Emergent Rigidity in Randomly Cross-Linked System

Umi Yamamoto
University of Illinois, Urbana-Champaign, IL 61820

December 19, 2008

Abstract

In a randomly cross-linked macromolecular system, a liquid state undergoes the phase transition to amorphous solid states as one increases the number of cross-links. However, the statistical mechanical formulation of this system has been challenging due to its quenched randomness. In this review, I will outline the technique to describe such a system, and demonstrate how the essential properties of vulcanized matter can be derived.

1 Introduction

Amorphous solids, such as rubbers and chemical gels, are interesting materials. It is indeed solid, but not quite like a crystalline solid since it has a freedom to be deformed. Technically, amorphous solids are distinguished from crystalline solids[1] based on the following criteria[3]; it is a solid because

(i) it has a non-zero static shear modulus[2], i.e. produces non-zero restoring force in response to zero-frequency shear stress.

(ii) translational symmetry is at least partially broken, so a fraction of particle is localized to some mean position.

but it is not crystalline in a sense that

(i) there is no long-range order of the position of constituent molecules.

A transition from liquid states to amorphous solid states, called *vulcanization*, was first discovered in 1839 by Goodyear[5] in the chemical reaction with sulfur. Accordingly, it has been known from experiments that vulcanization occurs due to the effect of permanent cross-linking of constituent molecules, and the phase transition occurs as one increases the number of these cross-links.

As for the theory of such a random-networking system, an early work was done in 1940's by Guth and Kuhn, followed by its variants, but a full statistical treatment had not been given until 70's due to its intrinsic difficulty, which comes from quenched randomness. It was in 1976 that Deam and Edwards developed an elegant formulation of the randomly cross-linked system[7], with the help of the technique developed in the study of spin-glass systems.

In this review, I will outline how to build a statistical model of the vulcanization transition in a randomly cross-linked system, based on the the discussion presented in [1], [2], and [3]. In particular, I will demonstrate that the model exhibits the following properties upon the vulcanization;

1. A non-zero fraction of molecules get localized above the critical cross-link density, and none of them below it.
2. Non-zero shear modulus emerges at a critical cross-link density.

Although I will not cover detailed calculations, some equations will be quoted where appropriate.

---

[1] Crystalline solids are sometimes called *morphous solids*, as opposed to amorphous solids.

[2] The significance of staticness is that the shear modulus has to exist as long as the shear stress is applied; a liquid state does exhibit restoring force when a shear deformation is made, but it disappears as we wait for long enough time.

2 Random Constraints on the System

As mentioned before, the central difficulty in a statistical treatment of the vulcanization comes from the randomness due to the cross-links, not from the thermal fluctuation. We will clarify the nature of these randomness in this section, so we can propose a possible treatment in the next section.

A randomly cross-linked macromolecular system is described by two classes of variables; *annealed variables* and *quenched variables*. Quenched variables are defined as a quantity that does not evolve in time, while those which have time-evolution are called annealed variables. In our model, typical annealed variables are the position of polymers or molecules and the quenched variables are those determined by the structure of the random network. There are three quenched variables that concern us;

1. A catalog of points that are to be tied by the cross-links.
2. A topology of the network.

Since these two information limit the possible configurations of the system, we shall call 1, 2 as a random *constraint* and represent it as χ. The third randomness comes from

3. A distribution $P[\chi]$ of the random constraints.

3 generally depends on an experimental setting, but we will model it later. 1 and 2 are distinguished since there is a number of inequivalent topologies that can be generated from the same paring of points. Here networks (configurations) are said to be topologically inequivalent if one cannot be transformed to the other only by dynamics, so a configuration of a given topology cannot evolve to the one that belongs to an inequivalent topology.

To enable a mathematical description, let us now focus on a macromolecular system with N monomers in d-dimensional space. We shall represent the position of each monomer by d-dimensional curve $\boldsymbol{c}_i(s)$, where $i = 1, ..., N$ is the label for the monomer and $0 \leq s \leq 1$ is the parameter along the curve. Then, when M cross-links are present, the random constraint χ is characterized by a set of points $\{(\boldsymbol{c}_{i_e}(s_e), \boldsymbol{c}_{i'_e}(s'_e))\}$ $(e = 1, 2, ...M)$ (i.e. e-th cross-link connects a point s_e of the i_e-th monomer and a point s'_e of the i'_e-th monomer) and some topology, which we denote by S.

Before proceeding to the next section, we shall remark on one simplification that we *have to* make. Although we have defined the topology of the network as a quenched variable, no approach that can account for this effect has been known[3]. Therefore, we shall treat the fluctuation of the topology as an annealed variable, assuming that its effect is not very significant. In fact, this assumption is not too indefensible; as it will turn out, the vulcanization happens at rather small cross-link density (about one cross-link per molecule), so the fluctuation of topology is expected to be very small.

3 Statistical-Mechanical Model for Vulcanization

Now we will briefly demonstrate how one can build a statistical model that can describe vulcanization. For later use, let us define two kinds of "averages";

$$\begin{aligned}\langle ...\rangle_\chi &\equiv \text{thermal average} = \mathrm{Tr}_\chi(\rho\ ...),\\ \overline{(...)} &\equiv \text{disorder average} = \int \mathscr{D}\chi P[\chi]\ ...,\end{aligned}$$

where the trace is taken over all the microstates obeying the constraint χ and ρ is the density matrix with the Boltzmann weight.

We will first discuss a general approach to the system with quenched disorders, and then construct a model for the randomly cross-linked system according to the formulation by Deam and Edwards[7]. We will propose a form of the order parameter by an analogue to the spin-glass system, and verify its consistency in terms of the mean field theory. As a result, we will see that the consistency condition near the transition indicates the spontaneous breakdown of the translational symmetry.

3.1 Replica Method

Since the system has a quenched randomness (in our case, random constraint), the statistical nature of a physical quantity depends on a certain realization of the random constraint. However, instead of considering only one specific case, we would consider an average *over the realization of the constraints.* This idea, called self-averaging, is justified as long as the system is sufficiently large and no long-range order is present[3].

Here we have the problem with quenched disorders. As the configuration space is affected by the constraint, the partition function itself depends on a

---

[3] For more detailed discussion, see Ref.[4].

quenched random information. However, the disorder average of the Boltzmann weight $e^{-\beta H}/Z_\chi$ (times some observable) is quite hard to compute since we will have to average the *quotient* of a random variable[4].

The remedy is given as follows; instead of the partition function, we can construct the disorder average of the *free energy*

$$f = -\frac{1}{\beta N}\overline{\ln Z_\chi},$$

which, with the help of the replica trick[4], is calculated by

$$f = -\frac{1}{\beta}\lim_{n\to 0}\frac{\overline{{Z_\chi}^n}-1}{nN}, \tag{1}$$

where ${Z_\chi}^n$ is the n-th power of the original partition function, i.e. we virtually introduced $n-1$ replicas of the original system.

The entire effect of the disorder average is now in the $\overline{{Z_\chi}^n}$ term, so it is convenient to define the effective (replicated) free energy through

$$\overline{{Z_\chi}^n} = \mathscr{N}\int \mathscr{D}\Omega \exp\left(-ndN\mathscr{F}_n\right),$$

where $\mathscr{N}$ is a normalization factor that is irrelevant to our problem.

In terms of mean-field theory, the order parameter is determined by the self-consistency condition[5], i.e. $\Omega(\hat{k}) = \langle\Omega\rangle$, but we would make use of the stationary point approximation[2] for its convenience[6]. In this approximation, the replicated free energy and the physical free energy are related by

$$f = d\lim_{n\to 0}\mathscr{F}_n\left(\Omega(\hat{k})\right)\Big|_{\Omega=\bar{\Omega}}, \tag{2}$$

where $\bar{\Omega}$ is the field at which $\mathscr{F}_n$ is stationary. It also determines the order parameter according to

$$\Omega(\hat{k}) = \lim_{n\to 0}\bar{\Omega}(\hat{k}), \tag{3}$$

Thus we obtain a systematic method to derive the order parameter. (i)Compute the random partition Z_χ function with a random constraint χ (ii)find the replicated free energy $\mathscr{F}_n$ by taking the disorder average (iii)apply the stationary point approximation and find the parameter that minimizes the free energy (iv)take a limit $n \to 0$ to obtain the order parameter. Therefore, all we need is the replicated free energy $\mathscr{F}_n$.

---

[4] This idea is inspired by the discussion with P. M. Goldbart.

[5] Here the thermal average is taken with the replicated free energy.

[6] By convenience it means that it is easy to improve the model by the field-theoretic approach. For example, we can include the loop contribution to improve the stationary point approximation.

3.2 Free Energy Functional

To obtain $\mathscr{F}_n$ for the randomly cross-linked system, we need an appropriate Hamiltonian H and the distribution $P[\chi]$ of the random constraint. These quantities are proposed by the formulation of Deam and Edwards[7], where the Hamiltonian is given by

$$H = \frac{1}{2}\sum_{i=1}^{N}\int_0^1 ds \left|\frac{d\boldsymbol{c}_i(s)}{ds}\right|^2 + \frac{\lambda^2}{2}\sum_{i,i'}\int_0^1 ds \int_0^1 ds' \delta\left(\boldsymbol{c}_i(s) - \boldsymbol{c}_{i'}(s')\right).$$

λ^2 (> 0) is a coupling constant for the repulsive interaction between monomers and is generally temperature-dependent. In computing the partition function, a random constraint is imposed by multiplying a suitable product of Dirac delta functions[2];

$$Z_\chi = \int \mathscr{D}\boldsymbol{c}\; e^{-H}\prod_{e}^{M}\delta\left(\boldsymbol{c}_{i_e}(s_e) - \boldsymbol{c}_{i'_e}(s'_e)\right). \tag{4}$$

For the disorder-averaging, we would use the Deam-Edwards distribution of the random constraints[7]. It is constructed on the assumption that all cross-links are equivalent, i.e. at a given moment, a cross-link is created to any pair of monomers that happen to be close to each other, according to some "cross-linking probability" parametrized by μ^2. The resulting formula is proportional to $(\mu^2 V/N)^M$, showing that the average cross-link density $\overline{M}/N$ is simply increasing in the parameter μ^2.

Given these ingredients, we are ready to calculate the replicated free energy $\mathscr{F}_n$, but we shall focus on the case of the stationary point approximation and will not use the exact form. The explicit form of $\mathscr{F}_n$ is presented in Ref.[2].

3.3 Order Parameter

As explained above, the order parameter is given through the stationary point of the free energy. However, instead of solving the stationary point equation, we shall try to guess the form of the order parameter. As it will turn out, the construction is quite analogous to that of the spin-glass system.

Since we are interested in the transition to an (amorphous) solid state, the order parameter is expected to be a certain measure of the localization of the monomers. Then it is natural to consider the following;

$$\int d^d r\, \langle\delta(\boldsymbol{r} - \boldsymbol{c}_i(s))\rangle_\chi \exp\left(i\boldsymbol{k}\cdot\boldsymbol{r}\right) \equiv \langle\exp\left(i\boldsymbol{k}\cdot\boldsymbol{c}_i(s)\right)\rangle_\chi,$$

i.e. the probability density that a particular monomer (i, s) be located at $\boldsymbol{r}$. The average of this quantity over the monomers, i.e. $\frac{1}{N}\sum_{i=1}^{N}\langle \exp\left(i\boldsymbol{k}\cdot\boldsymbol{c}_i(s)\right)\rangle$ is, however, not a good order parameter since it fails to distinguish a set of delocalized monomers and that of (partially) localized monomers; due to the randomness of their mean position, it gives $\delta_{\boldsymbol{k},\boldsymbol{0}}$ in either case[3]. This situation is analogous to the magnetization in the spin-glass system, and in fact, an analogous approach works in the case of vulcanization. Instead of summing over the mean value, we can take a sum of a *product* of them[8]

$$\Omega(\hat{k}) = \overline{\frac{1}{N}\sum_{i=1}^{N}\int_0^1 ds\ \langle \exp\left(i\boldsymbol{k}^{(1)}\cdot\boldsymbol{c}_i(s)\right)\rangle_\chi \ldots \langle \exp\left(i\boldsymbol{k}^{(g)}\cdot\boldsymbol{c}_i(s)\right)\rangle_\chi},$$

where g is any integer and we wrote $\{\boldsymbol{k}^{(1)}, \ldots, \boldsymbol{k}^{(g)}\}$ as $\hat{k}$. One can deduce the following properties of $\Omega(\hat{k})$[3]:

1. If all monomers are delocalized, $\Omega(\hat{k}) \neq 0$ only if $\{\boldsymbol{k}^{(\alpha)} = \boldsymbol{0}\}$.
2. If a fraction of monomers are localized, $\Omega(\hat{k}) \neq 0$ only if $\sum_\alpha \boldsymbol{k}^{(\alpha)} = \boldsymbol{0}$

Thus at the limit $\{\boldsymbol{k}^{(\alpha)} \to \boldsymbol{0}\}$ (while keeping $\sum_\alpha \boldsymbol{k}^{(\alpha)} = \boldsymbol{0}$), the order parameter yields the fraction of localized monomers. In fact, assuming that the monomers are isotropically localized within some localization length ξ from its mean position, we have[3]

$$\Omega\left(\hat{k}\right) = (1-q)\prod_\alpha \delta_{\boldsymbol{k}^{(\alpha)},\boldsymbol{0}} + q\,\delta_{\sum_\alpha \boldsymbol{k}^{(\alpha)},\boldsymbol{0}}\int d\xi\ p(\xi)\exp\left(-\frac{\xi^2}{2}\sum_\alpha |k^{(\alpha)}|^2\right), \tag{5}$$

where $p(\xi)$ is the distribution of the localization length and q is the fraction of localized monomers.

3.4 Consistency Condition; Phase Transition

Let us now verify the validity of our proposal (5) for the order parameter. We will first check its consistency with the stationary point equation (2) and then focus on the region near the critical point.

3.4.1 Stationary point approximation

For our model to be self-consistent, the order parameter (5) should minimize the replicated free energy functional $\mathscr{F}_n$. It can be shown that this is indeed the case, provided that a number of self-consistency equations are satisfied[7]. In particular, at the limit $\hat{k}^2 \to 0$ while keeping $\sum_\alpha \boldsymbol{k}^{(\alpha)} = 0$, we can obtain the self-consistency condition for the fraction q of localized monomers[3]

$$1 - q = e^{-\mu^2 q}.$$

This equation has only a trivial solution $q = 0$ when $\mu^2 \leq 1$, but has non-zero solution $q = \bar{q}(\mu^2)$ when $\mu^2 \geq 1$, which corresponds to the amorphous solid state. The spectrum of $\bar{q}(\mu^2)$ ensures that q emerges continuously from zero at $\mu^2 = 1$ and approaches unity for large μ^2.

Thus we have seen that (i)at some critical cross-link density characterized by $\mu^2 = 1$, a phase transition to the amorphous solid state happens, and a fraction of monomers get localized (ii)the transition is continuous, and (iii)all (and not more than all) monomers get localized at large enough cross-link density. This is a reasonable result. Also, a linear stability analysis shows that the liquid state $\Omega(\hat{k}) = \delta_{\hat{k},\hat{0}}$ is unstable when $\mu^2 > 1$, ensuring that it cannot be a liquid state[2].

3.4.2 Near the Transition

Near the transition point $\mu^2 = 1$, more detailed behavior of q can be extracted by making an appropriate approximation[8]. The smallness of q near transition allows us to expand the free energy up to the quadratic order in Ω, yielding[2]

$$nd\mathscr{F}^n = \sum_{\hat{k}} \left(-\epsilon + \frac{1}{2}|\hat{k}|^2\right) |\Omega_{\hat{k}}|^2 - \sum_{\hat{k}_1,\hat{k}_2,\hat{k}_3} \Omega_{\hat{k}_1}\Omega_{\hat{k}_2}\Omega_{\hat{k}_3}\delta_{\hat{k}_1+\hat{k}_2+\hat{k}_3,\hat{0}}$$

where $\epsilon = 3(\mu^2 - 1)$ measures the excess cross-link density. The saddle point equation for this functional is then

$$\frac{d\mathscr{F}^n}{d\Omega(\hat{k})} = 2\left(-\epsilon + \frac{1}{2}|\hat{k}|^2\right)\Omega_{\hat{k}} + 3 \sum_{\hat{k}_1,\hat{k}_2 \in \mathscr{R}} \Omega_{\hat{k}_1}\Omega_{\hat{k}_2}\delta_{\hat{k}_1+\hat{k}_2,\hat{k}} = 0. \qquad (6)$$

The consistency of the order parameter (5) at $\hat{k}^2 \to 0$ then requires that[2]

$$q = \frac{2\epsilon}{3}$$

---

[7] These are discussed in detail in Ref.[2]

[8] As shown in Ref.[10], the Gintzburg-Landau criterion works in our model, too, and it yields the same form of the saddle-point equation.

i.e. the fraction q grows linearly in the excess cross-link density. In addition, the other consistency condition tells that the distribution $p(\xi)$ of the localization length scales as $\epsilon^{-1/2}$[2]. The divergence of this quantity at $\epsilon = 0$ also characterizes the phase transition at this point.

4 Emergence of Rigidity

In this section, we will briefly summarize the result of the Chap.III, Ref.[2].

4.1 Brief Summary

Since the shear modulus is determined from the expansion of the free energy in powers of the deformation, we are mainly interested in the free energy change due to the deformation. We can use the same physical and mathematical argument as in the previous section to obtain the free energy, etc., except that several impacts due to the deformation have to be taken into accounts.

To proceed, we would make two major assumptions; (i)the shear deformation is applied before taking the thermodynamic limit, and more importantly, (ii)all the localized monomers remain localized after deformation. Also, we shall consider the infinitesimal shear strain.

When the system size is finite, the Fourier representation of the order parameter is characterized by a discrete set of the wave vectors, in other words, $\Omega(\hat{k})$ is defined at discrete points in the (replicated) wave vector space. However, since the shear deformation changes the boundary condition in the position space, the wave vector space (i.e. domain of the order parameter) changes correspondingly. As a consequence, the solution to the the saddle point equation (6) has to be taken from the different domain of $\Omega(\hat{k})$. Also, the deformation affects the mean position of the localized monomers, as well as the shape of the localization region. Recalling the dependence of $\Omega(\hat{k})$ on these information, it is intuitively clear that the form of $\Omega(\hat{k})$ itself should be changed correspondingly.

After the detailed calculation, we see that the self-consistency condition for the saddle-point equation yields $q = 2\epsilon/3$, which is unchanged as consistent with our assumption. The change in the free energy is found as

$$\Delta f \propto \frac{2}{27}\epsilon^3$$

and the shear modulus as

$$E \propto k_B T N \epsilon^3$$

i.e. the static shear modulus is characterized by the exponent $t = 3$ near the transition. Its temperature dependence indicates that the entropic origin of the elasticity.

The exponent t for the rubber elasticity has been measured in experiments[6], and the results range from $t \simeq 2$ to $t \simeq 3$, i.e. some discrepancy does exist. However, since these experiments are done for gelation rather than vulcanization, a more direct measurement on the vulcanized media may provide a more or less consistent result.

5 Summary and Discussion

In this review, we have presented a statistical mechanical formulation of the randomly cross-linked macromolecular system, based on the replica trick and the Deam-Edwards Hamiltonian. At the level of the stationary point approximation, it was seen that a continuous phase transition from a liquid state to an amorphous solid state happens when the cross-link density exceeds certain critical value, so a non-zero fraction of monomers get localized to some mean position. The ratio of localized monomers approaches unity as we increase the number of cross-links, which agrees with our expectation.

In the vicinity of the critical point, it was shown that the localization ratio emerges from zero and linearly increases with the excess cross-link density ϵ. The divergence of the typical localization length, which we saw scales as $\epsilon^{-1/2}$, provides another characteristics of the phase transition. One of the main predictions of this model is the exponent of the static shear modulus. However, the prediction $t = 3$ has a little discrepancy from the experiments that need to be examined.

Thus, the model is able to describe the essential properties of the vulcanization transition that we stated at the beginning of this review, and therefore provides a successful statistical model of the randomly cross-linked system.

However, there is a couple of issues that we may want to improve. (i)beyond-the-mean-field theory calculation: So far the entire work has been done in the framework of the mean-field theory, but a further improvement could be made, say, by the renormalization group method. This work is done by Peng and Goldbart[9]. (ii)Universal properties: Our near-transition discussion can be replaced by the famous Gintzburg-Landau approach[10]. In the virtue of its model-independence, we may be able to find a universality about the properties of the amorphous solids. (iii)Treatment of topology: We have left out the issue of the topology at the beginning of the review. I am not sure how significant it is for the critical behavior of the amorphous solids. A quantitative discussion on this issue, if any, may be interesting.

At last, it should be stressed that the presented approach should not be limited to only the glassy system; the setting of the problem was quite general, so it may be applied to other network systems that involve some kind of permanent cross-links. In fact, an analogous approach has been applied to a number of researches, say, from neural network to so-called eco-physics. To me, therefore, it seems interesting to investigate the possible application/extension of this model.

References

[1] P. M. Goldbart and N. D. Goldenfeld, Phys. Rev. Lett. **58**, 2676 (1987)

[2] H. E. Castillo and P. M. Goldbart, Phys. Rev. E **62**, 8159 (2000)

[3] P. M. Goldbart, Journal of Physics, Cond. Matt. **12**, 6585 (2000)

[4] V. Dotsenko, *Introduction to the Replica Theory of Disordered Statistical Systems* (Cambridge, 2001)

[5] L. R. G. Treloar, *The Physics of Rubber Elasticity* (Oxford, London, 1975)

[6] M. Adam *et al.*, Pure Appl. Chem. **53**, 1489 (1981)

[7] R. T. Deam and S. F. Edwards, Phil. Trans. R. Soc. **280 A** 317 (1976)

[8] S. F. Edwards and P. W. Anderson, J. Phys. F **5**, 965 (1975)

[9] W. Peng and P. M. Goldbart, Phys. Rev. E **61**, 3339 (2000)

[10] W. Peng, H. E. Castillo, P. M. Goldbart, and A. Zippelius, Phys. Rev. B **57**, 839 (1998)