Elastic constants of nematic solutions of rod-like and semi-flexible polymers

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Elastic constants of nematic solutions of rod-like and semi-flexible polymers

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Analytical expressions for the elastic constants of nematic polymer solutions are derived when the macromolecules are monodisperse rod-like, bidisperse rod-like or semi-flexible. These expressions are derived in the gaussian approximation so that they constitute exact leading terms of a general asymptotic expansion for high degree of nematic ordering although the results are justifiable only within the range of validity of the second virial approximation. The limiting forms are in complete agreement with recent numerical work for monodisperse rods.

1. Introduction

Because the Frank elastic constants of liquid crystals depend on derivatives of the particle distribution functions these material constants are expected to be quite sensitive to the degree of molecular order, probably more so than the usual statistical thermodynamic quantities. This expectation is even stronger for polymeric liquid crystals since they are, in the main, more highly ordered than their monomeric counterparts. In addition, the dependence on molar mass is very interesting because it is bound to reflect universal properties just as it does for dilute isotropic solutions of linear polymers.

Here, our interest centres on sufficiently slender polymer chains, i.e. both the persistence length and the contour length are much larger than the effective diameter. Thus, we start from the classical virial expansion [7], formal expressions for the elastic constants having been derived first by Straley [2] and Priest [3]. The leading order solution of the Onsager integral equation for the orientational distribution function is simply gaussian and we show that it is feasible therefore to obtain the leading terms for the elastic constants for monodisperse and bidisperse rods. However, the calculations for semi-flexible polymers of arbitrary contour length are very complicated although a scaling analysis is straightforward as will be shown.

2. Monodisperse rods

Our starting point is an expression for the dimensionless elastic constants K_i first derived by Straley [2] and corrected by Lee and Meyer [4],

$$K_i = -\frac{4c_a^2}{3\pi^2} \iint d\Omega_1 \, d\Omega_2 \, f'(\cos\theta_1) \, f'(\cos\theta_2) \, |\sin\gamma| H_i. \tag{1}$$

Here, the actual $K_i' = K_i D/kT$, and $c_a = b\varrho$ is the number density ϱ of the nematic phase, scaled with respect to the isotropic excluded volume $b = (\pi/4)L^2 D$ with L the length and D the diameter of the rods ($L \gg D$). The single-rod orientational

distribution function $f(\cos\theta)$ depends on the angle θ between a rod and the director **n**. The coupling between two rods (denoted by indices 1 and 2; the solid angle $\Omega = (\theta, \phi)$ with ϕ the angle between a test rod and a chosen axis perpendicular to the director) is proportional to the terms H_i specific to the type of deformation, and the orientational part of the excluded volume $|\sin\gamma|$ were γ is the angle between the two probe rods.

Splay

$$H_1 = G(\sin^2\theta_1\cos^2\phi_1 + \sin^2\theta_2\cos^2\phi_2), \qquad (2)$$

Twist

$$H_2 = G(\sin^2\theta_1\sin^2\phi_1 + \sin^2\theta_2\sin^2\phi_2), \qquad (3)$$

Bend

$$H_3 = G(\cos^2\theta_1 + \cos^2\theta_2), \qquad (4)$$

$$G \equiv \sin\theta_1\sin\theta_2\cos\phi_1\cos\phi_2. \qquad (5)$$

These expressions are not very enlightening but, fortunately, they can be greatly simplified in view of the following points.

(a) If we change to the new variables $\psi_1 = \phi_2$, $\psi_2 = \phi_1 - \phi_2 \equiv -\phi'$ the effect of $\cos\phi_1\cos^3\phi_2$ on the integration is the same as that of $\cos^3\phi_1\cos\phi_2$ because

$$\gamma = \gamma(\phi') = \gamma(-\phi') = \gamma(\psi_2).$$

(b) Next, we write

$$\cos\phi_2 = \cos\phi_1\cos\phi' - \sin\phi_1\sin\phi',$$

the sine term yields zero on integrating over ϕ' because $\gamma = \gamma(\cos\phi')$.

(c) The integrations over ϕ_1 are elementary yielding the factors

$$\langle\cos^2\phi_1\rangle = \tfrac{1}{2}, \quad \langle\sin^2\phi_1\cos^2\phi_1\rangle = \tfrac{1}{8}, \quad \langle\cos^4\phi_1\rangle = \tfrac{3}{8}.$$

(d) The combination $\sin\theta_1\sin\theta_2\cos\phi'$ is replaced by $(\cos\gamma - \cos\theta_1\cos\theta_2)$.

In this way it is easy to show that, in equation (1), the H_i can be replaced by $H_{i,0}$ obtained from equations (2)-(5)

$$H_{1,0} = 3H_{2,0} \qquad (6)$$

$$H_{2,0} = \tfrac{1}{4}\sin^2\theta_1(\cos\gamma - \cos\theta_1\cos\theta_2), \qquad (7)$$

$$H_{3,0} = \cos^2\theta_1(\cos\gamma - \cos\theta_1\cos\theta_2). \qquad (8)$$

Accordingly, we have the exact relation

$$K_1 = 3K_2. \qquad (9)$$

Furthermore, we note that pre-averaging of equations (6)-(8) over the angle ϕ' causes the elastic constants to vanish. The constants are non-zero because the ϕ' distribution due to the $|\sin\gamma|$ term is non-random although only slightly so. In general, this or analogous ϕ' distributions should be sensitive to molecular structure, interactions, etc.

It is now possible to calculate K_i for any distribution that can be represented by the asymptotic form

$$f(\cos \theta) \sim \exp\left(-\tfrac{1}{2}\alpha\theta^2\right) \left(\sum_{k=0}^{r} c_k \theta^{2k}\right),$$

$$\alpha \gg 1 \quad (0 \leqslant \theta \leqslant \tfrac{1}{2}\pi; \text{ otherwise the mirrored version}). \tag{10}$$

Here, α and c_k are parameters which could be obtained, for example, by minimizing the free energy. Hence, if we expand all functions in the integrand of equation (1) for small θ_1, θ_2 and γ, all that is needed are gaussian averages of the type

$$\langle \theta_1^{2m} \theta_2^{2n} \gamma^{2p+1} \rangle_0 = \iint d\Omega_1 \, d\Omega_2 \, \theta_1^{2m} \theta_2^{2n} \gamma^{2p+1} g(\theta_1) g(\theta_2) \tag{11}$$

where

$$g(\theta_1) = \left(\frac{\alpha}{4\pi}\right) \exp\left(-\tfrac{1}{2}\alpha\theta^2\right), \quad (0 \leqslant \theta \leqslant \tfrac{1}{2}\pi) \quad (\alpha \gg 1),$$

$$= \left(\frac{\alpha}{4\pi}\right) \exp\left(-\tfrac{1}{2}\alpha(\pi - \theta)^2\right), \quad (\tfrac{1}{2}\pi \leqslant \theta \leqslant \pi). \tag{12}$$

We can evaluate equation (11) for any m, n and p by appealing to an interesting theorem deduced by Onsager [1]

$$J(\alpha_1, \alpha_2) = \iint d\Omega_1 \, d\Omega_2 \cosh\left(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2\right) F(\sin \gamma),$$

$$= \frac{8\pi^2}{\alpha_1 \alpha_2} \int_{\gamma=0}^{\gamma=\pi} d(F(\sin \gamma)) \cosh\left(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos \gamma\right)^{1/2}. \tag{13}$$

The function F must depend solely on $\sin \gamma$ and furthermore $F(0) = 0$.

Let us outline the calculation of several averages. Firstly, we let

$$F(x) = x^{2p+1};$$

then $\langle \gamma \rangle_0^{2p+1}$ is obtained from equation (13) by retaining the leading term of the asymptotic expansion of J for large $\alpha = \alpha_1 = \alpha_2$,

$$\langle \gamma^{2p+1} \rangle_0 = 4^{p+\frac{1}{2}} \Gamma(p + \tfrac{3}{2}) \alpha^{-p-\frac{1}{2}}. \tag{14}$$

The quantity $\langle \gamma^{2p+1} \theta_1^2 \rangle_0$ can be derived by differentiating equation (14) in addition to

$$\langle \gamma^{2p+1} \rangle_0 = \iint d\Omega_1 \, d\Omega_2 \, \gamma^{2p+1} g(\theta_1) g(\theta_2),$$

using equation (12). Note that this is possible because differentiation and asymptotic expansion are commuting operations. Cross terms like $\langle \theta_1^2 \theta_2^2 \gamma \rangle_0$ are a little more tedious to calculate. We have to differentiate both the formal expression for $\langle \gamma \rangle_{12}$ with respect to α_1 and α_2 and the explicit one derived from equation (13)

$$\langle \gamma \rangle_{12} = \left(\frac{\pi}{2}\right)^{1/2} (\alpha_1 + \alpha_2)^{1/2} \alpha_1^{-1/2} \alpha_2^{-1/2}.$$

Other averages are obtained in the same way. In this paper we do not go beyond the purely gaussian approximation, the averages we need are given in the Appendix.

From equations (1), (6)–(9) and (15) we find the leading terms for the elastic constants, eliminating α via the relation $\alpha = 4\pi^{-1}c_a^2$ which is valid in the gaussian approximation [1, 5]

$$K_1 = 4\pi^{-2}c_a^2\alpha^2 \langle \tfrac{1}{8}\gamma\theta_1^2(\gamma^2 - \theta_1^2 - \theta_2^2)\rangle_0,$$

$$= \tfrac{7}{4}\pi^{-3/2}c_a^2\alpha^{-1/2} = \frac{7c_a}{8\pi}, \tag{15}$$

$$K_2 = \frac{7c_a}{24\pi}, \tag{16}$$

$$K_3 = \tfrac{4}{3}\pi^{-2}c_a^2\alpha^2 \langle \tfrac{1}{2}\gamma(\gamma^2 - \theta_1^2 - \theta_2^2)\rangle_0,$$

$$= \tfrac{2}{3}\pi^{-3/2}c_a^2\alpha^{1/2} = \frac{4c_a^3}{3\pi^2}. \tag{17}$$

In the table equations (16) and (17) are compared with $K_{2,N}$ and $K_{3,N}$ obtained numerically by Lee and Meyer [4]. For large c_a, the ratios K_2/K_{2N} and K_3/K_{3N} converge nicely to unity. Note that the correction factors should be of the form $(1 + \text{constant } c_a^{-2} + \ldots)$ as is indeed the case. Furthermore, the numerical work satisfies $K_1 = 3K_2$.

Ratios of the elastic constants given by equations (16) and (17) to those calculated numerically [4]. They converge to unity as c_a increases. The first order deviation from unity is linear in c_a^{-2} (or α^{-1}) in accord with the general form of equation (10).

c_a	$K_2/K_{2,N}$	$K_3/K_{3,N}$
3·6	2·16	4·05
4	1·51	2·19
4·5	1·30	1·66
5	1·21	1·44
5·5	1·15	1·32
6	1·12	1·24
6·5	1·10	1·19
7	1·08	1·15
7·5	1·07	1·12

3. Bidisperse rods

A theory of the nematic ordering of bidisperse rod-like macro-molecules has been developed by Odijk and Lekkerkerker [5]. The system is now characterized by the parameters α_1, α_2, $Q = \alpha_2/\alpha_1$, rod lengths L_1 and L_2, $q = L_2/L_1$, rod diameter D, the total number density c_a and the mole fraction x of longer rods (index 1 denotes shorter rods; 2 longer rods). In the second virial and gaussian approximations we have [5]

$$\tfrac{1}{2}\pi^{1/2}c_a^{-1}\alpha_1^{1/2} = 1 - x + 2^{1/2}xq\left(\frac{Q}{1 + Q}\right)^{1/2}, \tag{18}$$

$$Q^{1/2} = \frac{q[2^{1/2}(1 - x)(1 + Q)^{-1/2} + xq]}{1 - x + 2^{1/2}xqQ^{1/2}(1 + Q)^{-1/2}}. \tag{19}$$

With the help of various gaussian averages (cf. the Appendix) it is straightforward to extend the results of the previous section to obtain

$$K_1 = 3K_2, \tag{20}$$

$$K_2 = K_{2,1}\left[(1 - x)^2 + \frac{2^{3/2}q^2x(1 - x)(3 + 8Q + 3Q^2)}{7Q^{1/2}(1 + Q)^{3/2}} + x^2Q^{-1/2}q^4\right], \tag{21}$$

$$K_3 = K_{3,1}[(1 - x)^2 + 2^{3/2}q^2x(1 - x)Q^{1/2}(1 + Q)^{-1/2} + x^2Q^{1/2}q^4], \tag{22}$$

with

$$K_{2,1} = \tfrac{7}{12}\pi^{-3/2}c_a^2\alpha_1^{-1/2}$$

and

$$K_{3,1} = \tfrac{2}{3}\pi^{-3/2}c_a^2\alpha_1^{1/2}.$$

4. Semi-flexible polymers

When polymers can no longer be regarded as rods, i.e. when the contour length is longer than the deflection length [6], we have to analyse the configurational statistics of a semi-flexible chain in a space-dependent nematic field in order to obtain formal expressions analogous to equation (1). Such an analysis is complicated even for constant nematic fields (cf. [7–9]). Here, we assess the elastic constants qualitatively by extending the scaling analysis of [6].

Firstly, a qualitative derivation of the elastic constants for rods is useful. If the director is forced to turn through a slight angle ε, the original, typically small angle θ_1, of rod 1 is slightly altered to θ_1'

$$\theta_1'^2 \simeq \theta_1^2 + \varepsilon^2 - 2\varepsilon\theta_1\cos\phi_1,$$

where the angle ϕ_1 is measured with respect to the plane of the two directors. Thus, the first order change in the gaussian distribution (cf. equation (12)) can be written as

$$\delta f \simeq (\alpha\theta_1\varepsilon\cos\phi_1)f,$$

so that the increment in excluded volume between two probe rods 1 and 2 is given by

$$\Delta B_2 \simeq L^2D\iint d\Omega_1\,d\Omega_2\,|\gamma|\,\delta f(\theta_1)\,\delta f(\theta_2),$$

$$\simeq \varepsilon^2L^2D\alpha^{1/2}, \tag{23}$$

(if the solution is nematic). The resulting increment in free energy density is

$$\frac{\Delta F}{V} \simeq kT\varrho^2\Delta B_2 \simeq (kTD^{-1})c_a^2\varepsilon^2\alpha^{1/2}L^{-2}. \tag{24}$$

When the deformation is a bend, we have

$$\varepsilon_3 \simeq L|\mathbf{n} \times \nabla \times \mathbf{n}| \tag{25}$$

otherwise the two test rods would not interact. For twist, we must have

$$\varepsilon_2 \simeq L\alpha^{-1/2}|\mathbf{n}.\nabla \times \mathbf{n}| \tag{26}$$

because the rods interact only when the typical distance perpendicular to both axes is of order γL. For splay, an analogous relation holds. The elastic constants derivable from the free energy density (cf. equation (24)) are in agreement with equations (15)–(17).

In [6], the deflection length λ was introduced for nematically confined polymers

$$\lambda = P\alpha^{-1}, \tag{27}$$

where P is the persistence length; for an extensive review, see [9]. Each chain can be thought of as a sequence of L/λ units. Hence, a chain will align on the average along some tortuously changing director field but only for length scales longer than λ. Clearly, we are dealing with a solution containing effectively $NL\lambda^{-1}$ rod-like units where N is the number of polymer molecules in solution. Hence, whenever $L \gg \lambda$, we can write

$$K_2 \simeq \varrho_\lambda^2 \lambda^4 D^2 \alpha^{-1/2},$$

$$\simeq \varrho_P^2 P^4 D^2 \alpha^{-5/2} \simeq c_{a,P}^{1/3}, \tag{28}$$

$$K_3 \simeq \alpha K_2 \simeq c_{a,P}. \tag{29}$$

The indices λ and P in ϱ and c_a refer to counting with the respective segments, i.e. $\varrho_l = NL/lV$ and $c_{a,l} = (\pi/4)l^2 D\varrho_l$ where l denotes either λ or P and V is the volume of the system. The relation $\alpha^{3/2} \simeq c_{a,P}$ [6] has also been employed.

The splay modulus deserves special attention. A tacit assumption when writing equation (23) is that the spatial density of macromolecules remains homogeneous after the director field has been altered. This assumption is envisaged to be reasonable for the bend and twist distortions but is untenable otherwise in view of the ideas of de Gennes [10] and Meyer [11]. Indeed, naive application of the reasoning behind equations (28) and (29) leads to the incorrect result $K_1 \simeq K_2 \simeq c_{a,P}^{1/3}$ whereas K_1 is certainly contour-length dependent [10, 11]. Our scaling arguments do not, however, influence Meyer's analysis of the distribution of chain ends under splay; slight fluctuations in chain shapes will not change figure 3 of [11]. We stress also that the dimensionless splay constant derived by Meyer [11]

$$K_1 = \tfrac{1}{4} c_{a,L} \tag{30}$$

is almost identical with equation (15) for rods, as it may be expected to be (Meyer's $d = (\varrho_L L)^{-1/2}$). De Gennes' result [10] disagrees with equations (15) and (24) confirming Meyer's criticism of it. The author hopes to complete a full statistical mechanical analysis of all three elastic constants for worm-like chains in the future.

5.   Concluding remarks

Let us stress the limitations of the calculations expounded in this analysis. Firstly, the second virial approximation must hold ($\alpha \ll (L/D)^2$, cf. [9]; for long worm-like chains, $\alpha \ll (P/D)^2$). The calculations for rods are useful only when $L \lesssim \tfrac{1}{2}\lambda$ ($= P/2\alpha$). In practice, extremely stiff biopolymers satisfy this condition [9]. The gaussian approximation itself should be viewed as a limiting law towards which other theories or numerical calculations ought to converge. Tedious preliminary work shows that, eventually, it will be possible to go beyond the gaussian approximation and formulate analytical theories very close to the numerical data.

At the present stage of experimental work any comparison of theory with experiments must be viewed as very tentative. Thus, it is doubtful whether tobacco mosaic virus is long enough to justify the use of the second virial approximation and it is certain that poly-γ-benzyl-L-glutamate is too short for the limit of very long contour lengths to be valid. Nevertheless, the ratios $K_3/K_2 = 43$ and $K_1/K_2 = 2\cdot5$ for tobacco

mosaic virus, from [12], and $K_3/K_2 = 13$ for poly-γ-benzyl-L-glutamate from [13] are not too far from the ratios given by equations (16), (17), (28) and (29)

$$K_3/K_2 = \frac{8\alpha}{7} = \frac{32c_a^2}{7\pi} \simeq 17; \quad K_1/K_2 = 3$$

and

$$K_3/K_2 \simeq \alpha \simeq 6 \cdot 5$$

respectively. These α values are taken from [9]. In a qualitative sense we can explain why partial flexibility lowers K_3/K_2; simply because the ordering parameter α decreases.

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Appendix
For convenience we quote several gaussian averages

$$\langle \gamma \theta_1^2 \rangle_0 = \tfrac{5}{2}\pi^{1/2}\alpha^{-3/2}, \quad \langle \gamma^3 \rangle_0 = 6\pi^{1/2}\alpha^{-3/2},$$

$$\langle \gamma^3 \theta_1^2 \rangle_0 = 21\pi^{1/2}\alpha^{-5/2}, \quad \langle \gamma \theta_1^2 \theta_2^2 \rangle_0 = \tfrac{23}{4}\pi^{1/2}\alpha^{-5/2},$$

$$\langle \gamma \theta_1^4 \rangle = \tfrac{47}{4}\pi^{1/2}\alpha^{-5/2},$$

$$\langle \gamma^3 \rangle_{12} = 3\left(\frac{\pi}{2}\right)^{1/2}\left(\frac{\alpha_1 + \alpha_2}{\alpha_1 \alpha_2}\right)^{3/2},$$

$$\langle \gamma(\theta_1^2 + \theta_2^2) \rangle_{12} = \left(\frac{\pi}{2}\right)^{1/2}\left[\frac{3\alpha_1^2 + 4\alpha_1\alpha_2 + 3\alpha_2^2}{\alpha_1^{3/2}\alpha_2^{3/2}(\alpha_1 + \alpha_2)^{1/2}}\right],$$

$$\langle \gamma^3(\theta_1^2 + \theta_2^2) \rangle_{12} = 3\left(\frac{\pi}{2}\right)^{1/2}\alpha_1^{-5/2}\alpha_2^{-5/2}(\alpha_1 + \alpha_2)^{1/2}(5\alpha_1^2 + 4\alpha_1\alpha_2 + 5\alpha_2^2),$$

$$\langle \gamma(\theta_1^2 + \theta_2^2)^2 \rangle_{12} = \left(\frac{\pi}{2}\right)^{1/2}\alpha_1^{-5/2}\alpha_2^{-5/2}(\alpha_1 + \alpha_2)^{1/2}$$

$$\times \left(15\alpha_1^2 + 4\alpha_1\alpha_2 + 15\alpha_2^2 + 2\alpha_1\alpha_2\left[\frac{\alpha_1^2 + \alpha_2^2}{(\alpha_1 + \alpha_2)^2}\right]\right).$$

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