

Nematic ordering in anisotropic elastomers: Effect of frozen anisotropy

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Abstract. Nematic ordering in *anisotropic non-Gaussian* elastomers is considered theoretically using mean field approximation. We focus on the effect of anisotropy during network cross-linking on the system elasticity and, in particular, on the so-called soft deformation mode. As the main result, we calculate the dependence of the elastomer free energy on the angle between the axis of “frozen” anisotropy and the nematic director. The dependence of the isotropic-nematic transition point on the orientational field acting on the monomers during the cross-linking process is also calculated.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.30.-v Liquid crystals

1 Introduction

Nematic polymer networks show remarkable elastic properties which have been extensively studied recently both theoretically [1–14] and experimentally [15–18]. One of the most striking features of these systems is the existence of soft deformation modes, *i.e.* certain shear deformations coupled with rotation of the nematic director that cost very low (or zero) energy [9–11]. As follows from simple symmetry arguments [19], these modes are absolutely soft (*i.e.* zero energy) for those elastomers that have been cross-linked entirely in the isotropic state. On the other hand, the softness is lost to semi-softness if crosslinking is performed in anisotropic state: in this case the initial anisotropy direction is frozen in the elastomer [11,12,17]. The free energy of the system increases when the director rotates on angle ω with respect to the axis of quenched anisotropy [11]:

$$F = F_i + F_a \sin^2 \omega \quad (1)$$

where F is the free energy density, and F_a characterizes the effect of the intrinsic network anisotropy.

The soft modes are closely related to the stripe domain pattern that has been observed in nematic elastomers under extension deformations perpendicular to the director [16,17]. The deformation is also semi-soft, and is characterized by a small threshold strain $\epsilon_1 \sim 0.02 \div 0.15$ [13,16,17]. Theoretically [11] the threshold is nearly proportional to the anisotropic modulus F_a .

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Theoretical studies of soft modes [11,13,14] show that $F_a \equiv 0$ for ideal elastic networks with identical Gaussian homopolymer strands (*i.e.* no quenched orientational memory): in this case all network strands are deformed in the same way and the elastomer can return to isotropic state after appropriate macroscopic deformation. Two models were proposed in order to explain the observed non-zero values of F_a and ϵ_1 . One model [11,13] takes into account that polymer sub-chains are sometimes random copolymers [18], rather than homopolymers. The anisotropic modulus is proportional to the degree of compositional disorder in this case. The other model [14] assumes bulky rod-like cross-linkers which also show orientational order in anisotropic state.

It is important however that a finite threshold/modulus for soft deformations has been observed for all systems studied (provided these were cross-linked in anisotropic state). This suggests a possibly universal mechanism for this effect. The aim of the present paper is to analyze the simplest model of nematic elastomer with point-like cross-links and compositionally homogeneous strands. However we take into account that the chain statistics are not exactly Gaussian as the chains are mesogenic and hence are semiflexible (note that truly Gaussian chains must be infinitely flexible, *i.e.* unable to form nematic order). We consider the simplest case of freely-jointed rod model for semiflexible sub-chains. We show that the hardening of the soft deformations can be explained by non-linear elasticity of individual sub-chains which is due to the fact that the chains are semi-rigid.

The theoretical problem and the model are set up in the next section. Three subsequent sections are devoted to the details of calculation of the anisotropic part of the free energy, F_a . We consider both the angular dependence

of the anisotropic free energy and its dependence on both effective orientational fields during cross-linking and in the final state. The results are discussed and compared with predictions of other theories in Section 8.

2 The model

Let us consider a melt (or a concentrated solution) of mesogenic polymer chains. Each chain is modeled by a freely-jointed sequence of rods (segments) of fixed length b . This is the simplest model for semiflexible chains which is adequate for *e.g.* side-chain mesogenic polymers [20]. The segment orientations are not correlated *a priori*.

An isotropic Gaussian network can be easily obtained by cross-linking the polymer system (polymer statistics are nearly Gaussian due to Flory theorem) into the elastomer sample. Detailed theoretical investigation of nematic ordering and elastic effects in these *isotropically* formed polymer networks consisting of mesogenic units has been independently conducted at the end of the 1980s by two groups [3,4] and [5,6].

In order to obtain an anisotropic network one has to conduct a more complicated procedure: a system of precursor polymer chains must be orientationally ordered during cross-linking. An orientational order may be induced *e.g.* by (1) application of external magnetic or electric field if the monomers are characterized by anisotropic polarizability; (2) application of external mechanical stress to the system; (3) decreasing the temperature below the clearing point of the precursor system, *i.e.* cross-linking in nematic state (in the latter case the order is due to nematic molecular field). The first way is inefficient as very high fields are normally required. The third way is the most efficient one. The last two ways has been actually realized experimentally [16,17].

In all cases the ordering field can be described by a quadrupole molecular potential

$$U_{ext}(\mathbf{n}) = -U_0(\mathbf{nu})^2 \quad (2)$$

acting on each polymer segment, where U_0 is the field amplitude, \mathbf{n} is unit vector along the segment, and \mathbf{u} is unit vector defining the field orientation; $U_0 > 0$ corresponds to orientational ordering along the \mathbf{u} axis. Note that in case (3) U_{ext} is actually the Maier-Saupe nematic molecular field [21–23]. The probability distribution of the subchain end-to-end vector,

$$\mathbf{R} = \sum_{i=1}^N b\mathbf{n}_i$$

where N is the number of segments per sub-chain, must depend on the orientational field U_0 . We will assume that the probability distribution functions of precursor polymer chains (prior cross-linking) and those of network strands are the same¹.

¹ Recently Rubinstein and Panyukov [24] showed that cross-linking process could affect the probability distribution of \mathbf{R} .

We assume that the orientational field is switched off after cross-linking, and the system relaxes to an equilibrium state under null orientational field. It is convenient to consider this state as a reference (*i.e.* formally undeformed) state², although it is not necessary to realize it in practice (in particular, the system might be nematically ordered both during cross-linking and afterwards, see below). Thus, we distinguish the *formation* state, where the network is prepared (cross-linked) in presence of nematic field, from the *reference* state, which is attained after (1) crosslinking, (2) turning off nematic interactions and (3) relaxation with no fields.

It is important that the subchain statistics (both with and without the field) are not exactly Gaussian: the Gaussian statistics are recovered in the limit $N \rightarrow \infty$, which is not assumed here (*i.e.* N is finite)³. Therefore, the subchain conformation does not have to be exactly isotropic even in the reference state: the network ‘remembers’ the direction of the initial orientational field U_{ext} . The corresponding memory effects are considered below.

Now let us allow for mesogenic interactions between polymer segments after cross-linking, and assume a nematic order of network strands. We employ the Maier-Saupe mean-field model [21–23] for nematic interactions, which are described in terms of molecular field $U_{nem}(\mathbf{n})$ acting on each segment:

$$U_{nem}(\mathbf{n}) = -U'_0\eta P_2(\mathbf{nd}) = -T\beta(\mathbf{nd})^2 + \frac{1}{3}T\beta \quad (3)$$

where $\beta = \frac{3}{2}\frac{U'_0}{T}\eta$, U'_0 is the Maier-Saupe nematic interaction constant, $U'_0 > 0$, and \mathbf{d} , the director. The order parameter η is the mean over all segments of the second Legendre polynomial $P_2(\mathbf{nd})$:

$$\eta = \left\langle \frac{3}{2}(\mathbf{nd})^2 - \frac{1}{2} \right\rangle. \quad (4)$$

As we show below, the network anisotropy in the reference state is *weak* (of the order of $1/N$). Therefore the nematic director \mathbf{d} can be oriented *arbitrarily* with respect to the elastomer anisotropy axis \mathbf{u} . Then the free energy of the system depends on the angle ω between the director \mathbf{d} and the \mathbf{u} -axis. This dependence is calculated in the next sections.

A (possibly formal) transition of the elastomer from the reference state to the nematic state is always supplemented by its macroscopic mechanical deformation (elongation along \mathbf{d}), as any subchain tends to adopt a prolate shape with its ends constrained by junctions. Therefore, when the angle ω between \mathbf{u} and \mathbf{d} changes, the shape

This effect is neglected here: it is small if the network functionality is high, and even in general case it does not affect qualitatively the results of the present study.

² Note that the total orientational field including molecular field must be null in the reference state, *i.e.* mesogenic interactions are switched off in this state.

³ Below we show that within our model the terms of the order of $1/N$ and higher are important for the main effects considered here, and thus, must be taken into account.

of the elastomer must also change, yielding semi-soft deformation modes discussed in the introduction.

In general case both the deformation and the molecular orientational field in the final state are slightly non-uniaxial. It is possible to show however that all effects of biaxiality are negligible with respect to the anisotropic free energy considered in the present paper.

We also employ the so-called affine model of network deformation, *i.e.* assume that end-to-end vectors of all subchains change during deformation according to the same law: $\mathbf{R} \rightarrow \mathbf{R}' = \hat{\lambda}\mathbf{R}$, where $\hat{\lambda}$ is the macroscopic strain tensor. The physics of this assumption is that we neglect fluctuations of junction points, so that they are deformed in the same way as the whole sample, which is the case if the network functionality is high. However, even in general case the affine deformation assumption does not affect the main qualitative results of the present paper, as discussed in Section 8.

We also assume that the system is incompressible: $\lambda_x\lambda_y\lambda_z = 1$, where $\lambda_{x,y,z}$ are the principal values of the strain tensor $\hat{\lambda}$.

3 Probability distributions under orientational field

The probability distribution of the end-to-end vector \mathbf{R} of a Gaussian strand under external orientational field U_{ext} , equation (2), is

$$P_0^G(\mathbf{R}) = \left(\frac{C_0}{\pi}\right)^{3/2} \frac{1}{K_{\parallel}^{1/2}K_{\perp}} \exp\left(-\frac{C_0R_{\parallel}^2}{K_{\parallel}} - \frac{C_0R_{\perp}^2}{K_{\perp}}\right). \quad (5)$$

where $C_0 = 3/(2Nb^2)$, \mathbf{R}_{\parallel} is the component of \mathbf{R} parallel to \mathbf{u} , \mathbf{R}_{\perp} is the perpendicular component, $K_{\parallel}(\alpha) \equiv 3\langle\cos^2\theta\rangle$, $K_{\perp}(\alpha) \equiv \frac{3}{2}\langle\sin^2\theta\rangle$, θ is the angle between \mathbf{n} and \mathbf{u} , $\alpha \equiv U_0/T$ is the reduced field magnitude (the Boltzmann constant is set to be 1 here, $k_B = 1$), and the following averaging procedure is used here and below:

$$\langle f(\cos\theta) \rangle(\alpha) = \frac{\int_0^1 e^{\alpha t^2} f(t) dt}{\int_0^1 e^{\alpha t^2} dt}. \quad (6)$$

Note that $K_x = K_{\perp}^{1/2}$, $K_y = K_{\perp}^{1/2}$ and $K_z = K_{\parallel}^{1/2}$ are the diagonal components of the shape deformation tensor for the subchains in the formation state with respect to their unperturbed isotropic Gaussian conformation (note that the deformation tensor is diagonal). Then $K^{3/2} \equiv K_x K_y K_z = K_{\parallel}^{1/2} K_{\perp}$ defines the change of subchain volume, *i.e.* $K^{3/2}(\alpha)$ is the swelling factor. The distribution, equation (5), has been used in all previous studies [3–6].

The distribution of end-to-end vector of a freely-jointed chain is close to Gaussian, equation (5), however,

up to corrections of order $1/N$ [25]. Let us calculate these corrections.

The *a priori* orientational distribution of a subchain segment \mathbf{n} in the external field is proportional to the Boltzmann factor $\exp(-U_{ext}(\mathbf{n})/T)$. Therefore the probability distribution for the end-to-end vector is [25]:

$$P_0(\mathbf{R}) = \frac{1}{c_{ext}^N} \int \delta\left(\mathbf{R} - \sum_{j=1}^N b\mathbf{n}_j\right) \times \exp\left(-\sum_{j=1}^N \frac{U_{ext}(\mathbf{n}_j)}{T}\right) \prod_{j=1}^N d^2\mathbf{n}_j \quad (7)$$

with

$$c_{ext} = \int \exp\left(-\frac{U_{ext}(\mathbf{n})}{T}\right) d^2\mathbf{n}. \quad (8)$$

For the quadrupole field $U_{ext}(\mathbf{n})$ (Eq. (2)) this expression can not be evaluated analytically in the general case. Let us expand the distribution function P_0 as a series in $1/N$ assuming that $N \gg 1$. The second-order result is:

$$\begin{aligned} P_0(\mathbf{R}; \alpha, \mathbf{u}) &= \left(\frac{C_0}{\pi}\right)^{3/2} \frac{1}{K_{\parallel}^{1/2}K_{\perp}} \\ &\times \exp\left(-\frac{C_0R_{\parallel}^2}{K_{\parallel}} - \frac{C_0R_{\perp}^2}{K_{\perp}}\right) \\ &\left\{ 1 - \frac{1}{5N} \left[L_2^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) (5 - 3C_4) \right. \right. \\ &+ L_2^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) (5 - 3S_4) \\ &+ L_1^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) L_1^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) (5 - 3G_{22}) \left. \right] \\ &- \frac{1}{35N^2} \left[L_3^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) (9C_6 - 63C_4 + 70) \right. \\ &+ L_3^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) (9S_6 - 63S_4 + 70) \\ &+ L_2^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) L_1^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) (9G_{42} - 21C_4 - 42G_{22} + 70) \\ &+ L_1^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) L_2^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) (9G_{24} - 21S_4 - 42G_{22} + 70) \left. \right] \\ &+ \frac{1}{25N^2} \left[L_4^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) 3(5 - 3C_4)^2 \right. \\ &+ L_4^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) 3(5 - 3S_4)^2 \\ &+ L_2^{-1/2} \left(\frac{C_0R_{\parallel}^2}{K_{\parallel}}\right) L_2^0 \left(\frac{C_0R_{\perp}^2}{K_{\perp}}\right) (2(5 - 3G_{22})^2 \end{aligned}$$

$$\begin{aligned}
& + (5 - 3C_4)(5 - 3S_4) \\
& + L_3^{-1/2} \left(\frac{C_0 R_{\parallel}^2}{K_{\parallel}} \right) L_1^0 \left(\frac{C_0 R_{\perp}^2}{K_{\perp}} \right) 3(5 - 3C_4)(5 - 3G_{22}) \\
& + L_1^{-1/2} \left(\frac{C_0 R_{\parallel}^2}{K_{\parallel}} \right) L_3^0 \left(\frac{C_0 R_{\perp}^2}{K_{\perp}} \right) 3(5 - 3S_4)(5 - 3G_{22}) \\
& + O \left(\frac{1}{N^3} \right) \}
\end{aligned} \tag{9}$$

where

$$\begin{aligned}
C_4(\alpha) &\equiv \frac{5}{9} \frac{\langle \cos^4 \theta \rangle}{\langle \cos^2 \theta \rangle^2} \\
S_4(\alpha) &\equiv \frac{5}{6} \frac{\langle \sin^4 \theta \rangle}{\langle \sin^2 \theta \rangle^2} \\
G_{22}(\alpha) &\equiv \frac{5}{3} \frac{\langle \cos^2 \theta \sin^2 \theta \rangle}{\langle \cos^2 \theta \rangle \langle \sin^2 \theta \rangle} \\
C_6(\alpha) &\equiv \frac{7}{27} \frac{\langle \cos^6 \theta \rangle}{\langle \cos^2 \theta \rangle^3} \\
G_{42}(\alpha) &\equiv \frac{35}{27} \frac{\langle \cos^4 \theta \sin^2 \theta \rangle}{\langle \cos^2 \theta \rangle^2 \langle \sin^2 \theta \rangle} \\
S_6(\alpha) &\equiv \frac{35}{54} \frac{\langle \sin^6 \theta \rangle}{\langle \sin^2 \theta \rangle^3} \\
G_{24}(\alpha) &\equiv \frac{35}{18} \frac{\langle \cos^2 \theta \sin^4 \theta \rangle}{\langle \cos^2 \theta \rangle \langle \sin^2 \theta \rangle^2}
\end{aligned}$$

(the averaging procedure is the same, Eq. (6)) and $L_n^m(x)$ are the generalized Laguerre polynomials⁴. The numerical coefficients in K_{\parallel} , K_{\perp} , C_i , S_j , G_{ij} are chosen so that these functions are equal to 1 for $\alpha = 0$.

As we discussed earlier, we assume that the probability distribution does not change during cross-linking, so in the *formation* state it is given by the same expression (9). However the distribution does change after the orientational field is switched off: the system relaxes to the *reference* state. This relaxation process is supplemented by a macroscopic uniaxial deformation of the sample $\hat{\lambda}_0^{-1}$,

⁴ We use the standard definition of $L_n^m(x)$:

$$L_n^m(x) = \frac{1}{n!} x^{-m} e^x \frac{d^n}{dx^n} [x^{m+n} e^{-x}]$$

which leads to the following first few cases:

$$L_0^0(x) = L_0^{-1/2}(x) = 1 \quad L_1^0(x) = -x + 1 \quad L_1^{-1/2}(x) = -x + \frac{1}{2}$$

$$L_2^0(x) = \frac{1}{2} [x^2 - 4x + 2] \quad L_2^{-1/2}(x) = \frac{1}{2} \left[x^2 - 3x + \frac{3}{4} \right]$$

$$L_3^0(x) = \frac{1}{6} [-x^3 + 9x^2 - 18x + 6] \quad \text{etc.}$$

where

$$\hat{\lambda}_0 = \begin{pmatrix} \frac{1}{\sqrt{\lambda_0}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda_0}} & 0 \\ 0 & 0 & \lambda_0 \end{pmatrix}$$

and $1/\lambda_0$ is the strain value along the direction \mathbf{u} . Minimization of the free energy per unit volume $F = -T n_s \int \ln P_0(\mathbf{R}; 0, \mathbf{u}) P_0(\hat{\lambda}_0 \mathbf{R}; \alpha, \mathbf{u}) d^3 \mathbf{R}$ (where n_s is the number density of subchains) with respect to λ_0 leads to the following strain:

$$\begin{aligned}
\lambda_0(\alpha) &= \left(\frac{K_{\parallel}(\alpha)}{K_{\perp}(\alpha)} \right)^{1/3} \left\{ 1 - \frac{K(\alpha)}{25N^2} [4S_4(\alpha) - 3C_4(\alpha) \right. \\
&\quad \left. - G_{22}(\alpha)] + O \left(\frac{1}{N^3} \right) \right\}
\end{aligned} \tag{10}$$

where

$$K(\alpha) \equiv K_{\parallel}^{1/3}(\alpha) K_{\perp}^{2/3}(\alpha) = (3 \langle \cos^2 \theta \rangle)^{1/3} \left(\frac{3}{2} \langle \sin^2 \theta \rangle \right)^{2/3}. \tag{11}$$

Thus, the probability distribution function in the *reference* state is $P(\mathbf{R}) = P_0(\hat{\lambda}_0 \mathbf{R})$, *i.e.*

$$\begin{aligned}
P(\mathbf{R}; \alpha, \mathbf{u}) &= \left(\frac{C_0}{\pi K(\alpha)} \right)^{3/2} \exp \left(-\frac{C_0 R^2}{K(\alpha)} \right) \\
&\times \left\{ 1 - \frac{1}{5N} [\mathcal{P}] - \frac{1}{35N^2} [\mathcal{P}] + \frac{1}{25N^2} [\mathcal{P}] + \frac{1}{25N^2} \right. \\
&\times \left. \left[C_0 (2R_{\parallel}^2 - R_{\perp}^2) (4S_4 - 3C_4 - G_{22}) \right] + O \left(\frac{1}{N^3} \right) \right\}.
\end{aligned} \tag{12}$$

with $\mathcal{P} =$ the same terms as in P_0 but where $K(\alpha)$ substitutes for $K_{\parallel}(\alpha)$ and $K_{\perp}(\alpha)$.

Note that in the main approximation the chain statistics in the reference state are both Gaussian and isotropic (see the main exponential factor in Eq. (12)). Consideration of Gaussian chains yields no dependence of $P(\mathbf{R})$ on the field direction \mathbf{u} . However the $O(1/N)$ corrections are indeed anisotropic. It is these corrections that determine the ‘memory’ of the elastomer about its orientation during cross-linking.

Note also that the chains in the reference state are shrunk with respect to their unperturbed Gaussian conformation. The dependence $K(\alpha)$ of the swelling factor on the orientational field is shown in Figure 1 (although the genuine swelling factor is $K^{3/2}(\alpha)$, it is more convenient for our purposes to plot $K(\alpha)$ instead since it enters all final results).

4 Free energy

Now let us switch on the orientational (nematic) interactions between segments. The interactions are assumed

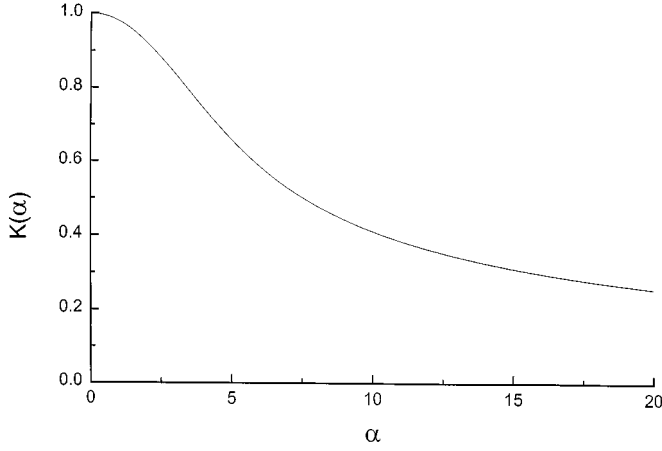


Fig. 1. The swelling factor $K(\alpha)$ as a function of the external field α (see Eq. (11)).

to be strong enough to induce nematic order in the system. Then each segment is influenced by mean orientational field $U_{nem}(\mathbf{n})$, equation (3), created by all the other segments. Partition function of a strand with a given end-to-end vector \mathbf{R} in this field is:

$$Z(\mathbf{R}) = \int \delta\left(\mathbf{R} - \sum_{j=1}^N b\mathbf{n}_j\right) \exp\left(-\sum_{j=1}^N \frac{U_{nem}(\mathbf{n}_j)}{T}\right) \times \prod_{j=1}^N \frac{d^2\mathbf{n}_j}{4\pi} = \left(\frac{c_{nem}}{4\pi}\right)^N P_0(\mathbf{R}; \beta, \mathbf{d}) \quad (13)$$

where the function $P_0(\mathbf{R}; \beta, \mathbf{d})$ is formally defined in equation (9),

$$c_{nem} = \int \exp\left(-\frac{U_{nem}(\mathbf{n})}{T}\right) d^2\mathbf{n} \quad (14)$$

and $\beta = \frac{3}{2} \frac{U'_0}{T} \eta$. Note that equation (13) is similar to equation (7) where $U_{ext}(\mathbf{n})$ is substituted by $U_{nem}(\mathbf{n})$.

As we discussed in the second section, nematic ordering (at equilibrium under null external stress) is supplemented by a macroscopic deformation of the sample with (yet unknown) strain $\hat{\lambda}$,

$$\hat{\lambda} = \begin{pmatrix} \frac{1}{\sqrt{\lambda}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

and λ is the strain value along the director \mathbf{d} (*i.e.* we assume here that z axis is parallel to \mathbf{d}) measured from the *reference* state. The value $\lambda_{\perp} = 1/\sqrt{\lambda}$ is given by the incompressibility condition $\lambda_{\perp}^2 \lambda_{\parallel} = 1$, where $\lambda_{\parallel} = \lambda$. Therefore the distribution of the end-to-end vectors in the nematic state is

$$P_{nem}(\mathbf{R}) = P(\hat{\lambda}^{-1}\mathbf{R}). \quad (15)$$

Following the usual mean field recipe, we obtain the free energy per unit volume of elastomer averaging the free

energy of a subchain over all \mathbf{R} (distributed according to Eq. (15)), and multiplying the result by the number density of strands n_s :

$$F = n_s \left\{ -T \overline{\ln Z(\mathbf{R})} - \frac{1}{2} \overline{\sum_{i=1}^N \langle U_{nem}(\mathbf{n}_i) \rangle} \right\} \quad (16)$$

where averaging over \mathbf{R} is defined as

$$\overline{f(\mathbf{R})} = \int f(\hat{\lambda}\mathbf{R}) P(\mathbf{R}; \alpha, \mathbf{u}) d^3\mathbf{R} \quad (17)$$

and $\sum_{i=1}^N \langle U_{nem}(\mathbf{n}_i) \rangle = -\frac{\partial}{\partial(1/T)} \ln Z(\mathbf{R})|_{U'_0}$ is the average potential energy of a subchain with a given end-to-end vector \mathbf{R} in the field U_{nem} which is formally treated as an external field (note that the formerly used averaging procedure, equation (6), is not relevant here).

Let us explain again why we subtract a half of the average *potential* energy of a subchain (in the field U_{nem} , Eq. (3)) from $-T \overline{\ln Z(\mathbf{R})}$ (although this procedure is quite standard [26]). The idea is simple: Assuming that units do not interact directly, one can write the free energy of the system of subchains in the field U_{nem} (formally treated as an external field) as $-T \overline{\ln Z(\mathbf{R})}$, where the partition function, equation (13), takes into account both the entropic part and the potential energy of the segments in the field. Recalling that the potential $U_{nem}(\mathbf{n})$ is actually a molecular field created by all the other units, we note that the interaction energy of any two segments i and j is counted twice in $-T \overline{\ln Z(\mathbf{R})}$: for the first time as the energy of segment i in the potential created by segment j , and for the second time as the energy of the particle j in the potential created by segment i . So, in order to avoid double counting of the interaction energy, one should subtract a half of the formal potential energy from $-T \overline{\ln Z(\mathbf{R})}$.

There is no need to conduct any special calculation in order to obtain the second term in the free energy, equation (16). Indeed,

$$\overline{\sum_{i=1}^N \langle U_{nem}(\mathbf{n}_i) \rangle} = -N U'_0 \eta \overline{\langle P_2(\mathbf{nd}) \rangle} = -N U'_0 \eta^2$$

where we take into account that $\eta = \overline{\langle P_2(\mathbf{nd}) \rangle}$. The last equation can be rewritten as

$$\frac{\overline{\sum_{i=1}^N \langle U_{nem}(\mathbf{n}_i) \rangle}}{T} = -N \frac{4}{9} \frac{\beta^2}{\gamma} \quad (18)$$

where $\gamma = U'_0/T$ and $\beta = \frac{3}{2} \eta \gamma$.

Thus, making use of equations (13, 16–18), the free energy of the elastomer can be written as

$$\begin{aligned} \frac{F}{T n_s} &= -N \ln \frac{c_{nem}}{4\pi} - \int \ln P_0(\hat{\lambda}\mathbf{R}; \beta, \mathbf{d}) P(\mathbf{R}; \alpha, \mathbf{u}) d^3\mathbf{R} \\ &\quad - \frac{1}{2} \left(-N \frac{4}{9} \frac{\beta^2}{\gamma} \right) \\ &= N \left\{ \frac{2}{9} \frac{\beta^2}{\gamma} + \frac{1}{3} \beta - \ln \int_0^1 e^{\beta t^2} dt \right\} + I(\alpha, \beta, \lambda, \omega) \end{aligned} \quad (19)$$

where $I(\alpha, \beta, \lambda, \omega) \equiv -\int \ln P_0(\hat{\lambda}\mathbf{R}; \beta, \mathbf{d})P(\mathbf{R}; \alpha, \mathbf{u}) d^3\mathbf{R}$ and ω is the angle between the director \mathbf{d} and the frozen anisotropy direction \mathbf{u} .

The free energy of the system is calculated using equations (19, 9, 13) in the Appendix. The result is

$$\begin{aligned} \frac{F}{Tn_s} &= NA(\beta, \gamma) + B(\alpha, \beta, \lambda) \\ &+ \frac{1}{N} \left(\text{terms not depending on } \omega \right) \\ &+ \frac{1}{N^2} C(\alpha, \beta, \lambda, \omega) + \frac{1}{N^2} \left(\text{terms not depending on } \omega \right) \\ &+ O\left(\frac{1}{N^3}\right) \end{aligned} \quad (20)$$

where

$$\begin{aligned} A(\beta, \gamma) &= \frac{2}{9} \frac{\beta^2}{\gamma} + \frac{1}{3} \beta - \ln \int_0^1 e^{\beta t^2} dt, \\ B(\alpha, \beta, \lambda) &= \text{const.} + \frac{3}{2} \ln K(\beta) + K(\alpha) \\ &\quad \times \left(\frac{\lambda^2}{2} \frac{1}{K_{\parallel}(\beta)} + \frac{1}{\lambda} \frac{1}{K_{\perp}(\beta)} \right), \\ C(\alpha, \beta, \lambda, \omega) &= \frac{1}{25} P_2(\cos \omega) f_{ext}^{(2)}(\alpha) \\ &\quad \times \left(\lambda^2 \frac{1}{K_{\parallel}(\beta)} - \frac{1}{\lambda} \frac{1}{K_{\perp}(\beta)} \right) \\ &\quad - \frac{1}{350} P_2(\cos \omega) f_{ext}^{(2)}(\alpha) \\ &\quad \times \left(3\lambda^4 X_C(\beta) - \frac{4}{\lambda^2} X_S(\beta) + \lambda X_G(\beta) \right) \\ &\quad - \frac{9}{875} P_4(\cos \omega) f_{ext}^{(4)}(\alpha) \\ &\quad \times \left(\lambda^4 X_C(\beta) + \frac{1}{\lambda^2} X_S(\beta) - 2\lambda X_G(\beta) \right) \end{aligned}$$

and the following functions are used in $C(\alpha, \beta, \lambda, \omega)$:

$$\begin{aligned} f_{ext}^{(2)}(\alpha) &= K^2(\alpha) (4S_4(\alpha) - 3C_4(\alpha) - G_{22}(\alpha)) \\ f_{ext}^{(4)}(\alpha) &= K^2(\alpha) (2G_{22}(\alpha) - C_4(\alpha) - S_4(\alpha)) \\ X_C(\beta) &= \frac{5 - 3C_4(\beta)}{K_{\parallel}^2(\beta)} \\ X_S(\beta) &= \frac{5 - 3S_4(\beta)}{K_{\perp}^2(\beta)} \\ X_G(\beta) &= \frac{5 - 3G_{22}(\beta)}{K_{\parallel}(\beta)K_{\perp}(\beta)} \end{aligned}$$

$P_m(x)$, the Legendre polynomials.

The main term in the r.h.s. of equation (20), $NA(\beta, \gamma)$, corresponds to the usual Maier-Saupe free energy of uncross-linked system of freely-jointed chains (per one chain, hence the factor N).

Combination of the first two terms $NA(\beta, \gamma) + B((\alpha = 0), \beta, \lambda)$ represents the result of Abramchuk and

Khokhlov [3,4]. The second term corresponds to the elastic response of a whole subchain and hence it does not depend on N . Both terms do not depend on the orientations \mathbf{u} and \mathbf{d} (on the angle ω). The next term, representing an $O(1/N)$ correction due to non-Gaussian elasticity of individual sub-chains, also does not depend on ω . The angular (ω -) dependence of the free energy shows only in the $O(1/N^2)$ order. The corresponding (fourth) term is a combination of the second and the fourth Legendre polynomials (F depends on even powers of $\cos \omega$ only since the directions \mathbf{u} and $-\mathbf{u}$, \mathbf{d} and $-\mathbf{d}$ are equivalent, so that the physical quantities must be invariant with respect to the transformation $\omega \leftrightarrow (\pi - \omega)$, *i.e.* $\cos \omega \leftrightarrow -\cos \omega$).

Thus, we have obtained the free energy as a function of α , β , λ , and ω . The parameters β (the reduced amplitude of the molecular orientation field) and λ (equilibrium elongation of the elastomer in the \mathbf{d} direction) are not fixed, but rather should be obtained self-consistently. The corresponding procedure is considered in the next section.

5 Minimization of the free energy

Obviously the free energy should be minimized with respect to the deformation λ . The situation with respect to the molecular field parameter β is more subtle, as β is a formal parameter, rather than a function of the system macroscopic state. The corresponding self-consistency equation is

$$\beta = \frac{3}{2} \gamma \eta,$$

where $\eta = \eta(\beta)$ is the orientational order parameter induced by the field β . Using equations (13, 16, 18) it is easy to show that this condition is equivalent to $\frac{\partial F}{\partial \beta} = 0$, where F is defined in equation (20).

Thus the two unknown parameters are defined by equations

$$\frac{\partial F}{\partial \beta} = 0 \quad (21)$$

$$\frac{\partial F}{\partial \lambda} = 0. \quad (22)$$

These equations might seem to mean that the equilibrium state corresponds to the minimum of the free energy, equation (20), with respect to both parameters, λ and β . This is not the case, however: the physical state of the system corresponds to a saddle point (a minimum along λ coordinate, and a maximum along β coordinate).

Equations (20–22) define the free energy as a function of external parameters α , ω (and also γ which is not shown explicitly):

$$F(\alpha, \omega) = F_i(\alpha) + F_a(\alpha, \omega)$$

where $F_i(\alpha)$ is the ‘isotropic’ part of the free energy which does not depend on ω . Obviously the anisotropic term,

$F_a(\alpha, \omega)$, originates from the fourth term in the r.h.s. of equation (20). Treating $1/N$ as a small parameter, and employing the theorem on small increments [28], we get in the main approximation

$$\frac{F_a(\alpha, \omega)}{Tn_s} = \frac{1}{N^2} C(\alpha, \beta_0, \lambda_1, \omega) \quad (23)$$

where β_0 and λ_1 are independent of ω as they are determined by the saddle point of the main ‘isotropic’ part of free energy, equation (20), *i.e.* without the fourth term in the r.h.s. In fact, it is enough to get β_0 and λ_1 in the main (zero’s) order in $1/N$, *i.e.* in the limit $N \rightarrow \infty$. Thus equations (21, 22) could be simplified as

$$\frac{\partial}{\partial \beta} A(\beta_0, \gamma) = 0 \quad (24)$$

$$\frac{\partial}{\partial \lambda} B(\alpha, \beta_0, \lambda_1) = 0. \quad (25)$$

The first equation is the same as in the standard Maier-Saupe theory [21–23]: in the limit $N \rightarrow \infty$ the network structure does not affect nematic ordering at all. This equation is known to be analytically unsolvable, so it was solved numerically. Generally, equation (24) has two solutions: the first is trivial $\beta_0 = 0$ (it corresponds to the isotropic phase) and the second $\beta_0 = \beta_0(\gamma)$ describes the nematic phase we are interested in.

The second equation (25) yields λ_1 :

$$\lambda_1(\gamma) = \left(\frac{K_{\parallel}(\beta_0(\gamma))}{K_{\perp}(\beta_0(\gamma))} \right)^{1/3} \quad (26)$$

(compare with $\lambda_0(\alpha)$, Eq. (10)). Note that λ_1 depends neither on α nor on ω . Equation (26) defines the temperature dependence of the spontaneous deformation of the sample. This dependence numerically coincides with the expression obtained in the reference [4] (for the case of not stressed networks) although the latter was calculated by somewhat different method and has a distinct final form.

Thus the anisotropic part of the free energy, F_a , is defined by equation (23) with $\beta_0(\gamma)$ and $\lambda_1(\gamma)$ defined by equations (24, 26). After some algebra we obtain F_a as a function of the angle ω , the external field $\alpha = U_0/T$ and the interaction parameter $\gamma = U'_0/T$:

$$\begin{aligned} \frac{F_a}{Tn_s} = & -\frac{3}{1750N^2} \left\{ 5P_2(\cos \omega) f_{ext}^{(2)}(\alpha) f_{nem}^{(2)}(\gamma) \right. \\ & \left. + 18P_4(\cos \omega) f_{ext}^{(4)}(\alpha) f_{nem}^{(4)}(\gamma) \right\} \\ & + O\left(\frac{1}{N^3}\right) \end{aligned} \quad (27)$$

where

$$\begin{aligned} f_{ext}^{(2)}(\alpha) &= K^2(\alpha) (4S_4(\alpha) - 3C_4(\alpha) - G_{22}(\alpha)) \\ f_{ext}^{(4)}(\alpha) &= K^2(\alpha) (2G_{22}(\alpha) - C_4(\alpha) - S_4(\alpha)) \\ f_{nem}^{(2)}(\gamma) &= K^{-2}(\beta_0) (4S_4(\beta_0) - 3C_4(\beta_0) - G_{22}(\beta_0)) \\ f_{nem}^{(4)}(\gamma) &= K^{-2}(\beta_0) (2G_{22}(\beta_0) - C_4(\beta_0) - S_4(\beta_0)) \end{aligned}$$

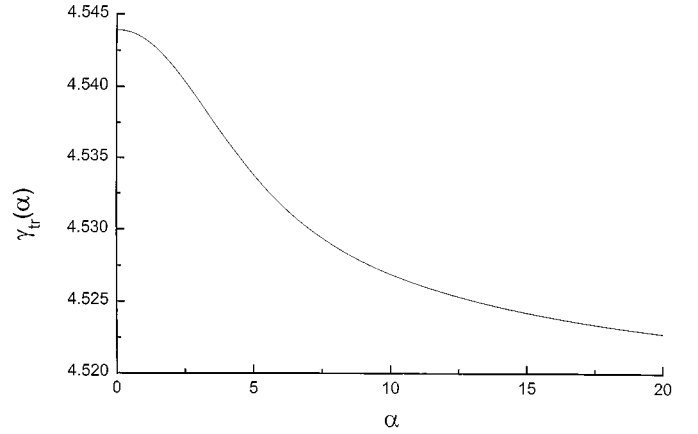


Fig. 2. Dependence of the nematic-isotropic transition point on the external field $\gamma_{tr}(\alpha)$ for the subchain length $N = 100$.

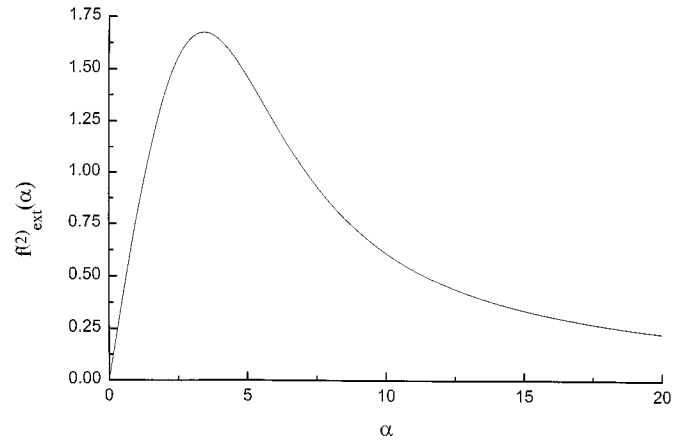


Fig. 3. The factor $f_{ext}^{(2)}(\alpha)$ versus α (Eq. (27)).

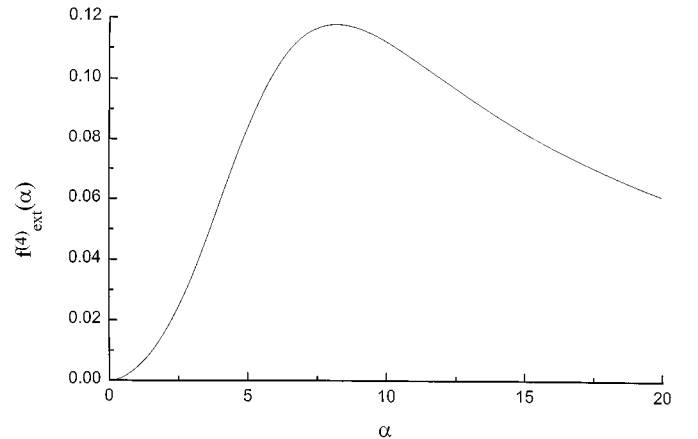


Fig. 4. The factor $f_{ext}^{(4)}(\alpha)$ versus α (Eq. (27)).

$\beta_0 = \beta_0(\gamma)$, and the function $K(\beta)$ is defined in equation (11): $K(\beta) = K_{\parallel}^{1/3}(\beta) K_{\perp}^{2/3}(\beta)$.

Dependencies $f_{ext}^{(2)}(\alpha)$, $f_{ext}^{(4)}(\alpha)$, $f_{nem}^{(2)}(\gamma)$, $f_{nem}^{(4)}(\gamma)$ have been calculated numerically and are presented in Figures 3–6. The maximum of the function $f_{ext}^{(2)}(\alpha)$

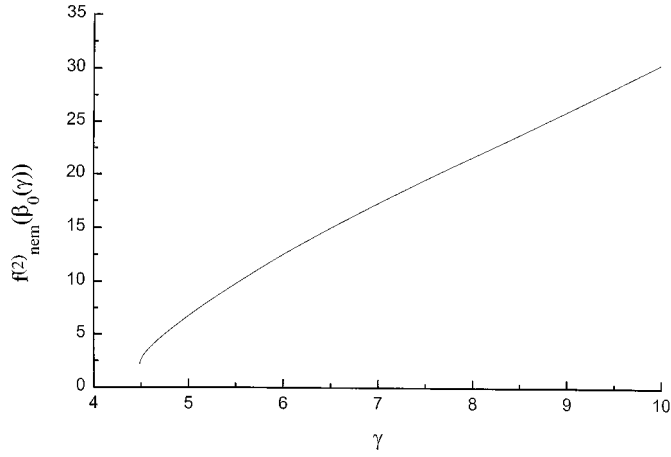


Fig. 5. The factor $f_{nem}^{(2)}(\gamma)$ versus Maier-Saupe interaction parameter γ (Eq. (27)).

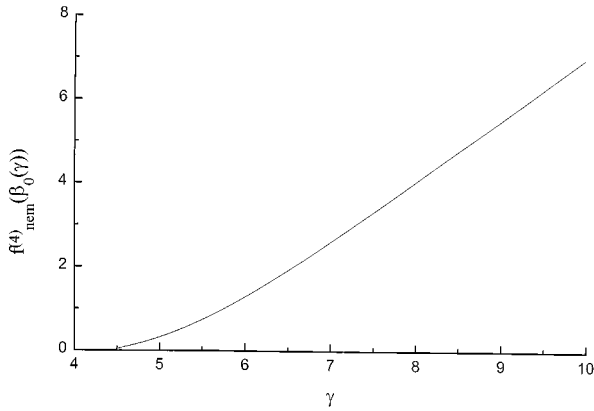


Fig. 6. The factor $f_{nem}^{(4)}(\gamma)$ versus γ (Eq. (27)).

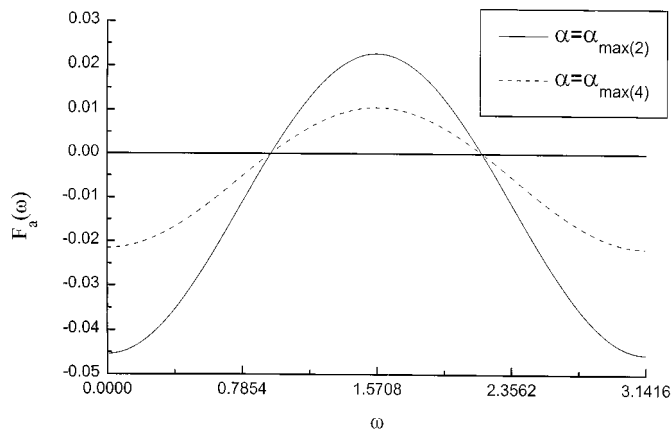


Fig. 7. Typical dependencies $F_a(\omega)$ (in units of Tn_s/N^2). The plots are presented for $\alpha = \alpha_{max(2)} = 3.451$, $\gamma = \gamma_{tr}(N = 100, \alpha = 3.451) = 4.538$ (Eq. (28)) and $\alpha = \alpha_{max(4)} = 8.225$, $\gamma = \gamma_{tr}(N = 100, \alpha = 8.225) = 4.529$ (Eq. (29)).

is attained at $\alpha_{max(2)} = 3.451$ and that of $f_{ext}^{(4)}(\alpha)$ — at $\alpha_{max(4)} = 8.225$. If the external field is weak, $|\alpha| \ll 1$, then $f_{ext}^{(2)}(\alpha) = \frac{4}{5}\alpha + O(\alpha^2)$, $f_{ext}^{(4)}(\alpha) = O(\alpha^2)$. If $\alpha = \alpha_{max(2)} = 3.451$ and $\gamma = \gamma_{tr}(N = 100, \alpha = 3.451) = 4.538$, then $f_{ext}^{(2)}(3.451) = 1.675$, $f_{ext}^{(4)}(3.451) = 0.045$, $f_{nem}^{(2)}(4.538) = 3.156$, $f_{nem}^{(4)}(4.538) = 0.063$ and

$$\frac{F_a}{Tn_s} = -\frac{1}{N^2} \left\{ 0.04531P_2(\cos \omega) + 0.00009P_4(\cos \omega) \right\}. \quad (28)$$

If $\alpha = \alpha_{max(4)} = 8.225$ and $\gamma = \gamma_{tr}(N = 100, \alpha = 8.225) = 4.529$, then $f_{ext}^{(2)}(8.225) = 0.818$, $f_{ext}^{(4)}(8.225) = 0.118$, $f_{nem}^{(2)}(4.529) = 3.044$, $f_{nem}^{(4)}(4.529) = 0.058$ and

$$\frac{F_a}{Tn_s} = -\frac{1}{N^2} \left\{ 0.02134P_2(\cos \omega) + 0.00021P_4(\cos \omega) \right\}. \quad (29)$$

The dependencies $F_a(\omega)$ (Eqs. (28, 29)) are shown in Figure 7 (in units of Tn_s/N^2).

It is obvious that the term containing $P_2(\cos \omega)$ dominates in both cases: the ratio of the coefficients at $P_2(\cos \omega)$ and $P_4(\cos \omega)$ in equations (28, 29) is more than 500 and 100 respectively. It means that if one intends to reveal and measure experimentally the dependence $F_a(\omega)$ near the transition point γ_{tr} , the external field while cross-linking should be chosen close to the value $\alpha_{max(2)} = 3.451$, maximizing $f_{ext}^{(2)}(\alpha)$. In case of cross-linking in a nematic melt, the optimum molecular field parameter is $\gamma_{opt} = 4.640$ (the optimum order parameter is $\eta_{opt}(\gamma_{opt}) = 0.496$, so that $\alpha = \frac{3}{2}\gamma_{opt}\eta_{opt} = \alpha_{max(2)}$). Furthermore, it is clear that the deeper in the nematic phase the network is (that is the larger γ and η are), the stronger the dependence $F_a(\omega)$ is (see Figs. 5, 6).

6 Anisotropy of the nematic network elasticity

Expressions (20, 27) enable us to describe elastic properties of anisotropic networks. As it is clear from equation (27) and Figure 7, the elastomer attains the *equilibrium* state (corresponding to the minimum of the free energy) when the director \mathbf{d} is parallel to the network anisotropy \mathbf{u} , *i.e.* when $\omega = 0$ or $\omega = \pi$. Since the dependence $F(\omega)$ is very weak (see Eqs. (28, 29)), a rotation of the director by some angle ω from its equilibrium orientation costs very little energy. On the other hand, deformation implied by the rotation of \mathbf{d} can be represented as basically a compression $1/\lambda_1$ (see Eq. (26)) along one axis (initial \mathbf{d}) followed by an elongation λ_1 along another axis (final \mathbf{d}), *i.e.* this is a *shear* deformation which is also *semi-soft*. [10–12] Equivalently, a weak dependence $F(\omega)$ implies that shear modulus $\mu^{(xz)}$ (axis z is parallel to \mathbf{u} , axis x is in the plane $\mathbf{u}-\mathbf{d}$) is much lower than *e.g.* shear modulus $\mu^{(xy)}$ or extensional modulus $\mu^{(zz)}$. Let us demonstrate that quantitatively.

At equilibrium the director \mathbf{d} is parallel to \mathbf{u} . Deformation induced by a small rotation of the director by the angle ω is equivalent to a shear Γ in the xz plane,

$$\Gamma = \omega \left(\lambda_1^{3/2} - \lambda_1^{-3/2} \right)$$

where $\lambda_1 = \lambda_1(\gamma)$ is given by equation (26)⁵.

Hence the elastic modulus corresponding to the xz shear deformation is

$$\mu^{(xz)} = \left. \frac{\partial^2 F}{\partial \Gamma^2} \right|_{\Gamma=0} = \left(\lambda_1^{3/2} - \lambda_1^{-3/2} \right)^{-2} \left. \frac{\partial^2 F}{\partial \omega^2} \right|_{\omega=0} \quad (30)$$

which upon substitution of F_a , equation (27), leads to

$$\mu^{(xz)} = \frac{9}{350} \frac{Tn_s}{N^2} \left(\lambda_1^{3/2}(\gamma) - \lambda_1^{-3/2}(\gamma) \right)^{-2} \times \left\{ f_{ext}^{(2)}(\alpha) f_{nem}^{(2)}(\gamma) + 12 f_{ext}^{(4)}(\alpha) f_{nem}^{(4)}(\gamma) \right\}. \quad (31)$$

For typical values of parameters (*e.g.* for those used in Eqs. (28, 29)) this gives an estimate

$$\mu^{(xz)} \simeq (0.03 \div 0.2) \frac{Tn_s}{N^2}.$$

Meanwhile, the extensional modulus

$$\mu^{(zz)} = \left[\lambda \frac{\partial}{\partial \lambda} \left(\lambda \frac{\partial F}{\partial \lambda} \right) \right]_{\lambda=\lambda_1(\gamma)} \quad (32)$$

($\lambda_1(\gamma)$ is the equilibrium deformation) in the main order in $1/N$ (*i.e.* generated by the term $B(\alpha, \beta_0(\gamma), \lambda)$ in Eq. (20)) is⁶

$$\mu^{(zz)} = 3Tn_s \frac{K(\alpha)}{K(\beta_0(\gamma))} \quad (33)$$

with typical values

$$\mu^{(zz)} \simeq (1.5 \div 3) Tn_s.$$

So, characteristic values of the xz -shear modulus are much smaller than those of the extensional one:

$$\mu^{(xz)} \sim \frac{\mu^{(zz)}}{N^2}.$$

The same conclusion holds true for $\mu^{(xy)}$ since $\mu^{(xy)} \sim \mu^{(zz)} \sim Tn_s$. Hence the xz -shear can be considered as a semi-soft deformation mode.

⁵ Note that ω is the angle between \mathbf{d} and \mathbf{u} in the *reference* state while in the *nematic* state the angle ω' between these vectors is different: $\tan \omega' = \frac{\tan \omega}{\lambda_1^{3/2}}$.

⁶ For isotropic networks ($\alpha = \beta_0 = 0$) equation (33) for $\mu^{(zz)}$ reduces to the well known classical result $\mu_0^{(zz)} = 3Tn_s$ [25].

7 The isotropic-nematic transition

So far we considered the case of free elastomers, *i.e.* with no external stress: $\sigma = 0$. In order to characterize non-linear thermoelastic behavior of the system, *i.e.* to find the stress-strain relationship for *e.g.* uniaxial deformation (when the stress σ is applied along the director \mathbf{d}), one should minimize the expression $F - \sigma \ln \lambda$ instead of just F (Eq. (20)). The resultant thermoelastic diagrams are similar to those obtained in references [4,6] for elastomers cross-linked in isotropic state. In fact, the effect of anisotropy during cross-linking could be taken into account by a simple modification: thermoelastic diagrams calculated for isotropic networks remain valid for anisotropic elastomers (at least, in the main order in $1/N$) if one substitutes the reduced stress $\sigma/K(\alpha)$ for the stress σ calculated in references [4,6] (the function $K(\alpha)$ is defined in Eq. (11) and is shown in Fig. 1).

Now, having calculated the free energy of the system (Eq. (23)) one can locate the isotropic-nematic transition. Using equation (20) we obtain the difference of free energies in nematic ($\beta \simeq \beta_0(\gamma)$) and isotropic ($\beta = 0$) states:

$$\begin{aligned} \frac{\Delta F(\alpha, \gamma)}{Tn_s} = N & \left\{ \frac{2}{9} \frac{\beta_0^2}{\gamma} + \frac{1}{3} \beta_0 - \ln \int_0^1 e^{\beta_0 t^2} dt \right\} \\ & + \frac{3}{2} \left\{ \ln K(\beta_0) + K(\alpha) \left(\frac{1}{K(\beta_0)} - 1 \right) \right\} \\ & + O\left(\frac{1}{N}\right) \end{aligned} \quad (34)$$

where $\beta_0 = \beta_0(\gamma)$. It is clear, that the value of γ at the point of nematic-isotropic transition, γ_{tr} , which is determined by the condition $\Delta F = 0$, depends on the external field α and on the number of segments in a strand N . The N -dependence of the transition point has been considered in reference [4]; it is very weak if N is large. The dependence of the transition point on the external field α calculated using equation (34) is also weak; it is shown in Figure 2 (for $N = 100$). Obviously the orientational field applied to the system during cross-linking favors nematic ordering: the Maier-Saupe parameter at the transition, γ_{tr} , decreases as α increases. This effect has been already qualitatively discussed in reference [5].

Thus, our consideration of anisotropic networks with mesogenic units enables us to describe their elastic behavior and to locate the isotropic-nematic transition point for arbitrary values of the external field constant α .

8 Discussion

In this paper we considered nematic elastomers cross-linked in anisotropic state. We show that the system 'remembers' the direction of its initial anisotropy, so that the free energy of the elastomer depends on the director orientation according to equation (27) which is our main

result. This dependence is weak, however, yielding semi-soft deformation modes [10–12]: the shape of the sample changes considerably as the director rotates. In fact, deformation associated with director rotation on angle ω can be reduced to compression of the sample by a factor λ_1 along one axis (\mathbf{u}) and subsequent elongation by the same factor along another axis (\mathbf{d}); ω is the angle between \mathbf{u} and \mathbf{d} .

The quenched anisotropy of the network is related to non-Gaussian elasticity of network strands. In fact, we show that the anisotropic part of the free energy is proportional to the square of deviation of the strand end-to-end vector distribution from Gaussian law, *i.e.* to square of $1/N$, where N is the number of segments per strand.

The angular dependence of the free energy is given by two terms, one is proportional to $P_2(\cos\omega)$ and the other to $P_4(\cos\omega)$ (see Eq. (27)). However the P_4 term is practically negligible as it is ~ 100 times smaller than the P_2 term. Therefore the angular dependence essentially takes the form of equation (1), first predicted in reference [11], *i.e.* $F(\omega) = \text{const.} + F_a \sin^2 \omega$. The anisotropic energy F_a depends on both the order parameter during cross-linking (related to the orientational field $\alpha = U_0/T$, see Eq. (2)) and that in the final state (related to the Maier-Saupe parameter $\gamma = U'_0/T$, see Eq. (3)):

$$F_a = \frac{9}{700} \frac{n_s T}{N^2} f_{ext}^{(2)}(\alpha) f_{nem}^{(2)}(\gamma) \quad (35)$$

where n_s is the number concentration of strands. The dependence of F_a on the initial order parameter is non-monotonic: it shows a maximum corresponding to the order parameter $\simeq 0.5$ at the crosslinking stage. This value of 0.5 is close to the order parameter at the isotropic-nematic transition point ($\eta \simeq 0.44$) as predicted by the Maier-Saupe theory [26]. Thus we predict that the most anisotropic network is formed when cross-linked in the nematic state slightly below the clearing temperature.

The anisotropic free energy (F_a) also determines the threshold ϵ_1 for formation of stripe domains in elastomers under extension ($1 + \epsilon_1$) perpendicular to the director [11, 12]. Using theoretical results of references [11, 12] it is easy to show that the threshold is $\epsilon_1 \simeq \frac{2}{3} F_a / (n_s T)$, *i.e.*

$$\epsilon_1 \simeq \frac{3}{350 N^2} f_{ext}^{(2)}(\alpha) f_{nem}^{(2)}(\gamma). \quad (36)$$

Assuming the optimal order parameter $\eta \simeq 0.5$ during cross-linking and the same η in the final state, we thus obtain $\epsilon_1 \simeq \frac{0.93}{N^2}$. For a typical $N \sim 10$ this amounts to ϵ_1 values which are much smaller than the experimentally observed values of $0.02 \div 0.15$.

Thus, the network anisotropy due to non-Gaussian statistics of strands considered in this paper results in a small effect, which is however universal as real subchains are always slightly non-Gaussian. The same problem of quenched network anisotropy was also considered theoretically in references [11, 13, 14]. Very roughly their result for the threshold is $\epsilon_1 \sim 1/N$, *i.e.* much larger values, in qualitative agreement with observations. However the models considered in references [13, 14] (rod-like cross-linkers

and compositionally heterogeneous strands) are not exactly universal.

At this point it is reasonable to consider the question: are there any *universal* effects that could give rise to stronger network anisotropy and higher thresholds than those predicted in this paper?

Let us consider the simplifying assumptions adopted in our model.

(1) Strands considered as freely-jointed chains of rod-like segments. In reality main-chain mesogenic polymers are better described by worm-like persistent chain models. Qualitatively we expect our main results to be valid also for persistent strands, however with different numerical prefactors. It is known that persistent chains become effectively more rigid in the nematic state. This implies smaller effective number N of rigidity (Kuhn) segments, *i.e.* higher threshold $\epsilon_1 \propto 1/N^2$ (see Eq. (36)). However the above comment does not apply to side-chain mesogenic polymers which are well described by the freely-jointed model.

(2) Monodisperse system of precursor polymers. The effect of polydispersity could be easily taken into account in the model: in the final equations (like Eqs. (35, 36)) the factor $1/N^2$ should be replaced by the number averaged value $\langle 1/N^2 \rangle_n$. If the degree of polydispersity is high enough (which is the case in practice), then $\langle 1/N^2 \rangle_n$ might be much larger than $1/N_n^2$, where $N_n = \langle N \rangle_n$. In particular, for $N_w/N_n = 2$ (Flory molecular weight distribution) even the exponent is different: $\langle 1/N^2 \rangle_n \simeq 1/N_n$. In this case we predict $\epsilon_1 \sim 0.03/N_n$, *i.e.* the threshold is still small due to numerical prefactor.

(3) Affine deformations. In general case network junction points do not exactly follow the macroscopic deformation of the sample as they do fluctuate and also the network structure is irregular. However we expect little effect of these complications on the network ‘orientation memory’. The reason is that even in this general case the memory is solely due non-Gaussian corrections to the statistics of sub-chains. In fact, it is possible to show that irregular and non-affine network formed by strictly Gaussian chains do not remember its orientational state imposed during cross-linking. The reason is that (nematic) orientational field affects conformation of all chains in the same way. In particular the ratio R_{\parallel}/R_{\perp} is the same for all chains, even if their molecular weights are different. Therefore the network anisotropy induced during cross-linking can be exactly canceled by its appropriate deformation afterwards.

(4) Topological effects. So far we assumed that the chains are fantom, *i.e.* could possibly intersect each other. Real polymer chains can form knots which might be trapped between junction points. It is well-known [27] that the effect of these knots (entanglements) could strongly affect elastic properties of ordinary networks. In particular entanglements act like effective junction points thus renormalizing the effective sub-chain length: $1/N \rightarrow 1/N + 1/N_e$, where N_e is the number of monomers per entanglement. A similar renormalization of the anisotropic energy is also expected, *i.e.* the threshold ϵ_1 should be proportional to $(1/N + 1/N_e)^2$ instead of $1/N^2$.

Further measurements of the sub-chain molecular weight (N -) dependence of the anisotropic energy (and/or of the threshold ϵ_1) would be very desirable in order to clarify the underlying molecular mechanisms.

9 Conclusions

(1) An elastomer cross-linked in the nematic state retains memory about its anisotropy during cross-linking yielding a dependence of the elastomer free energy on the director orientation.

(2) The effect is due to non-Gaussian elasticity of network strands.

(3) For monodisperse network formed by freely-jointed chains the anisotropic free energy is inversely proportional to the square of subchain molecular weight.

(4) The strongest memory effect is predicted for a moderate orientational order during cross-linking: the optimal order parameter for freely-jointed chains of rods with Maier-Saupe nematic interaction is close to $\eta = 0.5$.

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Appendix

Our aim here is to find the angular dependence of the integral

$$I(\alpha, \beta, \lambda, \omega) = - \int \ln P_0(\hat{\lambda}\mathbf{R}; \beta, \mathbf{d}) P(\mathbf{R}; \alpha, \mathbf{u}) d^3\mathbf{R}$$

with functions P_0 , equation (9), and P , equation (12). Let us consider the integrand structure:

$$\ln P_0 = [(1)] - \frac{1}{N} [(2)] + \frac{1}{N^2} [(3)]$$

$$P = \left(\frac{C_0}{\pi K}\right)^{3/2} \exp\left(-\frac{C_0 R^2}{K}\right) \times \left\{ 1 - \frac{1}{N} [(4)] + \frac{1}{N^2} [(5)] + \frac{1}{N^2} [(6)] \right\}$$

where we have combined the first two terms of the order of $1/N^2$ in the r.h.s. of equation (12), defining the function $P(\mathbf{R}; \alpha, \mathbf{u})$, into the term [(5)]; the last (third) term is [(6)]. Obviously there are 7 terms of the order not higher than $1/N^2$ in the integral I :

1. The term $\int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot [(1)] \cdot 1 d^3\mathbf{R}$ is the main one as it depends neither on N nor on ω . It yields

$$\text{const.} + \frac{3}{2} \ln K(\beta) + K(\alpha) \left(\frac{\lambda^2}{2} \frac{1}{K_{\parallel}(\beta)} + \frac{1}{\lambda} \frac{1}{K_{\perp}(\beta)} \right)$$

i.e. the function $B(\alpha, \beta, \lambda)$ in the free energy (see Eq. (20)).

2. The terms $\int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot [(2)] \cdot 1 d^3\mathbf{R}$ and $\int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot [(3)] \cdot 1 d^3\mathbf{R}$ do not depend on ω and are proportional to $1/N$ and $1/N^2$ respectively. Thus both terms are not important⁷.
3. The terms $\int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot [(1)] \cdot [(4)] d^3\mathbf{R}$ and $\int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot [(1)] \cdot [(5)] d^3\mathbf{R}$ are identically equal to zero. Indeed, the term [(1)] is a linear combination of R_{\parallel}^2 and R_{\perp}^2 only, *i.e.* it is the sum of terms like $L_i^{-1/2}(R_x^2) L_j^{-1/2}(R_y^2) L_k^{-1/2}(R_z^2)$ where $i + j + k \leq 1$. On the other hand, terms [(4)] and [(5)] contain combinations of Laguerre polynomials like $L_l^{-1/2}(R_x^2) L_m^{-1/2}(R_y^2) L_n^{-1/2}(R_z^2)$ with $l + m + n \geq 2$. Therefore the corresponding integrals are always equal to 0 due to orthonormality of the system of Laguerre polynomials.
4. Thus, the only terms to be calculated are:

$$- \left(\frac{C_0}{\pi K}\right)^{3/2} \int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot [(1)] \cdot \frac{1}{N^2} [(6)] d^3\mathbf{R}$$

and

$$- \left(\frac{C_0}{\pi K}\right)^{3/2} \int \exp\left(-\frac{C_0 R^2}{K}\right) \cdot \frac{1}{N} [(2)] \cdot \frac{1}{N} [(4)] d^3\mathbf{R}.$$

The result is:

$$\text{The first} = \frac{1}{25N^2} P_2(\cos \omega)$$

$$\times f_{ext}^{(2)}(\alpha) \left(\lambda^2 \frac{1}{K_{\parallel}(\beta)} - \frac{1}{\lambda} \frac{1}{K_{\perp}(\beta)} \right)$$

$$\text{The second} = - \frac{1}{1750N^2} \left[5P_2(\cos \omega) f_{ext}^{(2)}(\alpha) \right.$$

$$\times \left(3\lambda^4 X_C(\beta) - \frac{4}{\lambda^2} X_S(\beta) + \lambda X_G(\beta) \right)$$

$$+ 18P_4(\cos \omega) f_{ext}^{(4)}(\alpha)$$

$$\times \left(\lambda^4 X_C(\beta) + \frac{1}{\lambda^2} X_S(\beta) - 2\lambda X_G(\beta) \right) \Big]$$

$$+ \left[\text{terms not depending on } \omega \right].$$

(A.1)

⁷ The first one is:

$$\frac{1}{40} \left[3 \left(1 - \frac{K(\alpha)}{K_{\parallel}(\beta)} \lambda^2 \right)^2 (5 - 3C_4(\beta)) \right.$$

$$+ 8 \left(1 - \frac{K(\alpha)}{K_{\perp}(\beta)} \frac{1}{\lambda} \right)^2 \times (5 - 3S_4(\beta))$$

$$\left. + 4 \left(1 - \frac{K(\alpha)}{K_{\parallel}(\beta)} \lambda^2 \right) \left(1 - \frac{K(\alpha)}{K_{\perp}(\beta)} \frac{1}{\lambda} \right) (5 - 3G_{22}(\beta)) \right].$$

The functions X_C , X_S , *etc.* are defined in the main text after equation (20).

Adding these 7 terms to $NA(\beta, \gamma)$ leads to equation (20).

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