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The tumbling or flow-aligning nature of nematics as predicted from the Slightly Bending Rod molecular model

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Existing calculations of the Leslie coefficients for rigid rods endowed with the Maier–Saupe potential are here extended to investigate the consequences of relaxing the constraint of a complete molecular rigidity. In particular, the recently proposed model of the Slightly Bending Rod (SBR) is used to calculate the ratio α_3/α_2 , the sign of which controls whether the nematic is of the tumbling or flow-aligning type. The results show that SBRs are more prone to tumbling than fully rigid rods. The flow-aligning to tumbling transition, which takes place by increasing the order parameter (e.g. by decreasing the temperature) is shifted, for SBRs, to a smaller value of the order parameter.

1. Introduction

The development of molecular theories of the nematic state has been mainly based on the rigid rod model, both for statics [1, 2] and dynamics [3, 4]. More specifically, the rigid rod model has been very successful in predicting the essential features of nemato-dynamics. Indeed, this molecular model properly reduces to the continuum theory of Leslie and Ericksen [5, 6] in the limit of slow flows, allowing for explicit predictions of the Leslie coefficients [7, 8]. Also the non-linear properties, which are particularly relevant for the polymeric nematics, are well described, qualitatively at least, by the model [9].

On the other hand, actual nematogenic molecules are not always rigid and rod-like. Often some degree of flexibility is present, and an understanding of how that might affect the observed behaviour could be useful. In particular we would like to know in which ‘direction’ some characteristic transitions are shifted with decreasing rigidity of the molecule. Relevant transitions, beyond the well-known thermodynamic one from the isotropic to the nematic state, are that from a tumbling-type (non-flow-aligning type) nematic to a flow-aligning one, which occurs by decreasing the strength of the nematogenic potential [7], and its dynamic analogue which takes place with increasing shear rate in the non-linear range [9, 10]. We would expect that the critical values of the relevant parameters (temperature, concentration or shear rate, etc.) at these transitions are affected by molecular flexibility, though we do not even know whether they would increase or decrease.

In order to obtain some qualitative information on the problem outlined above, we need to relax the rigidity constraint of the rod-like molecular model. For the equilibrium situation, various theories of nematic behaviour which account for flexibility are in fact available (see, e.g. [11–15]). These models, however, which allow the molecule to deviate substantially from the straight rod-like configuration, are too complicated for solving, or even formulating, dynamical problems. Then, a simple way of dealing with flexibility is by using a perturbation approach, that is, by modelling the molecules as slightly bending rods.

For this purpose, the SBR model was introduced in previous work [16], where also a two-dimensional version of the dynamical equation was written down, though no explicit solutions were derived. For the full three-dimensional SBR model, only equilibrium calculations have been made so far [17]. Since dynamic calculations in three dimensions remain difficult even with this simple model, we reconsider here the two dimensional version of the theory in order to derive a first dynamical result, namely the tumbling to flow-aligning transition in weak shear flows.

The paper is organised as follows. In a first section, together with recalling the SBR model itself, the solution of the equilibrium problem in two dimensions is given, which of course differs from the three-dimensional one previously derived [17]. On the other hand, the equilibrium solution is indispensable for solving the dynamical problem considered in this paper, where an expansion around the equilibrium state is in fact required. The dynamical problem is dealt with in two sections. First the dynamical equation is written down, and specified

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for the case of a steady shear flow. Next, the explicit solution in the linear limit of slow flows is derived, and compared with that for the rigid rod model. A short discussion concludes the paper.

2. Equilibrium of the two-dimensional SBR model

The SBR model assumes that the rod is at any instant a circular arc of small non-dimensional curvature $\varepsilon = L/r$, where L is rod length and r is the curvature radius. Of course r , hence ε , is a dynamic variable. The model is completed by specifying the configurational energy which, under equilibrium conditions and for the two-dimensional case considered in this work, is written as [16]

$$\frac{E(\varphi, \varepsilon)}{kT} = -U \left(S - \frac{\varepsilon^2}{6} S_M \right) \cos 2\varphi + B \frac{\varepsilon^2}{2} \quad (1)$$

where φ is the angle that the rod, at its mid-point, makes with the director. One great advantage of working in two dimensions is that the dynamic variables of the SBR model reduce to the curvature ε and the angle φ only.

The two terms in equation (1) are the nematic and the bending energies, respectively. Indeed B is the non-dimensional bending modulus which the SBR model assumes to be large, so that the curvature ε remains small at all times. In the nematic term, U is the non-dimensional strength of the Maier–Saupe interaction [2], and S and S_M are the following averages:

$$S = \left\langle \left(1 - \frac{\varepsilon^2}{6} \right) \cos 2\varphi \right\rangle \quad (2)$$

$$S_M = \langle \cos 2\varphi \rangle \quad (3)$$

The first of the two averages is the order parameter S of the nematic; the second, i.e. S_M , is the pseudo-order parameter of the mid-points only. Both these averages are made with the equilibrium distribution which, of course, is a Boltzmann distribution with the energy given in equation (1).

Since the energy expression again contains the averages S and S_M , the procedure for determining these averages is one of self-consistency, conceptually analogous to the classical Maier–Saupe case [2]. The problem is somewhat more complex here only because the two averages must be calculated simultaneously. A drastic simplification is obtained, however, by virtue of the weak bending assumption which allows expansion in power series of the ‘small parameter’ $1/B$. After straightforward calculations, the self-consistency equations then become

$$S = \left(1 - \frac{1}{6B} \right) S_M \quad (4)$$

$$S_M = \frac{I_1}{I_0} - \frac{U}{6B} \frac{I_1}{I_0} \left(\frac{I_2}{I_0} - \frac{I_1^2}{I_0^2} \right) \quad (5)$$

where the I_p s are the following integrals:

$$I_p = \int_0^\pi d\varphi (\cos 2\varphi)^p \exp(US \cos 2\varphi) \quad (6)$$

Of course S_M can be eliminated from equations (4) and (5), so that the self-consistency problem reduces to the single equation:

$$S = \frac{I_1}{I_0} - \frac{1}{6B} \frac{I_1}{I_0} \left[1 + U \left(\frac{I_2}{I_0} - \frac{I_1^2}{I_0^2} \right) \right] \quad (7)$$

Equation (7) generalizes the self-consistency equation of Maier and Saupe (in two dimensions) to the SBR case, and reduces to the classical result for $B \rightarrow \infty$.

Solution of a self-consistent equation is generally found by trial and error. However, once the result for the rigid rod case is found (left hand curve in figure 1; also see [10]), no further trial and error procedure is required for the SBR. Indeed, in view of the expansion procedure implicit in the model, the ‘correction’ can be obtained in terms of rigid rod results only. To proceed, equation (7) is further elaborated to a form where all the I_p s are calculated at the zeroth order, that is, by using rigid rod values. The I_p s appearing in the last

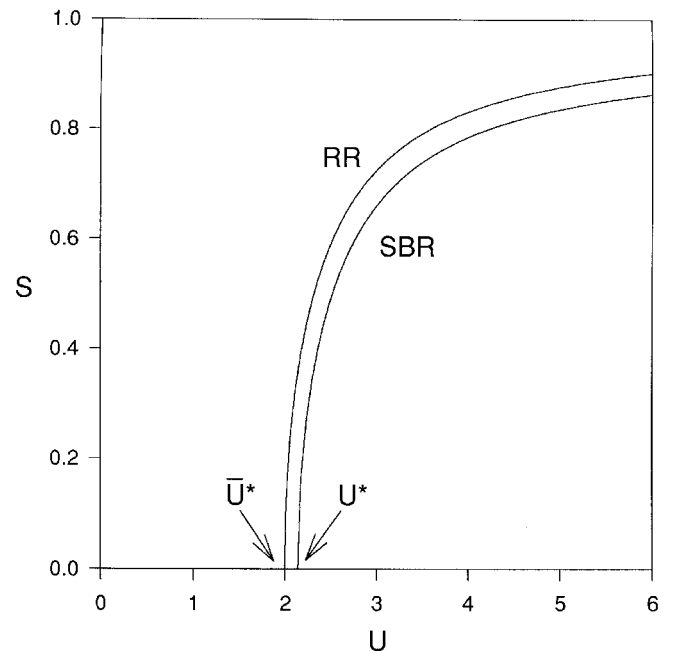


Figure 1. Equilibrium order parameter S as a function of the Maier–Saupe potential intensity U . The left hand curve is for rigid rods (RR) while the right hand one is for an SBR having $B=5$; U^* marks the isotropic–nematic transition which, in two dimensions, is second order.

term of that equation can already be calculated at the zeroth order, since the whole term is of order $1/B$. Conversely, the other term in equation (7) (i.e. I_1/I_0) needs further expansion into the rigid rod contribution plus a correction of order $1/B$.

A conceptual complication in this expansion procedure arises, however, because of the infinite steepness of the $S(U)$ curve at the isotropic–nematic transition (see figure 1), which is second order in two dimensions. It appears convenient, therefore, to invert the role of the S and U variables, that is to expand the function $U(S)$ instead of $S(U)$. We then write, at any given S

$$U = \bar{U} + \delta \quad (8)$$

where U and \bar{U} refer to the SBR and rigid rod cases, respectively, and δ is an S -dependent correction, of order $1/B$. Substituting equation (8) into equation (7) and performing the expansion we obtain

$$\delta = \frac{1}{6B} \left(U + \frac{1}{I_2/I_0 - S^2} \right) \quad (9)$$

where all quantities are now calculated at the zeroth order, i.e. for the rigid rod. Equation (9) gives the ‘horizontal distance’ between the two curves in figure 1. Of course, in view of the linearity in $1/B$, a single value of B can be used to portray the SBR correction. The curve in figure 1 has been drawn for $B=5$.

Figure 1 shows that, as expected, at equal intensity U of the interaction, the SBR system is more disordered than the rigid rod one. Conversely, if we require that the two systems attain the same value of the order parameter S , larger U values are needed for the SBR system. In particular, since the isotropic–nematic transition for the rigid rod in two dimensions occurs at $S=0$ and $\bar{U}^*=2$ [10], where equation (9) gives $\delta=2/3B$, we obtain at the transition

$$U^* = \bar{U}^* \left(1 + \frac{1}{3B} \right) \quad (10)$$

3. Dynamical equation in shear flow

As stated in the previous section, the configuration variables of the two-dimensional SBR are only two, namely an orientation angle and a curvature. In formulating the dynamical problem, it proves convenient to measure molecular orientation from some fixed direction, rather than from the director (as in statics), because the latter is generally unknown beforehand. Thus, we shall indicate with θ the angle between the tangent to the rod mid-point and the shear direction (θ should not be confused with φ of the previous section). As discussed in [16], the two dynamic variables θ and ε change in time at a different rate. The curvature ε is a ‘fast’ variable, whereas θ is ‘slow’. Hence, by averaging over the fast

variable, a Smoluchowski equation for the orientational part alone of the distribution function can be written as [16]

$$\frac{\partial \Psi_s}{\partial t} = \frac{\partial}{\partial \theta} \left[D \left(\frac{\partial \Psi_s}{\partial \theta} - \Psi_s \frac{\partial \ln Z_f}{\partial \theta} \right) - \Psi_s \omega \right] \quad (11)$$

where $\Psi_s(\theta, t)$ is the ‘slow’ orientational distribution, and D is a rotatory diffusion coefficient. The pseudo-potential, $-\ln Z_f$, and the flow-induced angular velocity ω are defined as follows:

$$Z_f = \int_{-\infty}^{+\infty} d\varepsilon g^{1/2} \exp(-E/kT) \quad (12)$$

$$\omega = \frac{\int_{-\infty}^{+\infty} d\varepsilon g^{1/2} \exp(-E/kT) g_{\theta\theta}^{-1} V_\theta}{Z_f} \quad (13)$$

Here, E is the energy of the SBR, a function of θ , ε , and t (a somewhat different function from that in equation (1), because of the different angle; cf. equation (6) in [16]), and g is the determinant of the metric tensor, the elements of which are given by

$$\begin{aligned} g_{\theta\theta} &= \frac{1}{L} \int_{l/2}^{l/2} ds \frac{\partial \mathbf{R}}{\partial \theta} \cdot \frac{\partial \mathbf{R}}{\partial \theta}; \\ g_{\varepsilon\varepsilon} &= \frac{1}{L} \int_{l/2}^{l/2} ds \frac{\partial \mathbf{R}}{\partial \varepsilon} \cdot \frac{\partial \mathbf{R}}{\partial \varepsilon}; \\ g_{\varepsilon\theta} &= g_{\theta\varepsilon} = 0 \end{aligned} \quad (14)$$

where \mathbf{R} is the vector joining the rod mid-point to the running point located at s along the SBR. Finally, V_θ in equation (13) is linked to the velocity gradient κ in the following way:

$$V_\theta = \frac{1}{L} \int_{l/2}^{l/2} ds \frac{\partial \mathbf{R}}{\partial \theta} \cdot \kappa \cdot \mathbf{R} \quad (15)$$

The expansion procedure which is inherent to the SBR model greatly simplifies the mathematics outlined in these equations. To begin with, V_θ is immediately calculated through the expansion of $\mathbf{R}(s)$. For a shear flow with the shear rate γ , the result, up to second order in ε , is

$$V_\theta = -\gamma \frac{L^2}{12} \left(\sin^2 \theta - \frac{7 \sin^2 \theta - 3}{80} \varepsilon^2 \right) \quad (16)$$

In a similar way, the metric tensor is readily calculated (again, up to second order in ε). Of special relevance is the $\theta\theta$ -component which comes out $g_{\theta\theta} = (L^2/12)(1 - \varepsilon^2/80)$, from which we obtain

$$g_{\theta\theta}^{-1} V_\theta = -\gamma \sin^2 \theta \left[1 - \frac{3}{80} \left(1 - \frac{\cos^2 \theta}{\sin^2 \theta} \right) \varepsilon^2 \right] \quad (17)$$

This expression is all that is needed to calculate ω from equation (13) to within order $1/B$. Indeed, since $g^{1/2}$ appears in both the numerator and denominator, it only contributes higher order terms. For a similar reason, the Boltzmann factor effectively reduces in this calculation to the simple form $\exp(-1/2B\epsilon^2)$. We then obtain

$$\omega = -\gamma \sin^2 \theta \left[1 - \frac{3}{80} \frac{1}{B} \left(1 - \frac{\cos^2 \theta}{\sin^2 \theta} \right) \right] \quad (18)$$

With respect to the case of the rigid rod model, for which $\omega = -\gamma \sin^2 \theta$, the ‘correction’ introduced by the SBR model, though of order $1/B$, is in fact very important. Mathematically, it is seen immediately that in the neighbourhood of $\theta=0$ the correction term is dominant. Physically, this is due to a direct effect of curvature. Indeed, while the rigid rod at $\theta=0$ is not acted upon by the flow, the SBR has a sort of effective thickness (due to inflection) which causes the flow to exert a non-zero rotating torque even in the horizontal position (see figure 2). In other words, the SBR molecule is more prone to tumbling in a shear flow than its fully rigid counterpart. Since the tumbling period of a slender rod is largely determined by the slowing down which takes place in the neighbourhood of $\theta=0$, we envisage a significantly shorter period for the SBR than for the rigid rod. We also expect that this property will be reflected in the characteristic ratio α_3/α_2 of the Leslie coefficients, to be explicitly calculated in the following section.

To conclude on the Smoluchowski equation, we finally report the expression for the pseudo-potential $-\ln Z_f$ which, to within terms of order $1/B$, comes out as

$$\ln Z_f = U \left(1 - \frac{1}{3B} \right) (\langle \cos 2\theta \rangle \cos 2\theta + \langle \sin 2\theta \rangle \sin 2\theta) \quad (19)$$

where it is understood that the average $\langle \dots \rangle$ is here made through the slow distribution function $\Psi_s(\theta, t)$.

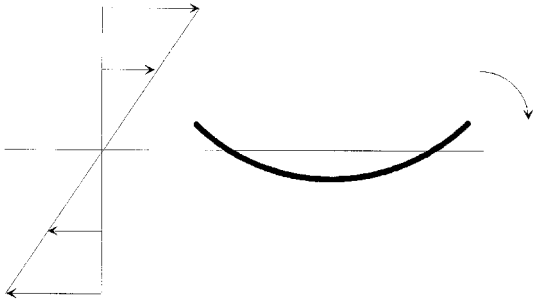


Figure 2. Differently from the rigid rod, a bending rod aligned to the shear direction remains subjected to a torque due to flow.

4. Stationary solutions

Similarly to the rigid rod case [10], stationary solutions of equation (11) (with ω and $\ln Z_f$ given by equations (18) and (19), respectively) are readily found. Actually to solve the equation, it proves convenient (see [10]) to change back again from the angular variable θ measured with respect to the shear direction to the angle φ from the director. We then obtain for the stationary distribution function $\Psi_s(\varphi)$

$$\Psi_s(\varphi, \beta) = \frac{N}{h(\varphi, \beta)} \left[\int_0^\varphi dx h(x, \beta) + \frac{\int_0^\pi dx h(x, \beta)}{\exp(\pi\gamma/2D) - 1} \right] \quad (20)$$

$$\begin{aligned} \ln h(\varphi, \beta) = & -U \left(1 - \frac{1}{3B} \right) \langle \cos 2\varphi \rangle \cos 2\varphi \\ & + \frac{\gamma}{2D} \left[\varphi - \left(\frac{1}{2} - \frac{3}{80} \frac{1}{B} \right) \sin(2\beta + 2\varphi) \right] \end{aligned} \quad (21)$$

where N is the normalisation factor, and the parameter β is the (yet unknown) angle between the director and the shear direction. For given values of U , B , and γ/D , the angle β must be determined (generally by trial and error) from the symmetry condition

$$\langle \sin 2\varphi \rangle \equiv \int_0^\pi d\varphi \Psi_s(\varphi, \beta) \sin 2\varphi = 0 \quad (22)$$

The problem, however, does not require trial and error procedures in the limit of slow flows, i.e. for $\gamma \rightarrow 0$. Indeed, by expanding in the small parameter γ (as well as by again using the smallness of $1/B$, whenever required), cumbersome but straightforward calculations give for the Leslie angle β the result

$$\begin{aligned} \cos 2\beta = & \frac{I_0}{I_1} \left(1 - \frac{\pi^2}{I_0^2} \right) + \frac{1}{6B} \left[\frac{I_0}{I_1} \left(1 - \frac{\pi^2}{I_0^2} \right) \left(U \frac{I_2}{I_0} + \frac{9}{20} \right) \right. \\ & \left. - U \frac{I_1}{I_0} \left(1 + \frac{\pi^2}{I_0^2} \right) \right] \end{aligned} \quad (23)$$

where the I_p s are the same S -dependent integrals appearing in the equilibrium problem, given in equation (6). Of course, since we are in the limit of slow flows, the S value appearing in the I_p s is itself the equilibrium order parameter. In obtaining the result of equation (23), we also used the equilibrium relationship, equation (4), linking S to $S_M = \langle \cos 2\varphi \rangle$, the latter being the average which originally appears in equation (21).

The Leslie angle β can be converted into the ratio α_3/α_2 of Leslie coefficients through the well known

relationship [18]:

$$\frac{\alpha_3}{\alpha_2} = \frac{1 - \cos 2\beta}{1 + \cos 2\beta} \quad (24)$$

Figure 3 reports α_3/α_2 as a function of S for both the rigid rod case ($B = \infty$) and the SBR. Here (as in figure 1 for the equilibrium situation), a single representative curve ($B = 5$) suffices, because of the expansion in $1/B$. Of course, only the positive branch of the α_3/α_2 versus S curve could be obtained in this way, i.e. from equation (23) for the Leslie angle. The solution reported in equation (20) holds only for the stationary case, and a different one would apply to the tumbling situation. On the other hand, the important message is already contained in the result reported in figure 3, namely that the flow-aligning to tumbling transition in the linear limit takes place at *smaller* values of the order parameter for the semi-rigid molecule.

It should here be mentioned that the SBR curve in figure 3 was not computed directly from equation (23); in fact, that equation is not the last step of the expansion in $1/B$. On the one hand, the first term on the right hand side of equation (23) is not strictly the zero order contribution of the expansion (i.e. the rigid rod result), because the I_p integrals there appearing themselves contain a contribution of order $1/B$. Secondly, because we are interested in the situation where α_3/α_2 approaches zero (marking the transition from flow-aligning behaviour to tumbling), again the $1/B$ correction term becomes

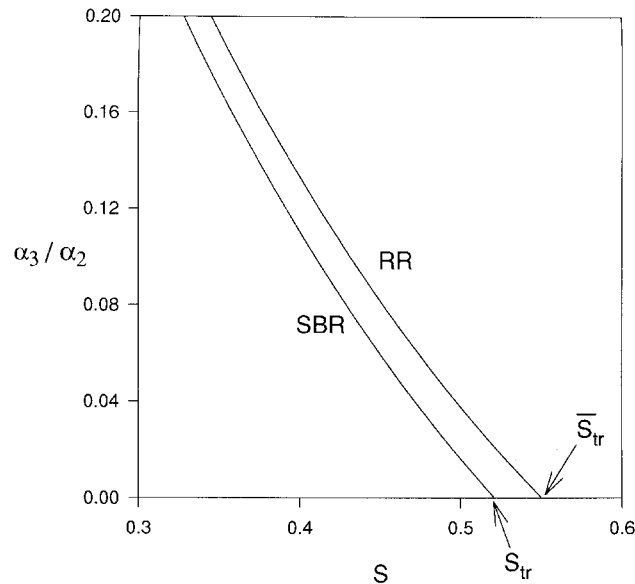


Figure 3. The characteristic Leslie coefficient ratio α_3/α_2 as a function of the equilibrium order parameter for both rigid rod (RR) and SBR molecules. The left hand curve is for an SBR with $B = 5$; S_{tr} marks the flow-aligning to tumbling transition.

dominant in that neighbourhood. The situation is similar to the one discussed previously for the order parameter curve in figure 1. In a close analogy, we can here switch to the ‘horizontal distance’ ε defined as

$$S = \bar{S} + \varepsilon \quad (25)$$

where S and \bar{S} refer to the SBR and rigid rod cases, respectively, at an equal value of the Leslie ratio α_3/α_2 . In calculating ε from equations (23) and (25), it is to be kept in mind that, since the I_p integrals contain both S and U , U must also be expanded as

$$U(S) = \bar{U}(\bar{S}) + \delta(\bar{S}) + \left. \frac{d\bar{U}}{d\bar{S}} \right|_{\bar{S}} \varepsilon \quad (26)$$

where $\delta(S)$ is given by equation (9), and $dU/dS = [(I_2/I_0 - S^2)^{-1} - U]/S$. Straightforward calculations then give for the horizontal distance between the curves in figure 3:

$$\varepsilon = -\frac{S}{6B} \left\{ 1 - \frac{9}{20} \left[\frac{(I_2/I_0 - S^2)}{(I_0/I_0 - I_0^2 - \pi^2 S^2)} \right] \right\} \quad (27)$$

In this equation, the quantity in braces is always positive, hence ε is negative. In particular, therefore, the transition value S_{tr} for the SBR is smaller (see figure 3) than that for the rigid rod ($\bar{S}_{tr} = 0.55$ in two dimensions [9]).

5. Conclusions

The main results of this paper can be summarized as follows. As regards equilibrium, the SBR model qualitatively reproduces (in two dimensions as well as in three [17]) the result which is also obtained from more sophisticated models of semi-rigid chains [11–15], namely that, for equal values of the potential intensity U , the order parameter S in the semi-rigid case is smaller than for the rigid rod.

The important new information concerns the effect of molecular semi-rigidity upon the tumbling tendency of the nematic phase which, perhaps contrary to intuition, turns out to be enhanced. As shown by figure 3, the tumbling range (from $S = S_{tr}$ to $S = 1$) is more extended in the SBR case. It is plausible that this effect is due to the change in the quantity ω given by equation (18). Of course, by imagining that molecular flexibility is progressively increased, the tumbling character of the nematic phase must give way to flow aligning behaviour throughout the S range, since we must recover the asymptotic results for fully flexible nematogenic chains [19, 20]. Thus, we may conclude that the behaviour of S_{tr} with increasing molecular flexibility is non-monotonic. On the other hand, a non-monotonic behaviour is also implicit in the result by Subbotin [21], which was obtained in the context of a considerably different

model, namely that of a fully entangled semi-rigid chain. It so appears that this non-monotonicity of S_{tr} with increasing molecular flexibility is a robust result.

Similarly to the rigid rod case [10, 22], we do not expect that the two dimensional character of the calculations affects the qualitative aspects of the results. Work is in progress to attempt analogous calculations in three dimensions, which seem to be considerably more difficult. In any event, two-dimensional nematics can be experimentally produced in the form of monolayers at interfaces [23], and for such a case two-dimensional models are directly relevant.

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