

## Statistical mechanics of permanent random atomic and molecular networks: Structure and heterogeneity of the amorphous solid state

Konstantin A. Shakhnovich\* and Paul M. Goldbart†

*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080*

(Received 19 January 1999)

Under sufficient permanent random covalent bonding, a fluid of atoms or small molecules is transformed into an amorphous solid network. Being amorphous, local structural properties in such networks vary across the sample. A natural order parameter, resulting from a statistical-mechanical approach, captures information concerning this heterogeneity via a certain joint probability distribution. This joint probability distribution describes the variations in the positional and orientational localization of the particles, reflecting the random environments experienced by them, as well as further information characterizing the thermal motion of particles. A complete solution, valid in the vicinity of the amorphous solidification transition, is constructed essentially analytically for the amorphous solid order parameter, in the context of the random network model and approach introduced by Goldbart and Zippelius [*Europhys. Lett.* **27**, 599 (1994)]. Knowledge of this order parameter allows us to draw certain conclusions about the structure and heterogeneity of randomly covalently bonded atomic or molecular network solids in the vicinity of the amorphous solidification transition. *Inter alia*, the positional aspects of particle localization are established to have precisely the structure obtained previously in the context of vulcanized media, and results are found for the analog of the spin glass order parameter describing the orientational freezing of the bonds between particles. [S0163-1829(99)12229-X]

### I. INTRODUCTION AND OVERVIEW

The purpose of this paper is to address the statistical structure of the amorphous solid state via a simple model of a three-dimensional vitreous medium consisting of covalently bonded atoms (or low-molecular-weight molecules).<sup>1</sup> We shall do so essentially analytically by making use of techniques drawn from the field of the statistical mechanics of systems having quenched randomness.<sup>2</sup> The model of vitreous media on which we shall focus is that introduced by Goldbart and Zippelius,<sup>3</sup> which takes as ingredients a thermodynamically large number of particles between which some large number of permanent random covalent bonds are introduced. The quenched randomness is encoded in the information describing which pairs of particles are covalently bonded; the remaining (annealed) degrees of freedom correspond to the unconstrained positions of the particles and the orientations of the orbitals. This model exhibits a continuous equilibrium phase transition from the liquid state to the amorphous solid state when the density of introduced bonds exceeds a certain critical value. It is on the structure and heterogeneity of this state that we hope to shed some light.

As an example of the type of medium we have in mind, consider networks formed by the polycondensation of  $\text{Si}(\text{OH})_4$  molecules, during which  $\text{H}_2\text{O}$  is eliminated between pairs of hydroxyl (OH) groups on certain randomly selected pairs of  $\text{Si}(\text{OH})_4$  molecules so as to form Si-O-Si bonds. The amorphous solidification of such media has been studied in many experiments; we cite as an example those of Gauthier-Manuel *et al.*<sup>4</sup> As it is our intention to develop a rather general model of random networks, and to focus on universal properties, it is not necessary for us to incorporate the specific details of the medium. For example, we shall not

be accounting for the bond geometry associated with the so-called bridging oxygen atoms between the silicon atoms. In the model, both types of Si orbitals, those connected to hydroxyl groups and those connected to bridging oxygen atoms, will simply be referred to as “orbitals.” A second example of the type of media we have in mind is provided by amorphous silicon networks,<sup>1</sup> especially those in which hydrogen passivates bonds unconnected to other silicon atoms.

The structural characterization of the vitreous state that we shall construct will be statistical in nature, reflecting the intrinsic heterogeneity of the environments that the constituent particles in vitreous media inhabit. It will take the form of a *joint probability distribution* characterizing the fraction of particles that are localized in the vitreous state, and will describe the spatial extent of the thermal fluctuations in their positions, the degree and character of the thermal fluctuations in the orientations of the orbitals that are capable of participating in covalent bonds, and the strength and nature of the correlations between the thermal fluctuations in the particle positions and the orbital orientations. Moreover, rather than dealing with media having a specific architecture (i.e., a specific realization of introduced bonds), we shall consider an ensemble of architectures, all characterized by a common parameter governing the probability that a permanent chemical bond was formed between any pair of nearby orbitals.

A statistical description of an amorphous solid state has previously been developed and explored in the context of vulcanized (i.e., randomly permanently crosslinked) *macromolecular* media.<sup>5,6</sup> This description, which addresses the distribution of spatial extents of thermal position fluctuations (i.e., localization lengths) has been confirmed by computer simulations,<sup>7</sup> and rather general, model-nonspecific arguments in favor of the broad applicability of the description have also been presented.<sup>8</sup> For any particular version of ran-

dom media (e.g., the macromolecular media of Refs. 5,6 or the vitreous media considered in the present paper), what determines the specific content of the statistical description of the amorphous solid state is the form of the random constraints that the permanent covalent bonding imposes, and the resultant form taken by the amorphous solid order parameter. In the present context of vitreous media, the constraints, as we shall see below, are more intricate than they are in the macromolecular vulcanization context and, accordingly, the order parameter is more intricate and the statistical content more elaborate: it accounts not only for the heterogeneity (i.e., the distribution over the sample) of positional localization lengths but also for the distribution of orbital-orientation thermal fluctuations, the strengths of the position-angle thermal fluctuation correlations, and the statistical correlations between these physical characteristics.<sup>9</sup>

In Ref. 3, in addition to introducing the model of random network forming media considered here, and formulating the question of the phase transition to (and structure of) the amorphous solid state via statistical-mechanical techniques, Goldbart and Zippelius made a simple variational mean-field theory for the amorphous solid state in which all particles shared a common localization length and all orbitals shared a common extent of their angular localization. The positional and angular localization parameters were then solved for, self-consistently, and it was found that, at a certain critical value of the density of formed bonds, a continuous transition to an amorphous solid state occurs, beyond which the inverse of the positional localization parameter grows continuously from zero. It was also found that, in response to the onset of positional localization, orientational localization of the orbitals sets in. Owing to the restricted form of the variational hypothesis for the order parameter adopted in Ref. 3, specifically that it did not allow for the possibility that only a fraction of the particles would become localized at the transition, the critical bond density was overestimated in Ref. 3. (The correct critical density was, however, known from the linear stability analysis of the fluid state.) Later work by Theissen *et al.*,<sup>10</sup> in addition to allowing for networks comprising particles of various valencies, cured the difficulty of the critical bond density, by broadening the variational hypothesis to allow for a localized fraction (although it still only allowed for a single value for the positional and orientation localization parameters, and did not account for correlations between the thermal fluctuations of positions and orientations).

What, then, is the nature of the amorphous solid state? If the number of permanent random covalent bonds introduced between particles is smaller than a certain critical value then the effect of these bonds is to bind at least some of the particles into random permanent molecules of a variety of types (varying in size and architecture), each of which, given sufficient time, will wander ergodically through the volume of the container, i.e., the equilibrium state of the system is fluid. If, however, the number of bonds introduced is greater than the critical value then their effect is to bind a nonzero fraction of the particles into a *macroscopically large disordered molecule* that extends throughout the container, the remaining fraction of particles remaining disconnected from the macroscopic molecule and capable of wandering across the container, given sufficient time. By contrast, the particles that constitute the extensive molecule will be localized in the

vicinity of random preferred spatial positions, about which their positions will undergo thermal fluctuations extending only over a limited spatial regime (which will vary randomly in magnitude from particle to particle, reflecting the random architecture of the network), and these particles will confer a rigidity on the entire system, so that the equilibrium state of the system will no longer be fluid and will, instead, be solid. Moreover, the orbitals attached to localized particles will exhibit most probable orientations, about which they will fluctuate thermally, the extent and nature of these fluctuations also varying randomly from orbital to orbital. In addition, the thermal fluctuations in the positions of the particles and the orientations of the bonds connecting them will be correlated, to an extent that varies randomly from particle to particle. The unconventional nature of this the amorphous solid state is worth emphasizing: (i) only a fraction of the particles will be localized; (ii) the mean positions of the localized particles will be random, as will be (iii) the spatial extent of the positional fluctuations of the particles, (iv) the orientational fluctuations of the orbitals, and (v) the correlations between these fluctuations (these parameters being characterized by a joint probability distribution); and (vi) there will be no hint of crystallinity beyond the shortest of lengthscales (i.e., the bond length), beyond these length scales the symmetries of the amorphous solid state being those of the liquid state.

Our principal aims are to construct a statistical characterization of the structure and heterogeneity of the amorphous solid state exhibited by a model of permanently randomly bonded vitreous media in the vicinity of the solidification transition, and to provide a physical interpretation of this characterization. We shall do this by constructing the self-consistency equation for the amorphous solid order parameter, valid in the vicinity of the solidification transition, and obtaining an exact solution of this self-consistent equation.

This paper is organized as follows. In Secs. II and III we shall proceed kinematically, describing the model that we shall be considering, and analyzing a suitable order parameter defined in terms of the positions of the constituent particles and the orientations of their orbitals. Continuing kinematically, we shall explore the structure of this order parameter, and elucidate the physical information that it encodes. Then, in Secs. IV and V, we shall address the model, regarding the formed bonds as quenched random variables that vary from realization to realization. By using equilibrium statistical mechanics, invoking the replica technique to deal with the quenched randomness, and making a mean-field hypothesis, we shall develop a self-consistent equation for the order parameter. By making a natural physical hypothesis for the form of the solution we shall, in Sec. VI, solve exactly for this order parameter in the regime in which the thermal fluctuations of the particle positions and orbital orientations are strong (i.e., near the solidification transition). Finally, in Sec. VII we shall extract from our solution a wide array of physical diagnostics characterizing the amorphous solid state and, in Sec. VIII we shall make some concluding remarks. We emphasize that throughout this work we shall be proceeding analytically, except that we shall make use of the numerically-obtained scaling function (of a single variable) central to the characterization of vulcanized macromolecular matter described in Refs. 5,6.

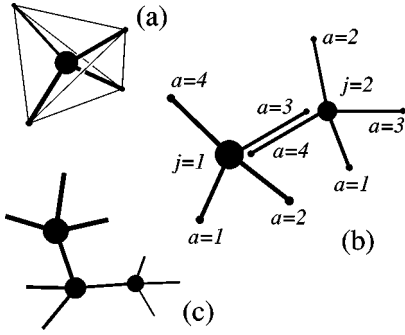


FIG. 1. Particle structure, bond, and network formation. (a) A single particle with the near-tetrahedral equilibrium structure of its orbitals. In this example the number of orbitals per atom  $A$  is 4 (as would be the case, e.g., for networks of Si atoms). (b) Formation of a covalent bond between two particles (the participating orbitals are slightly separated, for clarity). (c) A collection of three particles bonded together, forming the beginnings of a random network.

## II. ELEMENTS OF THE MODEL

The model of vitreous media which we shall focus on is that introduced in Ref. 3, which takes as its ingredients a thermodynamically large number  $N$  of particles, moving in a large three-dimensional cube of volume  $V$  (on which we impose periodic boundary conditions), at least some of which particles are permanently randomly bonded together to form a random network. At the kinematic level, the particles (labeled by  $j=1, \dots, N$ ) are characterized by their position vectors  $\{\mathbf{c}_j\}_{j=1}^N$ , along with the  $NA$  unit vectors  $\{\mathbf{s}_{j,a}\}_{a=1}^A$  describing the spatial orientations of the  $A$  orbitals that radiate from each of the particles  $j$ . Note that we shall be measuring lengths in units such that orbitals have length unity. Figure 1 illustrates the structure of the particles and the formation of a continuous random network out of them.

The orbitals radiating from a given particle tend to repel one another. For example, in the absence of any external perturbing forces, all things being equal, the orbitals of a four-orbital particle would point towards the vertices of a regular tetrahedron, as shown in Fig. 1(a). Rather than give a detailed specification of the interactions that embody this orbital-orbital repulsion, we shall encode the effects of such interactions into a sequence of parameters that characterize the correlations between the orientations of the orbitals of a single particle. For example, we shall find ourselves needing the correlator of the orientations of two *distinct* orbitals ( $a_1$  and  $a_2$ ) of a single particle (in the fluid state), say the  $j$ th:

$$\langle Y_{l_1 m_1}^*(\mathbf{s}_{j,a_1}) Y_{l_2 m_2}(\mathbf{s}_{j,a_2}) \rangle_{1,1} = \frac{1}{4\pi} \delta_{l_1, l_2} \delta_{m_1, m_2} C_{l_1}, \quad (2.1)$$

which we have parametrized in terms of the real numbers  $\{C_l\}_{l=0}^\infty$  (with  $C_0 \equiv 1$ ) that reflect the extent to which the orbitals interact.<sup>11</sup> The angle brackets  $\langle \dots \rangle_{1,1}$ , which we discuss below in Sec. IV A, denote thermal averaging with respect to a the single-particle Hamiltonian, which incorporates the intra particle interactions. The form of this correlator follows from the isotropy of the distribution of the orbital orientations in the fluid state. We shall not find ourselves making explicit use of the correlator of the orientations of *three* distinct orbitals of a single particle. However,

a simple symmetry-dictated form for it can readily be constructed, by making use of Wigner  $3-j$  technology, if one wishes to compute explicitly components of the order parameter that depend on it.

Having described the issue of a single particle and its orbitals, we now turn to the issue of the permanent random covalent bonds between pairs of particles, and how we are to describe them. We regard such bonding as introducing constraints on the relative location and relative orientation of the particles and orbitals participating in the bond. Specifically, we model the situation in which particles  $j$  and  $j'$  are bonded via orbitals  $a$  and  $a'$  by the constraints

$$\mathbf{c}_j + \frac{1}{2} \mathbf{s}_{j,a} = \mathbf{c}_{j'} + \frac{1}{2} \mathbf{s}_{j',a'}, \quad (2.2a)$$

$$\mathbf{s}_{j,a} = -\mathbf{s}_{j',a'}, \quad (2.2b)$$

as shown in Fig. 1(b). We denote by the number  $M$  and the collection  $\{j_e, j'_e; a_e, a'_e\}_{e=1}^M$  a specific realization of  $M$  bonds (i.e., a specific architecture).

Of course, the particles in the fluid interact with one another, regardless of whether or not bonds have been introduced. We shall assume that pairwise interactions, depending on the relative separation and orientation of the orbitals, exist between all particles. The crucial consequence that we assume these interactions to have is that they stabilize the system with respect to the formation of macroscopically inhomogeneous or anisotropic states, such as regular crystalline, liquid crystalline, molecular crystalline, or globular states.

## III. AMORPHOUS SOLID ORDER PARAMETER: RANDOM POSITIONAL AND ORIENTATIONAL LOCALIZATION

Following the ideas of Ref. 3, which represent an elaboration of ideas discussed in Ref. 12, we adopt as the order parameter characterizing the amorphous solid state the entity

$$\left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \prod_{\alpha=1}^n \langle e^{-i\mathbf{k}^\alpha \cdot \mathbf{c}_j} Y_{l^\alpha m^\alpha}^*(\mathbf{s}_{j,a}) \rangle \right], \quad (3.1)$$

where the angle brackets (with no subscripts) indicate a statistical-mechanical ensemble average over configurations of the particles, subject to a given collection of permanent random constraints (i.e., bonds), and the square brackets indicate an average over realizations of the bonds. This order parameter, which involves products of replicas of a single ensemble average, depends on the collections of wave vectors  $\{\mathbf{k}^\alpha\}_{\alpha=1}^n$  and angular momentum indices  $\{l^\alpha, m^\alpha\}_{\alpha=1}^n$ . Let us examine this order parameter, first, in order to ascertain the nature of the physical states that it is capable of diagnosing, and then to understand the type of statistical information that it encodes.

### A. Detection of random positional and orientational localization

Consider the order parameter given by Eq. (3.1), and suppose that we elect to set  $l^\alpha = 0$  (for  $\alpha = 1, \dots, n$ ). Then the order parameter becomes, up to irrelevant factors of  $4\pi$ :



$$\left[ \frac{1}{N} \sum_{j=1}^N \prod_{\alpha=1}^n \langle \exp(-i\mathbf{k}^\alpha \cdot \mathbf{c}_j) \rangle \right]. \quad (3.2)$$

As discussed in detail, e.g., in Ref. 6, and also below in Sec. VI D, these components of the order parameter are capable of detecting the spontaneous random freezing of particle positions (without regard to the behavior of the orbital orientations). More specifically, via the wave vector dependence, these order parameter components yield information about the fraction of particles that are positionally localized, as well as the statistical distribution of their positional localization lengths.

Suppose, instead, that we set  $\mathbf{k}^\alpha = \mathbf{0}$  (for  $\alpha = 1, \dots, n$ ) in Eq. (3.1). Then the order parameter becomes

$$\left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \prod_{\alpha=1}^n \langle Y_{l^\alpha m^\alpha}^*(\mathbf{s}_{j,a}) \rangle \right]. \quad (3.3)$$

As discussed, e.g., in Refs. 3,10, and also below in Sec. VI E 2, this component of the order parameter is capable of detecting the spontaneous random freezing of orbital orientations (without regard to the behavior of the particle positions). More specifically, via its dependence on the angular indices  $\{l^\alpha, m^\alpha\}_{\alpha=1}^n$ , this order parameter yields information about the extent and character of the orientational localization of the orbitals. It is via this component of the order parameter that the most direct contact is made with the Edwards-Anderson order parameter for Heisenberg spin glasses, which detects the random orientational freezing of magnetic moments. For example, choosing  $\{l^1, \dots, l^n\} = \{1, 1, 0, \dots, 0\}$ , and contracting appropriately on  $m^1$  and  $m^2$  we obtain

$$\sum_{m^1, m^2 = -1}^1 (-1)^{m^1} \delta_{m^1 + m^2, 0} \left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle Y_{1m^1}^*(\mathbf{s}_{j,a}) \rangle \right. \\ \left. \times \langle Y_{1m^2}^*(\mathbf{s}_{j,a}) \rangle \right] = \frac{3}{4\pi} \left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle \mathbf{s}_{j,a} \rangle \cdot \langle \mathbf{s}_{j,a} \rangle \right], \quad (3.4)$$

thus recovering the familiar Edwards-Anderson form. More generally, the order parameter for random networks exhibits the unconventional features that the index  $l$  can be greater than unity (so that higher multipole moments of the distribution of orientations can be accessed), as well as that a full characterization of the orientational freezing requires information from components with more than the familiar pair of thermal expectation values.

The third category of information results from examining the components of the order parameter corresponding to non-zero values of both  $\{\mathbf{k}^\alpha\}_{\alpha=1}^n$  and  $\{l^\alpha\}_{\alpha=1}^n$ . First, consider the subcase for which in every replica  $\alpha$  at most one of  $l^\alpha$  and  $\mathbf{k}^\alpha$  is nonzero. An example of such an order parameter component is

$$\left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle \exp(-i\mathbf{k}^1 \cdot \mathbf{c}_j) \rangle \right. \\ \left. \times \langle \exp(-i\mathbf{k}^2 \cdot \mathbf{c}_j) \rangle \langle Y_{l^3 m^3}^*(\mathbf{s}_{j,a}) \rangle \langle Y_{l^4 m^4}^*(\mathbf{s}_{j,a}) \rangle \right]. \quad (3.5)$$

Such components measure the statistical correlations between the strengths of positional and angular localization across the sample. *Inter alia*, such components address the question: if a certain particle is strongly localized positionally, how likely are the attached orbitals to be strongly localized orientationally.

Next, consider the general case in which some replicas  $\alpha$  have nonzero values for both  $\mathbf{k}^\alpha$  and  $l^\alpha$ . Such components provide information on the extent to which positional and orientational *thermal* fluctuations are correlated. For example, as is discussed in more detail below, by setting  $\mathbf{k}^\alpha = \mathbf{0}$  in all replicas  $\alpha$  except replicas 1 and 2, and by also setting  $l^1 = l^2 = 1, m^1 = m^2 = 0$ , and  $l^\alpha = m^\alpha = 0$  in the remaining replicas  $\alpha$ , we would obtain access to the disorder average of the quantity

$$\langle (\mathbf{c}_j - \langle \mathbf{c}_j \rangle) (\mathbf{s}_{j,a} - \langle \mathbf{s}_{j,a} \rangle)_z \rangle \cdot \langle (\mathbf{c}_j - \langle \mathbf{c}_j \rangle) (\mathbf{s}_{j,a} - \langle \mathbf{s}_{j,a} \rangle)_z \rangle, \quad (3.6)$$

which is a direct measure of the extent of the above-mentioned position-angle fluctuation correlations.

Let us pause to emphasize the three levels of randomness presented by random network forming media. There is *thermal* randomness, by which we mean the familiar thermal motion of the particles and orbitals. Then there is *architectural* randomness, resulting from the random manner in which covalent bonds are formed. Finally, there is *microstructural* randomness, i.e., the heterogeneity of the emergent solid state. This last level of randomness we capture statistically in a joint probability distribution that characterizes the nature of the thermal motions.

### B. Isolating the fraction of positionally localized particles

The most basic piece of information describing the amorphous solid state concerns the value of the fraction  $q$  of the  $N$  particles that are localized positionally, regardless of the value of their localization lengths and the angular localization of the orbitals attached to them. As shown in Refs. 3,6, this fraction  $q$  can be accessed via the order parameter (3.1) in the following way: set  $l^\alpha = m^\alpha = 0$  for  $\alpha = 1, \dots, n$ , and then pass to the limit  $\hat{\mathbf{k}} \rightarrow \hat{\mathbf{0}}$  via a sequence for which  $\sum_{\alpha=1}^n \mathbf{k}^\alpha = \mathbf{0}$ . The resulting quantity is the fraction  $q$ . The reason for this is that whereas the value of  $\langle \exp(-i\mathbf{k} \cdot \mathbf{c}_j) \rangle$  at  $\mathbf{k} = \mathbf{0}$  is strictly unity, the limiting value of  $\langle \exp(-i\mathbf{k} \cdot \mathbf{c}_j) \rangle$  (as  $\mathbf{k} \rightarrow \mathbf{0}$ ) is unity for positionally localized particles, but zero for delocalized particles. For the sake of convenience, we shall refer to the localized fraction  $q$  as the solid fraction, and the delocalized fraction  $1 - q$  as the liquid fraction.

### C. Distribution of positional and angular localization characteristics

To further elucidate the physical information regarding the positional and orientational localization of the particles and orbitals contained in the order parameter, we now construct a physically motivated form for the order parameter (3.1) in terms of certain *localizational characteristics*—quantities that describe the positional and orientational localization of particles and orbitals. We begin by considering the contribution from a single particle  $j$  and a single orbital  $a$  attached to it, i.e., the expectation value

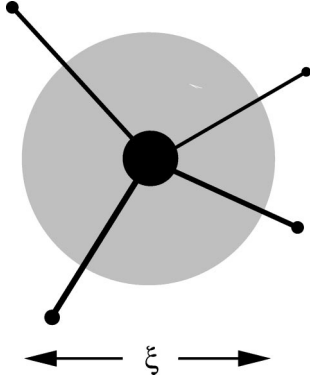


FIG. 2. Positional localization of particles. The characteristic extent of the thermal fluctuations of the position of the particle is represented by the gray circle and measured by the localization length  $\xi$ .

$$\langle e^{-i\mathbf{k}\cdot\mathbf{c}_j} Y_{lm}^*(\mathbf{s}_{j,a}) \rangle. \quad (3.7)$$

This function is the *characteristic function* of the joint thermal probability distribution describing the equilibrium localization of the position of the particle and the localization of the orientation of the orbital, as well as correlations between the thermal fluctuations between this position and orientation. First, we consider the  $(1-q)N$  particles in the delocalized fraction. For such particles we have  $\langle e^{-i\mathbf{k}\cdot\mathbf{c}_j} Y_{lm}^*(\mathbf{s}_{j,a}) \rangle = (4\pi)^{-1/2} \delta_{\mathbf{k},\mathbf{0}} \delta_{l,0} \delta_{m,0}$ . For the remaining  $qN$  localized particles we first extract from the expectation value (3.7) the phase factor associated with the mean position  $\boldsymbol{\mu}_j \equiv \langle \mathbf{c}_j \rangle$  of the particle, to obtain  $e^{-i\mathbf{k}\cdot\boldsymbol{\mu}_j} \langle e^{-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)} Y_{lm}^*(\mathbf{s}_{j,a}) \rangle$ , and then express the resulting quantity in terms of disconnected and connected pieces:

$$\begin{aligned} \langle e^{-i\mathbf{k}\cdot\mathbf{c}_j} Y_{lm}^*(\mathbf{s}_{j,a}) \rangle &= e^{-i\mathbf{k}\cdot\boldsymbol{\mu}_j} \{ \langle e^{-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)} \rangle \langle Y_{lm}^*(\mathbf{s}_{j,a}) \rangle \\ &\quad + \langle (e^{-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)} - \langle e^{-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)} \rangle) \rangle \langle Y_{lm}^*(\mathbf{s}_{j,a}) \rangle \\ &\quad - \langle Y_{lm}^*(\mathbf{s}_{j,a}) \rangle \}. \end{aligned} \quad (3.8)$$

On the right hand side of this expression, the disconnected (i.e., the first) piece contains two factors: (i)  $\langle \exp[-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)] \rangle$ , which describes the positional localization of the particle (see Fig. 2) and (ii)  $\langle Y_{lm}^*(\mathbf{s}_{j,a}) \rangle$ , which describes the

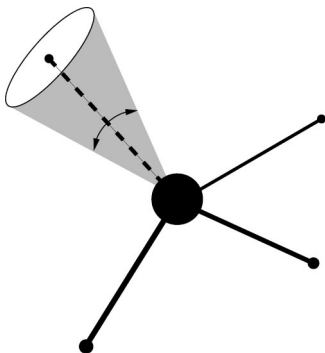


FIG. 3. Orientational localization of orbitals. The orientation of the orbital fluctuates thermally about its most probable value (broken line), the characteristic scale of these fluctuations being represented by the gray cone.

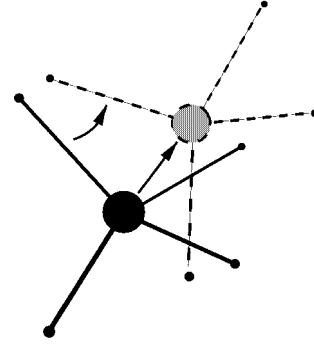


FIG. 4. Orientational-positional thermal fluctuation correlations. Imagine that the particle is connected to a rather immobile particle by the top left orbital. As the particle moves to the shaded position its orbitals reorient accordingly.

orientational localization of the orbital (see Fig. 3). If we approximate the first factor in the connected piece by making use of the standard cumulant expansion, by letting  $3\xi_j^2$  denote the (finite) mean square fluctuations  $\langle (\mathbf{c}_j - \langle \mathbf{c}_j \rangle) \cdot (\mathbf{c}_j - \langle \mathbf{c}_j \rangle) \rangle$  in the position of the particle, and by following this strategy to second order, then we arrive at the approximation

$$\langle \exp(-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)) \rangle \approx \exp(-k^2 \xi_j^2 / 2). \quad (3.9)$$

As for the connected (i.e., the second) term on the right-hand side of Eq. (3.8), it describes correlations between the fluctuations in the particle position and the orbital orientation (see Fig. 4). In the same way that we have introduced the diagnostic  $\xi$  to characterize positional localization, we now introduce two further diagnostics:

$$\Sigma_{lm;j,a} \equiv \langle Y_{lm}^*(\mathbf{s}_{j,a}) \rangle, \quad (3.10a)$$

$$\begin{aligned} e^{-|\mathbf{k}|^2 \xi_j^2 / 2} \Gamma_{lm;j,a}(\mathbf{k}) &\equiv \langle (e^{-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)} - \langle e^{-i\mathbf{k}\cdot(\mathbf{c}_j - \boldsymbol{\mu}_j)} \rangle) \\ &\quad \times (Y_{lm}^*(\mathbf{s}_{j,a}) - \langle Y_{lm}^*(\mathbf{s}_{j,a}) \rangle) \rangle. \end{aligned} \quad (3.10b)$$

The collection of complex-valued numbers  $\{\Sigma_{lm;j,a}\}$  characterizes the orientational localization of orbital  $a$  on particle  $j$ ; the collection of complex-valued functions  $\{\Gamma_{lm;j,a}(\mathbf{k})\}$  characterizes the correlations between the thermal fluctuations in the position of particle  $j$  and the orientation of orbital  $a$  attached to it. For example, consider  $\Gamma_{10;j,a}(\mathbf{k})$ . By expanding the exponential to first order (as we shall establish later, typical values of  $k$  are small near the transition), and recalling, that up to numerical factors  $Y_{10}(\mathbf{s})$  is  $s_z$ , we see, that

$$\begin{aligned} e^{-|\mathbf{k}|^2 \xi_j^2 / 2} \Gamma_{10;j,a}(\mathbf{k}) &= -i \sqrt{\frac{3}{4\pi}} \mathbf{k} \cdot \langle ((\mathbf{c}_j - \boldsymbol{\mu}_j) - \langle \mathbf{c}_j - \boldsymbol{\mu}_j \rangle) \\ &\quad \times ((\mathbf{s}_{j,a})_z - \langle (\mathbf{s}_{j,a})_z \rangle) \rangle + \mathcal{O}(\hat{\mathbf{k}}^2), \end{aligned} \quad (3.11)$$

which does indeed measure correlations between the positional and orientational thermal fluctuations, in accordance with the discussion of this component of the order-parameter, given at the end of Sec. III A.

By rewriting Eq. (3.8) in terms of these diagnostics, and making use of the approximation (3.9), we arrive at the form

$$\langle e^{-i\mathbf{k}\cdot\mathbf{c}_j} Y_{lm}^*(\mathbf{s}_{j,a}) \rangle \approx e^{-i\mathbf{k}\cdot\boldsymbol{\mu}_j} e^{-|\mathbf{k}|^2 \xi_j^2 / 2} \{ \Sigma_{lm;j,a} + \Gamma_{lm;j,a}(\mathbf{k}) \}. \quad (3.12)$$

By inserting this form, appropriate for particles  $j$  that comprise the localized fraction, into Eq. (3.1), and incorporating the contribution from the delocalized fraction, we arrive at the form

$$\begin{aligned} & \left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \prod_{\alpha=1}^n \langle e^{-i\mathbf{k}^\alpha \cdot \mathbf{c}_j} Y_{l^{\alpha m} a}^*(\mathbf{s}_{j,a}) \rangle \right] \\ & \approx (1-q) \prod_{\alpha=1}^n \delta_{\mathbf{k}^\alpha, \mathbf{0}} + \left[ \frac{1}{N} \sum_{j \text{ loc.}} \frac{1}{A} \sum_{a=1}^A \prod_{\alpha=1}^n \right. \\ & \quad \left. \times e^{-i\mathbf{k}^\alpha \cdot \boldsymbol{\mu}_j} e^{-|\mathbf{k}^\alpha|^2 \xi_j^2 / 2} \{ \Sigma_{l^{\alpha m} a; j, a} + \Gamma_{l^{\alpha m} a; j, a}(\mathbf{k}^\alpha) \} \right]. \end{aligned} \quad (3.13)$$

$$\begin{aligned} & = (1-q) \prod_{\alpha=1}^n \delta_{\mathbf{k}^\alpha, \mathbf{0}} \\ & + q \int d^3 \boldsymbol{\mu} \int d\tau d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\boldsymbol{\mu}, \tau, \{\Sigma\}, \{\Gamma\}) \\ & \times \exp -i \boldsymbol{\mu} \cdot \sum_{\alpha=1}^n \mathbf{k}^\alpha \exp -\frac{1}{2\tau} \sum_{\alpha=1}^n |\mathbf{k}^\alpha|^2 \\ & \times \prod_{\alpha=1}^n \{ \Sigma_{l^{\alpha m} a; j, a} + \Gamma_{l^{\alpha m} a; j, a}(\mathbf{k}^\alpha) \}, \end{aligned} \quad (3.14)$$

where we have made the definition  $\tau \equiv 1/\xi^2$ . The integration measures  $d\{\Sigma\}$  and  $\mathcal{D}\{\Gamma\}$ , respectively denote the multiple measure  $\prod_{lm} d\Sigma_{lm}$  and the multiple functional measure  $\prod_{lm} \mathcal{D}\Gamma_{lm}$ . We have also introduced the joint probability distribution  $P$ , central to our characterization of the localized particles in amorphous solid state, defined via

$$\begin{aligned} P(\boldsymbol{\mu}, \tau, \{\Sigma\}, \{\Gamma\}) & \equiv \left[ \frac{1}{N} \sum_j \frac{1}{A} \sum_{a=1}^A \delta(\boldsymbol{\mu} - \boldsymbol{\mu}_j) \delta(\tau - \xi_j^{-2}) \right. \\ & \quad \times \prod_{l=0}^{\infty} \prod_{m=-l}^l \delta(\Sigma_{lm} - \Sigma_{lm; j, a}) \\ & \quad \left. \times D(\Gamma_{lm} - \Gamma_{lm; j, a}) \right], \end{aligned} \quad (3.15)$$

in which the final factor  $D(\cdot)$  is a functional delta function.

The next step in our construction of a physically motivated form for the order parameter involves the identification of specific symmetries that we anticipate the amorphous solid state to possess, viz., macroscopic translational invariance (MTI) and macroscopic rotational invariance (MRI). MTI reflects the notion that although in the amorphous solid state translational invariance is spontaneously broken at the microscopic level (in any particular realization of the disorder), this invariance is restored at the macroscopic level, in the sense that no quantity computed by averaging over any macroscopic subvolume of the system exhibits any dependence on the particular subvolume chosen. Similarly, MRI reflects the notion that although rotational invariance is spontaneously broken at the microscopic level, it is restored at the macroscopic level in the sense that no quantity computed by

averaging over any macroscopic subvolume of the system exhibits any orientational preference. As for MTI, it amounts to the hypotheses: (i) that the disorder-averaged distribution  $P$  exhibits no correlation between the mean location of a particle and its other statistical characteristics; and (ii) that the distribution is translationally invariant (i.e., is independent of  $\boldsymbol{\mu}$ ).

Although MRI also imposes conditions on the joint probability distribution  $P$  we do not need to impose these conditions explicitly. The reason for that is that MRI for the component  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  is assured by the fact that  $\Sigma_{00; j, a}$  and  $\Gamma_{00; j, a}$  are constants (in fact, one is zero), and the assumption that the localization clouds of the particles are spherical and, accordingly, described by the single rms value of the fluctuation in the particle's position  $3\xi_j^2$ . MRI for the anisotropic components of  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  is a consequence of the fact that they, as we shall see below, are perturbed away from their zero values by MRI-satisfying couplings to the  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  component. Thus MRI is assured by the theory itself, and does not need to be explicitly incorporated into the proposed form of the order parameter.

By making use of the MTI hypotheses we arrive at the form

$$P(\boldsymbol{\mu}, \tau, \{\Sigma\}, \{\Gamma\}) = \frac{P(\tau, \{\Sigma\}, \{\Gamma\})}{V}, \quad (3.16)$$

which, when inserted into Eq. (3.14), leads to the expression

$$\begin{aligned} & (4\pi)^{n/2} \Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})|_{\mathbf{k}^0=\mathbf{0}, l^0=m^0=0} \\ & = (1-q) \prod_{\alpha=1}^n \delta_{\mathbf{k}^\alpha, \mathbf{0}} \delta_{l^\alpha, 0} \delta_{m^\alpha, 0} \\ & + q \delta \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \int_0^\infty d\tau \int d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\tau, \{\Sigma\}, \{\Gamma\}) \\ & \times \exp -\frac{1}{2\tau} \sum_{\alpha=0}^n |\mathbf{k}^\alpha|^2 \prod_{\alpha=0}^n \{ \Sigma_{l^{\alpha m} a; j, a} + \Gamma_{l^{\alpha m} a; j, a}(\mathbf{k}^\alpha) \}, \end{aligned} \quad (3.17)$$

where we have introduced the notation  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})|_{\mathbf{k}^0=\mathbf{0}, l^0=m^0=0}$  to denote the order parameter (3.1), and where hats indicate  $(n+1)$ -fold replicated versions of quantities. By extending the result of this approach to include the dependence on the zero-replica variables  $(\mathbf{k}^0, l^0, m^0)$  in a permutation-symmetry-dictated way we arrive at the form

$$\begin{aligned} & (4\pi)^{(n+1)/2} \Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m}) \\ & = (1-q) \prod_{\alpha=0}^n \delta_{\mathbf{k}^\alpha, \mathbf{0}} \delta_{l^\alpha, 0} \delta_{m^\alpha, 0} \\ & + q \delta_{\hat{\mathbf{k}}, \mathbf{0}} \int_0^\infty d\tau \int d\{\Sigma\} \mathcal{D}\{\Gamma\} p(\tau, \{\Sigma\}, \{\Gamma\}) \\ & \times e^{-\hat{\mathbf{k}}^2 / 2\tau} \prod_{\alpha=0}^n \{ \Sigma_{l^{\alpha m} a; j, a} + \Gamma_{l^{\alpha m} a; j, a}(\mathbf{k}^\alpha) \}. \end{aligned} \quad (3.18)$$

As we shall see below, for our solution we shall need an assumption for the form of the order-parameter component  $\Omega(\hat{\mathbf{k}}; \hat{0}, \hat{0})$ . To motivate this assumption, we set  $\hat{l} = \hat{m} = \hat{0}$  in Eq. (3.18). As is easy to see from the definitions (3.10a) and (3.10b),  $\Sigma_{00;j,a} = 1/\sqrt{4\pi}$  and  $\Gamma_{00;j,a} = 0$ , leaving us with the form

$$(4\pi)^{(n+1)/2} \Omega(\hat{\mathbf{k}}; \hat{0}, \hat{0}) = (1-q) \prod_{\alpha=0}^n \delta_{\mathbf{k}\alpha,0} + q \delta_{\mathbf{k},0} \int_0^\infty d\tau p(\tau) e^{-\hat{\mathbf{k}}^2/2\tau}, \quad (3.19)$$

where  $p(\tau)$  is a reduced form of the full joint probability distribution  $P(\tau, \{\Sigma\}, \{\Gamma\})$ , and describes only the positional localization of the particles:

$$p(\tau) \equiv \int d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\tau, \{\Sigma\}, \{\Gamma\}). \quad (3.20)$$

We note that, up to trivial factors of  $4\pi$ , the expression (3.19) is identical to the ansatz used in Refs. 6,5 in the context of vulcanized macromolecular media.

#### IV. DISORDER-AVERAGING; REPLICA STATISTICAL MECHANICS

Having described the relevant ‘‘kinematics,’’ i.e., the degrees of freedom and the constraints that characterize the model of randomly covalently bonded particles, we now formulate the statistical mechanics of the system, paying particular attention to the quenched (i.e., nonequilibrating) nature of the random constraints. At this stage we shall be following the method sketched in Ref. 3 which itself builds upon the general approach to macromolecular networks introduced in Ref. 13.

##### A. Partition function

The partition function of the system, subject to the constraints  $\{j_e, j'_e; a_e, a'_e\}_{e=1}^M$ , which we collectively denote by  $\mathcal{C}$ , relative to the partition function of the unconstrained system, is given by

$$\tilde{Z}(\mathcal{C}) = \left\langle \prod_{e=1}^M \delta^{(3)} \left( \mathbf{c}_{j_e} + \frac{1}{2} \mathbf{s}_{j_e, a_e} - \mathbf{c}_{j'_e} - \frac{1}{2} \mathbf{s}_{j'_e, a'_e} \right) \times \Delta^{(2)}(\mathbf{s}_{j_e, a_e} + \mathbf{s}_{j'_e, a'_e}) \right\rangle_{N,1}. \quad (4.1)$$

The angle brackets denote equilibrium averaging with respect to a Hamiltonian that incorporates interactions between distinct particles, as well as between the orbitals of a single particle. The subscript indicates that this average is taken over one copy of a system of  $N$  particles, and anticipates the introduction of replicas that we shall make shortly. The two types of delta function,  $\delta^{(3)}$  and  $\Delta^{(2)}$ , serve to eliminate configurations that fail to satisfy the constraints, and are appropriately defined in the following way:

$$\delta^{(3)}(\mathbf{c}_1 - \mathbf{c}_2) = \delta^{(3)}(\mathbf{c}_2 - \mathbf{c}_1) \equiv \sum_{\mathbf{k}} \left( \frac{\exp i\mathbf{k} \cdot \mathbf{c}_1}{\sqrt{V}} \right) \times \left( \frac{\exp i\mathbf{k} \cdot \mathbf{c}_2}{\sqrt{V}} \right)^*, \quad (4.2a)$$

$$\Delta^{(2)}(\mathbf{s}_1, \mathbf{s}_2) = \Delta^{(2)}(\mathbf{s}_2, \mathbf{s}_1) \equiv \sum_{l=0}^{\infty} \sum_{m=-l}^l Y_{lm}(\mathbf{s}_1) Y_{lm}^*(\mathbf{s}_2), \quad (4.2b)$$

where (corresponding to the periodic boundary conditions imposed on the system) the sum over  $\mathbf{k}$  is taken over the Cartesian components  $k_\nu = 2\pi n_\nu / V^{1/3}$ , with  $n_\nu$  being integers (both positive and negative), and the  $Y_{lm}$  are the usual spherical harmonic functions, the arguments of which are unit vectors.

Strictly speaking, the partition function  $\tilde{Z}$  is correct only up to the appropriate Gibbs factorial factor, and would not, as it stands, give rise to an extensive free energy hence the tilde. As we shall be focusing on the order-parameter self-consistency equation, in which (as is well known) the Gibbs factor plays no role it can be safely omitted here. For a detailed discussion of this issue, see Sec. 2.4 of Ref. 6.

##### B. Deam-Edwards distribution

At this stage, we introduce a statistical distribution characterizing the realization of the random bonds, following the elegant strategy of Deam and Edwards.<sup>13</sup> We take for the probability density that the collection of bonds  $\mathcal{C}$  is formed the quantity

$$\mathcal{P}_M(\mathcal{C}) \propto \frac{(2\pi V \mu^2 / NA^2)^M}{M!} \tilde{Z}(\mathcal{C}), \quad (4.3)$$

which is analogous to the probability density chosen by Deam and Edwards for the case of vulcanized macromolecular networks.<sup>13</sup> Instead of working with a fixed number of bonds, we allow their number to vary in a quasi-Poissonian way, and control the mean number of bonds by the control parameter  $\mu^2$ . For a given value of  $M$ , the Deam-Edwards distribution is proportional to the probability density for finding the set of pairs of orbitals  $\{j_m, j'_m; a_m, a'_m\}_{m=1}^M$  to be overlapping. The factor  $\mu^{2M}$  represents the probability that a bond is formed between each of these  $M$  overlapping pairs. Thus, the Deam-Edwards distribution provides a statistical characterization of a process of forming permanent bonds in which constraints are instantaneously introduced into the liquid state at equilibrium. As such, it is an idealization of the random-network-forming process, which generally takes place on a time scale during which at least some relaxation of the structure can occur. To handle the complication of relaxation would require the introduction of kinetics into the description, rather than purely equilibrium notions. Said another way, one can view the Deam-Edwards distribution as a strategy for freezing in liquid-state correlations, as process that is regarded as happening spontaneously in glass-forming systems, but here is introduced externally. The distribution encodes the physically attractive feature that the networks it gives appreciable weight to exhibit the macroscopic symme-



tries of the liquid state, inasmuch as the bond collections to which it gives appreciable weight correspond to likely configurations of the liquid state. With this distribution of bonds some of the correlations of the liquid state are *quenched in*, to a degree controlled by the mean number of bonds formed.

### C. Replica representation of the disorder-averaged free energy

We now set about constructing the disorder-averaged free energy per particle (relative to that of the system prior to random covalent bonding)  $f$ , which is defined via

$$N\beta f \equiv [\ln \bar{Z}(C)], \quad (4.4)$$

where  $\beta (\equiv 1/k_B T)$  measures the inverse temperature. As mentioned in the previous subsection, the Gibbs factor has been omitted, but this will have no consequences for the order-parameter self-consistent equation. By making use of the replica technique (see, e.g., Ref. 2),  $f$  can be obtained via

$$f = \lim_{n \rightarrow 0} f_n, \quad (4.5a)$$

$$-n\beta N f_n \equiv [\bar{Z}^n] - 1 = (\mathcal{Z}_{n+1} - \mathcal{Z}_1) / \mathcal{Z}_1, \quad (4.5b)$$

$$\mathcal{Z}_{n+1} \equiv \left\langle \exp \left( \frac{2\pi V \mu^2}{NA^2} \sum_{j,j'=1}^N \sum_{a,a'=1}^A \prod_{\alpha=0}^n \delta^{(3)}(\mathbf{c}_j^\alpha + \frac{1}{2}\mathbf{s}_{j,a}^\alpha - \mathbf{c}_{j'}^\alpha - \frac{1}{2}\mathbf{s}_{j',a'}^\alpha) \Delta^{(2)}(\mathbf{s}_{j,a}^\alpha, -\mathbf{s}_{j',a'}^\alpha) \right) \right\rangle_{N,n+1}. \quad (4.5c)$$

Here,  $\mathcal{Z}_{n+1}$  is the replicated partition function, arising from the averaging of  $\bar{Z}^n$  over the Deam-Edwards-type distribution (4.3), and the denominator  $\mathcal{Z}_1$  arises from the normalization of the Deam-Edwards distribution (see Ref. 10 for details). Notice the striking occurrence of a theory involving  $n+1$ , rather than the usual  $n$ , replicas, a feature, arising from the presence in the partition function in the Deam-Edwards distribution. (The extra replica ‘‘computes’’ the distribution of quenched random bonds.) The angle brackets  $\langle \dots \rangle_{n+1}$  indicate an  $(n+1)$ -fold replicated normalized average over the positions of the particles and the orientations of the orbitals, weighted suitably by a Hamiltonian that does not couple the replicas.

As one can see from the exponent in Eq. (4.5c), the replicated theory possesses the symmetries of independent translations and rotations of the replicas, i.e.,

$$\mathbf{c}^\alpha \rightarrow \mathcal{R}^\alpha \cdot \mathbf{c}^\alpha + \mathbf{a}^\alpha, \quad (4.6a)$$

$$\mathbf{s}_a^\alpha \rightarrow \mathcal{R}^\alpha \cdot \mathbf{s}_a^\alpha, \quad (4.6b)$$

where  $\{\mathbf{a}^\alpha\}$  are  $n+1$  independent arbitrary translation three-vectors, and  $\{\mathcal{R}^\alpha\}$  are  $n+1$  independent arbitrary 3-by-3 rotation matrices. As we shall see, the transition to the amorphous solid state is marked by the spontaneous breaking of the symmetries of the relative translations and rotations of the replicas; the common translations and rotations remain as residual symmetries. These residual symmetries correspond to the macroscopic translational and rotational symmetry of the amorphous solid state discussed in Sec. III C. The theory

also possesses the symmetry of the permutation of the  $n+1$  replicas, which remains intact in the amorphous solid state.

For the sake of convenience, we introduce the replicated delta functions, defined by

$$\hat{\delta}(\hat{\mathbf{c}}_1 - \hat{\mathbf{c}}_2) \equiv \prod_{\alpha=0}^n \delta^{(3)}(\mathbf{c}_2^\alpha - \mathbf{c}_3^\alpha), \quad (4.7a)$$

$$\hat{\Delta}(\hat{\mathbf{s}}_1, \hat{\mathbf{s}}_2) \equiv \prod_{\alpha=0}^n \Delta^{(2)}(\mathbf{s}_1^\alpha, \mathbf{s}_2^\alpha), \quad (4.7b)$$

where  $\hat{\mathbf{c}}$  denotes  $\{\mathbf{c}^0, \mathbf{c}^1, \dots, \mathbf{c}^n\}$  and  $\hat{\mathbf{s}}$  denotes  $\{\mathbf{s}^0, \mathbf{s}^1, \dots, \mathbf{s}^n\}$ , and also the replicated spherical harmonics  $\hat{Y}$ , defined by

$$\hat{Y}_{\hat{l}\hat{m}}(\hat{\mathbf{s}}) \equiv \prod_{\alpha=0}^n Y_{l^\alpha m^\alpha}(\mathbf{s}^\alpha), \quad (4.8)$$

where  $\hat{l}$  and  $\hat{m}$ , respectively, denote  $\{l^0, l^1, \dots, l^n\}$  and  $\{m^0, m^1, \dots, m^n\}$ .

## V. MEAN-FIELD APPROXIMATION

### A. Self-consistency condition for the order parameter

We now develop a mean-field approximation for the replica partition function, Eq. (4.5c). To do this, we rewrite the partition function as follows:

$$\begin{aligned} \mathcal{Z}_{n+1} &= \left\langle \exp \left( 2\pi N V \mu^2 \int_V d\hat{\mathbf{c}} \int_S d\hat{\mathbf{s}} \frac{1}{NA} \right. \right. \\ &\quad \times \sum_{j=1}^N \sum_{a=1}^A \hat{\delta}((\hat{\mathbf{c}}_j + \frac{1}{2}\hat{\mathbf{s}}_{j,a}) - \hat{\mathbf{c}}) \hat{\Delta}(\hat{\mathbf{s}}_{j,a}, \hat{\mathbf{s}}) \frac{1}{NA} \\ &\quad \times \sum_{j'=1}^N \sum_{a'=1}^A \hat{\delta}(\hat{\mathbf{c}} - (\hat{\mathbf{c}}_{j'} + \frac{1}{2}\hat{\mathbf{s}}_{j',a'})) \\ &\quad \left. \left. \times \hat{\Delta}(\hat{\mathbf{s}}, -\hat{\mathbf{s}}_{j',a'}) \right) \right\rangle_{N,n+1} \end{aligned} \quad (5.1a)$$

$$\begin{aligned} &= \left\langle \exp \left( 2\pi N V \mu^2 \int_V d\hat{\mathbf{c}} \int_S d\hat{\mathbf{s}} \frac{1}{NA} \right. \right. \\ &\quad \times \sum_{j=1}^N \sum_{a=1}^A \hat{\delta}(\hat{\mathbf{c}} - (\hat{\mathbf{c}}_j + \frac{1}{2}\hat{\mathbf{s}}_{j,a})) \hat{\Delta}(\hat{\mathbf{s}}, \hat{\mathbf{s}}_{j,a}) \\ &\quad \times \frac{1}{NA} \sum_{j'=1}^N \sum_{a'=1}^A \hat{\delta}(\hat{\mathbf{c}} - (\hat{\mathbf{c}}_{j'} + \frac{1}{2}\hat{\mathbf{s}}_{j',a'})) \\ &\quad \left. \left. \times \hat{\Delta}(-\hat{\mathbf{s}}, \hat{\mathbf{s}}_{j',a'}) \right) \right\rangle_{N,n+1}, \end{aligned} \quad (5.1b)$$

where  $\int_V d\hat{\mathbf{c}}$  denotes  $\prod_{\alpha=0}^n \int_V d^3 \mathbf{c}^\alpha$ , and  $\int_S d\hat{\mathbf{s}}$  denotes  $\prod_{\alpha=0}^n \int_S d^2 \mathbf{s}^\alpha$ , and where, to obtain the last form, we have used the symmetry properties of the delta functions.



Next, we introduce the (real-space version of the) amorphous solid order parameter,

$$\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}}) \equiv \left\langle \frac{1}{NA} \sum_{j=1}^N \sum_{a=1}^A \delta[\hat{\mathbf{c}} - (\hat{\mathbf{c}}_j + \frac{1}{2} \hat{\mathbf{s}}_{j,a})] \hat{\Delta}(\hat{\mathbf{s}}, \hat{\mathbf{s}}_{j,a}) \right\rangle. \quad (5.2)$$

Then, upon setting

$$\begin{aligned} & \frac{1}{NA} \sum_{j=1}^N \sum_{a=1}^A \delta[\hat{\mathbf{c}} - (\hat{\mathbf{c}}_j + \frac{1}{2} \hat{\mathbf{s}}_{j,a})] \hat{\Delta}(\hat{\mathbf{s}}, \hat{\mathbf{s}}_{j,a}) \\ & = \Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}}) + \delta\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}}), \end{aligned} \quad (5.3)$$

i.e., the order parameter  $\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}})$  plus the fluctuation  $\delta\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}})$ , expanding the exponent in powers of  $\delta\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}})$ , and omitting terms quadratic in  $\delta\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}})$ , we obtain

$$\begin{aligned} \mathcal{Z}_{n+1} \approx & \exp \left[ -2\pi NV\mu^2 \int_V d\hat{\mathbf{c}} \int_S d\hat{\mathbf{s}} \Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}}) \Omega(\hat{\mathbf{c}}; -\hat{\mathbf{s}}) \right. \\ & + N \ln \left\langle \exp \left( 4\pi V\mu^2 \int_V d\hat{\mathbf{c}} \int_S d\hat{\mathbf{s}} \Omega(\hat{\mathbf{c}}; -\hat{\mathbf{s}}) \frac{1}{A} \right. \right. \\ & \left. \left. \times \sum_{a=1}^A \delta[\hat{\mathbf{c}} - (\hat{\mathbf{c}}_1 + \frac{1}{2} \hat{\mathbf{s}}_{1,a})] \hat{\Delta}(\hat{\mathbf{s}}, \hat{\mathbf{s}}_{1,a}) \right) \right\rangle_{1,n+1} \left. \right], \end{aligned} \quad (5.4)$$

where the resulting expectation value involves only the position and orbital-orientations of a single particle.

The reader will have observed that the mean-field approximation strategy has yielded a one-particle problem, Eq. (5.4), as desired. However, there is a subtlety associated with the manner in which the various interactions present in Eq. (5.1b) are treated, which we now address. The angle brackets in Eq. (5.1b) denote averaging over  $n+1$  (coupled) replicas of the  $N$  (coupled) particle system. The intrareplica coupling originates in the interactions between particles present in the

liquid state; on the other hand, the inter-replica coupling originates in the random constraints. As discussed in detail in Sec. 5.1 of Ref. 6, it is useful to transfer the so-called one-replica sector contribution to the inter-replica coupling to the intrareplica coupling (which is thereby renormalized). (The intrareplica and inter-replica couplings both contain trivial contributions in the zero-replica sector, as does the order parameter; we ignore these contributions.) The subtlety is that the structure of the theory in the one-replica sector is quite different from that in the higher-replica sectors: whereas the constraints tend to destabilize *all* sectors, this tendency is counteracted in only the one-replica sector by the original intrareplica interactions. Consequently, at the amorphous solidification transition the one-replica sector component of the order parameter remains zero, whilst the higher-replica sector components become nonzero. Indeed, the competition between these two processes can be regarded as a form of frustration, which resolves itself by the formation of a state possessing MTI and MRI (see Sec. III C).

On a technical level, this discussion amounts to the following dictum: in all subsequent equations, e.g., Eqs. (5.4), (5.5), (5.7), the component of the order parameter lying in the one-replica sector is to be set to zero. Accordingly, the self-consistent equations that follow pertain to all sectors *except* the zero and one replica sectors. This notion is straightforward when the order parameter is expressed in the (plane and spherical) harmonic representation [as it is, e.g., in Eq. (5.7)]. In this representation, setting the one-replica sector contribution to zero refers to setting to zero the contribution in which nonzero entries in  $\{\hat{\mathbf{k}}; \hat{l}, \hat{m}\}$  appear in precisely one replica. (By the zero-replica sector we mean the sector with  $\hat{\mathbf{k}} = \hat{l} = \hat{m} = \hat{0}$ .)

We now return to the task of obtaining a self-consistent equation for the order parameter. By making the partition function (5.4) stationary with respect to  $\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}})$  we arrive at self-consistent equation (SCE) for the order-parameter:

$$\Omega(\hat{\mathbf{c}}_0; \hat{\mathbf{s}}_0) = \frac{\left\langle \frac{1}{A} \sum_{a=1}^A \delta\{\hat{\mathbf{c}}_0 - (\hat{\mathbf{c}}_1 + \frac{1}{2} \hat{\mathbf{s}}_{1,a})\} \hat{\Delta}(\hat{\mathbf{s}}_0, \hat{\mathbf{s}}_{1,a}) \exp \left( 4\pi V\mu^2 \int_V d\hat{\mathbf{c}} \int_S d\hat{\mathbf{s}} \Omega(\hat{\mathbf{c}}; -\hat{\mathbf{s}}) \frac{1}{A} \sum_{a=1}^A \delta\{\hat{\mathbf{c}} - (\hat{\mathbf{c}}_1 + \frac{1}{2} \hat{\mathbf{s}}_{1,a})\} \hat{\Delta}(\hat{\mathbf{s}}, \hat{\mathbf{s}}_{1,a}) \right) \right\rangle_{1,n+1}}{\left\langle \exp \left( 4\pi V\mu^2 \int_V d\hat{\mathbf{c}} \int_S d\hat{\mathbf{s}} \Omega(\hat{\mathbf{c}}; -\hat{\mathbf{s}}) \frac{1}{A} \sum_{a=1}^A \delta\{\hat{\mathbf{c}} - (\hat{\mathbf{c}}_1 + 1/2\hat{\mathbf{s}}_{1,a})\} \hat{\Delta}(\hat{\mathbf{s}}, \hat{\mathbf{s}}_{1,a}) \right) \right\rangle_{1,n+1}}. \quad (5.5)$$

The presence of  $\hat{\Delta}$ -function factors provides the option of replacing the dynamical variable  $\hat{\mathbf{s}}_{1,a}$  in the argument of the  $\delta$  functions by the parametric variable  $\hat{\mathbf{s}}$ , which replacement we sometimes make.

The transformation of the order parameter to a representation in terms of the plane wave and spherical harmonic coordinates, and the inverse transformation, are effected as follows:

$$\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m}) = \int_S d\hat{\mathbf{s}} \hat{Y}_{\hat{l}\hat{m}}^*(\hat{\mathbf{s}}) \exp(\frac{1}{2} i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}) \int_V d\hat{\mathbf{c}} \exp(-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}) \Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}}), \quad (5.6a)$$

$$\Omega(\hat{\mathbf{c}}; \hat{\mathbf{s}}) = \frac{1}{V^{n+1}} \sum_{\hat{\mathbf{k}}} \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}) \exp(-\frac{1}{2} i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}) \sum_{\hat{l}\hat{m}} \hat{Y}_{\hat{l}\hat{m}}(\hat{\mathbf{s}}) \Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m}). \quad (5.6b)$$

This choice of transformation has the effect of keeping the physical interpretation of the order parameter  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  free of any complicating factors of  $\exp(\frac{1}{2} i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}})$ , leaving the full factor  $\exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}})$  in the fluctuating variable to which the order parameter couples. Via this transformation, one arrives at a transformed self-consistent equation for the order parameter:

$$\Omega(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0) = \frac{\left\langle (1/A) \sum_{a=1}^A e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_a) \exp \left[ (4\pi\mu^2/V^n) \sum_{\hat{\mathbf{k}}, \hat{l}, \hat{m}} \Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} (1/A) \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}, \hat{m}}(-\hat{\mathbf{s}}_a) \right] \right\rangle_{1, n+1}}{\left\langle \exp \left[ (4\pi\mu^2)/V^n \sum_{\hat{\mathbf{k}}, \hat{l}, \hat{m}} \Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} (1/A) \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}, \hat{m}}(-\hat{\mathbf{s}}_a) \right] \right\rangle_{1, n+1}}. \quad (5.7)$$

We shall often refer to the triple  $(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0)$  as the ‘‘external variables.’’

### B. Instability of the fluid state

We now demonstrate that upon increasing the density of formed bonds the fluid state is rendered linearly unstable. To do this we follow Ref. 10, and expand the replica free energy,  $n\beta N f_n$  in Eq. (4.5b), to second order in the order parameter  $\Omega$ , thus obtaining

$$\begin{aligned} n\beta N f_n(\Omega) \approx & 2\pi\mu^2 NV \sum_{\hat{\mathbf{k}}} \sum_{\hat{l}_1, \hat{m}_1} \sum_{\hat{l}_2, \hat{m}_2} \\ & \times \Omega(\hat{\mathbf{k}}; \hat{l}_1, \hat{m}_1) \Omega(-\hat{\mathbf{k}}; \hat{l}_2, \hat{m}_2) M_{\hat{l}_1, \hat{m}_1, \hat{l}_2, \hat{m}_2}(\hat{\mathbf{k}}) \\ & - \left( \frac{4\pi\mu^2}{A} \right)^2 \frac{NV}{2V^n} \sum_{\hat{\mathbf{k}}, \hat{l}, \hat{m}} |\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})|^2 (-1)^{\bar{l}} \\ & \times \sum_{a_1, a_2} \prod_{\alpha=0}^n \left( \frac{\delta_{a_1, a_2} + (1 - \delta_{a_1, a_2}) C_{l^\alpha}}{4\pi} \right), \quad (5.8) \end{aligned}$$

where, as discussed in Sec. II, the coefficients  $C_l$  represent the effects of the interactions between the orbitals of a single particle (and are all less than 1 for  $l \geq 1$ ), and the kernel  $M$  is given by

$$M_{\hat{l}_1, \hat{m}_1, \hat{l}_2, \hat{m}_2}(\hat{\mathbf{k}}) = \int_S d\hat{\mathbf{s}} \hat{Y}_{\hat{l}_1, \hat{m}_1}(\hat{\mathbf{s}}) \hat{Y}_{\hat{l}_2, \hat{m}_2}(-\hat{\mathbf{s}}) \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}). \quad (5.9)$$

We remind the reader that this linear stability analysis applies only to the higher replica sectors of the order parameter, as per the discussion in Sec. V A. The corresponding analysis applied to the one-replica sector reveals the fact, anticipated in Sec. V A, that the one-replica sector remains stable at the transition, owing to the stabilizing effect of the interparticle interactions.

We expect the liquid state to become unstable first for long wavelengths, corresponding to  $\hat{\mathbf{k}} \rightarrow \hat{\mathbf{0}}$ . In this limit,  $M_{\hat{l}_1, \hat{m}_1, \hat{l}_2, \hat{m}_2}(\hat{\mathbf{k}}) \rightarrow \delta_{\hat{l}_1, \hat{l}_2} \delta_{\hat{m}_1, \hat{m}_2} (-1)^{\bar{l} + \bar{m}}$ . By examining the coefficients of the quadratic terms in Eq. (5.8), and specifically their signs, we see that for  $\mu^2 < \mu_c^2 \equiv 1$  the coefficients are positive for all components of the order parameter [i.e., for all values of  $(\hat{\mathbf{k}}, \hat{l}, \hat{m})$ ] and, therefore, that the free energy has a local minimum at  $\Omega = 0$ . Thus, for  $\mu^2 \leq \mu_c^2$  the fluid state is (at least locally) thermodynamically stable. On the other hand, for  $\mu^2 > \mu_c^2$ , certain coefficients become negative, starting with the longest length scale (and isotropic, corresponding to  $\hat{l} = \hat{0}$ ) modes. This sign change indicates

the loss of the (linear) stability of the fluid, and the concomitant acquisition of a nonzero value of the order parameter. As usual, the linear instability of one state does not sharply specify the nature of the stable state that replaces it, although the directions of instability do provide hints. In the present setting, the residual stability of the one-replica sector suggests that the primary characteristic of the new state is macroscopic translational and rotational invariance, which is the mechanism by which the induction of energetically costly order in the one-replica sector is avoided. Thus, it is reasonable to anticipate that the state that replaces the fluid state upon the formation of a sufficiently large density of bonds is the amorphous solid state. Furthermore, as the coefficients  $C_l$  are smaller than unity for  $l \geq 1$ , and become progressively smaller with increasing  $l$ , we may conclude that all anisotropic sectors remain stable, at least for bond densities in the vicinity of the amorphous solidification transition. Thus, it is reasonable to anticipate that anisotropic ordering (i.e., orientational localization) will arise only as a *response* to positional ordering, via nonlinear coupling between isotropic and anisotropic order-parameter components. Thus, as will be borne out below, we should anticipate that the form and extent of the anisotropic ordering will be computable algorithmically, as a perturbative correction to the nonperturbative result for the ordering in the isotropic sector.<sup>14</sup>

## VI. SOLUTION OF THE ORDER-PARAMETER SELF-CONSISTENT EQUATION

### A. General strategy

Having obtained the self-consistency equation (SCE) for the order parameter, Eq. (5.7), we now turn to the issue of solving it. We shall begin by extracting from the full SCE a transcendental self-consistency equation for the fraction of localized particles  $q$  by considering the SCE at external variables  $\hat{l}_0 = \hat{m}_0 = \hat{0}$  and taking the limit  $\hat{\mathbf{k}}_0 \rightarrow \hat{\mathbf{0}}$ . Solving this equation in the vicinity of the amorphous solidification transition (i.e., for small excess crosslink densities) we will find that  $q$  tends to 0 near the transition, allowing us to expand the SCE for the order-parameter in powers of  $q$  and truncate the expansion, retaining terms of order  $q^2$ .

We will then solve the SCE for individual order parameter components, starting with the only component with an unstable band, the isotropic component  $\Omega(\hat{\mathbf{k}}; \hat{0}, \hat{0})$  (the unstable band being those long wavelength modes for which  $\hat{\mathbf{k}}^2 < 2\epsilon$ ), which we shall obtain by utilizing the form of the solution, due to Refs. 5,6, and discussed in Sec. III C. The remaining (anisotropic) components are linearly stable and thus we can solve for their leading-order values perturba-

tively, by considering their couplings to  $\Omega(\hat{\mathbf{k}}; \hat{0}, \hat{0})$ . We shall obtain these anisotropic components by first solving for the leading-order contribution to the two lowest angular-momentum components, and then obtaining the solution in the general case by induction. The structure of the order parameter is illustrated in Fig. 5, showing the different components and bands.

Throughout the entire calculation we shall only be concerned with finding the leading-order contributions to the components of  $\Omega$ . This will generally imply (i) truncating the expansion in powers of  $q$  (typically at second order), (ii) ignoring the coupling of the components of the order parameter to higher angular-momentum components, and (iii) truncating expansions in powers of  $\hat{\mathbf{k}}$  (typically at linear order), as we expect typical values of  $\hat{\mathbf{k}}^2$  to be of order  $\epsilon$ . Many technical details of the calculations have been relegated to the appendices.

### B. Fraction of positionally localized particles

The first step in our solution of the order-parameter SCE is to determine the fraction of localized particles  $q$ . Following the discussion in Sec. III B, we first separate the delocalized and localized fractions in the full order parameter  $\Omega$  by writing

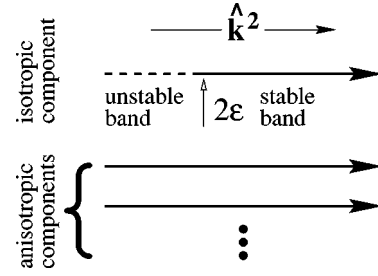


FIG. 5. Component and band structure of the order parameter (see text for explanation).

$$\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m}) \equiv (1-q) \prod_{\alpha=0}^n \left( \frac{\delta_{\mathbf{k}^{\alpha}, 0} \delta_{l^{\alpha}, 0} \delta_{m^{\alpha}, 0}}{\sqrt{4\pi}} \right) + q W(\hat{\mathbf{k}}; \hat{l}, \hat{m}), \quad (6.1)$$

where  $q W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  is the part of the order parameter describing the localized particles and is analytic at the origin, with  $W(\hat{0}; \hat{0}, \hat{0}) = 1/\sqrt{4\pi}$ . The delocalized contribution cancels from the numerator and denominator of the SCE, so we may rewrite Eq. (5.7), replacing  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  with  $q W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  in both the numerator and the denominator, obtaining

$$\Omega(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0) = \frac{\left\langle (1/A) \sum_{a=1}^A e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_a) \exp \left[ (4\pi\mu^2/V^n) \sum_{\hat{\mathbf{k}}, \hat{l}, \hat{m}} q W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} (1/A) \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}, \hat{m}}(-\hat{\mathbf{s}}_a) \right] \right\rangle_{1, n+1}}{\left\langle \exp \left[ (4\pi\mu^2/V^n) \sum_{\hat{\mathbf{k}}, \hat{l}, \hat{m}} q W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} (1/A) \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}, \hat{m}}(-\hat{\mathbf{s}}_a) \right] \right\rangle_{1, n+1}}. \quad (6.2)$$

Following the ideas of Refs. 6,5, to obtain a SCE for  $q$  we consider the SCE (6.2) for the order-parameter component  $\Omega(\hat{\mathbf{k}}_0; \hat{0}, \hat{0})$  in the limit  $\hat{\mathbf{k}}_0 \rightarrow \hat{0}$ . We start with the SCE for  $\Omega(\hat{\mathbf{k}}_0; \hat{0}, \hat{0})$ :

$$\Omega(\hat{\mathbf{k}}_0; \hat{0}, \hat{0}) = e^{-\mu^2 q} \left\langle e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \frac{1}{\sqrt{4\pi}} \exp \left( \frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}, \hat{l}, \hat{m}} q W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}, \hat{m}}(-\hat{\mathbf{s}}_a) \right) \right\rangle_{1, n+1}. \quad (6.3)$$

Note that the denominator of the right-hand side of Eq. (6.2) has been replaced by  $\exp(\mu^2 q)$  (see Appendix A for details). We now consider the limit  $\hat{\mathbf{k}} \rightarrow \hat{0}$  via a sequence for which  $\tilde{\mathbf{k}} = \mathbf{0}$ . The left-hand side, as can be easily seen from Eq. (6.1), becomes  $q/\sqrt{4\pi}$ . To evaluate the right-hand side we follow the procedure used in Appendix A to obtain the denominator of the right-hand side of the SCE.

We expand the exponential in a power series in  $q$  and consider the  $r$ -th order term, and pass to the replica limit  $n \rightarrow 0$ :

$$\left\langle \frac{1}{r!} (4\pi\mu^2)^r q^r \sum_{\mathbf{k}_1, l_1, m_1} \cdots \sum_{\mathbf{k}_r, l_r, m_r} W(\mathbf{k}_1; l_1, m_1) \cdots W(\mathbf{k}_r; l_r, m_r) e^{i\mathbf{k}_0 \cdot \mathbf{c}} e^{i\mathbf{k}_1 \cdot \mathbf{c}} \cdots e^{i\mathbf{k}_r \cdot \mathbf{c}} \right. \\ \left. \times \frac{1}{A^r} \sum_{a_1, \dots, a_r} e^{i\mathbf{k}_1 \cdot \mathbf{s}_{a_1}} \cdots e^{i\mathbf{k}_r \cdot \mathbf{s}_{a_r}} Y_{l_1 m_1}(-\mathbf{s}_{a_1}) \cdots Y_{l_r m_r}(-\mathbf{s}_{a_r}) \right\rangle_{1,1}. \quad (6.4)$$

By MTI of  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  we know that  $\tilde{\mathbf{k}}_r = \mathbf{0}$ , which means that  $\mathbf{k}_r = \mathbf{0}$ . Also, using MRI of  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  we see that if  $\hat{\mathbf{k}} = \hat{0}$  then Eq. (A3) can only be nonzero if  $\hat{l} = \hat{0}$  also. Knowing that  $W(\hat{0}; \hat{0}, \hat{0}) = 1/\sqrt{4\pi}$ , for the  $r$ th order contribution (with  $r \geq 1$ ) we get  $(1/r!)(\mu^2)^r q^r$ . For  $r=0$ , however, we get 0, because the limit of  $\langle \exp(-i\mathbf{k}_0 \cdot \mathbf{c}) \rangle$  as  $\mathbf{k}_0 \rightarrow \mathbf{0}$  is zero. Resumming the power series we finally obtain

$$\left\langle e^{i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \exp\left(\frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}\hat{l}\hat{m}} q W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}\hat{m}}(\hat{\mathbf{s}}_a)\right) \right\rangle_{1,n+1} = \sum_{r \geq 1} \frac{1}{r!} (\mu^2)^r q^r = \exp(\mu^2 q) - 1. \quad (6.5)$$

We thus find the following self-consistency equation for the fraction of localized atoms:

$$1 - q = \exp(-\mu^2 q). \quad (6.6)$$

This self-consistency condition is precisely that obtained in the case of vulcanized macromolecules,<sup>5,6</sup> and earlier, in the context of random graph theory, by Erdős and Rényi (see Ref. 6).

We will find it convenient to exchanging the control parameter  $\mu^2$  for  $\epsilon$ , defined via  $\mu^2 \equiv 1 + \epsilon/3$ , so that  $\epsilon$  vanishes as the transition is approached. The self-consistent equation for  $q$  is transcendental, but it is easy to analyze it graphically. Then, for  $\epsilon < 0$  we find that there is only one solution  $q = 0$ , corresponding to the liquid state of the system (no localized particles), and for  $\epsilon > 0$  we find that for  $\epsilon$  small  $q$  is small also, indicating that the fraction  $q$  of particles comprising the amorphous solid state tends to zero in the vicinity of the amorphous solidification transition. We can thus expand the exponential on the right-hand side of Eq. (6.6) obtaining the fraction  $q$  to first order in  $\epsilon$ :

$$q \approx \frac{2}{3} \epsilon. \quad (6.7)$$

### C. Perturbation expansion for the self-consistency equation

Having found the fraction  $q$  of localized particles to be small in the vicinity of the transition, we may expand the self-consistency equation for the order parameter, Eq. (6.2), in powers of  $q$ , to second order, obtaining

$$\begin{aligned} q W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0) + (1-q) \prod_{\alpha=0}^n \left( \frac{\delta_{\mathbf{k}^\alpha, \mathbf{0}} \delta_{l^\alpha, 0} \delta_{m^\alpha, 0}}{\sqrt{4\pi}} \right) \\ \approx e^{-\mu^2 q} \left\langle \frac{1}{A} \sum_{a_0=1}^A e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) \right\rangle_{1,n+1} + e^{-\mu^2 q} \left\langle \frac{1}{A} \sum_{a_0=1}^A e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) \frac{4\pi\mu^2}{V^n} \right. \\ \times \left. \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} q W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a_1=1}^A e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) \right\rangle_{1,n+1} \\ + \frac{e^{-\mu^2 q}}{2} \left\langle \frac{1}{A} \sum_{a_0=1}^A e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) \frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} q W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a_1=1}^A e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) \right. \\ \times \left. \frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}_2, \hat{l}_2, \hat{m}_2} q W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2) e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a_2=1}^A e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}} \hat{Y}_{\hat{l}_2 \hat{m}_2}(-\hat{\mathbf{s}}_{a_2}) \right\rangle_{1,n+1}. \end{aligned} \quad (6.8)$$

Cancelling the liquid contribution to  $\Omega$  on the left-hand side with the 0 th order contribution on the right-hand side, rearranging terms, and replacing  $\exp(-\mu^2 q)$  with  $1 - q$  we arrive at the form of the SCE that we shall focus on

$$\begin{aligned} q W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0) \approx (1-q) \frac{4\pi\mu^2}{V^n} q \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) \frac{1}{A^2} \sum_{a_0, a_1=1}^A \langle e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) \rangle_{1,n+1} \\ + \frac{1-q}{2} \left( \frac{4\pi\mu^2}{V^n} \right)^2 q^2 \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} \sum_{\hat{\mathbf{k}}_2, \hat{l}_2, \hat{m}_2} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2) \\ \times \frac{1}{A^3} \sum_{a_0, a_1, a_2=1}^A \langle e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}} \hat{Y}_{\hat{l}_2 \hat{m}_2}(-\hat{\mathbf{s}}_{a_2}) \rangle_{1,n+1}. \end{aligned} \quad (6.9)$$

### D. Self-consistency equation: Isotropic sector

Having obtained the localized fraction  $q$  and verified the consistency of the expansion of the SCE, we now turn to the issue of solving the SCE for individual components of the order-parameter. As discussed in Sec. V B, near to the amorphous solidification transition the only linearly unstable band

of  $W$  is the long-wavelength band of the isotropic component  $W(\hat{\mathbf{k}})$  [i.e.,  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})|_{\hat{l}=\hat{m}=\hat{0}}$  having sufficiently small (replicated) wave vectors, specifically,  $\hat{\mathbf{k}}^2 < 2\epsilon$ ]. Thus, the basic process occurring at the transition is the acquisition of a non-zero value by the unstable components of the order parameter, which in turn perturb the stable components away from



their zero values. The stable components include both the band of the isotropic component for  $\hat{\mathbf{k}}^2 > 2\epsilon$  and the anisotropic components for all values of  $\hat{\mathbf{k}}$ . As our aim is to calculate the leading contributions to each of the components of  $W$  at small positive  $\epsilon$ , we may, as a first step, proceed by computing the self-consistent value of  $W(\hat{\mathbf{k}})$ , neglecting the feedback on its value coming from the nonzero values that it induces in the (stable) anisotropic components [i.e.,  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})|_{\hat{l} \neq \hat{0}}$ ]. Although the  $\hat{\mathbf{k}}^2 > 2\epsilon$  band of the isotropic component  $W(\hat{\mathbf{k}})$  is linearly stable, it is necessary to treat it self-consistently together with the unstable band, owing to the fact that they constitute a continuum (see Fig. 5), and therefore the stable band includes elements with an arbitrarily large ‘‘susceptibility’’ to perturbations caused by their couplings to the elements of the linearly unstable band [i.e.,  $W(\hat{\mathbf{k}})$  for  $\hat{\mathbf{k}}^2 < 2\epsilon$ ].

We therefore consider the SCE for  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$ , Eq. (6.9), for isotropic external arguments (i.e.,  $\hat{l} = \hat{m} = \hat{0}$ ), and ignore the effects of all anisotropic components on the right hand side. We thus arrive at the closed, nonlinear SCE for  $W(\hat{\mathbf{k}}_0)$ :

$$W(\hat{\mathbf{k}}_0) = \left(1 - \frac{\epsilon}{3} - \frac{\hat{\mathbf{k}}^2}{6}\right) W(\hat{\mathbf{k}}_0) + \frac{\epsilon}{3} \frac{\sqrt{4\pi}}{V^n} \times \sum_{\mathbf{k}_1} W(\hat{\mathbf{k}}_1) W(\hat{\mathbf{k}}_0 - \hat{\mathbf{k}}_1). \quad (6.10)$$

Precisely this equation emerges in the context of randomly crosslinked macromolecular networks, from both semi-microscopic and Landau-type approaches.<sup>5,6</sup> In that context, the order parameter has only isotropic components, in contrast with the present context. To solve Eq. (6.10) we invoke the hypothesis for  $W(\hat{\mathbf{k}}_0)$  discussed in Sec. III C, viz., a parametrization in terms of the normalized probability distribution of localization lengths  $p(\tau)$ , along with the  $\delta_{\hat{\mathbf{k}}, \mathbf{0}}$  factor, enforcing MTI of the solution

$$W(\hat{\mathbf{k}}_0) = \frac{\delta_{\hat{\mathbf{k}}, \mathbf{0}}}{\sqrt{4\pi}} \int_0^\infty d\tau p(\tau) e^{-\hat{\mathbf{k}}^2/2\tau}. \quad (6.11)$$

As is shown in Ref. 6, this leads to the following nonlinear integrodifferential SCE for  $p(\tau)$ :

$$\frac{\tau^2}{2} \frac{dp}{d\tau} = \left(\frac{\epsilon}{2} - \tau\right) p(\tau) - \frac{\epsilon}{2} \int_0^\tau d\tau' p(\tau') p(\tau - \tau'), \quad (6.12)$$

i.e., precisely the equation found in Refs. 5,6. By making the rescalings

$$\tau \rightarrow \theta \equiv 2\tau/\epsilon, \quad (6.13a)$$

$$p(\tau) \rightarrow \pi(\theta) \equiv \frac{\epsilon}{2} p(\tau), \quad (6.13b)$$

as in Refs. 5,6, we determine that the universal scaling function  $\pi(\theta)$  satisfies the nonlinear integrodifferential equation

$$\frac{\theta^2}{2} \frac{d\pi}{d\theta} = (1 - \theta) \pi(\theta) - \int_0^\theta d\theta' \pi(\theta') \pi(\theta - \theta'), \quad (6.14)$$

together with the normalization condition  $\int_0^\infty d\theta \pi(\theta) = 1$ . The resulting scaled distribution  $\pi(\theta)$  can be obtained numerically, and the result is given in Refs. 5,6. (The prediction for this universal scaling function is compared with results from numerical simulations in Ref. 8.) Thus we have obtained the isotropic component  $W(\hat{\mathbf{k}})$  of the order parameter  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  in the vicinity of the transition. As we have discussed in Sec. III A, we are thus in possession of statistical information concerning the spatial localization of particles, regardless of the angular localization of the orbitals.

### E. Self-consistency equation: Anisotropic sectors

We now turn to the task of calculating the leading-order contributions to the *anisotropic* components of  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  [i.e.,  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})|_{\hat{l} \neq \hat{0}}$ ]. We remind the reader that the anisotropic components are all linearly stable near the transition, and not merely infinitesimally so (i.e., linear stability analysis indicates that none of these anisotropic components even become marginally stable at the transition). Note the contrast with the stable band of the isotropic component [ $W(\hat{\mathbf{k}})$  for  $\hat{\mathbf{k}}^2 > 2\epsilon$ ], which, though stable, do include marginally stable components (i.e., components of arbitrarily small ‘‘mass’’). Unlike the stable band of the isotropic component the (also stable) anisotropic components are separated by a ‘‘gap’’ from the unstable components, owing to the discreteness of the external variable  $\hat{l}$ , the components of which take on integer values only, in contrast with the components of  $\hat{\mathbf{k}}$ , which are continuous (in the thermodynamic limit). It is this ‘‘gap’’ that allows us to obtain the stable anisotropic components by means of perturbation theory, which we could not use to solve for the stable band of the isotropic component (see Fig. 5).

#### 1. Anisotropic sector: Angular momentum 1 in one replica channel

Rather than begin with generalities, we first consider the lowest angular momentum sector  $\{W(\hat{\mathbf{k}}; \hat{l}, \hat{m})\}_{\hat{l}^2=2}$  [i.e., the collection of order-parameter components  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  such that  $\hat{l}^2 \equiv \sum_\alpha l^\alpha (l^\alpha + 1) = 2$ ]. In this case  $\hat{l}$  is some permutation of the form  $(0, 1, 0, 0, \dots, 0)$ . We therefore consider the SCE for  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$ , i.e., Eq. (6.9) for the anisotropic external argument

$$\begin{array}{l} \text{replica} \\ \hat{l} \\ \hat{m} \end{array} \begin{array}{cccccc} 0 & 1 & \cdots & \alpha_1 & \alpha_1 + 1 & \cdots & n \\ \left( \begin{array}{cccccc} 0, & 0, & \cdots, & 1, & 0, & \cdots, & 0 \\ 0, & 0, & \cdots, & m_1, & 0, & \cdots, & 0 \end{array} \right) \end{array} \quad (6.15)$$

and arbitrary  $\hat{\mathbf{k}}$ , which, as we establish in Appendix C, reads

$$W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) = \mathcal{C}^{(0)} \left( -W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) + \frac{i}{\sqrt{3}} W(\hat{\mathbf{k}}_1) k_{m_1}^{\alpha_1*} - q \frac{\sqrt{4\pi}}{V^n} \sum_{\hat{\mathbf{k}}_1} W(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_1) \right). \quad (6.16)$$

The symbol  $k_m^{\alpha*}$  denotes the complex conjugate of the  $m$ th spherical tensor component of the vector  $\mathbf{k}^\alpha$  spherical component of the vector  $\mathbf{k}^\alpha$  and is defined via

$$k_m^{\alpha*} \equiv \sqrt{\frac{4\pi}{3}} k Y_{1m}^*(\mathbf{k}/k). \quad (6.17)$$

The parameter  $\mathcal{C}^{(0)}$  encodes physical information arising from orbital-orbital correlations of a single particle and is defined in Appendix B. Specifically,  $\mathcal{C}^{(0)}$  depends on the  $l=1$  value of the free-particle two-orbital orientation correlator  $\langle Y_{lm}^*(\mathbf{s}_a) Y_{l'm'}(\mathbf{s}_{a'}) \rangle_{1,1}$ . The permutation symmetry among the  $A$  orbitals and rotational invariance of the joint probability distribution of their orientations restrict this correlator to have the form

$$\langle Y_{lm}^*(\mathbf{s}_a) Y_{l'm'}(\mathbf{s}_{a'}) \rangle_{1,1} = \frac{1}{4\pi} \delta_{l,l'} \delta_{m,m'} \times (\delta_{a,a'} + (1 - \delta_{a,a'}) C_l), \quad (6.18)$$

characterized by the parameters  $\{C_l\}_{l=1}^\infty$  (with  $C_0=1$ , by normalization), introduced in Sec. II. As for the issue of what terms have been omitted in arriving at Eq. (6.16), we are concerned only with the leading-order values of the components of  $W$ , and therefore, here and elsewhere, shall omit terms that do not alter leading-order values. In particular, in arriving at Eq. (6.16) from Eq. (6.9) we have neglected all components of  $W$  having  $\hat{l} \geq 2$ . Such terms are sufficiently small that feedback from them would not alter the leading-order value of  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$ . We shall verify the internal consistency of this assumption below. In addition, we have only kept terms carrying sufficiently few powers of components of  $\hat{\mathbf{k}}$ . As the characteristic value of  $\hat{\mathbf{k}}^2$  is of order  $\epsilon$ , higher powers render terms subdominant. The steps leading from Eq. (6.9) to Eq. (6.16) are explained in detail in Appendix C.

To solve Eq. (6.16) we rewrite it in the form of a (type II inhomogeneous) integral equation by moving the first term on the right hand side to the left, regarding the second term as a known inhomogeneity, and the third term as a perturbation. We then solve this equation iteratively, thus obtaining

$$W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) = \frac{i}{\sqrt{3}} \mathcal{C}^{(1)} W(\hat{\mathbf{k}}) k_{m_1}^{\alpha_1*}, \quad (6.19)$$

where the parameter  $\mathcal{C}^{(1)}$  depends on  $A$  and  $C_1$  (see Appendix B). In fact, for this particular component of  $W$  our procedure merely amounts to truncating the Born series after the *zeroth* order (i.e., effectively ignoring the perturbation altogether), and solving the resulting algebraic equation. How-

ever, for certain other components it turns out to be necessary to retain the first-order term, for reasons that we shall explain below.

As we have discussed in Sec. III A, the result that we have just obtained about the value of the order-parameter component  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  yields statistical information concerning the variations, across the system, of the strength of the correlations between the thermal fluctuations of the positions of the localized particles and the thermal fluctuations of the orientations of their orbitals. We will discuss this information in more detail in Sec. VII C

## 2. Anisotropic sector: Angular momentum $l$ in two replica channels

Having obtained the leading-order contributions to the order-parameter components  $W(\hat{\mathbf{k}})$  and  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  [i.e., the isotropic (largest) and anisotropic (next largest) components], we now address the component of  $W$  corresponding to

$$\begin{array}{cccccccc} \text{replica} & 0 & 1 & \cdots & \alpha_1 & \alpha_1+1 & \cdots & n \\ \hat{l} & \left( 0, 0, \cdots, 1, 0, \cdots, 0 \right) \\ \hat{m} & \left( 0, 0, \cdots, m_1, 0, \cdots, 0 \right), \end{array} \quad (6.20)$$

which we denote by  $W_{1m_1 m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ . The motivation for examining this component is that, in contrast to the components  $W(\hat{\mathbf{k}})$  and  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$ , the limit  $\hat{\mathbf{k}} \rightarrow \hat{\mathbf{0}}$  of this component provides information purely about the orientational localization of the orbitals, independent of the positional localization properties, as we shall discuss in more detail in Sec. VII C.

As shown in Appendix D, the retention of all terms that give rise to leading-order contributions to  $W_{1m_1 m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$  leads to the following SCE for this component:

$$\begin{aligned} W_{1m_1 m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) &= \mathcal{C}^{(2)} W_{1m_1 m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) - \frac{1}{3} \mathcal{C}^{(3)} k_{m_1}^{\alpha_1*} k_{m_2}^{\alpha_2*} W(\hat{\mathbf{k}}) \\ &+ q \mathcal{C}^{(2)} \frac{\sqrt{4\pi}}{2V^n} \sum_{\hat{\mathbf{k}}_1} W(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_1 m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}_1) \\ &+ q \mathcal{C}^{(2)} \frac{\sqrt{4\pi}}{V^n} \sum_{\hat{\mathbf{k}}_1} W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}}_1), \end{aligned} \quad (6.21)$$

where the parameters  $\mathcal{C}^{(2)}$  and  $\mathcal{C}^{(3)}$  depend on  $A$  and  $C_1$  (see Appendix B). On the basis of the transformation properties of this equation under common rotations of the replicas (and bearing in mind the coupling between positional and orientational degrees of freedom), we propose that the solution has the form

$$\begin{aligned} W_{1m_1 m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) &= (-1)^{m_1} \delta_{m_1+m_2,0} w^{(1)}(\hat{\mathbf{k}}^2) \\ &+ k_{m_1}^{\alpha_1*} k_{m_2}^{\alpha_2*} w^{(2)}(\hat{\mathbf{k}}^2), \end{aligned} \quad (6.22)$$

parametrized in terms of the two as-yet unknown functions  $w^{(1)}$  and  $w^{(2)}$ , which each depend only on  $\hat{\mathbf{k}}^2$ . By inserting this proposed form into Eq. (6.21), contracting (on the indices  $m_1$  and  $m_2$ ), first with  $(-1)^{m_1} \delta_{m_1+m_2,0}$  and then with  $k_{m_1}^{\alpha_1*} k_{m_2}^{\alpha_2*}$ , and considering the limit  $\mathbf{k}^{\alpha^1} = \mathbf{k}^{\alpha^2} \rightarrow \mathbf{0}$  (with  $\hat{\mathbf{k}}^2$  fixed and arbitrary), and retaining only terms that contribute to the leading-order value of  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ , we arrive at the pair of coupled (type II inhomogeneous) integral equations

$$\mathcal{C}^{(4)} w^{(2)}(\hat{\mathbf{k}}^2) = -\frac{1}{3} \frac{\mathcal{C}^{(3)}}{\mathcal{C}^{(2)}} W(\hat{\mathbf{k}}), \quad (6.23a)$$

$$\begin{aligned} \mathcal{C}^{(4)} w^{(1)}(\hat{\mathbf{k}}^2) &= \frac{q \sqrt{4\pi}}{V^n} \sum_{\hat{\mathbf{k}}_1} W(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) w^{(1)}(\hat{\mathbf{k}}_1^2) \\ &+ q \frac{\sqrt{4\pi}}{V^n} \left\{ \sum_{\hat{\mathbf{k}}_1} W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}}_1) \right\}_{\delta} \\ &+ q \frac{\sqrt{4\pi}}{V^n} \left\{ \sum_{\hat{\mathbf{k}}_1} k_{1m_1}^{\alpha_1*} k_{1m_2}^{\alpha_2*} w^{(2)}(\hat{\mathbf{k}}_1^2) \right. \\ &\left. \times W(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) \right\}_{\delta}, \end{aligned} \quad (6.23b)$$

where the parameter  $\mathcal{C}^{(4)}$  depends on  $A$  and  $C_1$  (see Appendix B). The symbol  $\{\dots\}_{\delta}$  denotes the result of extracting from the quantity inside the braces the coefficient of the term proportional to the isotropic rank-2 spherical tensor  $(-1)^{m_1} \delta_{m_1+m_2,0}$ . [To extract this part, we take the limit  $\mathbf{k}^{\alpha^1} = \mathbf{k}^{\alpha^2} \rightarrow \mathbf{0}$  with  $\hat{\mathbf{k}}^2$  fixed and arbitrary, and contract with  $(-1)^{m_1} \delta_{m_1+m_2,0}/3$ .] To find the leading contributions to  $w^{(1)}$  and  $w^{(2)}$  we first read off the value of the latter from Eq. (6.23a). We then use this result to eliminate  $w^{(2)}$  from Eq. (6.23b), observing that we can omit the first term on the right hand side of Eq. (6.23b), and perform the remaining summations to arrive at the results

$$w^{(2)}(\hat{\mathbf{k}}^2) = -\frac{1}{3} \mathcal{C}^{(5)} \frac{1}{\sqrt{4\pi}} \int_0^{\infty} d\theta \pi(\theta) e^{-\hat{\mathbf{k}}^2/\epsilon\theta}, \quad (6.24a)$$

$$w^{(1)}(\hat{\mathbf{k}}^2) = \frac{\mathcal{C}^{(6)}}{\sqrt{4\pi}} \frac{\epsilon^2}{4} \int_0^{\infty} d\theta \kappa(\theta) e^{-\hat{\mathbf{k}}^2/\epsilon\theta}, \quad (6.24b)$$

where

$$\begin{aligned} \theta \kappa(\theta) &\equiv \int_0^{\infty} d\theta_1 \pi(\theta_1) d\theta_2 \pi(\theta_2) \theta_1 \theta_2 \delta[\theta - (\theta_1 + \theta_2)] \\ &= \{(\theta \pi(\theta)) * (\theta \pi(\theta))\}(\theta), \end{aligned} \quad (6.24c)$$

where the symbol  $*$  represents Laplace convolution. Note that, as can be anticipated from our perturbative approach to obtaining the anisotropic components, the results for  $w^{(1)}$  and  $w^{(2)}$  are constructed from the universal scaling function  $\pi(\theta)$ .

### 3. Self-consistency equation: General case

Having obtained the isotropic component of  $W$ , as well as the two lowest angular momentum anisotropic components, we now address the task of establishing the general form of  $W$ , along with an algorithm for obtaining the leading-order contributions to  $W$  for arbitrary values of its arguments. We begin by proposing the following structure for the general form of the leading-order contribution to  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$ :

$$\begin{aligned} W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) &\approx \mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}}) W(\hat{\mathbf{k}}) \\ &+ \epsilon^{1+(1/2)\hat{l}} \mathcal{T}_{\hat{l}, \hat{m}} \int_0^{\infty} d\theta \pi_{\hat{l}, \hat{m}}(\theta) e^{-\hat{\mathbf{k}}^2/\epsilon\theta}. \end{aligned} \quad (6.25)$$

Here  $\mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}})$  is a certain homogeneous polynomial in  $k_m^{(l)}$  in which all terms are of order  $\hat{l}$  in  $k$ . [We remind the reader that  $k_m^{(l)}$  stands for  $\sqrt{(2l+1)/4\pi} k^l Y_{lm}(\mathbf{k}/k)$ , and is thus of order  $l$  in  $k$ .] In addition,  $\mathcal{T}_{\hat{l}, \hat{m}}$  is a certain rotationally invariant tensor depending only on  $\hat{l}$  and  $\hat{m}$ , and  $\pi_{\hat{l}, \hat{m}}(\theta)$  is a distribution. All the unknown ingredients  $[\mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}}), \mathcal{T}_{\hat{l}, \hat{m}}$ , and  $\pi_{\hat{l}, \hat{m}}(\theta)]$  will be obtained below.

To illustrate these notions with a concrete example we note that  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ , constructed in Sec. VI E 2 has such a form, with

$$\mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}})|_{\hat{l}=(0, \dots, 0, 1, 1, 0, \dots, 0)} = -\frac{1}{3} \mathcal{C}^{(5)} k_{m_1}^{\alpha_1*} k_{m_2}^{\alpha_2*}, \quad (6.26a)$$

$$\mathcal{T}_{\hat{l}, \hat{m}}|_{\hat{l}=(0, \dots, 0, 1, 1, 0, \dots, 0)} = (-1)^{m_1} \delta_{m_1+m_2, 0}, \quad (6.26b)$$

$$\pi_{\hat{l}, \hat{m}}(\theta)|_{\hat{l}=(0, \dots, 0, 1, 1, 0, \dots, 0)} = \frac{\mathcal{C}^{(6)}}{4\sqrt{4\pi}} \kappa(\theta), \quad (6.26c)$$

where  $\hat{l}=(0, \dots, 0, 1, 1, 0, \dots, 0)$  indicates that  $l^{\alpha_1} = l^{\alpha_2} = 1$ , with  $l^{\alpha} = 0$  in all other replicas. Note that  $\mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}})|_{\hat{l}=(0, \dots, 0, 1, 1, 0, \dots, 0)}$  is of order  $\hat{l} = 2$  in components of  $\hat{\mathbf{k}}$ .

To show that the leading-order contribution to the general component  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  in the vicinity of the amorphous solidification transition does indeed have the form (6.25), for all values of  $\hat{l}$ ,  $\hat{m}$ , and  $\hat{\mathbf{k}}$ , we proceed by full mathematical induction on the multi-index  $\hat{l}^{15}$ . We note that  $W(\hat{\mathbf{k}})$  has this form with  $\mathcal{P}_{\hat{0}, \hat{0}}(\hat{\mathbf{k}}) = 1$  and  $\pi_{\hat{0}, \hat{0}}(\theta) = 0$ , thus establishing the *base* of induction. To establish the *step* of induction we assume that  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  has the form (6.25) for all values  $\hat{l} < \hat{l}_0$  (by which we mean  $l^{\alpha} \leq l_0^{\alpha}$  for all  $\alpha$ , and  $l^{\alpha} < l_0^{\alpha}$  for at least one  $\alpha$ ). We then examine the SCE for  $W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0)$ :

$$\begin{aligned}
W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0) &= (1-q) \frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) \frac{1}{A^2} \sum_{a_0, a_1=1}^A \langle e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) \\
&\times e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) \rangle_{1, n+1} + \frac{1}{2} \left( \frac{4\pi\mu^2}{V^n} \right)^2 q \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} \sum_{\hat{\mathbf{k}}_2, \hat{l}_2, \hat{m}_2} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2) \frac{1}{A^3} \\
&\times \sum_{a_0, a_1, a_2=1}^A \langle e^{-i\hat{\mathbf{k}}_0 \cdot \hat{\mathbf{c}}} \hat{Y}_{\hat{l}_0 \hat{m}_0}^*(\hat{\mathbf{s}}_{a_0}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}} \hat{Y}_{\hat{l}_2 \hat{m}_2}(-\hat{\mathbf{s}}_{a_2}) \rangle_{1, n+1}. \quad (6.27)
\end{aligned}$$

As we are only concerned with leading-order contributions to  $W$ , we truncate the  $\hat{l}$  sums in Eq. (6.27) so as to include only terms with  $\hat{l} \leq \hat{l}_0$ . We now examine the contributions to  $W(\hat{\mathbf{k}}_0, \hat{l}_0, \hat{m}_0)$  coming from linear couplings to lower-angular momentum components of  $W$  [i.e., the terms in the right-hand side of Eq. (6.27) that are linear in  $W$ ]. Consider the coupling to  $W(\hat{\mathbf{k}}, \hat{l}, \hat{m})$ . By the translational invariance of the correlator, performing the  $\hat{\mathbf{c}}$  average in Eq. (6.27) we establish that  $\hat{\mathbf{k}} = \hat{\mathbf{k}}_0$ . The remaining correlator factorizes on the replica index, becoming

$$\prod_{\alpha=0}^n \langle Y_{l_0 m_0}^*(\mathbf{s}_{a_0}^\alpha) Y_{l' \alpha m^\alpha}(-\mathbf{s}_{a_1}^\alpha) e^{i\mathbf{k}_0 \cdot \hat{\mathbf{s}}_{a_1}^\alpha} \rangle_{1, n+1}. \quad (6.28)$$

By introducing the Rayleigh plane-wave expansion for the factor  $\exp i\mathbf{k}_0 \cdot \hat{\mathbf{s}}_{a_1}^\alpha$  in terms of spherical Bessel functions and harmonics<sup>16</sup> we see that this correlator is nonzero only for the terms of order  $l'^\alpha$  in the Rayleigh expansion for which the angular momenta  $l'^\alpha, l_0^\alpha$ , and  $l^\alpha$  can sum to angular momentum 0. As we are only interested in the leading-order contributions to  $W$ , and the  $l'^\alpha$  term in the Rayleigh expansion is of order  $(k_0^\alpha)^{l'^\alpha}$ , we need only keep the lowest angular-momentum term (i.e.,  $l'^\alpha = l_0^\alpha - l^\alpha$ ). Thus, from each replica we shall pick up the factors  $(k_0^\alpha)^{l_0^\alpha - m^\alpha}$ , provided, of course, that  $|m_0^\alpha - m^\alpha| \leq l_0^\alpha - l^\alpha$ . Together from all replicas, these factors will give a factor, depending on the  $\{k_m^{(l)}\}$ , that will be of order  $\bar{l}_0 - \bar{l}$  in  $k$ . To leading order, the term that corresponds to the coupling of  $W(\hat{\mathbf{k}}_0, \hat{l}_0, \hat{m}_0)$  to  $W(\hat{\mathbf{k}}, \hat{l}, \hat{m})$  will thus become

$$\left( \prod_{\alpha=0}^n (k_0^\alpha)^{l_0^\alpha - l^\alpha} C_{l_0, \hat{m}_0; \hat{l}, \hat{m}}^\alpha \right) \mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}}_0) W(\hat{\mathbf{k}}_0), \quad (6.29)$$

where the  $C_{l_0, \hat{m}_0; \hat{l}, \hat{m}}^\alpha$  are constants, for which we cannot in general provide a closed-form result, but which we can, however, compute, should we decide to construct some component of the order parameter explicitly, as we have, e.g., done for  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}$ .

As  $\Pi_\alpha(k_0^\alpha)^{l_0^\alpha - l^\alpha}$  is of order  $\bar{l}_0 - \bar{l}$  in  $k_0$ , and as  $\mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}}_0)$  is, according to the inductive assumption, of order  $\bar{l}$ , we see that this contribution is of order  $\bar{l}_0$  in  $k_0$ . Taking the term

corresponding to  $\hat{l} = \hat{l}_0, \hat{m} = \hat{m}_0$  over to the left-hand side, adding all remaining terms, and making the definition

$$\mathcal{P}_{\hat{l}_0, \hat{m}_0}(\hat{\mathbf{k}}_0) \equiv \sum_{\hat{l} < \hat{l}_0} \sum_{\hat{m}} \left( \prod_{\alpha=0}^n C_{\hat{l}_0, \hat{m}_0; \hat{l}, \hat{m}}^\alpha (k_0^\alpha)^{l_0^\alpha - l^\alpha} \right) \mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}}_0), \quad (6.30)$$

we see that, to leading order in  $k_0$ , the linear contribution to  $W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0)$  is indeed of the form (6.25), with  $\mathcal{P}_{\hat{l}_0, \hat{m}_0}(\hat{\mathbf{k}}_0)$  being of the correct order in  $k_0$ . As, due to the fact that  $q$  is small near the transition, the linear contribution is of lower order in  $\epsilon$  than the quadratic terms for values of  $\hat{\mathbf{k}}^2$  of order  $\epsilon$ , we have thus also established a recursive algorithm for determining  $\mathcal{P}_{\hat{l}_0, \hat{m}_0}(\hat{\mathbf{k}}_0)$ . Illustrations of its use can be found in Appendixes C and D.

We now examine the *quadratic* contribution to  $W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0)$  in Eq. (6.25). This term is only the dominant one for  $\hat{\mathbf{k}}_0^2 \ll \epsilon$  and, hence, we need only obtain it in the limit  $\hat{\mathbf{k}}_0^2 \rightarrow 0$ , which is equivalent to extracting from it the leading-order contribution to the part proportional to the ( $\mathbf{k}$  independent) rotationally invariant tensor  $\mathcal{T}_{\hat{l}_0, \hat{m}_0}$ . As we are only interested in the leading-order behavior of  $W$ , in the summations over  $\hat{l}$  in the quadratic term of Eq. (6.27) we need only include the linear contributions to  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  [i.e., for the purposes of computing the quadratic term of  $W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0)$  we can set  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) = \mathcal{P}_{\hat{l}, \hat{m}}(\hat{\mathbf{k}}) W(\hat{\mathbf{k}})$  for  $\hat{l} \leq \hat{l}_0$ ]. We now study the quadratic coupling of  $W(\hat{\mathbf{k}}_0; \hat{l}_0, \hat{m}_0)$  to lower angular-momentum components. In each replica  $\alpha$  we have four sources of angular momentum: two ( $l_1^\alpha$  and  $l_2^\alpha$ ) coming from the two components of  $W$  [i.e.,  $W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1)$  and  $W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2)$ ]; and two ( $l_1'^\alpha$  and  $l_2'^\alpha$ ), one coming from each of the Rayleigh expansions of the ‘‘shift’’ factors  $\exp i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}$  and  $\exp i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}$ . As we are only interested in the leading-order behavior of  $W$ , we need only consider the case when  $l_1^\alpha + l_2^\alpha + l_1'^\alpha + l_2'^\alpha = l_0^\alpha$ . Each source of angular momentum  $l$  brings with it a factor of  $k^l$ . Hence, multiplying all factors from all replicas together and assembling all terms in the summations we shall obtain

$$q V^{-n} \left\{ \sum_{\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2} \mathcal{F}(\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) W(\hat{\mathbf{k}}_1) W(\hat{\mathbf{k}}_2) \delta_{\hat{\mathbf{k}}_1 + \hat{\mathbf{k}}_2, \hat{\mathbf{k}}_0} \delta_{\hat{\mathbf{k}}_1, 0} \delta_{\hat{\mathbf{k}}_2, 0} \right\}_T, \quad (6.31)$$



where the operation  $\{\dots\}_{\mathcal{T}}$  denotes the extraction, from  $\dots$ , of the part proportional to  $\mathcal{T}_{\hat{l}_0, \hat{m}_0}$ , and where  $\mathcal{F}$  is a polynomial function of  $k_1$  and  $k_2$  in which all terms are of order  $\tilde{l}_0$ . Provided, that  $\hat{l}_0$  and  $\hat{m}_0$  satisfy conditions for macroscopic rotational invariance (note, in particular, that MRI requires  $\tilde{l}_0$  to be even and, hence, that the quadratic contribution vanishes for  $\tilde{l}_0$  odd), we can perform the summations, indeed obtaining the claimed structure for the second-order term in Eq. (6.25). Thus, we have established a recursive procedure for obtaining  $\pi_{\hat{l}_0, \hat{m}_0}(\theta)$ . Keeping in mind that typical values of  $\hat{\mathbf{k}}_0^2$  are of order  $\epsilon$ , that  $q=2/3\epsilon$ , and that  $W(\hat{\mathbf{k}})$  is of order unity we verify the scaling of the quadratic term to be  $\epsilon^{(\tilde{l}_0/2)+1}$ , thus completing the *step* of induction, viz. the second and final element of our proof.

In conclusion of our discussion of the solution of the order-parameter SCE we note, in passing, that all the assumptions that we have made in Sec. VI A regarding the scaling (with  $\epsilon$ ) of various quantities are verified, *a posteriori*, by the solution that we have obtained, thus establishing the self-consistency of these assumptions.

## VII. PHYSICAL INFORMATION ENCODED IN THE ORDER PARAMETER

### A. Introduction

We have constructed the solution of the order-parameter self-consistency equation in the vicinity of the amorphous solidification transition, Eq. (6.25), and have obtained explicit solutions for the two lowest angular-momentum components of the order parameter, Eqs. (6.19), (6.24a), (6.24b). We are thus in possession of a range of statistical information about the amorphous solid state, this information being encoded in the order parameter, as discussed in Sec. III A. In this section we will extract some of this information explicitly, from the two lowest angular-momentum components of the order parameter, provide a strategy for obtaining other statistical information about the system from higher angular-momentum components, and discuss the scaling of the order parameter with  $\epsilon$  near the transition, as well as the implications of this scaling.

Our statistical diagnosis of the structure of the amorphous solid state in the vicinity of the amorphous solidification transition is made in terms of the moments of the joint distribution function  $P$  that collects together the localization characteristics of all the particles in the sample and their orbitals, averaged over realizations of the disorder. As we shall see, we are unable to construct the entire distribution function, or even to construct a closed-form expression for arbitrary moments. However, most of the useful information about the system can be obtained from low moments of the distribution, resulting from the two lowest angular-momentum components of the order parameter, which we have obtained explicitly. As for the information encoded in the higher angular-momentum components of the order parameter, we do not extract it explicitly. We do, however, describe the kind of information that could be obtained from them, as well as provide the general procedure for doing so.

### B. Encoded information: Isotropic sector

We begin by discussing the statistical information, encoded in the isotropic component of the order parameter  $W(\hat{\mathbf{k}}^2)$ . In Sec. VI D we have obtained this component in the vicinity of the amorphous solidification transition and, consequently, the reduced distribution of (inverse square) localization lengths  $p(\tau)$  associated with localized particles. The fact that  $p(\tau)$  takes on a scaling form, and that the scaling function  $\pi(\theta)$  has a well defined peak with location and width both of order unity, allows us to establish that (as  $\epsilon \rightarrow 0$ )  $\tau$  scales as  $\epsilon$  and, accordingly,  $\xi$  scales as  $\epsilon^{-1/2}$ . For example, any reasonable choice for a characteristic value of  $\xi$ , say  $\int_0^\infty d\tau p(\tau) \tau^{-1/2}$ , scales as  $\epsilon^{-1/2}$ .

In the present context, while the emergent distribution  $p(\tau)$  is found to have striking scaling properties, there is the suspicion that changes in the details of the model will lead to changes at least in the details of the scaling function  $\pi(\theta)$  or, perhaps, in the scaling property itself. However, it has been found in the context of vulcanized macromolecular matter that the scaling property, as well as the precise form of the scaling function, are robust, universal features of the mean-field theory, verified by independent computer simulations. Moreover, this universality has been found to have its origins in the symmetries of the appropriate Landau free energy and the divergence (at the transition) of the characteristic localization length.

Being in possession of the entire distribution of localization lengths provides us with a surprisingly rich characterization of the positional aspects of the amorphous solid state. It is striking that the distribution is universal, not only across the macromolecular systems where it was first found, but also in the present setting of vitreous media. Although we have obtained the distribution via analysis of a specific semi-microscopic model of vitreous media, we anticipate that, here too, the result will have a broader domain of applicability. Moreover, given the emerging picture of orientational order as order slaved to the underlying positional order, it is not surprising—and indeed we shall demonstrate this point below—that all other statistical descriptors of the amorphous solid state are also constructed from the universal function  $\pi(\theta)$ .

### C. Encoded information: Low angular-momentum anisotropic sectors

#### 1. Angular localization

We now discuss some of the specific physical information that can be obtained by examining our explicit solutions for the two lowest angular-momentum components of the order parameter, which we have obtained in Secs. VI E 1 and VI E 2. The first piece of information concerns the angular localization of the orbitals, without regard to the positional localization of the particles. As we recall from Sec. III A, such information is accessed via the order parameter for  $\hat{\mathbf{k}} = \hat{\mathbf{0}}$ , and is described by the distribution of the collection of characteristics  $\{\Sigma_{lm}\}$ . The lowest angular-momentum order-parameter component that provides access to this information is  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ , the solution for which is given by Eq. (6.22). Evaluating at  $\hat{\mathbf{k}} = \hat{\mathbf{0}}$  gives

$$q W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{0}}) = (-1)^{m_1} \delta_{m_1+m_2,0} \frac{\mathcal{C}^{(6)}}{\sqrt{4\pi}} \frac{\epsilon^3}{6} \int_0^\infty d\theta \kappa(\theta). \quad (7.1)$$

Now, recalling the interpretation of the order parameter developed in Sec. III A, we arrive

$$\begin{aligned} q \int d\tau d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\tau, \{\Sigma\}, \{\Gamma\}) \Sigma_{1,m_1} \Sigma_{1,m_2} \\ = \left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle Y_{1m_1}^*(\mathbf{s}_{j,a}) \rangle \langle Y_{1m_2}^*(\mathbf{s}_{j,a}) \rangle \right] \\ = (-1)^{m_1} \delta_{m_1+m_2,0} \frac{\mathcal{C}^{(6)}}{\sqrt{4\pi}} \frac{\epsilon^3}{6} \int_0^\infty d\theta \kappa(\theta). \quad (7.2) \end{aligned}$$

Notice that this characteristic of the angular localization of the orbitals is essentially the order parameter traditionally used to describe the directional localization of magnetic moments in the spin-glass state. In fact, if we recall the spherical-tensor decomposition of the scalar product of two unit vectors,  $\mathbf{s}_1 \cdot \mathbf{s}_2 = \sum_m (-1)^m Y_{1m}(\mathbf{s}_1) Y_{1-m}(\mathbf{s}_2)$ , then by appropriately contracting Eq. (7.2) over  $m_1$  and  $m_2$  we obtain the familiar characterization of directional localization:

$$\left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle \mathbf{s}_{j,a} \rangle \cdot \langle \mathbf{s}_{j,a} \rangle \right] = \frac{3 \mathcal{C}^{(6)}}{\sqrt{4\pi}} \frac{\epsilon^3}{6} \int_0^\infty d\theta \kappa(\theta). \quad (7.3)$$

## 2. Angle-position fluctuation correlations

Further specific physical information concerns the degree to which the thermal fluctuations in the orbital orientations are correlated with the thermal fluctuations of the particle positions. As discussed in Sec. III A, to extract this information, which is encoded in the distribution of the collection of functions  $\{\Gamma_{lm}(\hat{\mathbf{k}})\}$ , we examine the order-parameter component  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$ :

$$\begin{aligned} q W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) &= q \int d\tau d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\tau, \{\Sigma\}, \{\Gamma\}) \\ &\quad \times \Gamma_{1,m_1}(\mathbf{k}^{\alpha_1}) e^{-\hat{\mathbf{k}}^2/2\tau} \\ &= \left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle \langle e^{-i\mathbf{k}^{\alpha_1} \cdot (\mathbf{c}_j - \boldsymbol{\mu}_j)} \right. \\ &\quad \left. - \langle e^{-i\mathbf{k}^{\alpha_1} \cdot (\mathbf{c}_j - \boldsymbol{\mu}_j)} \rangle \rangle \right. \\ &\quad \left. \times (Y_{1m_1}^*(\mathbf{s}_{j,a}) - \langle Y_{1m_1}^*(\mathbf{s}_{j,a}) \rangle) \right] \\ &= \frac{2\epsilon}{3} \frac{i\mathcal{C}^{(1)}}{\sqrt{3}} k_{m_1}^{\alpha_1} * \frac{\delta_{\hat{\mathbf{k}},\mathbf{0}}}{\sqrt{4\pi}} \int_0^\infty d\theta \pi(\theta) e^{-\hat{\mathbf{k}}^2/\epsilon\theta}. \quad (7.4) \end{aligned}$$

By considering the derivative with respect to  $\mathbf{k}^{\alpha_1}$ , taking the limit  $\hat{\mathbf{k}} \rightarrow \hat{\mathbf{0}}$ , and contracting, we obtain

$$\left[ \frac{1}{N} \sum_{j=1}^N \frac{1}{A} \sum_{a=1}^A \langle \langle (\mathbf{c}_j - \langle \mathbf{c}_j \rangle) \cdot (\mathbf{s}_{j,a} - \langle \mathbf{s}_{j,a} \rangle) \rangle \rangle \right] \approx - \frac{\epsilon}{\sqrt{3\pi}} \mathcal{C}^{(1)} \quad (7.5)$$

characterizing the anticorrelation of the thermal orientation fluctuations of orbitals with the thermal position-fluctuations of the particles to which the orbitals are attached.

## D. Scaling and its indications

In the previous two subsections we have obtained explicit physical information about the amorphous solid state in the vicinity of the solidification transition from the three lowest angular-momentum components of the order parameter. We now address in more generality the manner in which various physical quantities reflecting the orientational ordering scale with  $\epsilon$ . To do this we examine the scaling of various components of the order parameter, established in Sec. VI E 3. Hence we have the following scaling for various moments<sup>17</sup> of the joint probability distribution  $P$  associated with localized particles ( $\bar{l} \neq 0$ ):

$$\int d\tau d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\tau, \{\Sigma\}, \{\Gamma\}) \hat{\Sigma}_{\hat{l}\hat{m}} \sim \epsilon^{1+\bar{l}/2}, \quad (7.6a)$$

$$\begin{aligned} \int d\tau d\{\Sigma\} \mathcal{D}\{\Gamma\} P(\tau, \{\Sigma\}, \{\Gamma\}) \\ \times \hat{\Gamma}_{\hat{l}\hat{m}}(\hat{\mathbf{k}}) \exp(-\hat{\mathbf{k}}^2/2\tau) \sim k^{\bar{l}} \sim \epsilon^{\bar{l}/2}, \quad (7.6b) \end{aligned}$$

the latter being valid for  $\hat{\mathbf{k}}^2 \sim \epsilon$ . Note the exponent  $1 + \bar{l}/2$  in Eq. (7.6a).

We now describe a plausible physical scenario that is consistent with this scaling of  $P$ . Near to the transition the network has many long chains consisting of twice-bonded particles, with only the occasional more highly bonded particles linking them. Most of the localized particles are on extremely mobile segments. Orbitals attached to particles on such segments are likely to be even less localized orientationally than orbitals on less mobile segments, such as those near junctions between chains. Consider, for the sake of illustration, a dangling chain (i.e., one attached to the network only at one end). The orientational fluctuations of successive orbitals compound the fluctuations of orbitals further away from the junction, causing them to be successively more delocalized. This compounding of fluctuations so heavily suppresses orientational localization that it causes the scaling (and not just the numerical value) of the orientational localization characteristics  $\Sigma_{lm}$  to vary according to location in the network. Moreover, because orientational localization is heavily suppressed for such a large fraction of orbitals, the leading-order scaling of the moments of  $\Sigma_{lm}$  is dominated by contributions from the small fraction of better-localized orbitals (e.g., those near chain junctions), and is blind to the much larger fraction of less well-localized orbitals (e.g., those far from chain junctions). This partitioning of localized orbitals into better and less well fractions yields a picture consistent with our results provided we assume that the better localized variety constitute a fraction of order  $\epsilon$  of the localized orbitals. This fraction manifests itself in the exponent  $1 + \bar{l}/2$  in Eq. (7.6a) as the additional 1. This picture

allows us to identify the following appealing scaling for the localization characteristics of the better localized orbitals:

$$\Sigma_{lm} \sim \epsilon^{l/2}, \quad (7.7a)$$

$$\Gamma_{lm}(\hat{\mathbf{k}}) \sim k^l \sim \epsilon^{l/2}, \quad (7.7b)$$

the latter being valid for  $\hat{\mathbf{k}}^2 \sim \epsilon$ . Note, in particular, that this scaling indicates that for a better localized orbital

$$\frac{\langle (\mathbf{c}_j - \langle \mathbf{c}_j \rangle) \cdot (\mathbf{s}_{j,a} - \langle \mathbf{s}_{j,a} \rangle) \rangle}{\sqrt{\langle (\mathbf{c}_j - \langle \mathbf{c}_j \rangle)^2 \rangle \langle \mathbf{s}_{j,a}^2 \rangle}} \sim 1, \quad (7.8)$$

implying that the orientational-positional thermal fluctuation correlations are strong for all bond densities in the vicinity of the amorphous solidification transition. Whilst we cannot be certain that this scenario is a necessary consequence of our results, it is both consistent with them and physically plausible.

### VIII. CONCLUDING REMARKS

The primary result of this Paper is a statistical characterization of the structure and heterogeneity of the equilibrium amorphous solid state that emerges due to the random permanent covalent bonding of the constituent particles. This statistical characterization takes the form of a joint probability distribution that ascertains the likelihood of finding a particle: (i) to be localized, (ii) to have a certain positional localization length, (iii) for a bond connected to this particle to have a certain orientational localization characteristics, and (iv) for the correlations between the thermal fluctuations in

particle position and orbital orientation to have certain characteristics.

We expect the emerging statistical characterization to be valid beyond the context of the model used to determine it. The reason for this is that, apart from certain simple dependences on physical parameters describing the particles in the network, this characterization is in fact a consequence of the order parameter that we have considered, the symmetries of the Landau-type free energy associated with this order parameter, and a limited number of further assumptions.

We have constructed an analytical approach to the equilibrium structure of the amorphous solid state of a class of materials, such as silica gels, formed by the permanent random covalent bonding of atoms or small molecules. However, the accuracy and scope of our results is limited in the following significant ways. We have focused on *equilibrium* structural properties, we have worked *near* to the amorphous solidification transition, and we have computed within the framework of a *mean-field* approximation. It would be interesting to have a better understanding of the implications of these limitations, and to be able to obtain results beyond them.

### ACKNOWLEDGMENTS

We thank Horacio Castillo, Reimer Kühn, Weiqun Peng and, especially, Annette Zippelius and Max Makeev for useful discussions. This work was supported by the U.S. National Science Foundation through Grants DMR94-24511 (P.M.G.) and GER93-54978 (K.A.S.), and the Campus Research Board of the University of Illinois at Urbana-Champaign through Grant No. 1-2-69454 (K.A.S.).

### APPENDIX A: DENOMINATOR FOR THE SELF-CONSISTENT EQUATION

In this appendix we evaluate the denominator of the right-hand side of the SCE for  $\Omega(\hat{\mathbf{k}}; \hat{l}, \hat{m})$ , Eq. (6.2), namely, the quantity

$$\left\langle \exp \left( \frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}\hat{l}\hat{m}} W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{l}\hat{m}}(-\hat{\mathbf{s}}_a) \right) \right\rangle_{1,n+1}. \quad (A1)$$

To do this, we expand the exponential in a power series and consider the  $r$ th order term

$$\begin{aligned} & \left\langle \frac{1}{r!} (4\pi\mu^2)^r q^r V^{-nr} \sum_{\hat{\mathbf{k}}_1 \hat{l}_1 \hat{m}_1} \sum_{\hat{\mathbf{k}}_2 \hat{l}_2 \hat{m}_2} \dots \sum_{\hat{\mathbf{k}}_r \hat{l}_r \hat{m}_r} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2) \dots W(\hat{\mathbf{k}}_r; \hat{l}_r, \hat{m}_r) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} \dots e^{i\hat{\mathbf{k}}_r \cdot \hat{\mathbf{c}}} \right. \\ & \left. \times \frac{1}{A^r} \sum_{a_1, \dots, a_r} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}} \dots e^{i\hat{\mathbf{k}}_r \cdot \hat{\mathbf{s}}_{a_r}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(-\hat{\mathbf{s}}_{a_1}) \dots \hat{Y}_{\hat{l}_r \hat{m}_r}(-\hat{\mathbf{s}}_{a_r}) \right\rangle_{1,n+1}. \quad (A2) \end{aligned}$$

Noticing that the quantity (A2) factorizes over the replicas, and passing to the replica limit  $n \rightarrow 0$ , we rewrite

$$\begin{aligned} & \left\langle \frac{1}{r!} (4\pi\mu^2)^r q^r \sum_{\mathbf{k}_1 l_1 m_1} \sum_{\mathbf{k}_2 l_2 m_2} \dots \sum_{\mathbf{k}_r l_r m_r} W(\mathbf{k}_1; l_1, m_1) W(\mathbf{k}_2; l_2, m_2) \dots W(\mathbf{k}_r; l_r, m_r) e^{i\mathbf{k}_1 \cdot \mathbf{c}} e^{i\mathbf{k}_2 \cdot \mathbf{c}} \dots e^{i\mathbf{k}_r \cdot \mathbf{c}} \right. \\ & \left. \times \frac{1}{A^r} \sum_{a_1, \dots, a_r} e^{i\mathbf{k}_1 \cdot \mathbf{s}_{a_1}} e^{i\mathbf{k}_2 \cdot \mathbf{s}_{a_2}} \dots e^{i\mathbf{k}_r \cdot \mathbf{s}_{a_r}} Y_{l_1 m_1}(-\mathbf{s}_{a_1}) \dots Y_{l_r m_r}(-\mathbf{s}_{a_r}) \right\rangle_{1,1}. \quad (A3) \end{aligned}$$

By the MTI of  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  we know that  $\tilde{\mathbf{k}}_i = \mathbf{0}$ , which means that  $\mathbf{k}_i = \mathbf{0}$ . Also, using MRI of  $W(\hat{\mathbf{k}}; \hat{l}, \hat{m})$  we see that if  $\hat{\mathbf{k}} = \hat{\mathbf{0}}$  then Eq. (A3) can only be nonzero if  $\hat{l} = \hat{\mathbf{0}}$  also. Knowing that  $W(\hat{\mathbf{0}}; \hat{\mathbf{0}}, \hat{\mathbf{0}}) = 1/\sqrt{4\pi}$ , we get, for the  $r$ th order contribution  $(\mu^2)^r q^r / r!$ . Resumming the power series we obtain, finally

$$\left\langle \exp \left( \frac{4\pi\mu^2}{V^n} \sum_{\hat{\mathbf{k}}\hat{m}} W(\hat{\mathbf{k}}; \hat{l}, \hat{m}) e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \frac{1}{A} \sum_{a=1}^A e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{s}}_a} \hat{Y}_{\hat{m}}(\hat{\mathbf{s}}_a) \right) \right\rangle_{1,n+1} = \sum_{r=0}^{\infty} \frac{(\mu^2)^r q^r}{r!} = \exp(\mu^2 q). \quad (\text{A4})$$

### APPENDIX B: DEFINITIONS OF THE $\mathcal{C}^{(N)}$ CONSTANTS

The  $\mathcal{C}^{(n)}$  constants are defined as follows:

$$\mathcal{C}^{(0)} \equiv A^{-1}(1 + (A-1)C_1), \quad (\text{B1a})$$

$$\mathcal{C}^{(1)} \equiv \frac{1}{1 + \mathcal{C}^{(0)}}, \quad (\text{B1b})$$

$$\mathcal{C}^{(2)} \equiv \frac{1}{A}(1 + (A-1)C_1^2), \quad (\text{B1c})$$

$$\mathcal{C}^{(3)} \equiv \mathcal{C}^{(2)} - 2\mathcal{C}^{(2)}\mathcal{C}^{(1)}, \quad (\text{B1d})$$

$$\mathcal{C}^{(4)} \equiv \frac{1 - \mathcal{C}^{(2)}}{\mathcal{C}^{(2)}}, \quad (\text{B1e})$$

$$\mathcal{C}^{(5)} \equiv \frac{\mathcal{C}^{(3)}}{3\mathcal{C}^{(2)}\mathcal{C}^{(4)}}, \quad (\text{B1f})$$

$$\mathcal{C}^{(6)} \equiv \frac{\mathcal{C}^{(3)}}{12\mathcal{C}^{(2)}\mathcal{C}^{(4)2}} + \frac{\mathcal{C}^{(1)2}}{8\mathcal{C}^{(4)}}. \quad (\text{B1g})$$

They encode information about the strength of the mutual repulsion of orbitals.

### APPENDIX C: ANISOTROPIC SELF-CONSISTENT EQUATION: ANGULAR MOMENTUM ONE IN ONE REPLICA CHANNEL

In this appendix we study in detail the SCE for the  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  component. We start with the full form

$$\begin{aligned} qW_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) &= (1-q) \frac{4\pi\mu^2}{V^n} q \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) \frac{1}{A^2} \\ &\times \sum_{a_0, a_1=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \prod_{\alpha \neq \alpha_1} (Y_{00}(\mathbf{s}_{a_0}^\alpha)) Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{m}}(-\hat{\mathbf{s}}_{a_1}) \right\rangle_{1,n+1} \\ &+ \frac{1}{2} \left( \frac{4\pi\mu^2}{V^n} \right)^2 q^2 \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} \sum_{\hat{\mathbf{k}}_2, \hat{l}_2, \hat{m}_2} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2) \\ &\times \frac{1}{A^3} \sum_{a_0, a_1, a_2=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \prod_{\alpha \neq \alpha_1} (Y_{00}(\mathbf{s}_{a_0}^\alpha)) Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \times \hat{Y}_{\hat{m}}(\hat{\mathbf{s}}_{a_1}) e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}} \hat{Y}_{\hat{m}}(\hat{\mathbf{s}}_{a_2}) \right\rangle_{1,n+1}. \end{aligned} \quad (\text{C1})$$

We now proceed to study this equation order by order, starting with the linear term. As we are not interested in feedback on this component from higher angular momentum components we may truncate the angular momentum sums to include only terms of  $\hat{l}^2 \leq 2$ . Thus we must include couplings to the components  $W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}})$  and  $W(\hat{\mathbf{k}})$  only. We study the coupling to  $W(\hat{\mathbf{k}})$  first (i.e.,  $\hat{l}_1 = \hat{m}_1 = 0$ ). Clearly then in replica  $\alpha_1$  we must Rayleigh-expand the shift-factor  $\exp(i\hat{\mathbf{k}}_1^\alpha \cdot \mathbf{s}_{a_1}^\alpha)$  to angular momentum 1 and put this factor equal to unity in all other replicas, obtaining



$$\begin{aligned}
& (1-q) \frac{4\pi\mu^2}{V^n} q \sum_{\hat{\mathbf{k}}_1} W(\hat{\mathbf{k}}_1) \frac{1}{A^2} \sum_{a_0, a_1=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) \left( \frac{1}{\sqrt{4\pi}} \right)^{(n+1)} 4\pi i j_1(k_1^{\alpha_1}) \right. \\
& \quad \left. \times \sum_{m'=-1}^1 Y_{1m'}(\mathbf{s}_{a_1}^{\alpha_1}) Y_{1m'}^* \left( \frac{\mathbf{k}_1^{\alpha_1}}{k_1^{\alpha_1}} \right) \right\rangle_{1,n+1} \\
& = (1-q) \mu^2 i \frac{\sqrt{4\pi}}{3} W(\hat{\mathbf{k}}) \frac{1}{A^2} \sum_{a_0, a_1=1}^A (\delta_{a, a_1} + (1 - \delta_{a, a_1}) C_1) k^{\alpha_1} Y_{1m_1}^* \left( \frac{\mathbf{k}^{\alpha_1}}{k^{\alpha_1}} \right) \\
& = \frac{i}{\sqrt{3}} \mathcal{C}^{(0)} W(\hat{\mathbf{k}}) k_{m_1}^{\alpha_1 *}. \tag{C2}
\end{aligned}$$

We now study the linear term corresponding to the coupling of  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  to  $W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}})$ . When  $\alpha_1 \neq \alpha_2$  this term, being of order  $\hat{\mathbf{k}}^2$ , is subdominant. Thus we need only consider the term in the angular momentum sum where  $l^{\alpha_1}=1$ ,  $\hat{l}_1$  being 0 in all other replicas. We examine this term in the sum, making use of the value of the two-orbital correlator, given by Eq. (6.18):

$$\begin{aligned}
& (1-q) \frac{4\pi\mu^2}{V^n} q \sum_{\hat{\mathbf{k}}_1} W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_1) \frac{1}{A^2} \sum_{a_0, a_1=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_1}(-\mathbf{s}_{a_1}^{\alpha_1}) \right\rangle_{1,n+1} \\
& = -(1-q) \mu^2 W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) \frac{1}{A^2} \sum_{a_0, a_1=1}^A (\delta_{a, a_1} + (1 - \delta_{a, a_1}) C_1) \\
& = -(1-q) \mathcal{C}^{(0)} \mu^2 W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}). \tag{C3}
\end{aligned}$$

We next proceed to examine the second-order term in Eq. (C1). Again, we truncate the angular momentum sums. As we are only interested in the leading-order contributions to  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  there are only two cases to consider:  $\hat{l}_1 = \hat{l}_2 = \hat{0}$  and  $\hat{l}_1^2 = 2, \hat{l}_2^2 = 0$ . The former case, however, results in a term that is subdominant to term (C2). We thus consider the latter case

$$\begin{aligned}
& \frac{1}{2} (1-q) \left( \frac{4\pi\mu^2}{V^n} \right)^2 q^2 \sum_{\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2} W(\hat{\mathbf{k}}_1) W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_2) \frac{1}{A^2} \\
& \quad \times \sum_{a_0, a_1=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} \left( \frac{1}{\sqrt{4\pi}} \right)^{(n+1)} \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_1}(-\mathbf{s}_{a_1}^{\alpha_1}) \right\rangle_{1,n+1} \\
& = -\frac{\sqrt{4\pi}}{2} (1-q) \frac{\mu^4}{V^n} \sum_{\hat{\mathbf{k}}_1} q^2 W(\hat{\mathbf{k}}_1) W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) \frac{1}{A^2} \sum_{a_0, a_1=1}^A (\delta_{a, a_1} + (1 - \delta_{a, a_1}) C_1) \\
& = -\frac{\sqrt{4\pi}}{2} (1-q) \mathcal{C}^{(0)} \frac{\mu^4}{V^n} \sum_{\hat{\mathbf{k}}_1} q^2 W(\hat{\mathbf{k}}_1) W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1). \tag{C4}
\end{aligned}$$

Keeping in mind that due to the symmetry  $\hat{l}_1 \leftrightarrow \hat{l}_2$  we must double the term (C4), we now assemble all the terms, dropping subleading contributions

$$q W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) = \mathcal{C}^{(0)} \left( -q W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) + \frac{i}{\sqrt{3}} q W(\hat{\mathbf{k}}_1) k_{m_1}^{\alpha_1 * *} - q^2 \frac{\sqrt{4\pi}}{V^n} \sum_{\hat{\mathbf{k}}_1} W(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_1) \right). \tag{C5}$$

Cancelling a factor of  $q$  leaves us with Eq. (6.16).

#### APPENDIX D: ANISOTROPIC SELF-CONSISTENT EQUATION: ANGULAR MOMENTUM ONE IN TWO REPLICA CHANNELS

In this appendix we study in detail the SCE for the  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$  component. We start with the full form:

$$\begin{aligned}
qW_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) &= (1-q) \frac{4\pi\mu^2}{V^n} q \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) \\
&\times \frac{1}{A^2} \sum_{a_0, a_1=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \prod_{\alpha \neq \alpha_1, \alpha_2} (Y_{00}(\mathbf{s}_{a_0}^\alpha)) Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) Y_{1m_2}^*(\mathbf{s}_{a_0}^{\alpha_2}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \hat{Y}_{\hat{l}_1 \hat{m}_1}(\hat{\mathbf{s}}_{a_1}) \right\rangle_{1,n+1} \\
&+ \frac{1}{2} \left( \frac{4\pi\mu^2}{V^n} \right)^2 q^2 \sum_{\hat{\mathbf{k}}_1, \hat{l}_1, \hat{m}_1} \sum_{\hat{\mathbf{k}}_2, \hat{l}_2, \hat{m}_2} W(\hat{\mathbf{k}}_1; \hat{l}_1, \hat{m}_1) W(\hat{\mathbf{k}}_2; \hat{l}_2, \hat{m}_2) \\
&\times \frac{1}{A^3} \sum_{a_0, a_1, a_2=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} \prod_{\alpha \neq \alpha_1, \alpha_2} Y_{00}(\mathbf{s}_{a_0}^\alpha) Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) Y_{1m_2}^*(\mathbf{s}_{a_0}^{\alpha_2}) e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}} \right. \\
&\left. \times \hat{Y}_{\hat{l}_1 \hat{m}_1}(\hat{\mathbf{s}}_{a_1}) e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_2 \cdot \hat{\mathbf{s}}_{a_2}} \hat{Y}_{\hat{l}_2 \hat{m}_2}(\hat{\mathbf{s}}_{a_2}) \right\rangle_{1,n+1}. \tag{D1}
\end{aligned}$$

As we did before in Appendix C for the SCE for  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  we proceed to study the linear terms of this equation. Again we truncate to include only the components of  $W$  of angular momentum smaller than the angular momentum of  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ , i.e.  $l^\alpha=0$  for  $\alpha \neq \alpha_1, \alpha_2$  and  $l^{\alpha_1}, l^{\alpha_2} \leq 1$ . Thus we find couplings to terms  $W(\hat{\mathbf{k}})$ ,  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$ ,  $W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}})$ , and  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ . Rayleigh expanding the shift factor  $\exp(i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{s}}_{a_1}^\alpha)$  to angular momentum 0 or 1 as appropriate in each replica, proceeding as in Eqs. (C3) and (C2), and, finally, inserting the value for  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}})$  that we obtained in Sec. VI E 1, we obtain the linear contribution (terms are in the order listed above):

$$\begin{aligned}
(1-q) \frac{4\pi\mu^2}{V^n} q \sum_{\hat{\mathbf{k}}_1} \frac{1}{A^2} \sum_{a_0, a_1=1}^A \left\langle e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}} e^{i\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{c}}} \left( \frac{1}{\sqrt{4\pi}} \right)^{n-1} Y_{1m_1}^*(\mathbf{s}_{a_0}^{\alpha_1}) Y_{1m_2}^*(\mathbf{s}_{a_0}^{\alpha_2}) \times \left\{ W(\hat{\mathbf{k}}_1) \left( \frac{1}{\sqrt{4\pi}} \right)^{n+1} (4\pi i)^2 j_1(k_1^{\alpha_1}) j_1(k_1^{\alpha_2}) \right. \right. \\
\times \sum_{m'_1, m'_2=-1}^1 Y_{1m'_1}(\mathbf{s}_{a_1}^{\alpha_1}) Y_{1m'_1}^* \left( \frac{\mathbf{k}_1^{\alpha_1}}{k_1^{\alpha_1}} \right) Y_{1m'_2}(\mathbf{s}_{a_1}^{\alpha_2}) Y_{1m'_2}^* \left( \frac{\mathbf{k}_2^{\alpha_2}}{k_1^{\alpha_2}} \right) + W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_1) \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_1} \\
\times (-\mathbf{s}_{a_1}^{\alpha_1}) 4\pi i j_1(k_1^{\alpha_2}) \sum_{m'=-1}^1 Y_{1m'}(\mathbf{s}_{a_1}^{\alpha_2}) Y_{1m'}^* \left( \frac{\mathbf{k}_1^{\alpha_2}}{k_1^{\alpha_2}} \right) + W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}}_1) \left( \frac{1}{\sqrt{4\pi}} \right)^n Y_{1m_2}(-\mathbf{s}_{a_1}^{\alpha_2}) 4\pi i j_1(k_1^{\alpha_1}) \\
\times \sum_{m'=-1}^1 Y_{1m'}(\mathbf{s}_{a_1}^{\alpha_1}) Y_{1m'}^* \left( \frac{\mathbf{k}_1^{\alpha_1}}{k_1^{\alpha_1}} \right) + W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}_1) \left( \frac{1}{\sqrt{4\pi}} \right)^{n-1} Y_{1m_1}(-\mathbf{s}_{a_1}^{\alpha_1}) Y_{1m_2}(-\mathbf{s}_{a_1}^{\alpha_2}) \left. \right\} \Bigg\rangle_{1,n+1} \\
= q\mathcal{C}^{(2)} \left( -\frac{1}{3} k_{m_1}^{\alpha_1} * k_{m_2}^{\alpha_2} * W(\hat{\mathbf{k}}) - \frac{i}{\sqrt{3}} k_{m_2}^{\alpha_2} * W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}) - \frac{i}{\sqrt{3}} k_{m_1}^{\alpha_1} * W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}}) + W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) \right) \\
= \mathcal{C}^{(2)} q W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) - \frac{q}{3} \mathcal{C}^{(3)} k_{m_1}^{\alpha_1} * k_{m_2}^{\alpha_2} * W(\hat{\mathbf{k}}). \tag{D2}
\end{aligned}$$

We next proceed to study the quadratic contribution to  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$  from Eq. (D1). Truncating the angular momentum sums as usual we see that there are the following four cases to consider (i)  $\hat{l}_1 = \hat{l}_2 = 0$ , corresponding to the coupling to  $W(\hat{\mathbf{k}}_1)W(\hat{\mathbf{k}}_2)$ , (ii)  $\hat{l}_1 = 0, \hat{l}_2^2 = 2$ , corresponding to the coupling to  $W(\hat{\mathbf{k}}_1)W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_2)$ , (iii)  $\hat{l}_1^2 = \hat{l}_2^2 = 2$ , corresponding to the coupling to  $W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_1)W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}}_2)$ , and (iv)  $\hat{l}_1 = 0, \hat{l}_2^2 = 4$  corresponding to the coupling to  $W(\hat{\mathbf{k}}_1)W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}_2)$ . We study these terms in more detail, as in Appendix C, Eq. (C4). Term (i) is clearly subdominant compared with the second term in Eq. (D2). Writing out the remaining terms

$$\text{term (ii): } -\frac{i}{\sqrt{3}} \frac{\sqrt{4\pi}}{2} (1-q) \mathcal{C}^{(2)} \frac{\mu^4}{V^n} \sum_{\hat{\mathbf{k}}_1} q^2 k_{m_2}^{\alpha_2} * W(\hat{\mathbf{k}}_1) W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1), \tag{D3}$$

$$\text{term (iii)}: \frac{\sqrt{4\pi}}{2} (1-q) \mathcal{C}^{(2)} \frac{\mu^4}{V^n} \sum_{\hat{\mathbf{k}}_1} q^2 W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}}_1) W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1), \quad (\text{D4})$$

$$\text{term (iv)}: \frac{\sqrt{4\pi}}{2} (1-q) \mu^4 \mathcal{C}^{(2)} \frac{\mu^4}{V^n} \sum_{\hat{\mathbf{k}}_1} q^2 W(\hat{\mathbf{k}}_1) W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1). \quad (\text{D5})$$

Term (ii) does not contribute to the leading-order behavior of  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$  as for  $\hat{\mathbf{k}}^2$  of order  $\epsilon$  or greater all quadratic terms are subleading compared to linear terms, and for  $\hat{\mathbf{k}}^2 \ll \epsilon$  it will, because of the  $k_{m_2}^{\alpha_2 *}$  factor, be subdominant compared to terms (iii) and (iv). Keeping in mind that because of the symmetry  $\hat{l}_1 \leftrightarrow \hat{l}_2$  we must double the term (iv), we reassemble the pieces of the SCE for  $W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}})$ , dropping subleading contributions:

$$\begin{aligned} q W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) &= \mathcal{C}^{(2)} q W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}) - \frac{1}{3} \mathcal{C}^{(3)} k_{m_1}^{\alpha_1 *} k_{m_2}^{\alpha_2 *} q W(\hat{\mathbf{k}}) + q^2 \mathcal{C}^{(2)} \frac{\sqrt{4\pi}}{V^n} \sum_{\hat{\mathbf{k}}_1} W(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_1 1m_2}^{\alpha_1 \alpha_2}(\hat{\mathbf{k}}_1) \\ &+ q^2 \mathcal{C}^{(2)} \frac{\sqrt{4\pi}}{2V^n} \sum_{\hat{\mathbf{k}}_1} W_{1m_1}^{\alpha_1}(\hat{\mathbf{k}} - \hat{\mathbf{k}}_1) W_{1m_2}^{\alpha_2}(\hat{\mathbf{k}}_1), \end{aligned} \quad (\text{D6})$$

Cancelling a factor of  $q$  leaves us with Eq. (6.21).

\*Electronic address: shakhnov@uiuc.edu

†Electronic address: goldbart@uiuc.edu

<sup>1</sup>For a review, see, e.g., Richard Zallen, *The Physics of Amorphous Solids* (J. Wiley, New York, 1983).

<sup>2</sup>See, e.g., M. Mézard, G. Parisi, and M. A. Virasoro, *Spin Glass Theory and Beyond* (World Scientific, Singapore, 1987); *Spin Glasses and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1997).

<sup>3</sup>P.M. Goldbart and A. Zippelius, *Europhys. Lett.* **27**, 599 (1994).

<sup>4</sup>B. Gauthier-Manuel, E. Guyon, S. Roux, S. Gits, and F. Lefauchaux, *J. Phys. (Paris)* **48**, 869 (1987).

<sup>5</sup>H.E. Castillo, P.M. Goldbart, and A. Zippelius, *Europhys. Lett.* **28**, 519 (1994).

<sup>6</sup>P.M. Goldbart, H.E. Castillo, and A. Zippelius, *Adv. Phys.* **45**, 393 (1996).

<sup>7</sup>S.J. Barsky and M. Plischke, *Phys. Rev. E* **53**, 871 (1996); S. J. Barsky, Ph.D. thesis, Simon Fraser University, Canada 1996; S. J. Barsky and M. Plischke (unpublished), see Ref. 8.

<sup>8</sup>W. Peng, H.E. Castillo, P.M. Goldbart, and A. Zippelius, *Phys. Rev. B* **57**, 839 (1998).

<sup>9</sup>What we, in fact, compute are moments of averages of such distributions over realizations of the quenched randomness. Although we have not checked this point in detail, we do not expect there to be sample-to-sample variations of the distribution.

<sup>10</sup>O. Theissen, A. Zippelius, and P.M. Goldbart, *Int. J. Mod. Phys. B* **11**, 1945 (1996).

<sup>11</sup>From the addition theorem for spherical harmonics, tracing Eq. (2.1) over  $m$  we find  $C_l = \langle P_l(\mathbf{s} \cdot \mathbf{s}') \rangle$ . We also note, in passing,

that the special case of uncorrelated (free) orbitals corresponds to the set of parameters  $C_l = (1, 0, \dots, 0)$ .

<sup>12</sup>P.M. Goldbart and N.D. Goldenfeld, *Phys. Rev. Lett.* **58**, 2676 (1987); *Phys. Rev. A* **39**, 1402 (1989); **39**, 1412 (1989).

<sup>13</sup>R.T. Deam and S.F. Edwards, *Proc. R. Soc. London, Ser. A* **280**, 317 (1976).

<sup>14</sup>As we are not able to compute the free energy for arbitrary values of the order parameter, we are unable to rule out the possibility that a discontinuous phase transition occurs at a bond density smaller than  $\mu_c^2$ . That the transition is continuous should be regarded as an additional assumption of ours.

<sup>15</sup>We remind the reader that *full mathematical induction* is the version of the technique of induction in which the validity of a statement for all integers  $n$  less than some integer  $N$  is required to establish the validity of the statement for  $N$ . Perhaps more familiar is *mathematical induction*, in which the validity of a statement for the integer  $N-1$  is all that is required to establish the validity of the statement for  $N$ . For a discussion, see, e.g., *Encyclopedic Dictionary of Mathematics*, edited by Kiyosi Itô (MIT Press, Cambridge, MA, 1993).

<sup>16</sup>See, e.g., A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1968).

<sup>17</sup>Note that we have not obtained an algorithm capable of yielding the leading-order scaling of *all* moments of the joint probability distribution  $P$ , even though we have obtained the leading-order behavior of all the components of the order parameter. Indeed, there is no reason for *every* moment of  $P$  to contribute to the leading-order behavior of the components of the order parameter.