Vulcanization and the Properties of Rubber

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Abstract

Rubber is composed of long stringlike polymer molecules, which are pinned together at random points by crosslinks. As the density of crosslinks is increased, the molecules get localized and the system undergoes a phase transition from a liquid to an amorphous solid state. The elastic properties of the resulting solid are very different from those of metals, and are primarily due to changes in the entropy of the chains upon stretching. This paper discusses why rubber solidifies, and why the solid has the properties it does.

1 Introduction

The substances known as rubber—natural rubber, gutta-percha, and various synthetic compounds—are amorphous solids composed of long polymers.[1] They vary somewhat in chemical composition, melting point, and so on; however, they have the same elastic properties, and for our purposes the distinctions between various kinds of rubber are unimportant. Pure rubber is a viscous liquid; it solidifies upon *vulcanization*, a chemical reaction between rubber and sulfur that produces cross-links between the polymer chains. The most important elastic properties of vulcanized rubber are the following: (1) it is much more extensible than crystalline solids, (2) it contracts when heated, and gives up heat when stretched.

Rubber becomes less elastic as it is cooled, and at a certain temperature (around $-70°$C for vulcanized rubber) it undergoes a continuous phase transition into a typical brittle glass-like state as the rotational degrees of freedom of the joints freeze out. (Confusingly, the literature sometimes refers to vulcanization as a kind of glass transition. There are in fact two unrelated transitions—from liquid to rubber, upon adding cross-links, which this paper is about; and from either liquid or rubber to a non-rubbery glass, upon cooling, which will not be discussed further.) If it is sufficiently pure, raw natural rubber (i.e. the viscous liquid) crystallizes when held at a temperature below $0°$ C for a long time. Neither of the amorphous solid states can crystallize, at least on the usual timescales, because the disorder in the positions of the chains is frozen in.

The distinctive (and useful) part of the phase diagram is, of course, the vulcanized solid. Its elastic properties are striking, and the physics behind them is quite different from that behind ordinary elasticity. As one might expect in the spirit of Landau theory, this goes together with the fact that the vulcanization transition is an unusual sort of phase transition. Vulcanization lies at the intersection of three areas of statistical physics—polymers, disordered systems, and critical phenomena—and yields important insights into all three. The basic questions a theory of vulcanization must explain are why, and how, a long-chain liquid turns into an amorphous solid; why crosslinking leads to rigidity; and how the usual ideas about spontaneous symmetry breaking are to be applied to systems in which the solid state is amorphous.

Besides, vulcanization is not unique to rubber, but is part of a more general class of transitions, known collectively as sol-gel or gelation transitions. Rubber is closely related to a substance like gelatin, which also consists of long chainlike polymers that crosslink to form an amorphous solid. The essential qualitative difference is that most of these gels are dilute solutions of polymers, while liquid rubber is a polymer melt. The field theoretic treatment of vulcanization extends straightforwardly to other gels;

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[1]This paragraph and the next summarize Chapter 1 of Treloar's book [1].

however, their elastic properties are different from those of rubber, and will not be considered here.

This paper is organized as follows: section 2 introduces relatively simple theories of rubber elasticity (the phantom chain model) and of vulcanization (percolation), and discusses their limitations; section 3 sketches how a Landau theory might be developed and used to derive the theories of section 2; and section 4 discusses extensions of these ideas to other problems in statistical physics. The reason for this arrangement is that the naive theories are substantially easier on the intuition than the Landau theory.

2 The Intuitive Picture

2.1 Entropy and Elasticity

A lot of things about rubber can be explained qualitatively by considering the statistical mechanics of a single chain. There are many more possible configurations with the chain partially stretched than with it fully stretched, so the entropy of the chain increases when it contracts; therefore, heating up the chain makes it contract (because $F = U - TS$, and entropy wins at higher temperatures). Similarly, a stretched polymer gives up heat because stretching reduces entropy, and the heat transfer $Q = T\Delta S$. The restoring force can be calculated from one of various thermodynamic identities, e.g. $f/a = P = T(\partial S/\partial V)_U$. While the statistics of a chain can be calculated exactly, the calculation simplifies if the chain is very far from being fully stretched, in which case one assumes a gaussian distribution of chain extensions.

The *phantom chain model* of Kuhn [1] is a simple extension of this model to deal with crosslinked networks of polymer chains. It treats each "free" segment between cross-links as an independent polymer, and assumes that: (1) stresses do not change the volume of the network (i.e. the bulk modulus is infinite, or at least much larger than the shear modulus), (2) the cross-link locations deform *affinely*,[2] (3) the cross-link locations do not fluctuate, and (4) the entropy of the network is the sum of the entropies of the segments, calculated as if they were free polymers [1].

To see why these assumptions are convenient, we sketch how one might compute the free energy change upon deformation.[3] Suppose we start with a unit cube of rubber, and deform it so that it has sides λ_i such that $\lambda_1\lambda_2\lambda_3 = 1$ (by assumption 1). Consider an individual polymer segment with one end at the origin and the other at (x, y, z). The origin is fixed by the deformation, and the other end goes to $(\lambda_1 x, \lambda_2 y, \lambda_3 z)$ by assumption (4). The entropy of a chain in the gaussian approxima-

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[2]This means that the shear is treated as a linear transformation. For example, a crosslink that's originally at the midpoint of a side moves to the midpoint of the deformed side.

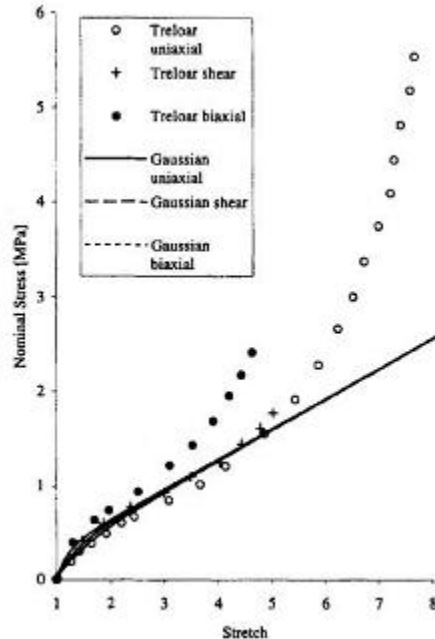[3]This is worked out in Chapter 3 of Treloar's book [1].

Figure 1: Theory vs. Treloar data for various kinds of stress [2]

tion is given by $c - br^2$, where r is the end-to-end length; therefore, we know the change in entropy of each chain, and we can add them all up by (4) to get the total entropy change. This entails some assumptions about where the crosslinks are, but this dependence drops out of the final answer, and we find that $\Delta S = -\frac{1}{2} N k_B (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)$ for the block of rubber. This gives us the free energy change upon deformation, which is $-T\Delta S$ because U is unaffected by the deformation. The restoring force, which is a thermodynamic quantity, is easy to calculate from the free energy.

The experimental data cited in Chapter 4 of Ref. [1] are in good agreement with this model for sufficiently small stresses. Treloar [1] compares the model with experiment for all sorts of shears, compressions, stretches, etc.; a typical plot is shown below. All the plots show two sorts of deviations—at intermediate stresses, explained later in this paper, and at very large stresses, where the gaussian approximation for individual chain statistics breaks down.

An essential feature of this model is that the chains are treated as non-interacting except at the cross-links. The reliability of this assumption obviously depends on the extent to which the chains get in one another's way. An intuitive picture is to think of a polymer as a self-avoiding random walk [3], in which case a polymer chain is a *branched* self-avoiding random walk. The phantom chain model approximates this as an ideal random walk; therefore it should be reliable when such an approximation

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is reliable—which it isn't, in fewer than six dimensions [3]. In practice things are not quite so bad because the two neglected effects—the self-avoiding character of the polymer, which makes it spread out, and the repulsion from the other polymers, which tends to squeeze it into as small a space as possible—cancel out. (This is not true for dilute polymer gels, in which self-avoidance is much stronger than interactions.) To include these effects would require a thoroughgoing field theoretic approach. Before we consider the field theoretic problem, though, let us discuss the vulcanization transition using the more intuitive percolation model.

2.2   Percolation and its Disconents

When does vulcanization take place? A reasonable hypothesis would be that it happens when a network of crosslinks extends over an appreciable fraction of the system size. We know it couldn't happen earlier, because it would take an enmeshing network to keep the crosslinked blobs of size $V' \ll V$ from sliding about. (One can construct special cases for which this isn't true, but it usually is.) This hypothesis reduces vulcanization to a case of *percolation*. A simpler case of percolation is the following: suppose we have a two-dimensional $N \times N$ grid of sites, and draw αN^2 lines at random between nearest-neighbor points. For small α the lines are sparse and isolated; for $\alpha \approx 1$, each point on the grid is connected to every other by many paths. At some critical value of α, there are on average just enough segments to join up and form one large path through the system. The extension to the case of rubber, in which the crosslinks form a network of chains that eventually encompasses the system, is conceptually straightforward.

Percolation has been extensively studied as a kind of critical phenomenon; the critical exponents are known, and agree with the direct renormalization group treatment of rubber, and also with experiment [13, 14]. However, the percolation model is unsatisfactory because it doesn't help us study the thermal fluctuations that determine rigidity and elasticity—and an account of elasticity is a *sine qua non* for any theory of rubber. Besides, while it is plausible that a phase transition should happen, a connected network isn't necessarily rigid [5]. This leads us to consider a different approach to the problem, which is to construct a Ginzburg-Landau theory of rubber. There are obvious obstacles to this program: it isn't obvious how one is to construct an order parameter or a coarse-grained Hamiltonian, for a start. These difficulties have been worked out; while the details are very technical, the following section sketches the most important steps.

3   A Landau Theory of Rubber

The practical objectives of developing a Landau theory of rubber are to show that the liquid is unstable to an amorphous solid, to derive the theory of elasticity from an effective equation for Goldstone modes, and to set up the renormalization group treatment of the critical behavior of rubber. In addition to these goals, it would be conceptually satisfying to understand how vulcanization relates to more elementary phase transitions.

3.1   The Order Parameter

How does one construct an order parameter for rubber? The nearest conventional ordered state is a crystal, which also breaks translational invariance, but unlike a crystal, rubber doesn't *look* ordered; there are, for instance, no Bragg peaks. The intuitive picture behind defining the order parameter is as follows. Suppose you took a snapshot of the microscopic system at a time $t = 0$ and then again at $t \to \infty$, and superimposed them. The strands in the liquid would have an entirely different configuration; in the amorphous solid, they would all be in roughly the same place. It is essential that our order parameter be sensitive to this distinction.

The order parameter generally used in the literature is:

$$\Omega(\mathbf{k}^n) = \frac{1}{N} \sum_i \int_0^1 ds \langle \exp(i\mathbf{k^1} \cdot \mathbf{c_i}(s)) \rangle_\chi \langle \exp(i\mathbf{k^2} \cdot \mathbf{c_i}(s)) \rangle_\chi \ldots \langle \exp(i\mathbf{k^g} \cdot \mathbf{c_i}(s)) \rangle_\chi$$

Here $\mathbf{c}_i(s)$ is the (suitably normalized) position vector of the point at arclength s on the ith polymer, and χ is a particular (random) distribution of crosslinks. In the liquid state, each of the terms is zero on average because the strands are delocalized; in the solid state, the strands fluctuate around well-defined mean positions, and therefore the average is nonzero, e.g. for gaussian fluctuations,

$$\langle \exp(i\mathbf{k} \cdot \mathbf{x}) \rangle = e^{i\mathbf{k} \cdot \overline{\mathbf{x}}} e^{-k^2 \xi^2} \neq 0.$$

The reason you need more than one k vector is that, in an amorphous system, $e^{i\mathbf{k} \cdot \overline{\mathbf{x}}}$ would average to zero because of destructive interference in the sum over chains. On the other hand, suppose we had multiple k vectors. Then each term in the average would be

$$e^{i(\mathbf{k_1} + \mathbf{k_2}) \cdot \overline{\mathbf{x}}} e^{-k^2 \xi^2} \neq 0$$

and therefore, for $\mathbf{k_1} + \mathbf{k_2} = 0$ the average would be nonzero. Goldbart [9] elegantly describes this as causing a a bump at $k = 0$ in the liquid state to turn into a fin of k-vectors such that $\sum \mathbf{k} = 0$ in the amorphous solid.
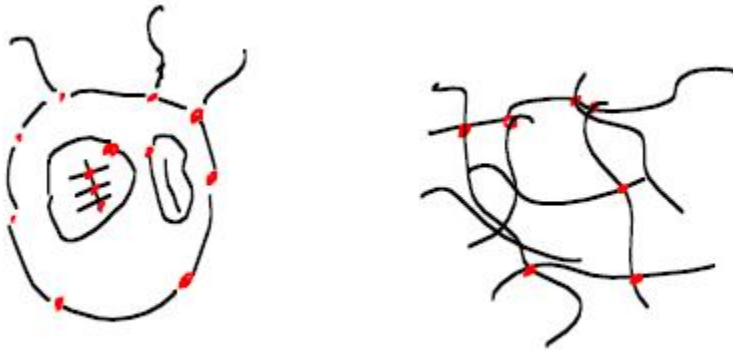
Figure 2: Improbable ("kaleidoscope eyes," L) and probable (R) **types** of crosslinked configurations. The crosslinks are shown as red dots.

To complete our definition of the order parameter, we must average it in the end over all possible realizations of the crosslink positions. This is done using the Deam-Edwards probability distribution [7, 8], which is based on the idea that the crosslinking process glues together strands that happen to be nearby in the uncrosslinked liquid. Therefore, the only crosslink distributions with statistical weight are those that (to quote Ref. [7]) "are compatible with some reasonably probable configuration of the uncrosslinked liquid."

Finally, one should note that the cross-link positions are defined by arclength along the crosslinked monomers (which are assumed to be distinguishable), and not by spatial coordinates; thus, crosslinking does not explicitly break translational invariance.

3.2   The Coarse-Grained Hamiltonian

Deam and Edwards [8] wrote down a Hamiltonian that accounts for the chain-chain interactions by a repulsive delta function pseudopotential that prevents the chains from sitting on top of each other. This is not quite realistic, but contains as much of the physics as we need. There are two parts to this Hamiltonian, called the Edwards Hamiltonian: the first, to penalize the stretching of individual links and "softly" enforce the integrity of each polymer, and the second to make the links avoid each other.

$$H_1^E = \frac{1}{2} \sum_{i=1}^{N} \int_0^1 ds \left| \frac{d\mathbf{c_i}(s)}{ds} \right|^2 + \frac{g}{2} \sum_{i,j=1}^{N} \int_0^1 ds \int_0^1 ds' \delta(\mathbf{c_i}(s) - \mathbf{c_j}(s'))$$

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Formally, the next step would be to compute the partition function Z subject to a specific realization of the crosslink positions, calculate the free energy, and then average the free energy over the Deam-Edwards crosslink probability distribution.[4] What we would really like, though, is to have a continuum representation of the Hamiltonian in terms of the order parameter. This is achieved through the **replica trick** [6], an odd but important technique in statistical mechanics. The replica trick relies on the identity

$$\log Z = \lim_{n \to 0} \frac{Z^n - 1}{n}$$

applied to the partition function. The idea is that Z^n, the partition function of n identical copies of the system, is easier to average than $\log Z$. If you were wondering what determines the n (the number of independent k vectors) in the order parameter, this is where it comes from. $Z^n = \exp(-S_n)$, and S_n can be written in terms of the n component piece of the order parameter. The expression here is derived in [9] from symmetry principles; we merely state the result:

$$S_n = N \sum_{\hat{k} \in HRS} (-a\tau + b|\hat{k}|^2/2)|\Omega(\hat{k})|^2 - Ng \sum_{\hat{k}_i \in HRS} \Omega(\hat{k}_1)\Omega(\hat{k}_2)\Omega(\hat{k}_3)\delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3}.$$

(The HRS, or higher replica sector, condition means that we need multiple k vectors to detect the amorphous solid, as discussed above. For our purposes, let a, τ and b be phenomenological parameters.) So far, we have not proved that the uniform liquid state, with $\Omega = 0$, is ever unstable; the theory hasn't yet predicted that vulcanization happens. One straightforward if tedious way to get at the transition is to apply a technique like linear stability analysis to the liquid state in the n-replica theory, locate the instability, and appropriately take the $n \to 0$ limit; see Ref. [6] for details.

3.3   Ergodicity and Topology

It is expected that the breaking of translational invariance should lead to breaking of ergodicity. In the case of rubber, there is a further breaking of ergodicity due to the fact that the strands cannot go through each other [4, 5]. Even with the same crosslink distribution, the two configurations in the figure belong to entirely separate parts of phase space. This feature is common to the liquid and the solid, and has nothing to do with vulcanization as such. It does establish, however, that if the crosslinks are permanent then the vulcanized solid really *is* an equilibrium amorphous state. Given a realization of crosslink locations and a region of phase space fixed by, say, the center

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[4]It won't do to average the partition function over the disorder, because that would imply that the system can explore disorder space, which it can't because the crosslinks are permanent.
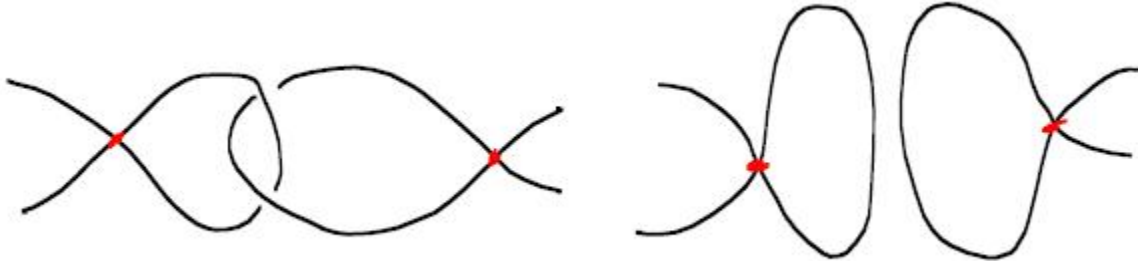
Figure 3: Two configurations with the same crosslinks but different topology. Adapted from [6].

of mass coordinate, there will be a minimum-free-energy configuration, perhaps with additional ordering; however, one might be permanently stuck in a bad neighborhood of configuration space from which this configuration is inaccessible.

It is clearly impractical to try to solve the Landau theory for a particular topology; in fact, there are no satisfactory techniques for dealing with the topological partitioning of phase space, and the literature [7] typically treats the different topological sectors of configuration space as separated by finite energy barriers, i.e. as analogous to topological defects. The consistency of this approach is questionable: it assumes that the topological constraints can relax on timescales where the crosslinks are permanent, which is not generally true because the polymers must break to go through each other.

3.4 Goldstone Modes

Now that we have a coarse-grained Hamiltonian, we should be able to find the Goldstone modes that determine rigidity. Since it is translational symmetry that is broken, we know that these will be phonon modes, and that the corresponding rigidities will be shear moduli. The detailed derivation is worked out in Ref. [11]. One possible strategy is to note that the order parameter is invariant under uniform translations of all the positions; therefore, since

$$\langle e^{i\mathbf{k}\cdot\mathbf{x}} \rangle = e^{i\mathbf{k}\cdot\bar{\mathbf{x}}} e^{-k^2\xi^2},$$

we could perform a displacement $\bar{\mathbf{x}} \mapsto \bar{\mathbf{x}} + \mathbf{v}(\mathbf{x})$, where v is a smooth slowly-varying function, and calculate an effective Hamiltonian for the elastic degrees of freedom. The upshot is that you can calculate the shear modulus, μ_n, in the n-replica theory and take $n \to 0$ to get a formula for the shear modulus.

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Deriving the phantom chain model from this theory takes a fair amount of work; see Ref. [11]. The strategy is to calculate the free energy increase upon deformation. One minimizes the Landau free energy, i.e. solves for $\delta L/\delta \Omega = 0$, subject to the constraint that the boundary of the system is deformed. Once this is done, the free energy change can be calculated, and the elastic properties can be deduced as before.

3.5   An Improved Theory of Elasticity

Related to this is the question of how rubber responds to a *large* static deformation. The phantom chain model predictions have been known to disagree with experiment for a fairly long time [1], but the mechanism was only recently explained [12]. The experimental result is that instead of being constant, the rigidity μ varies nonmonotonically with the strain.[5] The key to this behavior is in a fact that we didn't put into our model: that rubber is locally incompressible. In general, since each phonon mode carries $k_B T$ of energy, and the phonon density of states is $1/\xi^d$ where ξ is the average distance between crosslinks, there is a contribution of order $k_B T/\xi^d$ to the free energy from the phonons [12]. This affects the elastic properties because, for a locally incompressible system, the spectrum of phonon fluctuations is altered by large shear deformations. (This is because the crosslinks can't fluctuate as they please; they have to stay clear of all the other stuff. The effect is nonlinear and hard to describe intuitively.) The resulting change in free energy was taken into account using some fancy mathematics by Xing et al. [12], who found that the modified free energy density for a uniaxial stretch is

$$ f = \frac{1}{2}\mu_0(\lambda^2 + 2\lambda^{-1}) + \mu_1 \left[\frac{\tanh^{-1}\sqrt{1-\lambda^{-3}}}{\sqrt{1-\lambda^{-3}}} - \log\lambda \right]. $$

The stress-strain relation that follows from this equation is in excellent agreement with experiment.

3.6   Experiments on the Vulcanization Transition

While most of the experiments on rubber elasticity were done in the 1940s, studies of the vulcanization transition and its analogues in polymer gels have been quite active. Since, by an argument of de Gennes [3], the critical region in rubber is expected to be relatively small, most of these experiments have been done in dissolved polymer gels.[6]

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[5]The genteel term for "strain-dependent rigidity" is "Mooney stress."

[6]This is related to the argument in Section 2 that the effects of self-avoidance and interactions cancel out. In general, mean field theory works better for rubber than for gels. This fact is explicitly derived in Ref. [13] from the renormalization group.
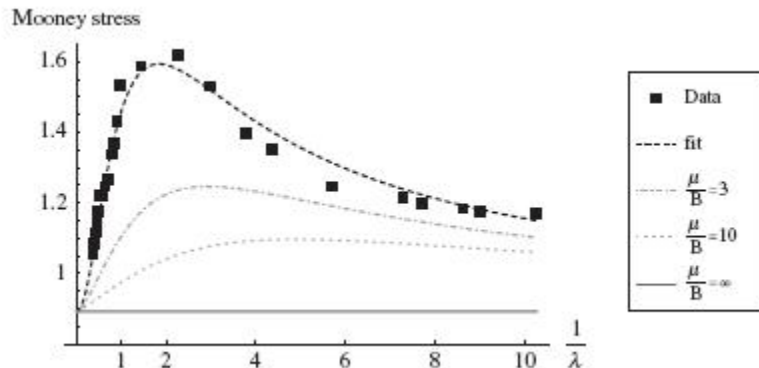
Figure 4: Theory vs. experiment for the strain-dependent rigidity. The horizontal line is the phantom chain model prediction. The dashed line fits the revised theory to the data. The other lines are interpolations for finite bulk moduli. [12]

If the liquid state is sufficiently viscous (as in some biological macromolecules) a very direct way to investigate critical properties is to measure the viscous/elastic response near the transition directly using a rheometer. Ref. [15] follows this procedure, and finds that the shear viscosity diverges with concentration of solute, with critical exponents that are consistent with percolation.

A more sophisticated technique is to inject a colored or fluorescent dye into the solution. Since the fluorescent properties of the dye molecules are strongly affected by the number of crosslinks [14], one can use the fluorescence yield to measure how far one is from the transition, and compare it against a transport coefficient (in this case, the speed of sound) that exhibits critical behavior.

4   Summary and Further Directions

We set out to understand how our ideas about spontaneous symmetry breaking could be applied to an amorphous solid like rubber. With the help of the replica trick, we were able to write down a coarse-grained Hamiltonian and an order parameter, which we (i.e. the references) then used to predict (1) that the liquid state is unstable to an amorphous solid state, (2) that the amorphous solid has incompressible phonon modes that determine its elastic properties, and (3) that the critical behavior is the same as that predicted by the percolation model. Essentially, the field theoretic treatment justifies, as limiting cases, both the phantom chain model and the percolation model, which are more intuitive ways to think about rubber, and gives us a systematic way to go beyond these limits.

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	a	I_c	υ_c	Gel time (min)
Gelatin	0.715	12.0	1.0085	35
TMOS pH = 5.6 $T = 22\,°C$ (fluorescein)	0.681	10.4	1.0418	13
TMOS pH = 5.6 $T = 22\,°C$ (uranile nitrate)	0.650	3.100	1.0418	13
TMOS pH = 5.6 $T = 25\,°C$ (fluorescein)	0.583	5.880	1.034	12
TMOS pH = 4.8 $T = 22\,°C$ (fluorescein)	0.637	0.187	1.0370	40
TMOS pH = 4.8 $T = 22\,°C$ (uranile nitrate)	0.642	1.640	1.0370	40

Figure 5: Critical exponent a of the ultrasound velocity for gelatin and tetramethoxysilane (TMOS) at various concentrations. Percolation predicts $a = 0.625$ [14].

While there are still aspects that need to be tested (e.g. some of the predictions of Ref. [12]), it seems clear that the theory described in this paper is substantially correct. One of the remaining weaknesses is the lack of any systematic procedure for dealing with the topological issues. The difficulties here seem related to some of the issues in loop models of topological quantum computation [17], and progress there might apply to rubber (or vice versa). Another difficulty is that our Landau theory works well only near the transition, and is less reliable deep in the solid state; there is still scope for an effective theory of the solid state [7]. Possible extensions proposed in Ref. [9] are to see if there are analogues to vulcanization in the theory of quantum phase transitions (quantum rubbers), and to study dynamic critical phenomena at the vulcanization transition [16]. An intriguing question along these lines is whether one can crosslink vortices in superfluid helium to produce a vortex rubber. In addition to these direct extensions, the general treatment of rigidity in polymer networks might apply to at least some of the myriad network problems in communications, engineer-

ing, geology, ecology etc.—particularly those with fluctuating degrees of freedom that cannot be treated by percolative methods.

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