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Semimicroscopic theory of elasticity near the vulcanization transition

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Randomly cross-linked macromolecules undergo a liquid to amorphous-solid phase transition at a critical cross-link concentration. This transition has two main signatures: the random localization of a fraction of the monomers and the emergence of a nonzero static shear modulus. In this paper, a semimicroscopic statistical mechanical theory of the elastic properties of the amorphous solid state is developed. This theory takes into account both quenched disorder and thermal fluctuations, and allows for the direct computation of the free energy change of the sample due to a given macroscopic shear strain. This leads to an unambiguous determination of the static shear modulus. At the level of mean field theory, it is found (i) that the shear modulus grows continuously from zero at the transition, and does so with the classical exponent, i.e., with the third power of the excess cross-link density and, quite surprisingly, (ii) that near the transition the external stresses do not spoil the spherical symmetry of the localization clouds of the particles.

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I. INTRODUCTION

The vulcanization transition is the equilibrium phase transition from a liquid state to a random solid state (known as the amorphous-solid state) that occurs when a sufficient density of randomly located, permanent cross-linking constraints is applied to the constituents of a liquid. The liquid may be a melt of macromolecules of various types (long or short, flexible or stiff) or even of a low molecular weight species, and our results will—*mutatis mutandis*—apply to this broad variety of systems. Corrections due to long-wavelength fluctuations of the order parameter, omitted in the mean field theory that we shall be developing do, however, tend to be important over a narrower range of cross-link densities for longer macromolecules and stronger concentrations of them [1–3]. For this reason, and for the sake of concreteness, we shall focus on cases involving long, linear, flexible macromolecules. There are two main equilibrium signatures of the vulcanization transition: (i) the structural signature that a nonzero fraction of the monomers (i.e., segments of the macromolecules) become localized around random mean positions and have random localization lengths; and (ii) the response signature that the system, as a whole, acquires a nonzero static shear modulus. The structural signature has been discussed previously; the purpose of this paper is to present a detailed analysis of the latter signature by developing a statistical–mechanical theory of the emergent elastic

properties of the amorphous solid state in the vicinity of the vulcanization transition. A core feature of this theory, a brief account of which was given in Ref. [4], is that it incorporates both annealed (i.e., thermally equilibrating) and quenched random (i.e., cross-link specifying) variables. Its main conclusions are (a) that the amorphous state emerging at the vulcanization transition, which is solid in the sense of the structural signature (i), is indeed solid in the sense of the response signature (ii); (b) that the elastic shear modulus vanishes continuously as the transition is approached, and does so with the third power of the excess crosslink density (i.e., the amount by which the cross-link density exceeds its critical value); and (c) that the shearing of the container associated with elastic deformations leads neither to a deterministic nor a stochastic shearing of the probability clouds associated with the thermal fluctuations of localized particles about their mean positions.

There has been considerable attention paid, over the years, to the elastic properties of vulcanized matter and related chemically bonded systems, especially those near the amorphous solidification transition. Amongst the most notable approaches are the classical ones [5], in which it was argued that near the transition the elastic entropy in the solid phase (and consequently the static shear modulus E) grow as the third power of the excess cross-link density ϵ , i.e., $E \sim \epsilon^t$ with $t=3$. More recently, it was proposed that the amorphous solidification transition of polymer systems be identi-

fied with a percolation transition [2,6]. This proposal led to the identification of the exponent t with the critical exponent μ for percolation of conductivity (with $\mu \approx 2.0$ in three spatial dimensions). In yet more recent work it was observed that the elasticity percolation exponent for a random network is substantially higher than μ when the forces are central [7]. Part of the ambiguity in the determination of the shear modulus of the randomly cross-linked system from percolative approaches stems from the fact that these approaches do not naturally lead to the computation of a free energy for the system.

Approaches of a more microscopic orientation have also been made to the elastic properties of vulcanized matter, in which macromolecular degrees of freedom feature explicitly. Among these are the ‘‘phantom network’’ [8] and ‘‘affine network’’ [9] approaches, as well as the comprehensive discussion of rubber elasticity by Deam and Edwards [10], and others [11]. These approaches focus on the well cross-linked regime rather than the lightly cross-linked regime near the vulcanization transition [12].

Experimentally, the exponent t has been addressed for several systems (although mostly for gelation rather than vulcanization): the results vary from $t \approx 2$ [13] to $t \approx 3$ [14]. This wide discrepancy remains unresolved.

The classical [15,16,5] and percolation [2,6] approaches to the physics of vulcanized matter are certainly stimulating. However, it must be recognized that neither explicitly includes both crucial ingredients: *thermal fluctuations* and *quenched disorder*. In addition, as was mentioned above, contradictory results have been obtained in the determination of the shear modulus of random amorphous solids from percolative formulations, due in part to the lack of a natural definition of an elastic free energy for the system. In the approach that we shall present, however, the free energy of the system emerges immediately as a physical quantity, and the value of the shear modulus is determined unambiguously by the change of the free energy due to deformations of the sample. Over the past few years, an approach to the vulcanization transition has been developed [17–20] that explicitly incorporates both thermal fluctuations and quenched disorder in the context of a semimicroscopic model for flexible, randomly cross-linked macromolecules. This approach is very much inspired by the work of Edwards and collaborators [10,21], as well as by ideas from the field of spin glasses. Emerging from this more recent approach has been a detailed picture of the *structure* of the amorphous solid state near to the vulcanization transition, including, in particular, an explicit form for the distribution of localization lengths. In this paper, we present a detailed exposition of the application of this approach to the second signature of the vulcanization transition, namely the emergence of static *response* to shear deformations. To our knowledge, this is the only existing computation of the static elastic properties of randomly cross-linked macromolecular systems near the vulcanization transition that starts from first principles and thereby includes both the effects of quenched disorder and thermal fluctuations.

The outline of the present paper is as follows. This introduction is followed by two long sections. In Sec. II we present the model that we use to describe systems of randomly cross-linked macromolecules, and review prior results

obtained from this model. In Sec. III we describe and implement the changes necessary to accommodate strained systems, construct the appropriate free energy, determine the resulting order parameter, and compute the elastic shear modulus. Finally, in Sec. IV, we give a short summary of our results.

II. MODEL

In this section we present the model that we use to analyze systems of randomly cross-linked macromolecules, and briefly summarize some of the results about the amorphous solidification transition in those systems that have been obtained previously within the framework of the same model [17–20]. We emphasize here those aspects of the model and the results that are modified when the system is deformed, and refer the reader interested in further details to those papers (especially Ref. [20], which gives a detailed account of the model).

A. Description of the system: macromolecules; Edwards Hamiltonian; random permanent cross links

We study a system of N macromolecules of arclength L and persistence length ℓ moving in a d -dimensional hypercubic volume V . The thermal degrees of freedom are the positions of the monomers $\mathbf{c}_i(s)$, where the index $i = 1, \dots, N$ labels the macromolecules and the arclength $0 \leq s \leq L$ labels the monomers on a given macromolecule. [For convenience, we measure arclengths in units of the total arclength L , and spatial positions in units of $\sqrt{L\ell/d}$, i.e., the root-mean-square (rms) end-to-end distance of a free macromolecule divided by \sqrt{d} .]

We model the system prior to cross linking by using the Edwards Hamiltonian [22],

$$H = \frac{1}{2} \sum_{j=1}^N \int_0^1 ds \left| \frac{d\mathbf{c}_j(s)}{ds} \right|^2 + \frac{\lambda^2}{2} \sum_{i,i'=1}^N \int_0^1 ds \int_0^1 ds' \delta(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')), \quad (2.1)$$

where $\lambda^2 (>0)$ characterizes the effect of the (repulsive) excluded-volume interaction between monomers and $\delta(\mathbf{c})$ is the d -dimensional Dirac delta function.

We suppose that permanent cross links are introduced between a random number M of randomly selected pairs of monomers: monomer s_e on chain i_e is cross linked to monomer s'_e on chain i'_e (with $e = 1, \dots, M$). These constraints, which enforce certain pairs of monomers to occupy common spatial locations, do not break translational symmetry, and the variables that specify the constraints, $\chi \equiv \{i_e, s_e; i'_e, s'_e\}_{e=1}^M$, play the role of quenched random variables.

For a particular realization of the disorder [23], the partition function reads

$$Z(\chi) \equiv \frac{\bar{Z}(\chi)}{\sigma(\chi)}. \quad (2.2)$$

Here, $\bar{Z}(\chi)$ is a naively computed sum of the thermodynamic weights for allowed macromolecular configurations, and is defined via

$$\bar{Z}(\chi) \equiv \int \mathcal{D}\mathbf{c} e^{-H} \prod_{e=1}^M \delta(\mathbf{c}_i(s_e) - \mathbf{c}_i'(s_e')), \quad (2.3)$$

where $\int \mathcal{D}\mathbf{c}$ indicates functional integration over all configurations of all macromolecules. The permutation symmetry factor $\sigma(\chi)$ in Eq. (2.2) depends on the realization of the disorder and compensates for the overcounting of configurations that only differ by permutations of the labels of macromolecules (Ref. [20], Secs. 2.4 and 2.6). This symmetry factor plays a role in ensuring that the free energy of the system has the proper extensive scaling (for example, in the simplest example of all molecules being identical, one has the well-known $1/N!$ prefactor to the partition function, without which one would have the Gibbs paradox). However, the symmetry factor *does not change* when the system is deformed after cross linking, and is thus *irrelevant* in the determination of elastic properties.

It should be pointed out that in the present approach the macromolecules are allowed to pass through one another and, therefore, the interlocking of loops is not explicitly considered [23]. There are reasons to believe that this is a good approximation. First, the transition regime, of interest here, is characterized by a rather low cross-link density—of order one cross link per macromolecule—so most of the macromolecules appear in “treelike” structures and therefore loops might reasonably be expected to have little impact. Second, under coarse graining the distinction between holonomic and anholonomic constraints tends to fade, with knots and cross links having rather similar effects. Third, a comparison of the results for the gel fraction and the distribution of localization lengths obtained from the present approach with those obtained in computer simulations that do include the interlocking of loops suggests that this interlocking effect is indeed negligible near the liquid to amorphous-solid transition [24–26].

B. Probability distribution of the quenched disorder

To model the distribution of the cross-link locations in a realistic vulcanization process, we make the following physical assumption (due to Deam and Edwards [10]): a “snapshot” of the semimicroscopic state of the uncross-linked system is taken, and, if a pair of monomers happen to be close to each other, there is a probability, determined by a control parameter μ^2 , of becoming permanently attached by a cross link. The mean number of cross links per macromolecule $[M]/N$ is a smooth, monotonically increasing function of μ^2 . Here and subsequently, square brackets $[\dots]$ denote averages over the cross-link distribution, i.e., disorder averaging. The replica technique is used to perform the disorder averages, with the peculiarity that the Deam–Edwards assumption leads to the presence of $n+1$ replicas $\alpha = 0, \dots, n$, with $n \rightarrow 0$. The additional replica $\alpha = 0$ represents the degrees of freedom of the original system before cross linking, or, equivalently, encodes the consequences of the cross-link distribution. Consequently, any external strain applied to the system *after the permanent constraints have been created* will affect replicas $\alpha = 1, \dots, n$, but not replica $\alpha = 0$ [10].

C. Order parameter for amorphous solidification

In this system there is a phase transition between a liquid phase at low cross-link densities ($\mu^2 < 1$) and an amorphous solid phase at high cross-link densities ($\mu^2 > 1$). Since the disorder-averaged particle density is uniform in both states, it cannot be used as an order parameter to detect the transition. The appropriate order parameter (inspired in the Edwards–Anderson [27] order parameter for spin glass systems), is the following [17]:

$$\Omega_{\mathbf{k}^1, \dots, \mathbf{k}^g} \equiv \left[\frac{1}{N} \sum_{j=1}^N \int_0^1 ds \langle e^{i\mathbf{k}^1 \cdot \mathbf{c}_j(s)} \rangle_\chi \dots \langle e^{i\mathbf{k}^g \cdot \mathbf{c}_j(s)} \rangle_\chi \right]. \quad (2.4)$$

Here, g is a positive integer, and $\{\mathbf{k}^1, \dots, \mathbf{k}^g\}$ are any g nonzero d -dimensional wave vectors. This order parameter is zero in the liquid phase and, for wave vectors chosen so that $\mathbf{k}^1 + \dots + \mathbf{k}^g = \mathbf{0}$, it is nonzero in the amorphous solid phase. The order parameter $\Omega_{\mathbf{k}^1, \dots, \mathbf{k}^g}$ is, in principle, experimentally accessible through scattering experiments: e.g., the incoherent contribution to the elastic neutron scattering cross section is proportional to $\Omega_{\mathbf{k}, -\mathbf{k}}$ [20,28]. Other experimental techniques that can be used to probe the order parameter are pulsed field gradient nuclear magnetic resonance (NMR) [29] and dynamic light scattering [30].

For the sake of computational simplicity, we adopt periodic boundary conditions on the coordinates to describe the microscopic configurations of our system. Consequently, the order parameter is only nonzero for $\mathbf{k}^a \in r^u$, $a = 1, \dots, g$, where r^u denotes the reciprocal lattice in d dimensions associated with the periodicity in real space arising from the boundary conditions. Here, the superscript u stands for “unstrained system.”

In the replica formalism, the definition of the order parameter translates into the following form:

$$\Omega_{\hat{\mathbf{k}}} \equiv \left\langle \frac{1}{N} \sum_{i=1}^N \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i) \right\rangle_{n+1}^P. \quad (2.5)$$

Here, hatted vectors denote replicated collections of vectors, viz., $\hat{\mathbf{v}} \equiv \{\mathbf{v}^0, \mathbf{v}^1, \dots, \mathbf{v}^n\}$, their scalar product being $\hat{\mathbf{v}} \cdot \hat{\mathbf{w}} \equiv \sum_{\alpha=0}^n \mathbf{v}^\alpha \cdot \mathbf{w}^\alpha$, 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. The set R^u of allowed replicated wave vectors $\hat{\mathbf{k}}$ is obtained by taking all combinations of $(n+1)$ allowed d -dimensional wave vectors. In the next section, when we discuss deformations of the system, these deformations will directly change the boundary conditions in real space and, consequently, the set of allowed wave vectors.

The presence in the replicated order parameter of products between quantities probing the replica $\alpha = 0$ and quantities probing the replicas $\alpha = 1, \dots, n$ makes it a useful tool to detect correlations between the state of the system *before* cross linking (or, equivalently, the distribution of cross-link locations) and the state of the system *after* cross linking (and possibly deformation).

D. Field theory

The fundamental quantity to be computed in the replica approach is the disorder averaged replicated partition function $[\bar{Z}^n]$. Starting from the microscopic Edwards Hamiltonian of Eq. (2.1) and the Deam–Edwards disorder distribution [10], and after performing a Hubbard–Stratonovich transformation that eliminates microscopic monomer position variables in favor of field variables $\Omega_{\hat{k}}$ [31], the following expression is obtained:

$$[\bar{Z}^n] = \mathcal{N} \int \mathcal{D}\Omega \exp\{-n dN \mathcal{F}_n(\{\Omega_{\hat{k}}\})\}. \quad (2.6)$$

Here $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$ is a replicated free energy functional and the symbol $\int \mathcal{D}\Omega$ denotes integration over all possible configurations for the field $\Omega_{\hat{k}}$, where the independent set of variables is the set of all complex-valued $\Omega_{\hat{k}}$ (for \hat{k} in the half-space determined by the condition that $\hat{k} \cdot \hat{n}$ be positive for a fixed unit vector \hat{n}). Outside of this half-space, $\Omega_{\hat{k}}$ is defined by the relation $\Omega_{-\hat{k}} = \Omega_{\hat{k}}^*$. \mathcal{N} is a normalization constant that will be ignored henceforth, as it does not affect the value of the order parameter [see Eq. (2.10)] or the dependence of the free energy on any shear deformations of the container (see Sec. III C). As for the free energy functional $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$, it is given by

$$\begin{aligned} n d\mathcal{F}_n(\{\Omega_{\hat{k}}\}) = & \tilde{\lambda}_n^2 \frac{N}{V} \sum_{\hat{p}}^{\dagger} |\Omega_{\hat{p}}|^2 + \frac{\mu^2}{V^n} \sum_{\hat{k}}^{\dagger} |\Omega_{\hat{k}}|^2 \\ & - \ln \left\langle \exp \left(i \tilde{\lambda}_n^2 \frac{2N}{V} \sum_{\hat{p}}^{\dagger} \text{Re} \Omega_{\hat{p}} \rho_{\hat{p}}^* \right. \right. \\ & \left. \left. + \frac{2\mu^2}{V^n} \sum_{\hat{k}}^{\dagger} \text{Re} \Omega_{\hat{k}} \rho_{\hat{k}}^* \right) \right\rangle_{n+1}^w, \quad (2.7) \end{aligned}$$

where the symbol $\bar{\Sigma}$ denotes a sum over replicated wave vectors in the higher replica sector, the symbol $\tilde{\Sigma}$ denotes a sum over replicated wave vectors in the one replica sector, and the superscript \dagger restricts a given sum to replicated wave vectors satisfying the condition $\hat{k} \cdot \hat{n} > 0$ for a fixed unit vector \hat{n} . The parameter $\tilde{\lambda}_n^2 \equiv \lambda^2 - V^{1-n} \mu^2/N$ gives the strength of the excluded volume interaction between the monomers after renormalization due to the effects of the crosslinking. The one-macromolecule Fourier-transformed density $\rho_{\hat{k}}$ is defined via

$$\rho_{\hat{k}} \equiv \int_0^1 ds e^{i\hat{k} \cdot \hat{c}(s)} \quad (2.8)$$

for a macromolecular configuration $\hat{c}(s)$, and the replicated Wiener average is defined by

$$\langle \mathcal{O} \rangle_{n+1}^w \equiv \frac{\int \mathcal{D}\hat{c} \mathcal{O} \exp\left(-\frac{1}{2} \int_0^1 ds \left| \frac{d\hat{c}(s)}{ds} \right|^2\right)}{\int \mathcal{D}\hat{c} \exp\left(-\frac{1}{2} \int_0^1 ds \left| \frac{d\hat{c}(s)}{ds} \right|^2\right)}. \quad (2.9)$$

Analogously, the order parameter can be obtained as [31]

$$\Omega_{\mathbf{k}^1, \dots, \mathbf{k}^g} = \lim_{n \rightarrow 0} \frac{\int \mathcal{D}\Omega \Omega_{\hat{l}} \exp\{-n dN \mathcal{F}_n(\{\Omega_{\hat{k}}\})\}}{\int \mathcal{D}\Omega \exp\{-n dN \mathcal{F}_n(\{\Omega_{\hat{k}}\})\}}, \quad (2.10)$$

where, once again, we choose \hat{l} so that $\mathbf{l}^\alpha = \mathbf{k}^\alpha$ for $\alpha = 1, \dots, g$ and $\mathbf{l}^\alpha = \mathbf{0}$ for $\alpha = 0$ and $\alpha = g+1, \dots, n$.

E. Stationary-point approximation

The simplest available method to evaluate the free energy and the order parameter is the stationary-point approximation, which also provides a starting point for possible improvement, for example, by way of the loop expansion [3]. In the stationary-point approximation [1], we have

$$\bar{f} = d \lim_{n \rightarrow 0} \min_{\{\Omega_{\hat{k}}\}} \mathcal{F}_n(\{\Omega_{\hat{k}}\}). \quad (2.11)$$

The value $\bar{\Omega}_{\hat{l}}$ of the field $\Omega_{\hat{l}}$ that provides the minimum also determines the order parameter according to

$$\Omega_{\mathbf{k}^1, \dots, \mathbf{k}^g} = \lim_{n \rightarrow 0} \bar{\Omega}_{\hat{l}}. \quad (2.12)$$

Proposing a general solution: As has been discussed in Refs. [19,20], the stationary-point equation for the free-energy functional near the transition is exactly solved by the following hypothesis:

$$\Omega_{\hat{l}} = (1-q) \delta_{\hat{l}, \hat{0}} + q \delta_{\hat{l}, \hat{0}} W^u(\hat{l}), \quad (2.13a)$$

$$W^u(\hat{l}) \equiv \int_0^\infty d\tau p(\tau) e^{-\hat{l}^2/2\tau}, \quad (2.13b)$$

with

$$\tilde{\mathbf{l}} \equiv \sum_{\alpha=0}^n \mathbf{l}^\alpha. \quad (2.14)$$

The physical motivation for this hypothesis comes from a picture in which a fraction q (the ‘‘gel fraction’’) of the monomers are localized around random mean positions $\mathbf{b}_j(s)$ about which they execute harmonic thermal fluctuations characterized by random localization lengths $\xi_j(s)$. In terms of the Fourier-transformed particle density for an individual monomer, this picture translates into the expression

$$\langle \exp(i\mathbf{k} \cdot \mathbf{c}_j(s)) \rangle_\chi = \exp(i\mathbf{k} \cdot \mathbf{b}_j(s)) \exp(-\xi_j(s)^2 \mathbf{k}^2/2). \quad (2.15)$$

The mean positions and localization lengths are assumed to be distributed independently, with a homogeneous distribution over the sample for the mean positions, and a statistical distribution $2\xi^{-3} p(\xi^{-2})$ for the localization lengths. By combining the contributions from all monomers in the system, we see that the proposed statistical distributions give rise to an order parameter of the form

$$\begin{aligned} \Omega_{\mathbf{k}^1, \dots, \mathbf{k}^s} &= (1-q) \delta_{\mathbf{k}^1, \mathbf{0}} \cdots \delta_{\mathbf{k}^s, \mathbf{0}} + q \int \frac{d\mathbf{b}}{V} e^{i(\mathbf{k}^1 + \dots + \mathbf{k}^s) \cdot \mathbf{b}} \\ &\times \int_0^\infty d(\xi^{-2}) p(\xi^{-2}) e^{-\xi^2((\mathbf{k}^1)^2 + \dots + (\mathbf{k}^s)^2)/2} \end{aligned} \quad (2.16a)$$

$$\begin{aligned} &= (1-q) \delta_{\mathbf{k}^1, \mathbf{0}} \cdots \delta_{\mathbf{k}^s, \mathbf{0}} + q \delta_{\mathbf{k}^1 + \dots + \mathbf{k}^s, \mathbf{0}} \\ &\times \int_0^\infty d\tau p(\tau) e^{-((\mathbf{k}^1)^2 + \dots + (\mathbf{k}^s)^2)/2\tau}. \end{aligned} \quad (2.16b)$$

The homogeneous distribution of the mean positions of the localized particles gives rise, in Eq. (2.16a), to an integral over \mathbf{b} , which represents the delta function that appears explicitly in the second term of the right-hand side (RHS) of Eq. (2.16b). In the second line we have also identified the variable $\tau = 1/\xi^2$. By taking the replica limit in the manner of Eq. (2.12), the order parameter hypothesis [of Eqs. (2.13a) and (2.13b)] reduces to Eq. (2.16b).

From our motivation of the order parameter hypothesis, it is evident that, in Eqs. (2.16a), (2.16b), and (2.13a), delocalized and localized particles are, respectively, represented by the first and second terms on the RHS. The function $W^u(\hat{k})$, which we refer to as the *continuous part* of the order parameter, encodes information about thermal fluctuations (the superscript u standing for ‘‘unstrained system’’).

The hypothesis of Eqs. (2.13a) and (2.13b) for the order parameter only allows for a liquid phase (for $q=0$) and for an amorphous solid phase (for $q>0$). It is useful to notice here that the order parameter is zero in the one replica sector, independently of the values of q and $p(\tau)$. This is to be expected, since the disorder averaged particle density is spatially uniform in both the liquid and amorphous solid phases.

F. Behavior near the amorphous solidification transition

For the regime close to the transition which occurs at $\mu^2=1$, it is convenient to define a variable $\epsilon \equiv 3(\mu^2-1)$ that measures the distance to the transition. For $\epsilon<0$ the system is in the liquid phase, and for $\epsilon>0$ the system is in the amorphous solid phase.

1. Free-energy functional

Close to the transition the order parameter is dominated by long localization lengths. This is to be expected on physical grounds, because the system is ‘‘barely solid,’’ allows the monomers to thermally fluctuate over long distances; and it has also been shown directly by computing $p(\tau)$ [19,20]. Here we take this as an assumption, and later show that the solution obtained for the order parameter is consistent with this assumption [32].

As that saddle point value of the order parameter is zero for wave vectors lying in the one replica sector, any term in the expansion of $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$ that contains it as a factor will automatically vanish. We therefore ignore all such terms henceforth.

By expanding Eq. (2.7) in powers of the order parameter and the wave vectors, assuming that the order parameter is zero in the one replica sector (and, in order to simplify later algebra, rescaling \mathcal{F} by an overall factor of 6), we obtain for the regime near the transition a free energy of the form:

$$\begin{aligned} n d\mathcal{F}_n(\{\Omega_{\hat{k}}\}) &= \overline{\sum}_{\hat{k} \in R^u} (-\epsilon + \frac{1}{2}|\hat{k}|^2) |\Omega_{\hat{k}}|^2 \\ &- \overline{\sum}_{\hat{k}_1 \hat{k}_2 \hat{k}_3 \in R^u} \Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{\hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}. \end{aligned} \quad (2.17)$$

This form for $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$ can be obtained either from a semimicroscopic model, as sketched here, or via an argument involving symmetries and the continuity of the transition in the context of a Landau theory. The same free-energy functional actually describes a universality class of physical systems that display liquid–amorphous-solid transitions similar to the one shown by vulcanized systems [26].

2. Stationary-point approximation

We now obtain the stationary-point approximation by demanding that variations of $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$ with respect to the order parameter should be zero. This results in the stationarity equation

$$0 = 2(-\epsilon + \frac{1}{2}|\hat{k}|^2) \Omega_{\hat{k}} - 3 \overline{\sum}_{\hat{k}_1 \hat{k}_2 \in R^u} \Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \delta_{\hat{k}_1 + \hat{k}_2, \hat{k}}. \quad (2.18)$$

The stationary-point equation Eq. (2.18) is satisfied (in the limit $n \rightarrow 0$) by the hypothesis Eqs. (2.13a) and (2.13b), provided that

$$\begin{aligned} 0 &= \delta_{\mathbf{k}, \mathbf{0}} \left\{ 2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\tau p(\tau) e^{-\hat{k}^2/2\tau} \right. \\ &\left. - 3q^2 \int_0^\infty d\tau_1 p(\tau_1) \int_0^\infty d\tau_2 p(\tau_2) e^{-\hat{k}^2/2(\tau_1 + \tau_2)} \right\}. \end{aligned} \quad (2.19)$$

3. Gel fraction

By taking the limit $\hat{k}^2 \rightarrow 0$, the above equation reduces to a condition for the gel fraction q ,

$$0 = -2q\epsilon + 3q^2. \quad (2.20)$$

For negative or zero ϵ , corresponding to a cross-link density less than or equal to its critical value, the only physical solution (i.e., with $0 \leq q \leq 1$) is $q=0$, corresponding to the liquid state. For positive ϵ , corresponding to a cross-link 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 [33], corresponds to a nonzero gel fraction, i.e., to the amorphous solid state,

$$q = \frac{2}{3}\epsilon. \quad (2.21)$$

As mentioned above, the gel fraction (and consequently the order parameter) change continuously at the transition, which means that at $\epsilon=0$ there is a continuous phase transition between the liquid and the amorphous-solid state. Moreover, the linear dependence of the gel fraction with ϵ implies a similar linear dependence with the excess of the cross-link density $[M]/N$ above the critical value M_c/N at the transition: $q \approx 2\epsilon/3 \sim ([M]/M_c - 1) = ([M]/M_c - 1)^\beta$, with $\beta=1$, i.e., we recover the classical exponent for the gel fraction.

4. Distribution of localization lengths

In the amorphous solid state, by assuming that Eq. (2.20) is satisfied, Eq. (2.19) reduces to a nonlinear integro-differential equation involving only the distribution of (inverse square) localization lengths $p(\tau)$:

$$\frac{\tau^2}{2} \frac{dp}{d\tau} = \left(\frac{\epsilon}{2} - \tau \right) p(\tau) - \frac{\epsilon}{2} \int_0^\tau d\tau_1 p(\tau_1) p(\tau - \tau_1). \quad (2.22)$$

The form of this equation immediately suggests that, to the present level of approximation, all ϵ dependence can be eliminated by the scalings [34]:

$$p(\tau) = (2/\epsilon) \pi(\theta), \quad \tau = (\epsilon/2)\theta. \quad (2.23)$$

Thus, the universal scaling function $\pi(\theta)$ satisfies the parameter free equation

$$\frac{\theta^2}{2} \frac{d\pi}{d\theta} = (1 - \theta)\pi(\theta) - \int_0^\theta d\theta' \pi(\theta') \pi(\theta - \theta'), \quad (2.24)$$

together with the normalization condition

$$1 = \int_0^\infty d\theta \pi(\theta). \quad (2.25)$$

This normalization condition directly follows from the fact that the order parameter of Eq. (2.4) has to be unity at the origin [19,20], and is consistent with the physical interpretation of $p(\tau)$ as a probability distribution.

The scaling function $\pi(\theta)$ determines the behavior of both the distribution of localization lengths and the order parameter near the transition. It has a peak at $\theta \approx 1$ of width of order unity, and decays rapidly both as $\theta \rightarrow 0$ and $\theta \rightarrow \infty$. The asymptotic forms of the decays are: $\pi(\theta) \sim a\theta^{-2} \exp(-2/\theta)$ (for $\theta \ll 1$) and $\pi(\theta) \sim 3(b\theta - 3/5) \exp(-b\theta)$ (for $\theta \gg 1$). These forms are obtained analytically from Eq. (2.24); the coefficients $a \approx 4.554$ and $b \approx 1.678$ can be extracted from the complete numerical solution of Eq. (2.24) [19].

Due to the fact that $\pi(\theta)$ has a well-defined, unique peak that concentrates most of the weight, it makes sense to define a *typical* localization length ξ_{typ} , and from Eq. (2.23) we see that it scales as $\xi_{\text{typ}} \sim \epsilon^{-1/2}$. In particular, it diverges at the transition, as anticipated above. It is interesting to notice that this typical length scales with the same exponent as the one obtained in the classical theory for the correlation length. However, ξ_{typ} is a quantity that describes the localized monomers, whereas the correlation length of the classical theory describes the delocalized monomers.

5. Order parameter

The order parameter also has a scaling form near the transition, which follows directly from its parametrization in terms of q and $p(\tau)$, Eqs. (2.13a) and (2.13b), and the scaling form for $p(\tau)$, Eq. (2.23):

$$\Omega_{\hat{k}} = (1 - 2\epsilon/3) \delta_{\hat{k}, \hat{0}} + (2\epsilon/3) \delta_{\tilde{\mathbf{k}}, \mathbf{0}} \omega(\sqrt{2\hat{k}^2/\epsilon}), \quad (2.26a)$$

$$\omega(k) = \int_0^\infty d\theta \pi(\theta) e^{-k^2/2\theta}. \quad (2.26b)$$

Hence, we see that the order parameter is also described in terms of a scaling function, in this case $\omega(k)$. As for $\pi(\theta)$, the asymptotic forms of $\omega(k)$ can be obtained analytically: $\omega(k) \sim 1 + ck^2 + dk^4$ (for $k \ll 1$) and $\omega(k) \sim (9\pi k^3/\sqrt{8b})^{1/2} \exp(-\sqrt{2bk^2}) \{1 + (27/40)\sqrt{2bk^2}\}$ (for $k \gg 1$). A numerical calculation yields $\omega(k)$ for all k , and determines the coefficients $c \approx -0.4409$ and $d \approx 0.1316$ (see Ref. [19]).

III. RESPONSE TO SHEAR STRAIN

In this section we discuss the effects of an externally applied strain, both on the semimicroscopic macromolecular structure of the system and on the value of its free energy. To do this, we repeat the preceding followed in the previous section to obtain the order parameter and the free energy of the system, but this time we consider in detail the effects of deforming the boundaries of the container. As we did before, we are going to concentrate on the behavior near the amorphous solidification transition, and we are going to employ the stationary-point approximation in order to obtain explicit results.

A. Description of the deformation

We characterize the deformation of the system by the ($d \times d$) deformation matrix \mathbf{S} , that describes the change in position of any point \mathbf{b} at the boundary of the system $\mathbf{b} \rightarrow \mathbf{S} \cdot \mathbf{b}$, with \mathbf{S} independent of \mathbf{b} . For any matrix \mathbf{S} , it is possible to find a diagonal matrix $\bar{\mathbf{S}}$ and two rotations \mathbf{U} and \mathbf{V} such that the decomposition $\mathbf{S} = \mathbf{U}\bar{\mathbf{S}}\mathbf{V}$ holds [35,36]. This decomposition can be interpreted in terms of a physical process performed in three steps: in the first, the system is rotated in space as described by \mathbf{V} ; in the second, it is deformed with the diagonal deformation matrix $\bar{\mathbf{S}}$; and in the third, it is rotated as described by \mathbf{U} . The only part of this process that represents a genuine strain, and can therefore possibly alter the free energy of the system, is the second step. Therefore, we may (and shall) always assume, without loss of generality, that the deformation matrix is diagonal. As an example of a deformation matrix for $d=3$, let us consider the case in which the x , y and z Cartesian components of the position vector are, respectively, elongated by the factors λ_x , λ_y , and λ_z , the matrix \mathbf{S} has the form $\text{diag}(\lambda_x, \lambda_y, \lambda_z)$. As we are concerned with the effects of pure shear strains, we shall consider only deformations that leave the volume V of the system unchanged, i.e.,

$$\det \mathbf{S} = 1. \quad (3.1)$$

For considering infinitesimal strains, it is convenient to define the (diagonal) strain tensor

$$\mathbf{J} \equiv \mathbf{S} - \mathbf{I}, \quad (3.2)$$

where \mathbf{I} is the identity matrix. For small shear deformations, we have

$$1 = \det \mathbf{S} = 1 + \text{tr}(\mathbf{S} - \mathbf{I}) + O((\mathbf{S} - \mathbf{I})^2), \quad (3.3)$$

and consequently

$$\text{tr } \mathbf{J} = 0, \quad (3.4)$$

to first order in the deformation.

B. Deformation and replicas

Before taking the thermodynamic limit, the system is finite in extent, and thus the Fourier representation of any function of position consists of a superposition of plane waves with wave vectors belonging to a discrete set. The precise set of wave vectors is determined by the periodic boundary conditions. In particular, the order parameter is represented by a function $\Omega_{\hat{k}}$ that is only defined at a discrete set of points in replicated Fourier space. Now, under strain the boundaries in position space are displaced and, as a consequence, the discrete set of points in replicated Fourier space move. As previously mentioned in Sec. II B, any external strain applied to the system after the permanent constraints have been created will affect replicas $\alpha=1, \dots, n$, but not replica $\alpha=0$ [10]. Therefore, the change in the discretization of the wave vectors occurs only for $\alpha=1, \dots, n$, but not $\alpha=0$. For replicas $\alpha=1, \dots, n$, the set of allowed d -dimensional wave vectors r^u corresponding to the unstrained system is replaced by a new set r^s corresponding to the strained system. Consequently, the set R^s of allowed *replicated* wave vectors in the strained system is composed of all replicated wave vectors $\hat{k} = \{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n\}$ such that $\mathbf{k}^0 \in r^u$ and $\mathbf{k}^\alpha \in r^s$ (for replicas $\alpha=1, \dots, n$).

C. Free-energy functional for the deformed system

Conceptually, there are two sources for the change in free energy, Eq. (2.11), under deformation: the change in the expression for the free-energy functional itself, and the consequent change in the value of the order parameter that solves the stationary-point equation. The free-energy functional for the strained system $\mathcal{F}_n^s(\{\Omega_{\hat{k}}\})$ is obtained by repeating, step-by-step, the procedure followed [20] to construct the free-energy functional for the unstrained system $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$. The only change resides in the fact that integrals over the positions of the monomers in replicas $\alpha=1, \dots, n$ now range over the region occupied by the strained sample instead of the region occupied by the unstrained sample and, consequently, the summations over replicated wave vectors now run over the new set R^s of wave vectors in replicated space:

$$\delta^s(\hat{c}) = \frac{1}{V^{1+n}} \sum_{\hat{p} \in R^s} \exp(i\hat{p} \cdot \hat{c}). \quad (3.5)$$

As a result, one has

$$\frac{\mu^2 V}{2N} \sum_{i,j=1}^N \int_0^1 ds \int_0^1 dt \delta^s(\hat{c}_i(s) - \hat{c}_j(t)) = \frac{\mu^2 N}{2V^n} \sum_{\hat{p} \in R^s} |Q_{\hat{p}}|^2, \quad (3.6)$$

and the expression for $[\bar{Z}^n]$ in terms of monomer densities becomes

$$[\bar{Z}^n] = \frac{e^{-Nn\phi} \int \mathcal{D}\hat{c} \exp \left\{ -\frac{1}{2} \sum_{j=1}^N \int_0^1 ds \left| \frac{d\hat{c}_j(s)}{ds} \right|^2 - N\tilde{\chi}_n^2 \frac{N}{V} \sum_{\hat{p} \in R^s}^\dagger |Q_{\hat{p}}|^2 + N \frac{\mu^2}{V^n} \sum_{k \in R^s}^\dagger |Q_{\hat{k}}|^2 \right\}}{\int \mathcal{D}\mathbf{c} \exp \left\{ -\frac{1}{2} \sum_{j=1}^N \int_0^1 ds \left| \frac{d\mathbf{c}_j(s)}{ds} \right|^2 - N\tilde{\chi}_0^2 \frac{N}{V} \sum_{\mathbf{p}}^\dagger |Q_{\mathbf{p}}|^2 \right\}}. \quad (3.7)$$

Two features should be noted here. One is that the denominator in formula (3.7) is not affected by the deformation, because it is the normalization factor for the disorder distribution, which is fixed before the system is deformed. Thus, the normalization constant \mathcal{N} in Eq. (2.6), which reads

$$\mathcal{N} = \frac{\exp(-Nn\phi)}{\int \mathcal{D}\mathbf{c} \exp \left\{ -\frac{1}{2} \sum_{j=1}^N \int_0^1 ds \left| \frac{d\mathbf{c}_j(s)}{ds} \right|^2 - N\tilde{\chi}_0^2 \frac{N}{V} \sum_{\mathbf{p}}^\dagger |Q_{\mathbf{p}}|^2 \right\}}, \quad (3.8)$$

is unchanged by the deformation, as anticipated in Sec. II D. The second feature is that the general form of the expression for $[\bar{Z}^n]$ in Eq. (3.7) is unchanged with respect to the corresponding expression in the unstrained system, even to the point that the values of the prefactors multiplying the sums over replicated wave vectors are unchanged. The only differences between the unstrained and strained system reside in

the region of integration for the variable \hat{c} and in that the summations over replicated wave vectors run over either the set R^u or the set R^s .

From Eq. (3.7) one immediately obtains, with the Hubbard–Stratonovich transformation as in Sec. II D, the free energy functional

$$\begin{aligned}
n d\mathcal{F}_n^s(\{\Omega_{\hat{k}}\}) &= \bar{\chi}_n^2 \frac{N}{V} \sum_{\hat{p} \in R^s}^\dagger |\Omega_{\hat{p}}|^2 + \frac{\mu^2}{V^n} \sum_{\hat{k} \in R^s}^\dagger |\Omega_{\hat{k}}|^2 \\
&\quad - \ln \left\langle \exp \left(i \bar{\chi}_n^2 \frac{2N}{V} \sum_{\hat{p} \in R^s}^\dagger \text{Re} \Omega_{\hat{p}} \rho_{\hat{p}}^* \right. \right. \\
&\quad \left. \left. + \frac{2\mu^2}{V^n} \sum_{\hat{k} \in R^s}^\dagger \text{Re} \Omega_{\hat{k}} \rho_{\hat{k}}^* \right) \right\rangle_{n+1}^W. \quad (3.9)
\end{aligned}$$

As in the case of the undeformed system, we are going to take one further step, and restrict ourselves to the regime near the amorphous solidification transition.

D. Free-energy and stationary-point equations near the vulcanization transition

In the regime close to the transition, we can expand the free energy functional in powers of the order parameter and the wave vectors, as we did in Sec. II F 1, and obtain the analog of Eq. (2.17) for the deformed system:

$$\begin{aligned}
n d\mathcal{F}_n^s(\{\Omega_{\hat{k}}\}) &= \sum_{\hat{k} \in R^s} (-\epsilon + \frac{1}{2} |\hat{k}|^2) |\Omega_{\hat{k}}|^2 \\
&\quad - \sum_{\hat{k}_1 \hat{k}_2 \hat{k}_3 \in R^s} \Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{\hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}. \quad (3.10)
\end{aligned}$$

As a result, the stationary-point equation for the strained system becomes

$$0 = 2(-\epsilon + \frac{1}{2} |\hat{k}|^2) \Omega_{\hat{k}} - 3 \sum_{\hat{k}_1 \hat{k}_2 \in R^s} \Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \delta_{\hat{k}_1 + \hat{k}_2, \hat{k}}. \quad (3.11)$$

Although, superficially, this equation looks the same as Eq. (2.18), they are actually different, as all the wave vectors entering in Eq. (2.18) belong to R^u , i.e., the set of replicated wave vectors corresponding to the undeformed system, and all the wave vectors entering in Eq. (3.11) belong to R^s , i.e., the set of replicated wave vectors corresponding to the deformed system. Therefore, while Eq. (2.18) is invariant under all permutations of the $1+n$ replicas, Eq. (3.11) is only invariant under permutations of the n replicas $\alpha = 1, \dots, n$.

E. Proposing a hypothesis for the order parameter

We shall obtain the order parameter for the strained state by finding a solution of Eq. (3.11). To do this, we shall use physical arguments similar to those used in the case of the unstrained system to motivate our guess for a possible solution. As our guess will turn out to solve Eq. (3.11) exactly, this justifies, *a posteriori*, our physical assumptions. As the shear modulus is determined by an expansion of the free energy to quadratic order in the deformation, for the moment we will only consider infinitesimal deformations.

For each localized monomer in the unstrained system we envisage that its old mean position $\mathbf{b}_j(s)$ is displaced to a new mean position $\mathbf{b}_j^s(s) = \mathbf{S} \cdot \mathbf{b}_j(s) + \mathbf{t}_j(s)$. Up to this point the only assumption is the physically intuitive one that those monomers that are localized in the undeformed system re-

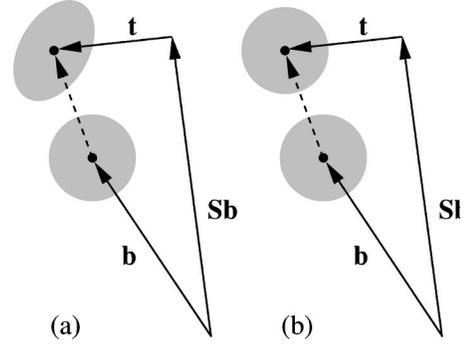


FIG. 1. Change of the localization region for an individual monomer due to an externally imposed strain: (a) assuming that the fluctuation region around the mean position deforms affinely; (b) assuming that the fluctuation region around the mean position stays spherically symmetric.

main localized in the deformed system. The vector $\mathbf{S} \cdot \mathbf{b}_j(s)$ is the affine displacement of the old position [9]. We now make the assumption that $\mathbf{t}_j(s)$ is a random additional displacement, uncorrelated with $\mathbf{b}_j(s)$.

For each localized monomer, we also need some conjecture about the behavior under strain of the size and shape of the region within which it thermally fluctuates. We assume that this localization region need not remain spherical (as it was in the unstrained system) but might be deformed due to the external strain (Fig. 1). We will consider the position fluctuations for the monomers:

$$\delta \mathbf{c}_j^u(s) = \mathbf{c}_j(s) - \mathbf{b}_j(s) \quad (3.12)$$

for the unstrained system, and

$$\delta \mathbf{c}_j^s(s) = \mathbf{c}_j(s) - (\mathbf{S} \cdot \mathbf{b}_j(s) + \mathbf{t}_j(s)) \quad (3.13)$$

for the strained system, and also the individual monomer densities for the unstrained and strained systems, $\rho_{j,s,\chi}^u(\mathbf{r})$ and $\rho_{j,s,\chi}^s(\mathbf{r})$, as defined by

$$\rho_{j,s,\chi}(\mathbf{r}) \equiv \langle \delta(\mathbf{r} - \mathbf{c}_j(s)) \rangle_\chi. \quad (3.14)$$

One possible assumption is that the fluctuation region deforms affinely, i.e., that

$$\delta \mathbf{c}_j^u(s) \rightarrow \delta \mathbf{c}_j^s(s) = \mathbf{S} \cdot \delta \mathbf{c}_j^u(s). \quad (3.15)$$

This gives rise to the individual monomer density

$$\rho_{j,s,\chi}^s(\mathbf{r}) = \rho_{j,s,\chi}^u(\mathbf{S}^{-1} \cdot (\mathbf{r} - \mathbf{b}_j^s(s)) + \mathbf{b}_j(s)) \quad (3.16)$$

in real space, and

$$\begin{aligned}
\langle e^{i\mathbf{k} \cdot \mathbf{c}_j(s)} \rangle_\chi^s &= \exp(i\mathbf{k} \cdot \{\mathbf{S} \cdot \mathbf{b}_j(s) + \mathbf{t}_j(s)\}) \\
&\quad \times \exp(-\xi_j^2(s) \mathbf{k} \cdot \mathbf{S}^2 \cdot \mathbf{k} / 2) \quad (3.17)
\end{aligned}$$

for the Fourier-transformed version. In what follows, we will replace the matrix \mathbf{S}^2 by its expansion to first order in the deformation

$$\mathbf{S}^2 \approx \mathbf{I} + 2\mathbf{J} + O(\mathbf{J}^2). \quad (3.18)$$

Thus, for an infinitesimal strain, the assumption of affine distortion of the fluctuation region gives the density

$$\begin{aligned} \langle e^{i\mathbf{k}\cdot\mathbf{c}_j(s)} \rangle_\chi^s &= \exp(i\mathbf{k}\cdot\{\mathbf{S}\cdot\mathbf{b}_j(s) + \mathbf{t}_j(s)\}) \\ &\times \exp(-\xi_j^2(s)\mathbf{k}\cdot\{\mathbf{I} + 2\mathbf{J}\}\cdot\mathbf{k}/2). \end{aligned} \quad (3.19)$$

An alternative assumption is that the fluctuation region remains spherical as in the unstrained system, i.e., that

$$\delta\mathbf{c}_j^u(s) \rightarrow \delta\mathbf{c}_j^s(s) = \delta\mathbf{c}_j^u(s). \quad (3.20)$$

This, in turn, gives rise to the individual monomer density

$$\rho_{j,s,\chi}^s(\mathbf{r}) = \rho_{j,s,\chi}^u(\mathbf{r} - \mathbf{b}_j^s(s) + \mathbf{b}_j(s)) \quad (3.21)$$

in real space, and

$$\langle e^{i\mathbf{k}\cdot\mathbf{c}_j(s)} \rangle_\chi^s = \exp(i\mathbf{k}\cdot\{\mathbf{S}\cdot\mathbf{b}_j(s) + \mathbf{t}_j(s)\}) \exp(-\xi_j^2(s)\mathbf{k}^2/2) \quad (3.22)$$

in wave-vector space.

Motivated by the above special cases, we propose the following parametrization for $\langle e^{i\mathbf{k}\cdot\mathbf{c}_j(s)} \rangle_\chi^s$, which contains Eqs. (3.19) and (3.22) as particular limits:

$$\begin{aligned} \langle e^{i\mathbf{k}\cdot\mathbf{c}_j(s)} \rangle_\chi^s &= \exp(i\mathbf{k}\cdot\{\mathbf{S}\cdot\mathbf{b}_j(s) + \mathbf{t}_j(s)\}) \\ &\times \exp(-\xi_j^2(s)\mathbf{k}\cdot\{\mathbf{I} + \eta_j(s)\mathbf{J}\}\cdot\mathbf{k}/2). \end{aligned} \quad (3.23)$$

The rationale for this generalization goes as follows. We know that in the undeformed system the probability cloud is asymptotically isotropic. For an infinitesimal deformation, one might expect the localization region to be slightly distorted. To lowest order in the deformation, the matrix characterizing the deformation is \mathbf{J} . The other ingredient that can influence the shape of the localization region is the disorder: thus we include a random factor $\eta_j(s)$ that weights the departure of the localization region from spherical symmetry. For example, if $\eta_j(s) = 2$, Eq. (3.23) would reduce to Eq. (3.19), meaning that the probability cloud is affinely distorted. By contrast, if $\eta_j(s) = 0$ Eq. (3.23) would reduce to Eq. (3.22), i.e., the probability cloud would remain spherically symmetric, as it is in the undeformed system. In the same spirit as in the undeformed case, we assume that the parameters η and ξ describing the extent (and shape) of the fluctuation region are uncorrelated with the original mean position \mathbf{b} .

By considering g real copies of the system, and adding the contributions of all monomers, we can explicitly construct the order parameter of Eq. (2.4):

$$\begin{aligned} \Omega_{\mathbf{k}}^1, \dots, \mathbf{k}^g &= (1-q)\delta_{\mathbf{k}^1, \mathbf{0}} \times \dots \times \delta_{\mathbf{k}^g, \mathbf{0}} \\ &+ q \int \frac{d\mathbf{b}}{V} e^{i(\mathbf{k}^1 + \dots + \mathbf{k}^g)\cdot\mathbf{S}\cdot\mathbf{b}} \\ &\times \int d\mathbf{t} \int_0^\infty d\tau \int_{-\infty}^\infty d\eta \psi(\mathbf{t}, \tau, \eta) e^{i(\mathbf{k}^1 + \dots + \mathbf{k}^g)\cdot\mathbf{t}} \\ &\times e^{-((\mathbf{k}^1)\cdot\{\mathbf{I} + \eta\mathbf{J}\}\cdot\mathbf{k}^1 + \dots + \mathbf{k}^g\cdot\{\mathbf{I} + \eta\mathbf{J}\}\cdot\mathbf{k}^g)/2\tau}. \end{aligned} \quad (3.24)$$

Here, $\psi(\mathbf{t}, \tau, \eta)$ is the joint statistical distribution for the parameters \mathbf{t} , τ , and η , i.e.,

$$\begin{aligned} \frac{1}{V} \psi(\mathbf{t}, \tau, \eta) &\equiv \left[\frac{1}{N} \sum_{j=1}^N \int_0^1 ds \delta(\mathbf{b} - \mathbf{b}_j(s)) \delta(\mathbf{t} - \mathbf{t}_j(s)) \right. \\ &\left. \times \delta(\tau - (\xi_j(s))^{-2}) \delta(\eta - \eta_j(s)) \right]. \end{aligned} \quad (3.25)$$

In order for Eq. (3.24) to reproduce the order parameter of Eq. (2.16b) in the limit of zero strain, the following condition on $\psi(\mathbf{t}, \tau, \eta)$ has to be satisfied:

$$\lim_{S \rightarrow \mathbf{I}} \psi(\mathbf{t}, \tau, \eta) = \delta(\mathbf{t}) p(\tau) \delta(\eta). \quad (3.26)$$

The integral over \mathbf{b} in Eq. (3.24) factorizes for the same reason as in the undeformed system, namely because \mathbf{b} is uncorrelated with all the other parameters.

In order to solve the stationary-point equations, we need an expression for $\Omega_{\hat{k}}$, where \hat{k} is a generic replicated wave vector in R^s . Obtaining this expression is less straightforward than in the undeformed case: we have to take into account the fact that replica $\alpha=0$ is different from all the others because it is not affected by the deformation. This suggests that for localized monomers we parametrize the Fourier-transformed individual particle density by using Eq. (2.15) for $\alpha=0$ and Eq. (3.23) for $\alpha=1, \dots, n$, and thus we obtain the following form for $\Omega_{\hat{k}}$:

$$\begin{aligned} \Omega_{\hat{k}} &= (1-q) \prod_{\alpha=0}^n \delta_{\mathbf{k}^\alpha, \mathbf{0}} + q \int \frac{d\mathbf{b}}{V} e^{i(\mathbf{k}^0\cdot\mathbf{b} + \sum_{\alpha=1}^n \mathbf{k}^\alpha\cdot\mathbf{S}\cdot\mathbf{b})} \\ &\times \int d\mathbf{t} \int_0^\infty d\tau \int_{-\infty}^\infty d\eta \psi(\mathbf{t}, \tau, \eta) e^{i(\sum_{\alpha=1}^n \mathbf{k}^\alpha)\cdot\mathbf{t}} \\ &\times e^{-((\mathbf{k}^0)^2 + \sum_{\alpha=1}^n \mathbf{k}^\alpha\cdot\{\mathbf{I} + \eta\mathbf{J}\}\cdot\mathbf{k}^\alpha)/2\tau} \end{aligned} \quad (3.27a)$$

$$= (1-q) \delta_{\hat{k}, \hat{0}} + q \delta_{\mathbf{k}^0 + \mathbf{S}\cdot\sum_{\alpha=1}^n \mathbf{k}^\alpha, \mathbf{0}} W^s(\hat{k}). \quad (3.27b)$$

To arrive at the second line we have observed that the product of wave-vector Kronecker delta functions corresponds to a delta function for replicated wave vectors, we have identified the integral over \mathbf{b} as a representation of a Kronecker delta function in wave-vector space, and we have denoted the integral over \mathbf{t} , τ and η as $W^s(\hat{k})$, i.e., the continuous part of the order parameter in the strained system.

Although it is not trivial to propose a general form for the probability distribution $\psi(\mathbf{t}, \tau, \eta)$, under fairly mild conditions it is possible to expand its Fourier transform with respect to the random displacement \mathbf{t} to first order in the strain and to lowest nontrivial order in wave vectors:

$$\int d\mathbf{t} e^{i\mathbf{P}\cdot\mathbf{t}} \psi(\mathbf{t}, \tau, \eta) = p(\tau) \delta(\eta) + m(\tau, \eta) \mathbf{P}\cdot\mathbf{J}\cdot\mathbf{P} + O(\mathbf{J}^2), \quad (3.28)$$

with $m(\tau, \eta)$ an unknown function. The correctness of this expansion can be justified as follows. The value of the right hand side of Eq. (3.28) in the limit of zero strain is dictated by Eq. (3.26). The first order correction in the strain is de-

terminated by assuming that it is invariant under a rotation of the coordinate system (which is equivalent to a simultaneous rotation of \mathbf{p} and \mathbf{J}). This condition only allows for the following terms: (i) a linear function of $\mathbf{p} \cdot \mathbf{J} \cdot \mathbf{p}$ times any function of \mathbf{p}^2 and (ii) a product of an invariant linear function of \mathbf{J} times any function of \mathbf{p}^2 . The only quantity linear in \mathbf{J} and invariant under rotations is $\text{tr} \mathbf{J}$, which is zero for infinitesimal shear strains, as mentioned above. Thus we only have term (i), which, to lowest nontrivial order in wave vectors, reduces to the contribution appearing in Eq. (3.28).

The integral over \mathbf{t} in Eq. (3.27a) is the same as that in Eq. (3.28), but with \mathbf{p} replaced by

$$\sum_{\alpha=1}^n \mathbf{k}^\alpha = -\mathbf{S}^{-1} \cdot \mathbf{k}^0 \approx -\mathbf{k}^0 \quad (3.29)$$

The approximation in the second line is consistent with our keeping only terms linear in the deformation in Eq. (3.28).

We are now in the position of being able to simplify the form of Eq. (3.27a) substantially, by taking the following steps: (i) we use Eqs. (3.28) and (3.29) to perform the integration over the random displacement \mathbf{t} ; (ii) we expand all terms consistently to linear order in \mathbf{J} ; and (iii) we define scaling variables in a way analogous to that shown in Eq. (2.23).

As a result of these manipulations, we arrive at the following hypothesis for the continuous part of the order parameter:

$$W^s(\hat{k}) = q \int_0^\infty d\theta e^{-\hat{k}^2/\epsilon\theta} \left(\pi(\theta) - \frac{\zeta(\theta)}{\epsilon} \mathbf{k}^0 \cdot \mathbf{J} \cdot \mathbf{k}^0 - \frac{\varpi(\theta)}{\epsilon} \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{J} \cdot \mathbf{k}^\alpha \right). \quad (3.30)$$

Here, $\zeta(\theta)$ and $\varpi(\theta)$ are new scaling functions, which describe the change in the continuous part of the order parameter due to the deformation. They are unknown at this point, but they will be determined later by demanding that the hypothesis (3.30) satisfy the stationary point equations for the deformed system, Eq. (3.11).

The motivation for the hypothesis, Eq. (3.30), can be rephrased in a more compact way as follows. Let us assume that for small strains $W^s(\hat{k})$ is unchanged by a rotation of the coordinate system (or, equivalently, by simultaneous rotations of \mathbf{S} and \hat{k}). This is evidently true for $W^u(\hat{k})$ (which is a function of \hat{k}^2). Therefore the difference between the two quantities $W^s(\hat{k})$ and $W^u(\hat{k})$ has the same property. If we further assume permutation symmetry among replicas $\alpha = 1, \dots, n$, this difference can only contain, up to lowest nontrivial order in the deformation and in the wave vectors, the following terms: (i) the product of an invariant linear function of \mathbf{J} and a linear combination of a constant, $(\mathbf{k}^0)^2$, and $\sum_{\alpha=1}^n (\mathbf{k}^\alpha)^2$; (ii) a linear function of $\mathbf{k}^0 \cdot \mathbf{J} \cdot \mathbf{k}^0$; (iii) a linear function of $\sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{J} \cdot \mathbf{k}^\alpha$; and (iv) a linear function of $(\sum_{\alpha=1}^n \mathbf{k}^\alpha) \cdot \mathbf{J} \cdot (\sum_{\beta=1}^n \mathbf{k}^\beta)$. The only quantity linear in \mathbf{J} and

invariant under rotations is $\text{tr} \mathbf{J}$, which is zero for infinitesimal shear strains, as mentioned above. In addition, by using Eq. (3.29), any term of type (iv) is reduced to a term of type (ii). Thus only terms of type (ii) and (iii) are left, and we recover Eq. (3.30). Note that in Ref. [4] the term (ii) was omitted from Eq. (9); the results, however, are not altered by this omission.

F. Solving the stationary-point equations

We now show that the hypothesis proposed does indeed satisfy the stationary-point equations in the deformed system, provided that the gel fraction q and the scaling functions $\pi(\theta)$, $\zeta(\theta)$, and $\varpi(\theta)$ satisfy appropriate conditions.

In order to perform the summation over wave vectors in the stationary-point equation, Eq. (3.11), one has to take into account the fact that the sum excludes vectors in the one and zero replica sectors. For any expression $f_{\hat{k}}$ that is zero in the one replica sector, the following identity is valid in the large volume limit:

$$\overline{\sum_{\hat{k}} f_{\hat{k}}} = V \int_{\hat{k}} f_{\hat{k}} - \lim_{\hat{k} \rightarrow 0} f_{\hat{k}}. \quad (3.31)$$

To simplify our notation, we make use of the following shorthand:

$$\int_{\hat{k}} f_{\hat{k}} \equiv V^n \int \frac{d\hat{k}}{(2\pi)^{(1+n)d}} f_{\hat{k}}, \quad (3.32)$$

the factor V^n in front of the integral will be irrelevant in the replica limit $n \rightarrow 0$, and we will ignore it from now on. Then the stationary point equation for the deformed system can be rewritten as:

$$0 = 2(3q - \epsilon + \frac{1}{2}|\hat{k}|^2)\Omega_{\hat{k}} - 3V \int_{\hat{p}} \Omega_{\hat{p}} \Omega_{\hat{k}-\hat{p}}. \quad (3.33)$$

Two observations are in order here. One is technical, namely that the volume prefactor in the second term, although it might appear dangerous, is in fact compensated by a factor of $1/V$ coming from the integrand. The second is more profound: at this point in the argument, all explicit dependence on the deformation has been removed from the stationary point equation. The only dependence that remains resides in the fact that the order parameter field entering in it has to be consistent with the boundary conditions for the strained system, i.e., it must be chosen so that for a system of large but finite volume the order parameter is nonzero for replicated wave vectors that belong to the discrete set R^s rather than R^u . This restriction has nontrivial effects: it will be shown in the penultimate paragraph in this section that a proposed order parameter of the form given by Eq. (2.13a), which would be perfectly acceptable if one completely neglected the discreteness of the set R^s , must be rejected because it cannot simultaneously satisfy the boundary conditions and depend continuously on the strain.

By inserting the hypothesis for the order parameter, Eqs. (3.27b) and (3.30), into the stationary-point condition, Eq. (3.33), and expanding to first order in the strain, we obtain

$$\begin{aligned}
0 = & \delta_{\tilde{\mathbf{k}}^s, \mathbf{0}} \left\{ 2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\theta \pi(\theta) e^{-\hat{k}^2/\epsilon\theta} - 3q^2 \int_{\hat{p}} \int_0^\infty d\theta_1 \pi(\theta_1) \int_0^\infty d\theta_2 \pi(\theta_2) e^{-\hat{p}^2/\epsilon\theta_1} e^{-(\hat{k}-\hat{p})^2/\epsilon\theta_2} \right. \\
& \times \int d\mathbf{m} e^{i\mathbf{m}\cdot\tilde{\mathbf{p}}^s} - 2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\theta \frac{\zeta(\theta)}{\epsilon} \mathbf{k}^0 \cdot \mathbf{J} \cdot \mathbf{k}^0 e^{-\hat{k}^2/\epsilon\theta} + 6q^2 \int_{\hat{p}} \int_0^\infty d\theta_1 \frac{\zeta(\theta_1)}{\epsilon} \mathbf{p}^0 \cdot \mathbf{J} \cdot \mathbf{p}^0 \\
& \times \int_0^\infty d\theta_2 \pi(\theta_2) e^{-\hat{p}^2/\epsilon\theta_1} e^{-(\hat{k}-\hat{p})^2/\epsilon\theta_2} \int d\mathbf{m} e^{i\mathbf{m}\cdot\tilde{\mathbf{p}}^s} - 2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\theta \frac{\varpi(\theta)}{\epsilon} \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{J} \cdot \mathbf{k}^\alpha e^{-\hat{k}^2/\epsilon\theta} \\
& \left. + 6q^2 \int_{\hat{p}} \int_0^\infty d\theta_1 \frac{\varpi(\theta_1)}{\epsilon} \sum_{\alpha=1}^n \mathbf{p}^\alpha \cdot \mathbf{J} \cdot \mathbf{p}^\alpha \int_0^\infty d\theta_2 \pi(\theta_2) e^{-\hat{p}^2/\epsilon\theta_1} e^{-(\hat{k}-\hat{p})^2/\epsilon\theta_2} \int d\mathbf{m} e^{i\mathbf{m}\cdot\tilde{\mathbf{p}}^s} \right\}. \quad (3.34)
\end{aligned}$$

Here we have made use of the notation

$$\tilde{\mathbf{k}}^s \equiv \mathbf{k}^0 + \mathbf{S} \cdot \sum_{\alpha=1}^n \mathbf{k}^\alpha, \quad (3.35)$$

and the integral representation for the Kronecker delta

$$\delta_{\mathbf{k}, \mathbf{0}} = \frac{1}{V} \int d\mathbf{m} e^{i\mathbf{m}\cdot\mathbf{k}}. \quad (3.36)$$

After performing the integrations, first over \hat{p} , then over \mathbf{m} , Eq. (3.34) reduces to

$$\begin{aligned}
0 = & \left[2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\theta \pi(\theta) e^{-\hat{k}^2/\epsilon\theta} - 3q^2 \int_0^\infty d\theta_1 \int_0^\infty d\theta_2 \pi(\theta_1) \pi(\theta_2) e^{-\hat{k}^2/\epsilon(\theta_1+\theta_2)} \right] \\
& - \frac{1}{\epsilon} \{ \mathbf{k}^0 \cdot \mathbf{J} \cdot \mathbf{k}^0 \} \left[2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\theta \zeta(\theta) e^{-\hat{k}^2/\epsilon\theta} - 6q^2 \int_0^\infty d\theta_1 \int_0^\infty d\theta_2 \left(\frac{\theta_1}{\theta_1+\theta_2} \right)^2 \zeta(\theta_1) \pi(\theta_2) e^{-\hat{k}^2/\epsilon(\theta_1+\theta_2)} \right] \\
& - \frac{1}{\epsilon} \left\{ \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{J} \cdot \mathbf{k}^\alpha \right\} \left[2(3q^2 - \epsilon q + q\hat{k}^2/2) \int_0^\infty d\theta \varpi(\theta) e^{-\hat{k}^2/\epsilon\theta} - 6q^2 \int_0^\infty d\theta_1 \int_0^\infty d\theta_2 \left(\frac{\theta_1}{\theta_1+\theta_2} \right)^2 \varpi(\theta_1) \pi(\theta_2) e^{-\hat{k}^2/\epsilon(\theta_1+\theta_2)} \right]. \quad (3.37)
\end{aligned}$$

Now, what conditions are forced on the unknown quantities q , $\pi(\theta)$, $\zeta(\theta)$, and $\varpi(\theta)$ by this stationary-point equation? First, by taking the limit $\hat{k}^2 \rightarrow 0$ we recover the condition for the gel fraction

$$0 = -2q\epsilon + 3q^2, \quad (3.38)$$

which implies that $q = 2\epsilon/3$ for $\epsilon > 0$. It is not surprising that we obtain the same gel fraction for the amorphous solid state as in the unstrained system, as in our motivation for the order parameter hypothesis we assumed that the monomers that were localized in the strained system would also be those that were localized in the unstrained system.

Next, we observe that demanding that Eq. (3.37) be valid for all $\hat{k} \in R^s$ is equivalent to the above equation for the gel fraction, together with the following integro-differential equations for the scaling functions $\pi(\theta)$, $\zeta(\theta)$, and $\varpi(\theta)$:

$$\frac{\theta^2}{2} \frac{d\pi}{d\theta} = (1-\theta)\pi(\theta) - \int_0^\theta d\theta' \pi(\theta') \pi(\theta-\theta'), \quad (3.39a)$$

$$\frac{\theta^2}{2} \frac{d\zeta}{d\theta} = (1-\theta)\zeta(\theta) - \frac{2}{\theta^2} \int_0^\theta d\theta' \theta'^2 \zeta(\theta') \pi(\theta-\theta'), \quad (3.39b)$$

$$\frac{\theta^2}{2} \frac{d\varpi}{d\theta} = (1-\theta)\varpi(\theta) - \frac{2}{\theta^2} \int_0^\theta d\theta' \theta'^2 \varpi(\theta') \pi(\theta-\theta'). \quad (3.39c)$$

As for the boundary conditions satisfied by the scaling functions $\pi(\theta)$, $\zeta(\theta)$, and $\varpi(\theta)$, they are obtained by studying the values of the order parameter in different regions of \hat{k} space. First, as noticed in Sec. II F 4 for the case of $p(\tau)$, the fact that the order parameter is unity at the origin (i.e., $\hat{k} = \hat{0}$) determines the following normalization condition for $\pi(\theta)$:

$$\int_0^\infty d\theta \pi(\theta) = 1. \quad (3.40)$$

Next, to derive boundary conditions for $\zeta(\theta)$ and $\varpi(\theta)$ we observe that, from Eq. (2.4),

$$\lim_{(\mathbf{k}^1)^2 + \dots + (\mathbf{k}^g)^2 \rightarrow \infty} \Omega_{\mathbf{k}^1, \dots, \mathbf{k}^g} = 0, \quad (3.41)$$

and consequently that

$$\lim_{\hat{k}^2 \rightarrow \infty} \Omega_{\hat{k}} = 0. \quad (3.42)$$

In order to benefit from this information, we perform the change of variables

$$\theta \rightarrow y \equiv \hat{k}^2 / \epsilon \theta \quad (3.43)$$

in Eq. (3.30), thus obtaining

$$W^s(\hat{k}) = q \int_0^\infty dy e^{-y} \left\{ \frac{\epsilon}{\hat{k}^2} \tilde{\pi} \left(\frac{\hat{k}^2}{\epsilon y} \right) - \tilde{\zeta} \left(\frac{\hat{k}^2}{\epsilon y} \right) \mathbf{x}^0 \cdot \mathbf{J} \cdot \mathbf{x}^0 - \tilde{\varpi} \left(\frac{\hat{k}^2}{\epsilon y} \right) \sum_{\alpha=1}^n \mathbf{x}^\alpha \cdot \mathbf{J} \cdot \mathbf{x}^\alpha \right\}. \quad (3.44)$$

Here, we have defined the functions $\tilde{\pi}(\theta)$, $\tilde{\zeta}(\theta)$, and $\tilde{\varpi}(\theta)$ by

$$\tilde{\pi}(\theta) \equiv \theta^2 \pi(\theta), \quad \tilde{\zeta}(\theta) \equiv \theta^2 \zeta(\theta), \quad \tilde{\varpi}(\theta) \equiv \theta^2 \varpi(\theta), \quad (3.45)$$

and the unit vector $\hat{\mathbf{x}} = \{\mathbf{x}^0, \dots, \mathbf{x}^n\}$ by

$$\mathbf{x}^\alpha \equiv \frac{\mathbf{k}^\alpha}{\sqrt{\hat{k}^2}} \quad (\alpha = 0, \dots, n). \quad (3.46)$$

From the expression (3.44) for the order parameter hypothesis, and the exponential decay of $\pi(\theta)$ for $\theta \rightarrow \infty$, it follows that

$$\lim_{\hat{k}^2 \rightarrow \infty} \Omega_{\hat{k}} = - \lim_{\theta \rightarrow \infty} \left(\tilde{\zeta}(\theta) \mathbf{x}^0 \cdot \mathbf{J} \cdot \mathbf{x}^0 + \tilde{\varpi}(\theta) \sum_{\alpha=1}^n \mathbf{x}^\alpha \cdot \mathbf{J} \cdot \mathbf{x}^\alpha \right). \quad (3.47)$$

However, this limit must be zero regardless of the direction of $\hat{\mathbf{x}}$, and consequently we obtain the following boundary conditions for $\zeta(\theta)$ and $\varpi(\theta)$:

$$\lim_{\theta \rightarrow \infty} \theta^2 \zeta(\theta) = 0, \quad (3.48a)$$

$$\lim_{\theta \rightarrow \infty} \theta^2 \varpi(\theta) = 0. \quad (3.48b)$$

To obtain boundary conditions at $\theta=0$, one only needs to examine the integro-differential equations (3.39a), (3.39b), and (3.39c) themselves. Near the origin, the integral terms can be neglected, and all three equations reduce to the form:

$$\frac{\theta^2}{2} \frac{df}{d\theta} = (1 - \theta)f(\theta), \quad (3.49)$$

where f stands for π , ζ , or ϖ . This is a first-order linear differential equation having the solution

$$f(\theta) = A \frac{e^{-2/\theta}}{\theta^2}, \quad (3.50)$$

with A an arbitrary constant. Consequently, all three scaling functions vanish rapidly at the origin.

As the reader has probably already noticed, the integro-differential equations and the boundary conditions that apply to both $\zeta(\theta)$ and $\varpi(\theta)$ are linear and homogeneous. This implies that one of two possibilities must hold for each one of these functions: either it is identically zero, or it is only determined up to an arbitrary multiplicative constant. [By contrast, in the case of $\pi(\theta)$, the integro-differential equation (3.39a) is nonlinear, and the condition of Eq. (3.40) is linear but inhomogeneous, and the scale of the solution is well determined.] The latter possibility does not seem to be easy to justify on physical grounds, as it would imply that the stationary-point equations leave the order parameter undetermined. In fact, if this were the case, there would be a continuous family of order parameters such that the continuous parts $W^s(\hat{k})$ for members of the family differ to varying degrees from the continuous part of the order parameter corresponding to the amorphous solid state of the unstrained system. One could, however, imagine that we are missing some additional physical constraint that fixes the scale of these two functions, and therefore the above argument is suggestive but not conclusive. To settle the issue of which of the two possibilities holds for $\zeta(\theta)$ and $\varpi(\theta)$, we show, in Appendix A, by analytic manipulation of the integro-differential equations and boundary conditions, that both $\zeta(\theta)$ and $\varpi(\theta)$ are identically zero.

The fact that both $\zeta(\theta)$ and $\varpi(\theta)$ are identically null implies the *a priori* most surprising result of this paper: the continuous part of the order parameter *does not change* to first order in the strain, i.e., $W^s(\hat{k}) = W^u(\hat{k})$. This conclusion is consistent with the phantom network picture [8,12]. It also suggests that $W^s(\hat{k}) = W^u(\hat{k})$ for finite (and not merely infinitesimal) deformations. Indeed, our order-parameter hypothesis turns out to satisfy the stationary-point equation for arbitrarily strained systems.

To see this, let us return to the stationary point equation (3.33). As was mentioned earlier, Eq. (3.33) applies both for the unstrained and for the strained systems, the only difference between the two cases being that in the unstrained case the ‘‘external’’ replicated wave vector \hat{k} belongs to the discrete set R^u , whereas in the strained case \hat{k} belongs to the set R^s . By inserting the form for the order parameter given by Eq. (3.27b), but now with $W^s(\hat{k}) = W^u(\hat{k})$ [i.e., given by Eq. (3.30) with $\zeta(\theta) = \varpi(\theta) = 0$] we find that the stationary point equation is satisfied provided $\pi(\theta)$ satisfies Eq. (2.24).

One way of understanding this result is to consider that in order for the shape of the fluctuation region to be affected by the externally imposed strain, this strain has to be somehow communicated to the individual monomers. This is most likely the effect of the deformation of the ‘‘cage’’ of surrounding polymers that form the local environment at each point. However, when the interlocking of loops is neglected, as in the present calculation, this ‘‘cage’’ exerts no effect. Therefore, this result should be taken with caution, as its validity might not extend beyond the region near the transi-

tion, in which the approximation of neglecting the interlocking of loops is fully justified.

At first sight, it might appear possible to propose alternative hypothesis for the structure of the deformed amorphous solid state. One possible alternative hypothesis would be to assume that the order parameter is completely unchanged when the system is deformed. However, this is not quite correct. In addition to the stationary-point equation, the order parameter has to satisfy the boundary conditions in real space for the deformed system. This means that the hypothesis of Eq. (3.27b) for $\Omega_{\hat{k}}$ is physically meaningful only for \hat{k} belonging to the set of allowed replicated wave vectors R^s . If the order parameter corresponding to the unstrained system were retained, there would be a factor $\delta_{\mathbf{k},0}$ in the term corresponding to the localized monomers that would be zero for generic values of the deformation matrix \mathbf{S} unless *both* $\mathbf{k}^0 = \mathbf{0}$ and $\sum_{\alpha=1}^n \mathbf{k}^\alpha = \mathbf{0}$. As in the undeformed system this same factor is nonzero for $\sum_{\alpha=1}^n \mathbf{k}^\alpha = -\mathbf{k}^0 \neq \mathbf{0}$, this would give rise to an unphysical discontinuity in the order parameter as a function of the deformation. On the other hand, the modified delta factor $\delta_{\tilde{\mathbf{k}},0}$ that appears in Eq. (3.27b) takes into account the shift in the reciprocal lattice due to the deformation, and displays no such discontinuity. In mathematical terms, finding the intersection between the set of measure zero in Fourier space that corresponds to macroscopically translation invariant states and the discrete set of points allowed by the strained boundary conditions plays a crucial role in selecting the correct order parameter for the deformed system. In more physical terms, the order parameter needs to somehow “remember” that when the system was cross linked, it had a different shape. The factor $\delta_{\tilde{\mathbf{k}},0}$ is the one that keeps this memory, by correlating the $\alpha=0$ replica (associated with the cross linking) with the replicas $\alpha = 1, \dots, n$ (associated with the present, strained state of the system) in a way that explicitly depends on the strain. If this information was lost, we would be computing the free energy of a system that was cross linked *after* being deformed, and this would be independent of the deformation.

A second possibility would be to keep for the order parameter the form proposed in Eq. (3.27b), and to choose for its continuous part the form $W^s(\hat{k}) = W^u(\{\mathbf{k}^0, \mathbf{S} \cdot \mathbf{k}^1, \dots, \mathbf{S} \cdot \mathbf{k}^n\})$ [37]. Although this hypothesis might appear natural, since it represents an affine deformation of the localization clouds for each monomer [in the manner of Eq. (3.19)], it turns out that it is not a stationary point of the free energy [38]. This nonstationary point does not represent a physical state because the thermal weights of the configurations are not peaked around it. Indeed, it is easy to show by direct insertion in Eq. (3.33) that this hypothesis would be a stationary point for a modified free energy in which the term quadratic in $\Omega_{\hat{k}}$ had a modified coefficient $[-\epsilon + \frac{1}{2}(\mathbf{k}^0)^2 + (\mathbf{S} \cdot \mathbf{k}^1)^2 + \dots + (\mathbf{S} \cdot \mathbf{k}^n)^2]$ instead of $(-\epsilon + \hat{k}^2/2)$. In more physical terms, since this state describes monomers that fluctuate in regions whose shape is not spherical, it fails to maximize the entropy, given the constraints imposed on the system.

G. Change in free energy with deformation; shear modulus

We now have all the ingredients necessary to calculate the change in the free energy Δf , to leading order in ϵ , due to the deformation of the system:

$$\Delta f = d \lim_{n \rightarrow 0} \{ \mathcal{F}_n^s(\{\Omega_{\hat{k}}^s\}) - \mathcal{F}_n^u(\{\Omega_{\hat{k}}^u\}) \}. \quad (3.51)$$

Here $\Omega_{\hat{k}}^s$ and $\Omega_{\hat{k}}^u$ are, respectively, the stationary-point values of the order parameter for the strained and unstrained systems. Similarly, \mathcal{F}_n^s and \mathcal{F}_n^u , respectively, denote the free-energy functionals for the strained and unstrained systems. As we show in Appendix B, the free-energy change due to the deformation is

$$\Delta f = \frac{2}{27} \epsilon^3 \text{tr}(\mathbf{S}^2 - \mathbf{I}). \quad (3.52)$$

Thus we can extract the value of the static shear modulus E of the amorphous solid state near the solidification transition (with physical units restored):

$$E = k_B T N C \epsilon^3, \quad (3.53)$$

where k_B is Boltzmann’s constant, T is the temperature, and C is a model-dependent positive constant. Hence, we see that the static shear modulus near the vulcanization transition is characterized by the exponent $t=3$, in agreement with the classical result [5,2]. A simple scaling argument, viz., that the modulus should scale as two powers of the order parameter (q^2) and two powers of the gradient (ξ_{typ}^{-2}), leads to the same value for the exponent t .

IV. CONCLUDING REMARKS

In this paper we have presented a microscopic derivation of the static elastic response of a system of randomly cross-linked macromolecules near the amorphous-solidification transition.

From the technical point of view, we have modeled the deformation of the system by changing the boundary conditions in real space. A point that required special care was how to include in our formulation the physical information that the system had been cross linked *before* it was deformed. This results in an asymmetry in the replica formulation of the problem: in the case we are studying, replica $\alpha = 0$ describes the system *before* the deformation is applied, and replicas $\alpha = 1, \dots, n$ describe the system in its actual state of deformation.

The physical picture that emerges from the results of this paper has the following features: (i) the amorphous-solid state, which had been previously shown to be characterized structurally by the localization of a nonzero fraction of particles, is also characterized by having a nonzero static shear modulus; (ii) the static shear modulus scales as the third power of the excess cross-link density (beyond its value at the transition) [39]; and (iii) the form of localization exhibited by the particles is left unchanged by the strain.

A possible explanation for the spherical localization regions that the particles exhibit even under externally applied stress might be that in the regime near the transition most monomers in the infinite cluster are very loosely connected, and thus their behavior is dominated by the maximization of entropy, which is obtained by allowing them to fluctuate in all directions. It is not implausible that strain-induced changes in the pattern of localization would emerge from a

more detailed analysis of the effects of the excluded-volume interaction, at least at higher cross-link densities. This is because at higher crosslinks densities, the macromolecular network is more tightly bound, and the topological barriers generated by interlocking of macromolecular loops are more significant.

Finally, let us point out that since the treatment presented here only depends on the form of the free-energy functional [26] near the transition, and not any specific semimicroscopic model, the approach to elasticity described here should be generally applicable not only to systems of randomly cross-linked flexible macromolecules, but also to other equilibrium amorphous solid forming systems.

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APPENDIX A: CORRECTION TO THE ORDER PARAMETER UNDER STRAIN

In this appendix we show that the only solution to Eq. (3.39b) that satisfies the boundary condition Eq. (3.48a) is the null function $\zeta(\theta) \equiv 0$ for all θ . Our approach is to assume that a nonzero solution exists, and then to arrive at a contradiction. As the equations and boundary conditions are identical for $\zeta(\theta)$ and $\varpi(\theta)$, showing that $\zeta(\theta)$ is identically null would imply that the same holds for $\varpi(\theta)$.

It is convenient to work with $\tilde{\zeta}(\theta)$ instead of $\zeta(\theta)$. In terms of $\tilde{\zeta}(\theta)$, the integro-differential equation reads:

$$\frac{\theta^2}{2} \frac{d\tilde{\zeta}}{d\theta} = \tilde{\zeta}(\theta) - 2 \int_0^\theta d\theta' \tilde{\zeta}(\theta') \pi(\theta - \theta'). \quad (\text{A1})$$

The boundary condition is simply

$$\lim_{\theta \rightarrow \infty} \tilde{\zeta}(\theta) = 0. \quad (\text{A2})$$

It turns out that it is possible to derive a simple differential equation for the Laplace transform $\hat{\varrho}(s)$ of the function

$$\varrho(\theta) \equiv \frac{d\tilde{\zeta}}{d\theta}. \quad (\text{A3})$$

By starting with Eq. (A1), and using properties of the Laplace transform, one obtains (after some algebra) the equation

$$\frac{d^2 \hat{\varrho}(s)}{ds^2} = \frac{2}{s} \hat{\varrho}(s) (1 - \hat{\pi}(s)), \quad (\text{A4})$$

and the boundary condition

$$\hat{\varrho}(0) = \int_0^\infty d\theta \frac{d\tilde{\zeta}}{d\theta} = \lim_{\theta \rightarrow \infty} \tilde{\zeta}(\theta) - \tilde{\zeta}(0) = 0. \quad (\text{A5})$$

The function $\hat{\pi}(s)$ appearing in Eq. (A4) is the Laplace transform of the scaled probability distribution $\pi(\theta)$ for the unstrained system. By using its expansion for small s , namely

$$\hat{\pi}(s) = 1 - s \langle \theta \rangle_\pi + O(s^2), \quad (\text{A6})$$

one can immediately show that Eq. (A4) has a regular singular point at the origin, and thence use the Frobenius method [40] to obtain the asymptotic forms near the origin of two linearly independent solutions:

$$\hat{\varrho}_1(s) = s - s^2 + O(s^3), \quad (\text{A7a})$$

$$\hat{\varrho}_2(s) = \frac{1}{2} - s \ln s + O(s). \quad (\text{A7b})$$

Any solution of Eq. (A4) can be written as a linear combination of these two. Due to the boundary condition (A5), the coefficient of $\hat{\varrho}_2(s)$ must be zero. Therefore $\hat{\varrho}(s)$ is some real multiple of $\hat{\varrho}_1(s)$.

We have not been able to integrate Eq. (A4) analytically. However, it is straightforward to integrate it numerically, using the behavior given by Eq. (A7a) as the initial condition. The numerical solution thus obtained diverges at infinity; but as $\hat{\varrho}(s)$ is the Laplace transform of a function, it goes to zero at infinity. Therefore, by assuming that a non-zero solution can be found satisfying both Eq. (3.39b) and Eq. (3.48a), we have arrived at a contradiction.

APPENDIX B: FREE-ENERGY CHANGE UNDER STRAIN

We need to compute the difference between the free energy of the deformed system, $\mathcal{F}_n^s(\{\Omega_{\hat{k}}^s\})$, and the undeformed system, $\mathcal{F}_n(\{\Omega_{\hat{k}}^u\})$, as a function of the deformation matrix \mathbf{S} . From Eq. (3.10) we see that $\mathcal{F}_n^s(\{\Omega_{\hat{k}}^s\})$ contains both a quadratic and a cubic term in $\Omega_{\hat{k}}^s$. We first study the quadratic term. We make use of Eq. (3.31) to write, in the large volume limit,

$$\bar{\sum}_{\hat{k} \in R^s} \left(-\epsilon + \frac{|\hat{k}|^2}{2} \right) |\Omega_{\hat{k}}|^2 \quad (\text{B1})$$

$$= \epsilon \lim_{\hat{k} \rightarrow \hat{0}} |\Omega_{\hat{k}}|^2 + V \int_{\hat{k}} \left(-\epsilon + \frac{|\hat{k}|^2}{2} \right) |\Omega_{\hat{k}}|^2. \quad (\text{B2})$$

The term associated with the limit $\hat{k} \rightarrow \hat{0}$ has the value ϵq^2 , independent of \mathbf{S} , and is thus irrelevant for the present purposes. We concentrate on computing the integral

$$I \equiv V \int_{\hat{k}} \left(-\epsilon + \frac{|\hat{k}|^2}{2} \right) |\Omega_{\hat{k}}|^2. \quad (\text{B3})$$

To make the analysis more digestible, we define the notations

$$\int_{\theta} \dots \equiv \int_0^\infty d\theta \dots \pi(\theta) \quad \text{and} \quad a \equiv \frac{2}{\epsilon} \left(\frac{1}{\theta_1} + \frac{1}{\theta_2} \right). \quad (\text{B4})$$

The first step is to insert the form of the order parameter for the solid phase, Eqs. (3.27b) and (3.30), and use the fact that $\zeta(\theta) = \varpi(\theta) \equiv 0$. We then have

$$\begin{aligned}
I &= V \int_{\hat{k}} \left(-\epsilon + \frac{|\hat{k}|^2}{2} \right) \left(q \delta_{\tilde{\mathbf{k}}^s, \mathbf{0}} \int_{\theta} e^{-\hat{k}^2/\epsilon\theta} \right)^2 \\
&= q^2 \int_{\theta_1} \int_{\theta_2} \int_{\hat{k}} \left(-\epsilon + \frac{|\hat{k}|^2}{2} \right) e^{-a\hat{k}^2/2} \\
&\quad \times \int d\mathbf{m} e^{i\mathbf{m} \cdot (\mathbf{k}^0 + \mathbf{S} \cdot \sum_{\alpha=1}^n \mathbf{k}^\alpha)} \\
&= q^2 V^n \int_{\theta_1} \int_{\theta_2} \left(-\epsilon - \frac{d}{da} \right) \int d\mathbf{m} \frac{e^{-m^2/2a}}{(2\pi a)^{d/2}} \left(\frac{e^{-(\mathbf{S}\mathbf{m})^2/2a}}{(2\pi a)^{d/2}} \right)^n \\
&= q^2 V^n \int_{\theta_1} \int_{\theta_2} \left(-\epsilon - \frac{d}{da} \right) \{ (2\pi a)^{nd} [\det(\mathbf{I} + n\mathbf{S}^2)] \}^{-1/2}
\end{aligned} \tag{B5}$$

$$= q^2 (1 + n \ln V) (-\epsilon + O(n)) \left(1 - \frac{n}{2} \text{tr}(\mathbf{S}^2) \right) + O(n^2), \tag{B6}$$

where we have only kept the lowest two powers of the number n of replicas in the result. The change in this term due to the deformation is

$$\Delta I = \frac{n}{2} \epsilon q^2 \text{tr}(\mathbf{S}^2 - \mathbf{I}) + O(n^2). \tag{B7}$$

Now, to compute the cubic term, we use Eq. (3.31) repeatedly to obtain

$$\begin{aligned}
& - \sum_{\hat{k}_1 \hat{k}_2 \hat{k}_3 \in R^s} \overline{\Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{\hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}} \\
&= -V^2 \int_{\hat{k}_1} \int_{\hat{k}_2} \overline{\Omega_{\hat{k}_1} \Omega_{\hat{k}_2} \Omega_{-\hat{k}_1 - \hat{k}_2}} + 3Vq \int_{\hat{k}} |\Omega_{\hat{k}}|^2 - 2q^3.
\end{aligned} \tag{B8}$$

Next, by inserting the form [Eqs. (3.27b) and (3.30)] of the order parameter, the first term on the right-hand side yields

$$\begin{aligned}
J &\equiv -q^3 \int_{\theta_1} \int_{\theta_2} \int_{\theta_3} \int_{\hat{k}_1} \int_{\hat{k}_2} e^{-\hat{k}_1^2/\epsilon\theta_1 - \hat{k}_2^2/\epsilon\theta_2 - (\hat{k}_1 + \hat{k}_2)^2/\epsilon\theta_3} \\
&\quad \times \int d\mathbf{m}_1 e^{i\mathbf{m}_1 \cdot (\mathbf{k}_1^0 + \mathbf{S} \cdot \sum_{\alpha=1}^n \mathbf{k}^\alpha)} \int d\mathbf{m}_2 e^{i\mathbf{m}_2 \cdot (\mathbf{k}_2^0 + \mathbf{S} \cdot \sum_{\alpha=1}^n \mathbf{k}^\alpha)} \\
&= -q^3 V^{2n} \int_{\theta_1} \int_{\theta_2} \int_{\theta_3} \int d\mathbf{m}_1 \int d\mathbf{m}_2
\end{aligned}$$

$$\begin{aligned}
& \times \frac{\exp[-\frac{1}{2}(\mathbf{m}_1 \mathbf{m}_2) \mathbf{A} \begin{pmatrix} \mathbf{m}_1 \\ \mathbf{m}_2 \end{pmatrix}]}{(4\pi^2 \det \mathbf{A})^{d/2}} \\
& \times \left(\frac{\exp[-\frac{1}{2}(\mathbf{S}\mathbf{m}_1 \mathbf{S}\mathbf{m}_2) \mathbf{A} \begin{pmatrix} \mathbf{S}\mathbf{m}_1 \\ \mathbf{S}\mathbf{m}_2 \end{pmatrix}]}{(4\pi^2 \det \mathbf{A})^{d/2}} \right)^n,
\end{aligned} \tag{B9}$$

where the 2×2 matrix \mathbf{A} is the inverse of the matrix

$$\frac{2}{\epsilon} \begin{pmatrix} \frac{1}{\theta_1} + \frac{1}{\theta_3} & \frac{1}{\theta_3} \\ \frac{1}{\theta_2} & \frac{1}{\theta_2} + \frac{1}{\theta_3} \end{pmatrix}. \tag{B10}$$

By performing the Gaussian integration over \mathbf{m}_1 and \mathbf{m}_2 , and expanding in powers of n , we obtain

$$\begin{aligned}
J &= -q^3 V^{2n} \int_{\theta_1} \int_{\theta_2} \int_{\theta_3} (4\pi^2 \det \mathbf{A})^{-nd/2} [\det(\mathbf{I} + n\mathbf{S}^2)]^{-1} \\
&= -q^3 (1 + 2n \ln V) (1 - n \text{tr}(\mathbf{S}^2)) (1 + O(n)) + O(n^2).
\end{aligned} \tag{B11}$$

For this term, the change due to the deformation is

$$\Delta J = nq^3 \text{tr}(\mathbf{S}^2 - \mathbf{I}) + O(n^2). \tag{B12}$$

Similarly, the second term on the right-hand side of Eq. (B8) can be evaluated to yield

$$\begin{aligned}
K &= 3Vq \int_{\hat{k}} |\Omega_{\hat{k}}|^2 \\
&= 3q^3 (1 + n \ln V) \left(1 - \frac{n}{2} \text{tr}(\mathbf{S}^2) \right) (1 + O(n)) + O(n^2),
\end{aligned} \tag{B13}$$

and its change under deformation is

$$\Delta K = -\frac{3n}{2} q^3 \text{tr}(\mathbf{S}^2 - \mathbf{I}) + O(n^2). \tag{B14}$$

By combining the contributions given in Eqs. (B7), (B12), and (B14), dividing by the number n of replicas, and taking into account the fact that $q = 2\epsilon/3$, we obtain the free-energy change due to the deformation given in Eq. (3.52).

[1] In the vulcanization of macromolecular melts, the width of the critical region, in which mean-field theory fails, is of the order of $L^{(d-2)/(d-6)}$ (where L is the length of a macromolecule), i.e., it vanishes in the limit of long macromolecules for dimen-

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- [31] As is conventional in statistical mechanics, we use the same notation, Ω , for the equilibrium value of the order parameter and for the fluctuating variable (of which it is the expectation value and which features in the Landau free energy). Which meaning is implied can be readily ascertained from the context.
- [32] One could speculate that the solution to the stationary-point equations is not unique, and that both a solution dominated by long localization lengths and a second solution dominated by shorter localization lengths are present. Even in that case, the physical argument already given would strongly suggest that the “long-localization-length” solution is the physically relevant one. Besides, to the best of our knowledge, no second solution has been found, despite attempts by the authors and by others.
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- [34] For any ϵ dependence to appear in the scaling function $\pi(\theta)$, terms of order ϵ^4 would have to be included in the free-energy functional, or equivalently terms of order ϵ^3 would have to be included in the stationary-point equation.
- [35] To see this, let us point out first that *any* real matrix \mathbf{S} can be decomposed as a product $\mathbf{S}=\mathbf{O}\mathbf{N}$, where \mathbf{O} is a real unitary (i.e., real, orthogonal) matrix and \mathbf{N} is a real, symmetric matrix with all its eigenvalues non-negative (see, e.g., Ref. [36], Chap. 9, particularly theorem 14). Clearly, the symmetric matrix \mathbf{N} can now be diagonalized by an orthogonal transformation \mathbf{V} : $\mathbf{N}=\mathbf{V}^T\bar{\mathbf{S}}\mathbf{V}$ (here, \mathbf{V}^T is the transpose of \mathbf{V}). Therefore, by defining $\mathbf{U}=\mathbf{O}\mathbf{V}^T$, we obtain the desired decomposition. As \mathbf{S} describes a deformation of an elastic solid, it is continuously connected to the identity. Consequently, the matrices \mathbf{U} and \mathbf{V} are also continuously connected to the identity, and therefore belong to the proper rotation subgroup.
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- [38] This (nonstationary) point has a replicated free energy that is identical to that of the stationary point for the unstrained system, i.e., *lower* than the one for the stationary point corresponding to the strained system. This apparently paradoxical situation is in fact quite common in calculations with replicas, and it sometimes has to do with the presence of a Hessian matrix for the true (stable) minimum of the free energy that has, in the $n\rightarrow 0$ limit, a negative number of degenerate positive eigenvalues. [See, e.g., Sec. I.3 of M. Mezard, G. Parisi, and M. Virasoro, *Spin Glass Theory and Beyond* (World Scientific, Singapore, 1987)].
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