

Universality and its origins at the amorphous solidification transition

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(Received 25 July 1997)

Systems undergoing an equilibrium phase transition from a liquid state to an amorphous solid state exhibit certain universal characteristics. Chief among these are the fraction of particles that are randomly localized and the scaling functions that describe the order parameter and (equivalently) the statistical distribution of localization lengths for these localized particles. The purpose of this paper is to discuss the origins and consequences of this universality, and in doing so, three themes are explored. First, a replica-Landau-type approach is formulated for the universality class of systems that are composed of extended objects connected by permanent random constraints and undergo amorphous solidification at a critical density of constraints. This formulation generalizes the cases of randomly cross-linked and end-linked macromolecular systems, discussed previously. The universal replica free energy is constructed, in terms of the replica order parameter appropriate to amorphous solidification, the value of the order parameter is obtained in the liquid and amorphous solid states, and the chief universal characteristics are determined. Second, the theory is reformulated in terms of the distribution of local static density fluctuations rather than the replica order parameter. It is shown that a suitable free energy can be constructed, depending on the distribution of static density fluctuations, and that this formulation yields precisely the same conclusions as the replica approach. Third, the universal predictions of the theory are compared with the results of extensive numerical simulations of randomly cross-linked macromolecular systems, due to Barsky and Plischke, and excellent agreement is found. [S0163-1829(98)04102-2]

I. INTRODUCTION

During the last decade there has been an ongoing effort to obtain an ever more detailed understanding of the behavior of randomly cross-linked macromolecular systems near the vulcanization transition.¹⁻⁴ This effort has been built from two ingredients: (i) the Deam-Edwards formulation of the statistical mechanics of polymer networks;⁵ and (ii) concepts and techniques employed in the study of spin glasses.⁶ As a result, a detailed mean-field theory for the vulcanization transition—an example of an amorphous solidification transition—has emerged, which makes the following predictions: (i) For densities of cross links smaller than a certain critical value (on the order of one cross-link per macromolecule) the system exhibits a liquid state in which all particles (in the context of macromolecules, monomers) are delocalized. (ii) At the critical cross-link density there is a continuous thermodynamic phase transition to an amorphous solid state, this state being characterized by the emergence of random static density fluctuations. (iii) In this state, a nonzero fraction of the particles have become localized around random positions and with random localization lengths (i.e., rms, displacements). (iv) The fraction of localized particles grows linearly with the excess cross-link density, as does the characteristic inverse square localization length. (v) When scaled by their mean value, the statistical distribution of localization lengths is universal for all near-critical cross-link densities, the form of this scaled distribution being uniquely determined by a certain integrodifferential equation. For a detailed review of these results, see Ref. 4; for an informal discussion, see Ref. 7.

In the course of the effort to understand the vulcanization transition for randomly cross-linked macromolecular systems, it has become clear that one can also employ similar approaches to study randomly *end-linked* macromolecular systems,⁸ and also randomly cross-linked *manifolds* (i.e., higher dimensional objects);⁹ in each case, a specific model has been studied. For example, in the original case of randomly cross-linked macromolecular systems, the macromolecules were modeled as flexible, with a short-ranged excluded-volume interaction, and the cross links were imposed at random arc-length locations. On the other hand, in the case of *end-linked* systems, although the excluded-volume interaction remained the same, the macromolecules were now modeled as either flexible or stiff, and the random linking was restricted to the ends of the macromolecules. Despite the differences between the unlinked systems and the styles of linking, in all cases identical critical behavior has been obtained in mean-field theory, right down to the precise form of the statistical distribution of scaled localization lengths.

Perhaps even more strikingly, in extensive numerical simulations of randomly cross-linked macromolecular systems, Barsky and Plischke^{10,11} have employed an off-lattice model of macromolecules interacting via a Lennard-Jones potential. Yet again, an essentially identical picture has emerged for the transition to and properties of the amorphous solid state, despite the substantial differences between physical ingredients incorporated in the simulation and in the analytical theory.

In light of these observations, it is reasonable to ask whether one can find a common theoretical formulation of

the amorphous solidification transition (of which the vulcanization transition is a prime example) that brings to the fore the emergent collective properties of all these systems that are model independent, and therefore provide useful predictions for a broad class of experimentally realizable systems. The purpose of this paper is to explain how this can be done. In fact, we approach the issue in two distinct (but related) ways, in terms of a replica order parameter and in terms of the distribution of random static density fluctuations, either of which can be invoked to characterize the emergent amorphous solid state.

The outline of this paper is as follows. In Sec. II we construct the universal replica Landau free energy of the amorphous solidification transition. In doing this, we review the replica order parameter for the amorphous solid state and discuss the constraints imposed on the replica Landau free energy by (a) symmetry considerations, (b) the smallness of the fraction of particles that are localized near the transition, and (c) the weakness of the localization near the transition. In Sec. III we invoke a physical hypothesis to solve the stationarity condition for the replica order parameter, thereby obtaining a mean-field theory of the transition. We exhibit the universal properties of this solution and, in particular, the scaling behavior of certain central physical quantities. In Sec. IV we describe an alternative approach to the amorphous solidification transition, in which we construct and analyze the Landau free energy expressed in terms of the distribution of static density fluctuations. Although we shall invoke the replica approach in the construction of this Landau free energy, its ultimate form does not refer to replicas. As we show, however, the physical content of this Landau theory is identical to that of the replica Landau theory addressed in Secs. II and III. In Sec. V we exhibit the predicted universality by examining the results of extensive numerical simulations of randomly cross-linked macromolecular networks, due to Barsky and Plischke. In Sec. VI we give some concluding remarks.

II. UNIVERSAL REPLICA FREE ENERGY FOR THE AMORPHOUS SOLIDIFICATION TRANSITION

We are concerned, then, with systems of extended objects, such as macromolecules, that undergo a transition to a state characterized by the presence of random static fluctuations in the particle density when subjected to a sufficient density of permanent random constraints (the character and statistics of which constraints preserve translational and rotational invariance). In such states, translational and rotational symmetry are spontaneously broken, but in a way that is hidden at the macroscopic level. We focus on the long-wavelength physics in the vicinity of this transition.

In the spirit of the standard Landau approach, we envisage that the replica technique has been invoked to incorporate the consequences of the permanent random constraints, and propose a phenomenological mean-field replica free energy, the $n \rightarrow 0$ limit of which gives the disorder-averaged free energy, in the form of a power series in the replica order parameter. We invoke symmetry arguments, along with the recognition that near to the transition the fraction of particles that are localized is small and their localization is weak. The control parameter ϵ is proportional to the amount by which the con-

straint density exceeds its value at the transition. As we shall see, the stationarity condition for this general, symmetry-inspired Landau free energy is satisfied by precisely the order-parameter hypothesis that exactly solves the stationarity conditions derived from semimicroscopic models of cross-linked and end-linked macromolecules. From the properties of this solution we recover the primary features of the liquid-amorphous solid transition.

In a system characterized by static random density fluctuations, one might naïvely be inclined to use the particle density as the order parameter. However, the disorder-averaged particle density cannot detect the transition between the liquid and the amorphous solid states, because it is uniform (and has the same value) in both states: a subtler order parameter is needed. As shown earlier, for the specific cases of randomly cross-linked^{1,3,4} and end-linked⁸ macromolecular systems, the appropriate order parameter is instead:

$$\Omega_{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g} \equiv \left[\frac{1}{N} \sum_{i=1}^N \langle e^{i\mathbf{k}^1 \cdot \mathbf{c}_i} \rangle_{\chi} \langle e^{i\mathbf{k}^2 \cdot \mathbf{c}_i} \rangle_{\chi} \dots \langle e^{i\mathbf{k}^g \cdot \mathbf{c}_i} \rangle_{\chi} \right], \quad (1)$$

where N is the total number of particles, \mathbf{c}_i (with $i = 1, \dots, N$) is the position of particle i , the wave vectors $\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g$ are arbitrary, $\langle \dots \rangle_{\chi}$ denotes a thermal average for a particular realization χ of the disorder, and $[\dots]$ represents averaging over the disorder.

We make the Deam-Edwards assumption⁵ that the statistics of the disorder is determined by the instantaneous correlations of the unconstrained system. (It is as if one took a snapshot of the system and, with some nonzero probability, added constraints only at those locations where two particles are in near contact.) This assumption leads to the need to work with the $n \rightarrow 0$ limit of systems of $n + 1$, as opposed to n , replicas. The additional replica, labeled by $\alpha = 0$, represents the degrees of freedom of the original system before adding the constraints, or, equivalently, describes the constraint distribution.

We assume, for the most part, that the free energy is invariant under the group S_{n+1} of permutations of the $n + 1$ replicas. In this replica formalism, the replica order parameter turns out to be

$$\Omega_{\hat{k}} \equiv \left\langle \frac{1}{N} \sum_{i=1}^N \exp(i\hat{k} \cdot \hat{c}_i) \right\rangle_{n+1}^P. \quad (2)$$

Here, hatted vectors denote replicated collections of vectors, viz., $\hat{v} \equiv \{\mathbf{v}^0, \mathbf{v}^1, \dots, \mathbf{v}^n\}$, their scalar product being $\hat{v} \cdot \hat{w} \equiv \sum_{\alpha=0}^n \mathbf{v}^{\alpha} \cdot \mathbf{w}^{\alpha}$, and $\langle \dots \rangle_{n+1}^P$ denotes an average for an effective pure (i.e., disorder-free) system of $n + 1$ coupled replicas of the original system. We use the terms *one-replica sector* and *higher-replica sector* to refer to replicated vectors with, respectively, exactly one and more than one replica α for which the corresponding vector \mathbf{k}^{α} is nonzero. In particular, the order parameter in the one-replica sector reduces to the disorder-averaged mean particle density, and plays only a minor role in what follows. The appearance of $n + 1$ replicas in the order parameter allows one to probe the correlations between the density fluctuations in the constrained system and the density fluctuations in the unconstrained one.

We first study the transformation properties of the order parameter under translations and rotations, and then make use of the resulting information to determine the possible terms appearing in the replica free energy. Under independent translations of all the replicas, i.e., $\mathbf{c}_i^\alpha \rightarrow \mathbf{c}_i^\alpha + \mathbf{a}^\alpha$, the replica order parameter, Eq. (2), transforms as

$$\Omega_{\hat{k}} \rightarrow \Omega'_{\hat{k}} = e^{i \sum_{\alpha=0}^n \mathbf{k}^\alpha \cdot \mathbf{a}^\alpha} \Omega_{\hat{k}}. \quad (3)$$

Under independent rotations of the replicas, defined by $\hat{R} \hat{v} \equiv \{R^0 \mathbf{v}^0, \dots, R^n \mathbf{v}^n\}$ and $\mathbf{c}_i^\alpha \rightarrow R^\alpha \mathbf{c}_i^\alpha$, the order parameter transforms as

$$\Omega_{\hat{k}} \rightarrow \Omega'_{\hat{k}} = \Omega_{\hat{R}^{-1} \hat{k}}. \quad (4)$$

As discussed in detail in Ref. 4, because we are concerned with the transition between liquid and amorphous solid states, both of which have uniform macroscopic density, the one-replica sector order parameter is zero on both sides of the transition. This means that the sought free energy can be expressed in terms of contributions referring to the higher-replica sector order parameter, alone.

We express the free energy as an expansion in (integral) powers of the replica order parameter $\Omega_{\hat{k}}$, retaining the two lowest possible powers of $\Omega_{\hat{k}}$, which in this case are the square and the cube. We consider the case in which no external potential couples to the order parameter. Hence, there is no term linear in the order parameter. We make explicit use of translational symmetry, Eq. (3), and thus obtain the following expression for the replica free energy (per particle per space dimension) $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$:¹²

$$\begin{aligned} nd\mathcal{F}_n(\{\Omega_{\hat{k}}\}) &= \sum_{\hat{k}} \overline{g_2(\hat{k})} |\Omega_{\hat{k}}|^2 \\ &- \sum_{\hat{k}_1, \hat{k}_2, \hat{k}_3} \overline{g_3(\hat{k}_1, \hat{k}_2, \hat{k}_3)} \\ &\times \Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{\hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}. \end{aligned} \quad (5)$$

Here, the symbol $\overline{\Sigma}$ denotes a sum over replicated vectors \hat{k} lying in the higher-replica sector, and we have made explicit the fact that the right-hand side is linear in n (in the $n \rightarrow 0$ limit) by factoring n on the left-hand side. In a microscopic approach, the functions $g_2(\hat{k})$ and $g_3(\hat{k}_1, \hat{k}_2, \hat{k}_3)$ would be obtained in terms of the control parameter ϵ , together with density correlators of an uncross-linked liquid having interactions renormalized by the cross linking. Here, however, we will ignore the microscopic origins of g_2 and g_3 , and instead use symmetry considerations and a long-wavelength expansion to determine only their general forms. In the saddle-point approximation, then, the disorder-averaged free energy f (per particle and space dimension) is given by⁶

$$f = \lim_{n \rightarrow 0} \min_{\{\Omega_{\hat{k}}\}} \mathcal{F}_n(\{\Omega_{\hat{k}}\}). \quad (6)$$

Bearing in mind the physical notion that near the transition any localization should occur only on long length scales, we examine the long-wavelength limit by also performing a low-order gradient expansion. In the term quadratic in the order parameter we keep only the leading and next-to-

leading order terms in \hat{k} ; in the cubic term in the order parameter we keep only the leading term in \hat{k} . Thus, the function g_3 in Eq. (5) is replaced by a constant and the function g_2 is expanded to quadratic order in \hat{k} . By analyticity and rotational invariance, g_2 can only depend on $\{\mathbf{k}^0, \dots, \mathbf{k}^n\}$ via $\{|\mathbf{k}^0|^2, \dots, |\mathbf{k}^n|^2\}$, and, in particular, terms linear in \hat{k} are excluded. In addition, by the permutation symmetry among the replicas, each term $|\mathbf{k}^\alpha|^2$ must enter the expression for g_2 with a common prefactor, so that the dependence is in fact on \hat{k}^2 . Thus, the replica free energy for long-wavelength density fluctuations has the general form:

$$\begin{aligned} nd\mathcal{F}_n(\{\Omega_{\hat{k}}\}) &= \sum_{\hat{k}} \overline{\left(-a\epsilon + \frac{b}{2} |\hat{k}|^2 \right)} |\Omega_{\hat{k}}|^2 \\ &- c \sum_{\hat{k}_1, \hat{k}_2, \hat{k}_3} \overline{\Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{\hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}}. \end{aligned} \quad (7)$$

To streamline the presentation, we take advantage of the freedom to rescale \mathcal{F}_n , ϵ , and \hat{k} , thus setting to unity the parameters a , b , and c . Thus, the free energy becomes

$$\begin{aligned} nd\mathcal{F}_n(\{\Omega_{\hat{k}}\}) &= \sum_{\hat{k}} \overline{\left(-\epsilon + \frac{|\hat{k}|^2}{2} \right)} |\Omega_{\hat{k}}|^2 \\ &- \sum_{\hat{k}_1, \hat{k}_2, \hat{k}_3} \overline{\Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{\hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}}. \end{aligned} \quad (8)$$

By taking the first variation with respect to $\Omega_{-\hat{k}}$ we obtain the stationarity condition for the replica order parameter:

$$0 = nd \frac{\delta \mathcal{F}_n}{\delta \Omega_{-\hat{k}}} = 2 \left(-\epsilon + \frac{|\hat{k}|^2}{2} \right) \Omega_{\hat{k}} - 3 \sum_{\hat{k}_1, \hat{k}_2} \overline{\Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \delta_{\hat{k}_1 + \hat{k}_2, \hat{k}}}. \quad (9)$$

This self-consistency condition applies for all values of \hat{k} lying in the higher-replica sector.

III. UNIVERSAL PROPERTIES OF THE ORDER PARAMETER IN THE AMORPHOUS SOLID STATE

Generalizing what was done for cross-linked and end-linked macromolecular systems, we hypothesize that the particles have a probability q of being localized (also called the ‘‘gel fraction’’ in the context of vulcanization) and $1 - q$ of being delocalized, and that the localized particles are characterized by a probability distribution $2\xi^{-3} p(\xi^{-2})$ for their localization lengths ξ . Such a characterization weaves in the physical notion that amorphous systems should show a spectrum of possibilities for the behavior of their constituents, and adopts the perspective that it is this spectrum that one should aim to calculate. This hypothesis translates into the following expression for the replica order parameter:^{3,4}

$$\Omega_{\hat{k}} = (1 - q) \delta_{\hat{k}, \hat{0}} + q \delta_{\hat{k}, \hat{0}}^{(d)} \int_0^\infty d\tau p(\tau) e^{-\hat{k}^2/2\tau}, \quad (10)$$

where we have used the notation $\widetilde{\mathbf{k}} \equiv \sum_{\alpha=0}^n \mathbf{k}^\alpha$. The first term on the right-hand side term represents delocalized particles, and is invariant under independent translations of each rep-

lica [cf. Eq. (3)]. In more physical terms, this corresponds to the fact that not only the average particle density but the individual particle densities are translationally invariant. The second term represents particles that are localized, and is only invariant under common translations of the replicas (i.e., translations in which $\mathbf{a}^\alpha = \mathbf{a}$ for all α). This corresponds to the fact that the individual particle density for localized particles is not translationally invariant, so that translational invariance is broken microscopically, but the average density remains translationally invariant, i.e., the system still is macroscopically translationally invariant.

By inserting the hypothesis (10) into the stationarity condition (9), and taking the $n \rightarrow 0$ limit, we obtain

$$0 = \delta_{\mathbf{k}, \mathbf{0}}^{(d)} \left\{ 2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\tau p(\tau) e^{-\hat{k}^2/2\tau} - 3q^2 \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) e^{-\hat{k}^2/2(\tau_1 + \tau_2)} \right\}. \quad (11)$$

In the limit $\hat{k}^2 \rightarrow 0$, the equation reduces to a condition for the localized fraction q , viz.,

$$0 = -2q\epsilon + 3q^2. \quad (12)$$

For negative or zero ϵ , corresponding to a constraint density less than or equal to its critical value, the only physical solution is $q=0$, corresponding to the liquid state. In this state, all particles are delocalized. For positive ϵ , corresponding to a constraint density in excess of the critical value, there are two solutions. One, unstable, is the continuation of the liquid state $q=0$; the other, stable, corresponds to a nonzero fraction,

$$q = \frac{2}{3} \epsilon \quad (13)$$

being localized. We identify this second state as the amorphous solid state. From the dependence of the localized fraction q on the control parameter ϵ and the form of the order parameter Eq. (10) we conclude that there is a continuous phase transition between the liquid and the amorphous solid states at $\epsilon=0$, with localized fraction exponent $\beta=1$ (i.e., the classical exponent¹³). It is worth mentioning that microscopic approaches go beyond this linear behavior near the transition, yielding a transcendental equation for $q(\epsilon)$, valid for all values of the control parameter ϵ ; see Refs. 3, 4.

From Eq. (8) it is evident that the liquid state is locally stable (unstable) for negative (positive) ϵ : the eigenvalues of the resulting quadratic form are given by $\lambda(\hat{k}) = -\epsilon + \hat{k}^2/2$.

Now concentrating on the amorphous solid state, by inserting the value of the localized fraction into Eq. (11), we obtain the following integrodifferential equation for the probability distribution for the localization lengths:

$$\frac{\tau^2}{2} \frac{dp}{d\tau} = \left(\frac{\epsilon}{2} - \tau \right) p(\tau) - \frac{\epsilon}{2} \int_0^\tau d\tau_1 p(\tau_1) p(\tau - \tau_1). \quad (14)$$

All parameters can be seen to play an elementary role in this equation by expressing $p(\tau)$ in terms of a scaling function:

$$p(\tau) = (2/\epsilon) \pi(\theta); \quad \tau = (\epsilon/2)\theta. \quad (15)$$

Thus, the universal function $\pi(\theta)$ satisfies

$$\frac{\theta^2}{2} \frac{d\pi}{d\theta} = (1 - \theta) \pi(\theta) - \int_0^\theta d\theta' \pi(\theta') \pi(\theta - \theta'). \quad (16)$$

Solving this equation, together with the normalization condition $1 = \int_0^\infty d\theta \pi(\theta)$, one finds the scaling function shown in Refs. 3,4. The function $\pi(\theta)$ has a peak at $\theta \approx 1$ of width of order unity, and decays rapidly both as $\theta \rightarrow 0$ and $\theta \rightarrow \infty$. By combining these features of $\pi(\theta)$ with the scaling transformation (15) we conclude that the typical localization length scales as $\epsilon^{-1/2}$ near the transition. The order parameter also has a scaling form near the transition:

$$\Omega_{\hat{k}} = [1 - (2\epsilon/3)] \delta_{\hat{k}, \hat{0}} + (2\epsilon/3) \delta_{\mathbf{k}, \mathbf{0}}^{(d)} \omega(\sqrt{2\hat{k}^2/\epsilon}),$$

$$\omega(k) = \int_0^\infty d\theta \pi(\theta) e^{-k^2/2\theta}. \quad (17)$$

Equation (16) and the normalization condition on $\pi(\theta)$ are precisely the conditions that determine the scaling function for the cross-linked and end-linked cases; they are discussed extensively, together with the properties of the resulting distribution of localization lengths and order parameter, in Refs. 3, 4, and 8.

As discussed in this section, the localized fraction $q(\epsilon)$ and the scaled distribution of inverse square localization lengths $\pi(\theta)$ are universal near the transition. We now discuss this issue in more detail.

First, let us focus at the mean-field level. Recall the mean-field theory of ferromagnetism¹⁴ and, in particular, the exponent β , which characterizes the vanishing of the magnetization density order parameter (from the ferromagnetic state) as a function of the temperature at zero applied magnetic field. The exponent β takes on the value of 1/2, regardless of the details of the mean-field theory used to compute it. The functions $q(\epsilon)$, $\pi(\theta)$, and $\omega(k)$ are universal in the same sense. The case of $q(\epsilon)$ is on essentially the same, standard, footing as that of the magnetization density. What is not standard, however, is that describing the (equilibrium) order parameter is a universal scaling function, $\omega(k)$ [or, equivalently, $\pi(\theta)$] that is not a simple power law. This feature arises because the usual presence of fields carrying *internal* indices, such as Cartesian vector indices in the case of ferromagnetism, is replaced here by the external continuous replicated wave-vector variable \hat{k} . There are two facets to this universal scaling behavior of the order parameter. First, for systems differing in their microscopic details and their constraint densities there is the possibility of collapsing the distribution of localization lengths on to a single function, solely by rescaling the independent variable. Second, there is a definite prediction for the dependence of this rescaling on the control parameter ϵ .

Now, going beyond the mean-field level, in the context of vulcanization de Gennes¹⁵ has shown that the width of the critical region, in which fluctuations dominate and mean-field theory fails, vanishes in the limit of very long macromolecules in space dimension $d=3$ or higher. Thus, one may anticipate that for extended objects the mean-field theory discussed here will be valid, except in an exceedingly narrow region around the transition. Nevertheless, if—as is usually the case—the effective Hamiltonian governing the fluctuations is the Landau free energy then the universality discussed here is expected to extend, *mutatis mutandis*, into the critical regime.

That the amorphous solid state given by Eq. (17) is stable with respect to small perturbations (i.e., is locally stable) can be shown by detailed analysis. Moreover, as we shall see in Sec. V, it yields predictions that are in excellent agreement with subsequent computer simulations. However, there is, in principle, no guarantee that this state is globally stable (i.e., that no states with lower free energy exist).

Up to this point we have assumed that the free energy is invariant under interchange of all replicas, including the one representing the constraint distribution ($\alpha=0$), with any of the remaining n , i.e., that the free energy is symmetric under the group S_{n+1} of permutations of all $n+1$ replicas. This need not be the case, in general, as the system can be changed, (e.g., by changing the temperature) after the constraints have been imposed. In this latter case, the free energy retains the usual S_n symmetry under permutations of replicas $\alpha=1, \dots, n$. The argument we have developed can be reproduced for this more general case with only a minor change: in the free energy, we can no longer invoke S_{n+1} symmetry to argue that all of the $|\mathbf{k}^\alpha|^2$ must enter the expression for g_2 with a common prefactor. Instead, we only have permutation symmetry among replicas $\alpha=1, \dots, n$ and, therefore, the prefactor b for all of these replicas must be the same, but now the prefactor b_0 for replica $\alpha=0$ can be different. This amounts to making the replacement

$$\hat{k}^2 \rightarrow \bar{k}^2 \equiv b_0 b^{-1} |\mathbf{k}^0|^2 + \sum_{\alpha=1}^n |\mathbf{k}^\alpha|^2 \quad (18)$$

in the free energy. Both the rest of the derivation and the results are unchanged, except that \hat{k}^2 needs to be replaced by \bar{k}^2 , throughout. We mention, in passing, that no saddle points exhibiting the spontaneous breaking of replica permutation symmetry have been found, to date, either for systems with S_{n+1} or S_n symmetry.

IV. FREE ENERGY IN TERMS OF THE DISTRIBUTION OF STATIC DENSITY FLUCTUATIONS

The aim of this section is to construct an expression for the disorder-averaged Landau free energy for the amorphous solidification transition, \mathcal{F} , in terms of the distribution of static density fluctuations. We present this approach as an alternative to the strategy of constructing a replica free energy \mathcal{F}_n in terms of the replica order parameter Ω . In the familiar way, the equilibrium state will be determined via a variational principle: $\delta\mathcal{F}=0$ and $\delta^2\mathcal{F}>0$. What may be less

familiar, however, is that in the present setting the *independent* variables for the variation (i.e., the distribution of static density fluctuations) themselves constitute a functional.

Our aim, then, is to work not with the replica order parameter $\Omega_{\hat{k}}$, but instead with the disorder-averaged probability density functional for the random static density fluctuations,^{16,4} $\mathcal{N}(\{\rho_{\mathbf{k}}\})$, which is defined via

$$\mathcal{N}(\{\rho_{\mathbf{k}}\}) \equiv \left[\frac{1}{N} \sum_{i=1}^N \prod_{\mathbf{k}} \delta_c(\rho_{\mathbf{k}} - \langle \exp(i\mathbf{k} \cdot \mathbf{c}_i) \rangle_\chi) \right]. \quad (19)$$

Here, $\prod_{\mathbf{k}}$ denotes the product over all d vectors \mathbf{k} , and the Dirac δ function of complex argument $\delta_c(z)$ is defined by $\delta_c(z) \equiv \delta(\text{Re } z)\delta(\text{Im } z)$, where $\text{Re } z$ and $\text{Im } z$, respectively, denote the real and imaginary parts of the complex number z . From the definition of $\mathcal{N}(\{\rho_{\mathbf{k}}\})$, we see that $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*$ and $\rho_{\mathbf{0}} = 1$. Thus we can take as independent variables $\rho_{\mathbf{k}}$ for all d vectors \mathbf{k} in the half-space given by the condition $\mathbf{k} \cdot \mathbf{n} > 0$ for a suitable unit d vector \mathbf{n} . In addition, $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ obeys the normalization condition

$$\int \mathcal{D}\rho \mathcal{N}(\{\rho_{\mathbf{k}}\}) = 1. \quad (20)$$

It is straightforward to check that, for any particular positive integer g , the replica order parameter $\Omega_{\hat{k}}$ is a g th moment of $\mathcal{N}(\{\rho_{\mathbf{k}}\})$:

$$\int \mathcal{D}\rho \mathcal{N}(\{\rho_{\mathbf{k}}\}) \rho_{\mathbf{k}^1} \rho_{\mathbf{k}^2} \cdots \rho_{\mathbf{k}^g} = \Omega_{\mathbf{k}^1, \mathbf{k}^2, \dots, \mathbf{k}^g}. \quad (21)$$

We use $\mathcal{D}\rho$ to denote the measure $\prod_{\mathbf{k}} d\text{Re}\rho_{\mathbf{k}} d\text{Im}\rho_{\mathbf{k}}$.

The merit of the distribution functional $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ over the replica order parameter $\Omega_{\hat{k}}$ is that, as we shall soon see, it allows us to formulate a Landau free energy for the amorphous solidification transition, depending on $\mathcal{N}(\{\rho_{\mathbf{k}}\})$, in which replicated quantities do not appear, while maintaining the physical content of the theory. At the present time, this approach is not truly independent of the replica approach, in the following sense: we employ the replica approach to derive the free energy, Eq. (8), and only then do we transform from the language of order parameters to the language of the distribution of static density fluctuations. We are not yet in possession of either an analytical scheme or a set of physical arguments that would allow us to construct the Landau free energy directly. Nevertheless, we are able, by this indirect method, to propose a (replica-free) free energy, and also to hypothesize (and verify the correctness of) a stationary value of $\mathcal{N}(\{\rho_{\mathbf{k}}\})$. It would, however, be very attractive to find a scheme that would allow us to eschew the replica approach and work with the distribution of static density fluctuations from the outset.

To proceed, we take the replica Landau free energy \mathcal{F}_n , Eq. (8), in terms of the replica order parameter $\Omega_{\hat{k}}$, and replace $\Omega_{\hat{k}}$ by its expression in terms of the $(n+1)$ th moment of $\mathcal{N}(\{\rho_{\mathbf{k}}\})$. Thus, we arrive at the replica Landau free energy:

$$\begin{aligned}
nd\mathcal{F}_n = & \epsilon - 2 + (3 - \epsilon) \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \left(\sum_{\mathbf{k}} \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right)^{n+1} + \frac{1}{2} (n+1) \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}} k^2 \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right) \left(\sum_{\mathbf{k}} \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right)^n - \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \mathcal{D}\rho_3 \mathcal{N}(\{\rho_{3,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}_1, \mathbf{k}_2} \rho_{1,\mathbf{k}_1} \rho_{2,\mathbf{k}_2} \rho_{3,-\mathbf{k}_1-\mathbf{k}_2} \right)^{n+1}. \tag{22}
\end{aligned}$$

In order to obtain the desired (replica-independent) free energy, we take the limit $n \rightarrow 0$ of Eq. (22):

$$\begin{aligned}
d\mathcal{F} = d \lim_{n \rightarrow 0} \mathcal{F}_n = & (3 - \epsilon) \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \left(\sum_{\mathbf{k}} \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right) \ln \left(\sum_{\mathbf{k}} \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right) + \frac{1}{2} \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}} k^2 \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right) \ln \left(\sum_{\mathbf{k}} \rho_{1,\mathbf{k}} \rho_{2,-\mathbf{k}} \right) - \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \mathcal{D}\rho_3 \mathcal{N}(\{\rho_{3,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}_1, \mathbf{k}_2} \rho_{1,\mathbf{k}_1} \rho_{2,\mathbf{k}_2} \rho_{3,-\mathbf{k}_1-\mathbf{k}_2} \right) \ln \left(\sum_{\mathbf{k}_1, \mathbf{k}_2} \rho_{1,\mathbf{k}_1} \rho_{2,\mathbf{k}_2} \rho_{3,-\mathbf{k}_1-\mathbf{k}_2} \right). \tag{23}
\end{aligned}$$

In deriving the above free energy we have employed the physical fact that the average particle density is uniform. In other words, the replica order parameter is zero if all but one of the replicated wave vectors is nonzero which, translated in the language of the distribution of static density fluctuations, means that the first moment of the static density distribution equals $\delta_{\mathbf{k},0}$. It is worth noting that, within this formalism, the replica limit can already be taken at the level of the free energy, prior to the hypothesizing of an explicit form for the stationary value of the order parameter. On the one hand, this is attractive, as it leads to a Landau theory in which replicas play no role. On the other hand, the approach is, at present, restricted to replica-symmetric states.

We now construct the self-consistency condition that follows from the stationarity of the replica-independent free energy. We then proceed to solve the resulting functional equation exactly, by hypothesizing a solution having precisely the same physical content as the exact solution of the replica self-consistency condition discussed in Sec. III.

To construct the self-consistency condition for $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ it is useful to make two observations. First, $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ obeys the normalization condition (20). This introduces a constraint on the variations of $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ which is readily accounted for via Lagrange's method of undetermined multipliers. Second, as mentioned above, not all the variables $\{\rho_{\mathbf{k}}\}$ are independent: we have the relations $\rho_{\mathbf{0}} = 1$ and $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*$. In principle, one could proceed by defining a new distribution that only depends on the independent elements of $\{\rho_{\mathbf{k}}\}$, and re-express the free energy in terms of this new distribution. However, for convenience we will retain $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ as the basic quantity to be varied, and bear in mind the fact that $\rho_{\mathbf{0}} = 1$ and $\rho_{-\mathbf{k}} = \rho_{\mathbf{k}}^*$. By performing the constrained variation of $d\mathcal{F}$ with respect to the functional, $\mathcal{N}(\{\rho_{\mathbf{k}}\})$

$$0 = \frac{\delta}{\delta \mathcal{N}(\{\rho_{\mathbf{k}}\})} \left(\mathcal{F} + \lambda \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \right), \tag{24}$$

where λ is the undetermined multiplier, we obtain the self-consistency condition obeyed by $\mathcal{N}(\{\rho_{\mathbf{k}}\})$:

$$\begin{aligned}
0 = & \lambda d + 2(3 - \epsilon) \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{1,-\mathbf{k}} \right) \ln \left(\sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{1,-\mathbf{k}} \right) + \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}} k^2 \rho_{\mathbf{k}} \rho_{1,-\mathbf{k}} \right) \ln \left(\sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{1,-\mathbf{k}} \right) \\
& - 3 \int \mathcal{D}\rho_1 \mathcal{N}(\{\rho_{1,\mathbf{k}}\}) \mathcal{D}\rho_2 \mathcal{N}(\{\rho_{2,\mathbf{k}}\}) \\
& \times \left(\sum_{\mathbf{k}, \mathbf{k}'} \rho_{\mathbf{k}} \rho_{1,\mathbf{k}'} \rho_{2,-\mathbf{k}-\mathbf{k}'} \right) \ln \left(\sum_{\mathbf{k}, \mathbf{k}'} \rho_{\mathbf{k}} \rho_{1,\mathbf{k}'} \rho_{2,-\mathbf{k}-\mathbf{k}'} \right). \tag{25}
\end{aligned}$$

To solve this self-consistency condition for $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ we import our experience with the replica approach, thereby constructing the normalized hypothesis

$$\begin{aligned}
\mathcal{N}(\{\rho_{\mathbf{k}}\}) = & (1 - q) \delta_c(\rho_{\mathbf{0}} - 1) \prod_{\mathbf{k} \neq \mathbf{0}} \delta_c(\rho_{\mathbf{k}}) \\
& + q \int \frac{d\mathbf{c}}{V} \int_0^\infty d\tau p(\tau) \prod_{\mathbf{k}} \delta_c(\rho_{\mathbf{k}} - e^{i\mathbf{c} \cdot \mathbf{k} - k^2/2\tau}), \tag{26}
\end{aligned}$$

in which q (which satisfies $0 \leq q \leq 1$) is the localized fraction and $p(\tau)$ (which is regular and normalized to unity) is the distribution of localization lengths of localized particles. It is straightforward to show that by taking the $(n+1)$ th moment of $\mathcal{N}(\{\rho_{\mathbf{k}}\})$ we recover the self-consistent form of the replica order parameter, Eq. (10).

By inserting the hypothesis (26) into Eq. (25), making the replacement $\rho_{\mathbf{0}} \rightarrow 1$, and performing some algebra, the self-consistency condition takes the form

$$0 = \int \frac{d\mathbf{c}}{V} \int_0^\infty d\tau \left(1 + \sum_{\mathbf{k} \neq 0} \rho_{\mathbf{k}} e^{-i\mathbf{c} \cdot \mathbf{k} - k^2/2\tau} \right) \ln \left(1 + \sum_{\mathbf{k} \neq 0} \rho_{\mathbf{k}} e^{-i\mathbf{c} \cdot \mathbf{k} - k^2/2\tau} \right) \left\{ 2q(-\epsilon + 3q)p(\tau) - q \frac{d}{d\tau} [2\tau^2 p(\tau)] - 3q^2 \int_0^\tau d\tau_1 p(\tau_1) p(\tau - \tau_1) \right\} - \frac{3}{2} dq^2 \int_0^\infty d\tau_1 p(\tau_1) d\tau_2 p(\tau_2) \ln \{ V^{2/d} \tau_1 \tau_2 / 2\pi e (\tau_1 + \tau_2) \} + \lambda d, \quad (27)$$

in terms of the undetermined multiplier λ . To determine λ we insert the choice $\rho_{\mathbf{k}} = \delta_{\mathbf{k},0}$, which yields

$$\lambda = \frac{3}{2} q^2 \int_0^\infty d\tau_1 p(\tau_1) d\tau_2 p(\tau_2) \ln \{ V^{2/d} \tau_1 \tau_2 / 2\pi e (\tau_1 + \tau_2) \}. \quad (28)$$

By using this result to eliminate λ from the self-consistency condition, and observing that this condition must be satisfied for arbitrary $\{\rho_{\mathbf{k}}\}$, we arrive at a condition on q and $p(\tau)$, viz.,

$$0 = 2q(-\epsilon + 3q)p(\tau) - q \frac{d}{d\tau} [2\tau^2 p(\tau)] - 3q^2 \int_0^\tau d\tau_1 p(\tau_1) p(\tau - \tau_1). \quad (29)$$

We integrate this equation over all values of τ and use the normalization condition on $p(\tau)$ to arrive at the same equation relating q and ϵ as was found in Eq. (12) of the previous section, the appropriate solution of which is given by $q = 2\epsilon/3$, i.e., Eq. (13). Finally, we use this result for q to eliminate it from Eq. (29), thus arriving at the same self-consistency condition on $p(\tau)$ as was found in Eq. (14) of the previous section. Thus, we see that these conditions, one for q and one for $p(\tau)$, are precisely the same as those arrived at by the replica method discussed in Sec. III.

V. COMPARISON WITH NUMERICAL SIMULATIONS: UNIVERSALITY EXHIBITED

The purpose of the present section is to examine the conclusions of the Landau theory, especially those concerning universality and scaling, in the light of the extensive molecular-dynamics simulations, performed by Barsky and Plischke.^{10,11} These simulations address the amorphous solidification transition in the context of randomly cross-linked macromolecular systems, by using an off-lattice model of macromolecules interacting via a Lennard-Jones potential.

It should be emphasized that there are substantial differences between ingredients and calculational schemes used in the analytical and simulational approaches. In particular, the analytical approach: (i) invokes the replica technique; (ii) retains interparticle interactions only to the extent that macroscopically inhomogeneous states are disfavored (i.e., the one-replica sector remains stable at the transition); (iii) neglects order-parameter fluctuations, its conclusions therefore being independent of the space dimension; and (iv) is solved via an ansatz, which is not guaranteed to capture the optimal solution.

Nevertheless, and rather strikingly, the simulations yield an essentially identical picture for the transition to and prop-

erties of the amorphous solid state, inasmuch as they indicate that (i) there exists a (cross-link–density-controlled) continuous phase transition from a liquid state to an amorphous solid state; (ii) the critical cross-link density is very close to one cross link per macromolecule; (iii) q varies linearly with the density of cross links, at least in the vicinity of this transition (see Fig. 1); (iv) when scaled appropriately (i.e., by the mean localization length), the simulation data for the distribution of localization lengths exhibit very good collapse on to a universal scaling curve for the several (near-critical) cross-link densities and macromolecule lengths considered (see Figs. 2 and 3); and (v) the form of this universal scaling curve appears to be in remarkably good agreement with the precise form of the analytical prediction for this distribution.

It should not be surprising that by focusing on universal quantities, one finds agreement between the analytical and computational approaches. This indicates that the proposed Landau theory does indeed contain the essential ingredients necessary to describe the amorphous solidification transition.

Let us now look more critically at the comparison between the results of the simulation and the mean-field theory. With respect to the localized fraction, the Landau theory is only capable of showing the linearity of the dependence, near the transition, on the excess cross-link density, leaving undetermined the proportionality factor. The simulation results are consistent with this linear dependence, giving, in addition, the amplitude. There are two facets to the universality of the distribution of localization lengths, as mentioned in Sec. III. First, that the distributions can, for different systems and different cross-link densities, be collapsed on to a universal scaling curve, is verified by the simulations, as pointed out above. Second, the question of how the scaling parameter depends on the excess cross-link density is difficult to address in current simulations, because the dynamic range for the mean localization length accessible in them is limited, so that its predicted divergence at the transition is difficult to verify.

VI. SUMMARY AND CONCLUDING REMARKS

To summarize, we have proposed a replica Landau free energy for the amorphous solidification transition. The theory is applicable to systems of extended objects undergoing thermal density fluctuations and subject to quenched random translationally invariant constraints. The statistics of the quenched randomness are determined by the equilibrium density fluctuations of the unconstrained system. We have shown that there is, generically, a continuous phase transition between a liquid and an amorphous solid state, as a function of the density of random constraints. Both states are described by exact stationary points of this replica free energy, and are replica symmetric and macroscopically trans-

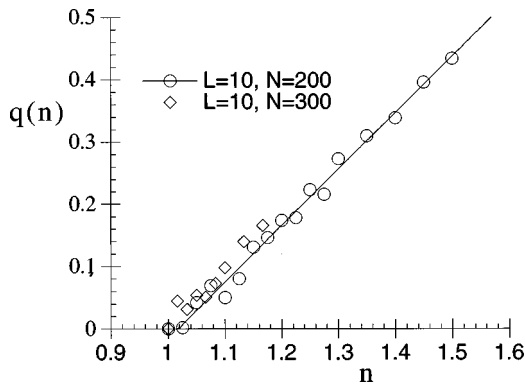


FIG. 1. Localized fraction q as a function of the number of cross links per macromolecule n , as computed in molecular-dynamics simulations by Barsky and Plischke (Ref. 11). L is the number of monomers in each macromolecule; N is the number of macromolecules in the system. The straight line is a linear fit to the $N=200$ data. Note the apparent existence of a continuous phase transition near $n=1$, as well as the apparent linear variation of q with n , both features being consistent with the mean-field description.

lationally invariant. They differ, however, in that the liquid is translationally invariant at the microscopic level, whereas the amorphous solid breaks this symmetry.

We have also shown how all these results may be recovered using an alternative formulation in which we focus less on the replica order parameter and more on the distribution of random static density fluctuations. In particular, we construct a representation of the free energy in terms of this distribution, and solve the resulting stationarity condition.

Lastly, we have examined our results in the light of the extensive molecular-dynamics simulations of randomly cross-linked macromolecular systems, due to Barsky and Plischke. Not only do these simulations support the general theoretical scenario of the vulcanization transition, but also they confirm the detailed analytical results for universal quantities, including the localized fraction exponent and the distribution of scaled localization lengths.

The ultimate origin of universality is not hard to understand, despite the apparent intricacy of the order parameter associated with the amorphous solidification transition. As we saw in Secs. II and III, there are two small emergent

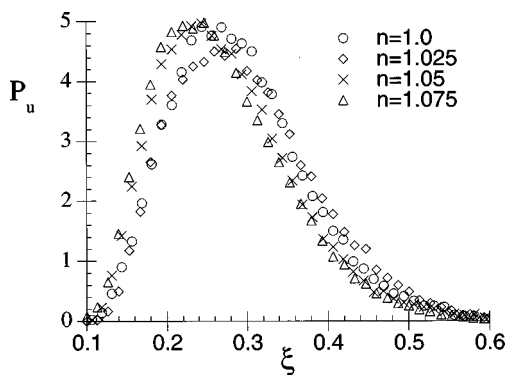


FIG. 2. Unscaled probability distribution P_u of localization lengths ξ (in units of the linear system size), as computed in molecular-dynamics simulations by Barsky and Plischke (Ref. 11). In the simulations the number of segments per macromolecule is 10; and the number of macromolecules is 200.

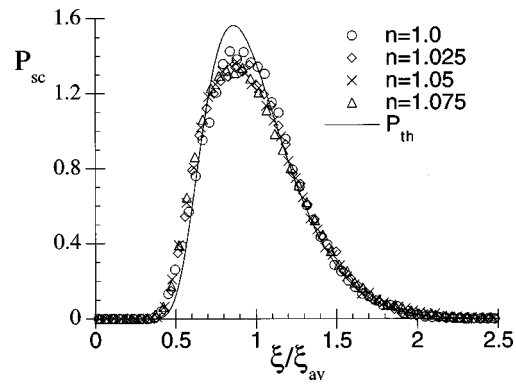


FIG. 3. Probability distribution (symbols) P_s of localization lengths ξ , scaled with the sample average of the localization lengths ξ_{av} , as computed in molecular-dynamics simulations by Barsky and Plischke (Ref. 11). Note the apparent collapse of the data on to a single universal scaling distribution, as well as the good quantitative agreement with the mean-field prediction for this distribution (solid line). In the simulation the number of segments per macromolecule is 10; and the number of macromolecules is 200. The mean-field prediction for $P_{sc}(\xi/\xi_{av})$ is obtained from the universal scaling function $\pi(\theta)$ by $P_{sc}(y) = (2s/y^3)\pi(s/y^2)$, where the constant $s \approx 1.224$ is fixed by demanding that $\int_0^\infty dy y P_{sc}(y) = 1$.

physical quantities, the fraction of localized particles and the characteristic inverse square localization length of localized particles. The smallness of the localized fraction validates the truncation of the expansion of the free energy in powers of the order parameter. The smallness of the characteristic inverse square localization length leads to a very simple dependence, $\sum_{\alpha=0}^n |\mathbf{k}^\alpha|^2$, on the $n+1$ independent wave vectors of the replica theory, well beyond the permutation invariance demanded by symmetry considerations alone. As a result, near the transition, the amorphous solid state is characterizable in terms of a single universal function of a single variable, along with the localized fraction.

Although throughout this paper we have borne in mind the example of randomly cross-linked macromolecular systems, the circle of ideas is by no means restricted to such systems. To encompass other systems possessing externally-induced quenched random constraints, such as networks formed by the permanent random covalent bonding of atoms or small molecules (e.g., silica gels), requires essentially no further conceptual ingredients (and only modest further technical ones).¹⁷

One may also envisage applications to the glass transition. Although it is generally presumed that externally-induced quenched random variables are not relevant for describing the glass transition, it is tempting to view the freezing-out of some degrees of freedom as the crucial consequence of the temperature-quench, with a form of quenched disorder thereby being developed spontaneously. The approach presented in the present paper becomes of relevance to the glass transition if one accepts this view of the temperature quench, and thus models the nonequilibrium state of the quenched liquid by the equilibrium state of a system in which some fraction of covalent bonds has been rendered permanent (the deeper the quench the larger the fraction).¹⁸ This strategy, viz., the approximating of pure systems by ones with ‘‘self-induced’’ quenched disorder, has also been invoked in very interesting work on the Bernasconi model for binary se-

quences of low autocorrelation.¹⁹ Interesting connections are also apparent with recent effective-potential approaches to glassy magnetic systems, in which one retains in the partition function only those configurations that lie close to the equilibrium state reached at the glass transition temperature.²⁰

ACKNOWLEDGMENTS

We thank Nigel Goldenfeld and David Hertzog for useful discussions. We gratefully acknowledge support from the U.S. National Science Foundation through Grant Nos.

DMR94-24511 (W.P., P.G.) and DMR91-57018 (P.G.), from the University of Illinois at Urbana-Champaign (H.C.), from NATO through CRG 94090 (P.G., A.Z.), and from the DFG through SFB 345 (A.Z.). Michael Plischke has generously provided us with unpublished results from his extensive computational studies of vulcanized macromolecular networks, performed in collaboration with Sandra J. Barsky, and has allowed us to report some of this work here. We are most grateful to him for this, and for his continued enthusiasm for the subject matter.

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