Cavity Approach to the Random Solid State

Xiaoming Mao,1 Paul M. Goldbart,1 Marc Mézard,2 and Martin Weigt3

1Department of Physics, University of Illinois at Urbana-Champaign, 1110 W. Green St., Urbana, IL 61801, USA
2CNRS et Université Paris Sud, LPTMS, Bât. 100, 91405 Orsay, France
3Institute for Scientific Interchange, Viale Settimio Severo 65, I-10133 Torino, Italy

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The cavity approach is used to address the physical properties of random solids in equilibrium. Particular attention is paid to the fraction of localized particles and the distribution of localization lengths characterizing their thermal motion. This approach is of relevance to a wide class of random solids, including rubbery media (formed via the vulcanization of polymer fluids) and chemical gels (formed by the random covalent bonding of fluids of atoms or small molecules). The cavity approach confirms results that have been obtained previously via replica mean-field theory, doing so in a way that sheds new light on their physical origin.

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Introduction—Permanent random chemical bonds, when introduced in sufficient number between the (atomic, molecular or macromolecular) constituents of a fluid, cause a phase transition—the vulcanization transition—
to a new equilibrium state of matter: the random solid state. In this state, some fraction of the molecules are spontaneously localized, and thus undergo thermal fluctuations about mean positions, the collection of which positions are random (i.e. exhibit no long-range regularity). As this is a problem of statistical mechanics (the constituents are undergoing thermal motion) in the presence of quenched randomness (the constraints imposed by the random bonding), it has been addressed via the replica technique. Indeed, the example of cross-linked macromolecular matter served as early motivation for Edwards’ development of the replica technique (see, e.g., Ref. [1]).

Our purpose in this Letter is to consider two central diagnostics of the random solid state: the fraction $Q$ of localized particles and the statistical distribution $\mathcal{N}(\xi^2)$ of squared localization lengths $\xi^2$ of these localized particles. Specifically, we show how results for these quantities can be obtained in an elementary and physically transparent way, via the cavity method. The cavity method has proven flexible and powerful in the analysis of a variety of other disordered systems, e.g., spin glasses [2]. The present work is based on the version used to address spin glasses having finite connectivity [3].

The results that we shall obtain via the cavity method are amongst those already known via a (less elementary and less physically transparent) application of the replica technique, together with a mean-field approximation; for reviews see Refs. [4,5]. Thus, it was already known [6] that (as is typical for mean-field theories) $Q$ obeys a transcendental equation, in this case

$$1 - Q = \exp(-\mu^2 Q),$$

where $\mu^2$ is a parameter that controls the density of cross-links. The instability of the fluid state and its replacement by the random solid state are signaled by the emergence, as $\mu$ is increased beyond a critical value (here unity), of a positive solution to Eq. (1), although the formulation is not restricted to the critical regime. This result for $Q$ was, in essence, found by Erdős and Rényi, in their classic work on the statistical properties of random graphs [6]. As for the distribution $\mathcal{N}(\xi^2)$, at the mean-field level and for near-critical values of the cross-link density, the replica approach yields the scaling form

$$\mathcal{N}(\xi^2) = \frac{2}{\epsilon\xi^4} \pi \left( \frac{2}{\epsilon\xi^2} \right),$$

where $\epsilon = [x (\mu^2 - 1)]$ measures the distance from the critical point, and in which the scaling function $\pi$ obeys the nonlinear integro-differential equation

$$\frac{d}{db} \left( \frac{1}{2} \theta^2 \pi(\theta) \right) = \pi(\theta) - (\pi \circ \pi)(\theta),$$

where $\pi \circ \pi$ indicates a Laplace convolution [9]. This result was obtained from a semi-microscopic approach by Castillo et al. [6] and re-derived via a Landau-type theory by Peng et al. [10]. Some support for the results for $Q$ and $\pi$ has been obtained numerically [11] and experimentally [12].

More recently, the mean-field level results have been improved in two directions: via renormalization-group analysis in the vicinity of the upper critical dimension (which is six for this random solidification transition) [13,14], and via analysis of the Goldstone fluctuations [15] (notably in two dimensions, where their consequences are—not surprisingly—dramatic). We pause to mention that we view the cavity method as complementing rather than supplanting the replica method: the latter provides access to the powerful array of field-theoretic tools, the former opens the way to a perturbative treatment of correlations beyond mean-field.

Cavity method for randomly cross-linked macromolecules, especially in the vicinity of the random solidification transition—We begin by considering a system of vulcanized macromolecules, as depicted in Fig. [11]. We characterize the system by the fraction $Q$ of localized chain segments
FIG. 1: (a) Snapshot of a cross-linked (open circles) macro-
molecular system, in which a fraction $Q$ of the macromolecules
belong to the infinite cluster (and are thus localized), and the
remaining fraction $1 − Q$ are delocalized. A localized segment
exhibits thermal position-fluctuations over a length-scale $\xi$ (i.e., its
localization length). Due to the heterogeneity of the
network, distinct segments have distinct localization lengths.
(b) Coupling of a new macromolecule (dashed) to the system
in order to probe the distribution $N(\xi^2)$. The new
macromolecule has $N_c$ contact points with the existing network,
and cross-links are introduced independently at these points.

and the statistical distribution $N$ of mean squared lo-
alization lengths $\xi^2$ of the localized particles. We then
envision adding a further macromolecule to the system,
as shown in Fig. 1b. Of all the segments on this chain, we
suppose that a certain number $N_c$ are sufficiently close
to segments of the original system to have a chance of
becoming cross-linked to them. We suppose that fluctu-
asations in this number are sufficiently small that we may
neglect them. Next, we consider a random cross-linking
process that results, with independent probability $p$, in
cross-links actually being introduced between each of the
$N_c$ close pairs. Within this framework, the probability
that exactly $k$ cross-links are introduced is then given by
the binomial formula: $\binom{N_c}{k} p^k (1 − p)^{N_c − k}$. We now ask
the question: What is the probability $P_k$ that exactly $k$
of these cross-links are made to localized segments? To
answer it, we make the approximation that the probabil-
ties for the segments of the original system to be localized
describe independent random variables, in which case the
probability of any one such segment being localized is $Q$.
Then, collecting together the contributions to this proba-
bility, which arise from $k'$ (with $k ≤ k' ≤ N_c$) cross-links
being formed, of which exactly $k$ are to localized seg-
ments, we arrive at the formula

$$P_k = \sum_{k' = k}^{N_c} \binom{N_c}{k'} p^{k'} (1 − p)^{N_c − k'} Q^{k'} (1 − Q)^{N_c − k'}. \quad (4)$$

Via a straightforward application of the binomial theo-
rem one can perform this summation, and hence arrive
at the result

$$P_k = \binom{N_c}{k} (pQ)^k (1 − pQ)^{N_c − k}. \quad (5)$$

Let us evaluate these probabilities for the three cases of
relevance, viz.,

$$P_0 = (1 − pQ)^{N_c}, \quad (6a)$$

$$P_1 = N_c pQ (1 − pQ)^{N_c − 1}, \quad (6b)$$

$$P_2 = \frac{1}{2} N_c (N_c − 1) (pQ)^2 (1 − pQ)^{N_c − 2}. \quad (6c)$$

In the limit of main interest, viz. $pQ ≪ 1$, these proba-
bilities simplify to

$$(P_0, P_1, P_2) \approx e^{−N_c pQ} \left(1, N_c pQ, \frac{1}{2} N_c (N_c − 1) (pQ)^2\right). \quad (7)$$

To arrive at a self-consistent equation for $Q$ (as a func-
tion of $p$ and $N_c$) we require that the probability of the added
macromolecule being cross-linked to exactly zero localized
segments be $1 − Q$, which gives

$$1 − Q = (1 − pQ)^{N_c}. \quad (8)$$

In the limit $pQ ≪ 1$ this becomes

$$1 − Q = \exp (−N_c pQ), \quad (9)$$

i.e., Eq. 4, provided we make the (physically sensible)
identification $pN_c ≡ \mu^2$.

To arrive at a self-consistent equation for $N$ (as a func-
tion of $p$, $N_c$ and $\xi^2$) we address the probability that the
segment at arc-length $\sigma$ (with $0 ≤ \sigma ≤ 1$) on the added
macromolecule has squared localization length $\xi^2$. As
the segments of the added macromolecule will only be local-
ized if they are attached to at least one localized segment
of the original system, we should replace the probabilities
$\{P_k\}_{k=0}^{\infty}$ by the probabilities conditioned on at least one
attachment being to a localized segment of the original
system (i.e., $k = 1, 2$). Thus we arrive at the probabilities
$\{P_1, P_2\}$ which we write in the form $(1 − a, a)$. Consider
the situation in which the added macromolecule is at-
tached at its arc-length $\sigma_1$ to a single segment of the
original system, that segment having squared localization
length $\xi^2_1$, as depicted in Fig. 1b. Furthermore, sup-
pose that the added chain is Gaussian. Then, by the el-
ementary properties of random walks, the mean squared
spatial separation of segments separated by arc-length
$|\sigma − \sigma_1|$ is given by $|\sigma − \sigma_1| R^2_k$, where $R^2_k$ is the mean
Now, supposing that the addition to the squared localization length, \(|\sigma - \sigma_1| R_g^2\), is small compared with the localization lengths that feature with appreciable weight in \(\mathcal{N}\), this approximates to

\[
\mathcal{N}(\xi^2 - |\sigma - \sigma_1| R_g^2) \approx \mathcal{N}(\xi^2) - |\sigma - \sigma_1| R_g^2 \mathcal{N}'(\xi^2). \tag{11}
\]

Next consider the situation in which the added macromolecule is attached at its arc-lengths \(\sigma_1\) and \(\sigma_2\) to two segments of the original system, as shown in Fig. 2b. In fact, as the probability that the added chain has two cross-links to localized segments of the original system is (in the limit of interest) much smaller than the probability that it has one cross-link, we shall not need to keep track of the arc-length locations of the cross-links; in this situation it will be adequate to treat the added chain as a point object. Then, as this object is attached to two localized objects, it is pinned more sharply than either, this parallel form of pinning giving rise to a smaller squared localization length \(\xi^2\), via the formula

\[
\xi^{-2} = \xi_1^{-2} + \xi_2^{-2}. \tag{12}
\]

So, assuming that \(\xi_1^2\) and \(\xi_2^2\) are independent (and thus governed by the joint distribution \(\mathcal{N}(\xi_1^2) \mathcal{N}(\xi_2^2)\)), the distribution of \(\xi^2\) is given by

\[
\int d\xi_1^2 \mathcal{N}(\xi_1^2) d\xi_2^2 \mathcal{N}(\xi_2^2) \delta \left( \xi^2 - (\xi_1^{-2} + \xi_2^{-2})^{-1} \right). \tag{13}
\]

We now put these results together to construct the distribution of squared localization lengths for segment \(\sigma\) of the added chain, arriving at

\[
(1-a) \left( \mathcal{N}(\xi^2) - |\sigma - \sigma_1| R_g^2 \mathcal{N}'(\xi^2) \right) + a \int d\xi_1^2 \mathcal{N}(\xi_1^2) d\xi_2^2 \mathcal{N}(\xi_2^2) \delta \left( \xi^2 - (\xi_1^{-2} + \xi_2^{-2})^{-1} \right). \tag{14}
\]

Finally, we average over the segment \(\sigma\) of the added chain, as well as the location \(\sigma_1\) of the cross-link, using \(\int d\sigma d\sigma' |\sigma - \sigma'| = 1/3\), thus arriving at the self-consistent equation obeyed by the distribution of squared localization lengths:

\[
\mathcal{N}(\xi^2) = (1-a) \left( \mathcal{N}(\xi^2) - \frac{1}{3} R_g^2 \mathcal{N}'(\xi^2) \right) + a \int d\xi_1^2 \mathcal{N}(\xi_1^2) d\xi_2^2 \mathcal{N}(\xi_2^2) \delta \left( \xi^2 - (\xi_1^{-2} + \xi_2^{-2})^{-1} \right). \tag{15}
\]

Observe that by integrating both sides over \(\xi^2\) and invoking the property that \(\mathcal{N}\) vanishes at the limits \(\xi^2 = 0\) and \(\infty\), we recover the normalization condition that \(\int d\xi^2 \mathcal{N}(\xi^2) = 1\). The scaling property of \(\mathcal{N}\) shows up via the following change of dependent and independent variables:

\[
\xi^2 \rightarrow \theta = \frac{2}{3} - \frac{a}{3} \frac{R_g^2}{\xi^2}, \tag{16a}
\]

\[
\mathcal{N}(\xi^2) \rightarrow \pi(\theta) = \frac{3}{2} - a \frac{R_g^2}{2} \xi^2 \mathcal{N}(\xi^2), \tag{16b}
\]

under which Eq. (15) becomes the sought integro-differential equation. We identify the parameter \(\epsilon\) in Eq. (16) with \(\frac{2}{\pi} \sqrt{\mathcal{N}(\xi^2)}\). Notice that the cavity method allows us to compute corrections to Eq. (16) perturbatively in \(1/R_g\).

Cavity method for randomly bonded Brownian particles at arbitrary bonding densities—The cavity approach can be extended to address the chemical gelation transition, i.e., the transition triggered by the introduction of random covalent bonds between atoms or small molecules (rather than macromolecules) in the liquid state. We shall address the model studied previously by Broderix et al. \cite{Broderix}, which consists of a collection of point particles undergoing Brownian motion at a certain temperature. Permanent bonds are then introduced at random between nearby particles, so that pairs of bonded particles become constrained softly (i.e. by a spring-like, harmonic...
potential), so that the probability distribution $\phi$ of their separations $r_j - r_k$ is Gaussian and characterized by a length-scale $l$:

$$\phi(r_j - r_k) \propto \exp \left( -|r_j - r_k|^2 / 2l^2 \right),$$  \hspace{1cm} (17)

where $r_{j,k}$ are the position vectors of particles $j$ and $k$. This model is sufficiently simple that the analysis of it need not be restricted to the critical region.

To approach the statistics of this system of randomly bonded Brownian particles using the cavity method, we consider the process of adding a new particle. The combinatorics of the bonding follows the form taken for the system of cross-linked macromolecules; we simply need to convert the notion of contact points into a spherical region of a certain radius in which the likelihood of particles being bonded to one another is concentrated. This sphere is centered on the new particle and, on average, includes $N_c$ of the existing particles. Then, bonds are randomly introduced, with probability $p$, between the new particle and some of the $N_c$ existing particles that are nearby. Thus, the foregoing combinatorics continues to apply, and we arrive at the formula for the probability of having exactly $k$ bonds with the infinite cluster given in Eq. (5). As a consequence, we obtain the foregoing result for the fraction of the infinite cluster $Q$, Eq. (9).

The physics of the localization lengths is, in fact, simpler for bonded Brownian particles. When the new particle is connected via a spring of length-scale $\xi$ to one localized particle, its localization length $\Xi_1$ is given by $\Xi_1^{-2} = (\xi^2 + l^2)^{-1}$. When it is connected in parallel, via identical springs to $k$ localized particles, its localization length $\Xi_k$ is given by

$$\frac{1}{\Xi_k^2} = \sum_{j=1}^{k} \frac{1}{\xi_j^2 + l^2},$$  \hspace{1cm} (18)

To construct the distribution of the squared localization length of the new particle, we shall average over all possible numbers of bonds, weighted with their corresponding probabilities. These probabilities follow from the probabilities $\hat{P}_k$ given by Eq. (5), but normalized by a factor $Q^{-1}$ because the new particle will only be localized if it is bonded to at least one particle in the infinite cluster. Hence, we arrive at a self-consistency equation for localization-length distribution for the randomly bonded Brownian particle model:

$$\mathcal{N}(\xi^2) = \sum_{k=1}^{\infty} \hat{P}_k \int_0^\infty d\xi_1^2 \mathcal{N}(\xi_1^2) \cdots d\xi_k^2 \mathcal{N}(\xi_k^2) \delta(\xi^2 - \Xi_k^2),$$  \hspace{1cm} (19)

where the conditional probabilities $\hat{P}_k$ are given by $\hat{P}_k = P_k/Q$ (for $k = 1, 2, 3, \ldots$). The distribution of localization lengths for the randomly bonded Brownian particle model was studied previously by Broderix et al. [10] using the replica method and a Mayer cluster expansion. To see that the cavity approach result (19) recovers their result, we take the limit $N_c \to \infty$ whilst keeping finite the mean number of bonds from the new particle (either to the infinite cluster or to delocalized particles), i.e. $pN_c$. In this limit, the binomial distribution tends to a Poisson distribution: $\hat{P}_k \to (pN_c)^k e^{-pN_c}/k!$. The result of Broderix et al. [12] then follows from Eq. (10) by (i) transforming to a distribution for $\tau = 1/\xi^2$, and (ii) making the identifications $\kappa = l^{-2}$ and $c = pN_c$ (i.e. the mean of number of bonds associated with a single particle).

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[9] As $\pi$ is a distribution it must be non-negative and normalized: $\int_0^\infty d\theta \pi(\theta) = 1$. Equation (5) is, however, self-normalizing, in the sense that solutions that behave reasonably, as $\theta$ tends to zero or infinity, are automatically normalized, as integrating the equation between these limits, term by term, reveals.