in the perpendicular direction. This could be associated with the formation of highly anisotropic domains perpendicular to the deformation direction.

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Solid State of Cross-Linked Macromolecules: Basic Concepts

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ABSTRACT: We present a simple physical picture of the way in which topological entanglements enter into a statistical mechanical theory for the solid state of randomly cross-linked macromolecules. Our approach, which does not require the use of invariants, focuses on the way in which the system explores its phase space. We summarize the results of a detailed calculation and briefly discuss their experimental consequences.

1. Introduction

It has long been recognized that cross-linked systems of flexible macromolecules pose extraordinary difficulties for statistical mechanics. These difficulties result from the combination of two factors: the chainlike nature of the molecules and the presence of permanent cross-links between the chains. These same two factors are also believed to be responsible for the spectacular elastic response of cross-linked systems such as gels and rubber.

We believe that a prerequisite for a genuine statistical mechanical theory of the elastic response of these systems is a sound understanding of the undeformed solid state. This paper is intended to explain the physical considerations underlying our recently proposed theory of the liquid-to-solid transition in cross-linked macromolecules.[1]

Although much has been understood about gels and rubbers from a phenomenological point of view,[2] a genuine microscopic theory must confront the topological complexity of cross-linked systems. The basic problem can be easily seen from Figure 1. Figure 1a shows a portion of a cross-linked system, where two chains, labeled A and B, are cross-linked to the network in such a way that chain A lies in front of chain B. The chains cannot pass through each other or the rest of the network. Consequently, it is impossible, as the system undergoes its dynamics, for the chains to move into the configuration depicted in Figure 1b. In this configuration, chain B lies in front of chain A, yet the chains are cross-linked at precisely the same points as in Figure 1a. The two configurations are said to be topologically inequivalent; if the system is formed in the configuration of Figure 1a, it will always preserve the topological relationships between the chains. A network of

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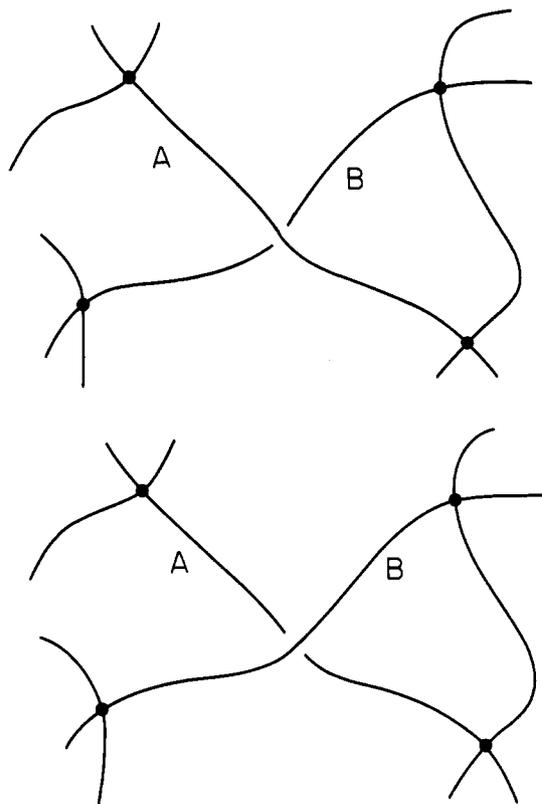[‡] Stanford University.

Figure 1. Two chains, A and B, in a network are cross-linked in such a way that their topological relationship with each other cannot change. The figure shows two topologically inequivalent configurations, (a, top) and (b, bottom).

cross-linked chains will have a well-defined, but complex, set of topological relationships between the chains, which we shall refer to as the topology of the network.

A corollary of this observation is that the specification of the positions of the cross-links does not uniquely specify the state of the system. To see this, recall how the cross-links might be specified in a statistical mechanical theory. The cross-links are not fixed in space; all that they do is to ensure that, e.g., monomer 174 on chain 18 is always constrained to be at the same point in space as, e.g., monomer 666 on chain 7. Proceeding in a similar fashion, one can construct a table which describes all the cross-links by listing, for each cross-link, which monomers on which chains are constrained to be at the same point in space. Such a table, however, does not contain enough information to reconstruct a given system. There are many different topologies that are consistent with the cross-links as specified by such a table. For example, in Figure 1 are shown two topologically inequivalent configurations, which nevertheless are specified by the same cross-link tabulation.

A related issue is the question of the definition of the term "entanglement". This term is often taken to mean a transient configuration in which a portion of one chain wraps around a portion of another chain in some complicated way. This configuration is transient, although possibly long-lived on the time scale of local motions, because the dynamics allows this configuration to become undone. Such configurations do not require special treatment if one is considering the thermal equilibrium of the system. The above definition of entanglement is *not* the one that we shall adopt here. By entanglement we shall refer only to configurations which cannot be undone by the dynamics, even if one waits forever. An example is the situation depicted in Figure 1a. The combination

of the cross-links and the impenetrability of the chains means that the dynamics of the system can never allow chain A to move behind chain B. They are entangled.

This, then, is the problem: how does one perform statistical mechanical calculations taking into account the fact that the network exists in one, and only one, topology? The purpose of the present paper is to explain in simple physical terms our recently proposed solution to this problem.

A variety of attempts have been made to answer the question above, most of which fall into one of three categories: (1) ignoring the problem,[3] (2) tube models,[4] and (3) topological invariants.[5] Approaches 1 and 2 have proven to be useful phenomenological tools but are not claimed to be systematic theories. Approach 3 has severe mathematical difficulties, to be discussed below, and it has not been possible to implement it beyond the simplest model problems.

The basic idea in the tube models is to restrict the chain to lie close to some notional mean position in the lattice by imprisoning it within a random tube. The random tube represents the confining effects of the neighboring chains. For a detailed review of this approach, see the articles cited in ref 4.

The approach using topological invariants assumes that there exists a set of invariants for each topology of the network. A topological invariant is a number, τ, which can be computed by a specified procedure for each configuration C of the chains of the network. We shall designate this procedure as if it were a function $T(C)$. Thus, $\tau = T(C)$. All those configurations which are topologically equivalent give the same value for the topological invariant. Furthermore, no two topologies of the network give the same value for the topological invariant. Thus, if one knows the value of the topological invariant, one can uniquely determine the topology of the network; conversely, if one knows the topology of the network, one can uniquely determine the value of the topological invariant. The statistical mechanics of the system in a given topology can then be calculated, respecting the requirement that the topology cannot change. The partition function, Z, depends on the particular topology chosen; thus Z is a function of τ. Z is calculated by performing a sum over all configurations of the chains, with their Boltzmann weights, but discarding configurations C' with $T(C') \neq \tau$:

$$Z(\tau) = \sum_{\{c\}} e^{-E(\{c\})/k_B T} \delta(\tau - T(C)) \qquad (1.1)$$

where k_B is Boltzmann's constant, T is temperature, and $E(\{C\})$ is the energy of the system in configuration C. Unfortunately, there are no known procedures which have all the properties required above of $T(C)$. All of the "invariants" which have been proposed in the past—including the Gaussian invariant and the Alexander polynomials—have many topologically inequivalent configurations which give the same numerical value for τ. Thus, these invariants cannot be used for $T(C)$. Even if this had not been the case, the task of implementing the constraint in eq 1.1 would almost certainly be impossible.

In this paper, we will argue that the difficulties mentioned above can be avoided by considering the space, S, of all configurations of the chains in the system. We will show that each topology of the system, consistent with a specified set of cross-links, defines a unique subregion of S. This is equivalent to the prescription of eq 1.1 and is thus impossible to implement, in general.

For many purposes, however, the partition function contains more information than is required. For example, in this paper, we shall concentrate on the question of

whether or not a system with a given number of cross-links is a liquid or a solid. We will show that it is possible to define an order parameter which has the following properties: (1) it can distinguish between the three possible thermodynamic phases, liquid, crystalline solid, and equilibrium amorphous solid, and (2) it can be expressed by summing a certain quantity over *all* configurations in S, and not just those configurations within one particular subregion of S which corresponds to one particular topology. This order parameter is constructed in such a way that it displays a signature of the way in which S is divided into subregions corresponding to the possible topologies of the network.

We have been able to calculate, approximately, this order parameter as a function of the density of cross-links in a gel or rubber and find that there is a second-order phase transition from a liquid to an equilibrium amorphous solid, as the cross-link density exceeds a critical value. These calculations have been described briefly elsewhere,[1] and are the subject of a forthcoming detailed report.[6] The present paper is intended to provide a physically motivated account of our theory, without the obfuscations of technical details. Accordingly, we shall mostly be content with descriptive arguments. It should be emphasized, however, that the reasoning presented in sections 2 and 3 is precise and in principle does not rely on any approximations. In particular, it is valid for realistic choices of $E(\{C\})$. In contrast, when we actually attempt to implement the ideas presented in sections 2 and 3 to compute the phase diagram for a system of randomly cross-linked macromolecules, we shall be forced to make approximations, as described in ref 1, among which is the use of the Edwards Hamiltonian for $E(\{C\})$.

This paper is organized in the following way. In section 2, we present elementary arguments showing that for a system of randomly cross-linked macromolecules S may be divided into two distinct classes of subregion. One class arises from the various topologies of a network with a given set of cross-links. The other class arises when there is a phase transition to the solid state. Section 3 describes how we construct the order parameter for the liquid–solid transition of the system, and section 4 summarizes the results of our detailed calculation using the Edwards Hamiltonian and briefly mentions some experimental consequences.

2. Structure of Configuration Space for a Cross-Linked System

We now present simple physical considerations which determine the structure of configuration space for a system of cross-linked macromolecules. There are two principal considerations. The first is related to the manifestation in configuration space of the many possible topologies available to a system once the cross-links have been specified. The second set of considerations is related to the possible occurrence of phase transitions in the system. In particular, we shall be concerned with the transition from a liquid state to a solid state.

The basic postulate from equilibrium statistical mechanics which we shall use is that of ergodicity. Loosely speaking, if, during an arbitrarily long time interval, a statistical mechanical system explores, with arbitrary accuracy, every configuration available to it, then the dynamics is said to be ergodic. For example, an ideal gas with infinitesimally weak interactions in a container of finite volume V is ergodic. During an infinitely long time interval, the particles may explore every point in the volume, with arbitrary momentum, subject only to the constraint that energy is conserved. As we shall see below, a system

composed of cross-linked macromolecules is not ergodic: in fact, the ergodicity can be broken to varying degrees, corresponding to the presence of topology and the phase of the system.

A. Topology. Consider a container of finite volume V, filled with long flexible chains. We shall suppose initially that the chains are not cross-linked and do not interact. All possible configurations are accessible to the system, and we shall designate the space of all possible configurations by S.

Now suppose that the system is cross-linked at random. The cross-links permanently constrain two monomers on two (or perhaps the same) chains to have the same position in space, although this position is, of course, not fixed. The constraint means that there are many configurations in S which are now inaccessible. For example, if there is a cross-link between chain 26 at monomer 135 and chain 14 at monomer 333, then no configurations are allowed where these two monomers do not occupy the same point in space. Thus, the system of cross-linked, but still noninteracting, chains explores a region of configuration space, S_1, which is a subset of S. The system is ergodic, but over a reduced set of configurations.

Next, we suppose that at a time t_0 we turn on the hard-core repulsions between the chains. We may still allow the cross-linked monomers to occupy the same point in space, or if the reader is uncomfortable with this, we might require that they are within one atomic distance from each other or that the chains are infinitesimally thin. The important point is that the chains are not able to pass through each other during the course of their dynamics. At the instant when the interactions are switched on, the chains are in a configuration C with some topology. Thereafter, the chains must be trapped permanently in that topology. This means that the set of configurations available to the chains is a subset of S_1. We shall refer to the set of configurations available to the cross-linked, interacting chains as S_2. The system is ergodic, but now over S_2, which is a subset of S_1. S_2 is the set of all configurations which are topologically equivalent to C.

At the time t_0, the system might have been in a different configuration, C'. In this case, if C and C' are not topologically equivalent, the system will be ergodic over the set of configurations topologically equivalent to C'. We might call this set S'_2. In general, then, we can see that there will be many possible subregions of configuration space in which the system can become trapped when we turn on the interaction. S_2 and S'_2 are but two subregions of an infinite set of subregions. We will denote these by $S_2{}^\mu$, $\mu = 1 ... \infty$. These subregions of configuration space will be disjoint, because it is not possible for a given configuration of the chains to be simultaneously in more than one topology. Thus, we see that the combination of cross-links and impenetrability of the chains has broken the original configuration space S into smaller, disjoint regions such as S_2 and S'_2. The system will be ergodic only over the configurations contained in one of these subregions.

To summarize, then, the effect of cross-links and impenetrability is to cause the system to become trapped into a subregion of the configuration space of a cross-linked but penetrable set of chains.

B. Phase Transition. Let us now ask what happens to a statistical mechanical system as it goes through a phase transition. We will start by considering a system of point particles; once we have exposed the principal ideas, we shall directly apply them to the system of cross-linked macromolecules. Our concern is the phase transition to the solid state, and accordingly we shall need to define

what we mean by a solid in statistical mechanics. We will define a solid in two closely related ways.

The first definition is that a solid resists infinitesimal static shear, while a liquid does not. In other words, if one slowly tries to shear a solid, it will exert a restoring force. The significance of the term static is this: if we shear a liquid, at first there will be a restoring force, but if we wait a sufficiently long time, then the force will die away. On the other hand, a solid will maintain a restoring force forever.

The second defintion is thermodynamic, and strictly applies to an infinite system in thermal equilibrium. It is that the solid state spontaneously breaks the translational invariance of the Hamiltonian of the system.[7] To see what this means, recall that the Hamiltonian H is simply the sum of the kinetic energy K and potential energy V of the system. Usually the potential energy will only depend on the difference in positions between the particles, not the absolute positions. Thus, if we shift the origin of coordinates, the potential energy is unchanged. Similarly, the kinetic energy, which depends on the time derivative of the coordinates of the particles, is also unchanged when we shift the origin of coordinates. Thus the Hamiltonian is translationally invariant. On the other hand, even though the Hamiltonian is translationally invariant, the state of the system need not be. A familiar example is the crystalline state. There, the atoms are localized in a periodic array, in contrast to the situation in a gas or liquid. In fact, even if the atoms are localized about positions which are randomly distributed in space, translational invariance is still broken. In summary, the onset of the solid phase occurs when the state of the system (as described by the density matrix, for example) spontaneously breaks the translational invariance of the Hamiltonian. The rigidity of the solid state is a feature which emerges from this symmetry breaking. A solid is not rigid because there are long-range forces holding it rigid. Instead, it is the preference for the atoms to localize themselves at certain poisitions with respect to their neighbors, in order to minimize the free energy, which confers the solid with rigidity.

Let us now see how the liquid-to-solid transition is manifested in configuration space. In the solid state, atoms are localized about their mean position. There are many configurations available to the liquid state which are not accessible to the solid state. We shall call the set of configurations available to the solid S_3. S_3 is a subset of S. However, this is not quite correct. There are many possible ways in which the system could solidify; in particular, because the Hamiltonian is translationally invariant, if all the atoms localized around a position, e.g., 10 in. away from their mean positions specified by S_3, then that configuration would be equally favorable energetically. In fact, once we have chosen a particular state of the system, which breaks the translational invariance, we may generate an infinite number of other, equally acceptable states by simply translating our original state. The same remarks also apply to rotations, since the Hamiltonian will usually be rotationally symmetric too.

Thus, when a liquid-to-solid transition occurs, the configuration space of the liquid is broken up into subsets S_3^i where $i = 1 \ldots \infty$. The configurations in each subset S_3^i are related by the symmetries of the Hamiltonian. That is to say, if we choose one configuration in one of the subsets, S_3^7 say, and translate it, e.g., 10 in., we will have generated a configuration in one of the other subsets, S_3^{99} say. In fact, if we take each configuration in turn from S_3^7 and translate it 10 in., we will generate all the configura-

tions in S_3^{99}. The fact that by applying symmetry operation of the Hamiltonian to all the configurations in one of the subsets generates all the configurations in all the other subsets is what we mean by saying that the subregions S_3^i are related by symmetry.

Now let us apply this picture to the case of the solidification of a cross-linked macromolecule. We have already seen that the presence of topology implies that the system explores a subregion of the configuration space available to a cross-linked but noninteracting set of chains. Let us suppose that the system is ergodic in the subregion called S_2. Now suppose that by adjusting a parameter in the Hamiltonian, such as the pH of the solvent, we can cause the system to become solid. Then the subregion of phase space S_2 will fragment further into a set of smaller subregions, S_3^i. Furthermore, these subregions are related by translational and rotational symmetry.

Thus, the original configuration space of the cross-linked but noninteracting set of chains, S_1, is now fragmented into subregions S_2^μ, which are themselves further fragmented into subregions S_3^i. Let us examine a particular subregion, S_2^{137} say, from the set of subregions S_2^μ. This contains a set of subregions of the S_3 type, which arose from the spontaneous breaking of translational invariance within the topology corresponding to S_2^{137}. Thus, this set of S_3 subregions are related by symmetry. On the other hand, suppose we consider two subregions of the S_3 type, S_3^{1557} and S_3^{17860}, say; we suppose that the former is contained with S_2^{137}, while the latter is contained with S_2^{26}. Since these S_3-type subregions have distinct topologies (because they are contained within different S_2-type subregions), they are not related by symmetry.

Finally, we remark that this ergodicity-breaking scheme is not the most general, although it is certainly the simplest which we can envisage. Indeed, this ergodicity-breaking scheme is our proposed interpretation of the calculation summarized in section 4. There is, however, no reason to assume a priori that all subregions contained within a given subregion of the S_2 type are related by symmetry; the calculation summarized in section 4 does not rule this out.

3. Construction of an Order Parameter

In the previous section, we showed that the configuration space for a set of cross-linked impenetrable macromolecules can become rather complicated, particularly when there is a transition to the solid state. However, when one performs statistical mechanical averages, one must only include in the averaging those configurations over which the system is actually ergodic. This requires knowing how to specify the configurations in each subregion of configuration space. In a complicated system such as that under consideration here, it is not known how to do this; although in simpler systems, such as Ising ferromagnets, this is possible.

In this section, we describe an order parameter which is calculable, within the mean-field theory, by performing a statistical mechanical average over *all* the configurations in S_1, and which detects whether or not S_1 is fragmented into subregions S_2 and S_3. The method is due originally to Parisi, who applied it to solve the problem of the infinite-range Ising spin glass.[8]

The basic idea is to construct a subregion detector $q^{\sigma\sigma'}$. The superscripts σ and σ' designate two subregions of configuration space. We call $q^{\sigma\sigma'}$ the overlap between subregions σ and σ', because it measures, in a sense to be discussed below, how similar the configurations are in the two subregions. For present purposes, we only need to know the following properties of $q^{\sigma\sigma'}$: (1) $q^{\sigma\sigma'}$ is zero only if either σ or σ' is a subregion of configuration space cor-

responding to the system being in the liquid state. (2) $q^{\sigma\sigma'}$ = $q^{\sigma\sigma}$ if σ and σ' are related by symmetry. This can only happen if σ and σ' describe states of broken translational symmetry, i.e., solids. In this case $q^{\sigma\sigma} \neq 0$.

In fact, $q^{\sigma\sigma'}$ is a function f of a set of quantities which compare the statistical mechanical average over the configurations in σ and σ' of the Fourier components of the monomer density fluctuations:

$$q^{\sigma\sigma'} = f(q^{\sigma\sigma'}_{kk'}) \qquad (3.1)$$

$$q^{\sigma\sigma'}_{kk'} = \frac{1}{LN} \sum_{\text{monomers}} \langle \exp(-i\mathbf{k}\cdot\mathbf{r}_i^s) \rangle^\sigma \langle \exp(-i\mathbf{k'}\cdot\mathbf{r}_i^s) \rangle^{\sigma'} \qquad (3.2)$$

Here, $\mathbf{r}_i^s$ is the position of the sth monomer on the ith chain, L is the degree of polymerisation, N is the number of chains in the system, and $\langle\ \rangle^\sigma$ denotes a statistical mechanical average taken over the configurations in the subregion σ. The wavevectors $\mathbf{k}$ and $\mathbf{k'}$ are nonzero. We chose the function f in such a way that $q^{\sigma\sigma'}$ did indeed satisfy properties 1 and 2.

The way in which $q^{\sigma\sigma'}$ works is as follows. In a region of configuration space which corresponds to the system being in the liquid phase, the equilibrium expection value of the monomer density is independent of position, and so Fourier components of the monomer density fluctuation are zero. Thus, if either of the regions σ or σ' in eq 3.2 corresponds to a liquid phase, then $q^{\sigma\sigma'}_{kk'} = 0$, yielding $q^{\sigma\sigma'}$ = 0. The only way to obtain a nonzero value for $q^{\sigma\sigma'}$ is if both σ and σ' correspond to solid phases, either crystalline or amorphous. The latter may be simply distinguished because the Fourier components of the density of a crystal are nonzero only for wavevectors satisfying the Bragg condition.

Now we consider the possible outcomes of computing $q^{\sigma\sigma'}$ for any pair of subregions σ and σ'. Note that at this stage, this computation is still impossible, in general, because we do not know how to specify the states in the subregions σ and σ'.

Case 1: If either or both σ and σ' describe the liquid phase, then $q^{\sigma\sigma'}$ is zero. Only when both σ and σ' describe solid phases is $q^{\sigma\sigma'}$ nonzero.

Case 2: If there is no topology present, as in the solidification of noncross-linked (or nonpolymeric) substances, then we would expect that a crystal can be formed at sufficiently low temperature. In this case, all the subregions could be generated from symmetry operations on just one of the subregions σ. Thus $q^{\sigma\sigma'}$ would be nonzero and would take on a value independent of σ and σ'.

Case 3: For the case at hand, however, when the system solidifies, there are two categories of subregion: S_2 and S_3. Thus, although $q^{\sigma\sigma'}$ will be nonzero, its value will depend on σ and σ'. Thus there will be a broad spectrum of values for $q^{\sigma\sigma'}$.

In conclusion, the way in which configuration space is broken up into ergodic subregions can be directly determined by computing $q^{\sigma\sigma'}$.

4. Discussion

Unfortunately, it is not possible to calculate $q^{\sigma\sigma'}$. Nor is it possible to calculate $P(q)$, the probability that, in thermal equilibrium, a pair of regions σ and σ' has an overlap $q^{\sigma\sigma'} = q$. However, it is possible, within a mean-field theory, to calculate $[P(q)]$, the value of $P(q)$ averaged over the possible ways of cross-linking the system. There are three possible functional forms for $P(q)$, corresponding to the three possible cases discussed in the previous section. These are sketched in Figure 2.

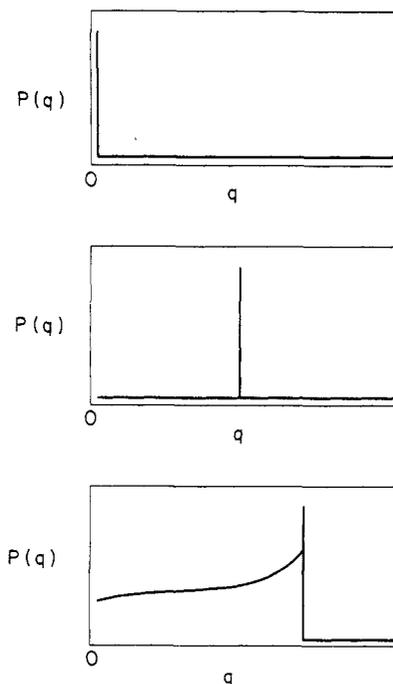In order to understand the phase diagram of the system, the strategy is to calculate $[P(q)]$ as a function of the

Figure 2. Schematic functional forms for the probability distribution of the overlap. The three possible cases are (a, top) the existence of subregions of configuration space corresponding to the liquid state; (b, middle) configuration space being fragmented into symmetry-related subregions, corresponding to the existence of only one type of solid phase; and (c, bottom) configuration space being fragmented into both symmetry-related and symmetry-unrelated subregions, corresponding to the existence of many possible types of solid phase.

density of cross-links. At the liquid-to-solid transition, $[P(q)]$ will change from one functional form to another. Based on the considerations of the preceding sections, we should expect to observe a transition between case 1 and case 3. The details of an approximate evaluation of $[P(q)]$ have been summarized in ref 1 and will be reported in detail in a forthcoming publication.[6]

The result of the calculation is as follows. We considered N chains with a mean number of cross-links N_x in a volume V, at fixed temperature. The chains are flexible and interact through the δ function pseudopotential introduced by Edwards.[9] Crudely speaking, this potential gives an energy penalty λ^2 whenever two chains intersect and thus mimics the excluded-volume interaction between the chains. This includes not just the self-avoidance of the chains but also the interaction with the solvent. It is the osmotic pressure due to the interaction with the solvent which prevents the network from collapsing. Indeed, when λ^2 is sufficiently small, we find that the network does collapse.

We study the regime where λ^2 is sufficiently large that the network is swollen and examine the behavior as we increase N_x from zero. We find that when $N_x \geq N/2$, the system is a thermodynamic solid, i.e., translational invariance is spontaneously broken, and the static shear modulus is nonzero. The transition is indeed between case 1 and case 3, indicating that the configuration space has fragmented not only into subregions related by symmetry but also into subregions which are unrelated by symmetry. Very close to the transition, the Landau free energy has the same form as that found by Parisi in the context of the infinite-range Ising spin glass. The existence of symmetry-unrelated subregions occurs there too and is often referred to as replica symmetry breaking. In light of the preceding considerations, we tentatively identify each symmetry-unrelated subregion of configuration space with

each possible topology of the network.

In addition to the considerations presented in the present paper, which support this conclusion, two other pieces of circumstantial evidence for this conclusion emerge from the calculation itself. First, the critical number of cross-links at the transition point is independent of λ^2. This implies that the transition to the solid state is not related to a finite energy scale but rather is due to a qualitative feature of the system; the increasingly complex topology with increasing N_x is the most obvious candidate. Second, it is possible to perform the calculation of $[P(q)]$ assuming the network is embedded in four-dimensional space. We do not find a transition to the solid state in this case, for any density of the cross-links. This is reasonable if the transition is related to the topology of the network, because in four dimensions, linear chains are not constrained by entanglements. This is perfectly analogous to the situation of a two impenetrable, concentric rings on a two-dimensional surface. If the rings are constrained to lie on the surface, then the inner ring is permanently trapped within the larger ring. If the rings may move into the third dimension, however, then the inner ring is no longer constrained by the outer ring. We remark, as a caveat, that at this stage we cannot rule out the possibility that renormalization effects not presently included in the calculation will alter the result in four dimensions.

At this juncture, it is pertinent to discuss the relationship between our theory and percolation models.[10] In the percolation models, it is assumed that the onset of rigidity occurs once there is an infinite network, and it is argued that gelation must be in the universality class of site-bond percolation. This assumption ignores the possible role of entangled chains in the transition to the solid state. In contrast, the present theory suggests that the transition to the solid state can occur as a result of a sufficiently complex topology rather than as a result of a sufficient degree of connectivity.[11] de Gennes suggested[12] that the shear modulus depends on the fraction of cross-links in the same way that the conductivity of a network of resistors depends upon the fraction of conducting bonds; this analogy is not a rigorous argument and has been criticized.[13] Moreover, the disorder in a randomly cross-linked macromolecule, which arises from the randomness of the cross-link positions, has no counterpart in percolation models. To see this, recall that each cross-link permanently constrains two particular monomers to be at the same point in space. Consequently, all allowed configurations of the polymer chains must respect this set of constraints, one for each cross-link. This constraint on the configurations—technically referred to as "quenched disorder" because the cross-link is not able to equilibrate or adjust its position along the arc length of the chains—is not present in percolation models. Consequently, we would not expect a priori that percolation models would be applicable to the case of irreversible gelation. Last, percolation models do not address the question of how rigidity emerges. In the simplest case, the elements of the model are rigid bonds on a lattice, so percolation models really address a question of *architecture*. On the other hand, the theory presented in ref 1 and in the present paper is a statistical mechanical theory. Rigidity is a consequence of *thermodynamics*. The elements of the theory are flexible chains, yet the system, in the thermodynamic limit, acquires the property of rigidity. In this sense, then, the present theory is a microscopic theory of the transition to the solid state, starting as it does from a physical model of flexible chains and solvent, without additional ad hoc assumptions about rigidity. Rigidity is an emergent feature

of the theory. An analogous situation occurs in the theory of superconductivity.[14] There, phenomenological models (London and Ginzburg–Landau theories) were developed, in which the superconductivity was put in by hand (i.e., London's rigidity of the wavefunction). Eventually, it was shown,[15] from a microscopic theory of the behavior of electrons, how superconductivity arose, without ad hoc assumptions. Superconductivity is, like rigidity, an emergent feature of a microscopic theory.

We now turn to some of the experimental consequences of our theory. We find that the transition to the solid state as the density of cross-links increases beyond the critical density is a continuous transition and not a first-order transition. This has important consequences for the shear modulus, which should consequently exhibit dynamical scaling behavior[16] at the critical cross-link density. Indeed, Winter and Chambon[17] have measured the real and imaginary parts of the frequency (ω)-dependent shear modulus $G(\omega)$ as a function of N_x for a PDMS gel and report that at the gel point, $G(\omega)$ is a power law function of ω over about 4 decades of ω. We interpret these observations as evidence for dynamic scaling at the transition to the solid state during gelation. It seems likely that similar behavior would occur during vulcanization. Work in progress is attempting to calculate the elastic response of cross-linked systems.

In the present theory, where a continuous thermodynamic phase transition occurs to the solid state, dynamical scaling of the linear response functions follows automatically. Power law behavior in dynamical response functions is predicted to occur *only* at the transition to the solid state. Away from the transition, other behavior can (but does not necessarily) occur. It is also important to note that in our theory, power law behavior in the time-dependent response functions does not arise from the existence of an assumed fractal structure, which is simply "put in by hand".[18] While it is certainly true that power law behavior can always be interpreted in terms of a fractal dimension, a genuine theory along these lines must account for the existence of a fractal structure—and hence power law correlations—only at the gel point. The present theory accomplishes this, in a sense, through the scale invariance which accompanies a second-order phase transition.

The question of how to predict the value for the exponent of ω in $G(\omega)$ is related to identifying the dynamic universality class: this is prescribed by the equations of motion for the cross-linked system. Work currently in progress is aimed at addressing this issue. On the other hand, percolation models do not have any intrinsic dynamics. This is reflected in the fact that it is a generating function, rather than a genuine partition function, which behaves in a nonanalytic way at the percolation threshold. Consequently, an additional assumption about the dynamics is required to understand dynamical scaling of the shear modulus in this model. It should be recalled that there may be many different dynamical universality classes which exhibit the same static critical phenomena.

Given all of the above, there remains the intriguing result that our calculation in ref 1 finds the same value for the critical number of cross-links ($N_x = N/2$) as the Flory–Stockmayer theory. Both calculations are mean-field calculations, but with apparently very different physics. A fuller understanding of this result would be very useful.

Finally, we wish to discuss the reason for the apparent success of the Edwards pseudopotential in accounting for the topology of the network, despite the absence of genuine hard-core interactions. Two observations are pertinent here. First, our calculation is based on a mean-field theory.

Second, the only interactions in the system occur when the chains intersect, always leading to an increase in energy. since mean-field theory recognizes only low-energy configurations (and not fluctuations around them), all that is required of the interaction is that it produces minima in the energy. Replacing the Edwards pseudopotential by a hard-core interaction would not alter the results of mean-field theory.

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On the Aggregation and Conformational States in Aqueous Solution of a Succinoglycan Polysaccharide

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ABSTRACT: Dilute solution properties of a succinoglycan sample from *Pseudomonas* sp. (purified SHELLFLO-S) have been studied by means of light scattering, viscosity, chiroptical spectroscopy, and differential scanning calorimetry experiments. The results collected working in a wide range of NaCl concentrations clearly show that the polysaccharide undergoes a thermally induced, highly cooperative conformational transition. The nature of the transition is discussed. All evidence favors an initial partially aggregated state for succinoglycan in which single, helical chains are laterally connected via side-chain interactions. Aggregation and conformational order are disrupted on heating. On cooling, only the pristine helical state of the polysaccharidic backbones would be recovered in aqueous NaCl, at a rate strongly dependent on the salt concentration.

Introduction

From the structural point of view, many microbial polysaccharides present a high degree of regularity, which seldom is encountered in polymeric carbohydrates from other sources. Such regularity of primary structure involves the possibility that the chains may assume ordered conformations, either single or multiple helices, both in the solid state and in solution, with important outcomes for mechanical properties, in the capability to form gels, and in rheological properties.[1-6] In this context, succinoglycans, a family of structurally closely related (when not identical) exocellular polysaccharides produced by a number of different soil bacteria, appear of particular relevance.[7,8]

In this paper we wish to present a rather detailed description of the dilute solution behavior of a succinoglycan sample (purified SHELLFLO-S).[9] Data collected regard

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