Microscopic theory for cross-linked macromolecules.
II. Replica theory of the transition to the solid state

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We investigate the statistical mechanics of a set of randomly cross-linked macromolecules. Using the replica method, we are led to consider a field theory for an order parameter which describes the breaking of the symmetry of independent translations and rotations between replicas. We construct the Landau free energy in this order parameter by systematically integrating out the polymer degrees of freedom. We find that the system can exhibit two transitions. The first corresponds to the collapse of a swollen rubber, while the second is a continuous transition to an equilibrium amorphous solid once the number of crosslinks exceeds a critical value. Very close to the latter transition, the Landau free energy is of the same form as that for the long-range Ising spin glass, enabling us to use Parisi's replica–symmetry-breaking scheme to describe the ordered state.

I. INTRODUCTION

In this paper, we shall apply the ideas developed in the preceding paper[1] (hereafter referred to as I) to a minimal model for the statistical mechanics of a system of randomly cross-linked macromolecules. Our goal is to describe how this system can become solid if it is sufficiently cross linked.[2] It is often assumed that this transition is related to the appearance of an infinitely large "percolation cluster," but this is not at all obvious, for two principal reasons. Firstly, a network can be connected by virtue of its topology, even in the absence of percolation; this is because regions may be topologically entangled without being cross linked. The possible role of topology in the transition to the rigid state has recently been studied analytically[3] and numerically.[4] Secondly, if the elements which comprise the percolation cluster were themselves rigid, then the percolation model might be justified. In this case, then, the question of rigidity of the system would be a question of architecture. However, the elements are not rigid; they are flexible polymer chains, in thermodynamic equilibrium. To answer the question of whether or not the system exhibits rigidity, it is the thermodynamics which must be considered. As is well known, and was elaborated in I, rigidity is a consequence of the spontaneous breakdown of translational symmetry. In order to describe the onset of rigidity, it is necessary to show explicitly that translational invariance can be spontaneously broken in the system, as the number of cross links exceeds a critical value. In other words, we propose to treat the transition to the solid state in exactly the same way that phase transitions in other systems are treated. This is the purpose of the present paper; a preliminary account of this calculation has already been published.[3]

For simple systems, the transition to the solid state can be achieved by, e.g., lowering the temperature, and the crystalline phase is described as a superposition of density waves. The transition is found to be first order, since there is no reason *a priori* for the absence of terms in the Landau free energy, which are cubic in the density.[5] Liquid and solid phases have different symmetries, and hence it is not possible to pass between them without encountering a transition of some sort. There is no reason for such a transition to be first order, other than that already mentioned; in principle, the transition could be second order. It is this possibility which transpires to be the case in systems of randomly cross-linked macromolecules; it turns out that there is a cubic term in the appropriate Landau free energy, but the restriction that the order parameter be positive ensures that a first-order transition does not occur. A similar situation exists in the Sherrington-Kirkpatrick model of the Ising spin glass.[6]

In systems of randomly cross-linked macromolecules, the transition can occur at fixed temperature as the number of cross links in the system is varied.[7] A prerequisite for a Landau theory is the identification of a suitable order parameter. In simple systems, the knowledge that the transition of interest is continuous, together with considerations of symmetry, allows the Landau theory to be constructed. An example is the Ginzburg-Landau theory of superconductivity,[8] where the microscopic interpretation of the order parameter was given some time after the theory.[9] In the present case, it is indeed possible to anticipate the relevant order parameter, as explained in I; however, the construction of the Landau theory is not straightforward, because there is quenched disorder

present, in the form of cross links. The present paper is concerned with the task of deriving the Landau theory from a microscopic model for randomly cross-linked macromolecules. In the course of the systematic development of the theory, an appropriate order parameter will naturally emerge, in much the same way that the magnetization emerges as an order parameter from a systematic treatment of a magnetic system.[10] In the present case, however, the relationship of the order parameter to the considerations of ergodicity discussed in I is far from obvious, and an adaption of an argument due to Parisi[11] is required to make the connection explicit.

Our procedure for eliminating the polymer degrees of freedom in favor of the order parameter is based on the theory of semidilute polymer solutions.[12] This theory has proved to be a reliable starting point for a renormalization-group treatment of semidilute polymer solutions,[13] which exhibits very good agreement with experiment[14] without any adjustable parameters.

Earlier work on the statistical physics of randomly cross-linked macromolecules has focused not so much on the onset of rigidity, but on the description of the behavior of cross-linked macromolecular solids under large deformations.[15] In this large body of literature, it is implicitly assumed that the system is solid, but the question of how this has arisen is finessed. The assumption of solidness can be traced back to the way in which it is assumed that the mean position of the cross links changes as the system is deformed. In a sense, then, the present work should be considered as complementary to the existing literature. Ultimately, we hope to be able to apply our approach to study the behavior of randomly cross-linked macromolecules under large deformations.

The contents of this paper are as follows. In Sec. II we write down the Hamiltonian for a cross-linked system of monodisperse chains. Quenched disorder is present because each cross link joins two specified monomers on two specified chains, according to a given probability distribution. For a particular choice of the probability distribution, disorder averages can be computed from a Hamiltonian describing n replicas of the system, in the limit that $n \to 0$. This latter Hamiltonian no longer contains random variables, and so the averages can be computed in a relatively straightforward way. We define for future use the disorder-averaged free energy of the system, and the disorder-averaged probability distribution for the symmetrized overlaps defined in I. Section III introduces a generalization of the Hubbard-Stratonovich transformation, which decouples the chains within each replica. We carefully explain the physical significance of the generalized Hubbard-Stratonovich field, and show how it can be used to compute the disorder-averaged probability distribution for the symmetrized overlaps. Then, in section IV, we proceed to integrate out the polymer degrees of freedom in order to derive the Landau free energy for the order parameter. In Sec. V we analyze the form of the Landau free energy, in an approximation which treats the most unstable mode only, and we exhibit the transition to the solid state. Exploiting the similarity between the present Landau free energy and that of the long-range Ising spin glass, we compute the disorder-

averaged probability distribution for the symmetrized overlaps at the transition. From its form, we deduce the way in which ergodicity has been broken at the onset of the solid state.

II. GENERAL FORMULATION

Consider N chains of length L, step length l, in a d-dimensional cube of volume V. Our starting point is the Hamiltonian[12,16]

$$H\{\mathbf{r}_i\} = \frac{d}{2l} \sum_{i=1}^{N} \int_0^L [\partial_s \mathbf{r}_i(s)]^2 ds$$
$$+ \frac{1}{2} \sum_{i,j=1}^{N} \int_0^L \int_0^L v_0[\mathbf{r}_i(s) - \mathbf{r}_j(t)] ds\, dt, \quad (2.1)$$

where $\mathbf{r}_i(s)$ is the position of the ith chain as a function of arc length s, $v_0(\mathbf{r})$ is the two-body potential, and the first term on the right-hand side of Eq. (2.1) represents the Wiener measure.[16] Implicit in the Hamiltonian is the constraint in the double summation, $|s - s'| > l$; this excludes self-interaction of monomers and multiple interactions between monomers on different chains. Let there be M cross links which permanently connect arclength positions $\{s_e, s_e'\}$ on chains $\{i_e, i_e'\}$ respectively, for $e = 1$, ..., M. If the system were to explore all possible microstates consistent with these constraints, then the partition function would be given by

$$Z \propto \int \prod_{i=1}^{N} D\mathbf{r}_i e^{-H} \prod_{e=1}^{M} \delta(\mathbf{r}_{i_e}(s_e) - \mathbf{r}_{i_e'}(s_e')) . \quad (2.2)$$

As explained in I, a system of cross-linked, mutually impenetrable chains cannot explore all of the possible configurations included in Eq. (2.2). The naive computation of statistical-mechanical averages over all the configurations would not account for the inescapable fact that the system has many disjoint sets of topologically equivalent configurations all of which satisfy the constraints. The reasons for this have been described in I. Any pair of equilibrium states with distinct topology cannot be related by a global symmetry operation. It is possible that within each set of topologically equivalent configurations there may exist pairs of equilibrium states which are not related by symmetry.

The method of preparation places the cross links at random throughout the sample and, in practice, we do not know which monomers the cross links will connect. The process of cross linking may be modeled as taking place simultaneously between randomly chosen pairs of monomers in contact. Consequently, the statistical distribution of cross links will reflect the instantaneous correlations of the un-cross-linked system. The probability distribution for the arc-length positions of the cross links is then[17]

$$\mathcal{P}_M(\{i_e, i_e'\}, \{s_e, s_e'\}) \propto \left\langle \prod_{e=1}^{M} \delta(\mathbf{r}_{i_e}(s_e) - \mathbf{r}_{i_e'}(s_e')) \right\rangle , \quad (2.3)$$

where the angular brackets denote averaging with respect to the un-cross-linked system. In the present case, we shall assume for simplicity that the cross links are uni-

formly distributed, and that the number of cross links M may vary about its mean value $\mu_0^2 N /2$ according to the Poisson distribution

$$\mathcal{P}_M = \frac{1}{M!} \left[\frac{\mu_0^2}{2NL^2} \right]^M \exp\left[-\frac{\mu_0^2 N}{2} \right] . \tag{2.4}$$

This is an approximation which neglects the correlations between cross links. The correlation arises because if two chains are cross linked, then they are constrained to be close, thus enhancing the likelihood of further cross linking. We expect that this effect will be small when chains overlap significantly, because within the volume occupied by a given chain, there are monomers from a large number of other chains.[2] Thus the bias introduced by the presence of a cross-linked chain is expected to be small.

This same argument ensures that mean-field theory will be a good approximation when chains overlap significantly, as they do during vulcanization. For strong gelation, on the other hand, corrections to mean-field theory are expected.[2] Furthermore, we shall eventually find that the average number of cross links per chain is close to $\frac{1}{2}$ at the transition to the solid state; with so few cross links in the system near to the transition, the difference between the distributions given by Eqs. (2.3) and (2.4) would not be expected to affect significantly the chain correlation functions.

As usual in problems with quenched disorder, we shall compute the disorder-average of quantities of interest, using the replica method.[17,18−21] Denote the disorder average of any variable O by square brackets $[\cdots]$, where

$$[O] \equiv \sum_{M=0}^{\infty} \sum_{i_1=1}^{N} \cdots \sum_{i_M=1}^{N} \sum_{i_1'=1}^{N} \cdots \sum_{i_M'=1}^{N} \int_0^L \cdots \int_0^L \prod_{e=1}^{M} ds_e \, ds_e' \, O \mathcal{P}_M . \tag{2.5}$$

Then, we find that

$$[Z^n] = \int \prod_{\alpha=1}^{n} \prod_{i=1}^{N} D\mathbf{r}_i^\alpha \exp(-\mathcal{H}) , \tag{2.6}$$

$$\mathcal{H} = \sum_{\alpha=1}^{n} H\{\mathbf{r}_i^\alpha\} - \frac{\mu_0^2}{2NL^2} \sum_{i,j=1}^{N} \int_0^L \int_0^L ds \, dt \prod_{\alpha=1}^{n} \delta(\mathbf{r}_i^\alpha(s) - \mathbf{r}_j^\alpha(t)) , \tag{2.7}$$

where we have ignored an irrelevant constant and used the fact that

$$\prod_{a=1}^{M} \left[\sum_{i_a=1}^{N} \sum_{i_a'=1}^{N} \right] \int_0^L \int_0^L \prod_{e=1}^{M} \prod_{\alpha=1}^{n} \delta(\mathbf{r}_{i_e}^\alpha(s_e) - \mathbf{r}_{i_e'}^\alpha(s_e')) ds_e ds_e' = \left[\sum_{i,j=1}^{N} \int_0^L \int_0^L ds \, ds' \prod_{\alpha=1}^{n} \delta(\mathbf{r}_i^\alpha(s) - \mathbf{r}_j^\alpha(s')) \right]^M . \tag{2.8}$$

It is convenient to introduce a rescaling of the variables,

$$s = \sigma L , \tag{2.9}$$

$$\mathbf{r} = \left[\frac{lL}{d} \right]^{1/2} \mathbf{c} , \tag{2.10}$$

$$v_0(\mathbf{r}) = v(\mathbf{c}) , \tag{2.11}$$

$$\mu^2 = \mu_0^2 \left[\frac{lL}{d} \right]^{-nd/2} . \tag{2.12}$$

In terms of these variables, the Hamiltonian in Eq. (2.6) becomes

$$\mathcal{H} = H_0 + H_I , \tag{2.13}$$

$$H_0 = \frac{1}{2} \sum_{i=1}^{N} \sum_{\alpha=1}^{n} \int_0^1 d\sigma (\partial_\sigma \mathbf{c}_j^\alpha)^2$$

$$+ \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\alpha=1}^{n} \int_0^1 \int_0^1 d\sigma \, d\sigma' v(\mathbf{c}_i^\alpha(\sigma) - \mathbf{c}_j^\alpha(\sigma')) , \tag{2.14}$$

$$H_I = -\frac{\mu^2}{2N} \sum_{i,j=1}^{N} \int_0^1 \int_0^1 d\sigma \, d\sigma' \prod_{\alpha=1}^{n} \delta(\mathbf{c}_i^\alpha(\sigma) - \mathbf{c}_j^\alpha(\sigma')) . \tag{2.15}$$

Note that after averaging over the disorder, we are now left with a pure theory (that is, one without random variables) for a replicated system. The process of averaging over the disorder has introduced an interaction between the replicas—the final term on the right-hand side of Eq. (2.15). The Hamiltonian is invariant under permutations of the replicas and independent translations and rotations of the replicas. The latter symmetry can be spontaneously broken, and leads to the solid phase of the system. The permutation symmetry—normally a discrete symmetry—nevertheless acts like a continuous symmetry in the limit $n \to 0$; it too becomes spontaneously broken at the transition to the solid state. This corresponds to the existence of equilibrium states which are unrelated by global translational and rotational symmetry.

In I we demonstrated how the nature of the equilibrium states can be inferred from correlation functions computed using the replica method, within mean-field theory. Explicitly we compute the disorder-averaged distribution function $[P_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{(m)}(q)]$ for the symmetrized overlaps $q_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{\sigma_1,\ldots,\sigma_m}$ defined by

$$[P_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{(m)}(q)]$$

$$\equiv \left[\sum_{\sigma_1,\ldots,\sigma_m} w^{\sigma_1} \cdots w^{\sigma_m} \delta(q - q_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{\sigma_1,\ldots,\sigma_m}) \right] , \tag{2.16}$$

where

$$q_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{\sigma_1,\ldots,\sigma_m} \equiv \left[\frac{\sum_{R_1,\ldots,R_m} |q_{R_1\mathbf{k}_1,\ldots,R_m\mathbf{k}_m}^{\sigma_1,\ldots,\sigma_m}|^2}{\sum_{R_1,\ldots,R_m} \delta_{R_1\mathbf{k}_1+\cdots+R_m\mathbf{k}_m,0}} \right]^{1/2} , \tag{2.17}$$

$$q_{\mathbf{k}_1,\ldots,\mathbf{k}_m}^{\sigma_1,\ldots,\sigma_m} = \frac{1}{N} \sum_{j=1}^{N} \int_0^1 d\tau \langle e^{-i\mathbf{k}_1\cdot\mathbf{c}_j(\tau)} \rangle^{\sigma_1} \cdots$$
$$\times \langle e^{-i\mathbf{k}_m\cdot\mathbf{c}_j(\tau)} \rangle^{\sigma_m} , \tag{2.18}$$

and

$$w^\sigma \equiv \frac{e^{-F^\sigma}}{\sum_\tau e^{-F^\tau}} . \tag{2.19}$$

The meaning of the symbols is as follows. The weight w^σ is the normalized Boltzmann weight for the equilibrium state σ, computed from the free energy

$$F^\sigma \equiv -\ln \mathrm{Tr}_\sigma e^{-H} , \tag{2.20}$$

where the trace includes only those microstates in the equilibrium state σ. $\{R_i\}$ is a set of cubic rotation matrices, introduced so that the rotation or translation of an equilibrium state leaves the symmetrized overlap invariant.

In the preceding equations, we only consider sets of wave vectors for which the denominator in Eq. (2.17) does not vanish, i.e., there is at least one set of rotations $\{R_i\}$ for which

$$\sum_{i=1}^{m} R_i\mathbf{k}_i = 0 . \tag{2.21}$$

This requirement is related to our notion of *macroscopic translational invariance* in an equilibrium amorphous solid, which is the statement that in any state of equilibrium, there is no distinguished wave vector. Loosely speaking, we expect that a snapshot of a solid with macroscopic translational invariance would be indistinguishable from a snapshot of a liquid, whereas a single snapshot of a crystal would be sufficient to distinguish it from a liquid. On the other hand, a solid with macroscopic translational invariance can be distinguished from a liquid only by taking a subsequent snapshot after a time interval t. As $t \to \infty$, the second snapshot is correlated with the first only in the case of the solid. To be precise, a necessary condition for an equilibrium state σ to possess macroscopic translational invariance is that the self-overlap $q_{\mathbf{k}_1,\ldots,\mathbf{k}_m}^{\sigma,\ldots,\sigma}$ has the form

$$q_{\mathbf{k}_1,\ldots,\mathbf{k}_m}^{\sigma,\ldots,\sigma} = \delta_{\mathbf{k}_1+\cdots+\mathbf{k}_m,0}$$
$$\times q^{\sigma,\ldots,\sigma}(k_1^2,\ldots,k_m^2;\mathbf{k}_1\cdot\mathbf{k}_2,\ldots,\mathbf{k}_{m-1}\cdot\mathbf{k}_m) . \tag{2.22}$$

As discussed in I, the information contained in the symmetrized overlap distributions is sufficient to deter-

mine the nature of the equilibrium states. In particular, the existence of equilibrium amorphous solid states is exhibited through the form of the overlap distributions.

In I, we show that within mean-field theory

$$[P_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{(m)}(q)] = \lim_{n\to 0} \langle \delta(q - Q_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{\alpha_1,\ldots,\alpha_m}) \rangle_n , \tag{2.23}$$

where

$$Q_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{\alpha_1,\ldots,\alpha_m} = \left[\frac{\sum_{R_1,\ldots,R_m} |Q_{R_1\mathbf{k}_1,\ldots,R_m\mathbf{k}_m}^{\alpha_1,\ldots,\alpha_m}|^2}{\sum_{R_1,\ldots,R_m} \delta_{R_1\mathbf{k}_1+\cdots+R_m\mathbf{k}_m,0}} \right]^{1/2} \tag{2.24}$$

and

$$Q_{\mathbf{k}_1,\ldots,\mathbf{k}_m}^{\alpha_1,\ldots,\alpha_m} = \frac{1}{N} \sum_{j=1}^{N} \int_0^1 d\tau \exp\left(-i\sum_{a=1}^{m} \mathbf{k}_a\cdot\mathbf{c}_j^{\alpha_a}(\tau) \right) . \tag{2.25}$$

Here, $Q_{\mathbf{k}_1,\ldots,\mathbf{k}_m}^{\alpha_1,\ldots,\alpha_m}$ is the microscopic overlap between configurations in the n distinct replicas of the system, each of which is subject to *identical* cross-linking constraints. $\langle \cdots \rangle_n$ denotes averaging over all configurations of the replicas, consistent with these constraints. Thus the replica method allows us to compute the desired distribution functions.

III. ELIMINATION OF THE POLYMER DEGREES OF FREEDOM

The systematic derivation of the Landau theory is accomplished by decoupling the interactions between the replicas in H_I using Hubbard-Stratonovich fields. We start with the representation of the distribution

$$[P_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{(m)}(q)] \propto \lim_{n\to 0} \int \prod_{\alpha=1}^{n} \prod_{j=1}^{N} D\mathbf{c}_j^\alpha \delta(q - Q_{\{\mathbf{k}_1,\ldots,\mathbf{k}_m\}}^{\alpha_1,\ldots,\alpha_m})$$
$$\times \exp(-\mathcal{H}) . \tag{3.1}$$

Now we introduce a notation to simplify the presentation. Sets of replicated vectors such as $\{\mathbf{c}_1,\ldots,\mathbf{c}_n\}$ will collectively be denoted $\hat{c}$. Inner products between replicated vectors will be denoted by $\hat{k}\cdot\hat{c}$, where

$$\hat{k}\cdot\hat{c} = \sum_{\alpha=1}^{n} \sum_{\mu=1}^{d} k_\mu^\alpha c_\mu^\alpha . \tag{3.2}$$

The measure in Eq. (3.1) becomes

$$D\hat{c} \equiv \prod_{\alpha=1}^{n} \prod_{j=1}^{N} D\mathbf{c}_j^\alpha . \tag{3.3}$$

To introduce the order parameter, we rewrite H_I as

$$-\frac{\mu^2}{2N} \sum_{j,h=1}^{N} \int_0^1 d\sigma\, d\tau\, \delta(\hat{c}_j(\sigma)-\hat{c}_h(\tau))$$
$$= -\frac{\mu^2}{2NV^n} \sum_{j,h=1}^{N} \int_0^1 d\sigma\, d\tau \sum_{\hat{k}} \exp\{i\hat{k}\cdot[\hat{c}_j(\sigma)-\hat{c}_h(\tau)]\} . \tag{3.4}$$

We separate from the summation over $\hat{k}$ the one term with $\hat{k} = \hat{0}$, which we subsequently drop as an irrelevant constant, and each of the n terms for which all but one wave vector in the set $\{k^1, \ldots, k^n\}$ is zero. We will

$$[P^{(m)}_{\{k_1, \ldots, k_m\}}(q)] \propto \lim_{n \to 0} \int D\hat{c}\, \delta(q - Q^{\alpha_1, \ldots, \alpha_m}_{\{k_1, \ldots, k_m\}})\,)\exp\left[-\tilde{H}_0 + \frac{\mu^2}{2NV^n} \overline{\sum_{\hat{k}}} \left| \sum_{j=1}^{N} \int_0^1 d\sigma \exp[-i\hat{k}\cdot\hat{c}_j(\sigma)] \right|^2 \right], \qquad (3.5)$$

where

$$\tilde{H}_0 = \sum_{\alpha=1}^{n} \tilde{H}\{c^\alpha\}\,, \qquad (3.6)$$

$$\tilde{H}\{c\} = \frac{1}{2} \sum_{j=1}^{N} \int_0^1 d\sigma [\partial_\sigma c_j(\sigma)]^2$$
$$+ \frac{1}{2} \sum_{j,h=1}^{N} \int_0^1 d\sigma\, d\tau\, \tilde{U}(c_j(\sigma) - c_h(\tau))\,, \qquad (3.7)$$

$$\tilde{U}(x) = U(x) - \frac{\mu^2 V}{N}\delta(x)\,. \qquad (3.8)$$

In the sum over $\hat{k}$ those terms for which $\hat{k}$ is of the form $(0, 0, \ldots, k, 0, \ldots)$ do not couple the replicas, and are simply absorbed as a contribution to a new interaction potential $\tilde{U}(x)$. It might appear that the δ-function subtraction can have no effect for a real potential. However, for a real potential, the representation of the cross-linking constraint as a product of δ functions is not adequate, due to the thickness of the chains, and must be replaced

by the necessary generalization. For the Edwards Hamiltonian,[12] where the potential $U(x)$ is modeled by $\lambda^2\delta(x)$, the representation in Eq. (2.2) is appropriate. The Hamiltonian $\tilde{H}$ describes a fictitious un-cross-linked polymer system with a pair potential which has been renormalized by the presence of cross links. As long as this fictitious system would be a homogeneous fluid, then the corresponding cross-linked system can only be unstable towards the formation of an equilibrium amorphous solid. If the fictitious fluid becomes unstable and loses homogeneity then the real cross-linked system can collapse.[22] Although interesting, we shall not discuss this phenomenon further.

The quadratic form of the term which couples the replicas can be eliminated by introducing complex variables $\Omega_{\hat{k}}$ for every term in the summation over $\hat{k}$. Making repeated use of the integral

$$\exp\tfrac{1}{2}|w|^2 = \int \frac{d(\mathrm{Re}z)d(\mathrm{Im}z)}{2\pi}\exp(-\tfrac{1}{2}|z|^2 + \mathrm{Re}\,\overline{w}z)\,, \qquad (3.9)$$

where $\overline{w}$ is the complex conjugate of w, we obtain

$$[P^{(m)}_{\{k_1, \ldots, k_m\}}(q)] \propto \lim_{n \to 0} \int \prod_{\alpha=1}^{n} \prod_{j=1}^{N} Dc_j^\alpha D\Omega\, \delta(q - Q^{\alpha_1, \ldots, \alpha_m}_{\{k_1, \ldots, k_m\}})$$

$$\times \exp\left[-\frac{N\mu^2}{2V^n} \overline{\sum_{\hat{k}}} |\Omega_{\hat{k}}|^2 - \tilde{H}_0 + \frac{\mu^2 N}{V^n}\mathrm{Re} \overline{\sum_{\hat{k}}} \Omega_{\hat{k}} \frac{1}{N} \sum_{j=1}^{N} \int_0^1 d\sigma \exp[i\hat{k}\cdot\hat{c}_j(\sigma)] \right], \qquad (3.10)$$

where the measure $D\Omega$ is given by

$$D\Omega = \overline{\prod_{\hat{k}}} d(\mathrm{Re}\Omega_{\hat{k}})d(\mathrm{Im}\Omega_{\hat{k}})\,. \qquad (3.11)$$

The field $\Omega_{\hat{k}}$ is related in a simple way to the order parameter of the system. To expose this connection we introduce a convenient notation. When $\hat{k}$ comprises exactly g nonzero wave vectors we write

$$\Omega_{\hat{k}} = \Omega^{\alpha_1, \ldots, \alpha_g}_{k_{\alpha_1}, \ldots, k_{\alpha_g}}\,, \qquad (3.12)$$

where the notation k_{α_1} refers to the k vector in $\hat{k}$ associated with the α_1th replica. In other words, this notation suppresses the wavevectors in $\hat{k}$ with zero magnitude, and the replica indices on $\Omega^{\alpha_1, \ldots, \alpha_g}_{k_{\alpha_1}, \ldots, k_{\alpha_g}}$ indicate with which replicas the nonzero wave vectors are associated. We will refer to terms with g nonzero wave vectors as

residing in the g-replica sector. As an example consider a term from the two-replica sector of the summation over $\hat{k}$ in equation (3.10) for which

$$\hat{k} = (0, h, 0, l, 0, 0, \ldots)\,, \qquad (3.13)$$

with $h, l \neq 0$ being the only non-zero components of $\hat{k}$. The variable $\Omega_{\hat{k}}$ for this value of $\hat{k}$ is written as Ω^{24}_{hl}. Of course, this construction only introduces

$$\Omega^{\alpha_1, \ldots, \alpha_g}_{k_{\alpha_1}, \ldots, k_{\alpha_g}}$$

for which $1 \leq \alpha_1 < \alpha_2 < \cdots < \alpha_g \leq n$. This ordering is implicit whenever we perform summations or products over α. Having defined this notation, let us mention some of its useful properties. First, the quadratic form in Eq. (3.10) becomes

$$\overline{\sum_{\hat{k}}} |\Omega_{\hat{k}}|^2 = \sum_{g=2}^{n} \sum_{\alpha} \sum_{k_1,\ldots,k_g \neq 0} |\Omega_{k_1,\ldots,k_g}^{\alpha_1,\ldots,\alpha_g}|^2 . \qquad (3.14)$$

The first sum in the preceding equation runs from 2 to n because the zero- and one-replica terms are absent from the summation, as discussed below Eq. (3.4). Second, the measure for integration over Ω becomes

$$D\Omega = \prod_{g=1}^{n} \prod_{\alpha} \prod_{k_1,\ldots,k_g \neq 0} d(\text{Re}\Omega_{k_1,\ldots,k_g}^{\alpha_1,\ldots,\alpha_g}) d(\text{Im}\Omega_{k_1,\ldots,k_g}^{\alpha_1,\ldots,\alpha_g}) .$$

$$(3.15)$$

Third, the Fourier transform in replicated real space is defined by

$$\tilde{\Omega}(\hat{x}) \equiv \frac{1}{V^n} \overline{\sum_{\hat{k}}} \Omega_{\hat{k}} e^{i\hat{k}\cdot\hat{x}}$$

$$= \frac{1}{V^n} \sum_{g=2}^{n} \sum_{\alpha} \sum_{k_1,\ldots,k_g \neq 0} \Omega_{k_1,\ldots,k_g}^{\alpha_1,\ldots,\alpha_g}$$

$$\times \exp\left[i \sum_{a=1}^{g} k_a \cdot x^{\alpha_a} \right]$$

$$= \sum_{g=2}^{n} \frac{1}{V^{n-g}} \sum_{\alpha} \Omega^{\alpha_1,\ldots,\alpha_g}(x^{\alpha_1},\ldots,x^{\alpha_g}) . \qquad (3.16)$$

Fourth, there are the following useful orthogonality properties:

$$\int d^{nd}\hat{x}\, \tilde{\Omega}(\hat{x}) = 0 , \qquad (3.17)$$

$$\int d^{nd}\hat{x}\, \tilde{\Omega}(\hat{x}) \sum_{\alpha} f^{\alpha}(x^{\alpha}) = 0 , \qquad (3.18)$$

for any functions $\{f^{\alpha}\}$.

This decomposition into sectors makes for a particularly simple interpretation of the order parameter. We will now show that $[P_{\{k_1,\ldots,k_m\}}^{(m)}(q)]$ can be exactly expressed in terms of Ω. In terms of the new variables, the last term in the exponent in Eq. (3.10) becomes

$$\text{Re} \sum_{g=2}^{n} \sum_{\alpha} \sum_{k_1,\ldots,k_g \neq 0} \Omega_{k_1,\ldots,k_g}^{\alpha_1,\ldots,\alpha_g} \overline{Q}_{k_1,\ldots,k_g}^{\alpha_1,\ldots,\alpha_g} = \text{Re} \overline{\sum_{\hat{k}}} \Omega_{\hat{k}} \overline{Q}_{\hat{k}} .$$

$$(3.19)$$

We can obtain the Q dependence in the δ function of Eq. (3.10) by differentiating with respect to Ω:

$$[P_{\{k_1,\ldots,k_m\}}^{(m)}(q)] \propto \lim_{n\to 0} \int D\Omega \exp\left[-\frac{N\mu^2}{2V^n} \overline{\sum_{\hat{k}}} |\Omega_{\hat{k}}|^2 \right]$$

$$\times \delta\left[q - \frac{V^n}{\mu^2} \frac{\partial}{\partial \overline{\Omega}_{\{k_1,\ldots,k_m\}}^{\alpha_1,\ldots,\alpha_m}} \right]$$

$$\times e^{NW\{\Omega\}} , \qquad (3.20)$$

where

$$\frac{\partial}{\partial \overline{z}} \equiv \frac{\partial}{\partial(\text{Re}z)} + i\frac{\partial}{\partial(\text{Im}z)} \qquad (3.21)$$

and

$$e^{NW\{\Omega\}} \equiv \int D\hat{c}\, \exp\left[-\tilde{H}_0 + (\mu^2 N/V^n)\text{Re} \overline{\sum_{\hat{k}}} \Omega_{\hat{k}} \overline{Q}_{\hat{k}} \right] \Big/ \int D\hat{c}\, e^{-\tilde{H}_0} \equiv \left\langle \exp\left[(\mu^2 N/V^n)\text{Re} \overline{\sum_{\hat{k}}} \Omega_{\hat{k}} \overline{Q}_{\hat{k}} \right] \right\rangle_n . \qquad (3.22)$$

The disorder-averaged free energy per chain is given by

$$-f = \lim_{n\to 0} \frac{1}{Nn}([Z^n]-1) , \qquad (3.23)$$

$$[Z^n] \propto \lim_{n\to 0} \int D\Omega \exp\left[-\frac{N\mu^2}{2V^n} \overline{\sum_{\hat{k}}} |\Omega_{\hat{k}}|^2 + NW\{\Omega\} \right] .$$

$$(3.24)$$

In the thermodynamic limit $N\to\infty$, the saddle-point approximation becomes exact, and we obtain

$$f\{\Omega\} = \lim_{n\to 0} \frac{1}{n} \left[\frac{\mu^2}{2V^n} \overline{\sum_{\hat{k}}} |\Omega_{\hat{k}}|^2 - W\{\Omega\} \right] , \qquad (3.25)$$

evaluated at the stationary value of Ω with positive semidefinite Hessian. The expectation value $\langle \cdots \rangle_n$ is taken with respect to the Hamiltonian of Eq. (3.6).

IV. LANDAU THEORY OF THE TRANSITION

The liquid phase corresponds to $\Omega = 0$. We are unable to compute $W\{\Omega\}$ for arbitrary Ω, but we can exhibit the instability of the liquid phase by expanding $W\{\Omega\}$ about $\Omega = 0$. To fourth order we obtain

$$f\{\Omega\} = \lim_{n\to 0} \left[\frac{\mu^2}{2V^n} \overline{\sum_{\hat{k}}} a_{\hat{k}} |\Omega_{\hat{k}}|^2 - \frac{1}{N} \left[\frac{\mu^2}{V^n}\right]^3 \overline{\sum_{\hat{k},\hat{l},\hat{m}}} \Omega_{\hat{k}} \Omega_{\hat{l}} \Omega_{\hat{m}} \Gamma_{\hat{k}\hat{l}}^{(3)} V^n \delta_{\hat{k}+\hat{l}+\hat{m},\hat{0}} - \frac{1}{N} \left[\frac{\mu^2}{V^n}\right]^4 \overline{\sum_{\hat{k},\hat{l},\hat{m},\hat{n}}} \Omega_{\hat{k}} \Omega_{\hat{l}} \Omega_{\hat{m}} \Omega_{\hat{n}} \Gamma_{\hat{k}\hat{l}\hat{m}}^{(4)} V^n \right.$$

$$\left. \times \delta_{\hat{k}+\hat{l}+\hat{m}+\hat{n},\hat{0}} \right] , \qquad (4.1)$$

$$\Gamma_{\hat{k}_1,\ldots,\hat{k}_{r-1}}^{(r)} V^n \delta_{\sum_{t=1}^{r} \hat{k}_t, \hat{0}} = \frac{N^r}{r!} \langle \overline{Q}_{\hat{k}_1} \cdots \overline{Q}_{\hat{k}_r} \rangle_n , \qquad (4.2)$$

$$a_{\hat{k}}(\mu^2) = 1 - \frac{2\mu^2}{N} \Gamma_{\hat{k}}^{(2)} . \qquad (4.3)$$

We have retained only those terms which contribute in the $n \to 0$ limit, and the linear term vanishes due to the translational invariance of the liquid phase.

If, for a given μ, any $a_{\hat{k}}$ is negative, then the liquid phase is unstable and the system will form an equilibrium amorphous solid. If, and when, this happens is determined by the correlations of the fictitious fluid, introduced earlier. Suppose the number of cross links, $N_x = \mu^2 N / 2$, is increased from zero. The instability will first set in when μ^2 exceeds $N / 2\Gamma_{\text{max}}^{(2)}$, where $\Gamma_{\text{max}}^{(2)}$ is the maximum value of $\Gamma_{\hat{k}}^{(2)}$ over all values of $\hat{k}$.

The important feature of the fictitious fluid is that the interactions between the chains can stabilize the homogeneous phase if the interactions between chains in the real system are sufficiently strong. Provided the homogeneous phase is stable, the correlation functions only determine the coefficients $\Gamma^{(r)}$ which themselves determine the coefficients in the Landau free energy of Eq. (4.1). We do not expect the precise numerical values to be important, and it may even be reasonable to approximate the correlation functions $\Gamma^{(r)}$ by the values they would have for noninteracting fictitious chains. For noninteracting chains and $n \geq 1$, we can use the result that $\hat{k}^2 \geq 8\pi^2 / V^{2/d}$ and $\Gamma_{\hat{k}}^{(2)}$ is a monotonic decreasing function of $\hat{k}^2$. Then for large V

$$\Gamma_{\text{max}}^{(2)} = \frac{N}{2V^n} \cdot \qquad (4.4)$$

Taking the $n \to 0$ limit, we find that the fluid phase is unstable when N_x exceeds $N / 2$.

The location and value of the maximum of $\Gamma_{\hat{k}}^{(2)}$ is straightforward when $n \geq 1$, but becomes a delicate issue when $n \to 0$. The maximum value of $\Gamma_{\hat{k}}^{(2)}$ is achieved at the smallest $\hat{k}^2$, which is no longer necessarily zero in the limit $n \to 0$. For example, in the noninteracting fictitious fluid approximation, $\Gamma_{\hat{k}}^{(2)}$ increases without bound for negative $\hat{k}^2$. We have not been able to resolve this issue, and in the remainder of this paper, we shall assume that $\Gamma^{(2)}$ is maximal near the origin; thus the instability sets in via the longest allowed wavelengths at finite μ^2. If this is the case, we expect that all coefficients in the Landau theory can be related to thermodynamic quantities by using the appropriate sum rules.

V. ONSET OF RIGIDITY IN THE TWO-REPLICA SECTOR

In this section we discuss a severe truncation of the complete problem: the two-replica sector. In fact, although this sector is far simpler than the complete problem, it is still too difficult. Here we shall treat the case of the onset of rigidity, examining only the very-longest-wavelength modes. We retain only modes in the two-replica sector, each with wavevectors of the minimum non-zero magnitude. We assume also that the saddle points are translationally invariant, and we choose the form of Ω to be $\Omega_{\mathbf{k}_1, \ldots, \mathbf{k}_g}^{\alpha_1, \ldots, \alpha_g} = 0$ unless $g = 2$, and $\mathbf{k}_1$ and $\mathbf{k}_2$ have the smallest nonzero magnitude $2\pi / V^{1/d}$. In this case,

$$\Omega_{\mathbf{k}l}^{\alpha\beta} = \omega^{\alpha\beta} \delta_{\mathbf{k}+l,0} \cdot \qquad (5.1)$$

Inserting this ansatz into the free energy, Eq. (4.1), we obtain[23]

$$f\{\omega\} = \lim_{n \to 0} \left[-\frac{d\mu^4}{n} \left[\gamma^{(2)} - \frac{1}{2\mu^2} \right] \text{Tr}(\omega^2) \right.$$

$$-\frac{2d\mu^6}{n} \gamma^{(3)} \text{Tr}(\omega^3) - \frac{6d\mu^8}{n} \gamma^{(4)} \text{Tr}(\omega^4)$$

$$+\frac{12d\mu^8}{n} \gamma^{(4)} \sum_{\alpha,\beta,\gamma} (\omega^{\alpha\beta})^2 (\omega^{\alpha\gamma})^2$$

$$\left. -\frac{3d\mu^8}{n} \gamma^{(4)} \sum_{\alpha,\beta} (\omega^{\alpha\beta})^4 \right], \qquad (5.2)$$

where the coefficients depend on the long-wavelength limits of the correlation functions,

$$\gamma^{(r)} \equiv \lim_{\mathbf{k}_1, \ldots, \mathbf{k}_{r-1} \to 0} \frac{\Gamma_{\mathbf{k}_1, \ldots, \mathbf{k}_{r-1}}^{(r)}}{N} \cdot \qquad (5.3)$$

The result obtained for $f\{\omega\}$ has the same form as that of the Sherrington-Kirkpatrick model, even up to the signs of the terms. This is crucial because it is the sign of the coefficient of $\sum_{\alpha\beta}(\omega^{\alpha\beta})^4$ which is responsible for the breaking of replica symmetry.

Writing $\epsilon \equiv 2\gamma^{(2)} - (\mu^2)^{-1}$, it follows that for $\epsilon < 0$,

$$P_{\{\mathbf{k},l\}}^{(2)}(q) = \delta(q) \qquad (5.4)$$

and the system is a fluid. For $\epsilon > 0$, we can use Parisi's solution[11] to obtain

$$[P_{\{\mathbf{k},l\}}^{(2)}(q)] = \frac{6\mu^2 \gamma^{(4)}}{\gamma^{(3)}} \theta \left[\frac{\epsilon}{12\mu^6 \gamma^{(3)}} - q \right]$$

$$+ \left[1 - \frac{\gamma^{(4)} \epsilon}{2\mu^4 (\gamma^{(3)})^2} \right] \delta \left[q - \frac{\epsilon}{12\mu^6 \gamma^{(3)}} \right] \qquad (5.5)$$

and, hence, the system forms an equilibrium amorphous solid. This is a good indication that the complete calculation would exhibit the solid phase with broken replica symmetry. A full treatment of the problem, without truncating to the longest-wavelength modes, and including all replica sectors is required.

VI. CONCLUSIONS

In I we showed that the statistical mechanics of randomly cross-linked macromolecules, taking into account both the topology of the network and the disorder of the cross linked, can be described by the probability distributions for the overlaps. In the present paper, we have attempted to evaluate these distributions using the replica method. We have demonstrated the instability of the cross-linked fluid of randomly cross-linked macromolecules to the formation of an equilibrium amorphous solid. Furthermore, we have found indications that the Landau theory has broken replica symmetry, which is consistent with the theory of I; this leads us to be optimistic about the applicability of the replica theory.

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