Rigidity and Ergodicity of Randomly Cross-Linked Macromolecules

Paul Goldbart and Nigel Goldenfeld

Loomis Laboratory of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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We consider a system of randomly cross-linked, interacting macromolecules, within the framework of replica field theory. We find that above a critical number of cross links, translational and replica symmetry are simultaneously broken, thus showning that the system is an equilibrium amorphous solid, with many pure phases unrelated by global symmetry. We argue that each symmetry-unrelated pure phase describes a separate realization of the topology of the network.

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Rubber elasticity is one of the most spectacular phenomena which can be exhibited by a solid.[1] In the phantom chain models,[1] these elastic properties are usually ascribed to the entropy of the long-chain molecules, modeled as a set of noninteracting random walks, which are constrained to meet at preassigned cross links. The partial success of this description, and its many variants, seems to us to be unjustified; a conceptually sound theory would include the strong interactions and topological entanglements which undoubtedly determine the behavior of cross-linked rubber.[2] In many respects the situation is reminiscent of the success of the free-electron theory of metals; ultimately we would like to understand the successes of the phantom-chain model at the level of many-body theory.

Although the startling elastic properties have attracted enormous attention, we believe that the very existence of the solid phase is equally remarkable. The nature of this solid phase poses a number of fascinating problems, which lie at the heart of condensed-matter physics; its elucidation requires explicit consideration of the relationship between the concepts of ergodicity, generalized rigidity, and spontaneous breaking in strongly interacting systems.[3]

In this paper, we propose that systems of cross-linked macromolecules, such as certain gels and vulcanized rubber, are in fact equilibrium amorphous solids. We will demonstrate how these systems become rigid as a consequence of the spontaneous breaking of translational symmetry and the ensuing loss of ergodicity. As we shall see, configuration space is fragmented into ergodic regions, known as pure phases,[4] according to two distinct principles. First, each pure phase is accompanied by others, generated from it by global symmetry operations. These pure phases result from the spontaneous breaking of translational symmetry and, in the case of crystallization for example, would exhaust configuration space. Second, we find an additional partitioning of configuration space into pure phases unrelated by symmetry. These result from the spontaneous breaking of replica symmetry,[5] as occurs in the case of the Sherrington-Kirkpatrick[6] infinite-range model of a spin-glass. In contrast to this case, our systems have genuine long-range interactions.

We shall see later how these pure phases may be related to the question of the topology of the network of cross-linked macromolecules.

Pure phases have a simple interpretation: A thermodynamic system explores the microstates within just one pure phase. The number of pure phases reflects the position on the phase diagram of the system, as given by the values of the external parameters. For example, in the case of liquid-gas transition, there is a single pure phase for all pressures and temperatures, except along the coexistence line, in which case there are two. In general, to decide whether or not a system in a given phase is rigid, one must calculate the restoring force with which the system responds to an infinitesimal shear; the shear response function is computed retaining *only* those states within the given pure phase. In pure systems,[3] rigidity arises either when the density-density correlation function decays exponentially to a nonzero value at infinity, or when it decays sufficiently slowly to zero. Spontaneous breaking of translational symmetry leads to the former case; the order parameter is the expectation value, in the given pure phase, of the Fourier components of the density. In a disordered system, such as a spin glass or, as we show, a cross-linked macromolecular network, where the system average of the order parameter is zero, rigidity is determined by the pair correlation function between microscopic degrees of freedom (i.e., single spins or monomers).

We now consider the equilibrium statistical mechanics of a d-dimensional network of randomly cross-linked macromolecules in a cube of volume V. The cross links, together with the hard-core interactions between macromolecules, give the network a permanent topology. Although the topology necessarily breaks ergodicity, it does not *a priori* imply rigidity. Only if the resulting pure phases had broken translational invariance would the system be rigid. The connectedness of the network is distinct from its rigidity; a connected but nonrigid system is not capable of transmitting an infinitesimal force.[3]

Our system consists of N chains, with trajectories $\{\mathbf{c}_i(s)\}$, $i=1,2,\ldots,N$, each of arclength L and persistence length l, parametrized by the arclength s. M

cross links permanently connect the pairs of points on chains $\{i_e, i_e'\}$ at arclength positions $\{s_e, s_e'\}$, $e=1,2,\ldots,M$. We use the Edwards Hamiltonian[2]

$$\mathcal{H}[\{\mathbf{c}_i\}] = \frac{d}{2l}\sum_{i=1}^{N}\int_0^L \left|\frac{d\mathbf{c}_i(s)}{ds}\right|^2 ds + \frac{1}{2}\lambda^2 \sum_{i,j=1}^{N}\int_0^L ds \int_0^L ds'\,\delta(\mathbf{c}_i(s)-\mathbf{c}_j(s')), \tag{1}$$

where λ^2 is a temperature-dependent parameter proportional to the second virial coefficient, and provides a Boltzmann weight for intersections of the chains. We shall say more about this term later. $\mathcal{H}$ is translationally invariant, and this feature is not violated when the cross-link constraints are imposed. For this system, configuration space is the space of all configurations of the chains which satisfy the cross-linking constraints. As we have seen above, rigidity is a consequence of the breaking of ergodicity. Thus, to address the question of rigidity, it is necessary to define an order parameter which describes how configuration space is spontaneously partitioned into pure phases. In principle, the thermodynamic properties of a given pure phase σ are obtained from the free energy

$$F^\sigma \equiv -\ln \mathrm{Tr}_\sigma \exp(-\mathcal{H}), \tag{2}$$

where the trace includes *only* those microstates within σ. However, we do not *a priori* have any information about the possible pure phases. Instead, we construct a quantity which can be calculated by a trace over *all* microstates consistent with the constraints, but which nevertheless displays a signature of the underlying pure phase structure of configuration space. A suitable quantity is the probability distribution, P, for a certain overlap, $q^{\sigma\sigma'}$, between pairs of pure phases. We choose the overlap to be a translationally and rotationally invariant function which compares the monomer densities in pure phases σ and σ':

$$(q^{\sigma\sigma'})^2 \sum_{\hat{\mathbf{e}},\hat{\mathbf{e}}'} \delta_{\hat{\mathbf{e}}\hat{\mathbf{e}}'} \equiv \sum_{\hat{\mathbf{e}},\hat{\mathbf{e}}'} |q^{\sigma\sigma'}_{\hat{\mathbf{e}}\hat{\mathbf{e}}'}|^2, \tag{3}$$

where

$$q^{\sigma\sigma'}_{\mathbf{k}\mathbf{k}'} \equiv \frac{1}{NL}\sum_{i=1}^{N}\int_0^L \langle e^{-i\mathbf{k}\cdot\mathbf{c}_i(s)}\rangle^\sigma \langle e^{-i\mathbf{k}'\cdot\mathbf{c}_i(s)}\rangle^{\sigma'} ds, \tag{4}$$

and the summation in Eq. (3) only includes the shortest wave vectors, $\{\hat{\mathbf{e}}\}$. Note that $q^{\sigma\sigma'}$ has been constructed to be numerically invariant if either pure phase is replaced by one of its global-symmetry-related counterparts.

Depending on the values of the physical parameters, the probability distribution

$$P(q) \equiv \sum_{\sigma,\sigma'} w^\sigma w^{\sigma'} \delta(q-q^{\sigma\sigma'}), \tag{5a}$$

$$w^\sigma = e^{-F^\sigma} / \textstyle\sum_\tau e^{-F^\tau} \tag{5b}$$

can show three qualitatively different types of behavior, according to whether and how the configuration space is partitioned. In case one, $P(q)=\delta(q)$, and translational symmetry is not broken. Hence, the system may either be fully ergodic, or there may be many translationally invariant (and hence nonrigid) pure phases unrelated by symmetry. In case two, there is a family of symmetry-related pure phases, corresponding to the spontaneous breaking of translational symmetry, and $P(q)=\delta(q-\bar{q})$. In the context of spin-glasses, $\bar{q}$ is the Edwards-Anderson order parameter.[7] The third case arises when there are pure phases which are unrelated by symmetry in addition to those related by symmetry; in this case $P(q)$ is a broad distribution.

While we are not able to calculate $P(q)$ for a given realization of the cross links, its disorder average, $[P(q)]$, emerges naturally[5] from the mean-field calculation by use of the replica method,[2,7] which we now present.

For simplicity, we choose a uniform distribution of cross-link positions allowing the number of cross links to fluctuate about its mean value, $\mu^2 N/2$, according to the Poisson distribution, $\mathcal{P}$. We define a generating function Z to be

$$Z \propto \int \prod_{i=1}^{N} \mathcal{D}\mathbf{c}_i \exp\{-\mathcal{H}[\{\mathbf{c}_i\}]\} \prod_{e=1}^{M} \delta(\mathbf{c}_{i_e}(s_e)-\mathbf{c}_{i_e'}(s_e')), \tag{6}$$

where the functional integral is over *all* chain configurations, and the product over δ functions enforces the cross-link constraints. In the context of mean-field theory, *all* saddle points are retained. If Z were the partition function of the actual problem then, in the broken symmetric state, only a restricted set of configurations would be included. Introducing n replicas, labeled by Greek superscripts α, β, ..., and performing the disorder average over the probability distribution

$$\mathcal{P}_M(\{i_e, i_e'\},\{s_e, s_e'\}) = (1/M!)\exp(-\tfrac{1}{2}\mu^2 N)(\mu^2/2NL^2)^M \tag{7}$$

yields an effective theory without disorder,

$$[Z^n] \propto \int \left(\prod_{i=1}^{N}\prod_{\alpha=1}^{n} \mathcal{D}\mathbf{c}_i^\alpha\right) \exp\left(-\sum_{\alpha=1}^{n}\mathcal{H}[\{\mathbf{c}_i^\alpha\}] + \frac{1}{2}\frac{\mu^2}{2NL^2}\sum_{i,j=1}^{N}\int_0^L ds \int_0^L ds' \prod_{\alpha=1}^{n}\delta(\mathbf{c}_i^\alpha(s)-\mathbf{c}_j^\alpha(s'))\right). \tag{8}$$

The replicas are coupled only through the term arising from the cross links. We distinguish between two classes of interaction: those which couple monomers within the same replica, and those which couple monomers in different replicas. The former category contains the excluded-volume interaction, weakened by a contribution from the one-replica sector of the cross-link term. Independent translations of the replicas leave this effective Hamiltonian invariant; it is the spontaneous breaking of this symmetry which leads to rigidity. The theory is also invariant under permutations of the replicas; the breaking of this symmetry leads to the existence of symmetry-unrelated pure phases.

We introduce real Gaussian random fields $\Psi^{\alpha}(\mathbf{x})$ to decouple the excluded-volume interaction and the one-replica sector of the cross-link interaction, and $\Omega(\hat{x})$ to decouple the remaining many-replica sectors.[8] The dn-dimensional vector $\{\mathbf{x}^1,\mathbf{x}^2,\ldots,\mathbf{x}^n\}$ is denoted by $\hat{x}$ and we define the scalar product $\hat{k}\cdot\hat{x}=\sum_{\alpha}\mathbf{k}^{\alpha}\cdot\mathbf{x}^{\alpha}$. We thus obtain

$$[Z^n]\propto\int\mathcal{D}\Omega\prod_{\alpha}\mathcal{D}\Psi^{\alpha}\exp\left[-\frac{1}{2}\sum_{\alpha}\int\{\Psi^{\alpha}(\mathbf{x})\}^2d^d\mathbf{x}-\frac{N\mu^2}{2V^n}\int\{\Omega(\hat{x})\}^2d^{dn}\hat{x}+N\Gamma\{\Psi^{\alpha},\Omega\}\right], \tag{9a}$$

$$\exp(\Gamma\{\Psi^{\alpha},\Omega\})=\int\mathcal{D}\hat{\mathbf{c}}\exp\left[-\frac{d}{2l}\int_0^L\left|\frac{d\hat{\mathbf{c}}(s)}{ds}\right|^2ds+i\lambda'\sum_{\alpha}\int_0^L\Psi^{\alpha}(\mathbf{c}^{\alpha}(s))ds+\frac{\mu^2}{LV^{n/2}}\int_0^L\Omega(\hat{\mathbf{c}}(s))ds\right], \tag{9b}$$

where $\lambda'=\lambda-\mu^2/(NL^2V^{n-1})$. For any field $\Theta(\hat{x})$, it is convenient to make the following unique decomposition into components:

$$\Theta(\hat{x})=\frac{1}{V^{n/2}}\Theta+\frac{1}{V^{(n-1)/2}}\sum_{\alpha}\Theta^{\alpha}(\mathbf{x}^{\alpha})+\frac{1}{V^{(n-2)/2}}\sum_{\alpha<\beta}\Theta^{\alpha\beta}(\mathbf{x}^{\alpha},\mathbf{x}^{\beta})+\cdots, \tag{10}$$

which are mutually orthogonal under integration over $\hat{x}$. When we decompose $\Omega(\hat{x})$ in this fashion, the one-replica term is absent, being accounted for in $\Psi^{\alpha}(\mathbf{x})$. The transition to the rigid state will manifest itself through a nonvanishing expectation value of Ω as μ is increased from zero. In fact, we find that the lowest-order many-replica field, $\Omega^{\alpha\beta}$, orders first. The nature of the ordered phase is obtained by calculating

$$[P(q)]=\langle\delta(q-\omega^{\alpha\beta})\rangle, \tag{11}$$

where

$$(\omega^{\alpha\beta})^2\sum_{\hat{\mathbf{e}},\hat{\mathbf{e}}'}\delta_{\hat{\mathbf{e}}\hat{\mathbf{e}}'}\equiv\sum_{\hat{\mathbf{e}},\hat{\mathbf{e}}'}|\Omega^{\alpha\beta}_{\hat{\mathbf{e}}\hat{\mathbf{e}}'}|^2, \tag{12}$$

and

$$\Omega^{\alpha\beta}_{\mathbf{k}\mathbf{k}'}=\frac{1}{V}\int d^d\mathbf{x}\int d^d\mathbf{x}'\,\Omega^{\alpha\beta}(\mathbf{x},\mathbf{x}')e^{-i\mathbf{k}\cdot\mathbf{x}-i\mathbf{k}'\cdot\mathbf{x}'}. \tag{13}$$

We employ the following strategy to integrate over the one-replica sector Ψ^{α} and thence derive systematically the effective Hamiltonian, H_{eff}, for Ω. First, we find the saddle point of the one-replica fields, for fixed translationally and rotationally invariant Ω. Second, we expand Γ to quadratic order in Ψ^{α}. Third, we perform the Gaussian integration over the one-replica sector, Ψ^{α}. Since Γ is not known exactly, it is computed in perturbation theory to quartic order in Ω, yielding H_{eff}. This procedure is valid if there is a continuous transition from $\langle\Omega\rangle=0$. We diagonalize the coefficient of the quadratic term in H_{eff}; the vanishing of one eigenvalue marks the onset of the broken-symmetry phase. This transition occurs when the mean number of cross links per chain exceeds one-half. In the thermodynamic limit, the system is rigid when the number of cross links exceeds this amount. We also require that $\lambda'>0$ to prevent the collapse of the network. At the onset of the transition, only $\Omega^{\alpha\beta}_{\hat{\mathbf{e}}\hat{\mathbf{e}}'}$ is nonzero; it is adequate to restrict attention to the manifold $\Omega^{\alpha\beta}_{\hat{\mathbf{e}}\hat{\mathbf{e}}'}=\omega^{\alpha\beta}\delta_{\hat{\mathbf{e}}-\hat{\mathbf{e}}'}$, which leads to

$$\frac{H_{\text{eff}}}{dN}=\frac{1}{n}\tau\operatorname{Tr}(\omega)^2-\frac{1}{3n}\operatorname{Tr}(\omega)^3-\frac{1}{8n}\sum_{\alpha\neq\beta}(\omega^{\alpha\beta})^4, \tag{14}$$

where $2\tau\equiv(1-\mu^2)$ and $|\tau|\ll1$. Here we take the $n\to0$ limit, and we have not written down the one-loop fluctuation corrections to the coefficients. These are small in $d=3$, but diverge in $d\geq4$. Notice that Eq. (14) has precisely the same form as the Landau free energy of the Sherrington-Kirkpatrick model of an Ising spin-glass.[6] The details of this calculation will be presented elsewhere.[9]

We now discuss the interpretation of our calculation. The form of $\omega^{\alpha\beta}$, as determined by its saddle-point value, dictates, via Eq. (11), the manner in which the entire configuration space is partitioned into pure phases. The three qualitatively different partitionings of configuration space correspond to the three possible types of solution to the saddle-point equation. In case 1, $\omega^{\alpha\beta}$ is zero and the system is either fully ergodic or composed of many coexisting translationally invariant pure phases. In case 2, $\omega^{\alpha\beta}$ is nonzero, but invariant under permutations of the replicas; there is a family of symmetry-related pure phases, corresponding to the spontaneous breaking of translational symmetry. This situation may be relevant to those macromolecules which reproducibly adopt a uniform conformation.[10] In case 3, $\omega^{\alpha\beta}$ is not invariant under permutations of the replicas; there are many pure phases unrelated by translational symmetry, in addition to those related by it. The transition which we report here is between cases 1 and 3, as the number of cross links exceeds one-half the number of chains. The replica symmetry-breaking scheme is identical to that discovered by Parisi,[5] and using this correspondence, we find

$$[P(q)] = 3\theta(-\tau - q)/2 + (1 + 3\tau/2)\delta(\tau + q).$$

What is the significance of the pure phase decomposition of configuration space? The energy barriers which demarcate the boundaries of the pure phases can only have arisen from the excluded-volume interaction: There is no other energy scale in the original problem. The configuration-space decomposition which we have found is independent of λ, and should not be affected by a more realistic treatment of the hard-core interactions than the Edwards Hamiltonian provides[9]: Ergodicity breaking requires infinite system size, not infinite energy scales. A sufficient degree of cross linking implies the existence of both topological entanglements and families of symmetry-unrelated pure phases; when there are insufficient cross links to cause rigidity, there may still be topological entanglements, corresponding to pure phases, unrelated by symmetry. In four dimensions, where the effects of topology are absent, ultraviolet-divergent fluctuation corrections in our theory prohibit the transition to the rigid state. Thus it is tempting to conclude that each family of symmetry-related pure phases corresponds to a unique topology of the network.

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