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DYNAMICS OF NEARLY RIGID POLYMER CHAINS IN A FLOW FIELD

Summary

The role of small flexibility of nearly rigid polymer chains in viscous media is considered. The method proposed in this paper is valid for the chain subjected to an external orienting field or an orienting flow gradient, for example uniaxial elongational flow. Worm-like chain model is used to describe dynamics and statistics of the chain.

Intrachain potential depends on curvature of the chain contour, while twisting at any point of the chain disappears on average due to thermal motion. Considering that relaxation of the twisting motion is much quicker than relaxation of curvature in such a rigid chain, one can treat such chain as a planar curve. With such an assumption, kinematic Darboux conditions are satisfied as an identity, and dynamics of the chain in can be described by Langevin type equation for the tangent vector at any point of the chain contour.

In the case of rigid chains, solution of the equation of motion of the chain tangent vector is found in the form of Fourier series expansion. Three first modes, corresponding to the longest relaxation times are considered in this paper. The main mode corresponds to rotational diffusion of the chain end-to-end vector. The next modes describe large scale bending vibrations, relaxation times of which decrease with increasing chain rigidity (decreasing flexibility). The elastic and viscous parts of steady state stress tensor for dilute solutions of the chains in elongational flow gradient are evaluated.

The partition function of the chain subjected to potential orienting flow field is obtained as a series expansion over small flexibility parameter. In the presence of elongational flow, the chains show molecular orientation and alignment. Order parameter (orientation factor) of chain tangent vector at steady state conditions is obtained as a function of flow gradient. Correlation between tangent vectors along the chain contour changes considerably with an increase of flow rate gradient (or external orienting field). Considerable enhancement of chain rigidity takes place as an effect of orienting forces of the flow or an external field.

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Dynamics of the chain segment in a flow field.

Let us consider small part of a chain length ds. A force **F**(s) acts upon the chain cross-section with coordinate s along the chain. It is a resultant of all *internal* forces acting in the chain. Thus, the equation of motion for the differential part of the chain reads

$$\mathbf{F}(s+ds) - \mathbf{F}(s) + \left[-\hat{\zeta}\cdot(\dot{\mathbf{r}} - \hat{\mathbf{K}}\cdot\mathbf{r}) + \mathbf{B}\right] ds = \mathbf{0} \qquad (1)$$

or

$$\mathbf{F}' - \hat{\zeta}\cdot(\dot{\mathbf{r}} - \hat{\mathbf{K}}\cdot\mathbf{r}) + \mathbf{B} = \mathbf{0} \qquad (2)$$

where we neglect inertia term. The term $-\hat{\zeta}(\dot{\mathbf{r}}-\hat{\mathbf{K}}\cdot\mathbf{r})+\mathbf{B}$ represents density (per unit contour length) of *external* forces affecting the chain motion, and symbol " ′ " denotes partial derivative along the chain contour, $\partial/\partial s$. **B**(s,t) is density of stochastic Brownian force, $\hat{\mathbf{K}}$ - flow gradient tensor, $\hat{\zeta}$ - friction coefficient tensor per unit contour length. Vector r(s,t) describes the position of the chain points in the laboratory coordinate system at the instant of time t.

In the slender body approach [1] it is suggested that the friction coefficient tensor in a local orthonormal basis {**u**, **n**, **b**}, connected with the chain, reads

$$\hat{\zeta} = \zeta \begin{bmatrix} 1/2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (3)$$

where **u, n, b** are the chain tangent, normal, and binormal unit vectors, respectively.

To evaluate the internal force **F** we note that potential energy U of persistent chain is known, and for asymptotic case of zero chain width it reads

$$U = \frac{\epsilon}{2} \int_{-L/2}^{L/2} (\mathbf{r}'' \cdot \mathbf{r}'')\, ds \qquad (4)$$

where L is the chain contour length, ϵ - the elasticity constant of chain bending which is related to the chain persistent length l:

$$\epsilon = \frac{k_B T}{2} l \qquad (5)$$

Hence, taking a small variation of the chain contour, $\delta\mathbf{r}(s)$, we find corresponding variation of the chain potential energy

$$\delta U = \in \int_{-L/2}^{L/2} (\mathbf{r}'' \cdot \delta \mathbf{r}'')\, ds = \in \mathbf{r}'' \cdot \delta \mathbf{r}' \Big|_{-L/2}^{L/2} - \in \int_{-L/2}^{L/2} (\mathbf{r}''' \cdot \delta \mathbf{r}')\, ds \tag{6}$$

On the other side, the work of internal forces corresponding to the variation of the chain contour, $\delta\mathbf{r}(s)$, is expressed as [2]

$$\delta W_I = \int_{-L/2}^{L/2} (\mathbf{F} \cdot \delta \mathbf{r}')\, ds \tag{7}$$

Thus, assuming the following condition of the chain free ends (zero curvature at the ends of the chain)

$$\mathbf{r}''(-L/2) = \mathbf{r}''(L/2) = 0 \tag{8}$$

we conclude that the force due to the bending potential reads (cf. eqs.(6-8))

$$\mathbf{F}(s) = -\in \mathbf{r}'''(s) = -\in \mathbf{u}''(s) = \in \left(k^2 \mathbf{u} - k'\mathbf{n} - k\tau\mathbf{b}\right) \tag{9}$$

where $k(s) \equiv [\mathbf{u}'(s) \cdot \mathbf{u}'(s)]^{1/2}$ is the chain curvature, and $\tau(s)$ - the chain twisting at the point s of the chain contour. But it is not enough to know the force component given by eq.(9) to describe the chain dynamics.

The chain inextensibility condition

$$\mathbf{r}'(s) \cdot \mathbf{r}'(s) \equiv \mathbf{u}^2(s) \equiv 1 \tag{10}$$

implies an additional, tension force at any point of the chain contour,

$$\mathrm{T}(s) = \mathrm{T}(s)\mathbf{u} \tag{11}$$

exerting along the chain axis.

Besides, there are subsequent terms in the expansion of the chain potential energy U into the series over the ratio of the chain width to the chain persistence length. Such terms are omitted in the statistics, but they also contribute to the dynamic properties. So, we should add the following contribution

$$\mathrm{N}(s)\mathbf{n} + \mathrm{M}(s)\mathbf{b} \tag{12}$$

Finally, the total force reads

$$\mathbf{F} = \epsilon\left(k^2\mathbf{u} - k'\mathbf{n} - k\tau\mathbf{b}\right) + \mathrm{T}\mathbf{u} + \mathrm{N}\mathbf{n} + \mathrm{M}\mathbf{b} \tag{13}$$

We evaluate now the correlation function of the chain tangent vectors using Langevin equation (2) with internal force given by eq.(13). Since the correlation function has been already calculated in the statistical theory of wormlike chains, we can compare the results and find the unknown term N**n** + M**b** in eq. (13). Such a task can be completed for the case of a planar chain.

Solution for a planar chain.

In the case of a planar chain, the **b**-component of all forces should vanish, and twisting disappears, $\tau = 0$. For convenience of notation, the variable $\mathbf{u} \equiv \mathbf{r}'$ in the equation of motion will be used. Then, from the Langevin equation we have

$$\mathbf{F}'' + \mathbf{B}' - \hat{\zeta}\cdot(\dot{\mathbf{u}} - \hat{\mathbf{K}}\cdot\mathbf{u}) = \mathbf{0} \tag{14}$$

The inextensibility condition (eq.10) leads to the following identity

$$\dot{\mathbf{u}}\cdot\mathbf{u} = 0 \tag{15}$$

For slender body approximation (eq.3), the eqs. (14, 15) reduce to

$$\mathbf{u}\cdot\mathbf{F}'' + \mathbf{u}\cdot\mathbf{B}' + \frac{1}{2}\zeta\,\mathbf{u}\cdot\hat{\mathbf{K}}\cdot\mathbf{u} = 0 \tag{16}$$

After substitution of eq.(13) for the force **F** we obtain tangential, **u**-component of eq.(14) in the form

$$\begin{aligned} &\mathrm{T}'' - \mathrm{T}k^2 - 2\mathrm{N}'k - \mathrm{N}k' + 2\epsilon(k^2)'' - \epsilon(k')^2 - \epsilon k^4 + \\ &+ \mathbf{u}\cdot\mathbf{B}' + \frac{1}{2}\zeta\,\mathbf{u}\cdot\mathbf{K}\cdot\mathbf{u} = 0 \end{aligned} \tag{17}$$

and normal, **n**-component of eq.(14) reads

$$\zeta\mathbf{n}\cdot\hat{\mathbf{K}}\cdot\mathbf{u} - \zeta\dot{\mathbf{u}}\cdot\mathbf{n} + \mathbf{B}'\cdot\mathbf{n} + 2\epsilon(k^3)' - \epsilon k''' + 2\mathrm{T}'k + \mathrm{T}k' + \mathrm{N}'' - k^2\mathrm{N} = 0 \tag{18}$$

Eq.(17) should be completed by the chain end conditions for the tension T. We consider here the case of chain with free ends which suggests

$$T(-L/2) = T(L/2) = 0 \tag{19}$$

at any instant of time.

All further discussion concerns *nearly rigid* chains, i.e. we are looking for a solution in the form of a series expansion over *small flexibility* parameter

$$L/l << 1 \tag{20}$$

defined as the ratio of the chain contour length, L, to the persistent length, l.

We use the following approximation for the unit tangent vector

$$\begin{aligned}\mathbf{u}(s,t) &= \mathbf{e}(t)\sqrt{1-Q^2(s,t)} + \mathbf{g}(t)Q(s,t) = \\ &= \mathbf{e}(t)\left[1-\frac{1}{2}Q^2(s,t)-\frac{1}{8}Q^4(s,t)+\ldots\right]+\mathbf{g}(t)Q(s,t)\end{aligned} \tag{21}$$

where e(t) and g(t) are orthonormal basis vectors in the plane of the chain, and the dimensionless function Q(s,t) supposed to be small as compared to unity for nearly rigid chain. Then, the chain curvature is evaluated as

$$k(s) \cong \kappa(s)\,Q'(s)\,(1+\frac{1}{2}Q^2(s)+\ldots)\ ; \qquad \kappa \equiv \operatorname{sign} Q' \tag{22}$$

and the normal unit vector

$$\mathbf{n}(s,t) = -\kappa\,\mathbf{e}(t)\,Q(s,t) + \kappa\,\mathbf{g}(t)\left(1-\frac{1}{2}Q^2(s,t)+\ldots\right) \tag{23}$$

Substituting eqs. (21-23) into eq. (17) we find in the approximation of first two orders of small flexibility parameter

$$\begin{aligned}&T'' - TQ'^2 - 2N'\kappa Q' - N\kappa Q'' + \\ &\in\left(2(Q'^2)'' - Q''^2 + 2(Q'^2Q^2)'' - Q'^4 - Q''(Q'Q^2)'\right) + \\ &+ \mathbf{e}\cdot\mathbf{B}' + Q\,\mathbf{g}\cdot\mathbf{B}' - \frac{1}{2}Q^2\,\mathbf{e}\cdot\mathbf{B}' + \\ &+ \frac{1}{2}\zeta\left[\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e} + Q\left(\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{g} + \mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right) + Q^2\left(\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{g} - \mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right)\right] = 0\end{aligned} \tag{24}$$

In eq.(24) we have taken into account that, as resulted from eq.(18), N should be of the order of $\sim\in k^3$ (the correction of the next order to main order term $\sim\in k$).

Solution of eq.(24) for the tension force T is obtained as a series

$$T = T^{(0)} + T^{(1)} + T^{(2)} + \dots \tag{25}$$

where each correction $T^{(i)}$ satisfies one of the following equations

$$T^{(0)''} + 2\in(Q'^2)'' - \in Q''^2 + \mathbf{e}\cdot\mathbf{B}' + \frac{1}{2}\zeta\,\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e} = 0 \tag{26}$$

$$T^{(1)''} + Q\,\mathbf{g}\cdot\mathbf{B}' + \frac{1}{2}\zeta\,Q\left(\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{g} + \mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right) = 0 \tag{27}$$

$$T^{(2)''} - T^{(0)}Q^2 - 2N^{(0)'}\kappa Q' - N^{(0)}\kappa Q'' + \in\left(2(Q'^2Q^2)'' - Q'^4 - Q''(Q'Q^2)'\right) - \\ - \frac{1}{2}Q^2\,\mathbf{e}\cdot\mathbf{B}' + \frac{1}{2}\zeta\,Q^2\left(\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{g} - \mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right) = 0 \tag{28}$$

The chain ends conditions, eq.(19), should be satisfied for each of eqs.(26-28). Different physical nature of the forces included in eq.(26) allows us to require that the chain end conditions are satisfied separately for each kind of the forces. Under such requirement, eq.(26) can be double integrated and it gives

$$T^{(0)} = -2\in Q'^2 + \in\int ds\int Q''^2 ds - \mathbf{e}\cdot\left[\int_{-L/2}^{s}\mathbf{B}(\xi,t)d\xi - \left(\frac{s}{L} + \frac{1}{2}\right)\int_{-L/2}^{L/2}\mathbf{B}(\xi,t)d\xi\right] + \\ + \frac{1}{2}\zeta\left(\frac{L^2}{8} - \frac{s^2}{2}\right)\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e} \tag{29}$$

It is easy to see that the chain end conditions (19) are satisfied for eq.(29).

In the same manner we obtain the solution of the equation of motion, eq.(18). In first order in Q, and taking into account that $\in Q^2$ is of the order of unity, we have for g and e projections, respectively

$$\zeta\left(\dot{\mathbf{e}}+\mathbf{g}\dot{Q}\right)=\mathbf{g}\Big\{2T^{(0)'}Q'+T^{(0)}Q''+N^{(0)''}\kappa+ \\ +\in\left(2(Q'^3)'-Q^{IV}+\frac{1}{2}Q^{IV}Q^2-\frac{1}{2}(Q'Q^2)'''\right)+\mathbf{g}\cdot\mathbf{B}'-Q\,\mathbf{e}\cdot\mathbf{B}'+ \\ +\zeta\,\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}+\zeta Q\left(\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{g}-\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right)\Big\} \tag{30}$$

and

$$\zeta\left(\dot{\mathbf{g}}-\mathbf{e}\dot{Q}\right)=-\mathbf{e}\Big\{2T^{(0)'}Q'+T^{(0)}Q''+N^{(0)''}\kappa+ \\ +\in\left(2(Q'^3)'-Q^{IV}+\frac{1}{2}Q^{IV}Q^2-\frac{1}{2}(Q'Q^2)'''\right)+\mathbf{g}\cdot\mathbf{B}'-Q\,\mathbf{e}\cdot\mathbf{B}'+ \\ +\zeta\,\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}+\zeta Q\left(\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{g}-\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right)\Big\} \tag{31}$$

Here we have taken into account that for the basis vectors

$$\dot{\mathbf{e}}\,||\,\mathbf{g}\;,\;\;\dot{\mathbf{g}}\,||\,\mathbf{e} \tag{32}$$

Note that eq.(31) does not provide any new information in addition to eq.(30). In fact, multiplying eq.(30) by **g**, and eq.(31) by **e**, we find after summation in the first order in Q the following identity

$$\dot{\mathbf{e}}\cdot\mathbf{g}+\mathbf{e}\cdot\dot{\mathbf{g}}=0 \tag{33}$$

So, it is enough to focus on eq.(30). In the main (zero) order in Q we have the following equation of motion

$$\zeta\left(\dot{\mathbf{e}}+\mathbf{g}\dot{Q}^{(0)}\right)=\mathbf{g}\left[-\in Q^{(0)^{IV}}+\mathbf{g}\cdot\mathbf{B}'+\zeta\,\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right] \tag{34}$$

which includes molecular friction, chain rigidity, contour density of Brownian forces and the flow field.

Equation (34) combines local motion resulting in changes of the chain contour, as well as rigid rotation of the chain. To separate the genuine change in the chain shape and angular motion of the chain "as a whole" we integrate eq.(34) over ds along the chain contour. It leads to the following set of two equations with separated angular and conformational motions

$$\zeta\dot{\mathbf{e}}=\mathbf{g}\left(\zeta\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}+\frac{1}{L}\mathbf{g}\cdot\int_{-L/2}^{L/2}\mathbf{B}'ds\right) \tag{35}$$

$$\zeta\dot{Q}^{(0)}=-\epsilon Q^{(0)^{IV}}+\mathbf{g}\cdot\left(\mathbf{B}'-\frac{1}{L}\int_{-L/2}^{L/2}\mathbf{B}'ds\right) \tag{36}$$

Eq.(35) describes Brownian rotation of a rigid rod subjected to a flow field of velocity gradient $\hat{\mathbf{K}}$, and eq.(36) corresponds to rod vibration under the influence of stochastic forces. In principle, we can solve eq.(35), and then substitute the solution for g(t) into eq.(36). Such separation of the motions takes place only in the main order approximation.

The solution of linear eq.(36) is found as a series expansion

$$Q^{(0)}(s,t)=\sum_{n=1}^{\infty}q_n(t)\,y_n(s) \tag{37}$$

where $y_n(s)$ are the eigenfunctions of the problem:

$$-\lambda_n^4 y_n+y_n^{IV}=0 \tag{38}$$

with the following end conditions, corresponding to free ends of the chain

$$y_n'(-L/2)=y_n'''(-L/2)=y_n'(L/2)=y_n'''(L/2)=0 \tag{39}$$

It is easily seen that

$$\lambda_n=\frac{\pi n}{L} \tag{40}$$

$$y_n(s)=\sqrt{\frac{2}{L}}\cos\frac{\pi n}{L}\left(s+\frac{L}{2}\right) \tag{41}$$

Further, the term in eq.(36)

$$\mathbf{B}' - \frac{1}{L}\int_{-L/2}^{L/2} \mathbf{B}' ds \qquad (42)$$

which is deviation of Brownian force density from its average value can also be expanded over orthonormal basis

$$\{y_n(s), \quad n = 1, 2, 3, \ldots\} \qquad (43)$$

as

$$\sum_{n=1}^{\infty} \mathbf{b}_n(t)\, y_n(s) \qquad (44)$$

Thus, the main order eq. (36) of the chain contour motion leads to

$$q_n(t) = q_{n0} \exp\left[-\frac{\in}{\zeta}\left(\frac{\pi n}{L}\right)^4 (t - t_0)\right] + \frac{1}{\zeta}\int_{t_0}^{t} d\tau \exp\left[-\frac{\in}{\zeta}\left(\frac{\pi n}{L}\right)^4 (t - \tau)\right] \mathbf{g}(\tau)\cdot \mathbf{b}_n(\tau) \qquad (45)$$

We are interested in steady-state behaviour. Thus, for $t_0 \to -\infty$ eq. (45) reduces to

$$q_n(t) = \frac{1}{\zeta}\int_{-\infty}^{t} d\tau \exp\left[-\frac{\in}{\zeta}\left(\frac{\pi n}{L}\right)^4 (t - \tau)\right] \mathbf{g}(\tau)\cdot \mathbf{b}_n(\tau) \qquad (46)$$

We note that the value

$$\frac{1}{\tau_0} \equiv \frac{\in}{\zeta}\left(\frac{\pi}{L}\right)^4 = \frac{\pi k T}{2\zeta}\left(\frac{\pi}{L}\right)^3 \left(\frac{L}{l}\right)^{-1} \qquad (47)$$

has a dimension of inversed time, and τ_0 is a characteristic time of vibration of rigid rod molecule. The characteristic time of vibrations increases with increasing chain flexibility, L/l, the length of the chain, L, medium friction coefficient, ζ, and with decreasing temperature, T.

To obtain the next order correction for the function Q(s,t):

$$Q(s,t) = Q^{(0)}(s,t) + Q^{(1)}(s,t) + \ldots \qquad (48)$$

we substitute zero order solution $Q^{(0)}(s,t)$ found above into the first order terms n eq.(30). Then, we obtain

$$\zeta\left(\dot{\mathbf{e}}+\mathbf{g}\dot{Q}^{(1)}\right)=\mathbf{g}\Big\{2T^{(0)\prime}Q^{(0)\prime}+T^{(0)}Q^{(0)\prime\prime}+N^{(0)\prime\prime}\kappa+$$

$$+\in\left(2(Q^{(0)\prime 3})'-Q^{(1)^{IV}}+\frac{1}{2}Q^{(0)^{IV}}Q^{(0)2}-\frac{1}{2}(Q^{(0)\prime}Q^{(0)2})'''\right)+\frac{1}{L}\mathbf{g}\cdot\int_{-L/2}^{L/2}\mathbf{B}'\,ds-Q^{(0)}\mathbf{e}\cdot\mathbf{B}'+$$

$$+\zeta\,\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}+\zeta Q^{(0)}\left(\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{g}-\mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right)\Big\} \tag{49}$$

We are looking for solution of eq.(49) in the form

$$Q^{(1)}(s,t)=\sum_{n=1}^{\infty}p_n(t)\,y_n(s) \tag{50}$$

Thus, all terms in eq.(49) should be expanded over the basis $\{y_n\}$ leading to

$$\zeta\dot{\mathbf{e}}=\mathbf{g}\left\{\frac{1}{L}\int_{-L/2}^{L/2}\left(2T^{(0)\prime}Q^{(0)\prime}+T^{(0)}Q^{(0)\prime\prime}+N^{(0)\prime\prime}\kappa+\frac{1}{2}\in Q^{(0)^{IV}}Q^{(0)^2}\right)ds+\right.$$

$$\left.+\frac{1}{L}\mathbf{g}\cdot\int_{-L/2}^{L/2}\mathbf{B}'\,ds+\zeta\,\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right\} \tag{51}$$

and

$$\zeta\,\dot{Q}^{(1)} + \in Q^{(1)^{IV}} = 2\,T^{(0)\prime}Q^{(0)\prime} - \frac{2}{L}\int\limits_{-L/2}^{L/2} T^{(0)\prime}Q^{(0)\prime}ds + T^{(0)}Q^{(0)\prime\prime} - \frac{1}{L}\int\limits_{-L/2}^{L/2} T^{(0)}Q^{(0)\prime\prime}ds +$$

$$+\,\kappa\,N^{(0)\prime\prime} - \frac{\kappa}{L}\int\limits_{-L/2}^{L/2} N^{(0)\prime\prime}ds + \in\left[\frac{1}{2}Q^{(0)^{IV}}Q^{(0)^2} - \frac{1}{2}(Q^{(0)\prime}Q^{(0)^2})^{\prime\prime\prime} + 2\,(Q^{(0)\prime 3})^{\prime}\right] -$$

$$-\frac{\in}{2L}\int\limits_{-L/2}^{L/2} Q^{(0)^{IV}}Q^{(0)^2}ds - Q^{(0)}\mathbf{e}\cdot\mathbf{B}^{\prime} + \zeta Q^{(0)}\left(\mathbf{g}\cdot\hat{\mathbf{K}}\cdot\mathbf{g} - \mathbf{e}\cdot\hat{\mathbf{K}}\cdot\mathbf{e}\right) \tag{52}$$

Then, eq.(52) gives

$$p_n(t) = \frac{1}{\zeta}\int\limits_{-\infty}^{t} d\tau\, \exp\left[-\frac{\in}{\zeta}\left(\frac{\pi n}{L}\right)^4 (t-\tau)\right]\left[X_n(\tau) + \zeta\, q_n(\tau)\left(\mathbf{g}(\tau)\cdot\hat{\mathbf{K}}\cdot\mathbf{g}(\tau) - \mathbf{e}(\tau)\cdot\hat{\mathbf{K}}\cdot\mathbf{e}(\tau)\right)\right] \tag{53}$$

where

$$X_n = \int\limits_{-L/2}^{L/2} y_n\left\{2T^{(0)\prime}Q^{(0)\prime} + T^{(0)}Q^{(0)\prime\prime} + N^{(0)\prime\prime}\kappa + \in\left(2(Q^{(0)\prime\,3})^{\prime} + \frac{1}{2}Q^{(0)^{IV}}Q^{(0)^2} - \frac{1}{2}(Q^{(0)\prime}Q^{(0)^2})^{\prime\prime\prime}\right) - Q^{(0)}\mathbf{e}\cdot\mathbf{B}^{\prime}\right\}ds \tag{54}$$

In derivation of eq.(51) we have used the condition

$$Q^{(0)}(-L/2) = Q^{(0)}(L/2) = 0 \tag{55}$$

The first term in eq.(51) expresses the correction to rigid rod rotation (eq.35) which results from the introduction of non-zero chain flexibility. The correction reduces, obviously, to zero at $Q \to 0$ and chain flexibility converging to zero.

Now we are able to evaluate the correlation functions for the chain tangent vector, $\mathbf{u}(s)$.

Tangent vectors correlation functions.

Using expansion of tangent vector **u**, given by eq.(21), we find correlation function of the tangent vector in first two orders of the approximation:

$$\langle \mathbf{u}(s_1,t)\cdot\mathbf{u}(s_2,t)\rangle \cong \left\langle\left(1-\frac{1}{2}Q^2(s_1,t)-\frac{1}{8}Q^4(s_1,t)\right)\left(1-\frac{1}{2}Q^2(s_2,t)-\frac{1}{8}Q^4(s_2,t)\right)\right\rangle +$$
$$+\langle Q(s_1,t)\,Q(s_2,t)\rangle \cong 1-\frac{1}{2}\left\langle(Q(s_1,t)-Q(s_2,t))^2\right\rangle-\frac{1}{8}\left\langle\left(Q^2(s_1,t)-Q^2(s_2,t)\right)^2\right\rangle \cong$$
$$\cong 1-\frac{1}{2}\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)^2\right\rangle-\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)\left(Q^{(1)}(s_1,t)-Q^{(1)}(s_2,t)\right)\right\rangle-$$
$$-\frac{1}{8}\left\langle\left({Q^{(0)}}^2(s_1,t)-{Q^{(0)}}^2(s_2,t)\right)^2\right\rangle \tag{56}$$

We start from the calculation of first order contribution (see eq.(48))

$$\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)^2\right\rangle=\frac{1}{\zeta^2}\sum_{n,m=1}^{\infty}\left(y_n(s_1)-y_n(s_2)\right)\left(y_m(s_1)-y_m(s_2)\right)\times$$
$$\times\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{t}d\tau_2\,\exp\left[-\frac{\in}{\zeta}\left(\frac{\pi n}{L}\right)^4(t-\tau_1)\right]\exp\left[-\frac{\in}{\zeta}\left(\frac{\pi m}{L}\right)^4(t-\tau_2)\right]\times \tag{57}$$
$$\times\left\langle \mathbf{g}(\tau_1)\cdot\mathbf{b}_n(\tau_1)\,\mathbf{g}(\tau_2)\cdot\mathbf{b}_m(\tau_2)\right\rangle$$

The last correlator in eq.(57) can be calculated by the standard technique [4] if we assume Gaussian distribution of the stochastic force components. In this case we have

$$\left\langle g_\alpha(\tau_1) b_{n\alpha}(\tau_1)\, g_\beta(\tau_2) b_{m\beta}(\tau_2)\right\rangle = \sum_{k=1}^{\infty}\sum_{\gamma=1}^{3}\int_{-\infty}^{\infty} d\tau \left\langle b_{n\alpha}(\tau_1) b_{k\gamma}(\tau)\right\rangle \times$$
$$\times \left\langle \frac{\delta}{\delta b_{k\gamma}(\tau)} \left(g_\alpha(\tau_1) b_{m\beta}(\tau_2) g_\beta(\tau_2)\right)\right\rangle \tag{58}$$

We use the following equality of δ-correlation

$$\left\langle b_{n\alpha}(\tau_1) b_{k\gamma}(\tau)\right\rangle = b_{nk}\ \delta_{\alpha\gamma}\ \delta(\tau_1 - \tau) \tag{59}$$

Then we have

$$\left\langle g_\alpha(\tau_1) b_{n\alpha}(\tau_1)\, g_\beta(\tau_2) b_{m\beta}(\tau_2)\right\rangle = \sum_{k=1}^{\infty} b_{nk} \left\langle \frac{\delta}{\delta b_{k\alpha}(\tau_1)} \left(g_\alpha(\tau_1) b_{m\beta}(\tau_2) g_\beta(\tau_2)\right)\right\rangle =$$
$$= \sum_{k=1}^{\infty} b_{nk} \left\{ \left\langle \frac{\delta b_{m\beta}(\tau_2)}{\delta b_{k\alpha}(\tau_1)} g_\alpha(\tau_1) g_\beta(\tau_2)\right\rangle + \left\langle \frac{\delta g_\alpha(\tau_1)}{\delta b_{k\alpha}(\tau_1)} g_\beta(\tau_2) b_{m\beta}(\tau_2)\right\rangle + \right.$$
$$\left. + \left\langle g_\alpha(\tau_1) \frac{\delta g_\beta(\tau_2)}{\delta b_{k\alpha}(\tau_1)} b_{m\beta}(\tau_2)\right\rangle \right\} \tag{60}$$

Using eq.(58) once again we receive

$$\left\langle g_\alpha(\tau_1) b_{n\alpha}(\tau_1)\, g_\beta(\tau_2) b_{m\beta}(\tau_2)\right\rangle = b_{nm}\ \delta(\tau_1 - \tau_2) + \sum_{k=1}^{\infty} b_{nk} \left\{ \left\langle \frac{\delta g_\alpha(\tau_1)}{\delta b_{k\alpha}(\tau_1)} g_\beta(\tau_2) b_{m\beta}(\tau_2)\right\rangle + \right.$$
$$\left. + \sum_{l=1}^{\infty} b_{ml} \left[\left\langle \frac{\delta g_\alpha(\tau_1)}{\delta b_{l\beta}(\tau_2)} \frac{\delta g_\beta(\tau_2)}{\delta b_{k\alpha}(\tau_1)}\right\rangle + \left\langle g_\alpha(\tau_1) \frac{\delta^2 g_\beta(\tau_2)}{\delta b_{l\beta}(\tau_2)\, \delta b_{k\alpha}(\tau_1)}\right\rangle \right] \right\} \tag{61}$$

Note that eq.(51) shows that

$$\frac{\delta e_{\alpha}(t)}{\delta b_{n\beta}(\tilde{t})}=0\ ,\quad t\le\tilde{t}\qquad\qquad n\ge 1 \tag{62}$$

and in the analogous way

$$\frac{\delta g_{\alpha}(t)}{\delta b_{n\beta}(\tilde{t})}=0\ ,\quad t\le\tilde{t}\qquad\qquad n\ge 1 \tag{63}$$

It means that in eq.(61)

$$\frac{\delta g_{\alpha}(\tau_1)}{\delta b_{k\alpha}(\tau_1)}=0 \tag{64}$$

and

$$\frac{\delta^2 g_{\beta}(\tau_2)}{\delta b_{1\beta}(\tau_2)\,\delta b_{k\alpha}(\tau_1)}=\frac{\delta}{\delta b_{k\alpha}(\tau_1)}\left(\frac{\delta g_{\beta}(\tau_2)}{\delta b_{1\beta}(\tau_2)}\right)=0 \tag{65}$$

The product in eq.(61)

$$\frac{\delta g_{\alpha}(\tau_1)}{\delta b_{1\beta}(\tau_2)}\cdot\frac{\delta g_{\beta}(\tau_2)}{\delta b_{k\alpha}(\tau_1)}=0 \tag{66}$$

since the fist factor is non-zero at $\tau_1 > \tau_2$, and the second one at $\tau_1 < \tau_2$.

We have proved the following formula

$$\langle \mathbf{g}(\tau_1)\cdot\mathbf{b}_n(\tau_1)\,\mathbf{g}(\tau_2)\cdot\mathbf{b}_m(\tau_2)\rangle = b_{nm}\,\delta(\tau_1-\tau_2) \tag{67}$$

where b_{nm} is the value of Brownian force correlation. Then, double integration in eq.(57) can be performed, and the result reads

$$\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)^2\right\rangle=\frac{1}{\zeta^2}\sum_{n,m=1}^{\infty}\frac{\left(y_n(s_1)-y_n(s_2)\right)\left(y_m(s_1)-y_m(s_2)\right)b_{nm}}{\frac{\epsilon}{\zeta}\left(\frac{\pi}{L}\right)^4\left(n^4+m^4\right)} \tag{68}$$

The value of Brownian force correlation function, b_{nm}, can be extracted from the condition, and it should give rise to correlation of the chain tangent vectors.

We know from the statistics that in two-dimensional case

$$\langle \mathbf{u}(s_1,t)\cdot\mathbf{u}(s_2,t)\rangle = 1 - \frac{L}{l}\frac{|s_1 - s_2|}{L} + \left(\frac{L}{l}\right)^2 \frac{(s_1 - s_2)^2}{2L^2} + \ldots \tag{69}$$

So, we require that

$$\left\langle \left(Q^{(0)}(s_1,t) - Q^{(0)}(s_2,t)\right)^2 \right\rangle = 2\,\frac{L}{l}\frac{|s_1 - s_2|}{L} \tag{70}$$

It should be noted that

$$\frac{|s_1 - s_2|}{L} = \frac{1}{3} + \sum_{n=1}^{\infty} \frac{1 + (-1)^n}{(\pi n)^2}\sqrt{2L}\,\left(y_n(s_1) + y_n(s_2)\right) - \sum_{n=1}^{\infty} \frac{2L}{(\pi n)^2}\, y_n(s_1) y_n(s_2) \tag{71}$$

It can be shown that the definition for Brownian force correlation

$$b_{nm} = 2k_B T\zeta \frac{(\pi n)^2}{L^2}\,\delta_{nm} \tag{72}$$

transfers eq.(68) to eq.(70).

Now we are able to calculate the following useful correlators

$$\langle q_n(t_1) q_m(t_2)\rangle = \delta_{nm}\,\frac{L}{l}\frac{2L}{(\pi n)^2}\exp\left[-\frac{\epsilon}{\zeta}\left(\frac{\pi n}{L}\right)^4 |t_1 - t_2|\right] \tag{73}$$

and

$$\left\langle Q^2(s,t)\right\rangle = \frac{L}{l}\left(\frac{1}{6} + 2\,\frac{s^2}{L^2}\right) \tag{74}$$

where s varies from $-L/2$ to $+L/2$ along the chain contour. It is seen from eq.(74) that the chain contour deviates at most from the rigid rod conformation at the chain ends, where $(s/L)^2=1/4$, and at the centre of the chain, $s=0$, the deviation is the smallest. The equation also proves that we correctly evaluated the order of smallness of Q^2 at the beginning of present considerations. The average value $\langle Q^2\rangle$ is of the order of flexibility parameter, $L/l \ll 1$.

Our next step consists in obtaining the second term of the series expansion (69) of the tangent vector correlation function using the following correlator

$$\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)\left(Q^{(1)}(s_1,t)-Q^{(1)}(s_2,t)\right)\right\rangle-\frac{1}{8}\left\langle\left({Q^{(0)}}^2(s_1,t)-{Q^{(0)}}^2(s_2,t)\right)^2\right\rangle \tag{75}$$

which appears in eq.(56). Expansion of the corresponding function over the basis $\{y_n\}$ has the form

$$\begin{aligned}\frac{(s_1-s_2)^2}{2L^2}&=\frac{1}{12}+\sum_{n=1}^{\infty}\frac{1+(-1)^n}{(\pi n)^2}\sqrt{\frac{L}{2}}\,(y_n(s_1)+y_n(s_2))-\\&-\sum_{n,m=1}^{\infty}\frac{2L}{\pi^2}\frac{\left((-1)^n-1\right)\left((-1)^m-1\right)}{n^2m^2}\,y_n(s_1)y_m(s_2)\end{aligned} \tag{76}$$

On the other side we have

$$\begin{aligned}&\left\langle\left({Q^{(0)}}^2(s_1,t)-{Q^{(0)}}^2(s_2,t)\right)^2\right\rangle=\sum_{n,m=1}^{\infty}\langle q_n(t)q_n(t)\rangle\langle q_m(t)q_m(t)\rangle\times\\&\times\left\{3y_n^2(s_1)y_m^2(s_1)+3y_n^2(s_2)y_m^2(s_2)-2y_n^2(s_1)y_m^2(s_2)-4y_n(s_1)y_m(s_1)y_n(s_2)y_m(s_2)\right\}=\\&=8\left(\frac{L}{l}\right)^2\left\{\frac{1}{20}+\sum_{n=1}^{\infty}\sqrt{\frac{L}{2}}\left((-1)^n+1\right)\left(\frac{5}{3\pi^2n^2}-\frac{52}{\pi^4n^4}\right)(y_n(s_1)+y_n(s_2))-\right.\\&\left.-2L\left[\sum_{n=1}^{\infty}\left(\frac{1}{3\pi^2n^2}-\frac{3}{\pi^4n^4}\right)y_n(s_1)y_n(s_2)+\sum_{n,m=1}^{\infty}\frac{\left(1+(-1)^n\right)\left(1+(-1)^m\right)}{\pi^4n^2m^2}+\sum_{\substack{n,m=1\\n\neq m}}^{\infty}\frac{2\left(1+(-1)^{n+m}\right)}{\pi^4(n^2-m^2)^2}\right]\right\}\end{aligned} \tag{77}$$

where the formula [4]

$$\langle q_nq_iq_jq_k\rangle=\langle q_nq_i\rangle\langle q_jq_k\rangle+\langle q_nq_j\rangle\langle q_iq_k\rangle+\langle q_nq_k\rangle\langle q_iq_j\rangle \tag{78}$$

has been used.

Eqs.(76,77) allow to determine the term

$$\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)\left(Q^{(1)}(s_1,t)-Q^{(1)}(s_2,t)\right)\right\rangle \tag{79}$$

necessary to calculate the unknown value $N^{(0)}(s,t)$.

Let us consider the correlator (79) more carefully

$$\left\langle\left(Q^{(0)}(s_1,t)-Q^{(0)}(s_2,t)\right)\left(Q^{(1)}(s_1,t)-Q^{(1)}(s_2,t)\right)\right\rangle=\frac{2}{L}\sum_{n=1}^{\infty}\langle q_n(t)\,p_n(t)\rangle+$$
$$+\frac{1}{\sqrt{2L}}\sum_{n=1}^{\infty}\sum_{k=1}^{\infty}\left(\langle q_{n+k}(t)\,p_k(t)\rangle+\left\langle \underset{n\neq k}{q_{|n-k|}}(t)\,p_k(t)\right\rangle\right)\left(y_n(s_1)+y_n(s_2)\right)-$$
$$-\sum_{n,m=1}^{\infty}\left(\langle q_n(t)\,p_m(t)\rangle+\langle q_m(t)\,p_n(t)\rangle\right)y_n(s_1)\,y_m(s_2) \tag{80}$$

To know the chain dynamics we need to know the correlation function $<q_n(t)\ p_m(t)>$. The correlation law (69) is valid in the case of isotropic chain or zero flow of the medium, $\hat{\mathbf{K}}\equiv\mathbf{0}$. In this case we have from eq.(53)

$$p_m(t)=\int_{-\infty}^{t}X_m(\tau)\exp\left[-\frac{\epsilon}{\zeta}\left(\frac{\pi m}{L}\right)^4(t-\tau)\right]d\tau \tag{81}$$

which allows to evaluate the integral

$$<q_n\ p_m>=\int_{-\infty}^{t}\langle q_n(t)X_m(\tau)\rangle\exp\left[-\frac{\epsilon}{\zeta}\left(\frac{\pi m}{L}\right)^4(t-\tau)\right]d\tau \tag{82}$$

where $X_m(\tau)$ is determined by eq.(54).

The stress tensor.

We use for stress tensor the formulation as

$$\sigma_{\alpha\beta} = -\int_{L/2}^{L/2} \left\langle \mathcal{F}_\alpha r_\beta \right\rangle ds \tag{83}$$

where the total contour density of the force acting on the chain includes Brownian force

$$\mathcal{F}_\alpha \equiv F'_\alpha + B_\alpha \tag{84}$$

and the force density satisfies equation of motion (2). As it is suggested above, the density of Brownian force

$$\mathbf{B}'(s,t) = \mathbf{b}_0(t) + \sum_{n=1}^{\infty} \mathbf{b}_n(t)\, y_n(s) \tag{85}$$

$$\mathbf{b}_{(0)}(t) \equiv \frac{1}{L}\int_{-L/2}^{L/2} \mathbf{B}'\, ds \tag{86}$$

or its integral at any point of the chain contour

$$\mathbf{B}(s,t) = \mathbf{b}_{-1}(t) + \mathbf{b}_0(t)\, s + \sum_{n=1}^{\infty} \mathbf{b}_n(t) \int y_n(s)\, ds \tag{87}$$

The main order of the Brownian term $-\int_{-L/2}^{L/2} \left\langle B_\alpha r_\beta \right\rangle ds$ gives .

$$-\int_{-L/2}^{L/2} \left\langle B_\alpha r_\beta \right\rangle ds = -\left\langle b_{0\alpha} e_\beta \right\rangle \frac{L^3}{12} \tag{88}$$

And the term $-\int_{-L/2}^{L/2} \left\langle F'_\alpha r_\beta \right\rangle ds$ leads to

$$-\int_{-L/2}^{L/2} \left\langle F'_\alpha r_\beta \right\rangle ds = \int_{-L/2}^{L/2} \left\langle T u_\alpha u_\beta + \in\left(k^2 u_\alpha u_\beta + k'' n_\alpha r_\beta - k' k\, u_\alpha r_\beta\right)\right\rangle ds \tag{89}$$

which in the main order gives

$$\sigma_{\alpha\beta} = \int_{-L/2}^{L/2} \left\{ \in \left[\left(-\left\langle Q'^2 \right\rangle + \left\langle \int\int (Q'')^2 ds \right\rangle - \left\langle Q'''Q \right\rangle s \right) \left\langle e_\alpha e_\beta \right\rangle + \left\langle Q''' \int Q\, ds \right\rangle \left\langle g_\alpha g_\beta \right\rangle \right] + \right.$$

$$\left. + \left(\frac{L^2}{8} - \frac{s^2}{2} \right) \left\langle \left(\mathbf{b}_0 \cdot \mathbf{e} + \frac{1}{2} \zeta \mathbf{e} \cdot \mathbf{K} \cdot \mathbf{e} \right) e_\alpha e_\beta \right\rangle \right\} ds \tag{90}$$

The terms which do not include correlators of $<(Q')^2>$-type result in the usual expression for the stress tensor of the solution of rigid rods

$$\sigma_{\alpha\beta}^{(rod)} = \frac{L^3}{12} \left[-\left\langle b_{0\alpha} e_\beta \right\rangle + \left\langle (\mathbf{b}_0 \cdot \mathbf{e})\, e_\alpha e_\beta \right\rangle + \frac{1}{2} \zeta \left\langle \left(\mathbf{e} \cdot \hat{\mathbf{K}} \cdot \mathbf{e} \right) e_\alpha e_\beta \right\rangle \right] \tag{91}$$

Eq.(91) can be transformed to standard form [3] by using Langevin eq.(35)

$$\zeta \dot{\mathbf{e}} = \zeta\, (\mathbf{g} \cdot \hat{\mathbf{K}} \cdot \mathbf{e})\, \mathbf{g} + (\mathbf{g} \cdot \mathbf{b}_0)\, \mathbf{g} \tag{92}$$

Eq.(91) provides general formulation for the stress tensor with the effects of chain flexibility for the case of $L/l \ll 1$. For zero flexibility it converges for rigid rod theorem. The formula can be applied for dilute solutions of such polymers under uniform flow field of the medium. For particular calculations with the series expansion over the small flexibility parameter, L/l , computations of the correlators $<q_n(t)\, p_m(t)>$ are required to determine the stress tensor from eq.(91).

Below, first order effects of chain flexibility on stress-orientation characteristics for elongational flow are deduced from this theory.

The chain in uniaxial elongational flow.

Nearly rigid polymer chains are considered in a dilute viscous solution subjected to uniaxial elongational flow characterized by the following velocity gradient tensor:

$$\hat{K} = q^* \begin{bmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{93}$$

where q* denotes the rate of elongation.

At steady-state conditions, i.e. for time $t \gg \tau_0$, steady orientation distribution of the tangent vectors, **u**, can be correlated with the stress tensor. The state of molecular orientation for uniaxial orienting fields is characterized by axial orientation factor characterizing molecular order in the system.

To characterize molecular orientation of nearly-rigid chains, an analogy chain-trajectory of Brownian particle is used [5]. In this approach, position s at the chain contour s is analogous to time, and inverse of the chain persistence length, $1/l$, to a diffusion coefficient. Partition function for the conformations with fixed chain end tangent vector, $\mathbf{u}_0$, is a solution of diffusion-type equation:

$$(L\frac{\partial}{\partial s}-\frac{L}{l}\nabla_u^2+\Phi(\mathbf{u}))\,G(\mathbf{u}_0,\mathbf{u};s)=\delta(\mathbf{u}_0-\mathbf{u})\,\delta(s) \tag{94}$$

where $\Phi(\mathbf{u})$ is a flow potential for thin rod particle. For uniaxial flow given by eq. (93) the flow potential is

$$\Phi(\mathbf{u})=-\frac{3}{4}\frac{q^*}{D_r}(\mathbf{u}\cdot\mathbf{e}_\Phi)^2 \tag{95}$$

D_r is the coefficient of rotational diffusion of a rigid rod, and $\mathbf{e}_\Phi$ is unit vector along the flow direction, $\nabla^2{}_u$ - Laplace operator on unit sphere. The solution of eq.(94) is a Green function which assumes the following form

$$G(\bar{u}_0,\bar{u};s)=\exp\left[-\frac{s\Phi(\mathbf{u})}{L}\right]\left[\delta(\mathbf{u}_0-\mathbf{u})+\sum_{n=1}^{\infty}\left(\frac{L}{l}\right)^n G_n\left(\frac{s}{L},\mathbf{u}_0,\mathbf{u}\right)\right] \tag{96}$$

The first order correction due to small flexibility of the chain will be taken for discussion.

Axial orientation factor (order parameter), calculated as a function of the position along the chain contour, with the first order correction for the chain flexibility in eq.(96) reads

$$\begin{aligned} f_{or}(s)=\frac{3}{2}\left\langle(\mathbf{u}(s)\cdot\mathbf{e}_\Phi)^2\right\rangle-\frac{1}{2}=f_{or}^{rod}-\frac{L}{l}\frac{q^*}{D_r}\Big[1+C_1\left\langle(\mathbf{u}_0\cdot\mathbf{e}_\Phi)^2\right\rangle_{rod}+\\ +C_2\left\langle(\mathbf{u}_0\cdot\mathbf{e}_\Phi)^4\right\rangle_{rod}+C_3\left\langle(\mathbf{u}_0\cdot\mathbf{e}_\Phi)^6\right\rangle_{rod}-6\frac{(L-s)\,s}{L^2}f_{or}^{rod}\Big] \end{aligned} \tag{97}$$

where $f_{or}{}^{rod}$ is the orientation factor for rigid rod-like molecule in the flow [3], and

$$C_1 = \frac{3q^*}{D_r} - \frac{15}{4} \quad C_2 = -\frac{7q^*}{4D_r} + \frac{9}{4} \quad C_3 = \frac{3q^*}{4D_r} \tag{98}$$

From eq.(97) we conclude that the molecular orientation factor decreases with increasing chain flexibility, at fixed flow rate gradient. The degree of molecular orientation is higher at the chain centre, and lower at the chain ends.

From the analysis of dynamics of nearly rigid chain, the first order correction accounting for the effects of chain flexibility on the chain curvature, chain tension, and stress are of the order of Q, where Q is of the order of $(L/l)^{1/2}$ (cf. eq.(74)). In first order approximation, the stress tensor, separated for elastic and friction contributions is:

a) the elastic contribution

$$\sigma^e_{\alpha\beta} = \sigma^e_{\alpha\beta,\,rod} + A_1 \left(\frac{L}{l}\right)^{1/2} \left(\langle g_\alpha e_\beta\rangle + \langle e_\beta g_\alpha\rangle\right) \tag{99}$$

b) the viscous (friction) contribution

$$\sigma^v_{\alpha\beta} = \sigma^v_{\alpha\beta,\,rod} + A_2 \left(\frac{L}{l}\right)^{1/2} K_{\mu\nu} \left\langle e_\mu e_\nu \left(g_\alpha e_\beta + g_\beta e_\alpha\right)\right\rangle \tag{100}$$

where A_1, A_2 are material constants, **e** is the chain end-to end unit vector, **q** is a unit vector in the plane of the chain, normal to **e.** The stress tensor contains shear-components at the correction term due to non-zero chain flexibility. Values of the stress shear components increase with increasing molecular orientation (e.g. elongational flow gradient).

Normal components of the stress tensor are not affected by chain flexibility in this approximation because for uniaxial symmetry of orientation distribution of vectors **e,** the average values $\langle g_\alpha e_\alpha \rangle = 0$. Then, the corrections to the normal components of the stress tensor are of higher order of the small flexibility parameter.

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