Randomly Crosslinked Macromolecular Networks

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May 2, 2000

Abstract

This essay explores a few aspects of randomly crosslinked macromolecular networks. Deam and Edwards' theory of rubber elasticity is explored. The so called Flory, James and Guth assumptions are tested via Deam and Edwards' theory. An order parameter that is capable of distinguishing between the fluid, crystalline solid, and amorphous solid states was developed, following the work of Paul Goldbart.

1 Indroduction

> *There is probably no other inert substance, the properties of which excite in the human mind, when first called to examine it, an equal amount of curiosity, surprise, and admiration. Who can examine, and reflect upon gum-elastic, without adoring the wisdom of the Creator?*
>
> Charles Goodyear,*Gum-Elastic and its Varieties, with a Detailed Account of its applications and Uses, and of the Discovery of Vulcanization* (1855)

This is a funny quotation. What kind of person is compelled to adore the "wisdom of the Creator" by thinking about rubber? The very idea that rubber could serve as a source of spiritual inspiration, in same way that the sky and oceans are sometimes thought to serve such a purpose, is a bit wacky. On the other hand, the first half of this quote probably rings true in the ear of any physicist that has studied random media. The physics of rubber is indeed amazing.

Why did Goodyear say that rubber excites admiration in the mind? A simple answer is that finding a good description of rubber is so difficult, and any good description is so complicated, that rubber earns the admiration of anybody who takes a stab at such tasks. In this paper I will try to lead the reader to a good description of rubber. There is no doubt that the reader will find this description complicated!

The media described in this paper is not rubber *per se*. We will examine networks of randomly crosslinked macromolecules in both the fluid phase and solid phase. The solid state of a randomly (semi-permanently) crosslinked network of macromolecules is rubber. In examining the liquid and the solid phases of these networks, we will come across the phase transition from one phase to the other via an order parameter. The order parameter will be found to depend on the density of crosslinks as well as the localization length of the crosslinks.

This paper consists of only three sections following the introduction. In sections two and three we explore rubber elasticity as described by Deam and Edwards in 1976.[1] The goal of section one is to calculate a partition function for $n+1$ sytems, each system consisting of a single long polymer in a box, the polymer crosslinked with itself. This partition function, and replica theory in general, is something that I find very hard to interpret. We will see that if we avoid discussing the meaning of replica theory, it will pop up again in section 3 in which we will have something very helpful to say about it.

A particularly important feature of the Deam and Edwards Partition function is the quantity known as the Edwards measure, which, from the time it was written down, has been used as the starting point for many subsequent theories of rubber elasticity. In section two we will see the results (but not the details) of the Deam and Edwards partition function as it is put to use. Deam and Edwards calculate thermodynamic quantities under various assumptions due to Flory[1], James and

Guth [1], as well as under assumptions of their own.

Section three, the most important as well as impressive part of this paper (due to Goldbart and colleagues, not myself), is devoted to calculating an order parameter that is capable of distinguishing between three states of matter: liquid, crystalline solid, and amorphous solid. The amorphous solid state of a network of randomly crosslinked macromolecule is defined as a state in which the macromolecules are localized about mean positions that are distributed homogeneously and randomly, and to an extent that varies randomly from monomer to monomer.[2] This order parameter, capable of distinguishing between these three states is a complicated, but amazing thing – just as Goodyear said.

Note: I warn the reader that this essay contains no figures, because no vizualization aids are necessary. All the reader needs is the ability to imagine a few pieces of string (sometimes tied together at random points along the strings) and an empty box that can be sheared.

2 The Edwards measure

In this section I will present an approach to the theory of amorphous solids, which, to the present time has served as the starting point for many other theories of amporphous solids. This approach was first taken by R.T. Deam and S.F. Edwards. I present one particular example of their work on the amporphous solid state of randomly crosslinked chain networks entitled *The Theory of Rubber Elasticity*.[1] Since the theory of Deam and Edwards served as the foudation for many other developements in the field of amorphous solids, I will take a reasonable amount of care to explain the mathematical, as well as the basic statistical mechanical, ideas that they present. This is for my own benefit, as well as the reader's.

We begin by describing a polymer. How does one define a polymer, mathematically? We could look at the atom by atom composition of hydrocarbons, proteins, DNA strands and the like, each being very different from the other on the microscopic level. However, this kind of detailed description would vary greatly across different types of polymers, and given the size of certain macromolecules the descriptions would be too complicated to be of any use to us. This is not what they do in stastical physics. Rather, we can save ourselves a lot of time by patiently finding a way to describe *all* polymers in terms of their more generic characteristics. How long is it? How hard is it to bend? Who cares what it's made of? So, I now define for you a physicist's view of a polymer. A polymer is

$$\mathbf{R}(s) \tag{1}$$

Simple enough. **R** is a position vector and s is an arclength. How is a position vector a polymer? Well, pick an arclength. We will start off assumimg s an integer. Say, $s = 1$. There is a point in space defined as $\mathbf{R}(1)$. At another arclength, say

$s = 2$, there is another position in space defined as $\mathbf{R}(2)$. Do this from $s = 0$ to $s = L$ (L is the length of the polymer), and you have just traced out the path of a polymer.

In this paper, we assume that polymers are long and floppy. This is due, once again, to our desire to describe as many polymers as possible with a few simple ideas. If the polymer was not floppy, then we might have to consider things like bond angles and other constraints that we don't want to deal with. Since this polymer is floppy, we say that $\mathbf{R}(\mathrm{s})$ is a Gaussian random vector. If $\mathbf{R}(\mathrm{s})$ is made in discrete steps of s, then in constructing $\mathbf{R}(\mathrm{s})$ we follow the routine given above, but at each increment of s, the direction in which we choose to step is completely random. The probability that a particular cofiguration is realised is given by the Wiener measure,

$$P[\mathbf{R}(s)] = Nexp\left(-\frac{3}{2l}\int_0^L |\dot{\mathbf{R}}(s)^2| ds\right) \tag{2}$$

Where does this come from? With respect to what variable is $\mathbf{R}(\mathrm{s})$ differentiated? It seemed quite mysterious to me until I saw the Wiener measure "derived" at a lecture by P. Goldbart.[3] Imagine, again, that the polymer is made in discrete units of s. Then one can see that the probalility for a given configuration is equal to the product of the probabilities associated with each step made in space (tracing out the polymer). Because of the Gaussian nature of our polymers, the product of exponentials becomes a sum in the argument of a single exponential and we get

$$P[\mathbf{R}_1\mathbf{R}_2 ... \mathbf{R}_s] = \left(\frac{d}{2\pi l^2}\right)^{\frac{Nd}{2}} \exp\left(-\frac{d}{2l^2}\sum_{s=1}^{N-1} |\mathbf{R_{s+1}} - \mathbf{R_s}|^{\mathbf{2}}\right) \tag{3}$$

This probability distribution is in d dimensions, for a polymer made in $N-1$ integer steps (and, therefore N vectors), each of length l. Now imagine taking the continuum limit ($l \to 0$). The difference $|\mathbf{R}(s+l) - \mathbf{R}(s)|^2/l^2$ is just the square of the derivative in the continuum limit. The sum, of course becomes an integral, and sweeping the multiplicative constants under the rug, we now see and understand the origin of the Weiner measure. This will soon be modified and renamed the Edwards measure, after S. F. Edwards.

Now that we have described a polymer as well as its probability distribution, we move on to Deam and Edwards' description of the phantom chain network. A phantom chain is an infinitely thin chain that can pass through itself and other chains. A network of such chains when crosslinked to the right extent will form an amorphous solid. The statisitcal mechanincs of such a solid must be developed because the standard statisitical mechanics of gasses, liquids and ordered solids can't describe random solids.

How is statisitcal mechanics usually done on ordered solids? The procedure is as follows. (1) Choose a lattice. (2) Transform your system into a phonon gas, calculate the free energy. (3) Change the shape of the lattice, do (2) again. (4) Use the change in free energy to calculate the modulus of the solid. A problem arises when one attempts this procedure on an amporphous solid: there is no lattice and no phonon gas to which we can transform. Instead, the notion of a topology must be used. The topology of an amorphous solid is nothing more than the particular arrangement and positioning of the chains making up the solid (including positions of crosslinks). The way that we do statisitcal mechainics on amorphous solids is as follows. (1) Pick a topology. (2) Calculate the free energy associated with that topology. (3) Change the shape of the system (assuming topology is conserved due to the microscopic constraints put in the system at the time of vulcanization), and calculate the free energy. (4) Calculate the modulus from the change in free energy.

There are two problems with this procedure. First, how is one to know which of infinitely many topologies the sample of amorphous solid has? This problem is solved by taking into account all possible topologies and doing a weighted average. The weights can be calculated and the averaging done via replica theory. The second problem (that I will not deal with) is that there is a chance that the number of possible topologies is small and that each has a very different free energy. In such a case, the calculation of the most probable modulus would not equal the actual modulus.

The replica method, as presented by Deam and Edwards, consists of using a partition function Z(n) to calculate the strained free energy, $\tilde{F}$. I must say that the method, as presented by Deam and Edwards, should be taken as a useful method for calculating the change in free energy associated with affine (topology preserving) deformations of a random solid, from which thermodynamic quantities can be found. Certain physically relevant features of this calculation can be discussed (such as the physical meaning of replicas and their interactions), but I will avoid discussing these features in the setting of the method discussed in this section. As I mentioned in the introduction, I will discuss such things in a later section in the setting of a particularly illuminating method presented in a paper by P. Goldbart.[4]

In the Deam and Edwards calculation, we are asked to consider without qualification the expression

$$Z(n) = \sum_m Z_m (\tilde{Z_m})^n, \tag{4}$$

where Z_m is the partition function for a single, long, self crosslinked polymer in a box of volume V with topology m, and $\tilde{Z}_m$ is the partition function for the equivalent polymer in a deformed box, the configuration of the replica polymer being affinely deformed. The motivation for using this somewhat strange object, $Z(n)$, is that $\tilde{F}$ is found by

$$\tilde{F} = -kT \left(\frac{\partial Z / \partial n|_{n=0}}{Z(n=0)} \right), \tag{5}$$

and as we know, $\tilde{F}$ is a necessary part of getting at the thermodynamic quantities.

One can see already the reason that this is called the replica method, having to do with the power n in $Z(n)$. One can replace the partition functions in 4 using the Gibbs distribution, and put in 'topology conservation' terms (delta functions) to arrive at

$$Z(n) = \int\int\ldots\int\prod_{\alpha=0}^{n} d\Omega^{(\alpha)}\exp\left(-\beta_A H^{(0)} - \sum_{\alpha=1}^{n}\beta_B H^{(\alpha)}\right)\prod_{\alpha=1}^{n}\delta(m(0)-m(\alpha)). \tag{6}$$

Notice the effect of the topology conservation terms. All possible configurations that lack the topology of system (0) are thrown out. If one expands $Z(n)$ in powers of n, one can find the desired free energy relationships. However, these relationships require us to know the free energy of the undeformed system, as well as the free energy of the deformed systems, which we will not attempt to find at the moment. We will instead take $Z(n)$, and show how Deam and Edwards calculate Z(n) using the Wiener measure and another term. Physicists today call the combination of these two terms the Edwards measure.

Now we imagine the same set of systems as just described (one undeformed box, n deformed boxes), but we construct Z(n) in a slightly different way.

$$\begin{aligned} Z(n) =& N\int_0^L ds_1\int_0^L ds_2\int_V \delta\mathbf{R}^{(0)}(s)\int_{V\lambda_x\lambda_y\lambda_z}\delta\mathbf{R}^{(\alpha)}(s)\int\ldots\int_{V\lambda_x\lambda_y\lambda_z}\delta\mathbf{R}^{(n)}(s) \\ &\times\prod_{\alpha=0}^{n}\delta(\mathbf{R}^{(\alpha)}(s_1)-\mathbf{R}^{(\alpha)}(s_2))\exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L|\dot{\mathbf{R}}(s)^2|ds\right). \end{aligned} \tag{7}$$

This contains the Wiener measure as well as a term that insures that each of the systems has the same *crosslink* topology. Remeber that the system described is just one long chain, self crosslinked at one position. Notice that the integrations over ds_1 and ds_2 scan through all possible positions for the crosslink. Adding N crosslinks and changing the order of integration, $Z(n)$ becomes

$$\begin{aligned} Z(n) =& N\int_V\int V\lambda_x\lambda_y\lambda_z\ldots\int\prod_{\alpha=0}^{n}\delta\mathbf{R}^{\alpha}(s)\left[\prod_{\alpha=0}^{n}\int_0^L ds_1\int_0^L ds_2\delta(\mathbf{R}^{(\alpha)}(s_1)-\mathbf{R}^{(\alpha)}(s_2))\right]^N \\ &\times\exp\left(-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L\dot{\mathbf{R}}(s)^2 ds\right). \end{aligned} \tag{8}$$

Finally, converting this into a pole integration, we get

$$\begin{aligned} Z(n) =& \oint\frac{d\mu N!}{\mu^{N+1}}N\int_V\int_V\lambda_x\lambda_y\lambda_z\ldots\int\prod_{\alpha=0}^{n}\delta\mathbf{R}^{\alpha}(s) \\ &\times\exp\left(\mu\int_0^L\int_0^L\prod_{\alpha=0}^{n}\int_0^L ds_1\int_0^L ds_2\delta(\mathbf{R}^{(\alpha)}(s_1)-\mathbf{R}^{(\alpha)}(s_2))-\frac{3}{2l}\sum_{\alpha=0}^{n}\int_0^L\dot{\mathbf{R}}(s)^2 ds\right)^N. \end{aligned}$$

Notice the argument of the exponential. It is the anticipated Edwards measure. The parameter μ is important. It appears to assign a strength to the crosslinking. Later on, we will see the importance of μ^2, which we will call the crosslink density parameter. Now that we've gone through the math to get to this particular form of Z(n), we will look quickly a couple of assumptions that can be made about our randomly crosslinked network, and compare the results that follow from these assumptions. It should be noted that in order to do these calculations, Deam and Edwards take Z(n) one step further by doing some averaging, which I will not do here.

3 Assumptions: Flory, James & Guth

Flory[1] assumed that the crosslinks in random network are fixed in space and randomly distributed throughout the volume. This assumption is consistent with assuming periodic boundary conditions, which result in a volume of rubber with uniform density. Deam and Edwards modified their partition function to account for these assumptions and found an upper bound on $\tilde{F}$ given by

$$\tilde{F} \leq NkT\left[\sum_i \lambda_i^2 - \ln \lambda_i\right]. \tag{9}$$

The Flory assumption, further, yields for the mean squared fluctuations of crosslinks from their affinely deformed positions

$$\langle \eta_i^{(\alpha)^2} \rangle = lL/6N. \tag{10}$$

Finally, Deam and Edwards calculated the mean square difference of $\mathbf{R}^{(0)}$ and $\overline{\mathbf{R}^{(0)}}$. This quantity is the variance of the point by point positions of the polymer, and can be thought of as the width of the polymer density in the box.

$$\langle (\mathbf{R}^{(0)} - \overline{\mathbf{R}^{(0)}})^2 \rangle = \frac{1}{4}V^{\frac{2}{3}} + lL/6N. \tag{11}$$

These quanties will carry more meanining when we have something to compare them to, which brings us to the James & Guth assumption.[1] James and Guth assumed that the crosslinks in the bulk of the rubber are free to move, but the crosslinks at the edges of the box are fixed in space. We predict that this leads to boxes of rubber with high density in the center, and lower density near the edges. The calculations just done for the case of the Flory assumption yields, for the James and Guth assumption (again using a modified Deam and Edwards' partition function),

$$\tilde{F} \leq NkT \sum_i \lambda_i^2, \tag{12}$$

$$\langle \eta_i^{(\alpha)^2} \rangle = lL/6N, \tag{13}$$

$$\langle (\mathbf{R}^{(0)} - \overline{\mathbf{R}^{(0)}})^2 \rangle = lL/6N. \tag{14}$$

The most important point to carry away from the comparison between the results of the two sets of assumptions is that the Flory assumption contradicts itself (the crosslinks aren't fixed), but does give the correct density behavior, due to the dominating V term in the width of the density. The James and Guth assumptions, on the other hand, produce the expected fluctuations, but give rise to a high polymer density at the center of the box, and low density at the edges of the box. As given in the definition of an equilibrium amorphous solid, such density behavior does not characterize the macroscopically homogeneous piece of rubber that we have in mind.

The natural 'fix it' one should propose is to allow for the fluctuations of crosslinks about their affinely deformed positions, and to require a polymer density evenly distributed throughout the box. This is just what Deam and Edwards did. Their results are

$$\tilde{F} \leq kT \frac{N}{2} \frac{1}{1 + c/\rho} \sum_i \lambda_i^2, \tag{15}$$

$$\omega_i = lL/6N, \tag{16}$$

These results are quite nice. Particularly, $1/(1+c/\rho)$ in (15) accounts for "wasted loops", i.e. loops frozen into the polymer by crosslinks that do not contribute to the rigidity of the network. Also, the factor of 1/2 distinguishes it from the other approaches. Eq.(16) gives the cross link localization (the same thing as $\langle \eta_i^{(\alpha)^2} \rangle$), and agrees with the results of Flory, James and Guth. It should be noted that Deam and Edwards calculated ω via a variational approach (by finding the value that minimized the free energy), which is why they changed symbols on us!

The question of density remains. Deam and Edwards found that the system undergoes an interesting change, which drastically effects the polymer density. One might even use (as they did) the words "phase transition" in scare quotes. The quantities involved are V,μ (the crosslink density parameter), and $A(\omega)$ given by

$$A(\omega) = \prod_i \left(\frac{\omega_i}{2\pi} \right)^{\frac{n}{2}}. \tag{17}$$

For $\mu A(\omega) - V$ greater than zero, the polymer density is like that of the James and Guth assumption, and for $\mu A(\omega) - V$ less than zero, the polymer density is evenly spread, as desired.

Deam and Edwards made further contributions, such as adding an 'excluded volume' term, which removes the phantom nature of the chains. They also did calculations for entanglements, i.e. certain configurations of the polymers which, although they are not true crosslinks, inhibit many configurations from being realised in the system. I now close this section by repeating myself. Quite a lot of work done in the field of amorphous solids was built on the foudation provided by the calculations discussed in the first two sections of this paper. The full treatment can be found in Ref[1].

4 Hunting down the order parameter

This section comes almost entirely from Ref [4]. The description of the order parameter for randomly crosslinked networks given in Ref [4] is the best and most accesible description that I've been able to find. So, at the cost of quantity (i.e., of offering a more diverse group of references), I've chosen to utilize, almost exclusively, the reference of highest quality. This choice will, hopefully, benefit the reader as much as it benfits myself. We will find, as the order parameter emerges, some ideas that will help us understand a bit about replica theory.

We begin from scractch, by considering a collection of point particles in a box of volume V. The position of each particle is given by a position vector, and the distribution of these particles is given by the distribution $\Pi(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$. We denote averages with respect to this distribution with angle brackets, and as a consequence of this choice, the probability of finding a single particle, i, at position $\mathbf{r}$ is written as $\langle \delta(\mathbf{r} - \mathbf{R}_i) \rangle$. Now comes an interesting and unexpected step. Instead of dealing with such a probability, we deal with a different object – the Fourier transform of the probability given by

$$\int_V d^3r \langle \delta(\mathbf{r} - \mathbf{R}_i) \rangle \exp i\mathbf{k} \cdot \mathbf{r} = \langle \exp i\mathbf{k} \cdot \mathbf{R}_i \rangle, \tag{18}$$

where $\mathbf{k}$ is a discrete lattice wave vector found in the usual way assuming periodic boundary conditions.

We now examine the properties of $\langle \exp i\mathbf{k} \cdot \mathbf{R}_i \rangle$, which we will call the characteristic function. Keep in mind that this characteristic function is associated with a *single* particle. If the characteristic function is to characterize one of the particles in a fluid state, then we begin by observing that an arbitrary translation of all of the particles in the system does not effect this quantity because configurations related by such a translation are equally probable. Writing this statement out explicitly will lead to the following:

$$\lim_{k \to 0} \langle \exp i\mathbf{k} \cdot \mathbf{R}_i \rangle_f = 0, \tag{19}$$

$$\langle \exp i\mathbf{k}\cdot\mathbf{R}_i\rangle_f|_{k=0} = 1, \tag{20}$$

Where the subscript f denotes a fluid. These result tell us that the characteristic function is discontinuous at $\mathbf{k} = 0$.

Now we examine the characteristic function's properties in the solid state. In the a solid state, the 'particles' become localized about some mean position. In the amorphous solid state, we have little to no information about the distribution of positions of the particles. To sidestep this potential problem we do a cumulant expansion, which looks like

$$\ln\langle \exp i\mathbf{k}\cdot\mathbf{R}_i\rangle_s = \ln\langle 1 + i\mathbf{k}\cdot\mathbf{R}_i + (i\mathbf{k}\cdot\mathbf{R}_i)^2/2 + \ldots\rangle_s. \tag{21}$$

Leaving out further (important) steps in the expansion, eventually one arrives at form of the equation which, when both sides are re-exponentiated (getting rid of the log), is

$$\langle \exp i\mathbf{k}\cdot\mathbf{R}_i\rangle_s \approx \exp i\mathbf{k}\cdot\langle\mathbf{R}_i\rangle_s \exp(-{\xi_i}^2 k^2/2), \tag{22}$$

where the subscript s denotes a solid. The localization length, ${\xi_i}^2$, emerged from the expansion, and one should check Ref[4] to see just how this was done. Its presence is vital. Equally important is the mean position of the particle, $\langle\mathbf{R}_i\rangle_s$. The importance of these quantities is demonstrated by considering a particle i to be either delocalized ($\xi_i = \infty$) or localized ($\xi_i < \infty$). Under such conditions the characteristic function behaves as

$$\lim_{k\to 0}\langle \exp i\mathbf{k}\cdot\mathbf{R}_i\rangle_{s,deloc} = 0 \tag{23}$$

$$\lim_{k\to 0}\langle \exp i\mathbf{k}\cdot\mathbf{R}_i\rangle_{s,loc} = 1 \tag{24}$$

So, we can see already that the characteristic function can tell the difference (in the large length scale, $k \to 0$, limit) between localized particles and delocalized particles.

Now we must utilize the behavior of the characteristic function as we look a systems of particles (remember that, so far we've only been talking about one particle). From this we will build an order parameter. Getting back into the mode of replicas (remembering the method's appearance in section two of this paper), we will take the product of g single particle characteristic functions, each associated with an arbitrary wave vector $\mathbf{k}^j$, we will average over a system of N particles, and finally we will average over all disordered configurations of the system:

$$\left[\frac{1}{N}\sum_{i=1}^{N}\langle \exp i\mathbf{k}^1\cdot\mathbf{R}_i\rangle\langle \exp i\mathbf{k}^2\cdot\mathbf{R}_i\rangle\ldots\langle \exp i\mathbf{k}^g\cdot\mathbf{R}_i\rangle\right], \tag{25}$$

where the square brackets denote the disorder averaging. Notice that the inner averages are equilibrium averages, while there is just one disorder average to be done. This quantity is the order parameter we've been seeking (although, it is for point particles, not macromolecules).

A few steps from here (with many steps left out), we will put this order parameter into the desired form, viz., one that can distinguish between liquid, crystalline solid, and random solid states of a network of randomly crosslinked macromolecules. We take the first of these steps by inserting (22) into (25) to arrive at

$$\int_V dR \int_0^\infty d\xi \left[\frac{1}{N} \sum_{i=1}^{N} \delta(R - \langle \mathbf{R}_i \rangle) \delta(\xi - \xi_i) \right] \exp\left(i\mathbf{R} \cdot \sum_{\alpha=1}^{g} |\mathbf{k}|^\alpha \right) \exp\left(-\frac{\xi^2}{2} \sum_{\alpha=1}^{g} |\mathbf{k}^g|^2 \right)$$

This order parameter is obvously a complicated object, and one can check Ref [4] for the details of what I will just state. If system is in a liquid state, the order parameter takes the values 1 or zero, depending upon whether all of the wave vectors are zero, or nonzero, respectively. If the system is in a crystalline solid state, the order parameter takes nonzero values, and one extracts a *single* localization length.

Now, we get to the heart of the matter. If system is in an amorphous solid state, the order parameter can be manipulated into the form

$$(1-q) \prod_{\alpha=1}^{g} \delta_{k^\alpha,0} + q\delta_{0,\sum_{\alpha=1}^{g} k^\alpha} \int d\xi p(\xi) \exp\left(-\xi_1^2 \sum_{\alpha=1}^{g} |k^g|^2/2 \right). \tag{26}$$

A few things need to be said about (26). First, it is has distinctly different behavior than its counterpart forms in the liquid and crystalline phases. Secondly, it is dependent upon the so called gel fraction, q and the distribution of localization lengths, $p(\xi)$ (which is distinctly different from such distributions in the other two phases). The gel fraction is simply the fraction of monomers (constituents of polymers) that are localized. The distribution of localization lengths should be self explanatory.

A final thing to mention about the order parameter, is that we can finally make make some sense of replica thoery. One can see that it is *necesary* that we consider More than one g in order to describe the amorphous solid phase of matter (using this order parameter, anyway). One can check that for the $g = 1$ case (alone), the order parameter cannont distinguish between the liquid and the amorphous solid state. This tells us that replica theory is more than just a trick to calcuate the thermodynamics of amorphous solids, as it seemed in the section two of this paper! This is a very exciting result, because the notion of replicas seems quite artificial at first.

This also comforts us when we talk about replicas interacting, which seems bizzare at first. For example, the phase transition that we have been considering, viz., the liquid to amorphous solid transition, is characterized by various types of replica symmetry breaking [5]. To the student, still wet behind the ears in statisitical physics, these ideas are difficult to digest. Although the symmetries are seen by just looking at the Hamiltonian of the system, the unsure graduate student now has another piece of information to force him to get used to replicas.

5 Conclusion

In this essay, I have introduced the reader to a small corner of the randomly crosslinked macromolecular network world. We have learned how to describe a polymer. We went through the steps of the Deam and Edwards theory of rubber elasticity, and had a brush with replica theory in the process. We saw how Deam and Edwards made good with the bad assumptions of others. Most importantly, we saw how Goldbart and colleagues found a most remarkable order parameter suitable for describing the phases of randomly crosslinked macromolecular networks. Finally, we improved our confidence in replica theory.

References

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