due to the fast decay of the exponential integrand those regions hardly make a contribution to the integral. Performing this integration then leads to

$$F = \frac{1}{2} \sum_{m=1}^{N} \left(k_0 \left(\Delta r_\parallel(m) - ls(m) \right)^2 + \frac{k_0 H_0}{H_0 + k_0 l^2 s^2} \left(\Delta r_\perp(m) \right)^2 \right) \tag{15}$$

It is convenient to introduce the following two elastic constants

$$k_\parallel \equiv k_0 \tag{16}$$

$$k_\perp(s) \equiv \frac{k_0 H_0}{H_0 + k_0 l^2 s^2} \tag{17}$$

or, by making use of $s^2 \equiv s$, rewrite this last expression as

$$\frac{1}{k_\perp(s)} = \frac{1}{k_0} + s \frac{1}{H_0 l^{-2}} \tag{18}$$

Notice that $k_\perp(0) = k_\parallel$. For later use we will denote $k_\perp(1)$ by $k_\perp$. From (18) it immediately follows that $k_\parallel \geq k_\perp(s)$. (15) can thus be written as

$$F\left[\Delta\mathbf{r}, \mathbf{n}, s\right] = \frac{1}{2} \sum_{m=1}^{N} \left(k_\parallel \left(\Delta r_\parallel(m) - ls(m) \right)^2 + k_\perp(s(m)) \left(\Delta r_\perp(m) \right)^2 \right) \tag{19}$$

Finally, to obtain the free energy that only depends on the slow variables we have to average over the set of fast variables $\{s(m), 1 \leq m \leq N\}$. Notice that we may take each $\Delta\mathbf{r}(m)$ to be a constant when we perform this average and that each term in (19) can be averaged separately. The fact that each $s(m)$ is a fast variable means that during the interval $\tau_{fast} \ll t \ll \tau_{Rouse}$ each spring will switch many times between a normal and a hairpin state. Hence, if we average the contribution to the free energy from the m-th spring over this time interval we get

$$\langle F_m\left[\Delta\mathbf{r}, \mathbf{n}, s\right] \rangle_{\tau_{fast} \ll t \ll \tau_{Rouse}} = w_1 F_m\left[\Delta\mathbf{r}(m), 1\right] + w_0 F_m\left[\Delta\mathbf{r}(m), 0\right] \tag{20}$$

By the ergodic hypothesis this time average is equal to an average over the ensemble generated by the set $\{s(m), 1 \leq m \leq N\}$. Thus, after summing over all the springs we find

$$\langle F\left[\Delta\mathbf{r}, \mathbf{n}, s\right] \rangle_s = w_1 F\left[\Delta\mathbf{r}(m), 1\right] + w_0 F\left[\Delta\mathbf{r}(m), 0\right] \tag{21}$$

which in a continuous formulation becomes

$$\langle F\left[\mathbf{r}, \mathbf{n}, s\right] \rangle_s = w_0 \frac{1}{2} k_\parallel \int_0^N dm \left(\frac{\partial r}{\partial m} \right)^2 + w_1 \frac{1}{2} \int_0^N dm \left(k_\parallel \left(\frac{\partial r_\parallel}{\partial m} - l \right)^2 + k_\perp \left(\frac{\partial r_\perp}{\partial m} \right)^2 \right) \tag{22}$$

In the sequel we will denote $\langle F\left[\mathbf{r}, \mathbf{n}, s\right] \rangle_s$ by $F\left[\mathbf{r}, \mathbf{n}\right]$. The resulting Rouse-like free energy (22) describes a chain containing hairpins in the limit of strict nematic order. The hairpins are thereby accounted for in an averaged manner. One readily recognizes that this free energy interpolates between the free energy of a directed LCP and that of a anisotropic Gaussian chain.

In the next section we will formulate the dynamics of such a chain because it is the rheological behavior that we are ultimately interested in. For this we will use the language of Langevin equations as the remaining slow variables characterising the configurations of the chain are subject to noise originating from the solvent degrees-of-freedom and the chain's fast variables that were eliminated from the description. Also we will derive an expression for the stress tensor on the basis of the well-known Kramers-Kirkwood formula.

2.2 Derivation of the Langevin equation

We will assume that the chains are subject to an imposed homogeneous flow field whose local velocity is described by a possibly time-dependent rate-of-deformation or velocity gradient tensor $\boldsymbol{\kappa}$, i.e.

$$\mathbf{v}(\mathbf{r}) \equiv \boldsymbol{\kappa} \cdot \mathbf{r} \tag{23}$$

The Langevin equation describing the dynamics of a chain on the so-called Brownian time-scale follows from a balance between frictional drag, entropy elasticity and noise. The frictional drag force acting on bead m of the chain is given by

$$\mathbf{f}_{drag}(m) \equiv -\boldsymbol{\zeta}(\mathbf{n}) \cdot \left(\frac{\partial \mathbf{r}(m)}{\partial t} - \boldsymbol{\kappa} \cdot \mathbf{r}(m) \right) \tag{24}$$

where

$$\boldsymbol{\zeta}(\mathbf{n}) = \zeta_{\parallel} \mathbf{nn} + \zeta_{\perp} (\mathbf{I} - \mathbf{nn}) \tag{25}$$

is an anisotropic friction tensor. The frictional drag on a chain is anisotropic because the beads are modeled by rigid rods, which themselves have anisotropic frictional properties. The elastic force on bead m is related to the elastic free energy $F[\mathbf{r}, \mathbf{n}]$ (22) via

$$\mathbf{f}_{elas}(m) \equiv -\frac{\delta F[\mathbf{r}, \mathbf{n}]}{\delta \mathbf{r}(m)} \tag{26}$$

On the Brownian time-scale the sum of both these forces will be balanced by a force $\mathbf{f}(m, t)$ related to the noise in the system. From this balance we obtain the following Langevin equation

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot \left(\frac{\partial \mathbf{r}(m)}{\partial t} - \boldsymbol{\kappa} \cdot \mathbf{r}(m) \right) = -\frac{\delta F[\mathbf{r}, \mathbf{n}]}{\delta \mathbf{r}(m)} + \mathbf{f}(m, t) \tag{27}$$

This Brownian stochastic force $\mathbf{f}(m, t)$ is assumed to have white noise characteristics, i.e.

$$\langle \mathbf{f}(m, t) \rangle = 0 \tag{28}$$

$$\langle \mathbf{f}(m, t) \mathbf{f}(m', t') \rangle = 2\boldsymbol{\zeta}(\mathbf{n}) T \delta(m - m') \delta(t - t') \tag{29}$$

where T is the temperature in energy units.

In the previous section we found that this elastic free energy $F[\mathbf{r}, \mathbf{n}]$ appearing in in (26) consists of two contributions

$$F[\mathbf{r}, \mathbf{n}] = w_0 F_0[\mathbf{r}, \mathbf{n}] + w_1 F_1[\mathbf{r}, \mathbf{n}] \tag{30}$$

with

$$F_0[\mathbf{r}, \mathbf{n}] = \frac{1}{2} k_{\parallel} \int_0^N dm \left(\frac{\partial r(m)}{\partial m} \right)^2 \tag{31}$$

and

$$F_1[\mathbf{r}, \mathbf{n}] = \frac{1}{2} \int_0^N dm \left(k_{\parallel} \left(\frac{\partial r_{\parallel}(m)}{\partial m} - l \right)^2 + k_{\perp} \left(\frac{\partial r_{\perp}(m)}{\partial m} \right)^2 \right) \tag{32}$$

If we now introduce the following two auxilliary elasticity tensors

$$\mathbf{K}_0 = k_{\parallel} \mathbf{I} \tag{33}$$

$$\mathbf{K}_1 = k_{\parallel} \mathbf{nn} + k_{\perp} (\mathbf{I} - \mathbf{nn}) \tag{34}$$

we can write these two contributions as

$$F_0\left[\mathbf{r}, \mathbf{n}\right] = \frac{1}{2}\int\limits_0^N dm \frac{\partial \mathbf{r}(m)}{\partial m} \cdot \mathbf{K}_0 \cdot \frac{\partial \mathbf{r}(m)}{\partial m} \tag{35}$$

and

$$F_1\left[\mathbf{r}, \mathbf{n}\right] = \frac{1}{2}\int\limits_0^N dm \left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1 \cdot \left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) \tag{36}$$

To evaluate the variational derivative of $F\left[\mathbf{r}, \mathbf{n}\right]$ consider first the variation of $F_1\left[\mathbf{r}, \mathbf{n}\right]$, i.e. $\delta_{\mathbf{r}}F_1\left[\mathbf{r}, \mathbf{n}\right] \equiv F_1\left[\mathbf{r} + \delta\mathbf{r}, \mathbf{n}\right] - F_1\left[\mathbf{r}, \mathbf{n}\right]$

$$\delta_{\mathbf{r}}F_1\left[\mathbf{r}, \mathbf{n}\right] = \frac{1}{2}\int\limits_0^N dm \left(\frac{\partial \delta\mathbf{r}(m)}{\partial m} \cdot \mathbf{K}_1 \cdot \left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) + \left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1 \cdot \frac{\partial \delta\mathbf{r}(m)}{\partial m}\right) \tag{37}$$

Because of the symmetry of $\mathbf{K}_1$ both terms in the variation are equal, hence

$$\delta_{\mathbf{r}}F_1\left[\mathbf{r}, \mathbf{n}\right] = \int\limits_0^N dm \left(\left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1 \cdot \frac{\partial \delta\mathbf{r}(m)}{\partial m}\right) \tag{38}$$

If we now integrate by parts we obtain

$$\delta_{\mathbf{r}}F_1\left[\mathbf{r}, \mathbf{n}\right] = \left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1 \cdot \delta\mathbf{r}(m)\Big|_0^N - \int\limits_0^N dm \left(\frac{\partial^2 \mathbf{r}(m)}{\partial m^2} \cdot \mathbf{K}_1 \cdot \delta\mathbf{r}(m)\right) \tag{39}$$

From this last expression we immediately obtain the variation of $F_0\left[\mathbf{r}, \mathbf{n}\right]$ by changing $\mathbf{K}_1$ to $\mathbf{K}_0$ and putting l to 0, i.e.

$$\delta_{\mathbf{r}}F_0\left[\mathbf{r}, \mathbf{n}\right] = \frac{\partial \mathbf{r}(m)}{\partial m} \cdot \mathbf{K}_0 \cdot \delta\mathbf{r}(m)\Big|_0^N - \int\limits_0^N dm \left(\frac{\partial^2 \mathbf{r}(m)}{\partial m^2} \cdot \mathbf{K}_0 \cdot \delta\mathbf{r}(m)\right) \tag{40}$$

The variation of $F\left[\mathbf{r}, \mathbf{n}\right]$ therefore becomes

$$\delta_{\mathbf{r}}F\left[\mathbf{r}, \mathbf{n}\right] = \left(w_0\frac{\partial \mathbf{r}(m)}{\partial m} \cdot \mathbf{K}_0 + w_1\left(\frac{\partial \mathbf{r}(m)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1\right) \cdot \delta\mathbf{r}(m)\Big|_0^N -$$

$$- \int\limits_0^N dm \frac{\partial^2 \mathbf{r}(m)}{\partial m^2} \cdot \left(w_0\mathbf{K}_0 + w_1\mathbf{K}_1\right) \cdot \delta\mathbf{r}(m) \tag{41}$$

The boundary terms must vanish because if they would be present then the force on bead m due to entropy elasticity and nematic interactions would depend on the positions of the chain ends and hence be non-local. Therefore this gives rise to the following two conditions for $\frac{\partial \mathbf{r}}{\partial m}$ at each end of the chain

$$w_0\frac{\partial \mathbf{r}(0)}{\partial m} \cdot \mathbf{K}_0 + w_1\left(\frac{\partial \mathbf{r}(0)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1 = 0 \tag{42}$$

$$w_0\frac{\partial \mathbf{r}(N)}{\partial m} \cdot \mathbf{K}_0 + w_1\left(\frac{\partial \mathbf{r}(N)}{\partial m} - l\mathbf{n}\right) \cdot \mathbf{K}_1 = 0 \tag{43}$$

and hence to

$$
\begin{aligned}
\frac{\partial \mathbf{r}(0)}{\partial m} &= l w_1 \left(w_0 \mathbf{K}_0 + w_1 \mathbf{K}_1\right)^{-1} \cdot \mathbf{K}_1 \cdot \mathbf{n} \\
&= \frac{w_1}{w_0 + w_1} l \mathbf{n} \\
&\equiv l' \mathbf{n}
\end{aligned}
\tag{44}
$$

and similarly

$$
\frac{\partial \mathbf{r}(N)}{\partial m} = l' \mathbf{n}
\tag{45}
$$

These boundary conditions can easily be understood in the limit of $w_0 \longrightarrow 0$. In that case when there are no hairpins present, the nematogens at the chain ends will be completely oriented along the director, i.e. $\frac{\partial \mathbf{r}(0)}{\partial m} = \frac{\partial \mathbf{r}(N)}{\partial m} = l \mathbf{n}$. However, in the more general case when the chain contains hairpins, in particular near the chain ends, this apparently leads to a kind of partial orientation of these end nematogens, i.e. $\frac{\partial \mathbf{r}(0)}{\partial m} = \frac{\partial \mathbf{r}(N)}{\partial m} = l' \mathbf{n}$ with $l' < l$.

Now, as the variational derivative $\frac{\delta F}{\delta \mathbf{r}(m)}$ is defined through $\delta_\mathbf{r} F[\mathbf{r}, \mathbf{n}] \equiv \int\limits_0^N dm \frac{\delta F}{\delta \mathbf{r}(m)} \cdot \delta \mathbf{r}(m)$,

we readily obtain from (41) that

$$
\begin{aligned}
\frac{\delta F}{\delta \mathbf{r}(m)} &= -\left(w_0 \mathbf{K}_0 + w_1 \mathbf{K}_1\right) \cdot \frac{\partial^2 \mathbf{r}(m)}{\partial m^2} \\
&\equiv -\mathbf{K} \cdot \frac{\partial^2 \mathbf{r}(m)}{\partial m^2}
\end{aligned}
\tag{46}
$$

With the help of (33) and (34) this effective elasticity tensor $\mathbf{K} \equiv \mathbf{K}(\mathbf{n})$ can be written in the form

$$
\mathbf{K}(\mathbf{n}) \equiv k'_\parallel \mathbf{nn} + k'_\perp (\mathbf{I} - \mathbf{nn}) \equiv k_\parallel \mathbf{nn} + (k_\perp + w_0(k_\parallel - k_\perp))(\mathbf{I} - \mathbf{nn})
\tag{47}
$$

This all leads to the following explicit Langevin equation for the chain dynamics including the appropriate boundary conditions and characteristics of the stochastic force

$$
\begin{cases}
\boldsymbol{\zeta}(\mathbf{n}) \cdot \left(\frac{\partial \mathbf{r}}{\partial t} - \boldsymbol{\kappa} \cdot \mathbf{r}(m)\right) = \mathbf{K}(\mathbf{n}) \cdot \frac{\partial^2 \mathbf{r}(m)}{\partial m^2} + \mathbf{f}(m, t) \\
\frac{\partial \mathbf{r}(0)}{\partial m} = l' \mathbf{n} \\
\frac{\partial \mathbf{r}(N)}{\partial m} = l' \mathbf{n} \\
\langle \mathbf{f}(m, t) \rangle = 0 \\
\langle \mathbf{f}(m, t) \mathbf{f}(m', t') \rangle = 2\boldsymbol{\zeta}(\mathbf{n}) T \delta(m - m') \delta(t - t')
\end{cases}
\tag{48}
$$

To conclude, the presence of hairpins leads in the model to a modification of the entropy elastic constants and the persistence length of the chain in comparison to the case without hairpins.

2.3   Solution by normal mode expansion

The Langevin equation we derived in the previous section (48) is in fact a stochastic partial differential equation. In general such equations are difficult to analyse and "exact" solutions or "exact" methods to obtain such solutions are very rare. However, if we assume that the director $\mathbf{n}$ is fixed in space and time, as is the case for instance in a homogeneous elongational (see furtheron), then this Langevin equation is linear in $\mathbf{r}$ and it is possible to construct an "exact" solution in the form of a normal mode expansion. The idea behind this method is that any motion of the chain can be described as a superposition of independent motions of a particular form, the so-called normal modes. Let ϕ_p be the function corresponding to the p-th normal mode. To find the explicit form of this function we multiply the Langevin equation (48) by $\phi_p(m)$ and integrate over m along the entire chain. If we now introduce the following quantities

$$\mathbf{r}_p(t) \equiv \int_0^N dm\, \mathbf{r}(m,t)\, \phi_p(m) \tag{49}$$

$$\mathbf{f}_p(t) \equiv \int_0^N dm\, \mathbf{f}(m,t)\, \phi_p(m) \tag{50}$$

$$\boldsymbol{\tau}^{-1}(\mathbf{n}) \equiv \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{K}(\mathbf{n}) \tag{51}$$

$$\boldsymbol{\tau}^{-1}(\mathbf{n}) \equiv \frac{1}{\tau_\parallel}\mathbf{nn} + \frac{1}{\tau_\perp}(\mathbf{I} - \mathbf{nn}) \tag{52}$$

we readily obtain

$$\frac{\partial \mathbf{r}_p}{\partial t} = \boldsymbol{\kappa} \cdot \mathbf{r}_p + \boldsymbol{\tau}^{-1}(\mathbf{n}) \cdot \left(\phi_p \frac{\partial \mathbf{r}}{\partial m}\Big|_0^N - \mathbf{r}\frac{\partial \phi_p}{\partial m}\Big|_0^N + \int_0^N dm \mathbf{r}(m)\frac{\partial^2 \phi_p}{\partial m^2} \right) + \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{f}_p(t) \tag{53}$$

In order for the normal modes to be independent, it is necessary that the functions ϕ_p are a solution of the following eigenproblem

$$\begin{cases} \frac{\partial^2 \phi_p}{\partial m^2} = -k_p^2 \phi_p \\ \frac{\partial \phi_p(m=0)}{\partial m} = 0 \\ \frac{\partial \phi_p(m=N)}{\partial m} = 0 \end{cases} \tag{54}$$

These solutions or eigenfunctions are given by
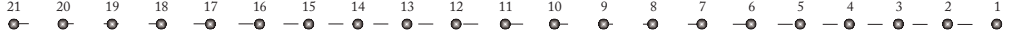
$$\phi_p(m) = \cos(k_p m) \tag{55}$$

with
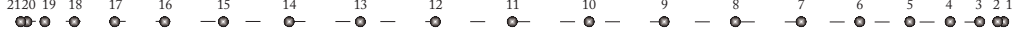
$$k_p \equiv \frac{\pi p}{N} \tag{56}$$

and $p \in (1, 2, 3, ..., N)$. N is the number of nematogens in the chain. So here the normal mode expansion coincides with the (cosine) Fourier series of the function $\mathbf{r}(.,t)$. Formally the number of eigenfunctions is infinite, but the eigenfunctions ϕ_p for $p > N$ correspond to deformations of the chain on scales smaller than l the size of the rigid nematogens. From the mathematical perspective these modes are inconsistent with the assumptions of the model and hence they should be absent in the description. From the point of view of physics, however, they are not forbidden but they will typically be too energetic to be excited during flow. Therefore we will represent $\mathbf{r}(m,t)$ by a normal mode expansion with a finite number of terms, i.e.

$$\mathbf{r}(m,t) = l' m \mathbf{n} + \frac{1}{N}\mathbf{r}_0(t) + \frac{2}{N}\sum_{p=1}^N \mathbf{r}_p(t)\cos(k_p m) \tag{57}$$
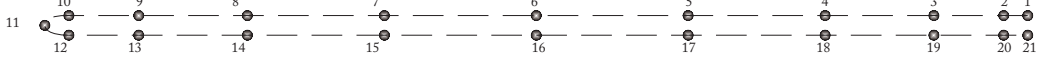
The unperturbed chain with a uniform distribution of bead centers.

21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

mode $p = 1$.
2120 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

mode $p = 2$.
10 9   8   7   6   5   4   3   2 1
11
12 13 14 15 16 17 18 19 20 21

mode $p = 3$.
7   6   5   4   3   2   1
8   9   10 11 12 13 14
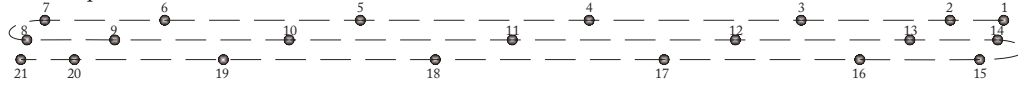21 20 19 18 17 16 15

Figure 3: Configuration of the bead centers corresponding to modes $p = 1, 2, 3$

It is instructive to show which bead configuration correspond to a given normal mode. In fig.3 some of these configurations are shown.

Substituting now (44), (45), (54) and (55) into (53) gives the following Langevin equation for the $p - th$ normal mode:

$$\tfrac{\partial}{\partial t}\mathbf{r}_p + \left(k_p^2 \boldsymbol{\tau}^{-1}(\mathbf{n}) - \boldsymbol{\kappa}\right) \cdot \mathbf{r}_p = -\left(1 - (-1)^p\right) l' \boldsymbol{\tau}^{-1}(\mathbf{n}) \cdot \mathbf{n} + \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{f}_p(t) \tag{58}$$

The properties of the random force $\mathbf{f}_p(t)$ in (58), in particular its time average and its two-time correlation function, can be easily obtained from its definition (50), the orthogonality of the $\{\phi_p\}$ and the properties of the real-space Brownian force $\mathbf{f}(m,t)$, (28) and (29).

$$\langle \mathbf{f}_p(t) \rangle = \left\langle \int_0^N dm\, \phi_p(m)\mathbf{f}(m,t) \right\rangle = \int_0^N dm\, \phi_p(m) \langle \mathbf{f}(m,t) \rangle = 0 \tag{59}$$

$$
\begin{aligned}
\langle \mathbf{f}_p(t)\mathbf{f}_{p'}(t') \rangle &= \left\langle \int_0^N dm \int_0^N dm'\, \phi_p(m)\phi_{p'}(m')\mathbf{f}(m,t)\,\mathbf{f}(m',t') \right\rangle \\
&= \int_0^N dm \int_0^N dm'\, \phi_p(m)\phi_{p'}(m') \langle \mathbf{f}(m,t)\,\mathbf{f}(m',t') \rangle \\
&= \int_0^N dm \int_0^N dm'\, \phi_p(m)\phi_{p'}(m') 2\boldsymbol{\zeta}(\mathbf{n})\, T\delta(m - m')\,\delta(t - t') \\
&= \int_0^N dm\, \phi_p(m)\phi_{p'}(m) 2\boldsymbol{\zeta}(\mathbf{n})\, T\delta(t - t') = N\boldsymbol{\zeta}(\mathbf{n})\, T\delta(t - t')\,\delta_{pp'} \tag{60}
\end{aligned}
$$

Now we will make the assumption that the director $\mathbf{n}$ is to be considered as a parameter in this last equation. In that case (58) becomes a linear inhomogeneous first order stochastic

ordinary differential equation. If the operator $\boldsymbol{\tau}_p(t)$ commutes with itself for all moments of time, then the solution can formally be written as

$$\frac{d}{dt}\mathbf{r}_p + \boldsymbol{\tau}_p^{-1}\mathbf{r}_p = \mathbf{v}_p^* \tag{61}$$

where $\mathbf{v}_p^*$ - is an additional rate of change of $\mathbf{r}_p$ due to the action of the stochastic force and the mean-field nematic and elastic interactions. The formal solution of this equation, subject to the initial condition $\mathbf{r}_p(0) = \mathbf{C}_p$, is given by

$$\mathbf{r}_p(t) = \exp\left(-\boldsymbol{\tau}_p^{-1}(t,0)t\right) \cdot \mathbf{C}_p + \int_0^t dt' \, \exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')(t-t')\right) \mathbf{v}_p^*(t') \tag{62}$$

where

$$\boldsymbol{\tau}_p^{-1}(t,t') \equiv k_p^2 \boldsymbol{\tau}^{-1}(\mathbf{n}) - \boldsymbol{\kappa}^*(t,t') \tag{63}$$

and

$$\boldsymbol{\kappa}^*(t,t') \equiv \frac{1}{t-t'} \int_{t'}^t \boldsymbol{\kappa}(t^*)dt^* \tag{64}$$

By directly inverting (63) we obtain

$$\boldsymbol{\tau}_p(t,t') = \frac{\boldsymbol{\tau}(\mathbf{n})}{k_p^2} \cdot \left[\mathbf{I} - \frac{\boldsymbol{\kappa}^*(t,t') \cdot \boldsymbol{\tau}(\mathbf{n})}{k_p^2}\right]^{-1} \tag{65}$$

Substituting

$$\mathbf{v}_p^*(t') \equiv -\left(1-(-1)^p\right)l'\boldsymbol{\tau}^{-1}(\mathbf{n}) \cdot \mathbf{n} + \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{f}_p(t') \tag{66}$$

into (62) gives

$$\begin{aligned}
\mathbf{r}_p(t) &= \exp\left(-\boldsymbol{\tau}_p^{-1}(t,0)t\right) \cdot \mathbf{C}_p + \\
&\int_0^t dt' \, \exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')(t-t')\right) \cdot \left[-\left(1-(-1)^p\right)l'\boldsymbol{\tau}^{-1}(\mathbf{n}) \cdot \mathbf{n} + \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{f}_p(t')\right]
\end{aligned} \tag{67}$$

From equation (67) it immediately follows that the average of $\mathbf{r}_p(t)$ is given by

$$\langle \mathbf{r}_p(t) \rangle = \exp\left(-\boldsymbol{\tau}_p^{-1}(t,0)t\right) \cdot \mathbf{C}_p - \int_0^t dt' \, \exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')(t-t')\right) \cdot \left(1-(-1)^p\right)l'\boldsymbol{\tau}^{-1}(\mathbf{n}) \cdot \mathbf{n} \tag{68}$$

Important remark should be made at this point. The solution can be represented this way only if $\boldsymbol{\tau}_p^{-1}(t,t')$ commutes with itself for different moments of time t,t'. This might not be the case for shear flow, because the orientation of director changes. But for elongational flow director aligns along the direction of elongation. For this case the exponent of operator $\boldsymbol{\tau}_p^{-1}(t,t')$ makes sense and (68) represents the solution of (58).

2.4 Derivation of the equation for director

In this section we derive the equation for the director dynamics. This equation is needed to close the set of equations of motion of a chain. The idea in the ground of this derivation is next: the free energy of the entire system should be minimized with respect to variations $\delta\mathbf{n}$ orthogonal to $\mathbf{n}$, i.e. $\delta\mathbf{n}\cdot\mathbf{n}=0$. The free energy of the system can be computed as the product of number of chains times the average free energy per chain. The function $F[\mathbf{r},\mathbf{n}]$ discussed above gives the free energy per chain for a given configuration of chains backbone. To get average free energy per chain we should average this function with respect to all possible backbone configurations. The minimization should be done under the condition that average configuration of the backbone of the chains is fixed. If we will take into account that $F_0[\mathbf{r},\mathbf{n}]$ is completely isotropic, then instead of $F[\mathbf{r},\mathbf{n}]$ we can consider $F_1[\mathbf{r},\mathbf{n}]$ from (30)

$$\delta_{\mathbf{n}}\langle F_1\rangle = \langle F_1[\mathbf{r},\mathbf{n}+\delta\mathbf{n}]\rangle - \langle F_1[\mathbf{r},\mathbf{n}]\rangle =$$

$$=\int_0^N dm\,\left\langle -l\delta\mathbf{n}\cdot\mathbf{K}_1(\mathbf{n})\cdot\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right)\right\rangle + \frac{1}{2}\int_0^N dm\,\left\langle\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right)\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right):\delta\mathbf{K}_1(\mathbf{n})\right\rangle$$

Here we used that the tensor of elasticity is symmetrical. Now we employ next two relations to get the equation for $\mathbf{n}$.

$$\delta\mathbf{K}_1 = \left(k_\parallel - k_\perp\right)\left(\mathbf{n}\delta\mathbf{n}+\delta\mathbf{n}\mathbf{n}\right) \tag{69}$$

$$\delta\mathbf{n}\cdot\mathbf{K}_1 = k_\perp\delta\mathbf{n} \tag{70}$$

Then,

$$\delta_{\mathbf{n}}\langle F_1\rangle = \int_0^N dm\,\left\langle -lk_\perp\delta\mathbf{n}\cdot\frac{\partial\mathbf{r}}{\partial m}\right\rangle + \frac{1}{2}\int_0^N dm\,\left\langle\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right)\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right):\delta\mathbf{K}_1(\mathbf{n})\right\rangle \tag{71}$$

$$\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right)\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right):\delta\mathbf{K}(\mathbf{n}) = \left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right)\left(\frac{\partial\mathbf{r}}{\partial m}-l\mathbf{n}\right):(k_\parallel-k_\perp)\left(\mathbf{n}\delta\mathbf{n}+\delta\mathbf{n}\mathbf{n}\right)=$$

$$= 2(k_\parallel-k_\perp)\left(\frac{\partial\mathbf{r}}{\partial m}\frac{\partial\mathbf{r}}{\partial m}:\mathbf{n}\delta\mathbf{n}-l\frac{\partial\mathbf{r}}{\partial m}\cdot\delta\mathbf{n}\right) \tag{72}$$

Finally we get the expression for $\delta_{\mathbf{n}}F_1$ (with the use of $\delta\mathbf{n}\cdot\mathbf{n}=0$). The condition for director is:

$$\delta_{\mathbf{n}}\langle F_1\rangle = (k_\parallel-k_\perp)\int_0^N dm\,\left\langle\frac{\partial\mathbf{r}}{\partial m}\frac{\partial\mathbf{r}}{\partial m}\right\rangle:\mathbf{n}\delta\mathbf{n}-lk_\parallel\int_0^N dm\,\left\langle\frac{\partial\mathbf{r}}{\partial m}\right\rangle\cdot\delta\mathbf{n}=0 \tag{73}$$

This equation is the same as $(\vec{s}\cdot\delta\mathbf{n})=0$. Comparing it with the condition for variations to be orthogonal to $\mathbf{n}$ we come to a conclusion, that $\vec{s}\parallel\mathbf{n}$. Consequently,

$$(k_\parallel-k_\perp)\int_0^N dm\,\left\langle\frac{\partial\mathbf{r}}{\partial m}\frac{\partial\mathbf{r}}{\partial m}\right\rangle\cdot\mathbf{n}-lk_\parallel\int_0^N dm\,\left\langle\frac{\partial\mathbf{r}}{\partial m}\right\rangle=\lambda\mathbf{n} \tag{74}$$

This is an eigenvector problem for nonlinear operator $\mathbf{A}(\mathbf{n})$

$$\mathbf{A}(\mathbf{n})\cdot\mathbf{n}=\lambda\mathbf{n} \tag{75}$$

where

$$\mathbf{A}(\mathbf{n}) = (k_\parallel-k_\perp)\int_0^N dm\,\left\langle\frac{\partial\mathbf{r}}{\partial m}\frac{\partial\mathbf{r}}{\partial m}\right\rangle - lk_\parallel\int_0^N dm\,\left\langle\frac{\partial\mathbf{r}}{\partial m}\right\rangle\mathbf{n} \tag{76}$$

For further use it would be convenient to write the derivative of $\mathbf{r}(m)$ in terms of normal modes expansion

$$\frac{\partial \mathbf{r}(m)}{\partial m} = -\frac{2}{N} \sum_{p=1}^{N} k_p \mathbf{r}_p \sin(k_p m) \tag{77}$$

Therefore

$$\int_0^N dm \, \frac{\partial \mathbf{r}(m)}{\partial m} = -\frac{2}{N} \sum_{p=1}^{N} (1 - (-1)^p) \, \mathbf{r}_p \tag{78}$$

$$\int_0^N dm \, \frac{\partial \mathbf{r}(m)}{\partial m} \frac{\partial \mathbf{r}(m)}{\partial m} = \frac{2}{N} \sum_{p=1}^{N} k_p^2 \mathbf{r}_p \mathbf{r}_p \tag{79}$$

Previous two results allow to simplify the expression for operator $\mathbf{A}(\mathbf{n})$

$$\mathbf{A}(\mathbf{n}) = \frac{2}{N} \sum_{p=1}^{N} \left[(k_\parallel - k_\perp) k_p^2 \langle \mathbf{r}_p \mathbf{r}_p \rangle + (1 - (-1)^p) \, l k_\parallel \langle \mathbf{r}_p \rangle \mathbf{n} \right] \tag{80}$$

This equation describes the dynamics of the director. For example, in the instance of the elongation flow it claims that the director should align along the eigen direction of flow gradient operator with the maximum eigenvalue.

2.5 Derivation of the stress tensor

The stress tensor $\boldsymbol{\sigma}$ in the solutions of the liquid crystalline polymers (LCP) consists of two parts: the stress tensor of the solvent $\hat{\sigma}_s$ and the stress tensor of the polymer beads $\hat{\sigma}_b$ in the solution. In the concentrated regime the main input in the stress tensor is due to the second term. In this section we will to calculate it by Kramers-Kirkwood formula

$$\boldsymbol{\sigma}_b = -\frac{1}{V} \sum_s \langle \mathbf{F}_s \mathbf{r}_s \rangle \tag{81}$$

here summation is done by the beads inside the volume V, $\mathbf{f}_s$ is the force acting on the bead with number s by other beads without the hydrodynamic force, $\mathbf{r}_s$ is the position of bead s. Averaging is made by all realizations of the process. In the case of continuous Rouse-like model formula (81) transforms into

$$\boldsymbol{\sigma}_b = -\frac{N_{ch}}{V} \int\limits_0^N dm \ \langle \mathbf{F}(m)\mathbf{r}(m) \rangle \tag{82}$$

where N_{ch} is the number of chains in volume V. The force $\mathbf{F}(m)$ is the righthand-side of the Langevin equation (48)

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot \left(\frac{\partial \mathbf{r}}{\partial t} - \boldsymbol{\kappa} \cdot \mathbf{r}(m) \right) = \mathbf{K}(\mathbf{n}) \cdot \frac{\partial^2 \mathbf{r}(m)}{\partial m^2} + \mathbf{f}(m, t) \tag{83}$$

So

$$\mathbf{F}(m) = \mathbf{K}(\mathbf{n}) \cdot \frac{\partial^2 \mathbf{r}(m)}{\partial m^2} + \mathbf{f}(m, t) \tag{84}$$

This force $\mathbf{F}(m)$ includes two terms. First is the force, which acts from the neighboring beads and the second one is a stochastic force.

When calculating the stress tensor it is also, as in previous subsections, better to use normal modes expansion.

$$\mathbf{r}(m) = \frac{1}{N}\mathbf{r}_0 + \frac{2}{N} \sum_{p=1}^N \mathbf{r}_p \cos{(k_p m)} \tag{85}$$

$$\mathbf{F}(m) = \frac{1}{N}\mathbf{F}_0 + \frac{2}{N} \sum_{p=1}^N \mathbf{F}_p \cos{(k_p m)} \tag{86}$$

where

$$\mathbf{F}_p = \int\limits_0^N dm \ \mathbf{F}(m) \cos{(k_p m)} = -k_p^2 \, \mathbf{K}\,(\mathbf{n}) \cdot \mathbf{r}_p - (1 - (-1)^p)\, l'k_\parallel \cdot \mathbf{n} + \mathbf{f}_p \tag{87}$$

Notice that it is incorrect to substitute the expansion of $\mathbf{r}(m)$ in form (85) into (84), in spite of converging of the series (85) to $\mathbf{r}(m)$, the second derivative of the series (85) by m does not converge to $\frac{\partial^2 \mathbf{r}}{\partial m^2}$. The correct expansion for $\mathbf{F}_p$ can be obtained by (87).

Expression for $\mathbf{r}_p$ can be taken from (67) (it is recapitulated here)

$$\mathbf{r}_p(t) = \int\limits_{-\infty}^t dt' \ \exp{\left(-\boldsymbol{\tau}_p^{-1}(t, t')\, (t - t') \right)} \cdot \left[-(1 - (-1)^p)\, l'\boldsymbol{\tau}^{-1} \cdot \mathbf{n} + \boldsymbol{\zeta}^{-1} \cdot \mathbf{f}_p\,(t') \right] \tag{88}$$

Substitution (85) and (86) into (82) gives

$$\boldsymbol{\sigma}_b = -\frac{N_{ch}}{V} \left(\frac{1}{N} \langle \mathbf{F}_0 \mathbf{r}_0 \rangle + \frac{2}{N} \sum_{p=1}^N \langle \mathbf{F}_p \mathbf{r}_p \rangle \right) \tag{89}$$

15

To use this formula it is necessary to calculate $\langle \mathbf{F}_0 \mathbf{r}_0 \rangle$ and $\langle \mathbf{F}_p \mathbf{r}_p \rangle$:

$$\langle F_{0,\alpha}(t) r_{0,\beta}(t) \rangle = \langle f_{0,\alpha}(t) r_{0,\beta}(t) \rangle = \left\langle \int\limits_{-\infty}^{t} dt' \left[\exp(-\boldsymbol{\tau}_0^{-1}(t,t')(t-t')) \boldsymbol{\zeta}^{-1} \right]_{\beta,\mu} f_\alpha(t) f_\mu(t') \right\rangle =$$

$$= NT \int\limits_{-\infty}^{t} dt' \left[\exp(-\boldsymbol{\tau}_0^{-1}(t,t')(t-t')) \boldsymbol{\zeta}^{-1} \right]_{\beta,\mu} \zeta_{\alpha,\mu} \delta(t-t')$$

$$(90)$$

The use of symmetry property $\zeta_{\alpha\mu} = \zeta_{\mu\alpha}$ gives

$$\langle \mathbf{F}_0(t) \mathbf{r}_0(t) \rangle = \frac{1}{2} NT\mathbf{I} \tag{91}$$

Similarly,

$$\langle \mathbf{F}_p(t)\mathbf{r}_p(t) \rangle = -k_p^2 \mathbf{K}(\mathbf{n}) \cdot \langle \mathbf{r}_p \mathbf{r}_p \rangle - (1 - (-1)^p) l' k_\parallel \mathbf{n} \langle \mathbf{r}_p \rangle + \langle \mathbf{f}_p \mathbf{r}_p \rangle \tag{92}$$

$$\langle f_{p,\alpha}(t) r_{p,\beta}(t) \rangle = \left\langle \int\limits_{-\infty}^{t} dt' \left[\exp(-\boldsymbol{\tau}_p^{-1}(t,t')(t-t')) \boldsymbol{\zeta}^{-1} \right]_{\beta,\mu} f_\alpha(t) f_\mu(t') \right\rangle =$$

$$= NT \int\limits_{-\infty}^{t} dt' \left[\exp(-\boldsymbol{\tau}_p^{-1}(t,t')(t-t')) \boldsymbol{\zeta}^{-1} \right]_{\beta,\mu} \zeta_{\alpha,\mu} \delta(t-t') = \frac{1}{2} NT \delta_{\alpha,\beta}$$

$$(93)$$

Here we take into account that the delta-function has singularity on the upper limit.

$$\langle \mathbf{f}_p(t) \mathbf{r}_p(t) \rangle = \frac{1}{2} NT\mathbf{I} \tag{94}$$

$$\langle \mathbf{F}_p(t)\mathbf{r}_p(t) \rangle = -k_p^2 \mathbf{K}(\mathbf{n}) \cdot \langle \mathbf{r}_p \mathbf{r}_p \rangle - (1 - (-1)^p) l' k_\parallel \mathbf{n} \langle \mathbf{r}_p \rangle + \frac{(N+1)}{2} T\mathbf{I} \tag{95}$$

Substitution (95) and (91) into (89) leads to

$$\boldsymbol{\sigma}_b = -\frac{N_{ch}}{V} \left((N + \frac{1}{2})T\mathbf{I} - \frac{2}{N} \sum_{p=1}^{N} k_p^2 \mathbf{K}(\mathbf{n}) \cdot \langle \mathbf{r}_p \mathbf{r}_p \rangle - \frac{2}{N} \sum_{p=1}^{N} (1 - (-1)^p) l' k_\parallel \mathbf{n} \langle \mathbf{r}_p \rangle \right)$$

As $N \gg 1$, we can neglect $\frac{1}{2}$ compared to N. Introducing the new notation

$$p_{id} = \frac{N_{ch} NT}{V}$$

gives

$$\boldsymbol{\sigma}_b = -p_{id}\mathbf{I} + \frac{2N_{ch}}{NV} \sum_{p=1}^{N} \left(k_p^2 \mathbf{K}(\mathbf{n}) \cdot \langle \mathbf{r}_p \mathbf{r}_p \rangle + (1 - (-1)^p) l' k_\parallel \mathbf{n} \langle \mathbf{r}_p \rangle \right) \tag{96}$$

To calculate correlation matrix at arbitrary moment of time it is useful to notice, that

$$\mathbf{r}_p = \langle \mathbf{r}_p \rangle + \int\limits_{0}^{t} dt' \, \mathbf{B}(t,t') \cdot \mathbf{f}_p(t') \tag{97}$$

where

$$\mathbf{B}(t,t') = \exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')(t-t')\right) \cdot \boldsymbol{\zeta}^{-1} \tag{98}$$

Therefore

$$\langle \mathbf{r}_p \mathbf{r}_p \rangle = \langle \mathbf{r}_p \rangle \langle \mathbf{r}_p \rangle + \mathbf{G}_p \tag{99}$$

where

$$\mathbf{G}_p = \left\langle \int\limits_{0}^{t} dt' \int\limits_{0}^{t} dt'' \left(\mathbf{B}(t,t') \cdot \mathbf{f}_p(t') \right) \left(\mathbf{B}(t,t'') \cdot \mathbf{f}_p(t'') \right) \right\rangle \tag{100}$$

and

$$\langle \mathbf{r}_p(t) \rangle = - \int\limits_{-\infty}^{t} dt' \, \exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')\,(t-t')\right) \cdot \left(1 - (-1)^p\right) l' \boldsymbol{\tau}^{-1} \cdot \mathbf{n} \tag{101}$$

Expression for $\mathbf{G}_p$ is next:

$$\mathbf{G}_p = NT \int\limits_{0}^{t} dt' \, \left[\zeta_{\perp}^{-1} \exp\left(-\left(\boldsymbol{\tau}_p^{-1}(t,t') + \boldsymbol{\tau}_p^{-1^T}(t,t')\right) t'\right) + \right.$$

$$\left. + \left(\zeta_{\parallel}^{-1} - \zeta_{\perp}^{-1}\right)\left(\exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')t'\right)\cdot\mathbf{n}\right)\left(\exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')t'\right)\cdot\mathbf{n}\right) \right] \tag{102}$$

The formulas (96), (99), (101) and (102) give the stress tensor at any arbitrary moment.

3 The elongation flow

3.1 The stress tensor for non-steady elongation flow

In this section we will derive explicit expression for the stress tensor in the instance of the simple elongation flow. In this case the direction of elongation remains constant, but the rate of elongation κ may vary in time.

$$\boldsymbol{\kappa}(t) = \frac{\kappa(t)}{2} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{103}$$

It is assumed here that $\kappa\tau N^2 < 1$, where τ - is the longest relaxation time. In the opposite case this model can not be applied, because the equilibrium state disappears. For polymers we are interested in $N \gg 1$, therefore $\kappa\tau \ll 1$. This allows to make further derivation by expansion with respect to $\kappa\tau_\parallel$ and $\kappa\tau_\perp$. The essential value, that characterizes anisotropy of stresses in the elongation flow, is, so called, tensile stress $\sigma_T = \sigma_{zz} - \sigma - xx$. We will focus on calculation of this quantity. Also we assume that initial moment of motion was infinite time ago. If we want to consider situation, when polymer starts to move at some moment of time t and before that moment it was at rest, then we can put velocity gradient to zero before moment t. So we can extend integration by time in expressions for the stress tensor till minus infinity and forget about initial conditions. Let's choose Oz axis along the direction of elongation. Then

$$\mathbf{r}_p(t) = \int_{-\infty}^{t} dt' \, \exp\left(-\boldsymbol{\tau}_p^{-1}(t,t')\,(t-t')\right) \cdot \mathbf{v}_p^*(t') \tag{104}$$

where

$$\mathbf{v}_p^*(t') = -\left(1-(-1)^p\right)l\boldsymbol{\tau}^{-1} \cdot \mathbf{n} + \boldsymbol{\zeta}^{-1} \cdot \mathbf{f}_p(t') \tag{105}$$

Expression for stress tensor is (96). Also we will omit the isotropic component of the stress tensor, which corresponds to the ideal gas pressure. Thus, we get

$$\boldsymbol{\sigma}_b^* = \frac{N_{ch}}{V}\frac{2}{N}\sum_{p=1}^{N}\left(k_p^2 \mathbf{K}\left(\mathbf{n}\right) \cdot \langle\mathbf{r}_p\mathbf{r}_p\rangle + \left(1-(-1)^p\right)l'k_\parallel \mathbf{n}\langle\mathbf{r}_p\rangle\right) \tag{106}$$

To obtain a tensile stress we have to calculate $\sigma_{b,zz}^*$ and $\sigma_{b,xx}^*$

$$\sigma_{b,zz}^* = \mathbf{n}\mathbf{n} : \boldsymbol{\sigma}_b^* = \frac{N_{ch}}{V}\frac{2}{N}\sum_{p=1}^{N}\left(k_p^2 k_\parallel \langle(\mathbf{n}\cdot\mathbf{r}_p)(\mathbf{n}\cdot\mathbf{r}_p)\rangle + \left(1-(-1)^p\right)l'k_\parallel \langle\mathbf{n}\cdot\mathbf{r}_p\rangle\right) \tag{107}$$

$$(\mathbf{n}\cdot\mathbf{r}_p) = \int_{-\infty}^{t} dt' \, \exp\left(-\tau_{p,\parallel}^{-1}(t,t')\,(t-t')\right)\left(\mathbf{n}\cdot\mathbf{v}_p^*(t')\right) \tag{108}$$

$$\left(\mathbf{n}\cdot\mathbf{v}_p^*(t')\right) = -\left(1-(-1)^p\right)l'\tau_\parallel^{-1} + \zeta_\parallel^{-1}\left(\mathbf{n}\cdot\mathbf{f}_p(t')\right) \tag{109}$$

Thus,

$$k_\parallel \langle(\mathbf{n}\cdot\mathbf{r}_p)(\mathbf{n}\cdot\mathbf{r}_p)\rangle = NT \int_{-\infty}^{t} \frac{dt'}{\tau_\parallel} \exp\left(-2k_p^2\frac{(t-t')}{\tau_\parallel}\right)\exp\left(2\int_{t'}^{t} dt^*\kappa(t^*)\right) +$$

$$+\left(1-(-1)^p\right)^2 k_\parallel l'^2 \left(\int_{-\infty}^{t} \frac{dt'}{\tau_\parallel}\exp\left(-k_p^2\frac{(t-t')}{\tau_\parallel}\right)\exp\left(\int_{t'}^{t} dt^*\kappa(t^*)\right)\right)^2 \tag{110}$$

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Let's integrate by parts the first term in (110), and assume that $\kappa\tau_\parallel \ll 1$ and $\int\limits_{t'}^{t} dt^* \kappa_\parallel(t^*) \ll 1$.

$$\int\limits_{-\infty}^{t} \frac{dt'}{\tau_\parallel} \exp\left(-2k_p^2 \frac{(t-t')}{\tau_\parallel}\right) \exp\left(\int\limits_{t'}^{t} dt^* 2\kappa_\parallel(t^*)\right) = \frac{1}{2k_p^2}\left(1 + 2\int\limits_{-\infty}^{t} dt' \exp\left(-2k_p^2 \frac{(t-t')}{\tau_\parallel}\right)\kappa(t')\right)$$

Similar treatment is applicable to the second term in (110) and to the expression for $\sigma_{b,xx}^*$

$$\sigma_{b,xx}^* = \mathbf{nn} : \boldsymbol{\sigma}_b^* = \frac{N_{ch}}{V}\frac{2}{N}\sum_{p=1}^{N} k_p^2 k_\perp' \left\langle (\mathbf{n}_\perp \cdot \mathbf{r}_p)(\mathbf{n}_\perp \cdot \mathbf{r}_p)\right\rangle \tag{111}$$

where $\mathbf{n}_\perp \cdot \mathbf{n} = 0$ and

$$(\mathbf{n}_\perp \cdot \mathbf{r}_p) = \int\limits_{-\infty}^{t} dt' \exp\left(-\tau_{p,\perp}^{-1}(t,t')(t-t')\right)\zeta_\perp^{-1}(\mathbf{n}_\perp \cdot \mathbf{f}_p(t')) \tag{112}$$

$$k_\perp' \left\langle (\mathbf{n}_\perp \cdot \mathbf{r}_p)(\mathbf{n}_\perp \cdot \mathbf{r}_p)\right\rangle = NT \int\limits_{-\infty}^{t} \frac{dt'}{\tau_\perp} \exp\left(-2k_p^2 \frac{(t-t')}{\tau_\perp}\right) \exp\left(-\int\limits_{t'}^{t} dt^* \kappa(t^*)\right) \tag{113}$$

Finally we will get expression for $\sigma_T = \sigma_{b,zz} - \sigma_{b,xx} = \sigma_{b,zz}^* - \sigma_{b,xx}^*$,

$$\sigma_T = \int\limits_{-\infty}^{t} dt' G(t-t')\kappa(t') \tag{114}$$

where

$$G(t) = \frac{N_{ch}T}{V}\sum_{p=1}^{N}\left[2e^{-2k_p^2\frac{t}{\tau_\parallel}} + e^{-2k_p^2\frac{t}{\tau_\perp}} + \frac{k_\parallel l'^2}{T}\frac{4(1-(-1)^p)}{Nk_p^2}e^{-k_p^2\frac{t}{\tau_\parallel}}\right] \tag{115}$$

The expression for the stress tensor is found. The function $G(t)$ is a linear response function. In order to simplify further analysis of the resulting expression we will make it dimensionless.

$$\tilde{G}(\tilde{t}) = \frac{\tilde{G}(\tilde{t}\,\tau_\parallel)}{P_{id}} \tag{116}$$

where

$$\tilde{t} = \frac{t}{\tau_\parallel} \tag{117}$$

$$\tilde{\tau} = \frac{\tau_\parallel}{\tau_\perp} \tag{118}$$

$$\tilde{q} = \frac{k_\parallel l'^2}{T} \tag{119}$$

Then

$$\tilde{G}(\tilde{t}) = \frac{1}{N}\sum_{p=1}^{N}\left[2\,e^{-2k_p^2\tilde{t}} + e^{-2k_p^2\tilde{\tau}\tilde{t}} + \tilde{q}\frac{4(1-(-1)^p)}{Nk_p^2}e^{-k_p^2\tilde{t}}\right] \tag{120}$$

The response function depends only on one argument $\tilde{t}$ and three parameters: the length of the chain N, the ratio of parallel and orthogonal relaxation times $\tilde{\tau}$ (which can vary only from 0 to 1) and the ratio of elastic energy to the thermal energy $\tilde{q}$. The graph for $\tilde{G}(\tilde{t})$ for different amount of beads in the chain is shown on figure (4). From this figure we see that the longer the chains are,
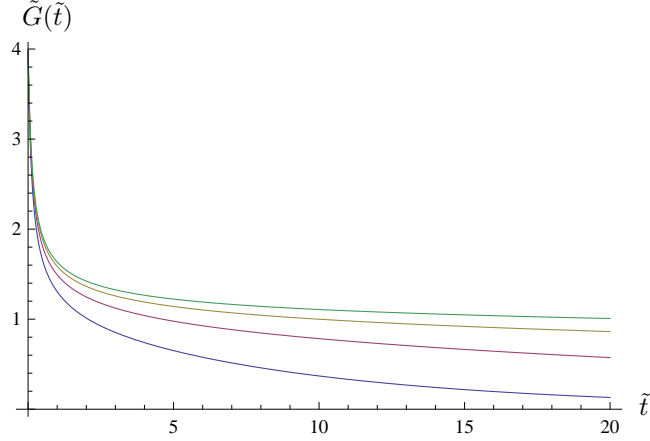
Figure 4: The response function $\tilde{G}(\tilde{t})$ on time for $\tilde{t}$ different amount of beads in the chain. N = 10 for the lowest curve, next are $N = 20$, $N = 40$, and $N = 80$ for the highest one. $\tilde{q} = 1$, $\tilde{\tau} = \frac{1}{2}$

the slower the decay of response. This result is in good agreement with common sense, because the relaxation of the longer chain should take more time, then a relaxation of the shorter one.

If we want to consider the dependence of elastic properties on the amount of hairpins, then we have to express the parameters $\tilde{\tau}$ and $\tilde{q}$ by original parameters of the model: k_0 - "entropy" elasticity of the springs, l - length of the beads, H_0 - strength of the nematic interaction, w_0 - fraction of the hairpins, $\zeta_{\parallel}$ and $\zeta_{\perp}$ - media friction coefficients to the motion along the bead and in orthogonal direction.

$$\tilde{\tau} = \frac{\zeta_{\parallel}}{\zeta_{\perp}} \frac{1 + w_0 \frac{k_0 l^2}{H_0}}{1 + \frac{k_0 l^2}{H_0}} \tag{121}$$

$$\tilde{q} = (1 - w_0)^2 \frac{k_0 l^2}{T} \tag{122}$$

Let's introduce the set of the original dimensionless characteristics of the system.

$$\zeta = \frac{\zeta_{\parallel}}{\zeta_{\perp}} \tag{123}$$

This parameter can change only from 0 to 1, because the resistance to the motion of the bead along itself is always less than in the orthogonal direction.

$$\epsilon = \frac{k_0 l^2}{T} \tag{124}$$

This parameter seems to be dependent on temperature, but if we recall that the elastic constant k_0 corresponds to the "entropy" springs and itself is proportional to T, then we can conclude that ϵ is a parameter describing the structure of the chain. It gives the "ratio" between rigid and flexible parts of the polymer. Increase of ϵ corresponds to increase persistence length of the chains.

And the last dimensionless parameter is temperature expressed in values of H_0. It gives the ratio between characteristic energies of thermal motion and energy of nematic ordering.

$$\Theta = \frac{T}{H_0} \tag{125}$$

Now we see, that originally in our model there are five dimensionless parameters: N, w_0, ζ, ϵ and Θ. But the macroscopic behavior of the system depends only on number of beads in the chain N and two combinations:

$$\tilde{\tau}(\zeta, w_0, \epsilon, \Theta) = \zeta \frac{1 + w_0 \epsilon \Theta}{1 + \epsilon \Theta} \tag{126}$$

20

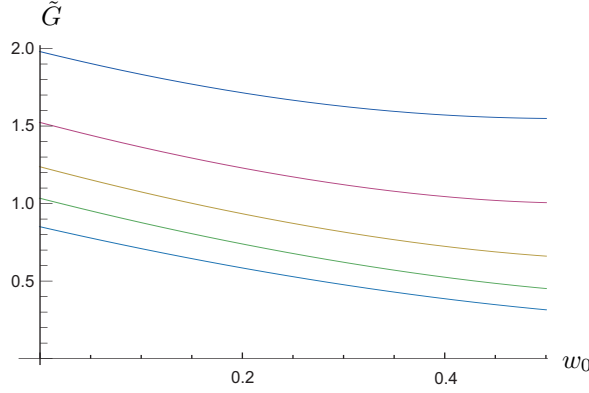$$\tilde{q}(\epsilon, w_0) = \epsilon(1 - w_0)^2 \tag{127}$$

Figure 5: The response function $\tilde{G}(\tilde{t}, w_0)$ on fraction of hairpins w_0 for different moments of time. Starting from the upper curve $\tilde{t} = \frac{1}{3}, 1, 3, 9, 27$ Here $N = 50$, $\zeta = \frac{1}{2}$, $\Theta = 1$, $\epsilon = 1$.

On figure (6) the influence of hairpins on elastic properties is shown. From this graph we can conclude, that small fraction of hairpins makes the response function decay faster. So the material becomes softer.

Next we compute the elongtion viscosity:

$$\tilde{\eta}_E = \int\limits_0^\infty d\tilde{t} \; \tilde{G}(\tilde{t}) \tag{128}$$
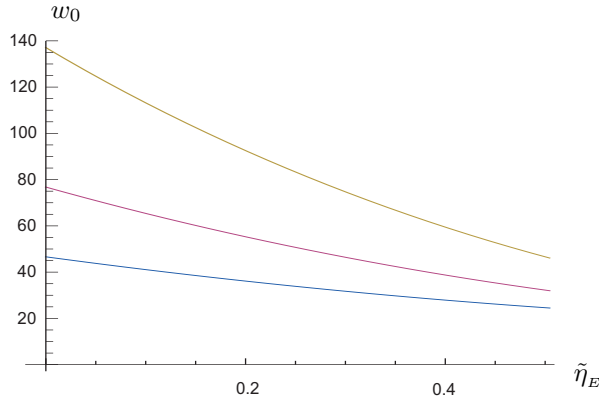

Figure 6: The elongation viscosity of the solution depending on the amount of hairpins. The elasticity of the springs starting from the lowest curve takes values: $\epsilon = \frac{1}{2}, 1, 2$. Here $N = 50$, $\zeta = \frac{1}{2}$, $\Theta = 1$.

On the basis of (120) we get the explicit expression for the tensile viscosity.

$$\tilde{\eta}_E = \frac{1}{N} \sum_{p=1}^N \left[\left(1 + \frac{1}{2\tilde{\tau}}\right) \frac{1}{k_p^2} + \frac{4\tilde{q}}{N} \frac{(1 - (-1)^p)}{k_p^4} \right] \tag{129}$$

3.2 The storage and loss moduli

In the case of oscillatory flow important characteristics of the linear response of the material are storage $\tilde{G}'$ and loss moduli $\tilde{G}''$. On the basis of the the expression for response function (120) from the previous section we may easily compute $\tilde{G}'$ and $\tilde{G}''$ by making *sin*- and *cos*-Fourier transform:

$$\tilde{G}'(\tilde{\omega}) = \tilde{\omega} \int_0^\infty d\tilde{t}\, \tilde{G}(\tilde{t}) \sin(\tilde{\omega}\tilde{t}) = \int_0^\infty d\tilde{\phi}\, \tilde{G}(\frac{\tilde{\phi}}{\tilde{\omega}}) \sin(\tilde{\phi}) \tag{130}$$

$$\tilde{G}''(\tilde{\omega}) = \tilde{\omega} \int_0^\infty d\tilde{t}\, \tilde{G}(\tilde{t}) \cos(\tilde{\omega}\tilde{t}) = \int_0^\infty d\tilde{\phi}\, \tilde{G}(\frac{\tilde{\phi}}{\tilde{\omega}}) \cos(\tilde{\phi}) \tag{131}$$

where $\tilde{\omega} = \omega\tau_\parallel$. Readily we obtain

$$\tilde{G}'(\tilde{\omega}) = \frac{1}{N} \sum_{p=1}^N \left[2\frac{\tilde{\omega}^2}{\tilde{\omega}^2 + 4k_p^4} + \frac{\tilde{\omega}^2}{\tilde{\omega}^2 + 4k_p^4\tilde{\tau}^2} + \frac{4\tilde{q}(1-(-1)^p)}{Nk_p^2}\frac{\tilde{\omega}^2}{\tilde{\omega}^2 + k_p^4} \right] \tag{132}$$

$$\tilde{G}''(\tilde{\omega}) = \frac{1}{N} \sum_{p=1}^N \left[2\frac{2k_p^2\tilde{\omega}}{\tilde{\omega}^2 + 4k_p^4} + \frac{2\tilde{\tau}k_p^2\tilde{\omega}}{\tilde{\omega}^2 + 4k_p^4\tilde{\tau}^2} + \frac{4\tilde{q}(1-(-1)^p)}{Nk_p^2}\frac{k_p^2\tilde{\omega}}{\tilde{\omega}^2 + k_p^4} \right] \tag{133}$$
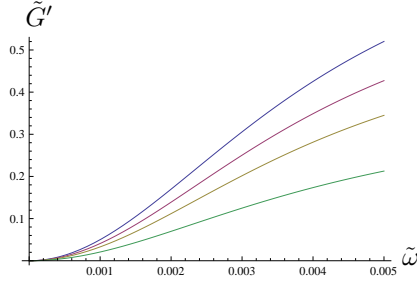

Figure 7: The storage module $\tilde{G}'(\tilde{\omega}, w_0)$ on frequency $\tilde{\omega}$ for different fractions of hairpins. Starting from the upper curve $w_0 = 0, 0.1, 0.2, 0.4$ Here $N = 50$, $\zeta = \frac{1}{2}$, $\Theta = 1$, $\epsilon = 1$.
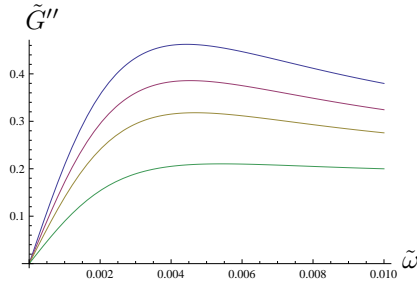

Figure 8: The loss module $\tilde{G}''(\tilde{\omega}, w_0)$ on frequency $\tilde{\omega}$ for different fractions of hairpins. Starting from the upper curve $w_0 = 0, 0.1, 0.2, 0.4$ Here $N = 50$, $\zeta = \frac{1}{2}$, $\Theta = 1$, $\epsilon = 1$.

From graphs (7) and (8) we see that as the amount of hairpins increases the material becomes less elastic and less viscous. In other words it becomes softer.

4 Summary

A model of the Rouse-like chain with hairpins has been presented here to describe the rheological properties of the highly-ordered LCP's. From the analysis of nematic and "entropic" interactions the equation for director orientation have been established. From this equation dynamics of the director can be found. It occurred that in the case of elongation flow the dynamics of the director is more simple. The director tends to align along the direction of elongation. This fact allowed to obtain the explicit expression for the tensile stress induced in material by the elongation flow. On the basis of the tensile stress the linear response modulus, storage and loss moduli and tensile viscosity have been computed. The main interest was directed on the influence of hairpins on the macroscopic mechanical properties. The plots from sections 3.1 and 3.2 show that the higher the fraction of the hairpins the weaker the response of the material to the external influences. In other words the material becomes softer.

The next aim is to investigate shear flow. The shear flow is more rich on non-trivial evolution of the director. The nematogens can have tumbling or flow-aligning behavior. Proposed here model has problems with describing tumbling of the nematogens, because in this case an assumption about high-ordering of the nematogens is not valid any more. Therefore for analysis of shear flow will be necessary either to improve somehow the approach by taking into account large deviations of nematogens from orientation of director, either to develop more suitable model.

Another weak point of this model is the absence of entanglements between the chains. But it is not a crucial factor in the highly-ordered regime.

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