From Vulcanization to Isotropic and Nematic Rubber Elasticity

Xiangjun Xing,1 Swagatam Mukhopadhyay,1 Paul M. Goldbart1 and Annette Zippelius2

1 Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, U.S.A.
2 Institut für Theoretische Physik, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37073 Göttingen, Germany

PACS. 82.70.Gg – Gels and sols.
PACS. 61.41.+e – Polymers, elastomers, and plastics.
PACS. 62.20.Dc – Elasticity, elastic constants.

Abstract. – A Landau theory is constructed for the vulcanization transition in cross-linked polymer systems with spontaneous nematic ordering. The neo-classical theory of the elasticity of nematic elastomers is derived via the minimization of this Landau free energy; this neo-classical theory contains the classical theory of rubber elasticity as its isotropic limit. Our work not only reveals the statistical-mechanical roots of these elasticity theories, but also demonstrates that they are applicable to a wide class of random solids. It also constitutes a starting-point for the investigation of sample-to-sample fluctuations in various forms of vulcanized matter.

The classical theory of rubber elasticity [1] has been remarkably successful. A blend of phenomenology and molecular-level reasoning, it is based on a few simple assumptions, and bears great predictive and descriptive power. By modeling rubbery materials (i.e. elastomers) as incompressible networks of entropic Gaussian chains, it gives their elastic free energy density \( f \) at temperature \( T \) as

\[
f = \frac{\mu}{2} \text{Tr} \Lambda^T \Lambda,
\]

for all uniform deformations \( \mathbf{r} \rightarrow \Lambda \cdot \mathbf{r} \) that conserve the volume (i.e. \( \det \Lambda = 1 \)). For most rubber-like materials the assumption of incompressibility is well satisfied.\(^1\) The shear modulus \( \mu \) is given by \( n_c T \), where the constant \( n_c \) is usually referred as “the density of effective chains in the network.” The classical theory [i.e. Eq. (1) and associated arguments] explain many essential features of rubbery materials, such as their stress-strain curves (at least for deformations that are not too large), and the striking temperature dependence of their shear moduli, as well as their strain-birefringence (i.e. the stress-optical effect).

\(^1\)This assumption may break down for swollen rubbers and gels. In this case, a finite-compressibility version of Eq. (1) remains valid. In fact, this is what we will derive in the paper.

© EDP Sciences
There are several important issues unresolved by the classical theory. First, for a given cross-link density, the shear modulus is not calculated within the theory.\(^2\) Second, in the intermediate-strain range there is universal and significant downward deviation of the experimental stress-strain curve, compared with the theoretical prediction. Finally, the issue of polymer entanglement is not addressed by the classical theory.

Subsequent efforts to improve the classical theory of rubber elasticity have focused on various directions (for one overview see Ref. \([2]\)). The non-Gaussian nature of the chain statistics, due to the finite extensibility of the polymers, has been taken into account, and explains the large-deformation behavior of the stress-strain curve. Purely mathematical modeling, as in the theories due to Mooney, Rivlin and others (see, e.g., Ref. \([1]\)), also provided useful insight. At the microscopic level, the effects of chain entanglement have long been emphasized and modeled via various approximation schemes, most notably by the Edwards tube model \([4]\) and its derivatives, although results from these models are often either inconclusive or contradictory. It seems fair to say that none of these efforts is as successful as the classical theory, either in terms of simplicity of assumptions, or in terms of broad descriptive power.

Recently, a simple anisotropic generalization of the classical model \([5, 6]\), known as the neo-classical model, was constructed to describe the highly unusual elasticity of nematic elastomers, i.e., rubbery materials with (spontaneously) broken rotational symmetry, and has done so with great success. In the presence of nematic order, the “step-length tensor” \(l\) characterizing the conformations of the polymer chains is anisotropic. Then, according to the neo-classical model, the elastic free energy of a nematic elastomer with deformation \(\Lambda\) is given by

\[
 f = \frac{\mu}{2} \text{Tr} l_0 \Lambda^T \Lambda^{-1} \Lambda, \tag{2}
\]

where \(l_0\) and \(l\) are the (in general anisotropic) step-length tensors in the initial and deformed states, and are functions of the nematic order parameter tensors \(Q^0\) and \(Q\) in these two states, respectively. A remarkable feature of Eq. (2) is that for a given \(l_0\) and \(l\) there exists a continuous manifold of deformations \(\Lambda\) that cost zero elastic free energy. These novel soft modes \([7, 8]\), as well as the thermal and quenched fluctuations associated with them, have been the focus of intensive study, both experimentally (see, e.g., Ref. \([6]\)) and theoretically \([6, 9, 10]\).

In a classic paper, Deam and Edward \([11]\) initiated a statistical-mechanical approach to the study of rubber elasticity that incorporates both thermal and quenched fluctuations, along with repulsive interactions. This replica-based approach, which has been called “vulcanization theory” (VT) \([12, 13]\), has been explored in great detail. Progresses in this direction includes, \(\text{inter alia:}\) (i) the calculation of the mean-field order parameter \([12]\); (ii) the derivation of a universal Landau theory \([14]\); (iii) the development of connections with percolation theory \([15]\); and (iv) the analysis of critical scaling for shear modulus \([16]\). A main virtue of VT is that it follows the Landau paradigm of modern condensed matter physics, inasmuch as it concentrates on order parameters, symmetries and length-scales. In particular, because of its independence on microscopic details, we view the Landau theory of the vulcanization transition as the right theory if one wishes to address the long length-scale physics of rubbery materials, especially near the vulcanization transition.

The aim of the present work is to establish connections between VT and the classical—as well as the neo-classical—elasticity of isotropic and nematic elastomers. We begin this task by generalizing the Landau theory for the vulcanization transition to systems with spontaneous

\(^2\)We remind the reader that the classical theory was developed before percolation theory was. Therefore, how an infinite network emerges during the random cross-linking process was not understood. In fact, near the vulcanization point, the “effective chains” of the classical theory bear little resemblance to the original polymer chains before cross-linking.
nematic ordering. As a saddle-point approximation to this theory, we derive the neo-classical model (2) for the elasticity of nematic elastomers. In the isotropic limit, this result reduces to the classical theory of rubber elasticity (1). Our work not only reveals the statistical-mechanical roots of these elasticity theories, but also demonstrates that they are applicable to a wide class of random solids. It also constitutes a starting-point for the investigation of sample-to-sample fluctuations in various forms of vulcanized matter.

We begin with the real-space version of the order parameter for the replica field theory of the VT [12,14,16,17] in d dimensions, which is a function of (1+n) d-vectors \( \hat{\delta} = (x^0, \ldots, x^n) \):

\[
\Omega(\hat{\delta}) = \sum_{j=1}^{N} \left( \prod_{\alpha=0}^{n} \delta(x^\alpha - c_\alpha^j) \right)_{1+n} - \frac{N}{V_0 V^n}.
\] (3)

Here, \( c_\alpha^j \) (with \( \alpha = 0, 1, \ldots, n \)) are the 1+n replicas of the position d-vectors of the N monomers (with \( j = 1, \ldots, N \)) that comprise the system. \( V_0 \) is the volume of the system in the preparation state, and \( V \) is the volume of the system in the measurement state (which may differ from \( V_0 \)). The brackets \( \langle \cdots \rangle_{1+n} \) denotes an average over the replica field theory given below. Up to a constant, the order parameter of VT gives the conditional probability distribution for the chain in the isotropic state. In the absence of any externally imposed deformation, the values of the order parameter should be such that they minimize the Landau free energy. For simplicity, we consider the case of equal pressures and bulk moduli in the preparation and measurement ensembles (i.e. \( p_0 = p \) and \( B_0 = B \)). Near the vulcanization transition, where the order parameter \( \Omega \) is small, this leads to 

\[
\frac{1}{2} B \Omega^2 = V^2 = B N^2 / 2 p,
\]

in the absence of deformation. The control parameter \( r \) triggers the transitions to the solid phase when it becomes negative (i.e. when the density of cross-links exceeds some critical value). This model has been analyzed extensively, both within and beyond the mean-field level(3). Last but not least,

(3) In the early literature, the model was usually expressed in momentum space rather than of real space. Furthermore, the one-replica sector of \( \Omega \) was excluded explicitly, which amounts to setting \( B_0 \) and \( B \) to infinity in Eq. (5). The asymmetry between the preparation and measurement ensembles, and its consequences, have been stressed only recently [16, 18].
we note that the order parameter \( \Omega(\hat{x}) \) of this Landau theory is a single-monomer quantity (albeit replicated). The original polymer degrees of freedom are integrated out in deriving the Landau theory and, consequently, the issue of topological entanglement becomes irrelevant in this theory. It is our belief that inclusion of entanglement in the original theory would simply lead to a quantitative modification of the parameters in the Landau theory Eq. (5), not an invalidation of the theory itself.

There are various ways to incorporate nematic ordering into VT. The simplest is to couple the VT order parameter \( \Omega \) to the replicated symmetric traceless tensor fields \( Q^\alpha \) (with \( \alpha = 0, 1, \ldots, n \)). Of these, \( Q^0 \) describes the nematic order in the preparation ensemble, whereas \( Q^\alpha \) (for \( \alpha = 1, \ldots, n \)) describe nematic order in the (\( n \)-fold replicated) measurement ensemble. The resulting free energy must be invariant under the simultaneous rotation of \( Q^\alpha \) and the spatial position vectors \( x^\alpha \), independently for each replica \( \alpha \). The lowest-order coupling (in \( Q \) and gradients) allowed by symmetry is

\[
H_{\Omega Q} = \int d\bar{x} \left( \frac{1}{2} \eta_0 Q^{0}_{ab} \nabla_a \nabla_b \Omega + \frac{1}{2} \eta \sum_{\alpha=1}^n Q^\alpha_{ab} \nabla_a \nabla_b \Omega \right),
\]

where \( \nabla_a \) indicates a derivative with respect to the \( a \)th cartesian component of the \( a \)th replicated position vector. The signs of the coupling constants \( \eta_0 \) and \( \eta \) depend on details of the chemical structure of nematic polymers under consideration. In a separate publication [19] we shall derive Eq. (6) from a lower-level description.

The total free energy should also be augmented by a part that depends only on \( Q^\alpha \), and accounts for the nematic interactions between neighboring (anisotropic) monomers. It is known, however, that the nematic energy-scale (roughly \( k_B T \) per monomer) is orders of magnitude larger than the energy-scale for the vulcanization transition (roughly \( k_B T \) per chain). Therefore, we may neglect the feedback of the \( \Omega \) ordering on the nematic order, and thus may treat \( Q^\alpha \) as given. More specifically, at the mean-field level, and under the assumption of that there is neither replica nor macroscopic translational symmetry breaking, we may set both \( Q^0 \) and \( Q^\alpha \) (\( \equiv Q \) for \( \alpha = 1, \ldots, n \)) to be constants, characterizing the uniform nematic order in both the preparation and measurement states. Additionally, large and positive values for \( B_0 \) and \( B \) guarantee that the saddle-point value of \( \Omega \) vanishes in the one-replica sector, i.e. Eq. (6) vanishes at the saddle point. By minimizing the total free energy over the VT order parameter \( \Omega \), we find the saddle-point equation

\[
0 = -l^{0}_{ab} \nabla_a \nabla_b \Omega - \sum_{\alpha=1}^n l_{ab} \nabla_a \nabla_b \Omega + r \Omega - \frac{1}{2} \Omega^2.
\]

As they stand, the tensors \( l_0 \) and \( l \) are short-hand for

\[
l^{0}_{ab} \equiv K_0 \delta_{ab} + \eta_0 Q^{0}_{ab}, \quad l_{ab} \equiv K \delta_{ab} + \eta Q_{ab}.
\]

However, as we shall see below, they are in fact the effective step-length tensors in the preparation and measurement ensembles that appear in the neo-classical elastic free energy, Eq. (2).

In the absence of any externally imposed deformation, the saddle-point equation (7) is solved by the following Ansatz(4):

\[
\bar{\Omega}(\hat{x}) = q \int dz \left\{ \int d\tau \frac{p(\tau)}{N(\tau)} \exp \left[ -\frac{\tau}{2} \left( \bar{y}^0 \cdot \bar{1}^{-1} \cdot \bar{y}^0 + \sum_{\alpha=1}^n \bar{y}^\alpha \cdot \bar{1}^{-1} \cdot \bar{y}^\alpha \right) \right] - \frac{1}{\sqrt{1+n}} \right\} (9a)
\]

\[
\bar{y}^0 \equiv x^0 - z, \quad \bar{y}^\alpha \equiv x^\alpha - z, \quad N(\tau) \equiv (\pi/\tau)^{(1+n)l/d} (\det \bar{1})^{1/2} (\det l)^{1/2}, \quad (9b)
\]

(4)A very similar Ansatz in real space has been used in Reference [18] for the isotropic case.
where the $d$-dimensional vector $\mathbf{z}$ is integrated over the interior of system $V_0$ in the preparation state. Obviously, if both the preparation state and the measurement state are isotropic (i.e. $Q^0 = Q = 0$ and $l_0 \propto 1 \propto I$, the above saddle-point Ansatz reduces to the earlier form appropriate to isotropic systems [12], with $p(\tau)$ the so-called distribution of inverse square localization lengths. The interpretation of this saddle point is as follows. A certain fraction of the monomers ($q$ per unit volume) belong to the infinite cluster (i.e. the gel fraction) and are localized. Such a monomer fluctuates around the point $\mathbf{z}$ with Gaussian variance-matrix $\tau^{-1} l_0$ in the preparation ensemble (i.e. the $0^{th}$ replica) and fluctuates around the same point $\mathbf{z}(\alpha)$ with variance-matrix $\tau^{-1} I$ in the measurement ensemble (i.e. replicas 1 to $n$). From Eq. (5) it is easy to see that the role of non-vanishing nematic order is to confer anisotropy on these fluctuations. Finally, because of the random nature of elastomers, there is a continuous distribution $p(\tau)$ of scales $\tau$.

In the gel phase (i.e. $r < 0$), we find that Eq. (9a) solves Eq. (7) provided that

$$q = 2|r|,$$

and that $p(\tau)$ satisfies the following integro-differential equation:

$$\frac{\tau^2}{2} \rho'(\tau) = \left( \frac{|r|}{4v} - \tau \right) p(\tau) - \frac{|r|}{4v} \int_0^\tau p(\tau') p(\tau - \tau') d\tau'.$$

Equations (10) and (11) are identical to those found for the isotropic case of VT [12]. The stability of this nematic saddle point can also be established in a way similar to the isotropic case (see Ref. [20]).

We now come to the main point of this Letter: obtaining the elastic free energy of isotropic and nematic random solids. To do this, we shall impose an arbitrary homogeneous deformation of the boundary of the system, which we encode in the matrix $\Lambda$ and illustrate in Fig. 1. We shall not make any assumptions about how the interior of the system changes in response to this deformation. Our aim is to determine the new saddle point $\Omega_\Lambda$ that minimises the free energy and is consistent with the deformation of the system. (We explain this consistency further, below.) We proceed by hypothesizing a modification of the original saddle-point solution (9a):

$$y^\alpha = x^\alpha - \mathbf{z} \rightarrow x^\alpha - \Lambda \cdot \mathbf{z} \quad (\alpha = 1, \ldots, n),$$

$$\frac{1}{V_0^{1+n}} \rightarrow \frac{1}{V_0 V_n}.$$  \hspace{1cm} (12a)

In general, $\det \Lambda (= V/V_0)$ may differ from unity, corresponding to a change in system volume. By substituting this modified Ansatz into Eq. (7), we find that the Ansatz is indeed a solution, provided $p(\tau)$ is the same distribution as defined by Eq. (11) (in the limit $n \to 0$).

\footnote{This automatically ensures that the measurement ensemble has the same volume as the preparation ensemble, i.e. $V = V_0$.}
The interpretation of this saddle point is as follows. After the deformation, the same fraction of the monomers (i.e. \( q \) per unit volume) are localized. In the preparation ensemble, a localized monomer continues to exhibit Gaussian fluctuations around the point \( z \) with an unchanged variance-matrix \( \tau^{-1} l_0 \). However, in the measurement ensemble it fluctuates around the new point \( \Lambda \cdot z \) but with the original variance-matrix \( \tau^{-1} l_0 \). This implies that the average position of each monomer, parametrized by \( z \), is deformed affinely, whereas the fluctuations around \( z \) remain intact (6). Note that \( z \), as well as \( x^0 \), are confined to the volume of the preparation ensemble (i.e. the range over which \( z \) is integrated; see Fig. 1). Observe, furthermore, that \( \bar{\Omega} \Lambda \) vanishes whenever \( x^\alpha \) and \( \Lambda \cdot x^0 \) are widely separated (for any \( \alpha = 1, \ldots, n \)). It follows that the \( x^\alpha \) are confined to the preparation ensemble transformed by the distortion \( \Lambda \) (i.e. the measurement ensemble), and this establishes that \( \Lambda \) is the homogeneous deformation imposed on the boundary of the system (see Fig. 1). (7) As we shall show in a forthcoming paper [22], the affine character of the deformation is destroyed by the fluctuations of nematic order \( Q^0 \) in the preparation ensemble that become frozen in at the time of cross-linking.

We now calculate the elastic free energy density of nematic elastomers \( f_{el}(\Lambda) \) at the mean-field level. To do this, we insert the deformed saddle point (9a), modified according to Eqs. (12), into the total free energy density (5), and subtract its value for the undeformed (\( \Lambda = I \)) saddle point. Then, dividing appropriately by \( n \) (recall that there are \( n \) replicas of the measurement ensemble), and taking the replica limit \( n \to 0 \), we find

\[
\begin{align*}
    f_{el}(\Lambda) &= \lim_{n \to 0} \frac{1}{n^2} (H[\bar{\Omega} \Lambda] - H[\bar{\Omega}]) \\
    &= \mu \text{Tr} l_0 A^T l^{-1} A + \frac{1}{2} \text{det} \Lambda \tilde{B} (\text{det} \Lambda - 1)^2, \\
    \mu &\equiv \frac{4}{3} |r|^3, \quad \tilde{B} \equiv B_0 \rho_0^2.
\end{align*}
\]

It is clear that the first term in Eq. (13a) coincides with the free energy density of the neo-classical theory of nematic elastomers, Eq. (2); the second term describes the energy cost for volume changes, with the bulk modulus \( \tilde{B} \) related to the parameter \( B_0 \), Eq. (13b). Consequently, what we have derived, Eqs. (13), is the neo-classical elasticity model of nematic elastomers, in fact generalized to finite bulk modulus systems. In the limit \( \tilde{B} \to \infty \), the incompressibility constraint \( \text{det} \Lambda = 1 \) is restored. Furthermore, if \( Q^0 \equiv Q = 0 \) we have \( l_0 \propto 1 \propto I \), and our result trivially reduces to the classical theory of rubber elasticity, Eq. (11). Finally, that the shear modulus, Eq. (13b), scales as \( |r|^3 \) is a mean-field result and has also been derived via other methods [21, 23].

We emphasize that Eq. (13a) is derived from the Landau theory of VT, which includes the the most relevant contributions. Therefore it is independent of short-distance details, and thus provides a universal mean-field description for the elasticity of all forms of vulcanized matter near the vulcanization point, provided that the corresponding transition is described by the Landau theory. This observation may explain, in part, the huge success of the classical theory of rubber elasticity, Eq. (1), and its anisotropic generalization, the neo-classical theory, Eq. (2).

The present work also constitutes a starting point for studying spatial fluctuations, both thermal and quenched, in vulcanized matter of various forms [24].
vulcanization point, critical fluctuations of the VT order parameter field $\Omega$ become important, and change qualitatively the scaling of $\mu$. (This issue was recently addressed; see Ref. [16].) Nevertheless, the form of the elasticity theory continues to hold, upon the incorporation of critical fluctuations. On the other hand, fluctuations of $Q_0$ in the preparation ensemble—which may be strong at short length-scales even deep in the isotropic phase—would provide a source for quenched random stresses in the random solid state, and these would couple directly to strain. Consequently, quenched-in fluctuations in $Q_0$, and their alignment by external stress, may change the elasticity qualitatively, and are likely to be responsible for the universal deviation of the stress-strain curves from the classical theory, observed for half a century. This issue will be explored in forthcoming work [22].

***

We thank T. C. Lubensky for stimulating discussions. This work was supported in part by grants NSF DMR02-05858 (XX, SM) and DOE DEFG02-91ER45439 (XX, PMG), and the Deutsche Forschungsgemeinschaft through SFB 602 (AZ) and Grant No. Zi 209/6-1 (AZ).

REFERENCES

[1] L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, Oxford, 1975).
[2] See, e.g., P. M. Goldbart and N. Goldenfeld, in Ref. [3], Chap. 17, and references therein.
[3] P. M. Goldbart, N. Goldenfeld and D. Sherrington, *Stealing the Gold – A Celebration of the Pioneering Physics of Sam Edwards* (Oxford University Press, 2005).
[4] S. F. Edwards and T. A. Vilgis, Rep. Prog. Phys. 51, 243-297 (1988).
[5] M. Warner and E. M. Terentjev, Prog. Polym. Sci. 21, 853 (1996).
[6] M. Warner and E. M. Terentjev, *Liquid Crystal Elastomers*, (Oxford University Press, 2003).
[7] L. Golubovic and T. C. Lubensky, Phys. Rev. Lett. 63, 1082(1989).
[8] P. D. Olmsted, J. Phys. II (France) 4, 2215(1994)
[9] O. Stenull and T. C. Lubensky, Europhys. Lett. 61, 776 (2003); Phys. Rev. E 69, 021807(2004).
[10] X. Xing and L. Radzihovsky, Europhys. Lett. 61, 769 (2003); Phys. Rev. Lett. 90, 166301(2003).
[11] R. T. Deam and S. F. Edwards, Phil. Trans. R. Soc. A, 280, 317 (1976).
[12] P. M. Goldbart, H. E. Castillo and A. Zippelius, Adv. Phys. 45, 393 (1996).
[13] P. M. Goldbart, J. Phys. Cond. Matt. 12, 6585 (2000).
[14] W. Peng, H. E. Castillo, P. M. Goldbart and A. Zippelius, Phys. Rev. B 57, 839 (1998); W. Peng and P. M. Goldbart, Phys. Rev. E 61, 3339 (2000).
[15] H.-K. Janssen and O. Stenull, Phys. Rev. E 64, 026119 (2001); W. Peng, P. M. Goldbart and A. J. McKane, Phys. Rev. E 64, 031105 (2001).
[16] X. Xing, S. Mukhopadhyay and P. M. Goldbart, Phys. Rev. Lett. 93, 225701 (2003).
[17] S. Mukhopadhyay, X. Xing and P. M. Goldbart, manuscript in preparation (2004).
[18] K. Broderix, M. Weight, and A. Zippelius, Eur. Phys. J. B 29, 441 (2002).
[19] S. Pfahl, X. Xing, S. Mukhopadhyay, P. M. Goldbart and A. Zippelius, manuscript in preparation (2004).
[20] H. E. Castillo, P. M. Goldbart and A. Zippelius, Phys. Rev. B 60, 14702 (1999).
[21] H. E. Castillo and P. M. Goldbart, Phys. Rev. E 58, R24-27 (1998); Phys. Rev. E 62, 8159 (2000).
[22] X. Xing and P. M. Goldbart, manuscript in preparation (2004).
[23] S. Mukhopadhyay, P. M. Goldbart and A. Zippelius, Europhys. Lett. 67, 49 (2004); P. M. Goldbart, S. Mukhopadhyay and A. Zippelius, Phys. Rev. B 70, 184201 (2004).
[24] For an example of such quenched-in fluctuations in the setting of polymer blends, see C. Wald, A. Zippelius and P. M. Goldbart, *Glassy states and microphase separation in cross-linked homopolymer blends*; cond-mat/0411056.