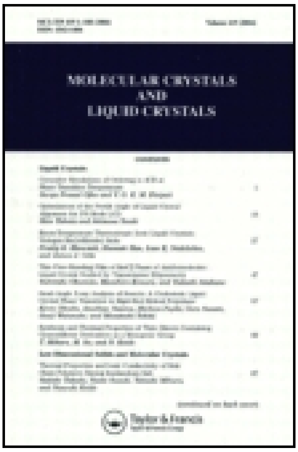

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# The Elastic Constants of Maier-Saupe Rodlike Molecule Nematics

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# The Elastic Constants of Maier-Saupe Rodlike Molecule Nematics

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The classical Maier-Saupe theory of spatially uniform nematics is here extended to the case of distorted configurations. Under the assumption that the molecules are rodlike, the mean field potential is here defined as an average over a suitable neighborhood of the test molecule. The energy density thereby calculated automatically accounts for the distortion energy, and properly reduces to the classical expression for the homogeneous situation. In the linear limit, contrary to existing predictions based on Maier-Saupe potential, the three constants of Frank elasticity are found to be different from one another, and ordered as $K_2 < K_1 < K_3$. The main variables determining the magnitude of the elastic constants are: the order parameter $S$, the molecular length $L$, and an interaction distance $\mathcal{L}$. A quantitative test of the theory on a standard nematic (PAA) shows good agreement with data for all three constants if $\mathcal{L}$ is of the order of 1 nanometer.

*Keywords: Maier-Saupe potential, rodlike molecules, Frank elasticity, distortion energy*

## 1. INTRODUCTION

Since the early sixties, several attempts[1–10] have been made to predict the constants of Frank elasticity from suitable models of the nematogen interaction. The main results refer either to the Onsager calculation of the excluded volume of long rodlike molecules[6] or to the Maier-Saupe mean field potential.[4]

As regards the latter case, of interest here, the following conclusions were reached: by assuming an isotropic center-of-mass correlation, the three elastic constants are predicted to be equal; by relaxing the center-of-mass correlation assumption in favor of an axially symmetric one (around the director), it is found that $K_1 = K_2 < K_3$.[4–8] The prediction that the first two constants are equal does not compare favorably with experiments,[11] not to speak of the prediction $K_1 = K_2 = K_3$.

We believe that these unsatisfactory results are due to an implicit assumption used in the calculations, namely that the Maier-Saupe mean field results from an average made over a *spherical* neighborhood of the "test" molecule. This assumption neglects the fact that, conceivably, the characteristic distance of the interactions (Van der Waals or otherwise) is smaller than the length of the rodlike molecule itself, so that a spherical neighborhood appears ill-suited.

Some confusion might arise here because the Maier-Saupe potential, having the form of a quadrupole interaction, seemingly accounts already for the anisotropy of the molecule. Now, while for the homogeneous situation the molecular anisotropy can be entirely represented through such an interaction, this is no longer assured when distortions are present. In the latter case, the geometrical features of the molecule are expected to enter explicitly. In particular, as mentioned above, molecular length and interaction distance should be compared.

In this work, a "natural" extension of the classical Maier-Saupe potential is considered, which accounts for spatial distortions in a system of rigid rodlike molecules. As shown in the following, even under the assumption of an isotropic center-of-mass correlation, the theory already predicts different values of the three constants. Thus, although an anisotropic center-of-mass correlation is perhaps more realistic for rodlike molecules in the nematic phase, for the sake of simplicity no other assumption will be considered here.

The paper is organized as follows. In Section 2, we present the physical motivation for the above mentioned extension, and provide its mathematical representation. In Section 3, we consider the expansion for weak distortions which, in Section 4, leads to the expressions for the constants of Frank elasticity. These are compared with data in Section 5. The last section contains a discussion about the limitations of the proposed model, as well as a brief comparison with results of continuum theories.

## 2. EXTENSION OF MAIER-SAUPE ENERGY DENSITY TO DISTORTED NEMATICS

The orientation of a rodlike molecule is specified by a unit vector **u** (actually a pseudo-vector, because **u** and -**u** are equivalent). In a spatially homogeneous system of such molecules, the orientational state is completely described by the distribution function f(**u**), giving the probability density that the molecules of the system are oriented along **u**. In view of normalization, it is

$$\int d\Omega f(\mathbf{u}) = 1 \qquad (2.1)$$

where the integral is made over all orientations **u**, i.e., over the solid angle $\Omega = 4\pi$.

When distortions are present, the orientational distribution function at a point **R** can be defined by using the concept of a statistical ensemble, in the following way. We consider a large collection of thermodynamically identical systems, in which also the macroscopic distortion is the same, and define f(**u**;**R**) as the probability density of the orientation **u** for the molecules of the ensemble centered at the fixed location **R**. The **R**-dependence of f(**u**;**R**) describes, at the molecular level, the distortion itself. The definition of f(**u**;**R**) reduces to that of f(**u**) in the homogeneous case.

The function f(**u**;**R**) is used to calculate ensemble averages at **R** of any **u**-dependent quantity $Q$:

$$\langle Q\rangle = \int \mathrm{d}\Omega \mathrm{f}(\mathbf{u};\mathbf{R})Q \tag{2.2}$$

Needless to say, $\langle Q\rangle$ may be **R**-dependent even if $Q$ is not, because of the **R**-dependence of f.

In a mean field approximation, the free-energy density $A$ is written as

$$A(\mathbf{R}) = \nu\left[kT\langle\ln \mathrm{f}(\mathbf{u};\mathbf{R})\rangle + \frac{1}{2}\langle V(\mathbf{u};\mathbf{R})\rangle\right] \tag{2.3}$$

where $\nu$ is the molecular density (independent of **R**), $kT$ is the Boltzmann constant times absolute temperature, and $V$ is the mean field potential acting on a molecule at **R** oriented along **u**. Because the potential is "internal," i.e., it gives the average interaction of the test molecule with the others, the $\frac{1}{2}$ factor prevents the interaction energy from being counted twice.

Under homogeneous equilibrium conditions, the Maier-Saupe mean field potential has the familiar form[12]

$$V(\mathbf{u}) = -2kTUS(\mathbf{n}\cdot\mathbf{u})^2 \tag{2.4}$$

$$S = \left(\frac{3}{2}\right)\langle(\mathbf{n}\cdot\mathbf{u}')^2\rangle - \frac{1}{2} \tag{2.5}$$

where $S$ is the order parameter, and **n** is the director. In Equation (2.4), $U$ is the (temperature dependent) nondimensional intensity of the potential, and the factor 2 is used for convenience. In order to mark the distinction from the argument of the function $V(\mathbf{u})$, the symbol $\mathbf{u}'$ has been used to indicate molecular orientations in the average square cosine of Equation (2.5).

Doi[13] extended the Maier-Saupe potential to non equilibrium conditions by writing

$$V(\mathbf{u}) = -2kTU\langle\mathbf{u}'\mathbf{u}'\rangle{:}\mathbf{uu} \tag{2.6}$$

where the time dependent average $\langle\mathbf{u}'\mathbf{u}'\rangle$ is, in this more general situation, a non-uniaxial tensor replacing **n** and $S$. Yet, just as Equation (2.4), to which it reduces at equilibrium, Equation (2.6) only applies to the spatially homogeneous case.

The average appearing in the Maier-Saupe potential is meant to portray the effect of the molecules surrounding the test rod (which is located at **R** and is oriented along **u**). In the spatially uniform case, this effect is correctly accounted for by an ensemble average, be it $\langle(\mathbf{n}\cdot\mathbf{u}')^2\rangle$ in Equation (2.4) or $\langle\mathbf{u}'\,\mathbf{u}'\rangle$ in Equation (2.6). In the distorted case, conversely, the ensemble averages *at a single point* (over the replicas of the distorted system) cannot describe what is going on *in the neighborhood* of the test rod.

What is needed in the distorted situation is a further step in the generalization such that the averaging process can explicitly account for points surrounding the given molecule. Clearly, the "shape" of this neighborhood should be linked to the molecular geometry. For rodlike molecules, as considered here, we have chosen the shape depicted in Figure 1a.

With the choice of coordinates indicated in Figure 1b, we propose the following generalization of the Maier-Saupe potential:

$$V(\mathbf{u};\mathbf{R}) = -2kTU\{\mathbf{u}'\mathbf{u}'\}:\mathbf{uu} \tag{2.7}$$

$$\{\mathbf{u}'\mathbf{u}'\} = \int d\Omega'\mathbf{u}'\mathbf{u}' \frac{1}{L}\int_{-L/2}^{L/2} ds \frac{1}{V}\int_V dV f(\mathbf{u}';\mathbf{R} + s\mathbf{u} + \mathbf{r}) \tag{2.8}$$

where $L$ is the length of the rodlike molecule, and $V$ is a spherical volume, centered at the current point (coordinate $s$) along the rod, and scanned by the $\mathbf{r}$ vector; the volume $V$ defines the range of the interactions.

It is worthwhile noting that the "neighborhood ensemble average" (NE-average) defined by Equation (2.8) not only depends on $\mathbf{R}$, but also on $\mathbf{u}$. In the homogeneous case, however, the NE-average loses the $\mathbf{u}$-dependence, and Equation (2.7) becomes coincident with Equation (2.6). Further comments on Equation (2.8) are postponed to Section 6.

## 3. SMALL DISTORTION EXPANSION

Under the assumption that the distortions developing over the neighborhood depicted in Figure 1 are small, the distribution function at $\mathbf{R} + \boldsymbol{\rho}$ can be expanded as

$$f(\mathbf{u}';\mathbf{R} + \boldsymbol{\rho}) = f(\mathbf{u}';\mathbf{R}) + \nabla f \cdot \boldsymbol{\rho} + \frac{1}{2}\nabla\nabla f:\boldsymbol{\rho\rho} + \ldots \tag{3.1}$$

where $\nabla$ is the spatial gradient ($\mathbf{u}'$ being fixed), and it is understood that $\nabla f$ and $\nabla\nabla f$ are calculated at $\mathbf{R}$. When Equation (3.1) is substituted in the integral of Equation (2.8), the first order term gives no contribution because of symmetry. Therefore, the expansion has been extended to the first non-zero contribution, i.e., to the second order term.

Substitution of Equation (3.1) into Equation (2.8) gives ($\boldsymbol{\rho} = s\mathbf{u} + \mathbf{r}$, see Figure 1b)

$$\{\mathbf{u}'\mathbf{u}'\} = \langle\mathbf{u}'\mathbf{u}'\rangle + \frac{1}{2}\int d\Omega'\mathbf{u}'\mathbf{u}'\, \nabla\nabla f: \frac{1}{L}\int_{-L/2}^{L/2} ds \frac{1}{V}\int_V dV(s^2\mathbf{uu} + \mathbf{rr}) \tag{3.2}$$

where the average $\langle\mathbf{u}'\mathbf{u}'\rangle$ arises from the function at $\mathbf{R}$, i.e., from the zeroth order term of the expansion. Due to symmetry, also the "mixed" terms of the $\boldsymbol{\rho\rho}$ product integrate to zero; they have therefore been omitted in Equation (3.2).

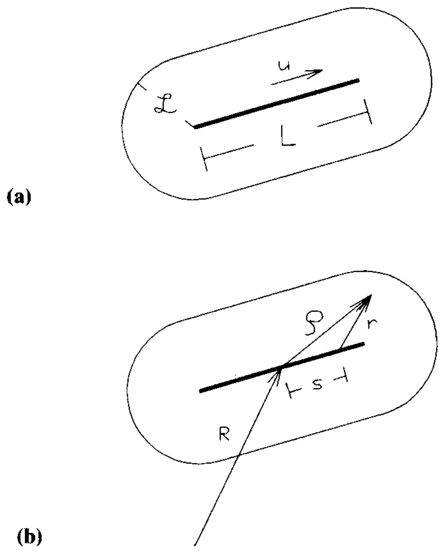

FIGURE 1 a) The relevant neighborhood of a rodlike molecule; b) The coordinates used in the NE-average of Equation (2.8).

The term $s^2\mathbf{uu}$, being independent of $\mathbf{r}$, is integrated over $s$ to give $(L^2/12)\mathbf{uu}$. Similarly, the term $\mathbf{rr}$ is independent of $s$, giving

$$\frac{1}{V}\int_V \mathrm{d}V\mathbf{rr} = C\mathbf{1} \tag{3.3}$$

where $\mathbf{1}$ is the unity tensor, and $C$ is a constant proportional to $V^{2/3}$. In view of the $L^2/12$ term resulting from the previous integration, we also write $C$ in the form $\mathcal{L}^2/12$ for convenience. The characteristic length $\mathcal{L}$, depicted in Figure 1a, is representative of the interaction distance. Equation (3.2) is then rewritten as

$$\{\mathbf{u'u'}\} = \langle\mathbf{u'u'}\rangle + \frac{1}{24}\int \mathrm{d}\Omega'\mathbf{u'u'}\ \nabla\nabla\mathrm{f}:(\mathcal{L}^2\mathbf{1} + L^2\mathbf{uu}) \tag{3.4}$$

By interchanging the spatial gradient and the integral over $\mathbf{u}'$ in Equation (3.4), we finally write (indicial notation is needed here)

$$\{\mathrm{u}_i'\mathrm{u}_j'\} = S_{ij} + \frac{1}{24}(\mathcal{L}^2\partial_\alpha\partial_\alpha S_{ij} + L^2\mathrm{u}_\alpha\mathrm{u}_\beta\partial_\alpha\partial_\beta S_{ij}) \tag{3.5}$$

where $S_{ij}$ is the 2nd moment of the orientational distribution function

$$S_{ij} = \langle\mathrm{u}_i'\mathrm{u}_j'\rangle \tag{3.6}$$

We now insert Equation (3.5) into the expression of the mean field potential, Equation (2.7), take the ensemble average of the result, and thus obtain the expression for the energy density $\varepsilon(\mathbf{R})$:

$$\varepsilon(\mathbf{R}) = \frac{1}{2}\nu\,\langle V(\mathbf{u};\mathbf{R})\rangle = -\nu kTU\,\langle\{\mathbf{u}'\mathbf{u}'\}:\mathbf{uu}\rangle$$

$$= -\nu kTU\left[S_{ij}S_{ij} + \left(\frac{\mathcal{L}^2}{24}\right)S_{ij}\partial_\alpha\partial_\alpha S_{ij} + \left(\frac{L^2}{24}\right)R_{\alpha\beta ij}\partial_\alpha\partial_\beta S_{ij}\right] \quad (3.7)$$

where $R_{\alpha\beta ij}$ is the 4th moment of the orientational distribution function

$$R_{\alpha\beta ij} = \langle u_\alpha u_\beta u_i u_j\rangle \quad (3.8)$$

In view of the objective of this work, that is to obtain predictions for the constants of Frank elasticity, Equation (3.7) might seem inadequate because it contains second, instead of first, gradients. (As is well known, Frank elasticity is formulated in terms of first gradients of the director field[14]). This is not a problem, however, since an expression containing no higher order gradients than the first can readily be obtained. Such an expression will differ from Equation (3.7) by "surface terms" only.

In order to clarify what is meant here, we recall that minimization of a volume integral of the energy density is implied in any equilibrium problem of bulk phases. It follows that energy density expressions which give rise to volume integrals only differing by a boundary surface term are in fact equivalent.

Let us then consider the following integration by parts:

$$\int_V S_{ij}\partial_\alpha\partial_\alpha S_{ij}\,\mathrm{d}V = \int_\Sigma S_{ij}\partial_\alpha S_{ij}p_\alpha\,\mathrm{d}\Sigma - \int_V \partial_\alpha S_{ij}\partial_\alpha S_{ij}\,\mathrm{d}V \quad (3.9)$$

where $V$ is the volume of the bulk phase, $\Sigma$ its bounding surface, and $\mathbf{p}$ the normal to this surface. Equation (3.9), together with a similar expression for the term $R_{\alpha\beta ij}\partial_\alpha\partial_\beta S_{ij}$, allow one to rewrite Equation (3.7) as

$$\varepsilon(\mathbf{R}) = \nu kTU\left[-S_{ij}S_{ij} + \left(\frac{\mathcal{L}^2}{24}\right)\partial_\alpha S_{ij}\partial_\alpha S_{ij} + \left(\frac{L^2}{24}\right)\partial_\alpha R_{\alpha\beta ij}\partial_\beta S_{ij}\right] \quad (3.10)$$

In view of the discussion to be made in Section 6, it is emphasized here that Equation (3.10) contains, together with the gradient of the second order moment $\nabla\mathbf{S}$, the gradient of the fourth order moment as well: the latter has been generated by the $\mathbf{u}$-dependence of the NE-average $\{\mathbf{u}'\mathbf{u}'\}$.

## 4. FRANK ELASTICITY

Consistently with the mean field potential of Equation (2.7), the equilibrium orientational distribution function is given by the Boltzmann expression

$$f(\mathbf{u};\mathbf{R}) = g(\mathbf{R})\exp(2U\{\mathbf{u}'\mathbf{u}'\}:\mathbf{uu}) \quad (4.1)$$

where the NE-average $\{\mathbf{u}'\mathbf{u}'\}$ is a function of both $\mathbf{u}$ and $\mathbf{R}$, and $g(\mathbf{R})$ is a factor that preserves normalization (compare Equation 2.1) at all points.

The orientational distribution problem drastically simplifies in the spatially uniform case, which enjoys a uniaxial symmetry. We simply need the average molecular orientation, i.e., the director $\mathbf{n}$, and the function $f_0(\mathbf{u} \cdot \mathbf{n})$ describing the equilibrium spread of orientations about the director. The function $f_0$ corresponds to the classical Maier-Saupe solution, to which Equation (4.1) reduces when there is no dependence on $\mathbf{R}$:

$$f_0(\mathbf{u} \cdot \mathbf{n}) = g \exp[2US(\mathbf{u} \cdot \mathbf{n})^2] \tag{4.2}$$

Of course, neither the order parameter $S$ nor the normalization factor $g$ depend on $\mathbf{n}$.

In the general case of an arbitrary distortion, $f(\mathbf{u};\mathbf{R})$ may depart considerably from $f_0(\mathbf{u} \cdot \mathbf{n})$. Work is in progress, for example, to determine how the distribution function changes in close proximity to defects. Conversely, in all cases where Frank elasticity is applicable, the distribution function differs negligibly from $f_0$, and the only effects that matter are linked to the gradients of the director $\mathbf{n}$.

Let us consider in more detail the following difference

$$\delta(\mathbf{u};\mathbf{R}) = f(\mathbf{u};\mathbf{R}) - f_0[\mathbf{u} \cdot \mathbf{n}(\mathbf{R})] \tag{4.3}$$

where $\mathbf{n}(\mathbf{R})$ is the director at $\mathbf{R}$ (a director can be defined also in the biaxial case).[15] Frank elasticity holds if $\delta(\mathbf{u};\mathbf{R})$ is small, in the sense that the free-energy minimum is the "same" (giving the "same" $\mathbf{n}(\mathbf{R})$ function) whether or not $\delta(\mathbf{u};\mathbf{R})$ is included in the minimization procedure. In other words, Frank elasticity corresponds to the possibility of minimizing free energy within a restricted class of distribution functions, i.e., those having the same orientational spread about the local director, as in the undistorted nematics; only the director itself is allowed to vary. The "sameness" referred to above is somehow arbitrary, however; as for all linear constitutive equations, Frank elasticity describes in fact an asymptotic behavior.

Priest,[5] who should be credited for most of the previous considerations, also notes that the restriction of the minimum problem to the class of $f_0$ functions cancels the orientational entropy term from the *distortion* free energy. Indeed, the entropy term $\langle \ln f(\mathbf{u};\mathbf{R}) \rangle$ in Equation (2.3) becomes in this case

$$\langle \ln f_0[\mathbf{u} \cdot \mathbf{n}(\mathbf{R})] \rangle = \ln g + 2US\langle [\mathbf{u} \cdot \mathbf{n}(\mathbf{R})]^2 \rangle = \ln g + \frac{4}{3} US^2 + \frac{2}{3} US \tag{4.4}$$

which, $g$ and $S$ being independent of $\mathbf{n}$, is a constant throughout.

In conclusion, the distortion free energy of Frank elasticity is made up only of the gradient terms in Equations (3.10), to be further specialized according to the uniaxial symmetry of the $f_0$ function.

The uniaxial forms of $S_{ij}$ and of $R_{\alpha\beta ij}$ are:

$$S_{ij} = S\mathrm{n}_i\mathrm{n}_j + S'\delta_{ij} \tag{4.5}$$

$$R_{\alpha\beta ij} = R_1\mathrm{n}_\alpha\mathrm{n}_\beta\mathrm{n}_i\mathrm{n}_j + R_2\overbrace{(\mathrm{n}_\alpha\mathrm{n}_\beta\delta_{ij} + \ldots)}^{\text{6 terms}} + R_3\overbrace{(\delta_{\alpha\beta}\delta_{ij} + \ldots)}^{\text{3 terms}} \tag{4.6}$$

where $S$, $S'$, $R_1$, $R_2$, $R_3$ are scalar constants to be calculated from $f_0$ (see Equations 4.11–4.13). The groups of six and three terms within the brackets in Equation (4.6) are obtained by changing indices in all possible meaningful ways.

Substitution of the uniaxial forms of Equations (4.5) and (4.6) into the two gradient terms appearing in Equation (3.10) gives, respectively:

$$\partial_\alpha S_{ij}\partial_\alpha S_{ij} = 2S^2\nabla\mathbf{n}:\nabla\mathbf{n}^{\mathrm{T}} \tag{4.7}$$

$$\partial_\alpha R_{\alpha\beta ij}\partial_\beta S_{ij} = 2S(R_2[(\nabla \cdot \mathbf{n})^2 + \nabla\mathbf{n}:\nabla\mathbf{n} + \nabla\mathbf{n}:\nabla\mathbf{n}^{\mathrm{T}}] + (R_1 + 2R_2)[(\mathbf{n} \cdot \nabla)\mathbf{n}]^2) \tag{4.8}$$

In deriving Equations (4.7) and (4.8), frequent use has been made of the identity $\mathrm{n}_i\partial_\alpha\mathrm{n}_i = 0$.

In order to obtain our result in the form of the Frank elasticity expression (as it is usually written), the following relationships are further required:

$$\begin{aligned} \nabla\mathbf{n}:\nabla\mathbf{n}^{\mathrm{T}} &= (\nabla \cdot \mathbf{n})^2 + (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + (\mathbf{n} \times \nabla \times \mathbf{n})^2 \\ \nabla\mathbf{n}:\nabla\mathbf{n} &= (\nabla \cdot \mathbf{n})^2 \\ [(\mathbf{n} \cdot \nabla)\mathbf{n}]^2 &= (\mathbf{n} \times \nabla \times \mathbf{n})^2 \end{aligned} \tag{4.9}$$

These equations are identities "to within surface terms," i.e., in the same sense as previously indicated (compare the discussion preceding Equation 3.9; see also Reference 11).

Back substitution of Equations (4.9) into Equations (4.7) and (4.8), and of the latter ones into Equation (3.10), gives the three elastic constants as

$$\begin{aligned} K_1 &= \frac{1}{6}\nu kTUS^2[\mathcal{L}^2 + 3L^2R_2/S] \\ K_2 &= \frac{1}{6}\nu kTUS^2[\mathcal{L}^2 + L^2R_2/S] \\ K_3 &= \frac{1}{6}\nu kTUS^2[\mathcal{L}^2 + L^2(R_1 + 3R_2)/S] \end{aligned} \tag{4.10}$$

In order to compute actual values of the elastic constants from these expressions, there remains to indicate the explicit forms of $R_1$ and $R_2$. From the definitions of Equation (4.6), and by setting the $z$-axis, say, of a Cartesian coordinate system along the director, we obtain

$$\begin{aligned} R_2 &= R_{3311} - \frac{1}{3} R_{1111} \\ R_1 + 3R_2 &= R_{3333} - 3R_{3311} \end{aligned} \tag{4.11}$$

Equation (2.5) for the order parameter $S$, and Equations (4.11) for $R_1$ and $R_2$, can be rewritten in the form

$$\begin{aligned} S &= \frac{3}{2} I_2/I_0 - \frac{1}{2} \\ M &= R_2/S = \frac{1}{4}(I_0 - 6I_2 + 5I_4)/(I_0 - 3I_2) \\ N &= (R_1 + 3R_2)/S = (3I_2 - 5I_4)/(I_0 - 3I_2) \end{aligned} \tag{4.12}$$

where $I_0$, $I_2$, $I_4$ are the integrals

$$I_q = \int_0^1 x^q \exp(2USx^2)\, dx; \quad (q = 0, 2, 4) \tag{4.13}$$

Thus, by calling $P$ the nondimensional front factor in Equations (4.10)

$$P = \frac{1}{6} US^2 \tag{4.14}$$

the expressions for the elastic constants are finally written as

$$\begin{aligned} K_1 &= vkTP[\mathcal{L}^2 + 3L^2M] \\ K_2 &= vkTP[\mathcal{L}^2 + L^2M] \\ K_3 &= vkTP[\mathcal{L}^2 + L^2N] \end{aligned} \tag{4.15}$$

It is worth noting that all three constants come out different in the general case. The equality $K_1 = K_2 = K_3$ holds true if $\mathcal{L} >> L$, i.e., if the "interaction neighborhood" of the molecule is essentially spherical (compare Figure 1a). This particular result of equal constants had been previously obtained,[4,8] apparently without recognizing its limiting status. At the opposite extreme, i.e., if $L >> \mathcal{L}$, we find $K_1 = 3K_2$ as in the result obtained with the Onsager excluded volume potential.[6]

The ratio of any two constants generally depends, through $M$ and $N$, on the strength $U$ of the potential, and therefore on the order parameter $S$. The absolute values of the elastic constants further depend on $S$ through $P$. These aspects, as well as some comparisons with data, are considered in the next section.

## 5. COMPARISON WITH EXPERIMENTS. THE PAA EXAMPLE

For any given value of $U$, the first of Equations (4.12) allows one to calculate $S$ by trial and error. Indeed, this equation represents the standard self-consistency condition of Maier and Saupe.[12] Once $S$ has been determined, the corresponding values of $M$, $N$, and $P$ are directly obtained from Equations (4.12–4.14). Figure 2 reports the functions $M$, $N$, $P$ *vs*. $S$. The smallest value of $S$ in Figure 2 is 0.429, that is the value at the isotropic-nematic transition predicted by the Maier-Saupe theory. In the fully oriented limit, i.e., as $S$ approaches unity, $M$ and $N$ approach 0 and 1, respectively, as they should (compare the definitions in Equations 3.6 and 3.8).

As shown in Figure 2, $N$ is larger than $M$ throughout the range of $S$-values: thus, from Equations (4.15), $K_3$ is found to be larger than $K_2$. Because Equations (4.15) also impose that the ratio $K_1/K_2$ be larger than unity (though smaller than 3), $K_2$ is predicted to be the smallest of the constants.

In fact, Figure 2 shows that $N > 3M$ everywhere, so that $K_3$ is found to be larger

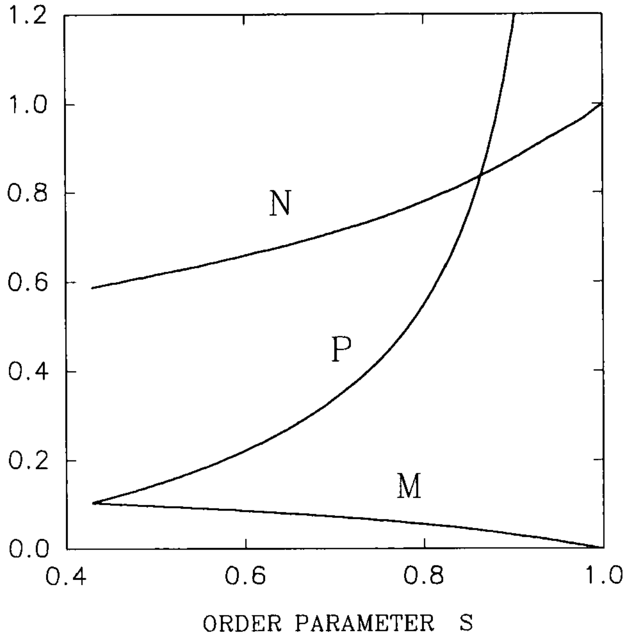

FIGURE 2 Dependence on the order parameter of the coefficients $M$, $N$, $P$, appearing in Equations (4.15) for the Frank elasticity constants.

than $K_1$ as well. In other words, the three elastic constants are predicted always to be ordered in the following way:

$$K_2 < K_1 < K_3 \tag{5.1}$$

Such an ordering of the elastic constants is well known experimentally for low molecular weight nematics.[11] For polymeric nematics, an inversion between $K_1$ and $K_3$ is observed in some cases, as well as a ratio $K_1/K_2$ larger than 3.[16] On the other hand, it is not expected that the present theory extends up to the polymeric limit; this point will be taken up again in the next section.

As regards temperature dependence, we note that temperature decreases from left to right in Figure 2, as $S$ increases. It is readily verified that the corresponding increase of the $P$ factor dominates over all other effects, so that a growth of all three elastic constants is predicted to occur with decreasing temperature. Also this behavior is in qualitative agreement with experiments.[11]

We now perform a quantitative comparison for the case of a well known nematic, $p$-azoxyanisole (PAA). The PAA molecule is rigid, and its length is $L = 17$ Å.[5] We choose in particular the temperature of 129°C at which we find both the value of the order parameter, $S = 0.54$ (Figure 2.8 in Reference 11), and that of the elastic constants, $K_1 = 3.85 \times 10^{-7}$ dynes, $K_2 = 2.4 \times 10^{-7}$ dynes, and $K_3 = 7.7 \times 10^{-7}$ dynes (Table 3.1 in Reference 11). Finally, the mass density[12] of PAA at 129°C is 1.156 g/cm$^3$, from which, the molecular weight being 258.3, we calculate $\nu kT = 14.9 \times 10^7$ dynes/cm$^2$.

From $S = 0.54$ we obtain: $M = 0.092$, $N = 0.632$, $P = 0.172$ (see Figure 2). In view of Equations (4.15), all that is now needed for a quantitative prediction of *all three* elastic constants is a value for the interaction distance $\mathcal{L}$. With $\mathcal{L} = 8.7$ Å, Equations (4.15) give:

$$K_1 = 4.0 \times 10^{-7} \text{ dynes}$$

$$K_2 = 2.6 \times 10^{-7}$$

$$K_3 = 6.6 \times 10^{-7}$$

The value of $\mathcal{L} = 8.7$ Å minimizes the mean square percentage difference between predicted and measured values of the three elastic constants. Such an average error is 10%; individual comparison shows, however, that $K_1$ and $K_2$ are in excess by 4% and 8%, respectively, whereas $K_3$ is 14% below the measured value.

These differences in precision, albeit minor, might possibly be ascribed to the assumption of an isotropic center-of-mass correlation, implicit in our mean field approach. Indeed, as mentioned in the Introduction, accounting for the anisotropic correlation raises $K_3$ with respect to the other two constants[4,8]; how important this correction might be in a situation where the order parameter is much less than unity remains to be established, however.

The point to be emphasized here is the good agreement obtained with *three* measured quantities by means of a theory containing a *single* adjustable parameter,

$\mathscr{L}$. Furthermore, the value obtained for this parameter from the best fit procedure shows the correct order of magnitude, i.e., about 10 Å.

## 6. DISCUSSION AND CONCLUSIONS

Let us first comment on our choice of the NE-average, particularly for what concerns the innermost integral in Equation (2.8) extending over the interaction volume $V$. At first sight, one might dislike the fact that the weight given to the point-to-point quadrupole interaction is a step function of $\mathbf{r}$: it is $1/V$ throughout $V$ and drops to zero outside. More realistically, one expects that the interaction gradually decays with increasing $\mathbf{r}$.

The use of a different weight would not change our results in any way, however, because of the expansion procedure inherent to Frank elasticity. Indeed, any different weight function, $W(r)$, would produce an integral similar to that of Equation (3.3), namely

$$\int_{R^3} \mathrm{d}V W(r)\, \mathbf{rr} = C'\, \mathbf{1} \tag{6.1}$$

where $R^3$ is whole space, and $W(r)$ is normalized, i.e., integration of $W(r)$ over $R^3$ gives unity. In Equation (6.1), the dimensions of the $C'$ factor still remain those of a square length, and therefore $C'$ would again be representable as $\mathscr{L}^2/12$. In conclusion, for whatever choice of the weighting function, $\mathscr{L}$ keeps the meaning of characteristic interaction distance (defined in detail by $W(r)$ itself), and the expressions of the elastic constants of Equations (4.15) are left unchanged.

A geometrical aspect of the molecule purposedly neglected in our NE-average is molecular "thickness." Although accounting for this feature would certainly modify the result for the elastic constants, we also expect that such a modification would be minor, at least as long as the "rod diameter" is less than $\mathscr{L}$. In any event, the possible inclusion of a diameter effect would become even more negligible as $L$ increases. Different, and more serious, complications arise when the ratio $L/\mathscr{L}$ grows considerably.

Indeed, we know that, if $L$ is large enough, the nematic state can exist even at low molecular concentrations, i.e., in dilute solutions. We also know that, in these limiting conditions, the "correct" mean field potential is that due to excluded volume,[17] and, consequently, the elastic constant expressions should be those calculated by Straley.[6] Now, just as the self consistency relationships of Maier-Saupe and Onsager are quite different, similarly different are the elastic constant expressions, even if $K_1/K_2 = 3$ in both theories. In other words, Equations (4.15) do not degenerate properly as $L \rightarrow \infty$ and $\nu \rightarrow 0$, just because the Maier-Saupe mean field does not apply in that limit.

Another limitation of our model is the complete neglecting of internal degrees of freedom. Further extensions of the Maier-Saupe potential to semi-flexible molecules are conceivable, which might go up to the polymeric chain. In this respect, it should be mentioned that predictions for semi-flexible polymers are already available,[18] albeit based on the use of the Onsager potential (defined on the persistence length in place of $L$). For whatever choice of the "intersegmental" potential, there are specific polymeric effects which must be separately included, however, such as the presence of "hairpins" induced by splay distortions.[16] It seems that the most prominent deviations from the ordering of Equation (5.1) are just due to the latter effects.[16]

Let us finally comment on the form of the distortion energy given by Equation (3.10), particularly on the appearance in it of the gradient of the fourth order moment $R_{\alpha\beta ij}$. We recall that, in the context of phenomenological theories, there has been a long-lasting debate about the form to be given to the distortion energy in order to obtain three different elastic constants. The main conclusions can be summarized as follows. In the original[19] Landau-de Gennes expansion in **S**, and using our notation, the distortion free energy $A_d$ is written as

$$A_d = \frac{1}{2}\left(a_1 \partial_\alpha S_{ij} \partial_\alpha S_{ij} + a_2 \partial_\alpha S_{\alpha i} \partial_\beta S_{\beta i}\right) \tag{6.2}$$

where $a_1$ and $a_2$ are constitutive parameters. From Equation (6.2), the following elastic constants are obtained[15]

$$\begin{aligned} K_1 &= K_3 = S^2(2a_1 + a_2) \\ K_2 &= 2S^2 a_1 \end{aligned} \tag{6.3}$$

Equations (6.3) show that three distinct elastic constants cannot be derived from the Landau-de Gennes expression. Poniewierski and Sluckin[15] therefore proposed that the constant coefficients $a_1$ and $a_2$ be replaced by invariant polynomial functions of the **S**-tensor. Three different elastic constants were thus obtained at the expense of a much larger number of arbitrary parameters, i.e., of the coefficients in the polynomials.

Still by using the Landau-de Gennes approach as a starting point, Rosciszewski[20] obtained three distinct elastic constants by a different "trick," i.e., by assuming an expansion in a fourth order tensor as well. It can readily be shown, however, that a complete list of all possible invariant terms of the distortion free energy, i.e., a list including all possible products of gradients, becomes hopelessly long in such a case. Rather arbitrarily, Rosciszewski himself cut those terms to a few.

Our result of Equation (3.10) "naturally" selects two gradient terms only, each of them bearing a constant coefficient. The term involving the product $\partial_\alpha S_{ij} \partial_\alpha S_{ij}$ corresponds to the first one in Equation (6.2), and, taken by itself, predicts in fact equal values of the three elastic constants (compare Equation 6.3 with $a_2 = 0$; see also Reference 21). The product $\partial_\alpha R_{\alpha\beta ij} \partial_\beta S_{ij}$ is the only fourth order tensor term; it provides the single source of distinction among the three elastic constants.

We wish to conclude by emphasizing the powerfulness, and the simplicity, of the molecular model approach as compared to the continuum mechanical one. Not only are the numerous possible gradient terms automatically selected and a few of them allowed to survive, but also the coefficients of those terms are explicitly linked to physically relevant parameters.

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