

Emergent Physics at the Vulcanization Transition

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Abstract

The Essay starts with an overview of the percolation approach and classical elasticity theory of the vulcanization transition of rubber, describing their assumptions and their limitations. Thereafter we discuss a third approach, the Vulcanization Theory (VT) which incorporates the effects of *thermal fluctuations* and *quenched random disorder*. The VT is an order parameter theory in the true Landau tradition. We discuss the very subtle type of spontaneous symmetry breaking that occurs in the transition from liquids to amorphous solids and we define a suitable order parameter that captures this symmetry breaking. This necessitates the introduction of *replica* field theory, and we discuss what these replicas represent physically. We also discuss the physical meaning behind the resulting Goldstone modes. We conclude the Essay by describing a few applications of VT.

1 Introduction: The Percolation Picture

This Essay will be a somewhat partisan introduction to that highly-relevant but oftentimes lightly disdained subset of physics known as rubber vulcanization. The partisan character necessarily emerges as the result of my highly selective and deficient knowledge of the field. I first encountered rubber vulcanization through the lenses of Vulcanization Theory (VT) [1], [20], [21], and only started learning about other more historical approaches such as percolation theory [8] and the classical theory of rubber elasticity (as outlined in [3]), mainly because I have to make this Essay reasonably objective and self-contained. VT follows the standard Landau paradigm (for more on paradigms in Physics, see [9]) insofar as it relies on order parameters, symmetries and length scales. It's independent of what we assume for the microscopic details, and hence is fully appropriate to describe the universal, long-wavelength properties of rubber, which means that any phenomenological theory of rubber elasticity should be derivable from it. VT has conceptually achieved for the vulcanization transition in rubber what BCS has achieved for the superconducting transition of the first type.

We shall understand the vulcanization transition in a highly specific sense, that of the vulcanized medium acquiring a non-vanishing shear modulus upon sufficient crosslinking. Crosslinking is the process by which reactants are added to an initially liquid solution of polymer strands that causes neighbouring strands to bond between various monomer pairs. In this sense the density of crosslinks functions as our external control parameter. There is another type of phase transition which is temperature-controlled, a transition from rubber to rubber-glass having to do with the freezing of degrees of freedom of chains to rotate about single bonds in the chain backbone. This type of transition won't be discussed in our Essay (see instead [3]).

As a first attempt at a theory of rubber elasticity, we may consider a hypercubic lattice of atoms, each atom being adjacent to z other neighbours (z is called the functionality), and

we randomly sprinkle "bonds" between pairs of atoms. Then denoting the fraction of bonds by p , we can ask at what value of $p = p_c$ we first obtain an infinitely long percolating cluster of bonds. Such an infinite percolating cluster can be thought of as our solid rubber, while a mere liquid-like melt of polymer chains will consist of many finite clusters. Polymer physicists typically work at the "tree level" approximation when they study the vulcanization transition in the percolation picture. This assumes there are no closed cycles or steric hindrances. This approximation *fails* to capture correctly below a certain critical dimension (six in this particular case) the critical behaviour (i.e. the scaling exponents of the transition, e.g. in $Q \sim (p - p_c)^\nu$, Q being the fraction of the infinite cluster) for *dilute* systems where the functionality z is small. However, for the particular case of rubber which is a *dense* system, where each monomer is essentially in touch with $N - 1$ other monomers, the functionality $z \sim N \gg 1$, and we get that fluctuation effects tending to make the system deviate from the tree level approximation are small. Thus tree-level percolation theory gives a fairly accurate description of the critical behaviour of rubber vulcanization. One result of percolation theory is that the critical value p_c at which the percolation transition occurs coincides with the critical fraction of crosslinks at which vulcanization occurs in VT (which we shall introduce later). The scaling behaviour is also in agreement with that predicted by VT. Writing the the density of bonds as η^2 , percolation theory gives us the following result:

$$1 - Q = \exp(-\eta^2 Q). \quad (1)$$

We shall see that this relation recurs later in VT. At the percolation transition threshold (the critical regime $0 \leq \eta^2 - 1 \ll 1$), it's convenient to exchange η^2 for another control parameter which we call ϵ defined by $\eta^2 \equiv 1 + \epsilon/3$ ($0 \leq \epsilon \ll 1$). Then we have

$$Q = 2\epsilon/3, \quad (2)$$

implying that it is a continuous phase transition, with the critical density of bonds $\eta_c^2 = 1$.

However, the percolation transition is a purely geometrical transition which neglects the effects of *thermal fluctuations*. Hence it cannot explain the origin of shear modulus which emerges from thermal fluctuations of the polymer chains. The percolation picture only addresses the problem of architecture, i.e. how the connectivity of the network of random bonds can lead to an infinite cluster; it doesn't address the issue of how this floppy network can acquire shear rigidity. That will have to emerge from thermodynamics. Rather hand-wavily, we can see this as follows. In an amorphous solid as rubber, there is both a breaking of translational invariance coming from the preference of crosslinks to localize themselves at particular positions with respect to their neighbours (in order to minimize the free energy), as well as a further breaking of ergodicity in that a system prepared in a certain topology is not able to evolve to a topologically inequivalent arrangement without breaking some of the crosslinks or polymer chains. It is this particle localization (because the system wants to minimize free energy, and topology) that "causes" the floppy network to acquire the property of stiffness.

2 Classical theory of rubber elasticity

Traditional wisdom has it that rubber elasticity is entropic. This assertion effectively means that the shear modulus of rubber is completely determined by temperature, and vanishes at zero temperature. (It is intriguing to think about whether this still holds true at the quantum level, where quantum fluctuations may renormalize the shear modulus to a finite value despite being at zero temperature). This can be seen in the following way. We can think of a polymer chain with N monomers each of length a as a random walk with a as the step length. Then in

three dimensions, the mean squared end-to-end vector for a random walk of N steps is given by

$$\langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R_z^2 \rangle = \langle R^2 \rangle / 3 = a^2 N / 3. \quad (3)$$

The random walk model of polymer chains leads to a Gaussian-shaped probability of finding that a *single* chain conformation has an end-to-end vector R :

$$P \sim \left(\frac{3}{2\pi R_0^2} \right)^{3/2} \exp(-3R^2/2R_0^2), \quad (4)$$

where R_0 is the variance. The single chain free energy $F = -k_B T \ln Z(R)$, and since the partition function is proportional to the probability distribution, for N chains we have that $F = Nk_B T(3R^2/2R_0^2) + Constant = U - TS$, U being the internal energy of the chains. The representation of polymer chains as a random walk neglects any internal energy between chains, so $U = 0$ and the free energy is entirely entropic. Then the tension per unit area in the polymer chain is given by $p = T(\partial S/\partial V)_U \sim -k_B T(3R^2/2R_0^2)$ (since $V \sim N$), which is Hooke's law with an entropic spring constant. Thus elasticity is entropic.

The classical theory of rubber elasticity developed e.g. by Kuhn, Wall and Flory (See e.g. [3]) takes over the assumption that polymer chains can be modeled as random walks, and in addition assumes (1) that there is no change of volume on deformation of the rubber, (2) the crosslinking points of the network of chains move under deformation *affinely*, i.e. the components of length of each chain change proportionately as the corresponding dimensions of the bulk medium, i.e. $R_i \rightarrow R'_i \equiv \Lambda_{ij} R_j$ (where Λ is a matrix representing shear deformation, and volume conservation implies $\det \Lambda = 1$) and (3) the entropy of the network is equal to the sum of the entropies of constituent chains. For a uniaxial shear deformation one can then write

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

where the first diagonal entry means the rubber is being stretched by a factor λ in one (longitudinal) direction while the second and third diagonal entries mean that it's simultaneously being shrunk by a factor $1/\sqrt{\lambda}$ in the two transverse directions. Then under uniaxial deformation, the average free energy cost for N chains becomes $F = 3Nk_B T \langle R^T \Lambda^T \Lambda R \rangle_{P(R)} / 2R_0^2 = Nk_B T T r(\Lambda^T \Lambda) / 2 = Nk_B T(\lambda^2 + 2/\lambda) / 2$, where $\langle \cdot \rangle_{P(R)}$ means we're averaging over the Gaussian distribution $P(R)$, so e.g. we get $\langle R_i R_j \rangle_{P(R)} = \delta_{ij} R_0^2 / 3$. This gives us

$$\begin{aligned} \frac{df}{d\lambda} &= \mu(\lambda - 1/\lambda^2) \\ \Rightarrow \frac{\lambda df/d\lambda}{\lambda - 1/\lambda^2} &= \mu(1/\lambda)^{-1}. \end{aligned} \quad (5)$$

This expression will be relevant to our comparison with experiments via the so-called Mooney-Rivlin plot, which is essentially a graphical plot of $\lambda(df/d\lambda)/(\lambda - 1/\lambda^2)$ versus $1/\lambda$. At this point we'll engage in an experimental digression in order to understand the conventions used in Fig. 1.

We define the total stress acting on a rubber sample as the difference $\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{el} - \Pi \delta_{\alpha\beta}$, where σ^{el} is the elastic stress obtained by differentiating the elastic free energy of the chain network (which is $F = k_B T(3R^2/2R_0^2)$) with respect to the strain imposed thereby: $\sigma_{\alpha\beta} \equiv \partial F / \partial \epsilon_{\alpha\beta} |_{\epsilon=0}$

for a strain $R_\alpha \rightarrow R_\alpha + \epsilon_{\alpha\beta}R_\beta$. The pressure Π arises e.g. from the internal pressure exerted by the crosslinks. For a uniaxial stress in the z direction, the total stress in the x and y directions is zero, and we may equate the pressure Π to e.g. σ_{xx}^{el} . Then (after [5]) we may characterize f^* as the "Mooney ratio" of the total stress $\sigma_{zz} - \sigma_{xx}$ to the functional dependence $\lambda^2 - 1/\lambda$, where for an affine deformation $R_\alpha \rightarrow \lambda_\alpha R_\alpha$. Observing that the variation $d\epsilon_{\alpha\alpha} = d\lambda_\alpha/\lambda_\alpha$, we can write $\sigma_{\alpha\alpha} \equiv \lambda_\alpha \partial F / \partial \lambda_\alpha$ and $\lambda_z = \lambda, \lambda_x = \lambda_y = 1/\sqrt{\lambda}$, whence $f^* = (\sigma_{zz} - \sigma_{xx}) / (\lambda^2 - 1/\lambda) = (\lambda_z (\partial f / \partial \lambda_z) - \lambda_x (\partial f / \partial \lambda_x)) / (\lambda^2 - 1/\lambda) = (3\lambda (\partial f / \partial \lambda)) / (\lambda^2 - 1/\lambda)$, which is essentially our Eq. (3).

How realistic is the classical theory of rubber elasticity? Eq. (5) indicates that we get a hyperbola tending towards ∞ as $1/\lambda \rightarrow 0$, and 0 as $1/\lambda \rightarrow \infty$ for the Mooney-Rivlin plot, but for the rubber samples studied in Fig. (1), what we see are gentle humps ... Thus the classical theory cannot be completely correct. The assumptions of affine deformation and Gaussian statistics are hard to believe for the case of real rubber, which is a heterogeneous random medium (brought about by the random nature of the vulcanization process). Thermal fluctuations have also been neglected; as we shall see later, it turns out that the Goldstone sector of these thermal fluctuations gives rise to the elastic shear moduli.

3 Describing the physics of quenched disorder

Any respectable theory of rubber vulcanization should have to begin with the observation that rubber is *amorphous*. Amorphous solids have the crucial feature that they involve two kinds of variables, *thermal* (or *annealed*) and *quenched*, which are defined by their vastly different time scales of relaxation: thermal variables relax on a time scale comparable to the time scale of the experiment, while quenched variables relax on a much longer time scale which means they can be approximated as being "frozen in", i.e. permanent to most appearances. This will be pertinent to constructing a microscopic model of rubber. From the renormalization group point of view, it is not important whether we start with a model of an extremely long polymer chain or an array of atoms randomly selected to be crosslinked, because at long length scales microscopic conformational details are irrelevant. We shall therefore introduce the *Randomly Linked Particle Model* (RLPM) [2] which is essentially an array of atoms or monomers with pairs randomly chosen to be crosslinked, augmented by two types of interactions between monomers: an excluded volume interaction which is basically a repulsive delta-function pseudopotential, and an attractive interaction between pairs of monomers that have been chosen to be crosslinked. The former arises from two sources: the self-avoidance of the chains and their interaction with the solvent. The first point is clear enough; for the second, we note that in good solvents the network is swollen, indicating that polymer chains are further apart; this may be represented as coming from a larger excluded volume interaction (i.e. a larger ν^2). In a poor solvent there is

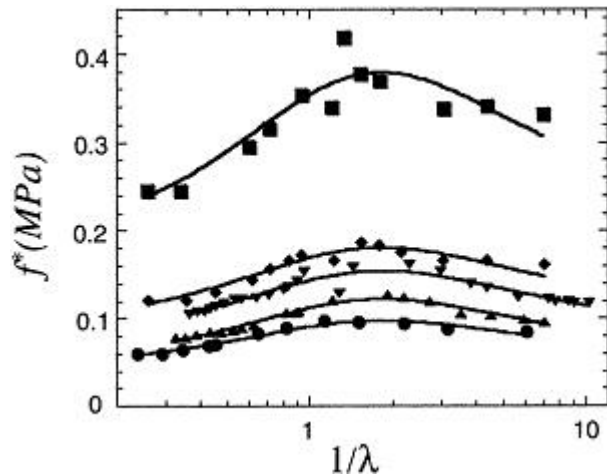


Figure 1: Mooney-Rivlin plot [5]. $\blacksquare, \blacklozenge$ represent natural rubber samples, $\blacktriangle, \blacktriangledown, \bullet$ represent poly(dimethylsiloxane) networks.

a higher likelihood of segregation of polymer species from solvent, polymer chains are clumped closer together which may be taken as a result of a smaller ν^2 . Fluctuating monomer positions are thermal variables and crosslink positions are quenched variables. The Hamiltonian of such a system reads as follows:

$$H_\chi = \frac{\nu^2}{2} \sum_{i,j=1}^N \delta(c_i - c_j) + \sum_{e=1}^M v_L(c_{i_e} - c_{j_e}). \quad (6)$$

c_i labels the monomer positions for N monomers, e labels the crosslinks in a given realization of quenched disorder, and M specifies the total number of crosslinks. v_L is the potential energy of a bond between a pair of monomers crosslinked together, which for the case of "Gaussian chains" (so-called because they lead to Gaussian statistics) may take the form

$$v_L(|r|) = \frac{k_B T |r|^2}{2a^2} \quad (7)$$

where a denotes the rest length of the bond (imagined to be a Hookean spring).

Quenched disorder arises in amorphous solids because of the inherent nature of the vulcanization process. To make a rubber, we can imagine first starting with a solution of polymer strands, onto which we sprinkle *instantaneously* and *simultaneously* chemical covalent bonds to initiate cross-linking, by which I mean different strands are conjoined together at various monomer positions. The act of sprinkling involves an element of randomness. The probability of finding a crosslink at a given monomer position can thus be described by some distribution. Intuitively, we expect that a high probability that pairs of chain segments happen to be near to each other will result in a large number of crosslinking constraints in the form of chemical bonds formed, and conversely: the probability depends on the average density of crosslinks η sprinkled into the liquid. This is precisely captured by the Deam-Edwards (DE) distribution [6], defined as follows:

$$P(\chi) = \frac{\left(\frac{\eta^2 V_0}{2N\Delta_0^{(0)}}\right)^M Z_\chi(V_0)}{M! Z_1} \quad (8)$$

Here $Z_\chi(V_0)$ is the partition function describing the equilibrium correlations of the liquid just before the crosslinking transition, with positions of monomers for its thermal variables. η is an external parameter that can be experimentally tuned, and this parameter controls the

VT transition. The factor $\left(\frac{\eta^2 V_0}{2N\Delta_0^{(0)}}\right)^M / M!$ is a Poisson distribution, we're assuming that the chemical crosslinking process is Poissonian. This product or probabilistic conjunction of factors assures us that only those configurations of crosslinks which are reasonably similar to the configuration of the liquid correlations just before crosslinking are more predominantly selected.

Now to make any further progress we need to construct the free energy by which we could then derive other macroscopic averaged physical quantities like pressure or entropy. This free energy has to involve averaging over two kinds of ensembles, the thermal variables and quenched disorder variables. Naively, we might think of treating both thermal and disorder variables on an equal footing and averaging over them (by means of a Boltzmann distribution) within the partition function. But this would mean that both types of variables relax to equilibrium on the same time scale, which is not what we want (since the disorder variables are meant to be quenched i.e. relaxing on a vastly longer time scale than the experimental time scale).

The alternative would be to Boltzmann-average only the thermal variables within the partition function, but average the free energy itself over the disorder variables by means of another, DE distribution. Why the free energy and not, say, the partition function? We disorder-average over the free energy because we expect that in the thermodynamic limit physical observables are *self-averaging*, i.e. they do not depend on a specific realization of disorder. Mathematically, self-averaging means that the relative fluctuations about the average thermal value of a physical quantity goes as $O(N^{-1/2})$, where N is the number of particles in the system. Physically, self-averaging quantities (such as the free energy) have to be extensive, which means that its additive property permits us to conceive of the disorder-averaging process as the consequence of dividing the macroscopic system into regions each bigger than the size of a fluctuation correlation length, which implies these regions are statistically independent of one another and therefore averaging over the system is equivalent to averaging over a probability distribution describing the disorder. This allows us to get the same results for experiments and also make it possible to compare theoretical predictions with what is observed experimentally. This rules out disorder-averaging the partition function, because it is not extensive, and hence not self-averaging. The disorder-averaged free energy is as follows:

$$[F] = \sum_{\chi} P(\chi) F_{\chi} = k_B T \sum_{\chi} P(\chi) \ln Z_{\chi} \quad (9)$$

where χ labels each specific realization of a disordered configuration of the crosslinked gel. The square brackets $[\cdot]$ is the standard way to denote disorder averaging.

4 Replicas and their physical interpretation

It is quite difficult to directly average a logarithm, but there is a mathematical trick (the "replica trick") to circumvent this difficulty. Essentially, it involves the following: For small n we may write, $x^n = \exp(n \ln x) \approx 1 + n \ln x$. Then

$$\ln x = \lim_{n \rightarrow 0} \frac{x^n - 1}{n} \quad (10)$$

$$\Rightarrow [F] = k_B T \sum_{\chi} P(\chi) \lim_{n \rightarrow 0} \frac{Z_{\chi}^n - 1}{n} = k_B T \lim_{n \rightarrow 0} \frac{[Z_{\chi}^n] - 1}{n}. \quad (11)$$

Then our problem becomes the evaluation of the following:

$$\begin{aligned} [Z_{\chi}^n] &= \sum_{\chi} P(\chi) Tr_{S_1} \exp(-\beta H_{\chi}(\{S_1\})) \dots Tr_{S_n} \exp(-\beta H_{\chi}(\{S_n\})) \\ &= \sum_{\chi} \frac{\left(\frac{\eta^2 V_0}{2N \Delta_0^{(0)}}\right)^M Z_{\chi}(V_0)}{M! Z_1} Tr_{S_1} \exp(-\beta H_{\chi}(\{S_1\})) \dots Tr_{S_n} \exp(-\beta H_{\chi}(\{S_n\})) \\ &\sim \sum_{M=0}^{\infty} \sum_{i_1 \neq j_1}^N \dots \sum_{i_M \neq j_M}^N \frac{\left(\frac{\eta^2 V_0}{2N \Delta_0^{(0)}}\right)^M}{M!} Tr_{S_0} Tr_{S_1} Tr_{S_n} \exp(-\beta H_{\chi}(\{S_0\})) \dots \\ &\times \exp(-\beta H_{\chi}(\{S_1\})) \dots Tr_{S_n} \exp(-\beta H_{\chi}(\{S_n\})), \end{aligned} \quad (12)$$

where S represents the possible microscopic states in the statistical ensemble of the system. (For magnetism, S represents spin orientation; for polymers S represents polymer conformations.) Thus we see that the replica trick entails making $n + 1$ replicas of the disordered, amorphous system, n of which are "copies" of the crosslinked or *measurement state* and one of which comes from the DE distribution and describes the pre-crosslinked or *preparation state*. Any two replicas are sufficiently distantly separated in time so that the thermal fluctuations of the localized particle about a common mean position in each replica are independent. This also means that we have translated the problem involving two types of variables relaxing on two vastly different time scales into one problem in which we are solely dealing with thermal variables, but which involves $n + 1$ replicated copies of the same system (and the disordered crosslinks have metamorphosed into interactions between different replicated thermal variables). More provocatively: quenched inhomogeneities of rubber structure in real space can be treated as thermal fluctuations in replica space and the problem of calculating frozen disorder can be attacked with the usual methods of equilibrium statistical physics!

5 Defining a suitable order parameter

We shall switch the order of averaging, by performing the disorder averaging $\sum_{\mathcal{X}} = \sum_{M=0}^{\infty} \sum_{i_1 \neq j_1}^N \dots \sum_{i_M \neq j_M}^N$ first and then doing the thermal averaging (tracing over the various "spins") later. This will *couple* different replicas of the thermally fluctuating monomer positions together, resulting in a complicated field theory. To *decouple* the different replicated terms, we need to do something called a *Hubbard-Stratonovich* transformation (which is a high-brow way of saying "completing the square") on the thermal variables which results in a new collective coordinate defined on replicated space, defined (for n replicas) as follows:

$$\Omega(\hat{x}) = \frac{Q}{N} \sum_{j=1}^N \delta^{(d)}(x^0 - c_j^0) \delta^{(d)}(x^1 - c_j^1) \dots \delta^{(d)}(x^n - c_j^n) - \frac{Q}{V_0 V^n} \quad (13)$$

$$\Omega(\hat{p}) = \frac{Q}{N} \sum_{j=1}^N \exp \left(i \sum_{\alpha=0}^n p^\alpha \cdot c_j^\alpha \right) \quad (14)$$

Q denotes the "gel fraction", which if we think of the vulcanized system as a sort of percolating cluster, then Q would be the fraction of molecules that are connected into an infinite cluster. Here we have abbreviated \hat{x} for the $n + 1$ times-replicated d -dimensional vector \vec{x} , and α labels the replicas. Now the Hubbard-Stratonovich transformation is done before thermal averaging, and the thermal averaging in turn is done before disorder averaging of Z^n . This ordered sequence will give us

$$[\langle \Omega \rangle] = \left[\frac{Q}{N} \sum_{j=1}^N \prod_{\alpha=0}^n \langle \exp(ip^\alpha \cdot c_j^\alpha) \rangle \right], \quad (15)$$

This both *disorder- and thermal-averaged* collective coordinate $[\langle \Omega \rangle]$ is the order parameter for the VT. In the case of a liquid where all N particles are delocalized, this fails to vanish only for the case where every wave-vector $p^\alpha_{\alpha=0}$ vanishes. But when some fraction Q of the particles are localized then the order parameter is non-vanishing if $\sum_{\alpha=0}^n p^\alpha = 0$.

How reasonable is $[\langle \Omega \rangle]$ as an order parameter that allows us to differentiate an amorphous solid from a liquid? We could have thought of using the disorder- and thermal-averaged

monomer density fluctuation as the order parameter, but this won't work, because in the amorphous state, owing to the randomness of the localized monomers, the macroscopic disorder-averaged density fluctuation remains zero on entering from the liquid phase. And this is not surprising: for amorphous systems, the order parameter tends to be a *distribution*, whereas for crystalline solids the order parameter has usually been a number. We need a more subtle characterization in terms of higher moments of the correlation function to capture the transition; this is reminiscent of the construction of the Edwards-Anderson order parameter in the spin glass problem (see e.g. [24]), only more complicated. Observing that in momentum space the density fluctuation for the j th monomer $\delta n(p_j) = \langle \exp(ip_j \cdot c_j) \rangle$, we can see that

$$\begin{aligned}\Omega^{(1)}(p) &\equiv \frac{Q}{N} \sum_{j=1}^N \delta n_j(p) = \frac{Q}{N} \sum_{j=1}^N \exp(ip \cdot c_j) \exp(-p^2 \xi_j^2/2) \\ \Omega^{(2)}(p, -p) &\equiv \frac{Q}{N} \sum_{j=1}^N \delta n_j(p) \delta n_j(-p) = \frac{Q}{N} \sum_{j=1}^N \exp(-p^2 \xi_j^2)\end{aligned}\quad (16)$$

where ξ_i^2 is the mean-squared fluctuation distance around the mean position of the i -th monomer. (We're dealing with an amorphous system, so different monomers are localized with different "spreads".) It can be seen that the first moment vanishes in the thermodynamic limit due to the addition of a large number of random phase factors, while the second moment doesn't. In the spin glass problem, the first and second moments completely specify the physics but in the vulcanization problem, we need all higher moments to gain a complete characterization of the physics. The order parameter in VT represents the condensation of many different replicas of the vulcanized system in replica space into a kind of "molecular bound state". This is certainly more awe-inspiring than the BCS order parameter which represents the condensation of merely two electrons in real space. If the particles are localized according to Eq. (16) with random spreads ξ , then we can write the order parameter $[\langle \Omega \rangle]$ as follows:

$$[\langle \Omega \rangle] = (-Q) \delta_{\hat{p}, \hat{0}}^{(n+1)d} + Q \delta_{\sum_{\alpha=0}^n \vec{p}^\alpha, \vec{0}}^{(d)} \int d\xi p(\xi) \exp(-\xi^2 |\hat{p}|^2/2), \quad (17)$$

where $p(\xi) = \left[\sum_{j, \text{localized}} \delta(\xi - \xi_j) / (QN) \right]$ is the distribution of the random spreads of the localized particles.

6 A Landau theory for the vulcanization transition

If we Taylor expand the free energy in terms of the small parameter $[\langle \Omega \rangle]$ (small, since we are at the threshold of VT), but before taking the replica limit $n \rightarrow 0$, we will obtain the following cubic Landau free energy,

$$ndF_n(\{\Omega_{\hat{p}}\}) = \sum_{\hat{p} \in HRS} \left(-a\epsilon + \frac{b}{2} |\hat{p}|^2 \right) |\Omega_{\hat{p}}|^2 - c \sum_{\hat{p}_1, \hat{p}_2, \hat{p}_3 \in HRS} \Omega_{\hat{p}_1} \Omega_{\hat{p}_2} \Omega_{\hat{p}_3} \delta_{\hat{p}_1 + \hat{p}_2 + \hat{p}_3, \hat{0}} \quad (18)$$

The ϵ -parameter controls the transition from the liquid to the amorphous solid state, and is related to the cross-link density via $\mu^2 = 1 + \epsilon/3$. Thus we can see that there is a phase transition at $\epsilon = 0$ or the critical crosslink density, $\mu_c^2 = 1$. Let us pause to consider how remarkable this result is. For one thing, the critical crosslink density does not involve the strength of excluded

volume interaction that we might naively expect. This seems to suggest that the transition does not relate to a finite energy scale, but stems instead from a qualitative aspect: possibly the increasing complexity of the topological network with increasing crosslink density. "HRS" denotes the "higher replica sector", as opposed to "one-replica sector" or "zero-replica sector". These terms are defined as follows: For an order parameter having n replicas for its argument, if all vectors in the argument are vanishing, then we say the order parameter resides in the *zero-replica sector*. If exactly one vector in the argument is non-vanishing, then it resides in the *one-replica sector*. If more than one vector is non-vanishing, it resides in the *higher replica sector*. The fact that our order parameter lies in the higher replica sector is a manifestation of the fact that averaged monomer density fluctuations are unable to distinguish amorphous solids from liquids, but higher moments of density-density correlators can. One final word about the Landau expansion. A field theorist may be disturbed by the negative sign on the prefactor of the cubic term as that seems to lead to a pathological field theory, e.g. a runaway trajectory in the renormalization group flow. The answer is that higher order terms will stabilize the theory; [22] have proved that the theory is locally stable.

By substituting the gel-fraction form of the order parameter into the Landau expansion, invoking stationarity and taking the replica limit $n \rightarrow 0$, one finds that at the VT transition threshold, ϵ is related to the gel fraction via

$$Q = 2\epsilon/3. \tag{19}$$

How correct is our taking a mean-field approach to vulcanization in the form of a Landau expansion? Renormalization group calculations done e.g. in [23] show that in less than six dimensions, fluctuations are non-dangerous and the mean field theory gives us fairly accurate critical indices, which turn out to match the analogous exponents in percolation theory.

7 Why Goldstone modes are important

In an amorphous solid such as rubber, it is the *relative* translational invariance between different replicas which is broken (and not their common translational invariance). This broken relative translational symmetry gives rise to Goldstone modes which are phonons, and it turns out that the rigidity associated with these phonons is manifested as their shear moduli. Let us give a heuristic argument why fluctuations of phonon modes are important. At long length scales (on sufficient coarse-graining), microscopic details such as polymer chain entanglements become irrelevant. The only important remaining degrees of freedom are the phonon modes. For soft amorphous solids like rubber the typical strain is of order unity, implying that the total elastic energy per unit volume scales as the shear modulus μ . At the vulcanization threshold the only important length scale is the mean localization length (or the vulcanization correlation length) ξ , thus in d dimensions, $f_{el} \sim \mu \sim k_B T \xi^{-d}$. Now if we denote $\Lambda \sim \xi^{-1}$ as the large momentum cut-off beyond which the system does not behave as a regular solid, we have that the number of phonon modes per unit volume is Λ^d . By the equipartition theorem, fluctuations of each phonon mode contribute $k_B T$ to the total free energy. Thus these phonon fluctuations (which are Goldstone fluctuations) contribute an energy of the order $\sim k_B T \Lambda^d \sim k_B T \xi^{-d}$ which is essentially the same as what we estimated for our total elastic free energy per unit volume based on scaling arguments! This should persuade a skeptic that the elastic free energy is mainly the emergent phenomenon of Goldstone fluctuations, which the classical theory of rubber elasticity has neglected. Furthermore, it has been shown that the classical theory is the saddle-point of VT [27].

To see how the relative translational symmetry of replicas is broken, let us first define a new basis of replicated vectors in terms of the Cartesian replica basis:

$$\hat{\epsilon}_L \equiv \frac{1}{\sqrt{1+n\zeta^2}}(\epsilon^0 + \zeta \sum_{\alpha=1}^n \epsilon^\alpha) \quad (20)$$

Then any $(1+n)d$ -dimensional vector \hat{x} may be decomposed as follows: $\hat{x} = \hat{x}_L + \hat{x}_T$, $\hat{x}_L = (\hat{x} \cdot \hat{\epsilon}_L)\hat{\epsilon}_L$, $\hat{x}_T = \hat{x} - \hat{x}_L$ (L denotes the longitudinal component and T the transverse component). The longitudinal component represents some kind of centre-of-mass coordinate and the transverse component the relative coordinate. This is apparent by working in two dimensions and setting $\zeta = 1$: then, $\hat{\epsilon}_L = (\hat{\epsilon}_1 + \hat{\epsilon}_2)/\sqrt{2}$, $\hat{\epsilon}_T = (\hat{\epsilon}_1 - \hat{\epsilon}_2)/\sqrt{2}$.

In a real d -dimensional rubber the volume in the measurement state (i.e. after vulcanization) will shrink (because of the inward directed pressure exerted by attractive crosslinks) by some factor ζ^d , which means that the mean position z of a localized particle in the measurement state will be modified by a factor ζ : $z \rightarrow \zeta z$; the mean position of the particle in the preparation state however, stays at the same value z . If we write $\tau \equiv 1/\xi^2$, where ξ is the localization length (i.e. random spread of a particle), the order parameter in real space can be expressed as

$$\Omega(\hat{x}) = Q \int \frac{dz}{V_0} \int d\tau P(\tau) \left(\frac{\tau}{2\pi}\right)^{(n+1)d/2} \exp\left(-\frac{\tau}{2}(|x^0 - z|^2 + \sum_{\alpha=1}^n |x^\alpha - \zeta z|^2)\right) - \frac{Q}{V_0 V^n} \quad (21)$$

By writing $\hat{z}_L = (z, \zeta z, \zeta z, \dots) = \sqrt{1+n\zeta^2} z \hat{\epsilon}_L$, this becomes:

$$\Omega_{SP}(\hat{x}) = Q \int d\tau P(\tau) \left(\frac{\tau}{2\pi}\right)^{(1+n)d/2} \left(\frac{2\pi}{\tau(1+n\zeta^2)}\right)^{d/2} \exp\left(-\frac{\tau}{2}|\hat{x}_T|^2\right) - \frac{Q}{V_0 V^n}. \quad (22)$$

Thus we see that the order parameter remains invariant for translations in the \hat{x}_L direction, which means that the system is invariant under common translations and rotations of all replicas; there is a Gaussian bump or hill in the \hat{x}_T direction though, representing relative translations between different replicas. Thus the relative translational symmetry is broken. Subjecting the replicas to a common translation does not alter the free energy, and the free energy depends only on the relative translational coordinate. The "gapless" Goldstone fluctuations will be in this broken symmetry direction. This is reminiscent of the situation of the water-air interface in a beaker in the absence of gravity (since gravity stabilizes the water surface), where a translation of the entire interface does not alter the free energy of the interface. The presence of the interface breaks translation invariance and gives rise to Goldstone modes which are capillary waves, i.e. "gapless" undulations of the interface [34]. See Fig. (2). The precise form of the energy due to such Goldstone fluctuations has been computed in [10] and [11] and shown to be equivalent to the energy for shear deformations in a phenomenological theory that involves replicating the disordered system n times and taking non-affine deformations into account.

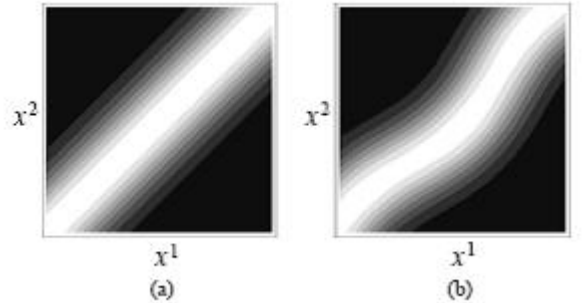


Figure 2: (a) Value of order parameter at saddle point, depicted in terms of brightness. x^1 and x^2 are the two replicas. (b) Goldstone deformation of the saddle point.

8 Conclusion

We have discussed the percolation approach and classical theory of rubber elasticity, and given an overview of their merits and shortcomings. We have also discussed a third approach in the guise of VT which appears to be more powerful than either of them, in the sense that it takes into account both thermal fluctuations and quenched disorder, and e.g. gives a satisfactory explanation of where the shear modulus comes from. One major drawback of VT is the following. A real rubbery network inhabits a certain sector of phase space consisting of topologically equivalent configurations, so strictly speaking, our partition function should respect this fact. Instead, VT does not distinguish between configurations with inequivalent interlocking closed loops. So while crosslinks are treated as being quenched or permanent, VT assumes that polymeric strands can somehow pass through each other to evolve to an inequivalent topological configuration. From a logical perspective, this is unsatisfactory.

However, VT has been applied to various physical situations involving vulcanization to give us a satisfactory understanding of what happens at the microscopic level. The extension of the classical theory of rubber elasticity to study liquid crystal elastomers in work done by Warner, Terentjev and co-workers (see, e.g. [31]) arises as a limiting case of a VT that's coupled to nematic order [28], [29]. VT has also been used to study glassy correlations in an isotropic melt of two species of homopolymers ("A" and "B") [32], [33]. The glassy correlations in nematic elastomers and quite possibly the polydomain structure can also naturally be analyzed using VT. [35] The non-affine generalization of VT [10] [11] [13] coupled to nematic order may also possibly shed light on the origin of semi-softness in nematic elastomers. [30]

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