

## Random solids and random solidification: what can be learned by exploring systems obeying permanent random constraints?

Paul M Goldbart<sup>†</sup>

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

E-mail: [goldbart@uiuc.edu](mailto:goldbart@uiuc.edu)

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**Abstract.** In many interesting physical settings, such as the vulcanization of rubber, the introduction of permanent random constraints between the constituents of a homogeneous fluid can cause a phase transition to a random solid state. In this random solid state, particles are permanently but randomly localized in space, and a rigidity to shear deformations emerges. Owing to the permanence of the random constraints, this phase transition is an equilibrium transition, which confers on it a simplicity (at least relative to the conventional glass transition) in the sense that it is amenable to treatment by established techniques of equilibrium statistical mechanics. In this paper I shall review recent developments in the theory of random solidification for systems obeying permanent random constraints, with the aim of bringing to the fore the similarities of and differences between such systems and those exhibiting the conventional glass transition. I shall also report new results, obtained in collaboration with Weiqun Peng, on equilibrium correlations and susceptibilities that signal the approach of the random solidification transition, discussing the physical interpretation and values of these quantities both at the Gaussian level of approximation and, via a renormalization-group approach, beyond.

### 1. Introduction

My aim in this article is to give a brief overview of recent developments in the theory of random solidification for systems obeying permanent random constraints. Along the way, I hope to bring to the fore the similarities of and differences between such systems and those exhibiting the conventional glass transition. I shall not dwell on detailed technical matters, as they can be found in a number of articles which I will cite and which are readily available<sup>‡</sup>. (Nor shall I attempt to provide a complete set of references.) Instead, I shall focus on what I regard as essential matters of principle.

The classic example of a system that undergoes random solidification in response to the imposition of a sufficient density of permanent random constraints on the motion of its constituents is vulcanized rubber. Prior to vulcanization, the system consists of a more or less viscous fluid of flexible macromolecules. Vulcanization amounts to the imposition of permanent covalent chemical bonds between randomly chosen atoms on the macromolecules. Both the chemical bonds defining the macromolecules and the bonds introduced by vulcanization will be regarded as permanent. Although, of course, no chemical bonds are

<sup>†</sup> <http://w3.physics.uiuc.edu/~goldbart>.

<sup>‡</sup> For a detailed account of work prior to 1996, emphasizing both concepts and techniques, see reference [1]. For informal accounts, stressing concepts more than techniques, see references [2, 3].

truly permanent, this means that we shall regard the breaking of these bonds to be extremely rare on the timescale needed for the unconstrained freedoms to equilibrate. This separation of timescales provides the window necessary for the applicability of equilibrium statistical mechanics to the unconstrained freedoms, subject to the vulcanization constraints which play the role of quenched random variables.

A second example is provided by chemical gels, such as silica gel, in which low-molecular-weight objects (rather than macromolecules) are permanently bonded together at random (e.g. by a condensation/elimination reaction) so as to build up a giant random molecule. It is useful to regard chemical gels, too, as systems that undergo random solidification in response to the introduction of a sufficient density of permanent random constraints (i.e. random covalent bonds).

What do we mean when we say: random permanent constraints lead to random solidification? We mean that the system undergoes a phase transition (as it happens, continuous), as the density of constraints is increased beyond some critical value, with the following characteristics. At subcritical densities the system is fluid in the following two senses: (i) it does not respond to an applied zero-frequency shear strain by developing a zero-frequency shear stress; and (ii) none of the particles in the system is localized and instead, given sufficient time, all wander throughout the (essentially infinite) container. On the other hand, at supercritical densities of constraints the system is a solid in both senses: (i) it responds to an applied zero-frequency shear strain by developing a zero-frequency shear stress; and (ii) at least a fraction of the particles in the system are localized, so instead of wandering throughout the container they remain in the vicinity of their mean positions, from which they make thermally driven excursions of only finite spatial extent. The fundamental competition leading to the transition is one between translational entropy, which favours delocalization, and crosslinking, which favours localization. Note that the transition is driven by crosslink density, not temperature.

As for the randomness of the emergent solid, this means that although translational symmetry is spontaneously broken—at least some particles acquiring random mean positions about which they undergo thermal motion—it is broken randomly, in the sense that there is no crystalline long-range order to the collection of mean positions: Fourier analysis, as we shall see more concretely in section 3, detects no long-range periodicity to the mean positions. Furthermore, there is a second level of randomness to the emergent solid. Not only are the mean particle positions distributed at random throughout the container but, also, every localized particle experiences a distinct environment. This shows up, e.g., via a statistical continuum of r.m.s. displacements of the localized particles (measured from their mean positions), i.e., a statistical distribution of localization lengths.

There is a subtlety here concerning the notion of localization that is worth commenting on. At temperatures below its melting temperature, the equilibrium state of, say, the element Cu is a crystalline solid, in the sense that an infinitesimal stress produces an infinitesimal strain (rather than strain *rate*, as it would in a fluid). However, the Cu atoms are not localized: vacancy motion causes them to diffuse, albeit slowly, throughout the crystal. In contrast, the permanence of the chemical bonds in vulcanized macromolecular systems, both intra- and inter-molecular, at least on the timescale of envisaged experiments, allows for true localization. In this sense, vulcanized matter forms solids that are simpler than ‘simple’ solids, such as crystalline Cu.

## 2. Connections with glasses: freezing in of correlations

Now, the title of the conference for which this paper was prepared is *Unifying Concepts in Glass Physics*, so I would like to make some general remarks about the relationship between vulcanized systems and the kinds of systems that are conventionally referred to as glassy. For

reasons that I hope will become apparent, I believe that it may be profitable to regard vulcanized systems as model glasses (see reference [2]).

Presumably, *conventional* glassy regimes emerge when certain structural correlations, characteristic of a liquid state and involving the positions of the particles, are unable to relax on the timescale of an experiment, and are therefore frozen in. (Note that I am sidestepping the fundamental question of whether or not such correlations can be frozen in on infinite timescales.) One of the central obstacles to the development of a sound theory of this phenomenon of glassiness is that, at least *prima facie*, it appears intrinsically dynamical (and perhaps is so at its very core). If so, this would confer on the subject a level of technical complexity, relative to issues that are amenable to treatment by the techniques of equilibrium statistical mechanics for systems possessing *extrinsic* (rather than *intrinsic*, i.e., spontaneously generated) quenched random constraints. The origin of the relative simplicity in the latter case is that one is presented with a wide (and evident) separation between the (short) timescale for the equilibration of unconstrained freedoms and the (long) timescale on which the constraints break. This separation yields a window of times in which equilibrium statistical mechanics is obviously applicable, and allows one to confidently finesse the task of statistical physics on timescales comparable to any that are intrinsic to the system, which is, of necessity, a matter of dynamics.

Extrinsic quenched random constraints, such as those introduced by the vulcanization process, have *precisely* the effect of freezing in certain structural correlations characteristic of a liquid state. However, not being intrinsic to the liquid, extrinsic constraints have an independence from it that allows one to tune their density and, hence, to *tune the state of the system in a controllable fashion right through the random solidification transition*. In this sense, with vulcanized matter one has access to a critical ‘glass’ transition that one does not have with intrinsically glassy systems. For the latter, the reliance on self-generated constraints necessarily creates a (presumably highly significant) ‘feedback loop’ between the correlations that are frozen in and the consequent state of the system. It does not seem unreasonable to suppose that this feedback effect is what causes the critical random solidification transition to be pre-empted by the conventional glass transition.

This point of view, which was elaborated in reference [2], served as the main motivation for an exploratory approach to structural glasses begun in reference [4] and developed in considerable detail in reference [5]. In this approach, one considers the equilibrium statistical mechanics of a network built from low-molecular-weight molecules connected at random by permanent covalent bonds. The formation of silica gel networks via a polycondensation/elimination reaction provides a concrete example of such networks; see, e.g., reference [6]. The essence of this approach is to identify correlations of the liquid state (i.e. particles separated by a bond distance), to freeze in some fraction of these correlations (as quenched random constraints) and to consider how the system responds. By this scheme, we are ‘pushing off to infinity’ the timescale for the relaxation of these correlations ‘by hand,’ and thereby establishing a setting amenable to treatment by the techniques of equilibrium statistical mechanics. This is a perfectly reasonable strategy for systems such as silica gel, in which there is a clear separation of timescales; for conventional glasses the strategy represents an idealization, and the question remains: To what extent is it a useful one?

What emerges from this approach to glassy systems? Put briefly (see reference [5] for details), one finds a phase transition from a liquid to a random solid state characterized by a rich order parameter, which encodes information not only about the positional localization of the particles in the system but also about the consequent orientational localization of the bonds that connect the particles (as well as thermal correlations between particle positions and bond orientations).

I think it is worth emphasizing that the approach to random solidification outlined here is in fact rather straightforward (at least in spirit, if not practice): a semi-microscopic model leads to a field theoretic representation that is amenable to treatment using a (rich and informative) saddle-point approximation and, as we shall see, systematic improvements via the application of renormalization-group ideas.

### 3. Detecting random solids: an order parameter

Let us briefly explore an order parameter capable of detecting the random solid state. For detailed discussions, see references [1–3]. Consider a collection of  $N$  particles, labelled  $j = 1, \dots, N$  and having  $d$ -dimensional positions  $\{\mathbf{R}_j\}_{j=1}^N$ . (The slight elaboration required to handle macromolecular freedoms rather than point particles is not of importance to the present discussion.) The basic element to focus on is the Fourier transform of the probability density of finding the particle to be at some position  $\mathbf{r}$  in the volume  $V$ , namely,

$$\int_V d^d r \langle \delta^{(d)}(\mathbf{r} - \mathbf{R}_j) \rangle \exp i\mathbf{k} \cdot \mathbf{r} = \langle \exp i\mathbf{k} \cdot \mathbf{R}_j \rangle \quad (1)$$

where  $\langle \dots \rangle$  denotes an equilibrium expectation value of a randomly constrained system, perhaps in a broken-symmetry state. If particle  $j$  is *delocalized*, then, by translational invariance,  $\langle \exp i\mathbf{k} \cdot \mathbf{R}_j \rangle = \delta_{\mathbf{k}, \mathbf{0}}$ . On the other hand, if it is *localized*, then a good model to bear in mind for later use is

$$\langle \exp i\mathbf{k} \cdot \mathbf{R}_j \rangle \approx \exp(i\mathbf{k} \cdot \langle \mathbf{R}_j \rangle) \exp(-\xi_j^2 k^2 / 2) \quad (2)$$

i.e., the Fourier transform of a Gaussian distribution for the particle position, characterized by the mean position  $\langle \mathbf{R}_j \rangle$  and the r.m.s. displacement (i.e. *localization length*)  $\xi_j$ . For future use, it is worth noting the distinction between the  $\mathbf{k} = \mathbf{0}$  value and the  $\mathbf{k} \rightarrow \mathbf{0}$  limit of  $|\langle \exp i\mathbf{k} \cdot \mathbf{R}_j \rangle|$ . Of course, regardless of whether or not particle  $j$  is localized, one obtains unity precisely at  $\mathbf{k} = \mathbf{0}$ ; by contrast, however, in the limit one finds zero if particle  $j$  is delocalized but unity if particle  $j$  is localized.

The first construct a statistical mechanician might examine is the average of  $\langle \exp i\mathbf{k} \cdot \mathbf{R}_j \rangle$  over the particles in the system:

$$\frac{1}{N} \sum_{j=1}^N \langle \exp i\mathbf{k} \cdot \mathbf{R}_j \rangle. \quad (3)$$

Not surprisingly, if all particles are delocalized, then this quantity takes the value  $\delta_{\mathbf{k}, \mathbf{0}}$ . However, if some fraction of the  $N$  particles are localized but their mean positions  $\langle \mathbf{R}_j \rangle$  are random, then, for no  $\mathbf{k}$  except  $\mathbf{0}$  do the contributions add constructively, so the sum continues to take the value  $\delta_{\mathbf{k}, \mathbf{0}}$ . Thus the entity (3) fails to distinguish between the delocalized liquid and the randomly localized solid, and does so in the much same way that the magnetization density fails to distinguish between, e.g., the spin-glass and paramagnetic states.

So, what is the remedy? As with the spin-glass case, to avoid destructive interference one considers more than one equilibrium expectation value under the average over particles (and then disorder averages; see section 4.1.3):

$$\left[ \frac{1}{N} \sum_{j=1}^N \prod_{\alpha=0}^g \langle \exp i\mathbf{k}^\alpha \cdot \mathbf{R}_j \rangle \right] \quad (4)$$

where  $[\dots]$  denotes disorder averaging. If all  $N$  particles are delocalized, then this entity only fails to vanish for the trivial case of all wave vectors  $\{\mathbf{k}^\alpha\}_{\alpha=0}^g$  vanishing. However, if some fraction  $q$  of the particles are localized with random mean positions, then the entity is non-zero

whenever  $\sum_{\alpha=0}^g \mathbf{k}^\alpha$  vanishes, i.e., the random solidification transition is associated with the change in form of (4) from being a ‘bump’ concentrated at the origin  $\{\mathbf{k}^\alpha = \mathbf{0}\}_{\alpha=0}^g$  of the replicated wave-vector space, to being a ‘fin’ concentrated on the hyper-surface  $\sum_{\alpha=0}^g \mathbf{k}^\alpha = \mathbf{0}$ . Thus we see that (4) serves as an order parameter for the liquid–amorphous–solid phase transition. Moreover, the limit  $\{\mathbf{k}^\alpha \rightarrow \mathbf{0}\}_{\alpha=0}^g$  (with  $\sum_{\alpha=0}^g \mathbf{k}^\alpha = \mathbf{0}$ ) determines the *fraction* of localized particles, and the shape of the fin determines the *distribution* of localization lengths. For example, if the localized fraction is localized according to equation (2) then the order parameter (4) will take the form

$$(1 - q) \prod_{\alpha=0}^g \delta_{\mathbf{k}^\alpha, \mathbf{0}} + q \delta_{\sum_{\alpha=0}^g \mathbf{k}^\alpha, \mathbf{0}} \int d\xi p(\xi) \exp\left(-\frac{\xi^2}{2} \sum_{\alpha=0}^g |\mathbf{k}^\alpha|^2\right) \quad (5)$$

where

$$p(\xi) \equiv \left[ (qN)^{-1} \sum_{j \text{ loc.}} \delta^{(1)}(\xi - \xi_j) \right]$$

is the statistical distribution of the random localization lengths of the localized particles.

We note, in passing, that under Fourier transformation to real space (via the operation  $V^{-1} \sum_{\mathbf{k}^0} \exp(-i\mathbf{k}^0 \cdot \mathbf{r}^0) \dots V^{-1} \sum_{\mathbf{k}^g} \exp(-i\mathbf{k}^g \cdot \mathbf{r}^g) \dots$ ) this order parameter becomes

$$\frac{1 - q}{V^{g+1}} + \frac{q}{(2\pi)^{d(g+1)/2}} \int d\xi p(\xi) \xi^{-d(g+1)} \int_V \frac{d^d \rho}{V} \exp\left(-\frac{1}{2\xi^2} \sum_{\alpha=0}^g |\mathbf{r}^\alpha - \rho|^2\right). \quad (6)$$

If we regard the  $g + 1$  replicas  $\{\mathbf{r}^\alpha\}_{\alpha=0}^g$  of the particle position as the positions of the  $g + 1$  ‘atoms’ of a ‘molecule’, then this joint probability distribution describes a *molecular bound state in replica space*. That it is bound follows from localization; invariance under common translations of the atoms follows from the randomness of the mean locations of the localized particles; the shape of the bound state follows from the distribution of localization lengths.

#### 4. Characteristics of the random solid state

So far, we have introduced an order parameter capable of detecting and diagnosing the random solid state. We now turn to the question of computing it within various frameworks and for various model settings.

##### 4.1. Semi-microscopic replica theory for vulcanized macromolecules

The most direct approach to the computation of the order parameter arises in the setting of randomly crosslinked macromolecular systems, and builds upon the formulation of the statistical mechanics of such systems established in the beautiful work of Deam and Edwards [7]. In the present article I shall just sketch the strategy, and encourage the reader to turn to references [1, 8] for technical details.

*4.1.1. Partition function.* We begin with the partition function for a system of  $N$  identical, interacting, flexible, uncrosslinked (and hence non-random) macromolecules, this partition function describing the fluid (i.e. melt or solution) of uncrosslinked macromolecules. (We view these macromolecules at the semi-microscopic level, which means that we ignore details of their chemical constitution and, instead, consider featureless strands of matter.)

*4.1.2. Crosslinks as quenched random constraints.* Now, how do we incorporate into this semi-microscopic description the effects of random crosslinking? In three spatial dimensions, at least, crosslinking has two distinct effects, which we may choose to call *holonomic* and *anholonomic*. The holonomic effect of each crosslink serves to *identify* the positions of two points on the macromolecules, chosen at random, i.e., to introduce a random constraint that identifies two positional freedoms that formerly were kinematically independent. The anholonomic effect serves to select a specific topological structure for the network: given the collection of macromolecules and the collection of holonomic constraints, how are the macromolecules ‘woven’ into a  $d$ -dimensional network? The *quenched random information* is then: (i) the catalogue of pairs of points that are identified by the crosslinks; and (ii) the specific topology of the macromolecular strands subject to the identification of the pairs of crosslinked points. As we shall discuss shortly, the holonomic aspect of crosslinking can readily be incorporated; however, we know of no scheme capable of accounting for the anholonomic aspect. Thus, in practice we shall treat the holonomic aspect as quenched random information, but shall treat fluctuations between distinct network topologies as annealed variables. This is not totally indefensible. First, the transition regime, which is the regime of interest to us here, is characterized by rather light crosslinking—of order one crosslink per macromolecule—so the effects of topology might reasonably be expected to be weak. Second, if one imagines coarse-graining one’s view of the system, then the distinction between holonomic and anholonomic constraints tends to blur, with knots and crosslinks having rather similar effects.

The next step is to specify, at random, a catalogue of pairs of points that are to be identified by the crosslinks, i.e., to specify the quenched random information that determines the holonomic aspect of the constraints. (Shortly, we shall discuss the issue of how to construct a reasonable model distribution for this quenched random information.) We use this information to remove from the sum over configurations (which constitutes the partition function for the uncrosslinked system of macromolecules) all configurations that fail to satisfy the (holonomic aspect of the) constraints. In practice this removal is accomplished by a suitable product of Dirac delta functions, which is zero for configurations that do not obey the constraints. The resulting partition function describes a specific realization of the randomly crosslinked system and, just as the partition function for a spin glass depends on the quenched random interactions, this partition function depends on the quenched random information describing the constraints. As such, it is impractical to handle directly and, for the usual reasons, one averages its logarithm, essentially the free energy of the randomly constrained system, over some distribution of the quenched random information.

*4.1.3. Distribution of crosslinks.* How might one ascribe a statistical weight to a specific realization of random crosslinks? One strategy, which is due to Deam and Edwards and which I regard as extremely elegant [7], is to imagine the following experimental procedure. Take the uncrosslinked liquid in equilibrium. Stop time. (Then the likelihood of finding any configuration will be proportional to its Boltzmann weight.) Examine the configuration that you have, and identify points of near-contact between macromolecules. Independently for each near-contact, either do or do not introduce a crosslinking constraint with some probability. The distribution of crosslinks thus constructed has the virtue of being determined by the equilibrium state of the uncrosslinked liquid, together with a single number, the crosslinking probability, the latter governing the (mean number) of crosslinks introduced and ultimately playing the role of the control parameter for the phase transition from the liquid to the random solid state.

In fact, by choosing this Deam–Edwards crosslink distribution one is conferring upon the system an additional—and highly convenient—symmetry. The origin of this symmetry is the fact, which will become obvious to the reader after a moment’s reflection, that the

Deam–Edwards crosslink probability distribution is itself proportional to the partition function of the randomly crosslinked system. Perhaps this observation is not of much comfort at the present stage, inasmuch as it only tells us that the theory contains one, rather than two, entities that we have not yet managed to compute. But at least it is one and not two! And shortly we shall see that this symmetry provides the reason why the replica theory turns out to have  $(n + 1)$ -fold, rather than the usual  $n$ -fold, permutation symmetry.

It should be stressed that there is much more to this choice of crosslink distribution than the enhanced symmetry it confers. Even more significantly, being based on a physical vulcanization process it ensures that appreciable statistical weight is only given to those realizations of the crosslinking that the macromolecules can accommodate, and thus it leads to reasonable, space-filling, statistically homogeneous (random solid) states.

*4.1.4. Replica statistical mechanics; replica field theory.* Taking stock of the situation, we see that we have a theory with: (i) annealed variables (the macromolecular coordinates), (ii) quenched variables (the number and specification of the crosslinks), (iii) a random partition function (containing random *constraints* on ‘street level’ rather than random *interactions* in the exponent of the Boltzmann weight) and (iv) a distribution for the quenched randomness based on a physical model for the vulcanization process. In the context of other random systems the distribution might, e.g., be a Gaussian distribution of exchange interactions (spin glasses) or of random impurity potentials (electronic transport).

Proceeding in the familiar way, we use the replica technique to compute the disorder average of the logarithm of the partition function. However, in our setting of randomly constrained systems, what emerges from this procedure may be quite unfamiliar. First, owing to the ‘street level’ location of the constraint delta functions, together with the random *number* of them, averaging over the quenched random variables yields a term in the exponent of the (effective, pure) Boltzmann weight featuring a *product over replicas*, in contrast with the more familiar *pairwise coupling* of replicas that commonly results from random *interactions* (cf. exchange interactions in spin glasses or random impurity potentials in electronic transport). This term has the effect of causing all pairs of segments of the replicated macromolecules to attract one another in replicated space. Second, as mentioned above, the equilibrium average involved in the construction of the crosslink distribution provides an additional replica, so we end up with the  $n \rightarrow 0$  limit of a theory involving  $n + 1$ , rather than the usual  $n$ , replicas.

Now, how can we address the resulting pure, replica theory? We may, as is often done for spin glasses, apply a Hubbard–Stratonovich decoupling transformation, which leads to a field theory representation. (The virtues of this procedure are manifold: it suggests the physically appropriate collective coordinates; it allows us to attack the problem using calculus; and it is exact, and thereby provides us with a framework for going beyond mean-field theory.) In the present context the necessary field turns out to be complex-valued and to live on  $(n + 1)$ -fold replicated space,  $\Omega(\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^n)$ ; it is precisely the Fourier transform of the order parameter introduced and motivated on physical grounds in section 3. A standard linear-stability analysis of this field theory reveals that there is indeed a phase transition, as the density of crosslinks is increased. Moreover, provided that the underlying fluid consists of adequately repulsive macromolecules, the stability analysis indicates that the instability is precisely of the physically anticipated form: the liquid state becomes unstable and the instability is in the direction of the random solid state.

But how does the instability actually get resolved? In other words, what is the precise form of the state that replaces it? Let us begin by addressing this question at the level of mean-field theory. (Going beyond mean-field theory will be discussed below, in section 7.) This natural starting point can be accomplished in several equivalent ways. One may treat the field theory

mentioned above at the saddle-point level. Or one can take the more direct route of replacing fluctuating collective coordinates by their average values plus departures, and then linearizing in the departures. Whatever the scheme, one ends up with a self-consistent equation for the order parameter: a functional equation for the field  $\Omega(\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^n)$ .

In general, this equation is highly complicated, even to write down let alone solve. However, in the random solid state, but near to the transition, the smallness of the fraction of localized particles provides a simplification, allowing us to discard all but the quadratic non-linearity in the self-consistent equation for the order parameter, which then reads

$$0 = 2 \left( -a\epsilon + \frac{b}{2} |\hat{k}|^2 \right) \Omega(\hat{k}) - 3c \sum_{\hat{k}_1 \hat{k}_2} \Omega(\hat{k}_1) \Omega(\hat{k}_2) \delta_{\hat{k}_1 + \hat{k}_2, \hat{k}}. \quad (7)$$

Here,  $a$ ,  $b$  and  $c$  are model-dependent coefficients,  $\epsilon$  measures the excess crosslink density (beyond the mean-field critical value of zero) and  $\Omega(\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n)$  is the Fourier transform of  $\Omega(\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^n)$ . To ease the notation we have taken to writing  $\hat{k}$  for  $\{\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n\}$  so that  $\Omega(\mathbf{k}^0, \mathbf{k}^1, \dots, \mathbf{k}^n)$  becomes  $\Omega(\hat{k})$  and  $\sum_{\alpha=0}^n \mathbf{k}^\alpha \cdot \mathbf{k}^\alpha$  becomes  $|\hat{k}|^2$ . The overbar on the summations indicates that a certain class of terms is to be omitted from the summations: the reason for this (vital) restriction will be discussed shortly. It is not difficult to verify that this equation is *exactly* solved by the function given in equation (5), provided that one chooses  $g = n$  (with  $n \rightarrow 0$ ), and (up to simple re-scalings involving  $a$ ,  $b$  and  $c$ ) the fraction of localized particles  $q$  and the normalized distribution of localization lengths  $p(\cdot)$  to be given by

$$q = 2\epsilon/3 \quad (8)$$

$$p(\xi) = (4/\epsilon\xi^3)\pi(2/\epsilon\xi^2) \quad (9)$$

where the scaling function  $\pi(\cdot)$  obeys the simple non-linear integro-differential equation

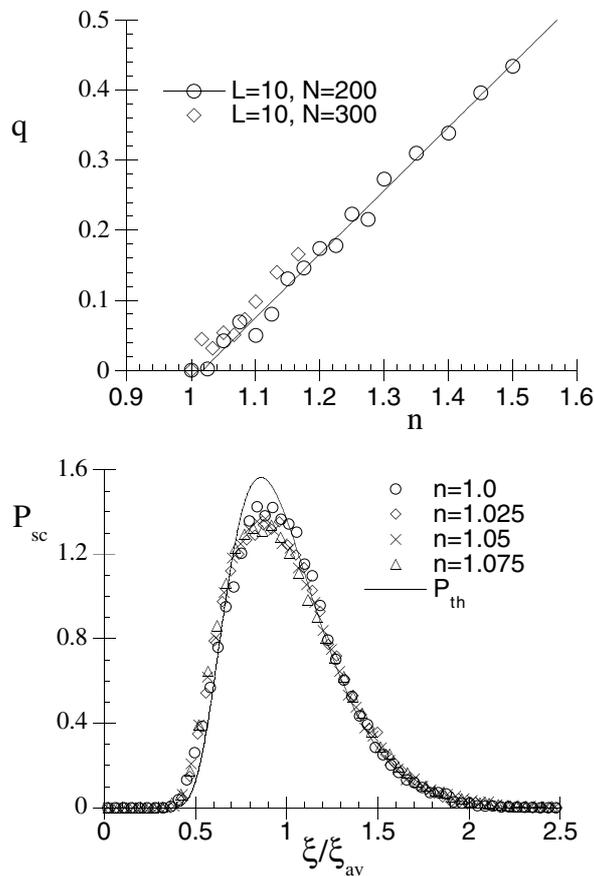
$$\frac{\theta^2}{2} \frac{d\pi}{d\theta} = (1 - \theta)\pi - \int_0^\theta d\theta' \pi(\theta')\pi(\theta - \theta') \quad (10)$$

whose solution gives rise to the parameter-free prediction shown as the full line in figure 1 (bottom).

So, what have we found? At this stage we have found that a mean-field treatment of a specific semi-microscopic model yields the following results:

- (i) For crosslink densities smaller than a certain critical value (of roughly one crosslink per macromolecule) the equilibrium state of the system is a liquid, with all particles (in the context of macromolecules, monomers) being delocalized.
- (ii) At the critical crosslink density there is a continuous thermodynamic phase transition to a random solid state characterized by the presence of random static density fluctuations.
- (iii) In this state, at least a fraction of the particles are localized near random positions about which they thermally fluctuate with random localization lengths.
- (iv) The fraction of localized particles grows linearly with the excess crosslink density, consistent with the mean-field theory of percolation. As the transition is approached, the characteristic localization length diverges as the inverse square root of the excess crosslink density.
- (v) When scaled by the mean value, the statistical distribution of localization lengths is universal for all near-critical crosslink densities, the form of this scaled distribution being uniquely determined by the integro-differential equation (10).

As one can see from figure 1, this picture has been rather well confirmed in molecular dynamics computer simulations of three-dimensional systems of randomly crosslinked, interacting macromolecules, undertaken at Simon Fraser University by Barsky and Plischke [9, 10].



**Figure 1.** Results from molecular dynamics simulations by Barsky and Plischke [10]. Top: localized fraction  $q$  versus number of crosslinks per macromolecule  $n$ .  $L$  is the number of monomers per macromolecule;  $N$  is the number of macromolecules in the system. The straight line is a fit to the  $N = 200$  data. Note the continuous phase transition at  $n = 1$  and the linear variation of  $q$  with  $n$ , both consistent with mean-field theory. Bottom: the distribution  $P_{sc}$  of localization lengths  $\xi$  (symbols), scaled with the sample-average localization lengths  $\xi_{av}$ . Note the collapse of the data onto a universal scaling distribution, and the quantitative agreement with the mean-field prediction (solid line). The number of segments per macromolecule was 10; the number of macromolecules was 200.

#### 4.2. Universality; simulations; a Landau theory

By repeating the strategy outlined above for several other systems that undergo random solidification, including end-linked (flexible and semi-flexible) macromolecular systems [11], chemically gelled low-molecular-weight systems [4, 5] and even crosslinked manifolds [12], we have learned that the critical properties (i.e. the exponent for the localized fraction and the scaling function for the distribution of localization lengths) are *universal* over a broad class of systems, at least at the mean-field level. (The extension of this universality beyond mean-field theory will be discussed in section 7.) Further evidence for this universality has come from the extensive sequence of computer simulations mentioned above.

This universality at the mean-field level can be understood from the perspective of a model-independent Landau approach [8]. Suppose we take for granted the idea that the

order parameter is a complex-valued field on  $(n + 1)$ -fold replicated Fourier space:  $\Omega(\hat{k})$ . Let us assume that near to the transition the fraction of localized particles is small and that the localization length of the localized particles is large. Let us also assume that macroscopic density fluctuations are suppressed by inter-particle interactions, and therefore do not fluctuate critically at the random solidification transition. As such fluctuations correspond to field configurations in which, e.g.,  $\Omega(\mathbf{0}, \mathbf{k}, \mathbf{0}, \dots, \mathbf{0})$  is non-zero, we should only allow equilibrium values of  $\Omega$  that vanish whenever all but one (or all) argument-vectors vanish. Then (up to simple coefficients) we arrive at the following Landau free energy (per object—e.g. macromolecule—being crosslinked):

$$\overline{\sum}_{\hat{k}} \left( -a\epsilon + \frac{b}{2} |\hat{k}|^2 \right) |\Omega(\hat{k})|^2 - c \overline{\sum}_{\hat{k}_1 \hat{k}_2 \hat{k}_3} \Omega(\hat{k}_1) \Omega(\hat{k}_2) \Omega(\hat{k}_3) \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}}. \quad (11)$$

The innocuous-looking condition that  $\Omega$  be zero whenever all but one (or all) argument-vectors vanish, alluded to just after equation (7), amounts to our incorporating into the theory the effects of inter-particle repulsions, and is vital.

As one can see from the quadratic term in the Landau theory, supercritical crosslinking causes the liquid state to become unstable. However, the instability cannot be resolved as it would be, say, in the case of ferromagnetism with its homogeneous ferromagnetic state, by the ‘condensation’ of (i.e. acquisition of a non-zero value by) the homogeneous mode, because there is no such mode in the theory. Instead, non-zero wave-vector modes acquire non-zero values, and do so in a delicate balance determined by the cubic interaction term, so as to form a kind of *domain wall in momentum space*. What is especially delicate is the scheme by which the system avoids condensing in the (forbidden) macroscopic density sector. By having condensation only of modes for which  $\sum_{\alpha=0}^n k^\alpha = \mathbf{0}$ , the cubic interaction term cannot induce the condensation of macroscopic density-sector fluctuations. One might say that the competing tendencies of the crosslinks (which cause attraction simultaneously in replica space) and the inter-particle repulsion (which acts separately in each replica) frustrate one another, this frustration resolving itself via random solidification. Owing to its macroscopic translational invariance, this state is a condensation that manages to avoid the energy cost that macroscopic density-sector fluctuations would bring.

The condition on the field is also vital from a symmetry standpoint, and embodies the notion that, provided inter-particle interactions are included, the only symmetry of the theory associated with the mixing of the replicas is the *permutation* symmetry  $S_{n+1}$ . The replica coupling arising from the disorder averaging of the replicated crosslinking constraints yields a term that has the special feature of being invariant under the larger group  $O((n + 1)d)$  of rotations that mix the (Cartesian components of the) replicas. However, this symmetry is explicitly broken down to a *permutation* symmetry by the inter-particle interactions. This reduced symmetry also plays vital roles in the analysis of the local stability of the random solid state and the determination of the universality class of the phase transition in the context of a renormalization-group approach to it, as we shall see further in section 7.

For specific values of the coefficients, this Landau theory is what emerges as the replica mean-field theory for each of the semi-microscopic models considered (except that the theory is a bit more elaborate for the gelation case). It is therefore not surprising that it, too, is made stationary by the form given in equation (10).

#### 4.3. Aside: broken symmetries and residual symmetries

In order to avoid confusion, let us be quite clear about the pattern of the symmetry breaking emerging from our picture of the random solidification transition. The liquid state, even

if crosslinks are present, is fully translationally invariant. Crosslinks do not, themselves, explicitly break translational symmetry, even though their presence in sufficient numbers can cause translational symmetry to break spontaneously, as occurs at the transition to the random solid state, in which particles become spontaneously localized in space. All this applies to specific realizations of crosslinking.

Now, what about the permutation symmetry of the replicated, disorder-averaged theory, i.e., what about replica symmetry? Whether or not this symmetry also spontaneously breaks at the transition is only an elaboration on top of the fundamental process, namely translational symmetry breaking. To date, limited searches have been undertaken (see references [13, 14]) but no stable saddle points having broken replica symmetry have been found. Moreover, local stability has been established (see reference [15]) for the saddle point described in section 4.1.4. This saddle point has the symmetries of the permutation of the replicas and the common translations and rotations of the replicas. What have been lost at the transition are the symmetries of the relative translations and rotations of the replicas.

## 5. Emergent elasticity

Perhaps the most remarkable (and certainly the most useful) feature of the phase of matter obtained via vulcanization is its elasticity. I will not dwell on this topic here; it is discussed in references [3, 16]. I will just mention that, at least at the level of mean-field theory, one can address rather directly the following question: By how much does the free-energy density increase when a shear (i.e. volume-preserving) deformation is applied to sample of vulcanized matter? In answering this question one finds that the random solid state is a homogeneous, isotropic elastic medium, characterized by a standard elastic free energy. Moreover, one finds that the shear modulus is (essentially) proportional to the temperature, confirming that the elasticity is primarily entropic in origin, and that this modulus vanishes as the third power of the excess constraint density, as the transition is approached from the liquid side. Some of the probabilistic features of how random solids deform under shear (which seem rather counter-intuitive, at least to me) are also discussed in references [3, 16].

## 6. Long-range correlations and divergent susceptibilities for random solidification

Let us now turn to the issue of long-range correlations that mark the onset of random solidification, and the attendant issue of diverging susceptibilities. In the simpler context of, say, the ferromagnetic Ising transition, the two-point spin-spin correlation function quantifies the notion that the 'by hand' alignment of one particular spin induces appreciable alignment of all the spins within roughly one correlation length of it, this distance growing as the transition is approached. Now imagine approaching the random solidification transition from the liquid side. The incipient order involves random localization and so, by analogy with the ferromagnetic case, the appropriate correlation function is the one that answers the question: Suppose that a particle is localized 'by hand'; to what extent and over what spatial region would other particles respond by becoming localized?

This scenario is, of course, the application to random solidification of the percolation theory question: What is the likelihood that two sites separated by a certain distance will be in the same cluster? After all, if two macromolecular segments are connected to the same cluster then the 'by hand' localization of one would cause the localization of the other. Note, however, the entire physical domain that is absent from any percolation picture, namely, the thermal fluctuations of the particles: not only do the relative separations of the particles on

the cluster fluctuate but also the state in question is liquid, so the particles are only relatively localized, not localized in space.

Bearing these remarks in mind, let us consider the basic correlator associated with the  $\Omega$  field theory:  $\langle \Omega(\hat{k}_1)\Omega(\hat{k}_2) \rangle$ . Not surprisingly, given that  $\Omega$  is about to acquire a non-zero expectation value, this correlator becomes long ranged at the transition. Indeed, at the Gaussian level one has

$$\langle \Omega(\hat{k}_1)\Omega(\hat{k}_2) \rangle \propto \delta_{\hat{k}_1+\hat{k}_2, \hat{0}} / (-2a\epsilon + b\hat{k}_1^2). \quad (12)$$

But what about a physical interpretation? Well, as we have discussed in section 4, the field  $\Omega$  is closely related to the order parameter capable of detecting the localization associated with random solidification and, thus, the growing correlations of  $\Omega$  should foretell incipient random localization, and they do. To see this, consider the construct

$$C_t(\mathbf{r} - \mathbf{r}') \propto \left[ \frac{1}{N} \sum_{j,j'=1}^N \langle \delta^{(d)}(\mathbf{r} - \mathbf{R}_j) \delta^{(d)}(\mathbf{r}' - \mathbf{R}_{j'}) \rangle \times \langle \exp(-it \cdot (\mathbf{R}_j - \mathbf{r})) \exp(it \cdot (\mathbf{R}_{j'} - \mathbf{r}')) \rangle \right]. \quad (13)$$

For  $t = \mathbf{0}$  this is simply proportional to the density–density correlation function and, as such, is not of central importance at the random solidification transition. However, for  $t \neq \mathbf{0}$  it addresses the question: If a particle near  $\mathbf{r}$  is localized on the scale  $t^{-1}$  (or more strongly), how likely is a particle near  $\mathbf{r}'$  to be localized on the same scale (or more strongly)? It is straightforward to show that  $C_t(\rho)$  is related to the  $\Omega$ – $\Omega$  correlator:

$$C_t(\rho) \propto \lim_{n \rightarrow 0} \sum_k e^{i(k+t) \cdot \rho} \langle \Omega(\mathbf{0}, t, \mathbf{k}, \mathbf{0}, \dots, \mathbf{0})^* \Omega(\mathbf{0}, t, \mathbf{k}, \mathbf{0}, \dots, \mathbf{0}) \rangle. \quad (14)$$

The  $t \rightarrow \mathbf{0}$  limit of  $C_t(\rho)$  determines how likely it is for two particles a distance  $|\rho|$  apart to be connected in a cluster, i.e., to be mutually localized, regardless of the strength of this localization. To construct the corresponding divergent susceptibility we integrate over space and pass to the  $t \rightarrow \mathbf{0}$  limit, thus obtaining a measure of the spatial extent over which pairs of particles are mutually localized:

$$\lim_{t \rightarrow \mathbf{0}} \int d^d \rho C_t(\rho) \propto \lim_{t \rightarrow \mathbf{0}} \lim_{n \rightarrow 0} \langle \Omega(\mathbf{0}, t, -t, \mathbf{0}, \dots, \mathbf{0})^* \Omega(\mathbf{0}, t, -t, \mathbf{0}, \dots, \mathbf{0}) \rangle \propto |\epsilon|^{-\gamma}.$$

At the Gaussian level of approximation, this susceptibility diverges with the classical exponent  $\gamma = 1$ .

## 7. Critical fluctuations

So far, our exploration of the random solidification transition has been at the level of mean-field theory (for the order parameter, elasticity and stability with respect to small fluctuations of the solid state), and the Gaussian approximation (for the correlations in the liquid state). What about critical fluctuations? In the present section I shall report some results on this issue that have been obtained very recently in collaboration with Weiqun Peng [17] and primarily concern critical fluctuations in the liquid state and at the critical point.

### 7.1. Replica field theory

Let us progress beyond mean-field theory and the Gaussian approximation by regarding equation (11) not as a Landau theory but as a Landau–Wilson effective Hamiltonian for a field theoretic approach to the issue of critical fluctuations. As such, it contains a Gaussian

term and a cubic interaction term which, by naïve dimensional analysis, can be seen to be the most relevant perturbation below six spatial dimensions (at least in the  $n \rightarrow 0$  limit).

It is worth noting the similarities of and differences between this field theory and the (cubic,  $(n + 1)$ -state Potts) field theory, the  $n \rightarrow 0$  limit of which can be invoked to study percolation [18]:

$$\int_V d^d r \left( \sum_{\alpha=1}^n \left( \frac{1}{2} t \psi_{\alpha}^2 + \frac{1}{2} |\nabla \psi_{\alpha}|^2 \right) - w^{(3)} \sum_{\alpha, \beta, \gamma=1}^n \lambda_{\alpha\beta\gamma}^{(3)} \psi_{\alpha} \psi_{\beta} \psi_{\gamma} \right) \quad (15)$$

where  $t$  controls the bond-occupation probability (and hence the percolation transition),  $w^{(3)}$  is the non-linear coupling and  $\lambda_{\alpha\beta\gamma}^{(3)}$  is the ‘Potts tensor’ (which controls the internal symmetry of the theory). As for similarities, there is the cubic nature of the interaction, the  $(n + 1)$ -fold permutation symmetry and the passage to the  $n \rightarrow 0$  limit. As for differences, the Potts field theory has a real multiplet of  $n$  fields on  $d$ -dimensional space; the vulcanization field theory has a real field living on  $(n + 1)$ -fold replicated  $d$ -dimensional space. Furthermore, the Potts field theory represents a setting involving a *single* ensemble, the ensemble of percolation configurations, whereas the vulcanization field theory describes a physical problem in which *two* distinct ensembles (thermal and disorder) play essential roles. As such, the latter is capable of providing a unified theory not only of the transition but also of the structure, correlations and (e.g. elastic) response of the emerging random solid state.

### 7.2. Recovering de Gennes’ Ginzburg criterion

As we report in detail in reference [17], suppose we take the  $\Omega$  field theory (11) and try to assess the range of constraint densities  $\delta\epsilon$  (around the critical constraint density) within which fluctuation corrections are significant, i.e., to construct a Ginzburg criterion. Then, provided that we correctly account for the non-critical nature of the density fluctuations, we find that fluctuations increase the critical crosslink density (as one would expect on general grounds), along with a Ginzburg criterion which, for the case of vulcanized macromolecular matter, reads

$$\delta\epsilon \sim (L/\ell)^{-(d-2)/(6-d)} \varphi^{-2/(6-d)} \quad (16)$$

where  $L/\ell$  is the number of (essentially independent) segments on each chain and  $\varphi$  is the volume fraction taken up by the macromolecules: e.g., for  $d = 3$ , shorter chains show stronger critical effects. This dependence on  $L/\ell$  is precisely that derived long ago by de Gennes on the basis of a percolative picture [19].

### 7.3. Expansion about six spatial dimensions

As we also report in detail in reference [17], we have, in addition, implemented a momentum-shell renormalization-group approach to the field theory (11) in order to construct universal quantities in an expansion around six spatial dimensions. Here, too, one has to exercise considerable care in handling the vital constraint on the fields associated with the suppression of density fluctuations by particle interactions. What emerges, at least to first order in  $6 - d$  (and probably beyond), is the following striking result: the critical state is governed by flow equations isomorphic to those emerging from the percolation limit of the Potts field theory. Thus, e.g., to first order in  $6 - d$  the critical exponents  $\eta$  ( $= -(6 - d)/21$ , which describes the decay of the order parameter fluctuation correlations at the vulcanization transition),  $\nu^{-1}$  ( $= 2 - (5(6 - d)/21)$ , which describes the divergence of the fluctuation correlation length) and  $\beta$  ( $= 1 - ((6 - d)/7)$ , which describes the growth of the localized fraction) take on precisely the values that one would expect from examining analogous quantities in percolation theory.

Although it is tempting to ask: ‘How could it be otherwise?’, it must be borne in mind that the vulcanization field theory is not the same as the Potts field theory. It is richer, as it emerges from an underlying semi-microscopic picture in which there are both quenched and annealed variables, and contains a detailed description of the structure of the emergent random solid state in addition to being capable of capturing the critical properties of the vulcanization transition.

The nature of the vulcanization transition and its relationship with the percolation transition in and around two spatial dimensions is an intriguing issue, as ongoing work with H E Castillo and W Peng is revealing [20]. Things become especially fascinating in two dimensions in view of the fact that there is a conventional percolation transition in there, whereas strong evidence (in the form of Goldstone modes resulting from the spontaneously broken *continuous* translational symmetry) suggests that two is the lower critical dimension for the vulcanization transition. Thus, it is tempting to speculate that the following scenario holds in two dimensions [20]:

- (i) With a subcritical density of constraints, the network does not percolate, there is no infinite cluster, the vulcanization order parameter is zero and its correlations decay exponentially with distance.
- (ii) By contrast, with a supercritical density of constraints, the network percolates and there is an infinite cluster; but thermal fluctuations in the positions of the constituents overwhelm the tendency for true localization, so the amorphous solidification order parameter remains zero and, instead, its fluctuations decay algebraically with distance. One might say that (constraint-density-controlled) cluster fragmentation, rather than thermally excited lattice defects, mediate the melting transition. If this scenario happens to be borne out, one would have a quasi-amorphous solid state—the random analogue of a two-dimensional solid [21]—exhibiting quasi-long-range positional order but of a random rather than regular type.

## 8. Where next?

In addition to a full renormalization-group-based exploration of amorphous solidification in and near two dimensions, touched upon in the previous paragraph, issues that I would very much like to see addressed further include:

- (i) dynamics near the vulcanization transition, including the divergence of the viscosity as the transition is approached from the liquid side;
- (ii) a full renormalization-group approach to the random solid state itself;
- (iii) the possibility of multifractality in the characterization of random network media, say, along the lines of that found in randomly diluted spin and resistor systems by Harris and Lubensky [22]; and
- (iv) quantized networks, perhaps a somewhat academic topic, but I think it would be fascinating to have at hand a model showing that rigidity (perhaps one might call it Casimir rigidity) can be acquired by random solids via *quantum* fluctuations, rather than the thermal fluctuations discussed here.

I would also very much welcome further experiments, such as quasi-inelastic neutron scattering ones, aimed, e.g., at extracting information about the distribution of localization lengths near the random solidification transition.

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