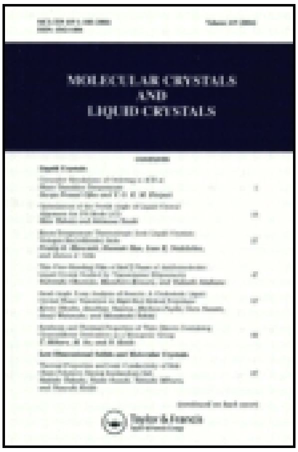

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Francesco Greco [a] & Giuseppe Marrucci [a]

[a] Chemical Engineering, University of Naples, Piazzale Tecchio, 80125, Napoli, Italy

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THE SLIGHTLY-BENDING-ROD MODEL OF NEMATIC POLYMERS

FRANCESCO GRECO and GIUSEPPE MARRUCCI
Chemical Engineering, University of Naples, Piazzale Tecchio, 80125 Napoli, Italy

Abstract A simple model for stiff polymers is here proposed to describe the flow behavior in the nematic phase. The model relaxes the usual assumption of a complete rigidity of the rodlike molecule. The dynamical equation is tractable if the molecular bending motion is much faster than rotation of the molecular axis.

INTRODUCTION

The flow behavior of liquid crystalline polymers has been interpreted in recent years from a microscopic point of view by using an extremely simple molecular model, namely, the rigid rod.[1,2] The rheological predictions obtained with such a molecular model are in very good qualitative agreement with many experiments, particularly for lyotropic polymers of high rigidity (cf., e.g., a recent review[3]). Nevertheless, the quantitative agreement is far from being satisfactory, especially for less rigid molecules such as the thermotropic polymers. Indeed, for the neat liquid crystalline phase of these polymers (which are by necessity somewhat flexible otherwise the liquid phase would not exist at all), discrepancies between experiments and theory are found. For example, the phenomenon of negative normal stresses which is predicted by theory[4] and observed in lyotropic systems,[5] is very rarely found, if at all, in thermotropic materials.

On the other hand, the use of models for stiff chains other than the rigid rod to study dynamical problems involves considerable mathematical difficulties. One source of difficulty is the large number of molecular degrees of freedom. For example, for the wormlike chain model of Kratky and Porod,[6] the whole function $\mathbf{R}(s)$ (position vector $\mathbf{R}$ vs. curvilinear coordinate s) is required. The ensuing use of functional analysis has been successful in statics,[7-9] but it appears prohibitive in dynamics. It should be mentioned that, by exploiting the reptation hypothesis for stiff chains in the isotropic phase, the functional analysis approach could in fact be avoided.[10] In the nematic phase, however, reptation does not seem a likely mechanism, since chain alignment is expected to reduce strongly the topological constraints.

In the model presented here, we also avoid all complexities of functional analysis. Indeed, we simply "perturb" the rigid rod model by including in it a very modest molecular flexibility. In other words, we adopt an expansion procedure which relaxes the complete rigidity of the molecule and allows for just a "slight" bending. The method can therefore be used to determine in which direction the characteristic features of the rigid-rod theory predictions "move" as a consequence of a partial molecular rigidity. In the present paper, only the model and the general dynamical equation are presented, leaving detailed results for specific flows to future work. For the sake of simplicity, a two-dimensional version of the theory is considered.

THE MODEL OF THE SLIGHTLY BENDING ROD

At any instant of time, the geometry of the Slightly Bending Rod (SBR in the following) is described by an arc of circle such that the length L of the arc is much smaller than the radius r of curvature (that is, the radius of the circle). Notice that, while L is the constant length of the rod, the radius of curvature r is a dynamic variable. The other dynamic variables of the SBR model are the "rod direction" **u**, defined as the unit vector tangent to the arc in its midpoint, and the unit vector **c**, orthogonal to **u**, which (together with **u**) identifies the plane containing the arc.

The just given geometrical definition of the SBR model is a consequence of the perturbative approach alluded to in the Introduction. Indeed, in the process of "relaxing" the complete rigidity of the rodlike model towards the well known persistent chain model of Kratky and Porod,[6] the SBR concept is the first significant step, corresponding to a finite but very large persistence length $(r >> L)$.

For the use to be made in the following, we need to introduce the unit vector **u**(s) tangent to the SBR at the current position s along the rod $(-L/2 \leq s \leq L/2)$. If **R**(s) is the position vector at s, $\mathbf{u}(s) = d\mathbf{R}/ds$ by definition. We now write **u**(s) as an expansion up to second order in s:

$$\mathbf{u}(s) = \left(1 - \frac{s^2}{2r^2}\right)\mathbf{u} + \frac{s}{r}\mathbf{c} \tag{1}$$

where we have oriented **c** towards the center of the circle. Notice that Equation (1) is the 2nd-order expansion for an arbitrary curve, if **u**, **c**, and r are values at s=0. Thus, while in the general case of a persistent chain this expansion would be applicable only locally, for the SBR we can use it throughout the length L. As presently shown, the expansion up to second order is what is needed to describe the energy in the SBR model.

The SBR energy is made up of two contributions. One of them is associated to bending, the other to the nematic interaction. As regards the first, it is customary to associate to the assumption of weak bending a Hookian elastic energy,[6] i.e., a quadratic form in the "deviation" from the undistorted state (the straight rod). Since this deviation is measured by d**u**/ds, the bending energy E_b of the chain is given by:

$$E_b = \mathcal{B} \int_{-L/2}^{L/2} ds \left(\frac{d\mathbf{u}}{ds} \right)^2 \approx \mathcal{B} \frac{L}{r^2} \qquad (2)$$

where $\mathcal{B}$ is the bending modulus (dimensions of force x square length) of the molecular structure. In this equation, the first equality defines the bending energy for the general wormlike chain of Kratky and Porod,[6] while the approximate equality only applies to the SBR, and is obtained by using Equation (1). In view of the smallness of L/r, in the approximate expression we have also neglected an additional term of order $\mathcal{B} L^3/r^4$.

For what concerns the nematic potential, we shall make use of a quadrupolar interaction of the form $\mathbf{u}(p)\mathbf{u}(p){:}\mathbf{u}(s)\mathbf{u}(s)$ between the local orientation of a molecule at a point p and that of another molecule at a point s. The total pair interaction energy will then involve an integration over both curvilinear coordinates, p and s. However, because we want to work within a mean-field approach analogous to that of Maier and Saupe,[11] the single-particle energy E_{MS} of a "test-molecule" (that with curvilinear coordinate s, say) requires averaging over all possible conformations of the p-molecule. We then write:

$$E_{MS} = -\mathcal{U} \left\langle \int_{-L/2}^{L/2} dp\, \mathbf{u}(p)\mathbf{u}(p) \right\rangle : \int_{-L/2}^{L/2} ds\, \mathbf{u}(s)\mathbf{u}(s) \qquad (3)$$

where the average $\langle \cdots \rangle$ makes use, in the SBR case, of a distribution function $\Psi(\mathbf{u}, \mathbf{c}, r, t)$ giving the probability density, at time t, of the conformation $(\mathbf{u}, \mathbf{c}, r)$, and the intensity $\mathcal{U}$ (dimensions of energy per square length) includes the effect of temperature and polymer concentration. In the rigid rod limit, where **u**(p) and **u**(s) are constants with p and s, respectively, Equation (3) reduces to the well known Maier-Saupe form $E_{MS} = -\mathcal{U} L^2 \langle \mathbf{uu} \rangle : \mathbf{uu}$, where $\langle \cdots \rangle$ is an angular average only. In our case, conversely, **u**(p) and **u**(s) obey Equation (1), and therefore:

$$E_{MS} = -\mathcal{U} L^2 \left\langle \mathbf{uu} + \frac{L^2}{12r^2}(\mathbf{cc} - \mathbf{uu}) \right\rangle : \left(\mathbf{uu} + \frac{L^2}{12r^2}(\mathbf{cc} - \mathbf{uu}) \right) \tag{4}$$

In conclusion, the molecular model of the SBR will make use of the following energy expression, sum of Equations (4) and (2):

$$\frac{E(\mathbf{u},\mathbf{c},\varepsilon)}{kT} = -U \left\langle \mathbf{uu} + \frac{\varepsilon^2}{12}(\mathbf{cc} - \mathbf{uu}) \right\rangle : \left(\mathbf{uu} + \frac{\varepsilon^2}{12}(\mathbf{cc} - \mathbf{uu}) \right) + B\varepsilon^2 \tag{5}$$

where we have introduced the nondimensional curvature of the rod $\varepsilon = L/r$ as a dynamical variable (replacing r), and the nondimensional energy intensities $U = \mathcal{U} L^2 / kT$ and $B = \mathcal{B} / LkT$. The SBR model assumes B to be a large number so that ε always remains much smaller than unity. Within the specified assumptions, only terms up to order ε^2 are meaningful in Equation (5). Thus, the fourth-order term implicit in the double-dot product of the "extended Maier-Saupe" expression must be neglected.

As mentioned in the Introduction, for reasons of simplicity we shall here limit our considerations to the "two-dimensional" case, corresponding to a fictitious situation where all molecules remain parallel to the same plane at all times. Going from three to two dimensions, the dynamical variables reduce from 4 to 2 (ignoring location in space). Indeed, together with the bending variable ε, a single angle θ is required, which gives the orientation within the fixed plane of the SBR midpoint.

In two dimensions, the energy expression reduces to:

$$\frac{E(\theta,\varepsilon)}{kT} = -\frac{U}{2}\left[\left(S - \frac{\varepsilon^2}{6} S_M\right)\cos 2\theta + \left(S' - \frac{\varepsilon^2}{6} S'_M\right)\sin 2\theta\right] + B\varepsilon^2 \tag{6}$$

containing the following averages:

$$S = \left\langle \left(1 - \frac{\varepsilon^2}{6}\right)\cos 2\theta \right\rangle \tag{7}$$

$$S_M = \langle \cos 2\theta \rangle \tag{8}$$

$$S' = \left\langle \left(1 - \frac{\varepsilon^2}{6}\right)\sin 2\theta \right\rangle \tag{9}$$

$$S'_M = \langle \sin 2\theta \rangle \tag{10}$$

Among the averages defined by Equations (7-10), those with the suffix M describe the average orientation of the SBR midpoint. Under conditions of (undistorted) equilibrium, and because the orientational distribution is then axially symmetric, it becomes convenient to measure θ from the symmetry axis (director) so that $S' = S'_M = 0$. In such a case, the two nonzero averages, S and S_M, represent the "order parameters" for the SBR model. More in detail, S_M describes the degree of orientational order of the rod midpoints, while S gives the "global" order, i.e., it accounts for all points of the bending rods. Needless to say, it is $S \le S_M$, where the equality applies to the rigid rod limit.

THE DYNAMICAL EQUATION OF THE SBR MODEL

Our starting point for SBR dynamics is a Smoluchowski equation for the distribution function $\Psi(\mathbf{u}, \mathbf{c}, r, t)$. We follow here the original Kirkwood approach,[12] in which a general method is prescribed to obtain the kinetic equation for objects with internal constraints. With reference to the two-dimensional case, for which the distribution function is $\Psi(\theta, \varepsilon, t)$, we write:

$$\begin{aligned} \frac{\partial \Psi}{\partial t} = {} & \frac{\partial}{\partial \theta}\left[D_{\theta\theta}\left(\frac{\partial \Psi}{\partial \theta} + \Psi \frac{\partial E}{\partial \theta} \right) - \Psi g_{\theta\theta}^{-1} V_\theta \right] \\ & + \frac{1}{\sqrt{g}} \frac{\partial}{\partial \varepsilon}\left\{ \sqrt{g}\left[D_{\varepsilon\varepsilon}\left(\frac{\partial \Psi}{\partial \varepsilon} + \Psi \frac{\partial E}{\partial \varepsilon} \right) - \Psi g_{\varepsilon\varepsilon}^{-1} V_\varepsilon \right] \right\} \end{aligned} \tag{11}$$

where θ and ε play the role of Lagrangean coordinates, E is the (nondimensional) energy of the SBR given by Equation (6), $D_{\theta\theta}$ and $D_{\varepsilon\varepsilon}$ are diffusivities, and the V's and g's are defined as follows:

$$V_\theta = \frac{1}{L} \int_{-L/2}^{L/2} ds \frac{\partial \mathbf{R}}{\partial \theta} \cdot \boldsymbol{\kappa} \cdot \mathbf{R} \quad ; \quad V_\varepsilon = \frac{1}{L} \int_{-L/2}^{L/2} ds \frac{\partial \mathbf{R}}{\partial \varepsilon} \cdot \boldsymbol{\kappa} \cdot \mathbf{R} \tag{12}$$

$$g_{\theta\theta} = \frac{1}{L} \int_{-L/2}^{L/2} ds \frac{\partial \mathbf{R}}{\partial \theta} \cdot \frac{\partial \mathbf{R}}{\partial \theta} \quad ; \quad g_{\varepsilon\varepsilon} = \frac{1}{L} \int_{-L/2}^{L/2} ds \frac{\partial \mathbf{R}}{\partial \varepsilon} \cdot \frac{\partial \mathbf{R}}{\partial \varepsilon} \tag{13}$$

$$g = \det\left(g_{\alpha\beta}\right) \tag{14}$$

Here, $\boldsymbol{\kappa}$ is the velocity gradient of the flow, and $\mathbf{R}(s;\theta,\varepsilon)$ is the position vector at the point s, parametric in the "coordinates" θ and ε of the SBR:

$$\mathbf{R}(s;\theta,\varepsilon) = \left(s - \frac{s^3}{6r^2}\right)\mathbf{u} + \frac{s^2}{2r}\mathbf{c} \tag{15}$$

Equation (15) is the integral of Equation (1). The variable θ is hidden in $\mathbf{u}$ and $\mathbf{c}$, while $\varepsilon = L/r$.

By using Equation (15), it is readily verified that the off-diagonal terms of the $g_{\alpha\beta}$-matrix are zero, and that $g = g_{\theta\theta}g_{\varepsilon\varepsilon}$ only depends on ε. The latter property explains why in the Smoluchowski equation, Equation (11), the $\sqrt{g}$ factor only appears in the last term of the equation.

Equation (11) for the distribution function $\Psi(\theta,\varepsilon,t)$ is by far too complex to be handled, so we need some additional approximation to proceed. Fortunately, we have a good physical motivation for an approximation which serves the purpose. In view of the high (though not infinite) rigidity of the SBR, we can reasonably surmise that the bending motion is much faster than the rotational motion of vector $\mathbf{u}$. That is, in terms of characteristic times, we can write:

$$\tau_{\mathrm{BEND}} \ll \tau_{\mathrm{ROT}} \tag{16}$$

Furthermore, we can assume that the magnitude κ of the velocity gradient $\boldsymbol{\kappa}$ is never large enough to influence the bending motion. That is, we can write:

$$\tau_{\mathrm{BEND}} \ll \frac{1}{\kappa} \tag{17}$$

This inequality is in fact implicit in the SBR model. Indeed, were the flow capable of "competing" with molecular flexibility, the hypothesis of having a single radius of curvature throughout the length of the molecule could not be maintained.

In view of the above-written inequalities, we can factorize the distribution function in the following way:

$$\Psi(\theta,\varepsilon,t) = \Psi_s(\theta;t)\Psi_f(\varepsilon;\theta,t) \tag{18}$$

where $\Psi_s(\theta;t)$ is the t-dependent distribution function of the "slow" variable θ, and $\Psi_f(\varepsilon;\theta,t)$ is the (θ,t)-dependent distribution function of the "fast" variable ε, which is assumed to describe a "local equilibrium" over ε. (As shown explicitly in the following, see Equation 19, the time dependence of $\Psi_f(\varepsilon;\theta,t)$ is due to the mean-field nature of the potential.) The meaning of Equation 18 is then as follows: In the dynamical evolution of the system, before the slow distribution function $\Psi_s(\theta;t)$ of the midpoint orientations may change significantly, the curvature distribution at each θ has all the time to reach equilibrium.

The fast distribution function has the Boltzmann expression:

$$\Psi_f(\varepsilon;\theta,t)=Z_f^{-1}(\theta,t)\exp(-E(\varepsilon;\theta,t))\ ;\quad Z_f(\theta,t)=\int_{-\infty}^{+\infty}d\varepsilon\exp(-E(\varepsilon;\theta,t)) \tag{19}$$

where $E(\varepsilon;\theta,t)$ is (in nondimensional form) the mean-field energy of Equation (6), which is time dependent because of $\Psi_s(\theta;t)$. Notice that in Equation (19) we have allowed for both positive and negative curvatures. Indeed, in two dimensions, "opposite" conformations are more easily accounted for by changing sign to r than by inverting **c** (cf. Equation 1). Notice further that, although the range of integration of the integral formally extends from $-\infty$ to $+\infty$, there is no contradiction with the central assumption of the SBR model, i.e., with the smallness of the curvature. Indeed, because the exponential form in Equation (19) depends on ε essentially as $\exp(-B\varepsilon^2)$, the "effective" integration range is in fact limited to very small (absolute) values of ε.

We can now go back to the Smoluchowski equation. By using Equations (18) and (19), and by integrating over ε, Equation (11) reduces to an equation for the slowly varying orientational distribution only:

$$\frac{\partial\Psi_s}{\partial t}=\frac{\partial}{\partial\theta}\left[D\left(\frac{\partial\Psi_s}{\partial\theta}-\Psi_s\frac{\partial\ln Z_f}{\partial\theta}\right)-\Psi_s\,\omega\right] \tag{20}$$

Here, the "effective" rotatory diffusivity D, and the "angular velocity" ω are given by the following integrals over the fast coordinate ε:

$$D=\int_{-\infty}^{+\infty}d\varepsilon\,\Psi_f\,D_{\theta\theta} \tag{21}$$

$$\omega = \int_{-\infty}^{+\infty} d\varepsilon\, \Psi_f\, g_{\theta\theta}^{-1} V_\theta \qquad (22)$$

While the diffusivity D plays in fact the role of an adjustable parameter, explicit expressions for the angular velocity $\omega(\theta, t)$ are readily obtained for any given flow field.

Equation (20), together with the expressions for the fast function Ψ_f and for the mean-field energy E (Equations 19 and 6, respectively), describe the dynamics of the SBR model in the general two-dimensional case. Specific results for a shear flow will be presented in a future publication. We expect that, within the approximations outlined here, also the full three-dimensional problem remains tractable.

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