Dynamics of Slightly Flexible Rods in the Liquid Crystalline State

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ABSTRACT: A molecular theory for the reptational dynamics of rods with a small persistent flexibility in the liquid crystalline state is developed. A closed diffusion equation for the orientational distribution function is obtained by expanding in the small parameter L/l, where L is the contour length of the rodlike polymer chain and l is the persistence length. The Leslie viscosities α_3 and α_2 are calculated, and it is found that the ratio α_3/α_2 is nonmonotonic with L/l. It is concluded that slightly flexible rodlike polymers are more prone to tumbling nematics than fully rigid rods.

1. Introduction

Dynamics of rigid-chain macromolecules in the nematic liquid crystalline state is one of the important and difficult fields of polymer physics. The problem is one of finding some simpler model of macromolecular motion such that, on the one hand, analytical or numerical solutions can be found, while, on the other hand, at least the main effects observed in flowing nematics are correctly described. The most popular model describing macromolecular motion is reptation.[1] Now, in the liquid crystalline state polymeric systems are certainly concentrated, so that side motion of the chains is difficult and the main relaxation processes take place along the chain contour.

On the basis of the model, the equations of motion for macromolecules in the liquid crystalline state have been written for rigid-rodlike polymers,[2,3] as well as for persistent chains.[4] In the linear limit, i.e., in slow flows, the Leslie coefficients and their dependence on the chain contour length L, on the persistent length l, and on the order parameter S are most important. The main role in the stability of flowing nematics is played by the two viscosities α_2 and α_3; thus, in the present paper, only these quantities will be considered.

Previous calculations have been carried out for two limiting cases $L/l \gg 1$[4] (very long persistent chains) and $L/l = 0$ (rigid rods).[5-8] They show the following behavior. For rigid rods, a range of values of the order parameter is found where $\alpha_3/\alpha_2 < 0$ and flow is unstable. On the contrary, for long persistent macromolecules ($L/l \gg 1$), the ratio α_3/α_2 is always positive, and tumbling behavior is absent. In the present work, the influence of a very limited flexibility ($L/l \ll 1$) on the Leslie viscosities α_2 and α_3 is considered.

2. Equation of Relaxation Dynamics

The starting point is the general relaxation equation of reptation dynamics in the presence of an orientational field. Similarly to the equation laid down by Semenov,[9,10] we can write

$$\frac{1}{D}\frac{\partial f_t(x,\mathbf{n})}{\partial t} = \frac{\partial^2 f_t(x,\mathbf{n})}{\partial x^2} +$$
$$\frac{1}{L}\frac{\partial}{\partial x^2}\int d\mathbf{n}' V(\mathbf{n}')\left[F_t\left(\begin{matrix}0\\\mathbf{n}'\end{matrix}\bigg|\begin{matrix}x\\\mathbf{n}\end{matrix}\right) - F_t\left(\begin{matrix}x\\\mathbf{n}\end{matrix}\bigg|\begin{matrix}L\\\mathbf{n}'\end{matrix}\right)\right] \quad (2.1)$$

with boundary conditions[10]

$$\frac{\partial f_t}{\partial x} + \frac{1}{l}\Delta_{\mathbf{n}}f_t = 0 \qquad \text{at } x = 0 \qquad (2.2)$$

$$\frac{\partial f_t}{\partial x} - \frac{1}{l}\Delta_{\mathbf{n}}f_t = 0 \qquad \text{at } x = L$$

Here $f_t(x,\mathbf{n})$ is the orientational distribution function at the point x along the chain ($0 \le x \le L$) at time t, F_t, is the pair correlation function which links orientations at two different points along the chain, D is the diffusion constant for the reptation motion along the "tube", $\Delta_{\mathbf{n}}$ is a Laplace operator in orientational space, and $V(\mathbf{n})$ is the orientational potential energy of a macromolecule with a uniform orientation $\mathbf{n}$ (made nondimensional with respect to kT). In eq 2.2, l is the Kuhn length, i.e., twice the persistence length of the polymer chain.

In the general case, the potential $V(\mathbf{n})$ consists of two parts: the external field V_{ext} and the molecular field V_{self}. The form used here for the total potential is of the quadrupole type, i.e.,

$$V(\mathbf{n}) = -A(\mathbf{n}\cdot\mathbf{u})^2 \qquad (2.3)$$

where $\mathbf{u}$ is the director and A is the field strength. The form of eq 2.3 corresponds to the Maier–Saupe approximation for the mean-field V_{self} of the nematic phase. Notice, however, that eq 2.3 is used here also for $S < S_{\text{IN}}$, where S_{IN} is the order parameter at the isotropic–nematic transition when no external field is present. In such a case, one should imagine that, for example, a magnetic field acts on the system, forcing S away from zero.

Equation 2.1 is not closed because of the presence of the pair correlation function F_t. In its turn, an equation of F_t would involve a three-point correlation function, and so on. In order to close the problem, the smallness of the parameter L/l will be used.

Let us first introduce an effective potential $\varphi(\mathbf{n})$ such that the distribution function $f_t(x,\mathbf{n})$, obeying eq 2.1, also coincides with the equilibrium distribution function for macromolecules acted upon by the external field $\varphi(\mathbf{n})$. Of course, because $f_t(x,\mathbf{n})$ is time dependent, so is $\varphi(\mathbf{n})$. Time must here be seen merely as a parameter, and the time dependence of most quantities, though not explicitly indicated, is understood from here on. A general theorem of statistical mechanics guarantees that $\varphi(\mathbf{n})$ exists and is unique.

If we now assume that the gradient of the potential $\varphi(\mathbf{n})$ is small (in some sense to be made more precise at the end of the calculations), one can get the connection between the distribution function $f_t(x,\mathbf{n})$ and the potential $\varphi(\mathbf{n})$ by an expansion procedure. To this aim, we divide the chain

in small segments of length λ, such that $\lambda \ll L$, and $N = L/\lambda$ is the total number of segments. Without the effect of the potential, the transition probability linking the orientations of two neighboring segments is

$$p(\mathbf{n}_1, \mathbf{n}_2) = \sum_{m=0}^{\infty} \sum_{|k| \le m} \exp\left(-\frac{m(m+1)\lambda}{l}\right) Y_m^{\ k}(\mathbf{n}_1)\ Y_m^{-k}(\mathbf{n}_2) \tag{2.4}$$

where the Y's are spherical harmonics. Under the action of the external field $\varphi(\mathbf{n})$, the total distribution function of the chain with segment orientations $\{\mathbf{n}_1, \mathbf{n}_2, ..., \mathbf{n}_N\}$ is

$$\rho(\mathbf{n}_1, ..., \mathbf{n}_N) = \exp\left(-\varphi(\mathbf{n}_1)\frac{\lambda}{L}\right)p(\mathbf{n}_1, \mathbf{n}_2) \times$$
$$\exp\left(-\varphi(\mathbf{n}_2)\frac{\lambda}{L}\right)p(\mathbf{n}_2, \mathbf{n}_3)\exp\left(-\varphi(\mathbf{n}_3)\frac{\lambda}{L}\right) \times ... \tag{2.5}$$

From eqs 2.4 and 2.5, and by using the smallness of L/l, one obtains the expression for the distribution function of the kth segment (see the appendix):

$$Qf_k(\mathbf{n}) = \exp(-\varphi(\mathbf{n}))\left[1 - \frac{1}{2}\frac{L}{l}\frac{k^2 + (N-k)^2}{N^2}\Delta_n\varphi + \frac{1}{3}\frac{L}{l}\frac{k^3 + (N-k)^3}{N^3}(\nabla_n\varphi)^2\right] \tag{2.6}$$

where Q is determined by the normalization condition and the operator ∇_n is the gradient in orientational space.

Further, it is convenient to work with a distribution function averaged over the chain length

$$f(\mathbf{n}) = \frac{1}{N}\sum_{k=1}^{N} f_k(\mathbf{n}) \tag{2.7}$$

Then, by inverting eq 2.6 and using eq 2.7, the potential $\varphi(\mathbf{n})$ can be expressed in terms of $f(\mathbf{n})$ as

$$\varphi(\mathbf{n}) = -\ln Q - \ln f(\mathbf{n}) + \frac{1}{3}\frac{L}{l}\Delta_n \ln f(\mathbf{n}) + \frac{1}{6}\frac{L}{l}(\nabla_n \ln f(\mathbf{n}))^2 \tag{2.8}$$

On the other hand, by again applying the expansion procedure for the pair correlation function and by averaging over the chain length, eq 2.1 can be rewritten in the form

$$\frac{1}{D}\frac{\partial f}{\partial t} = \frac{2}{Ll}\frac{1}{Q}\nabla_n[\exp(-\varphi(\mathbf{n}))\nabla_n(V(\mathbf{n}) - \varphi(\mathbf{n}))] \tag{2.9}$$

Then, by substituting the result of eq 2.8, we finally obtain

$$\frac{\partial f}{\partial t} = D_r\nabla_n[[1 + G(\mathbf{n})]f(\mathbf{n})\ \nabla_n[V(\mathbf{n}) + \ln f(\mathbf{n}) + G(\mathbf{n})]] \tag{2.10}$$

$$G(\mathbf{n}) = \frac{1}{6}\frac{L}{l}\left[\left(\frac{\nabla_n f}{f}\right)^2 - 2\frac{\Delta_n f}{f}\right]$$

where $D_r = 2D/Ll$ is a rotational diffusion constant.[11]

If we compare eq 2.10 with the general relaxation equation[12]

$$\frac{\partial f}{\partial t} = \nabla_n\left[D(\mathbf{n}|f)\ f(\mathbf{n})\ \nabla_n\left(\frac{\delta F}{\delta f}\right)\right] \tag{2.11}$$

where $F[f]$ is the free energy per macromolecule (in units of kT), and $D(\mathbf{n}|f)$ is the rotational diffusion coefficient, we can obtain the expression for the free energy and, more importantly, that for the rotational diffusion coefficient of semiflexible macromolecules:

$$F[f] = \int d\mathbf{n}\ \left[f(\mathbf{n})\ \ln f(\mathbf{n}) + \frac{1}{6}\frac{L}{l}\frac{(\nabla_n f)^2}{f} + V^*(\mathbf{n})\ f(\mathbf{n})\right] \tag{2.12}$$

$$V^*(\mathbf{n}) = V_{\text{ext}}(\mathbf{n}) + \frac{1}{2}V_{\text{self}}(\mathbf{n})$$

$$D(\mathbf{n}|f) = D_r[1 + G(\mathbf{n})] \tag{2.13}$$

where $G(\mathbf{n})$ is defined in eq 2.10.

3. Influence of Flow on Chain Dynamics

We now consider the influences of flow. If g_{ij} is the velocity gradient of the flow, the velocity $\mathbf{v}$ at the point $\mathbf{r}$ is given by

$$v_i = g_{ij}r_j \tag{3.1}$$

and the deformation of the continuum over a small time interval δt will be

$$\delta E_{ij} = g_{ij}\delta t \tag{3.2}$$

Flow then leads to deformation of the macromolecular contour and, as a consequence, to a change of the distribution function. Using the method of Doi and Edwards,[3] it is readily shown that the change of $f_t(x,\mathbf{n})$ due to deformation approximately is

$$\delta f_t(x,\mathbf{n}) = -\nabla_n[\delta \mathbf{n}\ f_t(x,\mathbf{n})] + f_t(x,\mathbf{n})\ \delta E_{ij}n_i n_j - \frac{1}{L}\int_0^L dx'\int dn'\ \delta E_{ij}n_i'n_j'F_t\left(\begin{matrix}x\\\mathbf{n}\end{matrix}\bigg|\begin{matrix}x'\\\mathbf{n}'\end{matrix}\right)$$

$$\delta n_i = \delta E_{ij}n_j - n_i\delta E_{jk}n_j n_k \tag{3.3}$$

The first term in eq 3.3 describes the rotation of chain segments, the second term accounts for the change in length of tube segments, and the third term corrects the second by accounting for the fact that the total chain length is a constant.

It is readily verified that eq 3.3 properly reduces to the expressions obtained in refs 3 and 4 for rigid rods and for large persistent macromolecules, respectively. We now simplify eq 3.3 by using the same expansion technique as used previously. In terms of the chain-length averaged function, it is obtained as

$$\delta f(\mathbf{n}) = -\nabla_n[\delta \mathbf{n}\ f(\mathbf{n})] - \frac{1}{3}\frac{L}{l}\nabla_n[f(\mathbf{n})\ \nabla_n(\delta E_{ij}n_i n_j)] \tag{3.4}$$

By inserting the influence of flow, eq 3.4, into the relaxation dynamics, given by eq 2.10, we can now write the general equation for the chain undergoing flow in the form

$$\frac{\partial f}{\partial t} + \nabla_n\left[\frac{d\mathbf{n}}{dt}f(\mathbf{n})\right] + \frac{1}{3}\frac{L}{l}\nabla_n[f(\mathbf{n})\ \nabla_n(g_{ij}n_i n_j)] =$$
$$D_r\nabla_n[[1 + G(\mathbf{n})]f(\mathbf{n})\ \nabla_n[V(\mathbf{n}) + \ln f(\mathbf{n}) + G(\mathbf{n})]] \tag{3.5}$$

where $d\mathbf{n}/dt$ is obtained from the second part of eq 3.3, and $G(\mathbf{n})$ is given by the second part of eq 2.10.

In order to calculate Leslie coefficients, we must first consider the elastic stress tensor. For monodomain systems, as considered here, the calculation of the elastic stress tensor can be made by using Doi's approach.[13] The starting point is the free energy per unit volume which, in the present case, is given by eq 2.12 times ckT where c is the concentration. In the following calculations, the stress tensor is made nondimensional with respect to ckT.

The elastic stress tensor is found from the condition

$$\delta F[f] = \sigma_{ij} \delta E_{ij} \qquad (3.6)$$

Straightforward calculations give

$$\sigma_{ij} = \left\langle n_j \nabla_i \phi + \frac{1}{3} \frac{L}{l} \nabla_n (n_i n_j) \nabla_n \phi \right\rangle \qquad (3.7)$$

where

$$\phi(\mathbf{n}) = \frac{dF}{dt} = V(\mathbf{n}) + \ln f(\mathbf{n}) + G(\mathbf{n}) \qquad (3.8)$$

At equilibrium $\phi = 0$, so that σ_{ij} vanishes as well.

4. Leslie Coefficients α_2 and α_3 of Short Semiflexible Chains

In the linear limit of slow flows, eq 3.5 must be expanded so as to find the first-order correction due to flow of the equilibrium distribution of short semiflexible chains. The latter is given by

$$f_{eq}(\theta) = C \exp(A \cos^2 \theta) \left[1 + \frac{2}{3} \frac{L}{l} A (1 - 3 \cos^2 \theta + A \sin^2 \theta \cos^2 \theta) \right] \qquad (4.1)$$

where C is a normalization constant.

Similarly to the results of Semenov[5] and Kuzuu and Doi,[6,7] the Leslie coefficients α_2 and α_3 are found to be

$$\alpha_2 = -\left\langle \cos^2 \theta \frac{dg}{d\theta} + \frac{\cos \theta}{\sin \theta} g + \frac{1}{3} \frac{L}{l} \left[(\cos^2 \theta - \sin^2 \theta) \frac{dg}{d\theta} + \frac{\cos \theta}{\sin \theta} g \right] \right\rangle$$

$$\alpha_3 = \left\langle \sin^2 \theta \frac{dg}{d\theta} - \frac{1}{3} \frac{L}{l} \left[(\cos^2 \theta - \sin^2 \theta) \frac{dg}{d\theta} + \frac{\cos \theta}{\sin \theta} g \right] \right\rangle \qquad (4.2)$$

where the averages are to be made by means of the equilibrium distribution, eq 4.1, and $g(\theta)$ is the solution of the equation

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dg}{d\theta} \right) - 2A \sin \theta \cos \theta \frac{dg}{d\theta} - \frac{1}{\sin^2 \theta} g = -$$
$$2A \sin \theta \cos \theta \left[1 - \frac{2}{3} \frac{L}{l} (3 - 2A + 5A \cos^2 \theta - A^2 \sin^2 \theta \cos^2 \theta) \right] \qquad (4.3)$$

It is readily verified that for rigid rods, i.e., for $L/l = 0$, eqs 4.2 and 4.3 coincide with those obtained by Semenov,[5] who also used the Maier–Saupe approximation. Notice that eq 4.2 gives α_2 and α_3 in nondimensional form, i.e., to within the factor $ckT/2D_r$.

We can now investigate the dependence of α_2 and α_3 or, more importantly, of their ratio α_3/α_2 on the order parameter S and on the flexibility ratio L/l. Equation 4.3 cannot be solved analytically in the general case. We then first consider the two limiting cases $A \ll 1$ and $A \gg 1$. Straightforward calculations give, for $A \ll 1$,

$$\alpha_2 = -\frac{2}{15} A \left(1 - \frac{4}{3} \frac{L}{l} + O(A) \right)$$

$$\alpha_3 = -\frac{2}{15} A \left(1 - \frac{4}{3} \frac{L}{l} + O(A) \right) = -S \left(1 + \frac{2}{3} \frac{L}{l} + O(S) \right) \qquad (4.4)$$

$$\alpha_3/\alpha_2 = 1 + O(A)$$
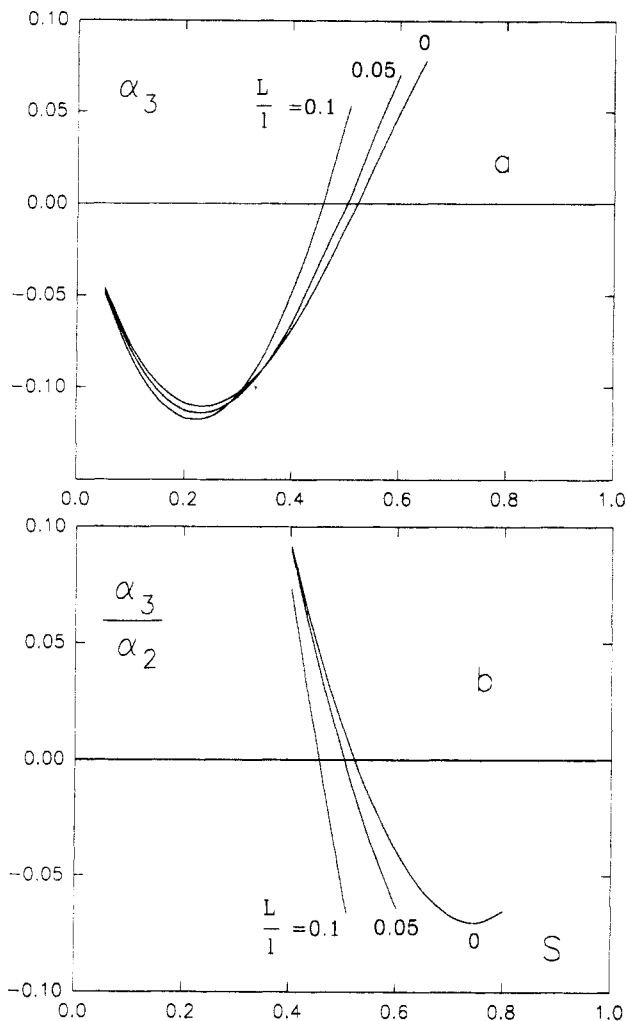
For $A \gg 1$, it is found that

Figure 1. Calculated values of α_3 and α_3/α_2 as a function of the order parameter S. Different curves refer to different values of the chain flexibility.

$$\alpha_2 = -2 \left(1 - \frac{1}{2A} - \frac{8}{9} \frac{L}{l} A \right)$$

$$\alpha_3 = \frac{1}{2A} \left(1 - \frac{4}{9} \frac{L}{l} A \right) \qquad (4.5)$$

$$\alpha_3/\alpha_2 = -\frac{1}{4A} \left(1 + \frac{4}{9} \frac{L}{l} A \right) = -\frac{1-S}{3} + \frac{1}{18} \frac{L}{l}$$

The interesting case is $A \gg 1$ because it corresponds to the liquid crystalline state. From eq 4.5 one can see that the Leslie viscosity α_3 begins to decrease with increasing L/l and can even become negative for large values of AL/l. However, large values of AL/l cannot be considered because the expansion procedure we have adopted fails in such a case. On the other hand, if $A \gg l/L$, the correlation length along the chain, x_c, obeys the inequality $x_c \sim l/A \ll L$, and the behavior of our chain is indistinguishable from that of the very long persistent chain considered by Semenov.[4] As shown in ref 4, for long persistent chains $\alpha_3/\alpha_2 > 0$; thus, the instability is absent in that case.

For intermediate values of A, numerical calculations are required. Results of these calculations, shown in Figure 1, indicate that the ratio α_3/α_2 has a nonmonotonic dependence on L/l in the nematic range, i.e., for not too small values of S. Indeed, for small values of L/l as reported in Figure 1, α_3/α_2 decreases (at a fixed S, see Figure 1b) by increasing the flexibility ratio L/l, becoming even more negative than it is for rigid rods. On the other hand, for
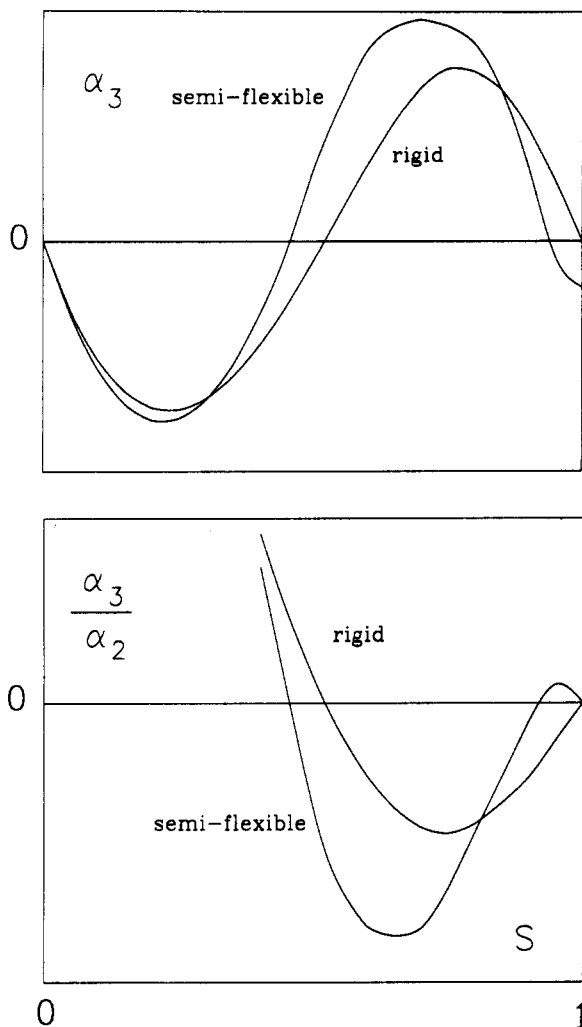
Figure 2. Qualitative dependence of α_3 and α_3/α_2 on S throughout the entire interval, showing the effect of chain flexibility. For small flexibilities, two crossovers are present with the curve for rigid rods.

large flexibilities, we must recover Semenov's result, whereby α_3/α_2 must become positive again.

As shown in Figure 1a, the "culprit" for the nonmonotonic behavior of α_3/α_2 is the Leslie coefficient α_3. The curves of α_3 vs the order parameter S show a crossover somewhere below $S = 0.4$, switching from the ordering predicted by eq 4.4 to the opposite one.

Figure 2 qualitatively shows the expected behavior throughout the range of S values. At large values of S, a second crossover is expected, as predicted by eq 4.5. The numerical calculations in that range would be prohibitively costly, however. On the other hand, we know for sure that, for not too small values of L/l, the limit considered by Semenov must be recovered.

5. Conclusions

The main conclusion of this paper is the prediction that semiflexible chains can in fact generate unstable non-

aligning nematics even more readily than rigid-rodlike ones. Starting from the rigid-rod situation, by increasing the chain flexibility, the tumbling range has been shown to begin at a smaller value of the order parameter and the characteristic ratio α_3/α_2 to become increasingly negative.

The recent experiments[14,15] show that the tumbling behavior of slightly flexible polymers takes place. Yet the problem of measuring the tumbling range dependence on molecular mass remains.

By further increasing the chain flexibility, or the chain length, the situation is inverted and the Semenov limit is eventually recovered.

Appendix

The distribution function of the kth segment $f_k(\mathbf{n})$ is defined as

$$f_k(\mathbf{n}) = \frac{1}{Q}\int d\mathbf{n}_1 \ldots d\mathbf{n}_{k-1} \, d\mathbf{n}_{k+1} \ldots d\mathbf{n}_N \, \rho$$

$$(\mathbf{n}_1, \ldots, \mathbf{n}_{k-1}, \mathbf{n}_{k+1}, \ldots, \mathbf{n}_N) \quad (A.1)$$

where Q is the normalization constant. After expanding the field $\varphi(\mathbf{n}_m)$ in eq A.1 around orientation $\mathbf{n}$

$$\varphi(\mathbf{n}_m) = \varphi(\mathbf{n}) + (\mathbf{n}_m - \mathbf{n})_\alpha \nabla_\alpha \varphi +$$

$$\frac{1}{2}(\mathbf{n}_m - \mathbf{n})_\alpha (\mathbf{n}_m - \mathbf{n})_\beta \nabla_\alpha \nabla_\beta \varphi + \ldots \quad (A.2)$$

and integration on $\{\mathbf{n}_m\}$, except the value $\mathbf{n}_k = \mathbf{n}$, and using the smallest of $(L/l\nabla_\alpha\varphi)$, one obtains the definitive expression (2.6).

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