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A rod-spring model for main-chain liquid crystalline polymers containing hairpins

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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,

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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 [3], [4], [5], [6]. 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 [7], [8], [9].

For sufficiently long main-chain LCPs in highly-ordered orientational states it was de Gennes [10] 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 [11].

2 Degrees of freedom of the rod-spring chain

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 rigid rods, which we will call nematogens or beads, connected by $N-1$ 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 nematogens. The springs connecting the rods reflect the partial flexibility of the chains.

The orientational ordering of the nematogens in the solution is usually described by a so-called order parameter $\mathbf{S}$, which is a tensor of the second order. But in the limit of strong ordering $\mathbf{S}$ can be represented by the diadic product of some unit vector $\mathbf{n}$. This vector is called the director.

The relaxation of the orientation of the nematogens happens much faster then the relaxation of the whole backbone of the chain, i.e. the orientational relaxation of the nematogens is a fast process. This means that in the limit of the high ordering and on the timescales of the relaxation of the chain backbone the orientation of the nematogens can be taken as parallel to the director. Thus, we will not need to specify the orientation of each nematogen.

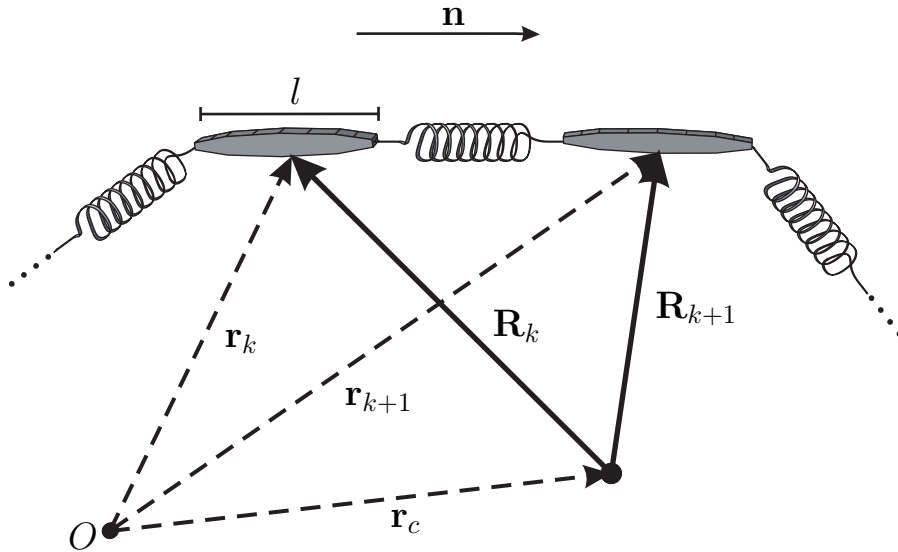Figure 1: The fraction of a chain around k-th nematogen. Here $\mathbf{r}_c$ is the center of mass of the chain, $\mathbf{R}_k$ is the vector connecting center of mass of the chain and the center of a k-th nematogen, O is the origin of the laboratory reference frame, $\mathbf{r}_k$ is the vector connecting the origin O with the center of a k-th nematogen, $\mathbf{n}$ is the director.

The set of coordinates describing the configuration of one chain may be easily deduced from the picture above (fig. 1). This set can be chosen in many different ways. The most obvious choice is $\{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$. Here all the vectors are connecting the origin of some chosen laboratory reference frame with the centers of nematogens. On the fig. 1 this origin is denoted as O.

Another way is to introduce the other set of variables: $\{\mathbf{r}_c, \mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N\}$. Here $\mathbf{r}_c$ is pointing from the origin O to the center of mass of the chain. Vectors $\mathbf{R}_k$ are connecting the center of mass of the chain with the center of its k-th nematogen. Among $N + 1$ vectors in this set only N are independent. This is because by definition of the center of mass $\sum_{m=1}^{N} \mathbf{R}_m = 0$. Of course we employ here the fact that all the nematogens have equal masses. The relation with the previous set is next:

$$\mathbf{r}_c = \frac{1}{N} \sum_{m=1}^{N} \mathbf{r}_m$$

$$\mathbf{R}_k = \mathbf{r}_k - \mathbf{r}_c$$

We can also introduce the set $\{\mathbf{r}_c, \mathbf{b}_1, \mathbf{b}_2, ..., \mathbf{b}_{N-1}\}$ consisting of the center-mass vector of the chain and $N-1$ connector vectors. They are defined in terms of the first set of vectors as

$$\mathbf{r}_c = \frac{1}{N} \sum_{m=1}^{N} \mathbf{r}_m$$

$$\mathbf{b}_k = \mathbf{r}_{k+1} - \mathbf{r}_k$$

The most convenient choice of the coordinates is usually dictated by the form of equations that are describing the system. But we will start the description in terms of the first set $\{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$, because of the very transparent meaning of all the vectors in it. Later, when the system of equations of motion for all nematogens will be stated we will change the coordinates to bring this system of equations to the most simple form.

3 Dynamics of the polymer chain

In this section we will state the set of equations that are governing the dynamics of a chain. The mechanical motion of an object in classical mechanics the Newton's second law of motion is used. It says that the sum of all generalized forces acting on the molecule or it's part is equal to the change of the corresponding generalized momentum.

$$\frac{d\mathbf{p}}{dt} = \mathbf{F}$$

The force on the righthand-side includes all the interactions exerted to the selected body. For example, if we select as a body one nematogen, then it is subjected to an action of the neighboring nematogens through "entropic springs" and to collisions with the other molecules due to thermal motion. The contribution from the collisions is usually separated into two parts. The average

force acting on the nematogen which we will call hydrodynamic force and the stochastic force with mean-value equal to zero and describing fluctuations of the momentum transfer caused by collisions. Our assumptions about the form of hydrodynamic force and stochastic force play essential role in the model. In this work we will consider the stochastic force to be a "time-derivative" of the Wiener process, i.e. white noise. The hydrodynamic force is taken in anisotropic Stocks form, i.e. linear dependence of the relative velocity with respect to the media and anisotropic viscosity coefficient. This assumption mimics the fact that nematogen experiences less resistance from the surrounding media when moves along itself, but not perpendicular to itself.

$$\mathbf{F}_{resist} = -\boldsymbol{\zeta}\left(\mathbf{n}\right) \cdot \mathbf{v}_{relative}$$

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

The interaction between parts of the same molecule is usually called intramolecular interaction. In our case this is the interaction with the neighboring nematogens through the "entropic springs". This interaction can be represented as the gradient of some potential. In the previous section it was mentioned that the orientational degrees of freedom of the nematogens are treated here as the fast variables. To average them out we first can consider each chain, if it is long enough, as a thermodynamic system with fixed positions of the centers of nematogens and "temperature" equal to the temperature of the surrounding media. In time of order of the angular relaxation time it will come to equilibrium with respect to fast angular variables. The potential which describes the energy of the chain in this case should be not the pure mechanical potential energy, but Helmholtz free energy which includes also the entropic contribution of the angular degrees of freedom. Analysis made in [1], [2] shows that the free energy of a single chain in the highly-ordered regime with the presence of hairpins can be taken in the next form.

$$
\begin{aligned}
F &= \frac{1}{2}w_0 \sum_{m=1}^{N-1} \left(\mathbf{r}_{m+1} - \mathbf{r}_m\right) \cdot \mathbf{K}_0 \cdot \left(\mathbf{r}_{m+1} - \mathbf{r}_m\right) + \\
&+ \frac{1}{2}w_1 \sum_{m=1}^{N-1} \left(\mathbf{r}_{m+1} - \mathbf{r}_m - l\mathbf{n}\right) \cdot \mathbf{K}_1 \cdot \left(\mathbf{r}_{m+1} - \mathbf{r}_m - l\mathbf{n}\right)
\end{aligned}
\tag{1}
$$

Here w_0 is a fraction of the hairpin states, $w_1 = 1 - w_0$. $\mathbf{K}_0 = k_0\mathbf{I}$ - "elasticity" matrix on the hairpin state, $\mathbf{K}_1 = k_0\mathbf{nn} + k_1\left(\mathbf{I} - \mathbf{nn}\right)$ - "elasticity" matrix on the normal state. The anisotropy in elasticity is caused by nematic interaction of the nematogens.

At this point it is necessary to specify what is meant here by hairpin state. The simplest way to explain this is by use of the fig. 2. In the previous section we have said that the orientation of the nematogen should be parallel to the director $\mathbf{n}$. But there is still two options left. If we introduce vector $\mathbf{u}_m$ as depicted on the fig. 2, then we call the state of the spring to be a hairpin state if the two consequent vectors $\mathbf{u}_m$ and $\mathbf{u}_{m+1}$ are pointing in the opposite direction. Otherwise, we call the state of spring to be normal.
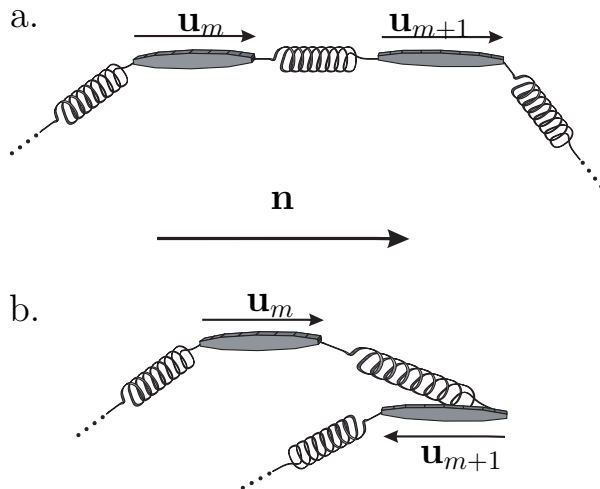
Figure 2: a. The normal state. u_m and u_{m+1} are pointing in the same direction. b. The hairpin state. u_m and u_{m+1} are pointing in the opposite directions.

After introducing a free energy of the chain we can now write equations for motion of the nematogens (for $s \in \{1, 2, ..., N\}$).

$$m\ddot{\mathbf{r}}_s(t) = -\frac{\partial F(\mathbf{r}_1, ..., \mathbf{r}_N)}{\partial \mathbf{r}_s} - \boldsymbol{\zeta}(\mathbf{n}) \cdot (\dot{\mathbf{r}}_s(t) - \mathbf{v}_{med}(\mathbf{r}_s, t)) + \mathbf{f}_s(t) \qquad (2)$$

Here m stands for the mass of the nematogen, $\mathbf{v}_{med}$ is the velocity of the surrounding media, $\mathbf{f}_s$ is the stochastic force acting on the s-th nematogen.

For the nematogen committing Brownian motion the inertial term in equation (2) is negligible compared to viscosity term. This allows us to omit the inertial term in the equation (2).

In most of the cases the flow can be considered to be uniform on the scale of the polymer chain. This motivates us to focus on the case of a uniform flow. In the uniform flow, i.e. the flow with the constant in space $\boldsymbol{\kappa} = \nabla \mathbf{v}_{med}$, the velocity of the flow at any point $\mathbf{r}$ can be found as $\boldsymbol{\kappa} \cdot \mathbf{r} + \mathbf{v}_{origin}$. The term $\mathbf{v}_{origin}$ can be eliminated by the proper choice of the origin. To do so we need to find a point which does not move during the whole time of the flow. This is always possible to do if $-\mathbf{v}_{origin}$ belongs to the range of operator $\boldsymbol{\kappa}$. However, it may happen that the still point is changing its position in time. Then we have to either take the system of reference following that point, either take into account the term $\mathbf{v}_{origin}$. For the cases of non-steady but uniform elongational or shear flows, which are of major interest here, there are always still points with zero velocity. That is why we omit $\mathbf{v}_{origin}$ in the foregoing calculations.

$$\mathbf{v}_{med}(\mathbf{r}_s, t) = \boldsymbol{\kappa} \cdot \mathbf{r}_s \qquad (3)$$

The expressions for $\frac{\partial F}{\partial \mathbf{r}_s}$ are readily obtained by the straightforward differentiation.

For $s = 1$

$$\frac{\partial F}{\partial \mathbf{r}_s} = -\left(\mathbf{K} \cdot (\mathbf{r}_2 - \mathbf{r}_1) - w_1 l \mathbf{K}_1 \cdot \mathbf{n}\right) \tag{4}$$

For $s \in \{2, ..., N-1\}$

$$\frac{\partial F}{\partial \mathbf{r}_s} = -\mathbf{K} \cdot (\mathbf{r}_{m+1} + \mathbf{r}_{m-1} - 2\mathbf{r}_m) \tag{5}$$

For $s = N$

$$\frac{\partial F}{\partial \mathbf{r}_s} = -\left(\mathbf{K} \cdot (\mathbf{r}_{N-1} - \mathbf{r}_N) + w_1 l \mathbf{K}_1 \cdot \mathbf{n}\right) \tag{6}$$

Here $\mathbf{K}$ stands for $w_0 \mathbf{K}_0 + w_1 \mathbf{K}_1$.

Finally, from (2),(3),(4),(5),(6) we get the set of equations governing the motion of the chain.

For $s = 1$

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot (\mathbf{r}_1 - \boldsymbol{\kappa} \cdot \mathbf{r}_1) = \mathbf{K} \cdot (\mathbf{r}_2 - \mathbf{r}_1) - w_1 l \mathbf{K}_1 \cdot \mathbf{n} + \mathbf{f}_1(t) \tag{7}$$

For $s \in \{2, ..., N-1\}$

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot (\mathbf{r}_s - \boldsymbol{\kappa} \cdot \mathbf{r}_s) = \mathbf{K} \cdot (\mathbf{r}_{m+1} + \mathbf{r}_{m-1} - 2\mathbf{r}_m) + \mathbf{f}_s(t) \tag{8}$$

For $s = N$

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot (\mathbf{r}_N - \boldsymbol{\kappa} \cdot \mathbf{r}_N) = \mathbf{K} \cdot (\mathbf{r}_{N-1} - \mathbf{r}_N) + w_1 l \mathbf{K}_1 \cdot \mathbf{n} + \mathbf{f}_N(t) \tag{9}$$

Now we have to specify the properties of the stochastic force $\mathbf{f}_s(t)$. By definition this force models a deviation of the instantaneous force acting on the nematogen due to the collisions with other particles from the average value of the collision force, which is called the hydrodynamic force. Thus, the average of the fluctuation force should be equal to zero. This holds for all $s \in \{1, ..., N\}$

$$\langle \mathbf{f}_s(t) \rangle = \mathbf{0} \tag{10}$$

The properties of the stochastic force are deduced from the equipartition theorem. This theorem says that the average thermal energy per each quadratic degree of freedom in thermal equilibrium should be $\frac{1}{2}T$. Boltzmanns constant is omitted here, because we express temperature in energy units.

$$\langle \mathbf{f}_s(t) \mathbf{f}_{s'}(t') \rangle = 2\boldsymbol{\zeta}(\mathbf{n}) \delta_{ss'} T \delta(t - t') \tag{11}$$

We finalize this section with the conclusion that the dynamics of a rod-spring chain in a presence of nematic field boils down to the system of stochastic differential equations (7),(8),(9) supplemented with a definition of the properties of stochastic forces (10), (11).

4 Normal modes expansion

In the previous section we have stated the system of stochastic differential equations describing the dynamics of a polymer chain. This system consists of N coupled equations. In this section our aim is to decouple those equations. In order to do that we will perform a sequence of changes of coordinates.

First, we want to separate the translational motion of the chain as a whole from the internal motions. This can be done by going to the set of variables $\{\mathbf{r}_c, \mathbf{b}_1, ..., \mathbf{b}_{N-1}\}$ described in section 2. Then equation for the $\mathbf{r}_c$ is obtained by taking sum of equations for all $\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_N$ and equations for $\mathbf{b}_s$ is obtained from the difference of equations for $\mathbf{r}_{s+1}$ and $\mathbf{r}_s$.

$$N\boldsymbol{\zeta} \cdot (\dot{\mathbf{r}}_c - \boldsymbol{\kappa} \cdot \mathbf{r}_c) = \mathbf{f}_c(t) \tag{12}$$

Here $\mathbf{f}_c(t) = \sum\limits_{s=1}^{N} \mathbf{f}_s(t)$.

$$\langle \mathbf{f}_c(t) \rangle = \sum_{s=1}^{N} \langle \mathbf{f}_c(t) \rangle = \mathbf{0} \tag{13}$$

$$\langle \mathbf{f}_c(t)\mathbf{f}_c(t') \rangle = \sum_{s=1}^{N} \sum_{s'=1}^{N} \langle \mathbf{f}_s(t)\mathbf{f}_{s'}(t') \rangle = 2N\boldsymbol{\zeta}(\mathbf{n}) T\delta(t - t') \tag{14}$$

Equation for internal degrees of freedom. For $s = 1$

$$\boldsymbol{\zeta} \cdot \left(\dot{\mathbf{b}}_1 - \boldsymbol{\kappa} \cdot \mathbf{b}_1 \right) = \mathbf{K} \cdot (-2\mathbf{b}_1 + \mathbf{b}_2) + w_1 l k_0 \mathbf{n} + \mathbf{f}_2 - \mathbf{f}_1 \tag{15}$$

For $s \in \{2, ..., N-2\}$

$$\boldsymbol{\zeta} \cdot \left(\dot{\mathbf{b}}_s - \boldsymbol{\kappa} \cdot \mathbf{b}_s \right) = \mathbf{K} \cdot (\mathbf{b}_{s+1} - 2\mathbf{b}_s + \mathbf{b}_{s-1}) + \mathbf{f}_{s+1} - \mathbf{f}_s \tag{16}$$

For $s = N-1$

$$\boldsymbol{\zeta} \cdot \left(\dot{\mathbf{b}}_{N-1} - \boldsymbol{\kappa} \cdot \mathbf{b}_{N-1} \right) = \mathbf{K} \cdot (\mathbf{b}_{N-2} - 2\mathbf{b}_{N-1}) + w_1 l k_0 \mathbf{n} + \mathbf{f}_N - \mathbf{f}_{N-1} \tag{17}$$

We introduce stochastic forces $\mathbf{g}_s = \mathbf{f}_{s+1} - \mathbf{f}_s$ for $s \in \{1, 2, ..., N-1\}$ and a Rouse matrix $A_{ps} = 2\delta_{p,s} - \delta_{p+1,s} - \delta_{p,s+1}$. Then equations (15),(16),(17) can be written in a general form for $p \in \{1, 2, ..., N-1\}$

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot \left(\dot{\mathbf{b}}_p - \boldsymbol{\kappa} \cdot \mathbf{b}_p \right) = -\mathbf{K}(\mathbf{n}) \cdot \sum_{s=1}^{N-1} A_{p,s} \mathbf{b}_s + w_1 l k_0 \mathbf{n} (\delta_{p,1} + \delta_{p,N-1}) + \mathbf{g}_p(t) \tag{18}$$

$$\langle \mathbf{g}_p(t) \rangle = \mathbf{0} \tag{19}$$

$$\langle \mathbf{g}_p(t)\mathbf{g}_{p'}(t') \rangle = 2A_{p,p'}\boldsymbol{\zeta}(\mathbf{n})T\delta(t - t') \tag{20}$$

By means of this change of variables we have separated translational motion of the center of mass (12) from the internal motions of the chain (18). We see that

$N-1$ equations for internal motions are coupled. The problem of decoupling of these equations boils down to diagonalization of Rouse matrix. It is known that Rouse matrix of sizes $(N-1) \times (N-1)$ can be diagonalized by matrix $\Gamma_{m,p} = \sqrt{\frac{2}{N}} \sin\left(\frac{\pi pm}{N}\right)$.

$$J_{m,s} = \lambda_m \delta_{m,s} = \sum_{p=1}^{N-1} \sum_{n=1}^{N-1} \Gamma_{m,p} A_{p,n} \left(\Gamma^{-1}\right)_{n,s}$$

where $\lambda_m = 4 \sin^2\left(\frac{\pi m}{2N}\right)$ - the eigenvalues of the Rouse matrix.

These considerations motivate us to perform the next change of variables.

$$\mathbf{q}_m = \sum_{s=1}^{N-1} \Gamma_{m,s} \mathbf{b}_s \tag{21}$$

Equations for coordinates $\mathbf{q}_m$ is derived from (18) by replacing of $\mathbf{b}_s$ in terms of $\mathbf{q}_m$ and by following multiplication by $\Gamma_{m,p}$ with following summation by index p. We get for $m \in \{1, ..., N-1\}$

$$\boldsymbol{\zeta}(\mathbf{n}) \cdot (\dot{\mathbf{q}}_m - \boldsymbol{\kappa} \cdot \mathbf{q}_m) = -\lambda_m \mathbf{K}(\mathbf{n}) \cdot \mathbf{q}_m + \alpha_m w_1 l k_0 \mathbf{n} + \mathbf{h}_m(t) \tag{22}$$

We used here some new notations.

$$\alpha_m = \sum_{p=1}^{N-1} \Gamma_{m,p} \left(\delta_{p,1} + \delta_{p,N-1}\right) = \sqrt{\frac{2}{N}} \left(1 - (-1)^m\right) \sin\left(\frac{\pi m}{N}\right) \tag{23}$$

$$\mathbf{h}_m(t) = \sum_{p=1}^{N-1} \Gamma_{m,p} \mathbf{g}_p(t) \tag{24}$$

$$\langle \mathbf{h}_m(t) \rangle = \mathbf{0} \tag{25}$$

$$\langle \mathbf{h}_m(t) \mathbf{h}_{m'}(t') \rangle = \sum_{p=1}^{N-1} \sum_{p'=1}^{N-1} \Gamma_{m,p} \Gamma_{m',p'} \langle \mathbf{g}_m(t) \mathbf{g}_{m'}(t') \rangle$$

We employ expression (20) and the fact that matrix Γ is orthogonal and symmetric to derive the expression for $\langle \mathbf{h}_m(t) \mathbf{h}_{m'}(t') \rangle$.

$$\langle \mathbf{h}_m(t) \mathbf{h}_{m'}(t') \rangle = 2 \boldsymbol{\zeta}(\mathbf{n}) \lambda_m T \delta_{m,m'} \delta(t - t') \tag{26}$$

We arrive to the set of $N-1$ independent equations for internal motion of the chain. The fact that all these equations are independent allows us to claim for new coordinates $\mathbf{q}_m$ to be normal modes.

$$\dot{\mathbf{q}}_m - \boldsymbol{\kappa} \cdot \mathbf{q}_m = -\lambda_m \boldsymbol{\tau}^{-1} \cdot \mathbf{q}_m + \alpha_m w_1 l \tau_{\parallel} \mathbf{n} + \mathbf{v}_m(t) \tag{27}$$

$$\boldsymbol{\tau}^{-1}(\mathbf{n}) = \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{K}(\mathbf{n}) = \tau_{\parallel}^{-1} \mathbf{nn} + \tau_{\perp}^{-1} (\mathbf{I} - \mathbf{nn}) \tag{28}$$

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$$\mathbf{v}_m(t) = \boldsymbol{\zeta}^{-1}(\mathbf{n}) \cdot \mathbf{h}_m(t) \tag{29}$$

$$\langle \mathbf{v}_m \rangle = \mathbf{0} \tag{30}$$

$$\langle \mathbf{v}_m(t)\mathbf{v}_{m'}(t') \rangle = 2\boldsymbol{\zeta}^{-1}(\mathbf{n})\lambda_m T \delta_{m,m'} \delta(t - t') \tag{31}$$

It is left to nondimensionalize these equations by the following transformation:

$$\tilde{\mathbf{q}}_m = \frac{\mathbf{q}_m}{l} \qquad\qquad \tilde{\mathbf{v}}_m(\tilde{t}) = \frac{\tau_\|}{l}\mathbf{v}_m(\tau_\| \tilde{t})$$

$$\tilde{t} = \frac{t}{\tau_\|} \qquad\qquad \tilde{\boldsymbol{\kappa}} = \boldsymbol{\kappa}\tau_\|$$

$$\tilde{\boldsymbol{\tau}}^{-1} = \boldsymbol{\tau}^{-1}\tau_\| \qquad\qquad \tilde{\boldsymbol{\zeta}}^{-1} = \boldsymbol{\zeta}^{-1}\zeta_\|$$

$$\tau = \frac{\tau_\perp}{\tau_\|} \qquad\qquad \zeta = \frac{\zeta_\perp}{\zeta_\|}$$

$$\Theta = \frac{2T}{k_0 l^2}$$

After these replacements we get following set of equations to describe internal motion of the chain.

$$\frac{d}{dt}\tilde{\mathbf{q}}_p = -\left(\lambda_p \tilde{\boldsymbol{\tau}}^{-1} - \tilde{\boldsymbol{\kappa}}\right) \cdot \tilde{\mathbf{q}}_p + \alpha_p w_1 \mathbf{n} + \tilde{\mathbf{v}}_p(\tilde{t}) \tag{32}$$

$$\langle \tilde{\mathbf{v}}_p(\tilde{t}) \rangle = \mathbf{0} \tag{33}$$

$$\langle \tilde{\mathbf{v}}_p(\tilde{t}) \tilde{\mathbf{v}}_{p'}(\tilde{t}') \rangle = \tilde{\boldsymbol{\zeta}}^{-1} \Theta \lambda_p \delta_{p,p'} \delta(\tilde{t} - \tilde{t}') \tag{34}$$

We finish this section with the set of equations (32), (33), (34). If the director dynamics is prescribed, these equations allow us to compute $\tilde{\mathbf{q}}_p$. On the basis of internal dynamics of the polymer chain we can deduce the macroscopic properties of the LCP solution, such as stress tensor, which are of major interest in this work. Formally (32) is a linear differential equation with respect to $\tilde{\mathbf{q}}_p$ and can be formally solved if $\tilde{\boldsymbol{\kappa}}(\tilde{t})$, $\mathbf{n}(\tilde{t})$ and $\tilde{\mathbf{v}}_p(\tilde{t})$ are given.

5 Ensemble average behavior of normal-modes coordinates

Our aim here is to write the analytical solution for the equation (32) and then to deduce the ensemble averages $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$, $\langle \tilde{\mathbf{q}}_p(\tilde{t})\tilde{\mathbf{q}}_p(\tilde{t}) \rangle$ from it. This can be done on the basis of derivations made in Appendix I.

First we introduce new notations

$$\mathbf{A}_p(\tilde{t}) \equiv -\left(\lambda_p \tilde{\boldsymbol{\tau}}^{-1}(\tilde{t}) - \boldsymbol{\kappa}(\tilde{t})\right) \tag{35}$$

$$\mathbf{a}_p(\tilde{t}) \equiv \alpha_p w_1 \mathbf{n}(\tilde{t}) + \tilde{\mathbf{v}}_p(\tilde{t}) \tag{36}$$

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$\mathbf{M}_p(t)$ is a matrix satisfying initial-value problem.

$$\begin{cases} \dot{\mathbf{M}}_p(\tilde{t}) = \mathbf{A}_p(\tilde{t}) \cdot \mathbf{M}_p(\tilde{t}) \\ \mathbf{M}_p(0) = \mathbf{I} \end{cases} \tag{37}$$

Then the solution of (32) is following from (63)

$$\tilde{\mathbf{q}}_p(\tilde{t}) = \mathbf{M}_p(\tilde{t}) \cdot \tilde{\mathbf{q}}_p(0) + \mathbf{M}_p(\tilde{t}) \cdot \int\limits_0^{\tilde{t}} ds\, \mathbf{M}_p^{-1}(s) \cdot \mathbf{a}_p(s) \tag{38}$$

where $\tilde{\mathbf{q}}_p(0)$ is the initial value.

Averaging (38) gives the behavior of $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$.

$$\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle = \mathbf{M}_p(\tilde{t}) \cdot \langle \tilde{\mathbf{q}}_p(0) \rangle + \alpha_p w_1 \mathbf{M}_p(\tilde{t}) \cdot \int\limits_0^{\tilde{t}} ds\, \mathbf{M}_p^{-1}(s) \cdot \mathbf{n}(s) \tag{39}$$

By taking the diadic product of (38) by itself we get an expression for $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$.

$$\langle \tilde{\mathbf{q}}_p(\tilde{t}) \tilde{\mathbf{q}}_p(\tilde{t}) \rangle = \langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle \langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle + \mathbf{M}_p(\tilde{t}) \cdot \mathbf{B}_p(\tilde{t}) \cdot \left(\mathbf{M}_p(\tilde{t}) \right)^T \tag{40}$$

where $\mathbf{B}_p(\tilde{t})$ satisfies the following initial-value problem.

$$\begin{cases} \dot{\mathbf{B}}_p(\tilde{t}) = \Theta \lambda_p \mathbf{M}_p^{-1}(\tilde{t}) \cdot \tilde{\boldsymbol{\zeta}}^{-1}(\tilde{t}) \cdot \left(\mathbf{M}_p^{-1} \right)^T \\ \mathbf{B}_p(0) = \langle \tilde{\mathbf{q}}_p(0) \tilde{\mathbf{q}}_p(0) \rangle - \langle \tilde{\mathbf{q}}_p(0) \rangle \langle \tilde{\mathbf{q}}_p(0) \rangle \end{cases} \tag{41}$$

These three quantities will be the major objects when computing stresses.

Now let's decide what initial conditions for $\langle \tilde{\mathbf{q}}_p(0) \rangle$ and $\langle \tilde{\mathbf{q}}_p(0) \tilde{\mathbf{q}}_p(0) \rangle$ are worthwhile being discussed. We will be interested in the cases when the polymer solution is at rest before moment of time $t = 0$ and after that moment is subjected to some deformation. Thus, we can take for the initial conditions $\langle \tilde{\mathbf{q}}_p(0) \rangle$ and $\langle \tilde{\mathbf{q}}_p(0) \tilde{\mathbf{q}}_p(0) \rangle$ their values in the equilibrium state. This means we have to derive an expressions for $\langle \tilde{\mathbf{q}}_p \rangle_{eq}$ and $\langle \tilde{\mathbf{q}}_p \tilde{\mathbf{q}}_p \rangle_{eq}$ in equilibrium, i.e. they should come from (39) and (40) in the limit $t \to \infty$ with $\boldsymbol{\kappa}(t) = \mathbf{0}$. In Appendix II the expression for $\langle \tilde{\mathbf{q}}_p \rangle_{eq}$ and $\langle \tilde{\mathbf{q}}_p \tilde{\mathbf{q}}_p \rangle_{eq}$ are obtained. They are given by (67) and (71). It follows that if the system was in equilibrium at moment $\tilde{t} = 0$, then

$$\mathbf{B}_p(0) = \Theta \, \tilde{\boldsymbol{\tau}} \cdot \tilde{\boldsymbol{\zeta}}^{-1} \tag{42}$$

To sum up the results derived in this section we want to make a remark. If the time-evolution of the director is prescribed, then by means of (37),(39),(40) and (41) we can track the evolution of ensemble averages $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$ and $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$. But, the evolution of the director is by itself determined by the evolution of the conformations of the chains, i.e. of ensemble averages of $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$, $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$ or even more complicated combinations. Therefore in the next section we focus on establishing the missing link between the evolution of $\mathbf{n}(\tilde{t})$ and the average conformations of the chains.

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6 Director orientation equation

As it was said in the end of the previous section we are aiming here to establish the equation for the director orientation evolution. The major physical principle that we will put in the ground is the minimization of the Helmholz free energy of the chains with respect to fast variables. Really, the relaxation of the orientational degrees of freedom happens much faster then the relaxation of the backbones conformation. This means that at the timescale of changes for $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$, $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$ we can consider the system to be in an equilibrium with respect to the orientation of the nematogens. In the highly-ordered limit orientation of the nematogens is determined by the orientation of the director. This brings us to a conclusion that the director should minimize the total free energy of the chains. In an earlier sections we have already stated the free energy of a single chain in a mean nematic of the surrounding molecules by (1). The total free energy of all chains is a sum of the free energy aver all chains plus the interaction term. But we have already taken the interaction between the chains in a mean-field way when writing the free energy of a single chain. The fact that each chain is subjected to a nematic field created by the surrounding is already taken into account. Thus the sum of free energies (1) over all chains already contains part of interactions modeled in a mean-field way. But we did not take into account the entanglements between chains, which are usually important in a concentrated solutions. On the other hand in the highly-ordered state these entanglements are expected to be much weaker than in a disordered state. As the first approach we will not take them into account and later from the comparisons of the current theory with experimental data we will see how good is this approach.

The free energy of the whole set of

$$F_{sys} = \sum_{i=1}^{N_{ch}} F_i \tag{43}$$

Here F_i is a free energy of an i-th chain. The assumption for all chains to have equal number of nematogens and the law of large numbers allows us to transform (43) into

$$F_{sys} = N_{ch} \langle F \rangle \tag{44}$$

Here F is a free energy of a single chain.

To simplify further derivations we make the expression for F_{sys} dimensionless by the following transformation.

$$\tilde{F}_{sys} = \frac{F_{sys}}{N_{ch} \frac{1}{2} k_0 l^2} \tag{45}$$

From (1) and derivations in the Appendix III, namely results (79),(80),(81), follows

$$\tilde{F}_{sys} = \sum_{m=1}^{N-1} 2w_1 \left(\mathbf{\Lambda} : \mathbf{nn} - \mathbf{p} \cdot \mathbf{n} \right) + C \tag{46}$$

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The problem is to minimize (46) with respect to $\mathbf{n}$ for given $\boldsymbol{\Lambda}$, $\mathbf{p}$, C, upon the constrain $\mathbf{n} \cdot \mathbf{n} = 1$. We use Lagrange multipliers method in order to find a minimizer. First we build Lagrange function

$$\mathfrak{L} = \boldsymbol{\Lambda} : \mathbf{nn} - \mathbf{p} \cdot \mathbf{n} + \mu \left(\mathbf{n} \cdot \mathbf{n} - 1\right) \tag{47}$$

Here μ is Lagrange multiplier. The multiplier $2w_1$ and constant C are omitted because they do not influence the position of the minimum. Let $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ be the normalized eigenbasis of operator Λ and $\{\Lambda_1, \Lambda_2, \Lambda_3\}$ are the eigenvlaues of $\boldsymbol{\Lambda}$. Then

$$\Lambda \;=\; \sum_{i=1}^{3} \Lambda_i \mathbf{e}_i \mathbf{e}_i \tag{48}$$

$$\mathbf{p} \;=\; \sum_{i=1}^{3} p_i \mathbf{e}_i \tag{49}$$

$$\mathbf{n} \;=\; \sum_{i=1}^{3} n_i \mathbf{e}_i \tag{50}$$

Here p_i and n_i are the coordinates of $\mathbf{p}$ and $\mathbf{n}$ in this basis. Now we look for a global minimum of $\mathfrak{L}$.

$$\frac{\partial \mathfrak{L}}{\partial n_i} \;=\; 2n_i \left(\Lambda_i + \mu\right) - p_i = 0 \qquad i \in \{1, 2, 3\} \tag{51}$$

$$\frac{\partial \mathfrak{L}}{\partial \mu} \;=\; \sum_{i=1}^{3} \left(n_i^2 - 1\right) = 0 \tag{52}$$

From (51,) follows the equation for μ

$$\sum_{i=1}^{3} \frac{p_i^2}{4 \left(\mu + \Lambda_i\right)^2} = 1 \tag{53}$$

If μ is found then coordinates of $\mathbf{n}$ can be easily found from the equations

$$n_i = \frac{p_i}{2 \left(\mu + \Lambda_i\right)} \tag{54}$$

From Sylvester's criteria follows that provided $\Lambda_i > 0$ for $i \in \{1, 2, 3\}$ expression (54) gives the minimum we were looking for.

The evolution of ensemble averages is dependent on the evolution of the director. The orientation of the director is determined by the ensemble averages $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$ and $\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle$. This means equations (39), (40) and (53), (54) should be used simultaneously.

7 The particle contribution to the stress tensor

In the concentrated polymer solutions usually the main contribution to the stress tensor is due to the polymer chains, but not due to a solvent. The

particle contribution to the stress tensor can be computed by a famous Kramers-Kirkwood formula

$$\boldsymbol{\sigma}^{(p)}(t) = -\frac{1}{V} \sum_{m=1}^{N_{beads}} \langle \mathbf{F}_m(t)\mathbf{r}_m(t) \rangle \tag{55}$$

Here V is a volume of the solution, N_{beads} - the total number of beads in the solution. In our case $N_{beads} = N_{chains}N$.

Our aim is to express (55) in terms of the set of normal coordinates $\{\tilde{\mathbf{q}}_1, \tilde{\mathbf{q}}_2, ..., \tilde{\mathbf{q}}_{N-1}\}$. The details of the derivation are in the Appendix IV. Here we give just the result.

$$\boldsymbol{\sigma}^{(p)}(t) = -P_{id}\mathbf{I} + \frac{2P_{id}}{N\Theta} \sum_{m=1}^{N-1} \left(\tilde{\mathbf{K}} \cdot \langle \tilde{\mathbf{q}}_p(\tilde{t})\tilde{\mathbf{q}}_p(\tilde{t}) \rangle - \frac{w_1\alpha_m}{\lambda_m}\mathbf{n} \langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle \right) \tag{56}$$

where

$$P_{id} = \frac{N_{chains}NT}{V} \tag{57}$$

$$\tilde{\mathbf{K}} = \tilde{\boldsymbol{\zeta}} \cdot \tilde{\boldsymbol{\tau}}^{-1} \tag{58}$$

8   Discussion

In the current work we have formulated a discrete microscopic model for a mono-domain highly-ordered nematic LCP solution. This model is the extension of the model formulated in the work [1]. The continuous limit of this model is studied in [2]. In the continuous limit the chain acquires an infinite number of degrees of freedom. In order to prevent the blow-up of the response functions the proper cut-off for the number of degrees of freedom is needed. The right mathematical way of doing this procedure is a subtle procedure. By considering the model for discrete chain we confirm that the cut-off introduced in the work [2] is properly done. Moreover, the discrete model is more suitable for the numerical studies which will be required in the most cases, besides very simple viscometric flows. These are the arguments in favor of the discrete formulation.

Appendix I. Formal solution of a linear matrix differential equation

In this appendix one of the methods of solving systems of linear inhomogeneous first order differential equations with time-dependent coefficients is shown. Let $\mathbf{x}$ be a time-dependent vector in $\mathbb{R}^n$ solving the initial-value problem.

$$\begin{cases} \dot{\mathbf{x}}(t) = \mathbf{A}(t) \cdot \mathbf{x}(t) + \mathbf{b}(t) \\ \\ \mathbf{x}(0) = \mathbf{x}_0 \end{cases} \tag{59}$$

Here $\mathbf{A}$ is a time-dependent matrix of size $n \times n$ and $\mathbf{b}$ is a given time-dependent vector in $\mathbb{R}^n$.

Our aim is to get an analytic expression for solution of the initial-value problem (59). In order to get the solution we will first solve a corresponding homogeneous equation and later use the modified method of variation of a constant. Our guess for the solution of the corresponding homogeneous equation is $\mathbf{x}(t) = \mathbf{M}(t) \cdot \mathbf{x}_0$, where $\mathbf{M}(t)$ is an unknown matrix to be found. Equation for $\mathbf{M}(t)$ can be established by direct substitution of $\mathbf{x}(t)$ into $\dot{\mathbf{x}}(t) = \mathbf{A}(t) \cdot \mathbf{x}(t)$.

$$\dot{\mathbf{M}}(t) \cdot \mathbf{x}_0 = \mathbf{A}(t) \cdot \mathbf{M}(t) \cdot \mathbf{x}_0$$

This equation should be satisfied for any initial conditions $\mathbf{x}_0$. Thus we obtain an equation for $\mathbf{M}(t)$. Supplemented with the initial condition $\mathbf{x}(0) = \mathbf{M}(0) \cdot \mathbf{x}_0 = \mathbf{x}_0$, i.e. $\mathbf{M}(0) = \mathbf{I}$, we obtain an initial-value problem for $\mathbf{M}(t)$.

$$\begin{cases} \dot{\mathbf{M}}(t) = \mathbf{A}(t) \cdot \mathbf{M}(t) \\ \\ \mathbf{M}(0) = \mathbf{I} \end{cases} \tag{60}$$

Now we turn back to the problem (59) with inhomogeneous equation. We will look for solution in the form $\mathbf{x}(t) = \mathbf{M}(t) \cdot \mathbf{c}(t)$, where $\mathbf{c}(0) = \mathbf{x}_0$ and $\mathbf{M}(t)$ is described by (60). By direct substitution of the suggested for $\mathbf{x}(t)$ expression into (59) we obtain an initial-value problem for $\mathbf{c}(t)$.

$$\begin{cases} \dot{\mathbf{c}}(t) = \mathbf{M}^{-1}(t) \cdot \mathbf{b}(t) \\ \\ \mathbf{c}(0) = \mathbf{x}_0 \end{cases} \tag{61}$$

If the matrix $\mathbf{M}^{-1}(t)$ is known and the a vector $\mathbf{b}(t)$ is given, then the problem (61) can be directly integrated.

$$\mathbf{c}(t) = \mathbf{x}_0 + \int_0^t ds\, \mathbf{M}^{-1}(s) \cdot \mathbf{b}(s) \tag{62}$$

From (62) we readily obtain an expression for $\mathbf{x}(t)$.

$$\mathbf{x}(t) = \mathbf{M}(t) \cdot \mathbf{x}_0 + \mathbf{M}(t) \cdot \int_0^t ds\, \mathbf{M}^{-1}(s) \cdot \mathbf{b}(s) \tag{63}$$

This expression contains both $\mathbf{M}$ and $\mathbf{M}^{-1}$. Sometimes it is more convenient to solve an evolution equation for $\mathbf{M}^{-1}$ instead of inverting $\mathbf{M}$ for every moment of time. Equation for $\mathbf{M}^{-1}$ is easily derived from (60) and by the use of the definition of inverse matrix $\mathbf{M}^{-1}(t) \cdot \mathbf{M}(t) = \mathbf{I}$.

$$
\begin{cases}
\dot{\mathbf{M}}^{-1}(t) = -\mathbf{M}^{-1}(t) \cdot \mathbf{A}(t) \\[2mm]
\mathbf{M}^{-1}(0) = \mathbf{I}
\end{cases}
\tag{64}
$$

We conclude this appendix giving the solution of the problem (59) in terms of (63), (60), (64).

Appendix II. Average quantities in equilibrium state

In the case of equilibrium $\tilde{\boldsymbol{\kappa}}(\tilde{t}) = \mathbf{0}$ and $\mathbf{n}$ does not change its direction in time. In this case system (37) can be explicitly solved.

$$\mathbf{M}_p(\tilde{t}) = \exp\left(-\lambda_p \tilde{\boldsymbol{\tau}}^{-1} \tilde{t}\right) \tag{65}$$

Then from (39)

$$\langle \tilde{\mathbf{q}}_p(\tilde{t}) \rangle = \exp\left(-\lambda_p \tilde{\boldsymbol{\tau}}^{-1} \tilde{t}\right) \cdot \langle \tilde{\mathbf{q}}_p(0) \rangle + \int_0^{\tilde{t}} ds \, \exp\left(-\lambda_p \tilde{\boldsymbol{\tau}}^{-1}(\tilde{t} - s)\right) \cdot \alpha_p w_1 \mathbf{n} \tag{66}$$

In the limit $t \to \infty$ this boils down to

$$\langle \tilde{\mathbf{q}}_p \rangle_{eq} = \frac{\alpha_p w_1}{\lambda_p} \mathbf{n} \tag{67}$$

In order to get an expression for $\langle \tilde{\mathbf{q}}_p \tilde{\mathbf{q}}_p \rangle_{eq}$ we can use the result (40).

$$\langle \tilde{\mathbf{q}}_p \tilde{\mathbf{q}}_p \rangle_{eq} = \langle \tilde{\mathbf{q}}_p \rangle_{eq} \langle \tilde{\mathbf{q}}_p \rangle_{eq} + \lim_{\tilde{t} \to \infty} \mathbf{M}_p(\tilde{t}) \cdot \mathbf{B}_p(\tilde{t}) \cdot \left(\mathbf{M}_p(\tilde{t})\right)^T \tag{68}$$

Expression for $\mathbf{B}_p(\tilde{t})$ can be found (41) by direct integration, because in equilibrium state matrices $\mathbf{M}_p(\tilde{t})$ are known and $\tilde{\boldsymbol{\zeta}}$ is just a constant matrix. Thus in equilibrium we get

$$\mathbf{B}_p(\tilde{t}) = \frac{1}{2} \Theta \, \tilde{\boldsymbol{\tau}} \cdot \tilde{\boldsymbol{\zeta}}^{-1} \cdot \exp\left(2\lambda_p \tilde{\boldsymbol{\tau}}^{-1} \tilde{t}\right) + \mathbf{B}_p(0) \tag{69}$$

and

$$\lim_{\tilde{t} \to \infty} \mathbf{M}_p(\tilde{t}) \cdot \mathbf{B}_p(\tilde{t}) \cdot \left(\mathbf{M}_p(\tilde{t})\right)^T = \frac{1}{2} \Theta \, \tilde{\boldsymbol{\tau}} \cdot \tilde{\boldsymbol{\zeta}}^{-1} \tag{70}$$

Finally we get an expression for $\langle \tilde{\mathbf{q}}_p \tilde{\mathbf{q}}_p \rangle_{eq}$

$$\langle \tilde{\mathbf{q}}_p \tilde{\mathbf{q}}_p \rangle_{eq} = \frac{\alpha_p^2 w_1^2}{\lambda_p^2} \mathbf{n}\mathbf{n} + \frac{1}{2} \Theta \, \tilde{\boldsymbol{\tau}} \cdot \tilde{\boldsymbol{\zeta}}^{-1} \tag{71}$$

This result is in agreement with equipartition theorem.

Appendix III. Free energy of the ensemble of chains

In this section we derive formula for dimensionless free energy of the system of chains expressed in normal-mode coordinates. We start from (1) and definition (45). First we turn from the set of coordinates $\{\tilde{\mathbf{r}}_1, ..., \tilde{\mathbf{r}}_N\}$ to $\tilde{\mathbf{R}}_c, \tilde{\mathbf{b}}_1, ..., \tilde{\mathbf{b}}_{N-1}$. They differ from the coordinated introduced in the section 2 just by division by the length-scale l.

$$\tilde{F}_{sys} = \frac{1}{k_0} \sum_{m=1}^{N-1} \left[w_0 \left\langle \tilde{\mathbf{b}}_m \cdot \mathbf{K}_0 \cdot \tilde{\mathbf{b}}_m \right\rangle + w_1 \left\langle \left(\tilde{\mathbf{b}}_m - \mathbf{n} \right) \cdot \mathbf{K}_1 \cdot \left(\tilde{\mathbf{b}}_m - \mathbf{n} \right) \right\rangle \right]$$

Then we open the brackets and employ the symmetry of operator $\mathbf{K}_1$

$$\tilde{F}_{sys} = \frac{1}{k_0} \sum_{m=1}^{N-1} \left[(w_0 \mathbf{K}_0 + w_1 \mathbf{K}_1) : \left\langle \tilde{\mathbf{b}}_m \tilde{\mathbf{b}}_m \right\rangle + w_1 \mathbf{K}_1 : \left(\mathbf{nn} - 2\mathbf{n} \left\langle \tilde{\mathbf{b}}_m \right\rangle \right) \right]$$

Then we employ the expressions $\mathbf{K}_0 = k_0 \mathbf{I}$ and $\mathbf{K}_1 = k_0 \mathbf{nn} + k_1 (\mathbf{I} - \mathbf{nn})$ to get

$$\tilde{F}_{sys} = 2w_1 \left(\mathbf{\Lambda} : \mathbf{nn} - \mathbf{p} \cdot \mathbf{n} \right) + C \tag{72}$$

where

$$\mathbf{\Lambda} = \frac{1}{2} \left(1 - \frac{k_1}{k_0} \right) \sum_{m=1}^{N-1} \left\langle \tilde{\mathbf{b}}_m \tilde{\mathbf{b}}_m \right\rangle \tag{73}$$

$$\mathbf{p} = \sum_{m=1}^{N-1} \left\langle \tilde{\mathbf{b}}_m \right\rangle \tag{74}$$

$$C = \left(w_0 + w_1 \frac{k_1}{k_0} \right) \sum_{m=1}^{N-1} \left\langle \tilde{\mathbf{b}}_m \cdot \tilde{\mathbf{b}}_m \right\rangle + w_1 \left(N - 1 \right) \tag{75}$$

Now we want to express $\mathbf{\Lambda}$, $\mathbf{p}$ and C in terms of the coordinates $\{\tilde{\mathbf{q}}_1, \tilde{\mathbf{q}}_2, ..., \tilde{\mathbf{q}}_{N-1}\}$.

$$\sum_{m=1}^{N-1} \left\langle \tilde{\mathbf{b}}_m \tilde{\mathbf{b}}_m \right\rangle = \sum_{m=1}^{N-1} \sum_{n=1}^{N-1} \sum_{s=1}^{N-1} \left(\Gamma^{-1} \right)_{m,s} \left(\Gamma^{-1} \right)_{m,n} \left\langle \tilde{\mathbf{q}}_s \tilde{\mathbf{q}}_n \right\rangle$$

We use $\Gamma^{-1} = \Gamma^T$ to get

$$\sum_{m=1}^{N-1} \left\langle \tilde{\mathbf{b}}_m \tilde{\mathbf{b}}_m \right\rangle = \sum_{n=1}^{N-1} \left\langle \tilde{\mathbf{q}}_n \tilde{\mathbf{q}}_n \right\rangle \tag{76}$$

Similarly,

$$\sum_{m=1}^{N-1} \left\langle \tilde{\mathbf{b}}_m \right\rangle = \sum_{m=1}^{N-1} \sum_{n=1}^{N-1} \left(\Gamma^{-1} \right)_{m,n} \left\langle \tilde{\mathbf{q}}_n \right\rangle = \sum_{n=1}^{N-1} \beta_n \left\langle \tilde{\mathbf{q}}_n \right\rangle \tag{77}$$

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where

$$\beta_n = \sum_{m=1}^{N-1} \Gamma_{m,n}^{-1} = \sqrt{\frac{2}{N}} \sum_{m=1}^{N-1} \sin\left(\frac{\pi n m}{N}\right)$$

We use formula

$$\sum_{m=1}^{N} \sin(am) = \frac{1}{\sin\left(\frac{a}{2}\right)} \sin\left(\frac{aN}{2}\right) \sin\left(\frac{a(N+1)}{2}\right)$$

to get

$$\beta_n = \frac{\alpha_n}{\lambda_n} \tag{78}$$

Thus we rewrite (73),(74),(75) in coordinates $\{\tilde{\mathbf{q}}_1, \tilde{\mathbf{q}}_2, ..., \tilde{\mathbf{q}}_{N-1}\}$

$$\boldsymbol{\Lambda} = \frac{1}{2}\left(1 - \frac{k_1}{k_0}\right) \sum_{m=1}^{N-1} \langle \tilde{\mathbf{q}}_m \tilde{\mathbf{q}}_m \rangle \tag{79}$$

$$\mathbf{p} = \sum_{m=1}^{N-1} \frac{\alpha_m}{\lambda_m} \langle \tilde{\mathbf{q}}_m \rangle \tag{80}$$

$$C = \left(w_0 + w_1 \frac{k_1}{k_0}\right) \sum_{m=1}^{N-1} \langle \tilde{\mathbf{q}}_m \cdot \tilde{\mathbf{q}}_m \rangle + w_1 (N - 1) \tag{81}$$

Results (79),(80),(81) allow us to express the free energy (72) in terms of coordinates $\{\tilde{\mathbf{q}}_1, \tilde{\mathbf{q}}_2, ..., \tilde{\mathbf{q}}_{N-1}\}$.

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