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Statistics of a polymer chain affected by orienting field. Influence of chain flexibility.

Introduction

An investigation of the behaviour of polymer chain placed into the orienting field is of great interest because this type of problem arise in connection with such an important system as Liquid-Crystalline Polymers, Polymers in the hydrodynamic flow and Polymers in the stress field. A series of theoretical methods in application to the rod-like particle was developed in classical works of Onsager [1], Flory [2-3], Kirkwood [4], Maier and Saupe [5].

However, in attempting to use these methods directly in the case of chains possessing some flexibility one faced essential difficulties. The consideration of flexibility effects has required to propose and develop special analytical approaches and models. Many authors have focused on these tasks for the last 25 years, and the present paper is devoted to reviewing and summarizing of contemporary knowledge on this subject.

The main formal aim is to obtain the relation connecting the orientational order characteristics with the magnitude of orienting field (external or self-consistent). It is desirable that these formulae would cover the whole range of variation of field and chain flexibility.

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Chain partition function as a solution of diffusion-type equation.

As usual, in order to obtain the thermodynamic properties of the chain molecules it is necessary to evaluate the partition function, i.e. the sum of the statistical weights of chain configurations over all possible configurations. This partition function can be evaluated in only a few idealized cases. The main suggestion which allows to do it is the possibility of representing a chain configuration as a trajectory of Markovian process. This classical idea of polymer physics (see, for example, work of Volkenstein [6], Birstein and Ptitsyn [7], Flory [8]) was developed in the most generalized form by Lifshitz in 1968 [9]. In fact, this method reflects these generic properties of polymer systems that are a result of the chain like structure of polymer molecules.

Let us focus on the Lifshitz formulation (we follow [10]). The chain is considered to be built from N+1 "elements", each is characterized by the "variable" α_i (subscript i varies from 0 to N). Generally speaking the element can be complex and the variable α can include for example the radius-vector of the centre of mass of element, the orientation of the element long axis, the spiralization, and so on. In this paper we are interested mainly in description of the chain orientation. Thus, we suppose below that $\alpha_i \equiv \vec{u}_i$ is a unit vector which is tangential to the element, considering as rod-like. The short range interaction between elements can be expressed in terms of the "linear memory function" $g(\vec{u}_i, \vec{u}_{i+1})$ which is the conditional probability that $i+1$-th element takes $\vec{u}_{i+1}$ orientation at given i-th element taking $\vec{u}_i$. The orienting field which acts upon chain element is denoted as $\varphi(\vec{u}_i)$. Note that in principle a long-range interaction between chain elements can also be effectively expressed as an additional field of such a type

The Green's function for the chain in which 0-th element is oriented as $\bar{u}_0$ and N-th as $\bar{u}_N$ is given by the summation over all possible configurations

$$G(\bar{u}_0,\bar{u}_N;N+1)=\int\prod_{i=1}^{N}\left[g(\bar{u}_{i-1},\bar{u}_i)\exp\left(-\frac{\varphi(\bar{u}_i)}{kT}\right)\right]d\bar{u}_1\ldots d\bar{u}_{N-1} \tag{1}$$

where $d\bar{u}_i$ implies integration in spherical co-ordinates.

The energy initial level in Eq. (1) in chosen so that $\varphi(\bar{u}_0)=0\,(*)$.

It is easily shown by adding one new element to the chain, that the Green's function should satisfy a recurrence equation of Markovian type

$$G(\bar{u}_0,\bar{u}_{N+1};N+2)=\int G(\bar{u}_0,\bar{u}_N)Q(\bar{u}_N,\bar{u}_{N+1})d\bar{u}_N \tag{2}$$

where the propagator $Q(\bar{u}_N,\bar{u}_{N+1})$ is defined as

$$Q(\bar{u},\bar{u}')\equiv g(\bar{u},\bar{u}')\exp\left(-\frac{\varphi(\bar{u}')}{kT}\right) \tag{3}$$

The equation (2) has a formal solution in the operator form

$$\hat{G}_{N+1}=\hat{G}^N \tag{4}$$

It should be noted that the symmetric type of propagator is also possible if the condition (*) is not introduced

$$Q(\bar{u},\bar{u}')\equiv\exp\left(-\frac{1}{2}\frac{\varphi(\bar{u})}{kT}\right)g(\bar{u},\bar{u}')\exp\left(-\frac{1}{2}\frac{\varphi(\bar{u}')}{kT}\right) \tag{3'}$$

However, the expression for the Green's function is more complicated in the case

$$\hat{G}_{N+1}=\exp\left(-\frac{1}{2}\frac{\varphi}{kT}\right)\hat{\tilde{Q}}^N\exp\left(-\frac{1}{2}\frac{\varphi}{kT}\right) \tag{4'}$$

We shall, use both form (3,3') depending on what is more convenient for a given problem.

The chain partition function is obtained by integration over orientation of the chain end elements

$$Z_N=\int d\bar{u}_o d\bar{u}_N G(\bar{u}_0,\bar{u}_N;N+1) \tag{5}$$

The orientational distribution function for the j-th element of the chain is found by using Eq. 2 as

$$f(\vec{u}_j) = \frac{\int d\vec{u}_0 d\vec{u}_N G(\vec{u}_0, \vec{u}_j; j+1) G(\vec{u}_j, \vec{u}_N; N-j)}{\int d\vec{u}_0 d\vec{u}_N G(\vec{u}_0, \vec{u}_N; N+1)} \tag{6}$$

The further evaluation is provided by the expansion of Green's function over its own basis of eigenvectors which are determined from the eigenvalue problems for propagator $\hat{Q}$ and conjugated propagator $\hat{Q}^+$

$$\hat{Q}\psi_m = \int Q(\vec{u}', \vec{u}) \psi_m(\vec{u}') d\vec{u}' = \Lambda_m \psi_m(\vec{u}) \tag{7}$$

$$\hat{Q}^+\psi_m^+ = \int Q(\vec{u}, \vec{u}') \psi_m^+(\vec{u}') d\vec{u}' = \Lambda_m \psi_m^+(\vec{u}) \tag{8}$$

Under the natural assumption of symmetry of the linear memory $g(\vec{u}', \vec{u}) = g(\vec{u}, \vec{u}')$ we have from (7-8)

$$\psi_m^+(\vec{u}) = \psi_m(\vec{u}') \exp\left(\frac{\varphi(\vec{u})}{kT}\right) \tag{9}$$

The operator $\hat{\tilde{Q}}$ appears to be self-conjugate $\left(\hat{\tilde{Q}}^+ = \hat{\tilde{Q}}, \quad \tilde{\psi}_m^+(\vec{u}) = \tilde{\psi}_m(\vec{u})\right)$ and has the same eigenvalues Λ_m. Symmetry of the kernel $g(\vec{u}, \vec{u}')$ provides also the ortonormalization of eigenvectors basis, i.e. it is fulfilled that

$$\int \psi_m(\vec{u}) \psi_{m'}^+(\vec{u}) d\vec{u} = \delta_{mm'}, \quad \sum_m \psi_m(\vec{u}) \psi_m^+(\vec{u}') = \delta(\vec{u} - \vec{u}') \tag{10}$$

As for the spectrum of the operators $\hat{Q}, \hat{Q}^+, \hat{\tilde{Q}}$, the only conclusion can be made in general case is that the spectrum is restricted by the upper value Λ_0 and corresponding eigensolutions $\psi_0, \psi_0^+ > 0$ because the function Q is nonnegative. The spectrum can be both discrete and continuous. However, in the case when vector $\vec{u}$ describes the orientation of element, i.e. belongs to unit sphere, the spectrum is discrete only $\Lambda_0 > \Lambda_1 > \Lambda_2 > \ldots$.

The operator $\hat{Q}$ is diagonal in its own basis. Hence, gives

$$Q(\vec{u}',\vec{u}) = \sum_m \Lambda_m \psi_m^+(\vec{u}')\psi_m(\vec{u}) \tag{11}$$

and

$$G(\vec{u}_0,\vec{u}_N;N+1) = \sum_m \Lambda_m^N \psi_m^+(\vec{u}_0)\psi_m(\vec{u}_N) \tag{12}$$

$$Z = \sum_m \Lambda_m^N \left[\int \psi_m^+(\vec{u}_0)d\vec{u}_0\right]\cdot\left[\int \psi_m(\vec{u}_N)d\vec{u}_N\right] \tag{13}$$

The ground state Λ_0 dominates in (12-13) if the following condition is fulfilled:

$$N \ln\left(\frac{\Lambda_0}{\Lambda_1}\right) >> 1 \tag{14}$$

As it will be seen below in some cases the condition (14) cannot be satisfied, even for long chain $(N \to \infty)$, if the eigenvalues Λ_0 and Λ_1 converge one to the other.

In the case of ground state domination Eq. (12) is transformed simply to

$$G(\vec{u}_0,\vec{u}_N;N+1) \cong \Lambda_0^N \psi_0^+(\vec{u}_0)\psi_0(\vec{u}_N) \tag{15}$$

Thus, we have for the distribution function (6) of the orientation of chain element which is far from the chain ends

$$f(\vec{u}_j) = \psi_0^+(\vec{u}_j)\psi_0(\vec{u}_j), \qquad 1 << j << N \tag{16}$$

It should be emphasized that the simple form of (16) is a direct consequence of the domination of the ground state (15). In a general case the expression (6) manifests dependence on the position index j.

Next part of the review includes some applications of general consideration developed in this paragraph.

Discrete chain model

As a simplest example we consider the model chain with free rotation of bonds and fixed bond angle γ in the absence of the external field. The linear memory function in this case is

$$g(\vec{u}',\vec{u}) = \delta\left((\vec{u}',\vec{u}) - \cos\gamma\right)\cdot\left(\frac{1}{2\pi}\right) \tag{17}$$

Then, using the summation formula for the Legendre's polynomials one can show that $\Lambda_m = P_m(\cos\gamma)$ and $\psi_m(\vec{u}) = P_m(\cos\theta)$, where the $\vec{u}$ vector is suggested to be in the spherical co-ordinate system $\vec{u} = (1,\theta,\varphi)$. The condition of domination of the ground state (14) is rewritten as

$$N\ln\left(\left|\frac{1}{\cos\gamma}\right|\right) >> 1 \tag{18}$$

Thus, the domination fails if the bond angle is as small as $\sqrt{\frac{2}{N}}$, i.e. if the chain is enough rigid.

More meaningful model was proposed by Rusakov and Shliomis in their work on the nematic LC polymers [11]. In this case the chain is built from rod like elements, and the flexibility of the chain is determined by the angular potential depending on the cosine of the angle between adjacent elements. The internal rotation is also free. The linear memory function is represented as

$$g(\vec{u}',\vec{u}) = \frac{1}{4\pi}\exp\{a(\vec{u}',\vec{u}) - 1\}, \quad a \equiv \frac{U}{kT} \tag{19}$$

U is the angular interaction energy defined by

$$U_{int} = \frac{U}{2}\sum_{i=1}^{N}\left[\vec{u}(i) - \vec{u}(i-1)\right]^2 \tag{20}$$

where U_{int} denotes total internal energy of the chain.

In the absence of orienting field the eigenfunction of kernel (19) can be evaluated exactly, and appear to be spherical functions:

$$g(\bar{u},\bar{u}') = \sum_{\ell=0}^{\infty} \lambda_\ell(a) \sum_{|m|\le\ell} Y_{\ell m}^{*}(\bar{u}) Y_{\ell m}(\bar{u}') \tag{21}$$

where

$$\lambda_\ell(a) = \frac{\exp(-a)}{2} \int_{-1}^{1} dx \exp(ax) P_\ell(x) = \exp(-a)\sqrt{\frac{\pi}{2a}}\, I_{\ell+\frac{1}{2}}(a) \tag{22}$$

$I_{\ell+\frac{1}{2}}$ is the Bessel's function of imaginary argument, which is expressed analytically.

$$\lambda_0 = \exp(-a)\frac{sh(a)}{a}; \quad \frac{\lambda_1}{\lambda_0} \equiv \mathcal{L}(a) = cth(a) - \frac{1}{a}; \ldots \tag{23}$$

At high rigidity of a chain $(a >> 1)$ the following asymptotic representation is valid

$$\lambda_\ell(a) \cong \frac{1}{2a}\left[1 - \frac{\ell(\ell+1)}{2a}\right] \tag{24}$$

The spectrum (24) coincides with that for the differential operator $\hat{g} \equiv \frac{1}{2a}\left(1 - \frac{\nabla_u^2}{2a}\right)$, where ∇_u^2 denotes the Laplace operator in spherical co-ordinates. It means that for the case of rather rigid chains the integral eigenfunction equation (7) can be substituted by the differential one with the operator $\hat{g}$. This substitution leads to Shrödinger-type equation and allow to use well developed apparatus of quantum mechanics, what makes this analogy very fruitful (see De Genne [12]). Note also that the equation (24) shows sensitivity of the spectrum levels with the rigidity increase, so that the ground state domination fails at N~a, or, introducing into consideration contour (L) and persistent lengths (ℓ) of the chain, at $L \sim \ell$.

The above model can be generalized for the case of external field of quadruple symmetry. Let the field potential be

$$\frac{\varphi(\bar{u})}{kT} = -\xi\, P_2((\bar{u},\bar{n})) \tag{25}$$

where $\bar{n}$ -is the unit vector parallel to the field symmetry axis (or LC director). The eigensolution problem (7) in this case is

$$\int \frac{d\bar{u}'}{4\pi} \exp\{a(\bar{u},\bar{u}') - 1 + \xi P_2((\bar{n},\bar{u}'))\}\psi_m(\bar{u}') = \Lambda_m \psi_m(\bar{u}) \tag{26}$$

Principally, Eq. (26) can be solved numerically by means of expansion of eigenfunctions as a series of spherical harmonics [11]. For the case of weak field $(a\xi << 1)$ the linearization of (26) is possible. Then in the first order it is found for the average degree of orientational order

$$\frac{1}{N}\sum_{j=1}^{N}\langle P_2(\bar{u}_j)\rangle = \frac{\xi}{5}\left\{1 + 2\left(\frac{a}{3\mathcal{L}(a)} - 1\right)\left[1 - \frac{1-\left(1-\frac{3\mathcal{L}(a)}{a}\right)^N}{\frac{3N\mathcal{L}(a)}{a}}\right]\right\} \tag{27}$$

Due to the condition $a\xi << 1$ the applicability of (27) is restricted to the region of small rigidity. For the strong rigidity case, Eq. (26) is transformed to differential one as mentioned above (Jähnig [13])

$$\left[\nabla_u^2 - 2a\xi P_2((\bar{n},\bar{u}'))\right]\psi_m(\bar{u}) = \varepsilon_m \psi_m(\bar{u}) \tag{28}$$

The spectrum levels ε_m are related to the above eigenvalues Λ_m:

$$\Lambda_m = \frac{1}{2a}\exp\left(-\frac{\varepsilon_m}{2a}\right) \tag{29}$$

The eigenfunctions of (28) are known as spheroidal functions and given in the tables (see Ref. [14]).

However, it should be pointed out that applicability of the expansion over eigensolution fails at $L \sim \ell$.

Persistent (worm-like) chain model

The transition to the continuous model can be made both in the eigenvalue equation (26) and in the initial equation for Green's function (1). The last approach is more general (Semenov, Khokhlov [15]).

Let us introduce into consideration a length of the chain element, b. Thus, the contour length is $L = (N+1)b$, and the transition to continuous limit consists as usual in putting $b \to 0$, $N \to \infty$ at L = Const. For the linear memory kernel one finds in the first order

$$\hat{g} \cong 1 + \frac{b}{\ell}\nabla_4^2 \tag{30}$$

where ℓ - is the persistent length of a chain. The only term which requires more attention is the interaction with orienting field $\varphi(\bar{u}_j)$. Strictly speaking it cannot be well defined at $b \to 0$. In fact, it is senseless to introduce the "anisotropic interaction" for the part of a chain which length is equal to its width (i.e. chain width d). Moreover, in the most physical systems the element can manifest essentially anisotropic properties only if its length to width ratio exceeds same value. For instance, as it was shown by Onsager [1] for rod like particles, the anisotropic part of interaction is noticeable at (length/width) > 3. In the case of charged chain in external electric field it is impossible to consider the orientational interaction of the chain portion which is less then elementary dipole dimension, etc.

By the above reasons it seems natural to introduce "interaction length" ℓ_{int}, which is the length of rod like part of a chain possessing energy $\varphi(\bar{u})$. Thus we can assume by definition that the orientational interaction energy of a chain part of length $\ell\ (\ell \le \ell_{int})$ is $\frac{\ell}{\ell_{int}}\varphi(\bar{u})$. It is obviously from the definition of interaction length ℓ_{int} that it should satisfy the inequalities

$$d < \ell_{int} \le \min(\ell, L) \tag{31}$$

Different suggestions about the interaction length ℓ_{int} correspond to different physical situations. For example, putting $\ell_{int} = d$ we obtain pure attractive type nematic potential which increases linearly with the rod-like element length. In this case the completely stretched chain has the energy $\frac{L}{d}\varphi(\bar{u})$. By contrast, supposing $\ell_{int} = \min(\ell, L)$ we obtain pure sterical interaction of Onsager type which does not depend on the rod-like element length at all. The orientation energies of rod-like part ℓ of semi-flexible chain and rod-like part of rigid chain of length L are equal to $\varphi(\bar{u})$. It seems that in the real polymer LC both types of interaction exist, but the influence of attraction is much smaller, especially for semi-rigid and rigid chains [16]. Hence, the statistical weight of chain element with orientation $\bar{u}$ in the field is (in the first order on $\ell \to 0$)

$$\exp\left(-\frac{\ell}{\ell_{int}} \cdot \frac{\varphi(\bar{u})}{kT}\right) \cong 1 - \frac{\ell}{\ell_{int}} \cdot \frac{\varphi(\bar{u})}{kT} \tag{32}$$

The final equation for the Green's function is obtained from (2) in the continuous limit. Then taking into account Eqs. (30, 32)

$$\frac{\partial G}{\partial L}(\bar{u}_0, \bar{u}_L; L) = \frac{1}{\ell}\nabla^2_{u_L} G(\bar{u}_0, \bar{u}_L; L) - \frac{1}{\ell_{int}}\frac{\varphi(\bar{u}_L)}{kT} G(\bar{u}_0, \bar{u}_L; L) \tag{33}$$

On the other side, let us consider the worm-like continuous model of a chain (Saitô et al [17], Freed [18]) from the beginning. The internal (bending) energy of the chain is given by

$$U_{bend} = \frac{1}{2} \in \int_0^L \left(\frac{\partial \bar{u}}{\partial s}\right)^2 ds \quad (34)$$

where s measures the distance along the chain contour. The Green's function can be expressed as a path integral over all trajectories of length L, for which initial and end tangential vectors $\bar{u}_0$ and $\bar{u}_L$ are fixed:

$$G(\bar{u}_0, \bar{u}_L; L) = \int_{\bar{u}(0)}^{\bar{u}(L)} D[\bar{u}(s)] \exp\left[-\frac{\in}{2kT} \int_0^L \left(\frac{\partial \bar{u}}{\partial s}\right)^2 ds\right] \quad (35)$$

Hence, the Green's function should satisfy the "diffusion equation" (the derivation is done by Weigl [19])

$$\left[\frac{\partial}{\partial L} - \frac{1}{\left(\frac{2 \in}{kT}\right)} \nabla_L^2\right] G(\bar{u}_0, \bar{u}_L; L) = \delta(L)\,\delta(\bar{u}_0 - \bar{u}_L) \quad (36)$$

from where it is found by comparison with Eq. (33) that a persistent length (or "diffusion coefficient") is obtained as

$$\frac{2 \in}{kT} = \ell = D^{-1} \quad (37)$$

The equation (36) for the isotropic case $(\varphi = 0)$ is easily solved, and it gives

$$G(\bar{u}_0, \bar{u}_L; L) = \sum_{n,m} e^{-n(n+1)DL} Y_{nm}(\bar{u}_0) Y^{*}_{nm}(\bar{u}_L) \quad (38)$$

It means in our above notation that

$$\Lambda_n = \exp[-n(n+1)D] \quad (39)$$

It can be derived from (38) that the chain end-to-end mean square distance is

$$\langle R^2 \rangle = \int_0^L ds \int_0^L ds' \left\langle \frac{\partial \bar{r}}{\partial s} \cdot \frac{\partial \bar{r}}{\partial s'} \right\rangle = \frac{2DL + e^{-2DL} - 1}{2D^2} \quad (40)$$

$$\frac{\partial \bar{r}}{\partial s} \equiv \bar{u}(s)$$

The expression (40) is identical to that in the Kratky-Porod model [20], which confirms again the definition (37) of the "persistent length".

In the orienting field of quadruple type (25) (see also (32)), the Boltzmann factor arises in the Green's function (35)

$$G(\bar{u}_0,\bar{u}_L;L)=\int_{\bar{u}(0)}^{\bar{u}(L)} D[\bar{u}(s)]\exp\left\{-\frac{\epsilon}{2kT}\int_0^L\left(\frac{\partial\bar{u}}{\partial s}\right)^2 ds\right\}\cdot\exp\left\{\frac{\xi}{\ell_{int}}\int_0^L ds\, P_2(\bar{n},\bar{u}(s))\right\} \tag{41}$$

which leads to partial differential equation (33) with the natural initial condition

$$G(\bar{u}_0,\bar{u}_L;L=0)=\delta(\bar{u}_0-\bar{u}_L) \tag{42}$$

As mentioned above the further treatment may consist in expansion of Green's and partition function into perturbation series or in solving equation (33). Rusakov and Shliamis [21] obtained first three terms of the partition function expansion

$$Z_L(\xi)\equiv\int d\bar{u}_0 d\bar{u}_L G(\bar{u}_0,\bar{u}_L;L)=1+\sum_{n=2}^{\infty} I_n\xi^n\left(\frac{1}{\ell_{int}}\right)^n \tag{43}$$

where

$$I_n=\int_0^L ds_1\int_0^{s_1} ds_2\ldots\int_0^{s_{n-1}} ds_n\left\langle P_2(\bar{u}(s_1))P_2(\bar{u}(s_2))\ldots P_2(\bar{u}(s_n))\right\rangle_0 \tag{44}$$

and averaging procedure in (44) is performed with the "unperturbed" propagator (38). It should be noted that in [21] the authors really assumed that $\ell_{int}=d$, because they considered only attractive interaction potential and neglected completely sterical interaction. Then first non-trivial term in (43) (which determines a Curie point of the system in the LC case) is found as

$$Z_L(\xi)=1+\frac{1}{30}\frac{L\ell}{\ell_{int}^2}\left[1-\frac{1-\exp\left(-\frac{6L}{\ell}\right)}{\left(\frac{6L}{\ell}\right)}\right]\xi^2+\ldots \tag{45}$$

Correspondingly we have for the order parameter (compare Eq. 27) in a weak field limit

$$S \equiv \frac{1}{L}\left\langle \int_0^L ds\, P_2(\vec{u}(s)) \right\rangle = \frac{\xi}{15}\left[1 - \frac{1-\exp\left(-\frac{6L}{\ell}\right)}{\left(\frac{6L}{\ell}\right)}\right]\frac{\ell}{\ell_{int}} \tag{46}$$

Eq. (46) gives for the case of slightly flexible chain $(L << \ell)$

$$S = \frac{\xi}{5}\left(1 - \frac{2L}{\ell}\right) \tag{46a}$$

and for the case of long persistent chain $(L >> \ell)$

$$S = \frac{\xi}{15}\left(1 - \frac{\ell}{6L}\right) \tag{46b}$$

if the Onsager type interaction $\ell_{int} = \min(\ell, L)$ is assumed. As for the equation (33) it can be analytically evaluated in two limiting cases of rigid $(LD \to 0)$ and semiflexible $(LD \to \infty)$ chain.

In the case of long semiflexible chain we put $G(L) \sim \exp(-\lambda_n L)$ and obtain after transformation the eigenvalue problem in the form (Warner et al. [22])

$$\left[\Lambda_n + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right) - |\Delta|^2 \sin^2\theta\right] W(\theta) = 0 \tag{47}$$

where $\Lambda_n \equiv \frac{1}{D}\lambda_n + \frac{2}{3}|\Delta|^2$ and $|\Delta|^2 \equiv \frac{3}{2}\xi\frac{1}{\ell_{int}D}$.

It was already mentioned that this equation has the solutions $Sp_n(\theta)$ (spheroidal wave functions). For the case of strong potential one obtains that the first eigenvalues are $(|\Delta| \to \infty)$

$$\begin{aligned} \Lambda_0 &= 2|\Delta| - 1 + \omega_0 \\ \Lambda_1 &= 2|\Delta| - 1 + \omega_1 \end{aligned} \tag{48}$$

where ω_0, ω_1 are small non-analytical parts for which it is fulfilled that

$$\omega_{01} \equiv \omega_0 - \omega_1 = 32|\Delta|^2 \exp(-2|\Delta|) \cdot \left[1 - \frac{1}{|\Delta|} + \dots\right] \tag{49}$$

Hence, there is no dominance of the ground state at the strong field limit even in the case of a long chain. Nevertheless, the second eigenfunction $Sp_1(\theta)$ does not contribute to the partition function and average order parameter being antisymmetrical, i.e. $\int_{-1}^{1} dx\, Sp_1(x) = 0 \quad (\cos\theta \equiv x)$. Thus, we have in the main order for the partition function at $|\Delta| >> 1$

$$Z_L \cong \left(\int_{-1}^{1} Sp_0(x)dx\right)^2 \cdot \exp\left\{\frac{3}{2}|\Delta|^2 DL - 2|\Delta|DL + DL\right\} \tag{50}$$

$$\left\langle \frac{1}{L}\int_0^L ds P_2(\vec{u}(s))\right\rangle \cong \int_{-1}^{1} dx\, Sp_0^2(x) P_2(x) \cong 1 - \frac{3}{2|\Delta|} + \dots \tag{51}$$

As for the calculation of mean square end-to-end distance, two eigenfunctions should be taken into account. For the projection on the external field symmetry axis it gives (compare Eq. (40))

$$\left\langle R_{11}^2 \right\rangle = \frac{2L}{D\omega_{01}}\left[1 + \frac{1}{LD\omega_1}\left(\exp(-LD\omega_{01}) - 1\right)\right]\left(\int_{-1}^{1} dx\, Sp_0(x)\, Sp_1(x) P_1(x)\right)^2 \tag{52}$$

We have seen from the expression (49) that $\omega_{01} \to 0$ as $|\Delta|$ becomes large. Therefore, there is a range of values of $|\Delta|$ where the chain becomes rigid (rod-like) with a dramatic expansion in $\left\langle R_{11}^2 \right\rangle$. This effect may be of high importance in some systems, but here we do not discuss any consequence of it.

Let us consider now the case of a rod-like chain with a characteristic ratio $L/\ell << 1$. Due to the self-adjustness of the kernel $g(\vec{u}, \vec{u}')$ we have the identity

$G(\vec{u}_0,\vec{u}_L,L)=G(\vec{u}_L,\vec{u}_0,L)$. Thus, one can obtain by integration of (33) over orientation of one end of the chain

$$\begin{cases}\dfrac{\partial Z(s,\vec{u})}{\partial s}-\dfrac{1}{\ell}\nabla_u^2 Z(s,\vec{u})+\dfrac{1}{\ell_{int}}\dfrac{\varphi(\vec{u})}{kT}Z(s,\vec{u})=0\\ Z(0,\vec{u})=1\end{cases} \tag{53}$$

where by definition $Z(s,\vec{u})\equiv\int d\vec{u}_0 G(\vec{u}_0,\vec{u};L)$. As mentioned above it is natural to put $\ell_{int}=L$. We search a solution of (53) in the form

$$Z(s,\vec{u})=\exp\left(-\frac{s}{L}\frac{\varphi(\vec{u})}{kT}\right)\left(1+B(s,\vec{u})\right) \tag{54}$$

which leads to the following equation for $B(s,\vec{u})$

$$\begin{cases}\dfrac{\partial B(s,\vec{u})}{\partial s}=\dfrac{1}{\ell}\left\{\left(-\dfrac{s}{L}\dfrac{\nabla^2\varphi}{kT}+\dfrac{s^2}{L^2}\left(\dfrac{\nabla\varphi}{kT}\right)^2\right)\left(1+B(s,\vec{u})\right)+\nabla_u^2 B(s,\vec{u})-2\dfrac{s}{L}\dfrac{\nabla\varphi}{kT}\nabla B(s,\vec{u})\right\}\\ B(0,\vec{u})=0 \qquad\qquad s\in[0,L]\end{cases} \tag{55}$$

The solution of (55) can be represented as a series

$$B(s,\vec{u})=\sum_{n=1}^{\infty}\left(\frac{L}{\ell}\right)^n B_n\left(\frac{s}{L},\vec{u}\right) \tag{56}$$

The first two terms of (56) are

$$\begin{aligned}B_1\left(\frac{s}{L},\vec{u}\right)&=-\frac{s^2}{2L^2}\frac{\nabla^2\varphi}{kT}+\frac{s^3}{3L^3}\left(\frac{\nabla\varphi}{kT}\right)^2\\ B_2\left(\frac{s}{L},\vec{u}\right)&=\frac{s^4}{8L^4}\left(\frac{\nabla^2\varphi}{kT}\right)^2-\frac{s^5}{6L^5}\frac{\nabla^2\varphi}{kT}\left(\frac{\nabla\varphi}{kT}\right)^2+\\ &+\frac{s^6}{18L^6}\left(\frac{\nabla\varphi}{kT}\right)^4-\frac{s^3}{6L^3}\nabla^2\nabla^2\frac{\varphi}{kT}+\frac{s^4}{12L^4}\nabla^2\left(\left(\frac{\nabla\varphi}{kT}\right)^2\right)+\\ &+\frac{s^4}{4L^4}\frac{\nabla\varphi}{kT}\nabla\left(\frac{\nabla^2\varphi}{kT}\right)-\frac{2}{15}\frac{s^5}{L^5}\frac{\nabla\varphi}{kT}\nabla\left(\left(\frac{\nabla\varphi}{kT}\right)^2\right)\end{aligned} \tag{57}$$

Expressions (56, 57) can be used for evaluation of the partition function.

Further taking into consideration Eq. (6) for the distribution function and definition $Z(s,\vec{u})$ one finds

$$f(s,\vec{u}) = \frac{Z(s,\vec{u})\, Z(L-s,\vec{u})}{Z} \tag{58}$$

where $Z \equiv \int d\vec{u} Z(L,\vec{u})$ is the partition function. Using (54) we have:

$$f(s,\vec{u}) = \frac{\exp\left(-\frac{\varphi}{kT}\right)}{Z}\left\{1+\frac{L}{\ell}\left[B_1\left(\frac{s}{L},\vec{u}\right)+B_1\left(\frac{L-s}{L},\vec{u}\right)-B_1(1,\vec{u})\right]+\right.$$
$$+\left(\frac{L}{\ell}\right)^2\left[B_2\left(\frac{s}{L},\vec{u}\right)+B_2\left(\frac{L-s}{L},\vec{u}\right)+B_1\left(\frac{s}{L},\vec{u}\right)B_1\left(\frac{L-s}{L},\vec{u}\right)-B_2(1,\vec{u})\right]+$$
$$\left.+\ldots+\frac{L}{\ell}B_1(1,\vec{u})+\left(\frac{L}{\ell}\right)^2 B_2(1,\vec{u})+\ldots\right\}$$

(58a)

and

$$Z = \int d\vec{u} \exp\left(-\frac{\varphi}{kT}\right)\left\{1+\frac{L}{\ell}B_1(1,\vec{u})+\left(\frac{L}{\ell}\right)^2 B_2(1,\vec{u})+\ldots\right\} \tag{58b}$$

The representation of $f(s,\vec{u})$ in the form (58a) allows to show that the normalization condition is satisfied

$$\int d\vec{u}\, f(s,\vec{u}) = 1 \tag{58c}$$

In fact, taking into account the equalities

$$
\begin{aligned}
&\frac{s^2+(L-s)^2-L^2}{L^2}=\frac{2s(s-L)}{L^2}\\
&\frac{s^3+(L-s)^3-L^3}{L^3}=\frac{3s(s-L)}{L^2}\\
&\frac{s^4+(L-s)^4-L^4}{L^4}=\frac{2(s(s-L))^2}{L^4}+\frac{4s(s-L)}{L^2}\\
&\frac{s^5+(L-s)^5-L^5}{L^5}=\frac{5(s(s-L))^2}{L^4}+\frac{5s(s-L)}{L^2}\\
&\frac{s^6+(L-s)^6-L^6}{L^6}=\frac{9(s(s-L))^2}{L^4}+\frac{6s(s-L)}{L^2}+\frac{2(s(s-L))^3}{L^6}
\end{aligned}
\tag{58d}
$$

one can show that

$$
B_1\left(\frac{s}{L},\bar{u}\right)+B_1\left(\frac{L-s}{L},\bar{u}\right)-B_1(1,\bar{u})=\frac{S(s-L)}{L^2}\nabla^2\exp\left(-\frac{\varphi}{kT}\right)
\tag{58e}
$$

and

$$
\begin{aligned}
&B_2\left(\frac{s}{L},\bar{u}\right)+B_2\left(\frac{L-s}{L},\bar{u}\right)+B_1\left(\frac{s}{L},\bar{u}\right)B_1\left(\frac{L-s}{L},\bar{u}\right)-B_2(1,\bar{u})=\\
&=\frac{s(s-L)}{L^2}\nabla^2\left\{\left(-\frac{1}{2}\nabla^2\frac{\varphi}{kT}+\frac{1}{3}\left(\nabla\frac{\varphi}{kT}\right)^2\right)\exp\left(-\frac{\varphi}{kT}\right)\right\}+\\
&+\frac{(s(s-L))^2}{L^4}\left\{\frac{1}{2}\nabla^2\nabla^2\exp\left(-\frac{\varphi}{kT}\right)-\nabla\exp\left(-\frac{\varphi}{kT}\right)\cdot\nabla\left(-\frac{1}{2}\nabla^2\frac{\varphi}{kT}+\frac{1}{3}\left(\nabla\frac{\varphi}{kT}\right)^2\right)\right.\\
&\left.-\exp\left(-\frac{\varphi}{kT}\right)\nabla^2\left(-\frac{1}{2}\nabla^2\frac{\varphi}{kT}+\frac{1}{3}\left(\nabla\frac{\varphi}{kT}\right)^2\right)\right\}
\end{aligned}
\tag{58f}
$$

The integration of expressions (58e, 58f) over unit sphere $d\bar{u}$ leads to zero in accordance with the Green's theorems for partial integration, which proves the normalization (58c).

Note that the expansion (58a) is valid for any field φ (not only for small one as it would be expected from the formulae (54, 57)). The only parameter which should be small is the extent of flexibility, L/ℓ.

For illustration of the above method we consider the case of dipole field with a potential

$$\frac{\varphi(\bar{u})}{kT} = -q\cos\theta \tag{59}$$

Then one obtains for the orientation parameter of the chain

$$\langle \cos\theta_s \rangle \equiv \int d\bar{u}\, f(\bar{u},s)\cos\theta = \mathcal{L}(q) + \frac{L}{\ell}\left\{\frac{1}{3}q\left(\mathcal{L}^2(q)-1\right) + 2\mathcal{L}(q)\frac{s(L-s)}{L^2}\right\} + \ldots \tag{59a}$$

where $\mathcal{L}(q) \equiv \mathrm{cth}\,q - \frac{1}{q}$ is the Langevin's function. In the strong field limit, $q \to \infty$, the expression in brackets in (59a) is finite and gives

$$\langle \cos\theta_s \rangle = 1 + \frac{L}{\ell}\left\{-\frac{2}{3} + 2\frac{s(L-s)}{L^2}\right\} + \ldots \qquad q \to \infty \tag{59b}$$

The central part of the chain (L/ℓ) appears to be more ordered then the end parts (0,L):

$$\begin{aligned} \langle \cos\theta_{L/2} \rangle &= 1 - \frac{1}{6}\frac{L}{\ell} \\ \langle \cos\theta_{0,L} \rangle &= 1 - \frac{2}{3}\frac{L}{\ell} \end{aligned} \tag{59c}$$

Returning to general consideration note that in some cases it is useful to introduce an averaged distribution function $f(\bar{u})$

$$f(\bar{u}) \equiv \frac{1}{L}\int_0^L ds\, f(s,\bar{u}) \tag{60}$$

Correspondingly, an averaged over the whole chain nematic order parameter is obtained as

$$\frac{1}{L}\left\langle \int_0^L P_2(\bar{u}(s))ds \right\rangle = \int d\bar{u}\, f(\bar{u}) P_2(\bar{u}) \tag{61}$$

Orientational free energy of a chain

The developed approach allows to reformulate our problem in a different form which may be more useful in some cases. Lifshitz was first who considered a question about the non-equilibrium free energy of a chain corresponding to a given distributions function. The general method was proposed by him in [9] and developed by Semenov and Khokhlov [15]. In this method one should consider the external field $\varphi(\bar{u})$ acting on macromolecules as fictious and then one must exclude the external field from the expression for the free energy. As a result one obtains the free energy of the system expressed solely in terms of the distribution function $f(\bar{u})$. It is clear that this procedure means physically taking away the work which was done by the fictious field.

Note that the functions $\varphi(\bar{u})$ and $f(\bar{u})$ are thermodynamically conjugated since they satisfy the equation

$$\frac{\delta}{\delta\varphi(\bar{u})} F[\varphi(\bar{u})] = -kT \frac{\delta}{\delta\varphi(\bar{u})} \ln Z[\varphi(\bar{u})] = f(\bar{u}) \tag{62}$$

where $F[\varphi(\bar{u})]$ is the free energy considered as a functional, and $\frac{\delta}{\delta\varphi(\bar{u})}$ is the functional derivative. Hence, the work done by the field $\varphi(\bar{u})$ is obtained as an integral

$$\int \varphi(\bar{u}) \frac{\delta}{\delta\varphi(\bar{u})} F d\bar{u} = \int \varphi(\bar{u})\, f(\bar{u}) d\bar{u}$$

Then, one should exclude this work from the equilibrium free energy which corresponds to the case of non-fictions field

$$\widetilde{F}[\varphi] = F[\varphi] - \int \varphi(\bar{u})\, f(\bar{u}) d\bar{u} = -kT \ln Z[\varphi] - \int \varphi(\bar{u})\, f(\bar{u}) d\bar{u} \tag{63}$$

The functional $\widetilde{F}[\varphi]$ is that we are interested in, but it is necessary to express the function $\varphi(\bar{u})$ by $f(\bar{u})$ using equation (62), and then substitute to (63). However, this procedure cannot be fulfilled in the most general form, but in two limiting cases: $\ell >> L$ and $\ell << L$.

Taking logarithm of both sides of Eq. (60) and using Eq. (58a) we have

$$\ln f(\bar{u}) = -\ln Z - \frac{\varphi(\bar{u})}{kT} + \ln\left(1 + \frac{L}{\ell}\left(-\frac{1}{3}\frac{\nabla^2 \varphi}{kT} + \frac{1}{6}\left(\frac{\nabla \varphi}{kT}\right)^2\right) + \ldots\right)$$

from where the function $\frac{\varphi(\bar{u})}{kT}$ is found as a series

$$\frac{\varphi(\bar{u})}{kT} = -\ln Z - \ln f(\bar{u}) + \sum_{m=1}^{\infty}\left(\frac{L}{\ell}\right)^m A_m[f] \tag{64}$$

Finally we obtain the orientational free energy of rigid chain $(\ell >> L)$ by substituting (64) into (63)

$$\frac{\widetilde{F}}{kT}[f] = \int f(\bar{u}) \ln f(\bar{u}) d\bar{u} + \frac{1}{6}\frac{L}{\ell}\int \frac{(\nabla_u f(\bar{u}))^2}{f(\bar{u})} d\bar{u} +$$
$$\frac{L^2}{\ell^2}\left[\frac{1}{72}\int \frac{(\nabla_u^2 f(\bar{u}))^2}{f(\bar{u})} d\bar{u} - \frac{1}{180}\int \frac{\nabla_u^2 f(\bar{u})(\nabla_u f(\bar{u}))^2}{f^2(\bar{u})} d\bar{u}\right] + \ldots\left(0\left(\frac{L}{\ell}\right)^3\right) \tag{65}$$

First term in (65) originates from an entropy of rod-like particle and the others provide correction which takes into account the chain flexibility.

In the opposite case $(\ell << L)$ the expansion over small parameter L/ℓ also can be obtained. It is natural to assume for such a system that the ground state is dominant. Thus, the variables in (53) can be separated, i.e. we put $Z(s, \bar{u}) = M(s) A(\bar{u})$.

It should be noted that the initial condition $Z(s,\bar{u})=1$ is not satisfied by this solution, so we have to consider $s \gg \ell$. Under this assumption one obtains

$$Z(s,\bar{u}) = \exp(\lambda s)A(\bar{u}); \quad \ell \ll s \ll L$$
$$\frac{1}{\ell}\nabla_u^2 A - \frac{1}{\ell_{int}}\frac{\varphi}{kT}A = \lambda A \tag{66}$$

Thus, it is found for the partition function and one-partial distribution function

$$Z_L = \exp(\lambda s)\int d\bar{u}A(\bar{u})$$
$$f(\bar{u}) \equiv \frac{1}{L}\int_0^L \frac{Z(s,\bar{u})Z(L-s,\bar{u})}{Z_L}ds = \frac{A^2(\bar{u})}{\int d\bar{u}A(\bar{u})} \tag{67}$$

On the other hand, the fictious field $\varphi(\bar{u})$ is expressed by the function $A(\bar{u})$ from (66) as

$$\frac{1}{\ell_{int}}\frac{\varphi(\bar{u})}{kT} = \frac{1}{\ell}\frac{\nabla_u^2 A(\bar{u})}{A(\bar{u})} - \lambda \tag{68}$$

which gives a relation between $f(\bar{u})$ and $\varphi(\bar{u})$ if equation (67) is taken into consideration. Finally, we have from (63)

$$\frac{\widetilde{F}}{kT} = -\lambda L - \ln\left(\int d\bar{u}A(\bar{u})\right) - \frac{L}{\ell_{int}}\int \frac{\varphi(\bar{u})}{kT}f(\bar{u})d\bar{u} =$$
$$= -\frac{L}{\ell}\int \frac{\nabla_u^2 A(\bar{u})}{A(\bar{u})}f(\bar{u})d\bar{u} - \ln\left(\int d\bar{u}A(\bar{u})\right) = \tag{69}$$
$$= \frac{L}{\ell}\int \frac{\left(\nabla_u^2 f(\bar{u})\right)^2}{f(\bar{u})}d\bar{u} - 2\ln\left(\int f^{\frac{1}{2}}(\bar{u})d(\bar{u})\right)$$

where the identity

$$\left[\int f^{\frac{1}{2}}(\bar{u})\,d(\bar{u})\right] = \int d\bar{u}A(\bar{u})$$

resulting from (67) has been used.

In order to evaluate the partition function in the intermediate region (L~ℓ) the solution (65) and (69) should be matched [15].

The representation of free energy as a functional of orientational distribution function is useful for the application of Onsager [1] method, in which the self-consistent interaction is also expressed in terms of orientational distribution function. Besides, this formulation can be applied to the case of real (non-fictious) external orienting field, when the direct solution of partial differential equation (53) is difficult. In such a situation one could try to guess the symmetry and shape of the distribution functions $f(\vec{u})$ in (65, 69) which becomes a kind of the "trial function" characterized by some parameters. By using this procedure one can obtain the ordinary differential equation for these parameters instead of an integro-differential equation or partial differential equation for the Green's function.

As an example we consider now the application of Onsager trial function

$$f_\alpha(\cos\theta) = \frac{\alpha}{2\,\mathrm{sh}\alpha}\,\mathrm{ch}(\alpha\cos\theta) \tag{70}$$

The order parameter calculated with distribution function (70) is

$$S = 1 + \frac{3}{\alpha^2} - \frac{3}{\alpha}\,\mathrm{cth}\,\alpha \tag{71}$$

Then, the equation for the chain free energy (63) gives in the case of rod-like, slightly flexible chain $(L << \ell)$ (see formula (65))

$$\begin{aligned}\frac{F_1}{kT}(\alpha) = & -\xi\left(1 + \frac{3}{\alpha^2} - \frac{3}{\alpha}\,\mathrm{cth}\,\alpha\right) + \ln\left(\frac{\alpha\,\mathrm{cth}\,\alpha}{2}\right) - 1 + \frac{\mathrm{arctg}(\mathrm{sh}\,\alpha)}{\mathrm{sh}\,\alpha} + \\ & + \frac{1}{6}\frac{L}{\ell}\left\{2\alpha\,\mathrm{cth}\,\alpha - 2 - \frac{\alpha^2\,\mathrm{arctg}(\mathrm{sh}\,\alpha)}{\mathrm{sh}\,\alpha} + \frac{1}{\mathrm{sh}\,\alpha}\int_0^\alpha \frac{y^2}{\mathrm{ch}\,y}\,dy\right\} + \ldots\end{aligned} \tag{72}$$

and for the case of long semiflexible chain $(L >> \ell)$ (see formula (69))

$$\frac{F_2}{kT}(\alpha)=-\xi\frac{L}{\ell}\left(1+\frac{3}{\alpha^2}-\frac{3}{\alpha}\text{cth}\,\alpha\right)+\frac{L}{\ell}\frac{1}{4}\left\{2\alpha\,\text{cth}\,\alpha-2-\frac{\alpha^2\text{arctg}(\text{sh}\,\alpha)}{\text{sh}\,\alpha}+\right.$$
$$\left.+\frac{1}{\text{sh}\,\alpha}\int_0^\alpha\frac{y^2}{\text{ch}\,y}dy\right\}-2\ln\left\{\sqrt{\frac{\alpha}{2\text{sh}\,\alpha}}\int_{-1}^{1}dx\sqrt{\text{ch}(\alpha x)}\right\}+\ldots \tag{73}$$

Further treatment consists in evaluation of the function $\alpha(\xi)$ from the condition of minimum of free energy (72) or (73). This can be done easily in the limiting cases of weak $(\xi << 1)$ and strong $(\xi >> 1)$ field. We have then

$$\frac{F_1}{kT}(\alpha)\cong\begin{cases}-\xi\frac{\alpha^2}{15}-\ln 2+\frac{\alpha^4}{90}+\frac{1}{6}\frac{L}{\ell}\left\{\frac{12}{90}\alpha^4\right\}, & \alpha<<1\\ -\xi\left(1-\frac{3}{\alpha}\right)+\ln\alpha+\frac{1}{6}\frac{L}{\ell}\{2\alpha\}, & \alpha>>1\end{cases} \tag{74}$$

and

$$\frac{F_2}{kT}(\alpha)\cong\begin{cases}-\xi\frac{\alpha^2}{15}\frac{L}{\ell}+\frac{1}{4}\frac{L}{\ell}\left\{\frac{12}{90}\alpha^4\right\}-\ln 2+\frac{\alpha^4}{180}, & \alpha<<1\\ -\xi\left(1-\frac{3}{\alpha}\right)\frac{L}{\ell}+\frac{1}{4}\frac{L}{\ell}\{2\alpha\}+\ln\alpha, & \alpha>>1\end{cases} \tag{75}$$

where we used for evaluations the following equalities:

$$\int_0^\alpha\frac{y^2}{\text{ch}\,y}dy=\frac{1}{3}\alpha^3-\frac{1}{10}\alpha^5+\ldots\qquad(\alpha\to0)$$
$$\int_0^\infty\frac{y^2}{\text{ch}\,y}dy=\frac{\pi^3}{8}$$
$$\int_{-1}^{1}dx\sqrt{\text{ch}(\alpha x)}=\frac{2\sqrt{2}}{\alpha}\left\{\int_0^\varphi\frac{d\beta}{\sqrt{1-\frac{1}{2}\sin^2\beta}}-2\int_0^\varphi\sqrt{1-\frac{1}{2}\sin^2\beta}\,d\beta\right\}+\frac{4}{\alpha}\frac{\text{sh}\,\alpha}{\sqrt{\text{ch}\,\alpha}} \tag{76}$$
$$\varphi\equiv\arcsin\left(\sqrt{\frac{\text{ch}\,\alpha-1}{\text{ch}\,\alpha}}\right)$$

Expressions (74-75) allows to determine the dependence $\alpha(\xi)$ for all interesting cases. Substituting this dependencies into the equation for the order parameter (71) we finally obtain:

$$S=\begin{cases}\dfrac{\xi}{15}\left(1-\dfrac{2L}{\ell}\right), & \xi\ll 1\\[2ex] 1-\dfrac{1+\sqrt{1+4\xi L/\ell}}{2\xi}, & \xi\gg 1\end{cases}\qquad L\ll\ell \tag{77}$$

$$S=\begin{cases}\dfrac{\xi}{15}\left(1-\dfrac{\ell}{6L}\right), & \xi\ll 1\\[2ex] 1-\sqrt{\dfrac{6}{\xi}}-\dfrac{\ell}{L}\cdot\dfrac{1}{2\xi}, & \xi\gg 1\end{cases}\qquad L\gg\ell \tag{78}$$

Note that the expressions (77-78) at $\xi \ll 1$ coincide with Eqs (46a-46b) obtained by different way.

It is interesting that the dependence of order parameter S, at fixed magnitude of field ξ, on the chain flexibility parameter L/ℓ is not monotonic, but shows a minimum (comp. [16]), as it is illustrated in the picture.

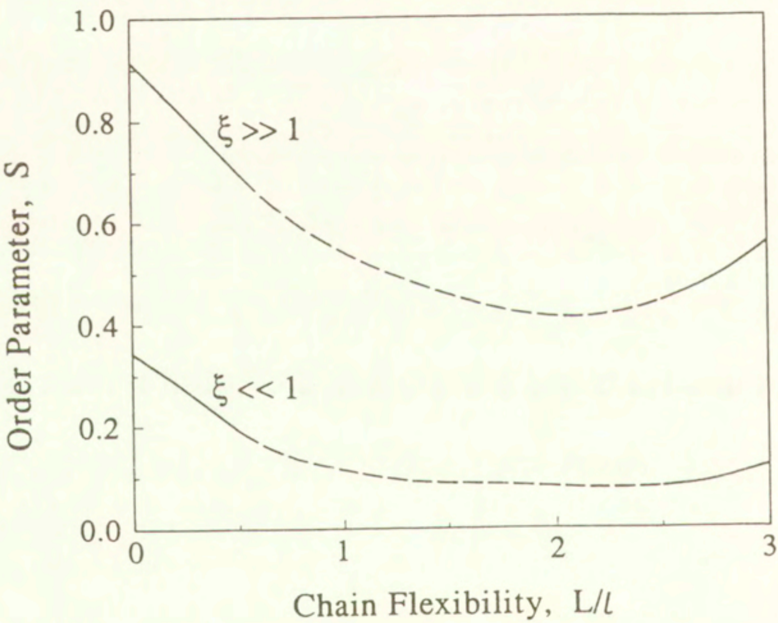

Figure. Order parameter S vs. chain flexibility, L/ℓ, at fixed field parameter ξ [16].

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