Nematic Elastomers: a New State of Matter?

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Abstract

Nematic elastomers (NE's) are polymer liquid crystals. They have mobile directors, which is coupled to the crosslinking network of polymers, thus give very nonlinear behavior in elasticity, like spontaneous change of shape, and nematic-isotropic transition under mechanical pressure. The basic experimental results are reviewed, and some theoretical work based on the neo-classical rubber elastic theory is also studied, with explaining the two categories of experiments.

1. Introduction: Liquid Crystal and Elastomers

Nematic liquid crystals are materials between liquid and solid. They have continuous translational symmetry, and can flow under applied stress like liquid. But their rotational symmetry is broken, because they have long-range orientational order of their director, and a goldstone elasticity associate with this spontaneous symmetry breaking[1, 2].

Liquid crystals are composed of certain organic molecules that have a rod like shape. In nematic phase these rod like molecules become parallel because of repulsion interaction, and thus break the rotational symmetry. In high temperatures, they are in isotropic phase and have no difference with conventional liquid, and exhibit continuous translation and rotational order. When the temperature is lowered, they have a cascade of transitions from isotropic state to nematic, smectic and eventually crystalline solid state.

Rubber is a soft amorphous solid. It has bulk modulus in the same scale with crystalline solid, but its shear modulus is about $10^{-4}-10^{-5}$ times that of the conventional solids, so they are able to have large deformation, but with constant volume, thus restore large amount of elastic energy[3].

Microscopically, rubber is composed of long, flexible polymers. These polymers (permanently in most situations) crosslink to each other, thus form a random network[4,5]. The section of polymer between crosslinks is long compared to the monomers of the polymer, so they can be seen as a random work. This property gives the small shear modulus of rubber. In this sense rubber is a marginal solid, with many liquid like characters.

Nematic elastomers, the subject of this paper, is a combination of liquid crystal and rubber[6,7,8]. The rod like molecules in liquid crystals are linked into polymers in nematic elastomers, either in the main-chain or in the side-chain fashion, as shown in Fig. 1. These materials are also called polymer liquid crystals (PLCs) and solid liquid crystals.

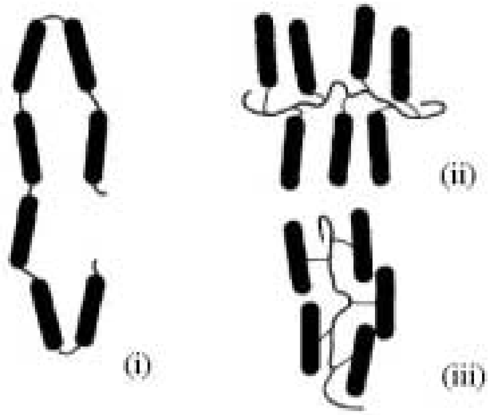

Fig. 1. Three types of polymer liquid crystals: (i) Main-chain (MC) with the nematic elements part of the backbone; the backbone has a prolate (elongated) shape; (ii) Side-chain (SC) with nematic elements

pendant to the backbone, then the backbone has an oblate (flattened) shape because of the character of the coupling of the rods to the backbone. (iii) Side-chain with the pendant nematic elements natrually parallel to the backbone, thus creating a prolate backbone.

Now we see that there are two kind of degrees of freedom in nematic elastomers: director of the nematic order, and the polymer random network. These two degrees of freedom are coupled together. Their coupling gives complicate and interesting behavier of the nematic elastomers, which will be reviewed in next section.

2. Basic Experimental Observation

There are mainly two category of experimental observations of nematic elastomers: spontaneous change of shape due to temperature change, and strain-induced nematic-isotropic transition.

In the first category of experiments, people prepare sample in temperature above the isotropic-nematic transition. The polymers got crosslinked in this isotropic state. Then they lower the temperature to below the nematic transition temperature. The sample will have a spontaneous shape change[9]. Fig. 2(a) is a schematic demonstration of this effect.

In this process of spontaneous shape change, microscopically the shape of the polymer is changed from isotropic to anisotropic, due to the nematic order, which cause the polymers prolong in the direction of the nematic order (for the case of main-chain polymer). Because the nematic molecules are embedded in the random network polymer matrix, the macroscopic shape of the nematic elastomer is also prolonged in this direction. See in Fig. 2(b) for a simple illustration. We will study this effect in detail in next section.

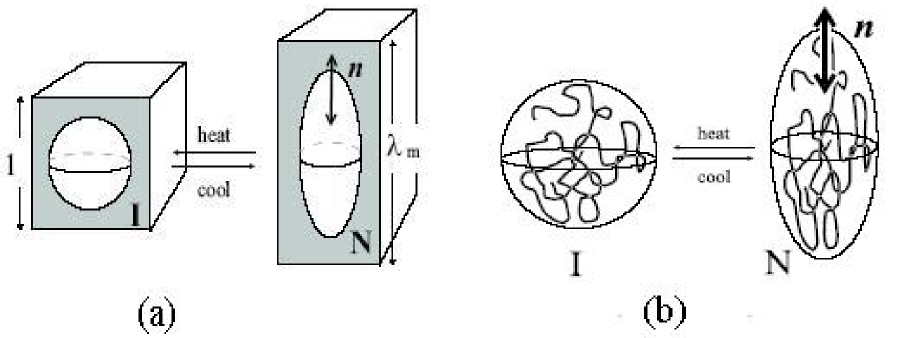

Fig. 2. (a) Macroscopic picture: A unit cube of rubber in the isotropic (I) state. It is prolonged in the Nematic state, by a factor λ_m, accommodating the now elongated chains.(b) Microscopic picture: Polymers are on average spherical in the isotropic (I) state and elongate when they are cooled to the nematic (N) state. The director **n** points along the long axis of the shape spheroid.

The second category of experiment is to apply strain on the nematic elastomer sample, and observe of influence on the nematic order[9]. A simple example of this kind of experimental is to clamp a long strip of monodomain (monodomain means a uniform nematic order) nematic rubber at its ends. The strip is cut so that its initial director $\mathbf{n}_0$ is in the plane of the strip, at and angle α to the imposed strain direction $\mathbf{u} = \hat{z}$. Since chains will be elongated along $\hat{z}$ by imposing strain, the director will rotate, by an amount θ, toward $\hat{z}$. The rotation axis is denoted by $\hat{y}$, see fig. 3 for a sketch of the experiment.

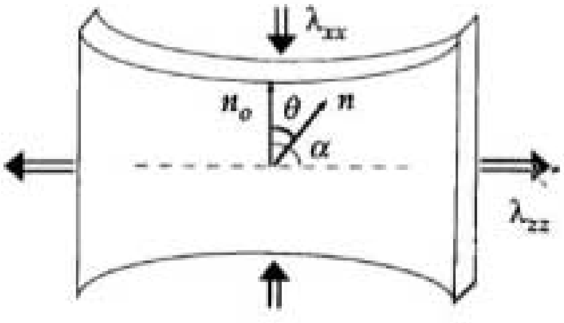

Fig. 3. A strip of nematic monodomain elastomer, clamped and extended. The original director is $\mathbf{n}_0$, in the plane of the strip, and at an angle α to the stretch director $\mathbf{u} = \hat{z}$. The director rotates about the $\hat{y}$ axis by an angle θ. Arrows on the clamps indicate the direction of extension λ_{zz}. The characteristic necking shape of the sample is emphasized.

In the data shown in fig. 4, people begin with $\alpha = \frac{\pi}{2}$, and call the angle between the nematic director and the alignment axis $\hat{z}$ (the direction of extension) as angle Φ. Then plot the angle Φ as a function of the extension ratio λ_{zz}. We can see that there is an initial rather small reduction in Φ with increasing strain, but at an extension ratio of ~ 1.13 (for side-chain elastomers in this experiment) there is a transition in the director alignment and a switch to value for $\Phi \sim 0$.

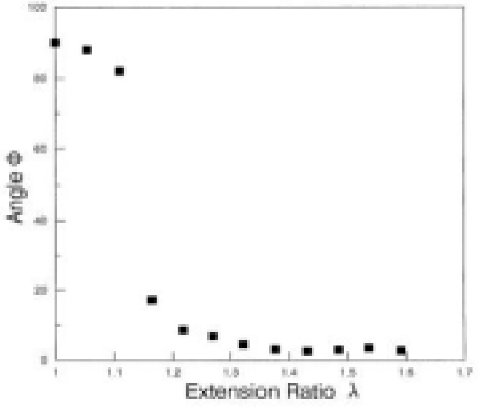

Fig. 4. A plot of the angle Φ between the director $\mathbf{n}$ and the extension axis against the extension ratio λ_{zz} for a monodomain liquid-crystal elastomer at $323K$.

3. Neo-classical rubber elasticity theory

3.1 Strains without couples: spontaneous distortions

The microscopic structure of nematic elastomers tells us, that the chain arc length $\mathcal{L}$ between crosslinking points is very long compared to the monomer length, so the chain trajectory between these crosslinking points can be considered a Gaussian random walk. This provides us the right conditions to apply and modify the classical theory of rubber elasticity into a "neo-classical" theory appropriate to nematic elastomers.

Nematic chains are anisotropic but, if sufficiently long, remain random walks. The distribution of separations of connected crosslinks is an anisotropic Gausian:

$$P(\mathbf{R}) \propto \exp\left(-\frac{3}{2\mathcal{L}}\mathbf{R}^T\mathbf{l}^{-1}\mathbf{R}\right) \tag{1}$$

In a symmetry broken state there is a matrix of effective step lengths l_{ij} . Notice if $l_{ij} = \delta_{ij}$, this distribution just recovers the usual isotropic random walk: $P(R) \propto \exp\left(-\frac{3R^2}{2l\mathcal{L}}\right)$. Now in the anisotropic assumption of effective step lengths, the shape of the polymer chain is characterized by:

$$\left\langle R_i R_j \right\rangle = \frac{1}{3} l_{ij} \mathcal{L} \tag{2}$$

For simplicity, we consider the effective step length in the principal frame of the uniaxial nematic director:

$$\mathbf{l} = \begin{pmatrix} l_\parallel & 0 & 0 \\ 0 & l_\perp & 0 \\ 0 & 0 & l_\perp \end{pmatrix} \tag{3}$$

The chain anisotropy (described by matrix $\mathbf{l}$) can be measured using neutron scattering. For main-chain nematic polymers, some $10°C$ below the phase transition one finds $l_\parallel / l_\perp \sim 15$, and became exponentially large in lower temperature[10].

Classical rubber elasticity theory[11] finds the free energy of a chain between two crosslinks $\mathbf{R}$ apart, is $F_R = -k_B T \log P(\mathbf{R})$. It is entropic. Using Equ. (1) we could see: the closer the two crosslinks are, the more configurations are available to the chain connecting them and the lower the free energy. So we can see the network resist extension.

$$F_R = -k_B T \log P(\mathbf{R}) = k_B T \frac{3}{2\mathcal{L}} Tr(\mathbf{R}^T \mathbf{l}^{-1} \mathbf{R}) + const \tag{4}$$

Now let us imaging an experimental process. First step, in temperature T_0 we prepare the sample by crosslink it. Now we have the step length matrix $\mathbf{l}_0$ (notice in our study of neo-classical rubber elasticity theory, this $\mathbf{l}_0$ is given as a known function of the nematic molecule shape), so we can write for the first step of experiment at T_0:

$$P(\mathbf{R}_0) \propto \exp\left(-\frac{3}{2\mathcal{L}}\mathbf{R}_0^T\mathbf{l}_0^{-1}\mathbf{R}_0\right) \tag{5}$$

After the crosslinking, we have a distribution of $\mathbf{R}_0$.

Second step, we change the temperature to T, so the step length matrix is changed into $\mathbf{l}$. The system will deform to accommodate this change of step length. But because it is crosslinked in first step, the system has a "quenched" disorder, so it can not just arrive to the distribution of a free chain, which just minimize the free energy in Equ (4).

To solve this problem, we assume the deformations are affine (deformation of polymer is proportional to deformation of the body), so given the strain tensor λ, we have, the deformation of the chain is described by

$$\mathbf{R} = \lambda\mathbf{R}_0 \tag{6}$$

And the probability of having $\mathbf{R}$ (not $P(\mathbf{R})$, but the probability of this realization of disorder) is the probability of $\mathbf{R}_0$ in the first step $P(\mathbf{R}_0)$. This argument gives us the free energy per network strand[12]

$$\begin{aligned}
F_R &= -k_BT\left\langle \log P(\mathbf{R})\right\rangle_{P(\mathbf{R}_0)} \\
&= -k_BT\int_0^\infty P(\mathbf{R}_0)\log P(\mathbf{R})d\mathbf{R}_0 \\
&= -k_BT\int_0^\infty \exp\left(-\frac{3}{2\mathcal{L}}\mathbf{R}_0^T\mathbf{l}_0^{-1}\mathbf{R}_0\right)\left[\left(-\frac{3}{2\mathcal{L}}\right)Tr(\mathbf{R}^T\mathbf{l}^{-1}\mathbf{R})+const\right]d\mathbf{R}_0 \\
&= k_BT\int_0^\infty \exp\left(-\frac{3}{2\mathcal{L}}\mathbf{R}_0^T\mathbf{l}_0^{-1}\mathbf{R}_0\right)\frac{3}{2\mathcal{L}}Tr(\mathbf{R}_0^T\lambda^T\mathbf{l}^{-1}\lambda\mathbf{R}_0)d\mathbf{R}_0+const \\
&= k_BT\frac{1}{2}Tr(\mathbf{l}_0\lambda^T\mathbf{l}^{-1}\lambda)+const
\end{aligned} \tag{7}$$

Suppose the strain tensor simply adopts the easiest direction, so its axis is also the nematic director $\mathbf{n}$. We have

$$\lambda = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{pmatrix} \tag{8}$$

This linear extension tensor λ is parallel to the nematic director $\mathbf{n}$, and conserves the volume, since $Det[\lambda]=1$. Plug this into the expression of free energy in Equ. (7), we arrive at (up to an additive constant)

$$\begin{aligned} F &= k_B T \frac{1}{2} Tr(\mathbf{l}_0 \lambda^T \mathbf{l}^{-1} \lambda) \\ &= \frac{1}{2} k_B T \left(\frac{l_\parallel^0}{l_\parallel} \lambda^2 + 2 \frac{l_\perp^0}{l_\perp} \frac{1}{\lambda} \right) \end{aligned} \tag{9}$$

A mechanically unconstrained sample is free to adopt an optimal deformed state, described by λ. Minimize this free energy giving us

$$\lambda_m = \left(\frac{l_\parallel l_\perp^0}{l_\parallel^0 l_\perp} \right)^{\frac{1}{3}} \tag{10}$$

We can consider two kind of experimental conditions from this point. One is $T_0 > T_{ni}$, and $T < T_{ni}$, where T_{ni} is the temperature of the isotropic nematic transition. This means we prepare the sample by crosslink it in the isotropic phase, and bring it to a temperature below the transition temperature. In this case we know above transition $l_\parallel^0 = l_\perp^0 = a$ because the chain is isotropic, but below the transition $l_\parallel \neq l_\perp$, so this gives us $\lambda_m = \left(l_\parallel / l_\perp \right)^{\frac{1}{3}}$. Obviously the elastomer is extended.

Another experiment is the reverse: crosslink at the nematic phase, and bring it to the isotropic phase. In this second case, $l_\parallel = l_\perp = a$, while $l_\parallel^0 \neq l_\perp^0$, so minimizing the free energy gives us $\lambda_m = \left(l_\perp^0 / l_\parallel^0 \right)^{\frac{1}{3}}$. This is a uniaxial contraction of the sample for a nematic elastomer with prolate chain conformation, or an elongation for an oblate case.

Both of these two experiments are examples of spontaneous shape changes. They result from the coupling between nematic order and the random network polymer matrix. Even when the elastomer has been held for several days in the isotropic state, there is a perfect reversible elongation/contraction on returning to the nematic phase. Despite liquid-like molecular mobility, nematic order is permanently imprinted in the network.

Up to now we take the step length tensor $\mathbf{l}$ as given. Actually, being a function of the backbone chain anisotropy, i.e. implicitly of the nematic order parameter Q, this tensor is strictly the result of minimization of the sum of nematic and elastic free energies. But sufficiently far away from T_{ni}, the free energy associate with nematic order is dominant, and unperturbed by the elastic random network, so we can just take the chain anisotropy $\mathbf{l}$ as given. $\mathbf{l}$ can rotate in space, which does not change the nematic free energy, but its principal values $l_\parallel(Q), l_\perp(Q)$ are not distorted.

3.2 Strains with couples: strain-induced transitions

In order to study the effect of strain not on the direction of nematic order $\mathbf{n}$, which can cause a nematic transition, we need to define the chain step length matrix $\mathbf{l}$ in a general coordinate

$$l_{ij} = l_\perp \delta_{ij} + \left(l_\parallel - l_\perp\right) n_i n_j \tag{11}$$

Imaging a process in which we clamp the elastomer (with means keep $\lambda = 1$), and re-orient the nematic director from $\mathbf{n}_0$ to $\mathbf{n}$. Apply Equ. (7) we have

$$\begin{aligned} F &= k_B T \frac{1}{2} Tr(\mathbf{l}_0 \lambda^T \mathbf{l}^{-1} \lambda) \\ &= k_B T \frac{1}{2} Tr\left(\left(l_\perp \delta_{ik} + \left(l_\parallel - l_\perp\right) n_i^0 n_k^0\right)\left(l_\perp^{-1} + \left(l_\parallel^{-1} - l_\perp^{-1}\right) n_k n_j\right)\right) \\ &= \frac{1}{2} k_B T \left(3 + \frac{\left(l_\parallel - l_\perp\right)^2}{l_\parallel l_\perp}\left[1 - \left(\mathbf{n} \cdot \mathbf{n}_0\right)^2\right]\right) \end{aligned} \tag{12}$$

In stead of clamping the sample, we can allow a strain on the sample. Our goal is to discuss the strain-induced nematic transition, so consider the experimental configuration in fig. 3: a strip of monodomain elastomer, with original nematic director $\mathbf{n}_0$ (also the x direction), is clamped and extended in direction $\mathbf{u}$ (also the z direction), at an angle α to the original director. Define the angle between the actual nematic director $\mathbf{n}$ is at angle θ with the z direction. In this case let $\alpha = \frac{\pi}{2}$ for simplicity. We expect a jump from $\theta = 0$ to $\theta = \frac{\pi}{2}$, to be aligned with the direction of stretch. We are not going to solve the exact process of the gradual change of θ. We just compare the free energy of $\theta = 0$ and $\theta = \frac{\pi}{2}$, and find the lower one. Actually we see from experiment (fig. 4) it is a sudden jump from $\theta = 0$ to $\theta = \frac{\pi}{2}$, so it's reasonable to just consider the free energy in these 2 states.

Now the strain tensor:

$$\lambda_{ij} = \lambda_{xx} \delta_{ij} + \left(\lambda_{zz} - \lambda_{xx}\right) u_i u_j \tag{13}$$

As for the chain shape tensor $\mathbf{l}$, we have $\mathbf{l}_0 = \begin{pmatrix} l_\parallel & 0 \\ 0 & l_\perp \end{pmatrix}$ (in xz plane), and $\mathbf{l}$ jump from $\begin{pmatrix} l_\parallel & 0 \\ 0 & l_\perp \end{pmatrix}$ to $\begin{pmatrix} l_\perp & 0 \\ 0 & l_\parallel \end{pmatrix}$ associate with the change of θ from $\theta = 0$ to $\theta = \frac{\pi}{2}$.

Thus the elastic free energies per network strand at $\theta = 0$ and $\theta = \frac{\pi}{2}$ are respectively

$$F_0 = \frac{1}{2} k_B T \left(\lambda_{zz}^2 + \lambda_{xx}^2 + \frac{1}{\lambda_{xx}^2 \lambda_{zz}^2}\right) \tag{14}$$

$$F_{\pi/2} = \frac{1}{2} k_B T \left(\frac{l_\perp}{l_\parallel} \lambda_{zz}^2 + \frac{l_\parallel}{l_\perp} \lambda_{xx}^2 + \frac{1}{\lambda_{xx}^2 \lambda_{zz}^2}\right) \tag{15}$$

The sample is clamped in z direction, so λ_{zz} is given. Let $\lambda_{zz} = \lambda$, and minimize the free energies (choose appropriate λ_{xx}) gives $\lambda_{xx} = 1/\lambda_{zz}$ for $\theta = 0$, and $\lambda_{xx} = 1/\left(\lambda_m^{3/2}\lambda_{zz}\right)$ for $\theta = \frac{\pi}{2}$. While the free energy

$$F_0 = \frac{1}{2}k_B T\left(\lambda^2 + \frac{1}{\lambda}\right) \tag{16}$$

$$F_{\pi/2} = \frac{1}{2}k_B T\left(\frac{\lambda^2}{\lambda_m^3} + \frac{2\lambda_m^{3/2}}{\lambda}\right) \tag{17}$$

At an imposed strain of $\lambda_t = \lambda_m\left(\frac{2}{\left(\lambda_m^{3/2}+1\right)}\right)^{1/3}$, these two free energies are equal. This marks the thermodynamic transition between the two states. But a more detail analysis shows that there is a hysteresis and the original state only become unstable at a higher strain $\lambda_c = \lambda_m$. The free energies are shown in fig. 5.

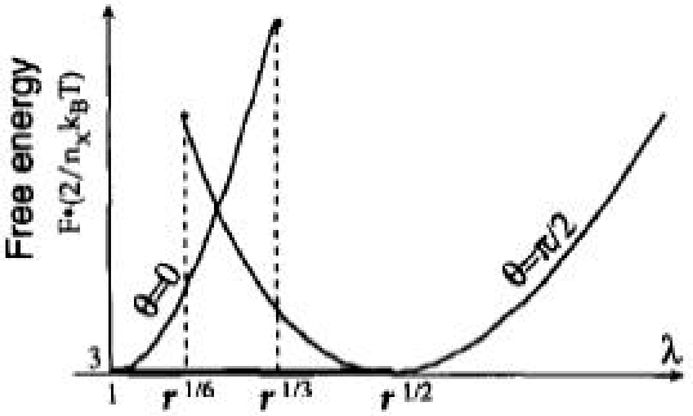

Fig. 5. Elastic free energy of the two different configurations in the ideal soft material. The transtion between the initial state $\theta = 0$ and the fully rotated state with $\theta = \frac{\pi}{2}$ takes place near the loss of stability point $\lambda_c = \lambda_m$.

4. Conclusion and discussion

In this brief review, we showed the basic experimental observation of nematic elastomers: spontaneous shape changes and strain-induced transition. We studied the foundations of neo-classical rubber elasticity theory for nematics and explain both experimental results using this theory.

This theory is successful in explaining these basic experiments, but it also has obvious limits. It can not explain polydomain nematic elastomers, which is a glassy state with local random nematic order. Also, in this theory, the nematic chain anisotropy is given fixed, and the theory just need to evaluate the elastic free energy, because people believe nematic free energy is dominant, and the nematic order is not changed if temperature is fixed.

A more complete theory of nematic elastomers, either microscopic or phenomenological, may be developed involving both nematic and elastic free energy, and their coupling. Interested readers can find new developments and some discussion of dynamics in ref. 7, 16.

5. Acknowledgments

We are grateful for discussions with X. Xing, P. M. Goldbart, and K. Sun, and thank N. Goldenfeld for teaching me the phenomena and theories of liquid crystal.

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