Phase Transition in Nematic Elastomers

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Abstract: Two kinds of phase transitions arising in nematic elastomers are discussed. It is also explained how the two different kinds of physics, one belonging to nematic liquid crystals, the other to nonlinear elasticity, mutually influence each other, resulting in the unexpected smoothening of the isotropic-nematic transition from first to second order, and the appearance of soft elasticity.

Introduction

Squalid stuff such as crystals and polymers can be more fascinating than supine supersymmetry and morbid M-theory. Certainly almost everything we see around us is in some fundamental sense the consequence of symmetry breaking, and squalid stuff is governed no less by the same physical principles of field theory as quarks and leptons. In writing my Essay I'm partly motivated by the wish to induce in the mind of my reader the sense of wonder that something as banal as nematic elastomers can exhibit unexpectedly rich properties, that are explainable only in terms of general symmetry principles and Goldstone's theorem, a central theorem in modern field theory. Furthermore, we shall see that elastic nonlinearities play an essential role in renormalizing the nature of elasticity. Nematic elastomers are essentially nematic liquid crystals embedded in rubbery polymer melt. Examples of nematic elastomers include artificial muscles and contact lenses.

Fig. 1: Nematic, Smectic-C and Tanaka gels with hard-rod dispersion

We shall be investigating the kind of phase transition encountered in nematic elastomers, but it is important to realize there are actually two kinds of phase transitions happening simutaneously in nematic elastomers. One is the **isotropic-nematic transition**[1] experienced by the nematogens embedded in the polymer melt of the elastomer. The presence of heterogeneities in the distribution of network crosslinks in the polymer melt probably influences the order of the IN transition and changes it from first to second order. The other phase transition occurring at the same time is the **isotropic-uniaxial transition** of the elastic medium itself. In ordinary situations the isotropic unstretched state is thermodynamically stable, and it is only on account of the existence of nematic order that the uniaxial, stretched state can become more thermodynamically stable than the isotropic state. Much of the interesting physics that we encounter in nematic elastomers, *e.g.* soft elasticity, comes from the interplay between the nematic and elastic components of the elastomer.

We shall find it highly instructive to compare the IN transition in nematic liquid crystals with that in nematic elastomers. We shall first begin by describing what nematic liquid crystals are, and how in the context of Landau theory an order parameter should be defined in order to describe the IN transition. We shall see that the transition is first order. Then we shall describe the physical properties of nematic elastomers, write down the Landau theory for an elastomer and see how the presence of nematic order manages to stabilize the uniaxial phase in an elastic solid. And because it

[1] Henceforth called the “IN transition”.

is now possible for the uniaxial phase to be made stable under a certain temperature, there can be a phase transition that involves the reduction of a symmetry group, and Goldstone's theorem tells us that the reduction results in “massless” Goldstone modes that manifest themselves as certain “soft directions” where we can achieve very large strains without energy cost. Finally we look at some experimental results concerning the order of the IN transition in nematic elastomers, which suggest that it is either continuous or a smooth cross-over not unlike that in a liquid-gas system at sufficiently high pressure. We shall touch on two possible explanations for the observed order, and also sketch the idea behind Petridis and Terentjev’s explanation of the “smoothing” of the first order IN transition into a continuous one.

Nematic Liquid Crystals and the Definition of an Order Parameter

First off, we have to understand what *nematic liquid crystals* are before embarking on a discussion of nematic *elastomers*. Nematic liquid crystals are essentially strands of polymer floating around in a solvent, made up of long rod-like molecules. It is liquid, meaning that it has no shear modulus. There are two phases, the isotropic phase and the nematic phase. In the isotropic phase, the molecules can point in any direction they want, there is no favoured orientation. In the nematic phase, locally each molecule is confined to a cone pointing in a certain direction labeled by a unit vector $\vec{n}$; statistically in the large they have orientational order along $\vec{n}$. Since these molecules “look the same” whether they point along $\vec{n}$ or $-\vec{n}$, we must have that the parameter describing nematic orientational order be even in $\vec{n}$. A vector order parameter is incapable of describing parity invariance, so the next best thing would be to look for a second-rank tensor. We also require any honest order parameter to be vanishing in the disordered, isotropic phase (the analogy being the magnetization M of Ising magnets), and we know that a symmetric traceless tensor will vanish when averaged over all space. Thus a suitable tensorial order parameter will be

$$\left\langle Q_{ij} \right\rangle = S\left(n_i n_j - \frac{1}{3}\delta_{ij} \right) \tag{1.1}$$

Close to the IN transition point, the order parameter $\langle Q \rangle$ has to be small, so we can approximate the Gibbs free energy in the Landau theory by a polynomial expression in powers of $\langle Q \rangle$, all indices contracted. It is not hard to see that the Landau free energy is given by (up to quartic order)

$$f = \frac{r_Q}{2} TrQ^2 - w_3 TrQ^3 + w_4 \left(TrQ^2 \right)^2 = \frac{r_Q}{3} S^2 - \frac{2}{9} w_3 S^3 + \frac{4}{9} w_4 S^4 \tag{1.2}$$

Here r_Q is temperature dependent, $r_Q = a(T - T^*)$, controlling how the order parameter evolves as T is lowered. The presence of the *cubic* term in $\langle Q \rangle$ indicates the IN transition is *first order* in nematic liquid crystals. $u > 0$ for the energy to be bounded from below. The minima of f can be found by requiring $\frac{\partial f}{\partial S} = 0$, and their relative stability is determined by finding the values of f at the minima. The global minimum stays at S=0 as temperature is lowered, but suddenly and

discontinuously jumps to a finite value when a certain temperature is reached. At that point we have a first order phase transition and co-existence of the nematic and isotropic phases.

Intermezzo on Nonlinear Elasticity

At this stage we shall introduce some rudimentary math to help us understand how a Lagrangian may be constructed in the theory of elasticity. A typical elastic solid is either undeformed (isotropic) or deformed; if it is undeformed, it is said to inhabit the reference space of points; if it is deformed, it is inhabiting the target space. These two spaces can be mapped into each other by a (generally) $d \times d$ matrix-valued function called the *Cauchy deformation tensor*, defined by

$$\Lambda_{i\alpha} = \frac{\partial R_i}{\partial x_\alpha} \approx \delta_{i\alpha} + \eta_{i\alpha} \tag{2.1}$$

Here *i* labels points in the target space and α labels points in the reference space, so $\Lambda_{i\alpha}$ is a mixed tensor. They transform differently under rotations in each space. We are assuming the case of small deformations: η is a small perturbation about undeformed isotropy. An infinitesimal displacement on the target space is related to an infinitesimal displacement on the reference space by

$$dR^2 - dx^2 = 2u_{\alpha\beta} dx_\alpha dx_\beta \tag{2.2}$$

Now we can think of the strain tensor $\underline{\underline{u}}$, defined by $\underline{\underline{u}} = \frac{1}{2}\left(\Lambda^T \Lambda - \delta\right)$, as being the "metric". This transforms as a second-rank tensor in reference space, but as a scalar in target space.

In prenematoelastomer physics a piece of rubber is just a piece of rubber and a liquid crystal is just a liquid crystal. There is no shear rigidity in a liquid crystal and the piece of rubber is always happy to stay in its unstretched isotropic state as long as pressure is not being applied to it. In harsher mathematical terms we say that the rubber is in the isotropic state when $\left\langle \underline{\underline{u}} \right\rangle = 0$ in the free energy,

$$f(\underline{\underline{u}}) = \frac{1}{2}\lambda\left(Tr\underline{\underline{u}}\right)^2 + \mu Tr\underline{\underline{u}}^2 - CTr\underline{\underline{u}}^3 + D'Tr\left(\underline{\underline{u}}^2\right)^2 - E'Tr\underline{\underline{u}}Tr\underline{\underline{u}}^2 \tag{2.3}$$

with $\lambda, \mu > 0$. Here λ, μ are the Lame coefficients from classical elasticity theory and there are cubic and quartic terms to take nonlinear effects into account.

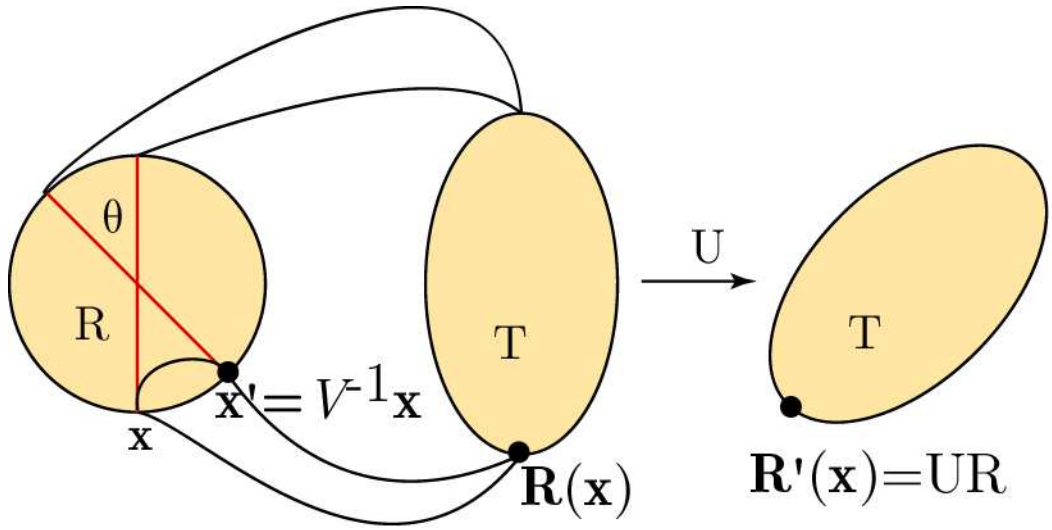

Fig. 2: **R** is the reference space and **T** is the target space. $u_{\alpha\beta}$ is invariant under rotations in **T** but transforms as a rank-two tensor in **R**. V denotes a rotation in **R**; U a rotation in **T**.

The general idea behind the Landau theory is that we are always entitled to ignore higher order terms if the lower order terms are sufficient to stabilize the energy, so if both Lame coefficients are positive, the cubic and quartic terms can be neglected, and we get that the energy is minimized for a configuration without strain (*i.e.*, $\langle \underline{\underline{u}} \rangle = 0$). In fact, for most elastic solids the two Lame coefficients have to be positive, since the case of no stretching strain is usually thermodynamically the most stable state.

However there can be a stable uniaxial phase if somehow we manage to get $\mu < 0$; then we have to include higher order terms for energy stability. Explicit calculations have been done (see *e.g.* Lubensky and Golubovic, 1989), we shall merely state the important result that in the uniaxial phase, the free energy of the elastic solid is given by

$$f_{uni} = \tfrac{1}{2} C_1 u_{zz}^2 + C_2 u_{zz}\left(u_{xx} + u_{yy}\right) + \tfrac{1}{2} C_3 \left(u_{xx} + u_{yy}\right)^2 + C_4\left(u_{xx}^2 + u_{yy}^2 + 2u_{xy}^2\right) + C_5\left(u_{xz}^2 + u_{yz}^2\right) \qquad (2.4)$$

This is automatically invariant under rotations in target space, since $\underline{\underline{u}}$ is a scalar in target space and f_{uni} is a function of $\underline{\underline{u}}$. The C_i's are called "moduli of elasticity".

Nematic Elastomers and the Return of the Goldstone Modes

How are nematic elastomers made? We shall now briefly describe a very popular way, the Kuepfer-Finkelmann method (Kuepfer and Finkelmann, 1991). In the first stage the nematic polymer melt is lightly sprinkled with crosslinks (chemical bonds) resulting in a weak gel. This is then stretched

uniaxially, either in the nematic (not elastic) isotropic phase at $T > T_{IN}$ or in the nematic phase. Still keeping the sample stretched, we do a second crosslinking reaction that fixes the enforced uniaxial alignment. If we impose a sufficiently high strain between the crosslinking stages, the resulting elastomer will be a nematic monodomain below T_{IN}.

At first sight it seems that nothing new has been gained, it appears that we have done is merely to combine two pieces of physics (nonlinear elasticity and liquid crystals), so the result should be the sum of both (hence by the look of it we should expect elastomer IN transition to be first-order like in liquid crystals and elastomers to display the same stretching behaviour as an ordinary rubber -- an initial Hookean regime followed by a curve then a dip). But contrary to such naïve expectations, it has been experimentally observed (Kuepfer and Finkelmann, 1994; Finkelmann *et al*, 1997) that for a certain regime, in certain planes, the elastomer undergoes very huge extensions for a small applied difference in shear stress, way more than is conceivable for normal rubber. The IN transition is also not first-order but continuous. In this section we shall understand this enormous extensibility (or "soft elasticity") in field theoretic terms, and also understand how the presence of nematic order can stabilize the transition of an elastic solid from an isotropic to a uniaxial state.

For now we shall restrict ourselves to truly isotropic elastomers, and neglect the fact that the Kuepfer-Finkelmann preparation method actually induces a residual anisotropy in the sample.[2] It will actually be easier for our present purpose to express the free energy density in terms of a symmetric traceless strain tensor $\underline{\underline{\tilde{u}}}$ defined by

$$u_{\alpha\beta} = \frac{1}{3}\delta_{\alpha\beta}u_{\gamma\gamma} + \tilde{u}_{\alpha\beta} \tag{3.1}$$

in which case it can be straight-forwardly worked out that the free energy density becomes (retaining the relevant terms)

$$\begin{aligned} f &= f_0 + f_1 \\ f_0 &= \frac{B}{2}\left(Tr\underline{\underline{u}} - \frac{E}{B}Tr\underline{\underline{\tilde{u}}}^2\right)^2 \\ f_1 &= \frac{A}{2}Tr\underline{\underline{\tilde{u}}}^2 - CTr\underline{\underline{\tilde{u}}}^3 + D\left(Tr\underline{\underline{\tilde{u}}}^2\right)^2 \end{aligned} \tag{3.2}$$

[2] Truly soft elasticity works only for the case of a truly isotropic sample; the nature of the preparation of monodomain real samples means that some preferred anisotropic direction is bound to be locked in, *e.g.* by the Kuepfer-Finkelmann procedure. We get instead *semi-soft* behaviour, where the stress-strain plateau occurs only at a finite but small value of the applied stress. We can think of this as being due to the introduction of a mechanical aligning field *h*, somewhat similar to an applied electric field, that endows the elastic modulus C_5 with a non-vanishing value. See Ye *et al*.

with $A = 2\mu, B = \lambda + \frac{2}{3}\mu, E = E' + C, D = D' - E^2/(2B)$. Observe that the really important term is f_1 since it will exhibit symmetry breaking, f_0 will vanish when we do an effective theory in terms of $\tilde{\underline{\underline{u}}}$ by integrating out the "massive" mode $\underline{\underline{u}}$.

In keeping with the spirit of the Landau theory of phase transitions, we shall now write down a free energy for a nematic elastomer with all terms allowed by symmetry and retaining only those terms up to the order necessary for symmetry breaking to occur and the system to be stabilized. The terms will include one that describes isotropic elasticity f_{el}, one that describes nematic order f_Q, and one that couples nematic order to elastic strain f_C, $f_{el-Q} = f_{el} + f_Q + f_C$.

We have already discussed the form of the elastic free energy density; the nematic free energy density is given by the Landau-de Gennes form,

$$f = \frac{r_Q}{2} TrQ^2 - w_3 TrQ^3 + w_4 \left(TrQ^2\right)^2 = \frac{r_Q}{3} S^2 - \frac{2}{9} w_3 S^3 + \frac{4}{9} w_4 S^4 \tag{3.3}$$

There are certain mathematical regulations concerning the precise form as to how nematic order tensors couple to elastic strain tensors. Thus far we have been using one form for the strain tensor, the *right Cauchy-Green tensor* $\tilde{\underline{\underline{u}}}$ which transforms as a second-rank tensor in reference space, and as a scalar in target space. However there is also another form, called the *left Cauchy-Green tensor* $\tilde{\underline{\underline{v}}}$ which transforms like a second-rank tensor in target space but is a scalar in reference space. Since the nematic order parameter Q also transforms as a second-rank tensor in target space, we really have to couple $\tilde{\underline{\underline{v}}}$ (not $\tilde{\underline{\underline{u}}}$) to Q. Thus for the coupling term we choose

$$\begin{aligned} f_C &= -sTr\underline{\underline{u}}TrQ^2 - 2tTr\tilde{\underline{\underline{v}}}Q \\ \tilde{v}_{ij} &= v_{ij} - \tfrac{1}{3}\delta_{ij} v_{kk} \end{aligned} \tag{3.4}$$

The quadratic terms in the full free energy density then read

$$\begin{aligned} f_{quadratic} &= \mu Tr\tilde{\underline{\underline{u}}}^2 + \tfrac{1}{2} r_Q Q^2 - 2tTr\tilde{\underline{\underline{v}}}Q \\ &= \mu Tr\tilde{\underline{\underline{u}}}^2 + \tfrac{1}{3} r_Q S^2 - \tfrac{4}{3} tS\sqrt{\tfrac{3}{2} Tr\tilde{\underline{\underline{u}}}^2} \\ &= \frac{1}{3}\left(S - \frac{2t}{r_Q}\sqrt{\tfrac{3}{2} Tr\tilde{\underline{\underline{u}}}^2}\right)^2 + \left(\mu - \frac{2t^2}{r_Q}\right) Tr\tilde{\underline{\underline{u}}}^2 \end{aligned} \tag{3.5}$$

where we have used the fact that the nematic order parameter Q can be expressed, in the uniaxial nematic state, by $Q_{ij} = S\left(n_i n_j - \frac{1}{3}\delta_{ij}\right)$, where $\vec{n}$ denotes the unit vector along the preferred axis.

To realize what effect the inclusion of the nematic order has on the elastic properties of the system, we must integrate out the nematic order such that we have an effective theory expressed

exclusively in terms of the elastic strain. "Integrating out" means that we do a Hubbard-Stratonovich transformation on S and integrate over the resulting Gaussian term on $\exp\left(\beta\int dV\ f\right)$. This enforces $S=(2t/r_Q)\sqrt{(3/2)Tr\underline{\underline{u}}^2}$ and renormalizes the shear modulus $\mu\mapsto\mu'\triangleq\mu-2t^2/r_Q$. In a theory of elasticity not involving coupling to any other piece of physics, μ must always be positive (because $\underline{\underline{u}}=0$ in thermodynamic equilibrium). Now r_Q in the nematic term is proportional to $T-T_{IN}$, where T_{IN} is the IN transition temperature for the *liquid crystal*. Cooling the temperature causes r_Q to decrease, and this decrease provides a mechanism whereby the effective renormalized μ' of the effective theory can also decrease, resulting in a *negative* effective shear modulus! The implications are clear: there is spontaneous symmetry breaking since now the global minimum of f is no longer at $\underline{\underline{u}}=0$ but at $\underline{\underline{u}}\neq 0$.

Now if we take fluctuations about the equilibrium state into account, we can derive that the corresponding change in f_{el-Q} takes the form

$$\begin{aligned}\delta f_{el-Q}&=\frac{1}{2}B\left(Tr\delta\underline{\underline{u}}-(4s/3B)S\delta S\right)^2+\mu\left(\delta v_0-(t/\mu)\sqrt{2/3}\delta S\right)^2\\&+\mu\sum_{\alpha=1}^{4}\left(v_\alpha-(t/\mu)Q_\alpha\right)^2+\frac{1}{2}A_1\left(\delta S\right)^2+\frac{1}{2}A_2\left(Q_1^2+Q_2^2\right)\end{aligned}\tag{3.6}$$

$O(2)$ rotational invariance of f_Q in *target space* means that terms in $Q_3^2\sim Q_{xz}^2, Q_4^2\sim Q_{yz}^2$ are absent in the nematic state. This is analogous to the case in quantum electrodynamics, where $U(1)$ gauge invariance forbids the photon fields from gaining a mass. Integrating out the "massive" modes $\delta S, Q_1, Q_2$ we get that the resulting free energy in terms of $\delta\underline{\underline{v}}$ (which is a scalar in reference space but a rank-two tensor in target space) takes the form

$$\begin{aligned}\delta f_v&=\frac{1}{2}B_1(\delta v_{zz})^2+B_2\delta v_{zz}(\delta v_{xx}+\delta v_{yy})+\frac{1}{2}B_3(\delta v_{xx}+\delta v_{yy})^2\\&+B_4(\delta v_{xx}^2+\delta v_{yy}^2+2\delta v_{xy}^2)+2\mu\left((\delta v_{xz}-(t/\mu)Q_{xz})^2+(\delta v_{yz}-(t/\mu)Q_{yz})^2\right)\end{aligned}\tag{3.7}$$

Again, $O(2)$ rotational invariance in target space means that the terms Q_{xz}, Q_{yz} have to be absent, they must be integrated out. But integrating over these variables also causes v_{xz}, v_{yz} to vanish, so the free energy takes the same form as that of a uniaxial elastic solid (cf. Eq. (2.5)), but with the elastic modulus C_5 missing. These "missing" terms correspond to "Goldstone modes" resulting from spontaneous reduction of the $O(3)$ symmetry group to $O(2)$. In particle physics an example of Goldstone particles would be the massless pions that emerge from the breaking of $SU(2)\times SU(2)\mapsto SU(2)$. In elasticity theory, the analogue of mass is shear modulus. We check that the counting of Goldstone modes does give the right number of missing degrees of freedom: the dimension of the matrix representation of the rotation group $O(N)$,

$\dim(O(N)) = N(N-1)/2 \Rightarrow \dim(O(3)) - \dim(O(2)) = 3-1 = 2$. As in high energy physics where Goldstone modes point to certain directions ("flat valleys") where a translation would not cost any energy, so here we have that our Goldstone modes correspond to energy-cost free shear directions in the *x*-*y* and *x*-*z* planes.

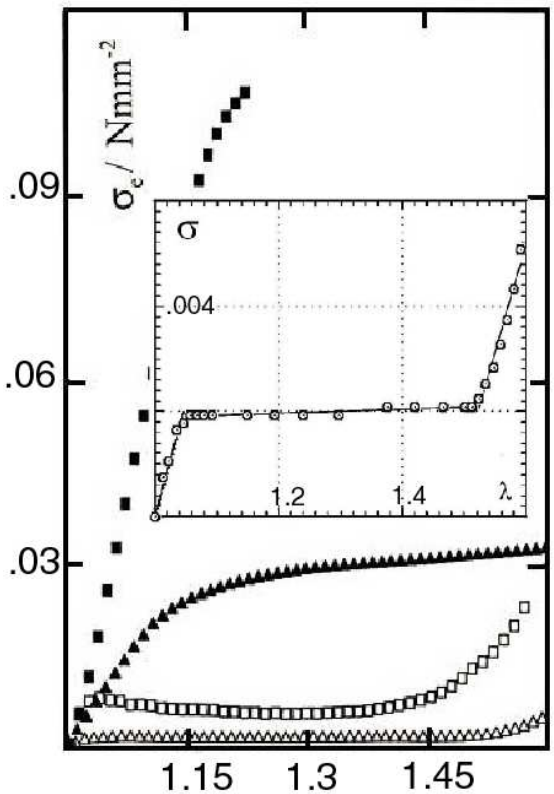

Fig. 3: Stress-deformation data of Kuepfer and Finkelmann (1994) for a series of elastomers with the same composition and crosslinking density, but varying in preparation history. Note the flat plateau in the stress-strain curve, indicating the presence of soft elasticity.

The IN transition has also been experimentally observed for *e.g.* nematic nanotube gels, see "Nematic nanotube gels," Islam MF, Alsayed AM, Dogic Z, Zhang J, Lubensky TC, Yodh AG, Phys. Rev. Lett. 92 (8): 2004.

The Order of the IN Transition in Nematic Elastomers

We have already seen how the IN transition in nematic liquid crystals is first order. Thus if we naively think that nematic elastomers are merely nematic liquid crystals embedded in rubber, and nothing more, then we would expect the IN transition for elastomers to be first order too, but this is not what is observed in experiment. Experiments and simulations (Lebar *et al*, 2005; Selinger, Jeon and Ratna, 2002; Selinger and Ratna, 2004) have shown that in the case of elastomers the transition is either continuous or a rapid nonsingular cross-over from the nematic to the isotropic phase. Thus the problem is to explain why we get a smooth transition for elastomers whereas we had a first-order transition for conventional liquid crystals. There are two possible explanations, to which we now turn.

The first explanation was due to de Gennes (1975). For a stress applied to an elastomer below a critical value, the nematic order parameter of an elastomer has a first-order discontinuity. As we increase the stress the size of the discontinuity decreases, until at the critical value itself there is no discontinuity and the elastomer evolves smoothly from the disordered to the ordered phase. The

stress can arise from both external application and internal stress caused by cross-linking the elastomer in the nematic phase, which fixes an orientational order on the distribution of cross-links. So we are assuming that such stresses have already put the elastomer in a "supercritical" state.

On the other hand, we can have quenched disorder present in the form of chemical heterogeneity of the elastomer. This means that chemical bonds used to cross-link the polymer strands in the elastomer are randomly distributed, and also, there could be impurities and defects arising from the less-than-perfect way the sample was prepared. There is a theorem due to Imry and Wortis (1979), that says that weak random-bond disorder would reduce the first-order discontinuity in a transition and increasing the disorder would completely get rid of the discontinuity. Model simulations done by Selinger, Jeon and Ratna (2002), Selinger and Ratna (2004) have indicated that this is a plausible mechanism for generating the smooth transition. Freezing the orientation of the chemical crosslinks by linking them to several tethered chains would constrain their orientational freedom, forcing the surrounding mesogens to be parallel to the long axis of the crosslinks. According to Fridrikh and Terentjev (1999), every crosslink adds an energy $\sim \frac{1}{2} g\vec{k}\cdot Q\cdot\vec{k}$ to the Hamiltonian, where g measures the coupling strength between the crosslink and the surrounding mesogens, and $\vec{k}$ measures the local orientation of the crosslink. The form of the term is determined by the quadrupolar symmetry of the problem.

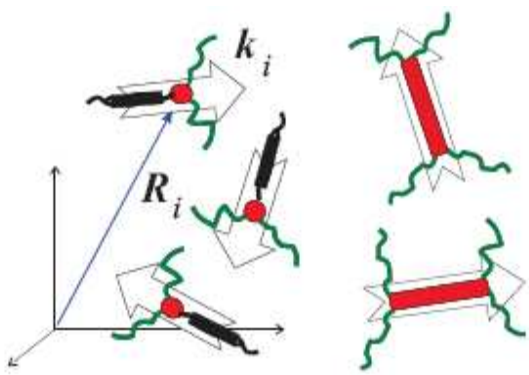

Fig. 4: Schematic representation of how crosslinks provide easy anisotropy axes $\{\vec{k}\}$. The nematic director is forced to be aligned, in the vicinity of the crosslink, with the axes, represented by the arrows. The orientation of $\{\vec{k}\}$ and the positions of the crosslinks $\{R_i\}$ are random. The crosslinks are constrained by the network topology, so they contribute quenched disorder to the nematic system. From Fridrikh and Terentjev (1999).

Introducing a continuum crosslink density $\rho\left(\vec{r}\right)=\sum_x \delta\left(\vec{r}-\vec{r}_x\right)$ and writing $\vec{k}=k\cdot\vec{n}$, where $\vec{n}$ denotes the direction where a crosslink is pointing locally, we have the *random field* contribution to the nematic free energy

$$f_{random-field} = -\int \tfrac{1}{2} gQ\rho\left(\vec{r}\right)\left(k\cdot\vec{n}\right)^2 d^3\vec{r} \tag{3.8}$$

Here both $\rho\left(\vec{r}\right)$ and $\vec{n}$ are randomly quenched variables, so if the crosslinks are uniformly distributed in space we have that $\rho\left(\vec{r}\right)$ follows a Gaussian distribution,

$$P\left[\rho\left(\vec{r}\right)\right] \sim \exp\left(-\int d^3\vec{r}\,\frac{(\rho-\rho_0)^2}{2\rho_0}\right) \tag{3.9}$$

with ρ_0 being the average density of impurities, proportional to the density of crosslinks. Since we are looking for results that do not depend on the specific distribution of $\rho(\vec{r})$ as it cannot be experimentally controlled, we have to average the free energy over the random distribution of $\rho(\vec{r})$. The way to do this is to use the replica trick, originally defined in the context of spin glass problems. Launching into this calculation (which has been done by Petridis and Terentjev, 2006) would bring us too far afield; however, we note the result that when replicas are taken into account, the Landau-de Gennes free energy gets (for small S (~ Q) and weak disorder) singularly renormalized to

$$f \approx \frac{1}{3} r_Q S^2 - \frac{2}{9} w_3 S^3 + \frac{4}{9} w_4 S^4 + \frac{3 g k_B T}{8\pi^2 (\kappa \beta a^2)^3} S^{-4} \tag{3.10}$$

where a is a small distance cut-off which is of the order of a monomer length and $\kappa \sim k_B T / a$ is the Frank elastic constant deep inside the nematic phase. We see that as the strength of the disorder g increases, the singular contribution in S^{-4} increases, and the discontinuity in S at the IN transition decreases and vanishes above a certain critical value, thus giving rise to a continuous phase transition. Figs. 5 and 6 offer us an easy way to visualize the progressive change in the transition as g is increased.

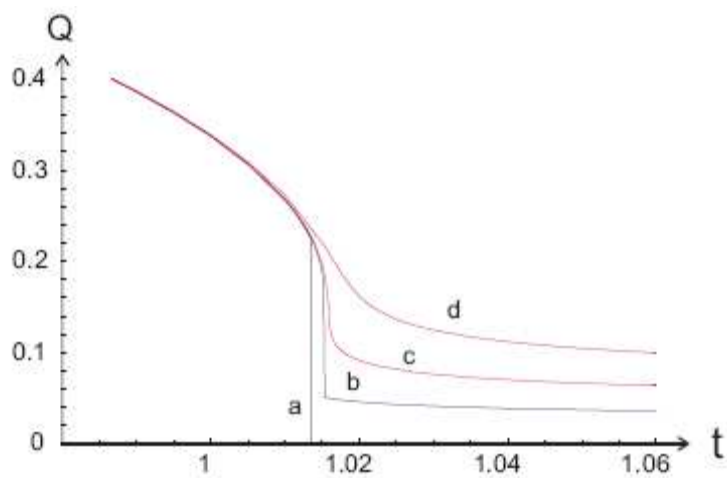

Fig. 5: The equilibrium order parameter $Q = 2S/3$ as a function of reduced temperature $t = T/T^*$ for a range of different disorder strength g. (a) is the first order transition for a system with no disorder (b) is a subcritical system (c) is a critical system (d) is a supercritical system. As the disorder strength increases the discontinuity gets smaller and eventually disappears.

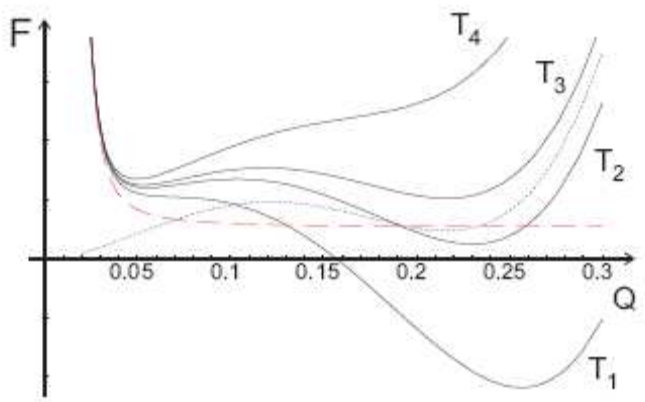

Fig. 6: Free energy against order parameter plots for a subcritical system for a range of temperatures, $T_1 < T_2 < T_3 < T_4$. The dotted line represents the Landau energy and the dashed line represents the disorder energy for $T = T_3$. We can see that the high-Q (high-S) minimum is due exclusively to the Landau energy, while the low-Q (low-S) minimum arises from competition between the S^2 term and the disorder term.

Conclusion

We round off our essay with a summary of what we have discussed. We have seen how nematic order and the elastic medium influence each other reciprocally. On the one hand, the presence of nematic order renormalizes the Lame constant μ in the *nematic-averaged effective strain-elastic free energy*, causing it to become temperature dependent and hence offering a possibility where the uniaxial state of the elastic medium could be stabilized. Since the symmetry is reduced, Goldstone's theorem tells us that there are certain "massless" degrees of freedom manifesting themselves as directions of soft elasticity. On the other hand, the presence of quenched disorder in the random distribution of network crosslinks and impurities gives rise to a singular renormalized contribution to the *disorder-averaged effective nematic free energy*, which is proportional to the strength of disorder, and increasing that disorder strength results in a continuous IN transition. Along the way, we have seen how symmetry plays a crucial role in determining the form of free energies and cause certain terms to be absent. We have exploited analogies with particle physics whenever possible, to aid clarity.

These considerations can also be extended to other classes of liquid crystal elastomers, *e.g.* smectics and columnar phases.

Acknowledgments

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Appendix

Let us consider whether the form (2.3) for our nonlinear free energy is reasonable, since this is a mathematically subtle point. There are no terms linear in $\underline{\underline{u}}$ because the reference state relative to

which $\underline{\underline{u}}$ is defined is always assumed to be in mechanical equilibrium, so imposing the condition $f'(\underline{\underline{u}})=0$ eliminates the linear term. There are no terms in $Tr\underline{\underline{u}}^3, Tr\underline{\underline{u}}^4, \left(Tr\underline{\underline{u}}\right)^2 Tr\underline{\underline{u}}^2, Tr\underline{\underline{u}}Tr\underline{\underline{u}}^3$ as they are of higher order than $\left(Tr\underline{\underline{u}}^2\right)^2$. To see this, assume the system is incompressible, described by the tensor Λ, $\underline{\underline{u}}=\frac{1}{2}\left(\Lambda^T\Lambda-\delta\right)=diag\left(\lambda^2-1,\lambda^{-1}-1,\lambda^{-1}-1\right)$, λ here being the eigenvalues of the deformation tensor Λ describing compression for the principal axis which has $\lambda<1$ and extension for the principal axis that has $\lambda>1$. Imagine that we are doing a small deformation, perturbing $\lambda=1+\delta+\delta^2$ for δ small. So $\underline{\underline{u}}\approx diag\left(2\delta+3\delta^2,-\delta,-\delta\right)$, and if we plug this in to $\left(Tr\underline{\underline{u}}^2\right)^2$ we see it is quartic order in δ, but (*e.g.*) $Tr\underline{\underline{u}}Tr\underline{\underline{u}}^3$ is of quintic order and so we ignore it. One other question could be: why are there apparently no terms in $Tr\underline{\underline{u}}^4$? There is a result from linear algebra (see *e.g.* Ogden, 1984), in three dimensions only $Tr\underline{\underline{u}}, Tr\underline{\underline{u}}^2, Tr\underline{\underline{u}}^3$ are linearly independent, and all other $Tr\underline{\underline{u}}^N$ for $N > 3$ can be expressed in terms of these three lower order invariants.

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