

## Microscopic theory for cross-linked macromolecules. I. Broken symmetry, rigidity, and topology

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This paper is concerned with the onset of rigidity in randomly cross-linked macromolecules. We discuss in detail the possible partitionings of configuration space, which may accompany the spontaneous breaking of translational invariance, treating separately the cases of crystals, amorphous solids, and cross-linked macromolecules. We describe the order parameters for these systems, drawing the distinction between solids with discrete translational symmetry and solids with macroscopic translational invariance, such as randomly cross-linked macromolecular solids. We show that the latter may be described by a sequence of probability distributions for the overlaps of equilibrium states. In a cross-linked system of impenetrable linear chains, the configuration space of the solid state is partitioned into two categories of equilibrium states: those related by translational and rotational symmetry, and those unrelated by these symmetries. The latter are a consequence of the distinct topologies of the network, which are consistent with a given set of cross links. We show how the overlap-probability distributions may be calculated.

### I. INTRODUCTION

In this and the accompanying paper<sup>1</sup> (hereafter referred to as I and II, respectively), we shall be concerned with the statistical mechanics of randomly cross-linked macromolecular solids. These systems are of special interest, not only because of their remarkable elastic properties<sup>2</sup> and consequent technological and biological importance, but also because of the unique difficulties which are encountered in the description of their topologically distinct configurations. Figure 1 illustrates this point: a set of permanent cross links at given arc-length positions on given polymer chains does not suffice to uniquely specify the topology of the network. Many different topologies are consistent with the given constraints. Due to the permanence of both the backbone of the chains and the cross links, the realized topology of the system is determined once and for all when the cross links are formed. The central problem is to calculate the statistical thermodynamic properties of the system, accounting not only for the cross-link constraints, but also for the restricted configuration space available to the system by virtue of its topology.

A related problem is the description of equilibrium amorphous solids. Their existence is debatable for unconstrained systems. However, the presence of quenched disorder in the form of randomly positioned cross links between macromolecules, and the consequent topological constraints, guarantees that if a system of randomly cross-linked macromolecules has a solid phase, then that phase is an equilibrium amorphous solid.

Recently, we showed how a system of randomly cross-linked macromolecules (RCM's) can become rigid as the

number of cross links is increased from zero.<sup>3</sup> We were able to demonstrate explicitly within a mean-field approximation that such a system spontaneously breaks translational invariance when the number of cross links exceeds

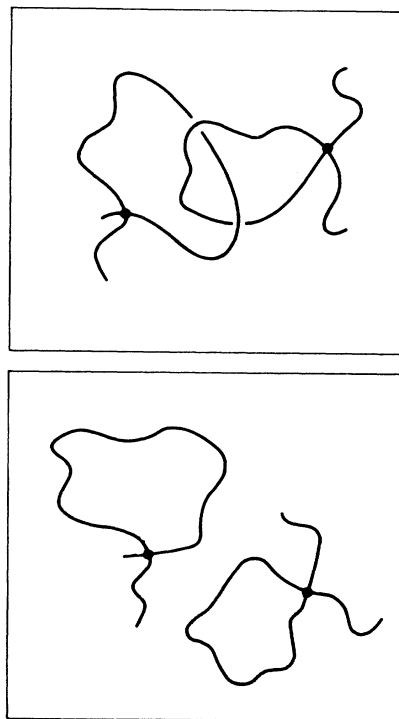


FIG. 1. Two topologically inequivalent configurations with identical cross-link locations.

one half the number of chains in the system. Furthermore, we showed that the solid phase is indeed an equilibrium amorphous solid, and we conjectured that the structure of configuration space which emerges from our calculation is a reflection of the role of topology in this system. The purpose of this series of papers is to present a detailed exposition of this work. In I, we explain the conceptual framework of our theory, for the most part without reference to a particular microscopic theory or approximation scheme. The principal theme is the description of the possible ways in which configuration space can be fragmented into ergodic regions (known as *equilibrium states*) when translational invariance is spontaneously broken.<sup>4</sup> These considerations lead us to define an appropriate order parameter which can distinguish between not only fluid and solid phases, but also between crystalline and amorphous solids. We also explain how this information regarding the nature of the equilibrium states may be obtained.

In II, we consider a minimal model of a network, which incorporates both the effects of interactions between the chains and the cross-link constraints.<sup>4</sup> This model is also capable of accounting for the topological constraints and we show explicitly how the theory established in I can actually be implemented. Subsequent papers in this series will study the static and dynamical elastic response of RCM's. In addition, we intend to report on a computer simulation which is currently in progress.

Real systems are only able to explore a single topology, and in principle we would like to be able to perform statistical-mechanical averages within that one topology. However, even for the simpler case of a knot or a link, this is presently impossible. The mathematical obstacles are worth recalling.<sup>5</sup> To perform averages within one topology requires that each nonintersecting configuration of a knot or link be uniquely specified by a quantity which depends only on the topology—a unique topological invariant.<sup>6</sup> Topological invariants for knots and links do indeed exist; examples are the Gauss invariant,<sup>7</sup> the Alexander polynomial,<sup>8</sup> and the Jones polynomial.<sup>9</sup> These are numbers or polynomials which are invariant under continuous, nonintersecting deformations. However, they are not unique. Many topologically distinct configurations may have the same topological invariant. For example, of the first 91 simple links of two closed curves, the Gauss invariant cannot distinguish 29 from the unlinked case. No unique topological invariants are presently known and a theory of RCM's which focuses on the properties of one topology is not possible at present.

The main part of the present paper is a discussion of the relationships between the concepts of broken ergodicity, spontaneously broken symmetry, and generalized rigidity.<sup>10</sup> It is convenient in conventional treatments of spontaneous symmetry breaking in systems without quenched disorder to rely on the method of small fields to generate nonzero order parameters. For example, in the case of a Heisenberg ferromagnet consisting of spins  $\mathbf{S}(\mathbf{x})$ , below temperature  $T_c$ , rotational invariance is spontaneously broken; the spontaneous magnetization,  $\mathbf{m} \equiv \langle \mathbf{S}(\mathbf{x}) \rangle$ , is nonzero and aligned along some direction

in spin space. It is usually calculated by applying a vanishingly small uniform external magnetic field along the *chosen direction*, thus ensuring that a nonzero magnetization results. The expectation value is computed using *all* configurations of the system and the thermodynamic limit must be taken before the zero-field limit is taken. In a system such as a spin glass, however, the analogous procedure cannot be followed because the spins order in random directions; thus the net magnetization is zero, and a uniform external field will not select any one equilibrium state.<sup>11</sup>

An alternative procedure is to consider the large-distance properties of the correlation functions  $\langle \mathbf{S}(\mathbf{x}) \cdot \mathbf{S}(\mathbf{y}) \rangle$ , computed using all the configurations of the system. As  $|\mathbf{x} - \mathbf{y}| \rightarrow \infty$ ,  $\langle \mathbf{S}(\mathbf{x}) \cdot \mathbf{S}(\mathbf{y}) \rangle \rightarrow \mathbf{m} \cdot \mathbf{m}$ . In a Heisenberg ferromagnet, this limit is nonzero only below  $T_c$ . In a spin glass, however, the equilibrium magnetization is a random function of position and, for large separations,  $\langle \mathbf{S}(\mathbf{x}) \cdot \mathbf{S}(\mathbf{y}) \rangle$ , evaluated over the entire configuration space, vanishes. For spin glasses, and as we shall show, for randomly cross-linked macromolecules, these methods have failed. An alternative to these methods is to consider explicitly the structure of configuration space. This is the approach presented here.

As a simple example of the relationship between symmetry breaking and configuration space, consider a system with degrees of freedom  $\{c_i\}$  with  $i = 1, \dots, N$  and Hamiltonian  $\mathcal{H}\{c_i\}$ . Suppose, for example, that  $\mathcal{H}\{c_i\}$  is translationally invariant. This means that configurations, which are identical apart from a translation by an arbitrary vector  $\mathbf{a}$ , have the same energy,

$$\mathcal{H}\{c_i\} = \mathcal{H}\{c_i + \mathbf{a}\} . \quad (1.1)$$

Suppose further that we are interested in computing the expectation value of some function  $f_{ik}$ ,  $\mathbf{k} \neq \mathbf{0}$ , taken, in this example, to be

$$f_{ik} = \exp(i\mathbf{k} \cdot \mathbf{c}_i) . \quad (1.2)$$

Then

$$\langle f_{ik} \rangle^\sigma = \frac{\text{Tr}_\sigma f_{ik}\{c_i\} \exp(-\mathcal{H}\{c_i\})}{\text{Tr}_\sigma \exp(-\mathcal{H}\{c_i\})} , \quad (1.3)$$

where the subscript  $\sigma$  denotes the microstates to be included in the trace. The issue is what microstates should be included in  $\sigma$ ? If  $\sigma$  includes all the microstates then

$$\langle f_{ik} \rangle^\sigma = e^{i\mathbf{k} \cdot \mathbf{a}} \langle f_{ik} \rangle^\sigma \quad (1.4)$$

and thus  $\langle f_{ik} \rangle^\sigma = 0$ . The only way in which  $\langle f_{ik} \rangle^\sigma$  can be nonzero is if  $\sigma$  does not include all the microstates. However, this is not sufficient. If all the microstates in the reduced set  $\sigma$  happen to remain in  $\sigma$  under the group of translations, then  $\langle f_{ik} \rangle^\sigma$  still vanishes. Therefore it is only if the reduced set  $\sigma$  is not invariant under the symmetry group of  $\mathcal{H}\{c_i\}$  that  $\langle f_{ik} \rangle^\sigma$  can acquire a nonzero value.

The requirement that the set of microstates included in the trace be restricted is known as *broken ergodicity*; when the restricted set is not invariant under the symmetry group of  $\mathcal{H}\{c_i\}$ , then that symmetry is a *spontaneously broken symmetry*. It is important to realize that broken ergodicity may occur without spontaneous symmetry

breaking; an example is the liquid-gas transition on the coexistence line. We will find it fruitful to think of RCM's in the following way. Imagine a network of randomly cross-linked macromolecules, which do not interact in any way at all (we will discuss later the complications due to the instability of this situation). All configurations consistent with the cross-linking constraints are accessible. Now impose the additional constraint that the polymers cannot pass through each other. Then the set of accessible configurations is reduced, and depends only on the state of the system at the time of imposition of the additional constraint. In this sense, then, imposition of topological constraints is associated with broken ergodicity.

When a system undergoes the spontaneous breaking of a symmetry, it also acquires a *generalized rigidity*. Examples are spin-wave stiffness, London rigidity of a superconductor, and the rigidity of solids. If the two-point correlation function either tends to a nonzero constant or exhibits power-law decay at long distances, then the divergence in the corresponding susceptibility is a signature of stiffness with respect to an appropriate external probe. A sufficient, but not necessary, condition for the occurrence of generalized rigidity is that a symmetry is spontaneously broken. We shall discuss in detail how various solids acquire their rigidity through the spontaneous breaking of translational symmetry. In particular, we shall discuss the application of these ideas to equilibrium amorphous solids, and to RCM's, where the effects of topology are important too.

We now give an overview of the present paper. Section II is devoted to a brief discussion of the description of configuration space for classical systems in the thermodynamic limit. In particular, we stress the logical relation between the concepts of ergodicity breaking, spontaneous symmetry breaking, and generalized rigidity. We begin by describing the equilibrium-state decomposition of configuration space for simple systems<sup>3</sup> and then for randomly cross-linked macromolecules. By the term "simple," we mean that the solid is formed from atoms or nonpolymeric molecules. In Sec. III we address the issue of how to define an order parameter for the solid state. This issue is problematic for equilibrium amorphous solids, where there are no distinguished Fourier components of the density. We show that a suitable description of an equilibrium amorphous solid is in terms of a certain overlap, which, loosely speaking, compares pairs of ergodic regions in configuration space. This concept has proved useful in the theory of spin glass.<sup>12</sup> We conclude, in Sec. IV, by discussing the practical implementation of the theory, by both Monte Carlo simulation and analytically, using the replica method. We have included an appendix, for completeness, which briefly summarizes the properties of equilibrium states on which our theory is based.

## II. PHASES, EQUILIBRIUM STATES, AND CONFIGURATION SPACE

### A. Configuration space for gases, liquids, and simple solids

Before we discuss our central topic, namely, the structure of configuration space for a system of RCM's, we

first consider the structure of configuration space for matter in the absence of topological constraints. The reader may wish to refer to the Appendix in which we briefly summarize the properties of equilibrium states.

For concreteness, consider a single atomic species whose phase diagram consists of the sequence gas to liquid to crystal as the temperature is reduced from a sufficiently high value. We are interested in qualitative features concerning the structure of configuration space, and accordingly, the discussion below requires the infinite-volume limit to be taken. In Sec. II C we shall contrast these features with those which we expect for a cross-linked system with topological constraints.

When the system is in either the liquid or the gas phase, all configurations are accessible and the system is ergodic. There is a unique translationally invariant equilibrium state; all correlation functions are isotropic. There is a special case to be considered, namely, the liquid-gas coexistence line. If the density is increased at constant temperature, there comes a point beyond which the pressure remains constant and a fraction of the system is found in the liquid phase. As the pressure is increased further, the fraction of the system which is liquid increases until eventually the entire system has been converted to the liquid state. Further increase in the density will be accompanied by an increase in the pressure. In this two-phase region, the system is in a mixed phase. There are two translationally invariant extremal measures,  $\rho_L$  and  $\rho_G$ , corresponding to the liquid and gas, respectively, and the measure in the two-phase region  $\rho_{TP}$  may be written in the form  $\rho_{TP} = \alpha\rho_L + (1-\alpha)\rho_G$ , where  $0 \leq \alpha \leq 1$ . The measure  $\rho_{TP}$  does not possess the cluster property, and thus there are large thermodynamic fluctuations, in accord with the physical interpretation of  $\rho_{TP}$ . At liquid-gas coexistence, there is no symmetry which is spontaneously broken, although ergodicity is broken.

Now let us assume that the liquid phase crystallizes below the melting temperature  $T_M$ . This transition involves a loss of symmetry, and so ergodicity is broken. The symmetry which is broken is continuous translational invariance. The resulting crystal is describable in terms of its center of mass, and the mean positions of all the atoms relative to the center of mass. The measure which describes the crystalline state is invariant under a subgroup of the original symmetry group, corresponding to discrete translations and rotations. The degeneracy of the system with respect to the position of the center of mass of the crystal implies that the configuration space must be fragmented into an infinite set of equilibrium states, which are related by global translations. In other words there is an equivalent set of microstates of the system for every possible position of the center of mass. In addition to the measures corresponding to the crystalline state, which we shall refer to as lattice-group-invariant extremal measures, there may be measures which are not even invariant under the crystal symmetry group. Such measures may be thought of as corresponding to crystals with a defect such as a stacking fault, for example, and have the same free-energy density as the perfect crystal. The set of microstates contained within the union of all

the extremal measures is equivalent to those over which the system is ergodic in the fluid phase. Each individual extremal measure, however, breaks translational invariance. If we perform a global lattice translation on the system, the set of microstates in a given lattice-group-invariant extremal measure  $\sigma$  maps in a one-to-one fashion on to the microstates in another lattice-group-invariant extremal measure  $\sigma'$ . Lastly, notice that if we perform thermal averages over the entire set of measures (i.e., the complete configuration space), the result is translationally invariant and isotropic.

### B. Configuration space for cross-linked macromolecules

Let us now consider the way in which configuration space can be fragmented for a specific realization of a system of cross-linked macromolecules. Notice that the imposition of cross links does not explicitly break the translational and rotational symmetry. Suppose that we are able, at will, to make the macromolecules penetrable or impenetrable to each other (but otherwise noninteracting) and, furthermore, suppose that we are able to control the number of cross links per chain  $N_x$  in the system.

If  $N_x = 0$ , then regardless of whether the chains are penetrable or impenetrable, the system is ergodic and the equilibrium state is translationally invariant. If  $N_x \neq 0$ , then we must consider the impenetrable and penetrable cases separately. In both cases, the number of degrees of freedom is reduced by each cross link. For the penetrable case, all of the configurations, consistent with the constraint imposed by the cross links, are available to the system. For the impenetrable case, however, there is a further reduction in the number of configurations available to the system, by virtue of the fact that the system is trapped within one topology. The topology in which the system is trapped is determined by the configuration of the chains at the precise time of formation of the cross links. Thus the microstates accessible to the system are neither the complete set, nor the restricted set consistent with the cross links, but a still smaller set, determined by both the cross-link positions and the configuration of the chains at the time of cross linking.

The problem of interest is to compute the properties of an impenetrable system trapped within a particular topology. Such a system can potentially be either solid or liquid. The set of microstates consistent with a particular topology is translationally and rotationally invariant, in the sense that any of these global symmetry operations acting on any microstate in the set yields another microstate in the set. If the system is ergodic over this set, then it is not solid. On the other hand, for the system to be solid, then ergodicity must be further reduced beyond the set of microstates of which the particular topology is composed, in order that translational symmetry be broken.

There are two possibilities for the fragmentation of configuration space in the solid phase. In both cases, configuration space is broken into sets of topologically equivalent configurations, each set being translationally invariant. In the solid phase, each set is decomposed further into equilibrium states which are not translationally invariant.

In the first and simpler case these equilibrium states owe their existence to the spontaneous breaking of translational invariance and, hence, are related by global symmetry operations. In this picture of the partitioning of configuration space, a given physical sample of a rubber would be solid in a unique way (up to global symmetry operations); this is analogous to the way that the ferromagnetic phase of a Heisenberg ferromagnetic is unique (up to global rotations in order parameter space). In this case, symmetry-unrelated ergodic regions of configuration space arise only when one considers the ensemble of all possible topologies for a fixed set of cross links.

The second possibility is that each of the sets of topologically equivalent configurations is broken up not into a single family of symmetry-related equilibrium states, but into more than one such families. There is no symmetry relationship between members of different families. Thus, even within the ergodic regions of configuration space defined by one topology, there is no unique way for a RCM to be solid.

In the usual case of simple liquids, the system is completely ergodic. Even in the liquid phase of RCM's there can be topologically inequivalent configurations and, hence, more than one equilibrium state, none of which has broken translational symmetry. An order parameter, such as that described in Sec. III, which only recognizes equilibrium states with broken translational invariance, cannot detect the difference between this case and the completely ergodic case.

## III. ORDER PARAMETERS FOR SOLIDS

The purpose of this section is to discuss the difficulties associated with defining an order parameter for an amorphous solid, and to show how these difficulties may be resolved. We begin by recalling the case of crystalline solids, where translational invariance is broken, but a discrete symmetry group, the lattice group, remains. Then we contrast this case with amorphous solids, where there is no residual symmetry, and yet an examination of the density over a sufficiently large region reveals no distinguished Fourier components. We shall find it convenient to use the normalized density

$$m^\sigma(\mathbf{r}) = \frac{1}{N} \sum_i \langle \delta(\mathbf{r} - \mathbf{r}_i) \rangle^\sigma. \quad (3.1)$$

Finally, we introduce the concept of a self-overlap,  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$ . The principle attributes of  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  are that (1) it vanishes if the external equilibrium state  $\sigma$  corresponds to a liquid; (2) it can take on nonzero values for a crystalline or amorphous solid; and (3) for a crystal it is nonzero when  $\mathbf{k}$  and  $\mathbf{k}'$  satisfy the Bragg condition, whereas for an amorphous solid  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  is zero unless  $\mathbf{k} + \mathbf{k}' = 0$ .

### A. Crystalline solids

A crystalline solid is a translationally invariant system whose equilibrium states retain only a discrete subset of this translational invariance, namely, the lattice group. Let us consider such a system, with  $N$  atoms located at

positions  $\mathbf{c}_i$  in the equilibrium state  $\sigma$ . The atoms have mean positions  $\langle \mathbf{c}_i \rangle^\sigma$  about which they fluctuate. The residual symmetry of the state yields mean atomic positions which lie on a regular lattice. The Fourier transform of the normalized microscopic density,

$$m_{\mathbf{k}}^\sigma = \frac{1}{N} \sum_{i=1}^N \langle \exp(-i\mathbf{k} \cdot \mathbf{c}_i) \rangle^\sigma, \quad (3.2)$$

transforms like Eq. (1.4) under lattice translations. Hence, in the thermodynamic limit,  $m_{\mathbf{k}}^\sigma$  vanishes unless  $\mathbf{k}=\mathbf{G}$ , where  $\mathbf{G}$  is an reciprocal lattice vector. On the other hand, for a liquid, which is translationally invariant,  $m_{\mathbf{k}}^\sigma=0$ , unless  $\mathbf{k}=\mathbf{0}$ . Thus  $\{m_{\mathbf{k}}^\sigma\}$  provide a suitable order parameter for the transition between liquids and crystals.

### B. Equilibrium amorphous solids

A system with a translationally invariant Hamiltonian is said to be an equilibrium amorphous solid when it is in an extremal equilibrium state  $\sigma$  in which the translational invariance is completely broken. Although the atoms are localized and fluctuate about mean positions  $\langle \mathbf{c}_i \rangle^\sigma$ , the mean positions do not lie on a regular lattice. Thus  $m_{\mathbf{k}}^\sigma$  is composed of a set of random phase factors, implying that  $m_{\mathbf{k}}^\sigma \sim O(1/N^{1/2})$ . In the thermodynamic limit,  $m_{\mathbf{k}}^\sigma=0$  unless  $\mathbf{k}=\mathbf{0}$ , and thus the normalized density is not a suitable order parameter for distinguishing between liquid and amorphous-solid states.

The failure of the conventional order parameter leads us to propose the following order parameter, which we call the self-overlap:

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma} = \frac{1}{N} \sum_{i=1}^N \langle e^{-i\mathbf{k} \cdot \mathbf{c}_i} \rangle^\sigma \langle e^{-i\mathbf{k}' \cdot \mathbf{c}_i} \rangle^\sigma. \quad (3.3)$$

We shall indicate some of its general properties and illustrate them with the simple example of an Einstein solid.

Firstly, if  $\sigma$  represents a liquid state, then for  $\mathbf{k}, \mathbf{k}' \neq \mathbf{0}$ ,  $\langle e^{-i\mathbf{k} \cdot \mathbf{c}_i} \rangle^\sigma$  vanishes, and thus  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  also vanishes. Secondly, if  $\sigma$  represents a crystalline state, then

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma} = \langle e^{-i\mathbf{k} \cdot \mathbf{u}} \rangle^\sigma \langle e^{-i\mathbf{k}' \cdot \mathbf{u}} \rangle^\sigma \sum_{\mathbf{G}} \delta_{\mathbf{k}+\mathbf{k}', \mathbf{G}}, \quad (3.4)$$

where  $\mathbf{u}$  is the displacement of any atom from its equilibrium position. Thus  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  detects the crystalline state, being the sum of Kronecker  $\delta$  functions, with temperature-dependent weights. Thirdly, if  $\sigma$  represents an amorphous state, then

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma} \propto \delta_{\mathbf{k}+\mathbf{k}', \mathbf{0}}. \quad (3.5)$$

Hence  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  differentiates between liquids, crystalline solids, and amorphous solids.

For an Einstein model of a  $d$ -dimensional amorphous solid with a mean-square atomic displacement,  $\xi^2 d$  we obtain the result

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma} = \begin{cases} 0 & \text{liquid} \\ e^{-(1/2)(k^2+k'^2)\xi^2} \sum_{\mathbf{G}} \delta_{\mathbf{G}, \mathbf{k}+\mathbf{k}'} & \text{crystalline solid} \\ e^{-(1/2)(k^2+k'^2)\xi^2} \delta_{\mathbf{0}, \mathbf{k}+\mathbf{k}'} & \text{amorphous solid} \end{cases} \quad (3.6)$$

These results explicitly display the way in which the symmetries of the state of the system are reflected in the order parameter.

We have seen that it is the random phases associated with the random atomic positions which render useless the simple density-order parameter. An analogous problem occurs in the theory of spin glasses. For example, in the Ising spin glass, a system of  $N$  spins  $S_i = \pm 1$  are subject to random interactions. At high temperature, the system is paramagnetic, but at low temperature, a spin-glass phase is found. There, the magnetization per unit volume  $m^\sigma$  is zero, despite the fact that each spin adopts a preferred direction

$$m^\sigma \equiv \frac{1}{N} \sum_{i=1}^N \langle S_i \rangle^\sigma = 0, \quad (3.7)$$

$$q^{\sigma\sigma} \equiv \frac{1}{N} \sum_{i=1}^N \langle S_i \rangle^\sigma \langle S_i \rangle^\sigma \neq 0.$$

If all the extremal states  $\{\sigma\}$  are related by global inversion, then  $q^{\sigma\sigma}$  is the Edwards-Anderson order parameter.<sup>13</sup>

In order to calculate  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$ , it is in fact necessary to generalize the definition of the overlap. Instead of considering just the self overlap  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$ , we consider the overlap  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'}$  between all pairs of states  $\sigma$  and  $\sigma'$ ,

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'} = \frac{1}{N} \sum_{i=1}^N \langle e^{-i\mathbf{k} \cdot \mathbf{c}_i} \rangle^\sigma \langle e^{-i\mathbf{k}' \cdot \mathbf{c}_i} \rangle^{\sigma'}. \quad (3.8)$$

This quantity arises naturally, when one recognizes that two configuration space averages are required to construct the nonvanishing order parameter  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$ .

### C. Cross-linked macromolecules

Although our primary interest is the case of randomly cross-linked macromolecules, we first consider the case of regularly cross-linked macromolecules. By this, we mean a set of macromolecules cross linked periodically along their arc length. The cross links are separated by an arc length large compared with the persistence length. We have in mind a picture of a tennis net of macromolecules, generalized to three dimensions, cross linked at every node, as illustrated in Fig. 2. It is plausible that the behavior of the system is as follows. Suppose the system is prepared in a microscopic state which has the same topology as a tennis net. We shall refer to this topology as the natural topology. The equilibrium state will be a crystalline solid, in the sense that the equilibrium mean values of the monomer positions will form the bonds of a periodic lattice and the mean positions of the cross links will lie on the vertices of the lattice. In equilibrium the system will, of course, fluctuate about the mean configuration, but only to configurations with the regular topology.

Now consider the set of all microscopic configurations irrespective of the topology, but still regularly cross linked. The overwhelming majority of the configurations will not possess the natural topology. A small fraction of the configurations may be characterized as having the natural topology apart from a finite number of isolated

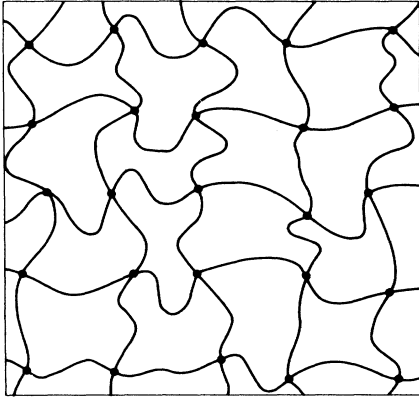


FIG. 2. Illustration of a regularly cross-linked macromolecular network.

topological defects, as shown in Fig. 3. (By the term “defect” we mean a local alteration of the topology which results from the passing of one chain segment through another, as occurs between Figs. 2 and 3.)

Typical configurations will not be of the form of a network in the natural topology, but with a small number of defects. Instead, they will be amorphous, with so many defects that they will not be recognizably crystalline.

If the system is prepared in a typical configuration the achievement of periodic ordering will be frustrated by the impenetrability of the chains, and the normalized equilibrium density, Eq. (3.2), will vanish. States having a finite number of defects will have a free energy which is larger by a finite amount than that of states in the natural topology. They will also be microscopically indistinguishable from states with the natural topology; their self-overlap will equal the self-overlap of states with the natural topology, which will also equal their mutual overlap.

Now consider states whose topology is macroscopically different from the natural topology. These cannot be generated by inserting a finite number of defects into the natural topology and have a free energy which is larger than that of states with the natural topology by an

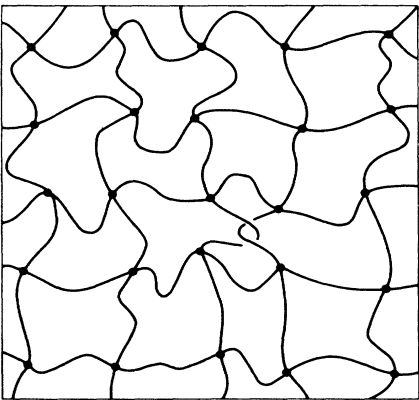


FIG. 3. Topological defect in a regularly cross-linked macromolecular network.

amount which diverges in the thermodynamic limit. We define the normalized Boltzmann weight of the equilibrium state  $\sigma$ , to be  $w^\sigma$ , where

$$w^\sigma \equiv \frac{e^{-F^\sigma}}{\sum_{\tau} e^{-F^\tau}} \quad (3.9)$$

and the free energy of  $\sigma$  is

$$F^\sigma \equiv -\ln \text{Tr}_\sigma e^{-\mathcal{H}}. \quad (3.10)$$

The Boltzmann weights of the amorphous states are negligible compared with those of the natural topology and those states which are microscopically identical to it.

We now turn to the case of randomly cross-linked macromolecules with sufficient cross links to cause rigidity. In this case, there is no counterpart to the unique natural topology that occurred for the regularly cross-linked case. For the randomly cross-linked case, there will be at least one amorphous equilibrium state with the lowest free energy. There will also be states whose free energy differs from this by a finite amount. However, in contrast to the regular case, we conjecture that these states do not necessarily bear any relation to the minimum energy states; they need not be generated from any of the states of lowest energy by a finite number of defects.

For the regular case, all states with nonvanishing weight can be obtained by inserting a finite number of defects into a state with natural topology; these states are microscopically identical. In the amorphous case, by contrast, there are states with nonvanishing weight which cannot be related by the insertion of a finite number of defects; these states are microscopically distinct.

Consider a system of  $N$  polymer chains, labeled  $i=1, \dots, N$ . Each chain has arc length  $L$  and persistence length  $l$ . This means that in the absence of interactions the orientation of the chains persists for an arc length of order  $l$ . Effectively, the total number of degrees of freedom is  $NL/l$ . A configuration of the system is described by the positions of the monomers at arc-length  $s$  on each chain,  $\mathbf{c}_i(s)$ . The normalized density in the equilibrium state  $\sigma$  is given by

$$m_{\mathbf{k}}^\sigma = \frac{1}{NL} \sum_{j=1}^N \int_0^L ds \langle \exp[-i\mathbf{k} \cdot \mathbf{c}_j(s)] \rangle^\sigma. \quad (3.11)$$

If  $\sigma$  describes either a liquid state or an amorphous solid state then  $m_{\mathbf{k}}^\sigma$  vanishes unless  $\mathbf{k}=0$ . The self-overlap is given by

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma} = \frac{1}{NL} \sum_{j=1}^N \int_0^L ds \langle \exp[-i\mathbf{k} \cdot \mathbf{c}_j(s)] \rangle^\sigma \times \langle \exp[-i\mathbf{k}' \cdot \mathbf{c}_j(s)] \rangle^\sigma. \quad (3.12)$$

If  $\sigma$  corresponds to a liquid state and both  $\mathbf{k}$  and  $\mathbf{k}'$  are not equal to zero, then  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}=0$ . If  $\sigma$  corresponds to a solid, either amorphous or crystalline, then  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  will not vanish. Between them,  $m_{\mathbf{k}}^\sigma$  and  $q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma}$  distinguish between liquid, crystalline, and amorphous solid states.

It is also convenient to define the overlap

$$q_{\mathbf{k}\mathbf{k}'}^{\sigma\sigma'} = \frac{1}{NL} \sum_{j=1}^N \int_0^L ds \langle \exp[-i\mathbf{k}\cdot\mathbf{c}_i(s)] \rangle^\sigma \times \langle \exp[-i\mathbf{k}'\cdot\mathbf{c}_i(s)] \rangle^{\sigma'}, \quad (3.13)$$

which, under the replacement of  $\sigma$  by a symmetry-related counterpart  $\hat{\sigma}$ , transforms as

$$q_{\mathbf{k}\mathbf{k}'}^{\hat{\sigma}\hat{\sigma}'} = \exp(-i\mathbf{k}\cdot\mathbf{a}) q_{\bar{R}\mathbf{k}\bar{R}\mathbf{k}'}^{\sigma\sigma'}, \quad (3.14)$$

where each configuration in  $\hat{\sigma}$  is obtained from a configuration in  $\sigma$  by first translating by  $\mathbf{a}$  and then rotating by  $R$ . The notation  $\bar{R}$  designates the inverse of  $R$ . So far, we have only introduced overlaps between two equilibrium states. As we shall see in paper II, these overlaps are only the lowest in an infinite sequence of overlaps between any number of equilibrium states whose disorder-averaged probability distributions emerge from the field-theoretical approach. Generalizing the two-state overlaps, we introduce the overlap between  $m$  equilibrium states  $\sigma_1, \dots, \sigma_m$  at nonzero wave vectors  $\mathbf{k}_1, \dots, \mathbf{k}_m$ , defined to be

$$q_{\mathbf{k}_1, \dots, \mathbf{k}_m}^{\sigma_1, \dots, \sigma_m} = \frac{1}{NL} \sum_{i=1}^N \int_0^L ds \langle e^{-i\mathbf{k}_1\cdot\mathbf{c}_i(s)} \rangle^{\sigma_1} \dots \times \langle e^{-i\mathbf{k}_m\cdot\mathbf{c}_i(s)} \rangle^{\sigma_m}. \quad (3.15)$$

As it stands, this overlap is not invariant under the replacement of  $\sigma$  by a symmetry-related equilibrium state. Since we would like to classify states into those which are related by symmetry and those which are not, we shall eliminate this dependence by using the symmetrized overlap

$$q_{\{\mathbf{k}_1, \dots, \mathbf{k}_m\}}^{\sigma_1, \dots, \sigma_m} \equiv \left[ \frac{\sum_{R_1, \dots, R_m} |q_{R_1\mathbf{k}_1, \dots, R_m\mathbf{k}_m}^{\sigma_1, \dots, \sigma_m}|^2}{\sum_{R_1, \dots, R_m} \delta_{R_1\mathbf{k}_1 + \dots + R_m\mathbf{k}_m, 0}} \right]^{1/2}, \quad (3.16)$$

where  $R_i$  are notation matrices for cubic symmetry, and the quantity is only defined whenever the denominator does not vanish. The modulus function eliminates the effect of translations and the summations eliminate the effect of cubic rotations. We have assumed that the system is in a cubic box with periodic boundary conditions.

The symmetrized overlaps  $\{q_{\{\mathbf{k}, \mathbf{k}'\}}^{\sigma\sigma'}\}$  yield two pieces of information. Firstly, if  $q_{\{\mathbf{k}, \mathbf{k}'\}}^{\sigma\sigma'}$  is nonzero, then  $\sigma$  describes an equilibrium amorphous solid. Secondly, if there is any variation in the numerical values of  $\{q_{\{\mathbf{k}, \mathbf{k}'\}}^{\sigma\sigma'}\}$ , then there are necessarily equilibrium states which are not related by a global symmetry operation. The symmetrized overlap and the symmetrized self-overlap enable us to compare equilibrium states at two levels of detail. If the configuration in two equilibrium states  $\sigma$  and  $\sigma'$  differ by only a finite number of topological defects, then we refer to the states as being microscopically identical. With probability 1, any given monomer will fluctuate in the same way about the same mean position, modulo global symmetry operations, in either equilibrium state. For such states,

$$q_{\{\mathbf{k}, \mathbf{k}'\}}^{\sigma\sigma} = q_{\{\mathbf{k}, \mathbf{k}'\}}^{\sigma\sigma'} = q_{\{\mathbf{k}, \mathbf{k}'\}}^{\sigma'\sigma'} \quad (3.17)$$

If the states are not microscopically identical, then one possibility is that they have different symmetrized self-overlaps. They they correspond to macroscopically observably different states, and we refer to them as being macroscopically distinct. A second possibility is that a pair of states may have identical symmetrized self-overlaps, which differ from the symmetrized overlap. In this case, the states are macroscopically identical, although microscopically distinct. Lastly, we note that there is no *a priori* necessity for there to be symmetry-unrelated equilibrium states in an equilibrium amorphous solid.

We shall now introduce a sequence of probability distributions, which describe how configuration space is decomposed into equilibrium states. The primary virtue of these distributions is that their disorder averages may be approximately calculated by averages over the entire ensemble of microscopic configurations consistent with the cross-link constraints, as shown in Sec. IV.

Define the set of probability distributions for the symmetrized overlaps

$$P_{\{\mathbf{k}_1, \dots, \mathbf{k}_m\}}^{(m)}(q) \equiv \sum_{\sigma_1, \dots, \sigma_m} w^{\sigma_1} \dots w^{\sigma_m} \delta(q - q_{\{\mathbf{k}_1, \dots, \mathbf{k}_m\}}^{\sigma_1, \dots, \sigma_m}). \quad (3.18)$$

This collection of probability distributions will serve as the order parameters. Notice that at this stage they have been defined for a particular realization of cross links. Furthermore, every microstate of the system consistent with the cross links is included on the right-hand side of Eq. (3.18).

Now suppose that we knew these probability distributions. What would they tell us about the system of cross-linked macromolecules? There are three possible cases for us to consider.

(i) Each of the probability distributions is a Dirac  $\delta$  function at the origin. This implies that all the equilibrium states (and there may only be one) with nonzero weight have zero symmetrized overlap and hence are translationally invariant and liquid. Notice that this case does not imply that there is only one fully ergodic equilibrium state. As one might anticipate for the case of a lightly cross-linked system, a choice of topology might exist. However, for each topology the system is liquid, and hence all overlaps vanish.

(ii) Each of the probability distributions is a Dirac  $\delta$  function, with weight at a nonzero value of the overlap. In this case, all equilibrium states with nonvanishing weights have a common value of the symmetrized overlap. This implies that they are all related to each other by symmetry, apart from a finite number of local differences which would not exhibit themselves in a macroscopic quantity such as an overlap. If we were considering the crystallization of a simple atomic fluid then single-peaked sharp distributions are what we would expect. Even though there may exist extremal equilibrium states with, for example, domain walls, the infinite increase in free energy due to the inhomogeneity would lead to vanishing normalized Boltzmann weights and these states would be completely suppressed from the distribution. For the simple Einstein solid of Sec. III,

$$P_{\{k_1, \dots, k_m\}}^{(m)}(q) = \delta(q - \bar{q}), \quad (3.19)$$

$$\bar{q} = \exp \left[ -\frac{1}{2} \xi^2 \sum_{i=1}^m |k_i|^2 \right]. \quad (3.20)$$

(iii) The probability distributions have weight at a variety of nonzero values of the overlap. This implies that there are equilibrium states with broken translational symmetry and nonzero Boltzmann weights which are microscopically distinct from each other. There are, of course, the symmetry related counterparts of these states and states which differ from them only by local defects. Each of the equilibrium states may or may not have the same value for its self-overlap.

#### IV. CALCULATION OF THE OVERLAP DISTRIBUTIONS

As we stated earlier, the two principal techniques for establishing the existence of broken symmetry—the

methods of small fields and of invariant correlation functions—are doomed to fail for equilibrium amorphous solids. In Sec. III we have introduced order parameters, in the form of probability distributions, which detect the existence of amorphous solid states. Superficially, it seems that these distributions are no more calculable than those quantities for which traditional methods fail. In this section, we shall show how one can approximate  $P_{\{k_1, \dots, k_m\}}^{(m)}(q)$  from a statistical-mechanical average over  $m$  copies of the entire configuration space. The technique developed in this section relies heavily on the work of Parisi on the infinite-range Ising spin glass.<sup>14</sup> For simplicity, we consider the distribution function  $P_{\{k, k'\}}^{(2)}$  defined in Eq. (3.18). The generalization to higher distributions is straightforward. For convenience, we work with the integral transform of  $P_{\{k, k'\}}^{(2)}(q)$  defined by

$$\Pi_{\{k, k'\}}^{(2)}(y) = \int_{-\infty}^{\infty} dq e^{yq^2} P_{\{k, k'\}}^{(2)}(q). \quad (4.1)$$

Expanding the exponential and inserting the definition of the symmetrized overlap, we obtain

$$\begin{aligned} \Pi_{\{k, k'\}}^{(2)}(y) = & \sum_{\sigma, \sigma'} w^\sigma w^{\sigma'} \sum_{a=0}^{\infty} \frac{(y/\beta)^a}{a!} \frac{1}{N} \sum_{i_1=1}^N \cdots \frac{1}{N} \sum_{i_a=1}^N \frac{1}{N} \sum_{i'_1=1}^N \cdots \frac{1}{N} \sum_{i'_a=1}^N \frac{1}{L} \int_0^L ds_1 \cdots \frac{1}{L} \int_0^L ds_a \frac{1}{L} \int_0^L ds'_1 \cdots \\ & \times \frac{1}{L} \int_0^L ds'_a \sum_{R_1, R'_1} \cdots \sum_{R_a, R'_a} \langle e^{-iR_1 k \cdot c_{i_1}(s_1)} \rangle^\sigma \langle e^{-iR'_1 k' \cdot c_{i'_1}(s'_1)} \rangle^{\sigma'} \cdots \langle e^{iR_a k \cdot c_{i_a}(s_a)} \rangle^\sigma \langle e^{iR'_a k' \cdot c_{i'_a}(s'_a)} \rangle^{\sigma'}, \end{aligned} \quad (4.2)$$

$$\beta = \sum_{R, R'} \delta_{Rk + R'k', 0}. \quad (4.3)$$

The next step is to use the cluster property of the equilibrium states to assemble the equilibrium state averages into a Gibbs average over  $m$  copies of the system (i.e., averages over all the microscopic configurations of  $M$  identical uncoupled copies of the original system, weighted by the sum of Hamiltonians, one for each copy of the system). The Gibbs average of a quantity  $O$  is given by

$$\langle O \rangle = \frac{1}{Z} \text{Tr}(e^{-HO}) = \sum_{\sigma} w^\sigma \langle O \rangle^\sigma, \quad (4.4)$$

where the Gibbs partition function is

$$Z = \text{Tr} e^{-H} \quad (4.5)$$

and Tr includes *all* configurations. Resumming the exponential series, and inverting the Laplace transform, we finally obtain

$$P_{\{k, k'\}}^{(2)}(q) = \langle \delta(q - Q_{\{k, k'\}}^{12}) \rangle_2, \quad (4.6)$$

$$Q_{\{k, k'\}}^{12} = \frac{1}{NL} \sum_{i=1}^N \int_0^L ds e^{-ik \cdot c_i(s) - ik' \cdot c_i^2(s)}, \quad (4.7)$$

where  $\langle \cdots \rangle_2$  denotes a Gibbs average over two independent copies of the system, with the cross links at the *same* arc-length positions in the two copies. A similar result applies in the general case

$$P_{\{k_1, \dots, k_m\}}^{(m)}(q) = \langle \delta(q - Q_{\{k_1, \dots, k_m\}}^{1, \dots, m}) \rangle_m, \quad (4.8)$$

where

$$Q_{\{\alpha_1, \dots, \alpha_m\}} = \left[ \frac{\sum_{R_1, \dots, R_m} |Q_{R_1 k_1, \dots, R_m k_m}^{\alpha_1, \dots, \alpha_m}|^2}{\sum_{R_1, \dots, R_m} \delta_{R_1 k_1 + \dots + R_m k_m, 0}} \right]^{1/2} \quad (4.9)$$

and

$$Q_{\{k_1, \dots, k_m\}}^{\alpha_1, \dots, \alpha_m} = \frac{1}{NL} \sum_{j=1}^N \int_0^L d\tau \exp \left[ -i \sum_{a=1}^m k_a \cdot c_j^{\alpha_a}(\tau) \right]. \quad (4.10)$$

Thus we have reduced the problem of calculating the overlap probability distributions to the problem of performing a Gibbs average over all the microstates of the system; in fact  $m$  such Gibbs averages. We are, of course, still unable to complete the calculation analytically, even approximately, because of the presence of the random cross-linking constraints. However, this form lends itself to evaluation using Monte Carlo methods; a calculation is currently in progress. This difficulty is resolved by the replica method, which we now describe.

The idea of the replica method is to calculate the overlap distributions, averaged over the probability distribution for the locations and number of constraints, by averaging over the disorder *before* performing the average over configuration space. However, this cannot be



done directly, since both the numerator and denominator in Eq. (4.7) depend on the quenched random constraints. The denominator in the expression for  $P_{\{k_1, \dots, k_m\}}^{(m)}$  is simply  $Z^m$ . The replica method exploits this observation by introducing a further factor of  $Z^{n-m}$  in both the numerator and denominator of Eq. (4.7), where  $n$  is an arbitrary integer greater than or equal to  $m$ . Thus the denominator becomes  $Z^n$ . If the dependence of the denominator on the disorder were eliminated, then the disorder average could be performed. This is achieved by taking the  $n \rightarrow 0$  limit. Denoting the disorder average by  $[\dots]$ , our expression for the disorder-averaged overlap distributions becomes

$$[P_{\{k_1, \dots, k_m\}}^{(m)}(q)] = \lim_{n \rightarrow 0} [\langle \delta(q - Q_{\{k_1, \dots, k_m\}}^1) \rangle_n]. \quad (4.11)$$

The form that these order parameters take, as the mean number of cross links and the Hamiltonian are varied, determines the equilibrium properties of the system.

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#### APPENDIX: BREAKING OF ERGODICITY AND CONTINUOUS SYMMETRY

Our approach to describing the equilibrium properties of RCM's relies on considering the sets of microstates which the system can explore for given constraints and values of the parameters in the Hamiltonian. As emphasized by Dobrushin, Lanford, Ruelle, and others, in equilibrium, the physical state of an infinite system can be described by a probability distribution, or measure,  $\rho$  on configuration space.<sup>3</sup> This measure is usually known as an *equilibrium state*. In this appendix, we shall summarize the properties of equilibrium states.

The equilibrium states satisfy a set of equations usually associated with the names of Dobrushin, Lanford, and Ruelle, whose physical content is that each subregion of the system is in local equilibrium with the rest of the system. Alternatively, the equilibrium states satisfy a variational principle, in the infinite-volume ( $V \rightarrow \infty$ ) limit. Physically, the variational principle requires that, at temperature  $T$ , equilibrium states  $\rho$  minimize the free energy density,  $f[\rho]$ , where

$$Vf[\rho] = F[\rho] = E[\rho] - TS[\rho], \quad (A1)$$

and the energy  $E$  and entropy  $S$  are given by

$$E[\rho] = \text{Tr} \rho \mathcal{H} \quad (A2)$$

$$S[\rho] = \text{Tr} \rho \ln \rho. \quad (A3)$$

For finite simple systems, the equilibrium state is unique and is just the familiar form

$$\rho \propto e^{-\mathcal{H}/T}. \quad (A4)$$

For a finite system of cross-linked macromolecules the equilibrium state is unique only for each set of topologically equivalent configurations. However, for infinite systems, the equilibrium state need not be unique.

Now consider systems with a Hamiltonian which is invariant under the elements of a symmetry group  $G$ . Let us first discuss the case when there is no spontaneous symmetry breaking. All of the equilibrium states are  $G$  invariant, and there is always at least one of them. These equilibrium states form a convex set, which is to say, if  $\rho_1$  and  $\rho_2$  are equilibrium states, then the convex sum

$$\rho = a\rho_1 + (1-a)\rho_2, \quad 0 < a < 1 \quad (A5)$$

is also a  $G$ -invariant equilibrium state. For our purposes, the most important result about these equilibrium states is the following: any equilibrium state  $\rho$  can be uniquely decomposed into a convex sum of *extremal equilibrium states*  $\rho_\alpha$ :

$$\rho = \sum_{\alpha} a_{\alpha} \rho_{\alpha}; \quad \sum_{\alpha} a_{\alpha} = 1, \quad 1 \geq a_{\alpha} \geq 0. \quad (A6)$$

The extremal equilibrium states have several distinguishing features. Firstly, they are extremal in the sense that they cannot be written in the form of Eq. (A6). Secondly, they are disjoint; each microstate of the system lies within only one extremal state. Thirdly, the extremal equilibrium states cluster. Clustering is a property of the correlation functions of the degrees of freedom  $\psi$ , namely, that

$$\lim_{a \rightarrow \infty} [\langle \psi(\mathbf{x}_1) \cdots \psi(\mathbf{x}_n) \psi(\mathbf{y}_1 + \mathbf{a}) \cdots \psi(\mathbf{y}_n + \mathbf{a}) \rangle^{\sigma} - \langle \psi(\mathbf{x}_1) \cdots \psi(\mathbf{x}_n) \rangle^{\sigma} \langle \psi(\mathbf{y}_1) \cdots \psi(\mathbf{y}_n) \rangle^{\sigma}] = 0, \quad (A7)$$

where  $\langle \dots \rangle^{\sigma}$  denotes an expectation value calculated with the measure for the extremal equilibrium state  $\sigma$ . Only the extremal states cluster; a convex sum of extremal equilibrium states does not possess the cluster property. Fourthly, extremal  $G$ -invariant equilibrium states all have the same free-energy density. The  $G$ -invariant extremal equilibrium states are called *equilibrium states*, because they have the physical interpretation that they describe a state of homogeneous equilibrium. The cluster property guarantees that the equilibrium states have small fluctuations and so have good thermodynamic behavior.

We now discuss spontaneous symmetry breaking. Suppose that at some value of the parameters in the Hamiltonian the system is in an equilibrium state with respect to  $G$ . It may happen that, for a different set of values of the parameters in the Hamiltonians, the correlation functions are such that the cluster properties of the original measure have been lost. Then there are no  $G$ -invariant extremal equilibrium states, but there will be extremal equilibrium states which are invariant under some subgroup  $H$  of  $G$ . For this value of the parameters, then, the system will be found in a state corresponding to one of the equilibrium states with respect to  $H$ . Since the extremal equilibrium states are disjoint, ergodicity has been broken. Furthermore, since the equilibrium states are

only invariant under a subgroup of the group of invariances of the Hamiltonian, symmetry has been broken. To summarize, the symmetry of the Hamiltonian is spontaneously broken when the symmetric measure is no longer extremal; instead each extremal measure is invariant under a small symmetry group.

It follows that the equilibrium states with respect to  $H$  are related by symmetric operations in  $G/H$ . Let us clarify what this means in the present context. Two regions are said to be symmetry related if the application of a symmetry operation in  $G/H$  to all the microstates within a given ergodic region of configuration space generates all the microstates within another distinct region of configuration space. Which symmetry operation in  $G/H$  is actually required depends on which two regions are being considered.

The loss of the cluster property of the  $G$ -invariant equilibrium states is associated with the acquisition of long range order. The  $H$ -invariant equilibrium states give rise to a nonzero order parameter, and although the connected correlation functions cluster, their large-distance behavior retains a vestige of the spontaneous symmetry breaking. A familiar example is the case of the  $O(3)$  Heisenberg model for a system of classical vector spins  $\mathbf{S}(\mathbf{x})$  in three dimensions. Above the transition temperature  $T_c$ , there is a single translationally invariant and  $O(3)$ -invariant extremal measure, corresponding to the paramagnetic phase. The magnetization  $M = \langle \mathbf{S}(\mathbf{x}) \rangle$  vanishes. The connected two-point correlation function  $G^{\mu\nu}(\mathbf{x}, \mathbf{y}) = \langle S^\mu(\mathbf{x}) S^\nu(\mathbf{y}) \rangle$  is isotropic in spin space and decays exponentially to zero as  $|\mathbf{x} - \mathbf{y}| \rightarrow \infty$ . We will shortly mention the implication that this behavior has for the spin-wave stiffness, or generalized rigidity of the order parameter  $M$ . Below  $T_c$ , there is a continuum of translationally invariant and  $O(2)$ -invariant extremal measures, corresponding to the degenerate family of ferromagnetic phases. The magnetization is nonzero and translationally invariant, and its direction in spin space  $\mathbf{n}$

labels the  $O(2)$ -invariant equilibrium states.  $G^{\mu\nu}(\mathbf{x}, \mathbf{y})$  is no longer isotropic, but instead may be separated into longitudinal and transverse components

$$G^{\mu\nu}(\mathbf{x}, \mathbf{y}) = G_L(\mathbf{x}, \mathbf{y}) n^\mu n^\nu + G_T(\mathbf{x}, \mathbf{y}) (\delta^{\mu\nu} - n^\mu n^\nu). \quad (\text{A8})$$

As  $|\mathbf{x} - \mathbf{y}| \rightarrow \infty$  both  $G_L$  and  $G_T$  decay to zero. However,  $G_L$  decays exponentially, while  $G_T$  decays with a power law. This power-law decay of the transverse correlation function is an example of Goldstone's theorem, which states that, in general, the spontaneous breaking of a continuous symmetry leads to long-range transverse correlations.

An important physical consequence of spontaneous symmetry breaking is the concept of the rigidity of the other parameter. In the example given above, the system is said to be rigid because the magnetization resists deformations which locally distort it from its equilibrium value. The change in the Gibbs free energy  $\delta G$  due to the distortion  $\delta \mathbf{M}$  is

$$\begin{aligned} \delta G &= \frac{1}{2} \sum_{\mathbf{k}} \left[ \frac{|\delta \mathbf{M}_{\mathbf{k}}^T|^2}{\lambda_{\mathbf{k}}^T} + \frac{|\delta \mathbf{M}_{\mathbf{k}}^L|^2}{\lambda_{\mathbf{k}}^L} \right] + O(\delta \mathbf{M}^4) \\ &= \frac{1}{2} \sum_{\mathbf{k}} [Rk^2 |\delta \mathbf{M}_{\mathbf{k}}^T|^2 + A(1 + k^2 \xi^2) |\delta \mathbf{M}_{\mathbf{k}}^L|^2] \\ &\quad + O(\delta \mathbf{M}^4, k^4), \end{aligned} \quad (\text{A9})$$

where  $\delta \mathbf{M}_{\mathbf{k}}^{L,T}$  are, respectively, the Fourier components of the longitudinal and transverse parts of the deviation of the magnetization from its uniform value,  $\lambda_{\mathbf{k}}^{L,T}$  are the eigenvalues of  $G^{L,T}(\mathbf{x}, \mathbf{y})$ , and  $A$  is a constant. The coefficient  $R$  is known as the spin-wave stiffness. A spatially uniform transverse fluctuation costs no Gibbs free energy, in contrast to the case for such a longitudinal fluctuation. Consequently the magnetization will rigidly rotate under the application of an infinitesimal transverse field.

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