Introduction. The vulcanization transition (VT) is the equilibrium phase transition from a liquid state of matter to an amorphous solid state. It occurs when a sufficient density of permanent random constraints (e.g. chemical crosslinks)—the quenched randomness—are introduced to connect the constituents (e.g. macromolecules), whose locations are the thermally fluctuating variables. Whilst a rather detailed description of the VT has emerged over the past few years within the context of a mean-field approximation \[ \chi \], the picture of this transition beyond the mean-field (MF) level is less certain.

The true (i.e. beyond-MF) critical properties of the VT (and the related chemical-gelation transition) have mostly been studied through approaches based on gelation/percolation perspectives \[ \chi \] \[ \chi \], in which the VT is directly or indirectly identified with the percolation transition. These approaches are associated with one single ensemble, accounting either for the quenched disorder or for the equilibrium thermal configurations (whose change in character mark the transition). Given that an essential aspect of the VT is the impact of the quenched random constraints on the thermal motion of the constituents, approaches based on a single ensemble cannot directly account for the effects of both types of fluctuations and are, thus, not entirely satisfactory.

The purpose of the present Letter is to apply renormalization-group (RG) ideas to a model in which both the quenched randomness and the thermal fluctuations of the constituents are naturally and directly incorporated. Our analysis provides a more complete way of obtaining the critical exponents, and therefore sheds light on the connection between gelation/percolation physics and the VT. A detailed account of this work can be found in Ref. \[ \chi \].

Our approach to the VT is based on a minimal Landau-Wilson effective Hamiltonian, which was constructed in Ref. \[ \chi \] and also shown to recover (at the mean-field level) the description of both the liquid and emergent amorphous solid states, known earlier from the analysis of various semi-microscopic models \[ \chi \] \[ \chi \]. The order parameter for the VT is a function that encodes both the gel fraction \( q \) (i.e. the fraction of monomers localized) and the distribution of localization length of the localized monomers (as well as other diagnostics). Support for the mean-field picture of the solid state has emerged from extensive molecular dynamics computer simulations of three-dimensional, off-lattice, interacting, macromolecular systems, due to Barsky and Plischke \[ \chi \].

Modeling the VT—the order parameter. The appropriate (dimensionless) order parameter for the VT, capable \( \textit{inter alia} \) of distinguishing between the liquid and amorphous solid states of randomly crosslinked macromolecular systems (RCMSs), is the following function of \( n \) wave-vectors \( \{ k^1, \ldots, k^n \} \):

\[
\left[ \frac{1}{N} \sum_{j=1}^{N} \int_0^1 ds \left( e^{ik^1 j c_j(s)} \cdots e^{ik^n j c_j(s)} \right)_\chi \right],
\]

where \( N \) is the total number of macromolecules, \( c_j(s) \) (with \( j = 1, \ldots, N \) and \( 0 \leq s \leq 1 \)) is the position in \( d \)-dimensional space of the monomer at fractional arclength \( s \) along the \( j^{th} \) macromolecule, \( \langle \cdots \rangle_\chi \) denotes a thermal average for a particular realization \( \gamma \) of the quenched disorder (i.e. the crosslinking), and \( \cdot \cdot \cdot \) represents a suitable averaging over this quenched disorder. It is worth emphasizing that the disorder resides in the specification of what monomers are crosslinked together: the resulting constraints do not explicitly break the translational symmetry of the system.

Modeling the VT—the minimal model. Following Deam and Edwards \[ \chi \], we adopt a constraint distribution appropriate to the situation of instantaneous crosslinking of the equilibrium melt or solution, and invoke the replica trick to incorporate the consequences of the permanent random constraints. Thus, we are led to the need to work with the \( n \to 0 \) limit of systems of \( n + 1 \) replicas. The additional (i.e. zeroth) replica incorporates the constraint distribution.

The form of the minimal model can be determined, in the spirit of the Landau approach, from the nature of the order parameter and the symmetries of the effective (i.e. pure but replicated) Hamiltonian, along with the assumptions of the analyticity of this Hamiltonian and the continuity of the transition \[ \chi \]. This scheme leads to the following minimal model, which takes the form of a cu-
bic field theory involving the order parameter field \( \hat{\Omega}(\hat{k}) \) living on \((n + 1)\)-fold replicated \(d\)-dimensional space:

\[
f \propto \lim_{n \to 0} n^{-1} \ln [Z^n], \quad [Z^n] \propto \int \mathcal{D}^d \hat{\Omega} \exp(-S_n),
\]

\[
S_n(\{\hat{\Omega}\}) = N \sum_{\hat{k} \in \text{HRS}} \left(-\bar{\alpha} \tau + \bar{b} |\hat{k}|^2\right) |\Omega(\hat{k})|^2
- Ng \sum_{\hat{k}_1, \hat{k}_2, \hat{k}_3 \in \text{HRS}} \Omega(\hat{k}_1) \Omega(\hat{k}_2) \Omega(\hat{k}_3) \delta_{\hat{k}_1+\hat{k}_2+\hat{k}_3,\hat{0}}. \tag{2b}
\]

Here, \( \tau \) is the control parameter, which measures the reduced density of random constraints, and the coefficients \( \bar{a}, \bar{b} \) and \( g \) encode the microscopic details of the system. We denote averages weighted with \( \exp(-S_n) \) by \( \langle \ldots \rangle^d \), use the symbol \( \hat{k} \) to denote the replicated wave-vector \( \{\hat{k}^0, \hat{k}^1, \ldots, \hat{k}^n\} \), and define the extended scalar product \( \hat{k} \cdot \hat{c} \) by \( \hat{k}^0 \cdot c^0 + \hat{k}^1 \cdot c^1 + \cdots + \hat{k}^n \cdot c^n \). The symbol \( \hat{\pi} \in \text{HRS} \) indicates that a summation over replicated wave-vectors is restricted to those containing at least two nonzero component-vectors \( \hat{k}^n \). (We say that this kind of wave-vector lies in higher-replica-sector, i.e. the HRS.) This condition reflects the important fact that no crystalline order (or any other kind of macroscopic inhomogeneity) is present in the vicinity of the VT; it changes the symmetry of the effective Hamiltonian and, hence, can (and in fact does) play a crucial role. Consequently, the functional integral is to be performed over fields obeying the linear constraint of lying in the HRS.

**Ginzburg criterion.** To estimate the range of \( \tau \) about the critical value, within which the effects of order-parameter fluctuations are relatively strong, we follow the conventional strategy of constructing a loop expansion (in the present setting, an expansion in the inverse monomer density) for the 2-point vertex function to one-loop order, examining its low-wave-vector limit, thus obtaining the inverse susceptibility \( \Xi \).

![FIG. 1. One-loop correction to the 2-point vertex function.](image)

The only one-loop correction comes from the diagram shown in Fig. 2, thus, we find

\[
\frac{1}{N \Xi} \approx -2\bar{a}(\tau - \tau_c) \left(1 - 18 \frac{Vg^2 J_d}{Nb^d/2} (-2\bar{\alpha} \tau)^{(d-6)/2}\right), \tag{3}
\]

where \( \tau_c > 0 \) is the critical value of \( \tau \), shifted due to the inclusion of one-loop corrections, and \( J_d \) is an unimportant dimensionless number. Equation (3) shows that the upper critical dimension for the VT is six. To determine the physical content of the Ginzburg criterion, we invoke the values of the coefficients appropriate for the semi-microscopic model of RCMSs, and find the following form of the Ginzburg criterion: for \( d < 6 \), fluctuations cannot be neglected for values of \( \tau \) satisfying:

\[
|\tau| \lesssim (L/\ell)^{-\frac{d-2}{2(d-6)}} \left(\varphi/g^2\right)^{-2/(6-d)}, \tag{4}
\]

Here, \( L \) is the arclength of each macromolecule, \( \ell \) the persistence length, and \( \varphi \equiv (N/V)(L/\ell)^d \) the volume fraction. Equation (4) shows that the fluctuation-dominated regime is narrower for longer macromolecules and higher densities (for \( 2 < d < 6 \)). Such dependence on the degree of polymerization \( L/\ell \) is precisely that argued for by de Gennes on the basis of a percolation picture.

**Epsilon expansion.** We now apply the \( \varepsilon \) \((\equiv 6 - d)\) expansion to derive the RG flow equations near the upper critical dimension, and discuss the resulting fixed-point structure and critical exponents. In order to streamline the presentation, we may, by suitably redefining the scales of \( \Omega(\hat{k}) \) and \( \hat{k} \) in Eq. (2), absorb the coefficients \( \bar{a} \) and \( \bar{b} \) (i.e. set \( \bar{a} = 1, \bar{b} = 1 \)).

![FIG. 2. Contributing one-loop diagrams. Full lines indicate bare HRS correlators for short-wavelength fields (i.e. fields lying in the momentum shell); wavy lines indicate long-wavelength fields.](image)

We shall be working to one-loop order and, correspondingly, the contributing diagrams are those depicted in Figs. a,b. After taking proper care of the constraints on the wave-vector summations, and passing to the \( n \to 0 \) limit, the flow equations are (with higher order terms omitted) found to be

\[
d\tau/d\ln b = 2\tau - C_0 g^2 - C_0' \tau g^2 - C_1 \tau g^2, \tag{5a}
\]

\[
dg/d\ln b = g(\varepsilon/2 - C_3 g^2 - \frac{3}{2} C_1 g^2), \tag{5b}
\]

\[
dz/d\ln b = \frac{1}{2}(d + 2 - C_1 g^2), \tag{5c}
\]

where \( b \) is the length-rescaling factor, \( z \) is the field-rescaling factor, and the (constant) coefficients in the flow equations are given by \( (C_0, C_0', C_1, C_3) = (V/N)(S_0/(2\pi)^6)(9\Lambda^2, 36, -6, 72) \) in which \( S_0 \) is the surface area of a 6-dimensional sphere of unit radius and \( \Lambda \) is the cut-off for replicated wave-vectors.

Proceeding in the standard way, we find that: (i) For \( \varepsilon \) negative (i.e. \( d > 6 \)), there is only the Gaussian fixed point (GFP), \( (\tau_c, g_c) = (0, 0) \), at which the
exponents take on their classical value: \( \nu = 2 \), \( \eta = 0 \). (ii) For \( \varepsilon \) positive (i.e. \( d < 6 \)), in addition to GFP, a new fixed point—the Wilson-Fisher fixed point (WFFP)—emerges, located at \( (\tau, g^2) = ((4\Lambda^2)/28, (1/126)(2\pi)^6/\mathcal{S}_0(V/N)^{-1}) \), controlling the critical behavior. The resulting critical exponents are (to first order in \( \varepsilon \)) \( \nu = 2 - (5\varepsilon/21) \) and \( \eta = -\varepsilon/21 \).

A standard scaling argument leads to the value of the critical exponent \( \beta \) for the gel fraction: for \( d > 6 \) we find \( \beta = 1 \); for \( d < 6 \) we find \( \beta = \nu (d + 2 - \eta)/2 = 1 - \varepsilon/7 \). In fact, under the (not unreasonable) assumption that, in the ordered state, the fluctuation correlation length-scale is the same as the localization length-scale, we can go further and propose a general scaling hypothesis for the (singular part of) \( \langle \Omega(k) \rangle^S \), viz.,

\[
\langle \hat{\Omega}(k) \rangle^S \sim \hat{\beta}^2 k^{2-2\nu},
\]

which is supported by the mean-field result \[8\]. There are, however, some fascinating subtleties here, which may instead yield multi-fractal characteristics for vulcanized matter similar to those explored by Harris and Lubensky in the setting of random \( xy \) models and resistor networks \[13\].

**Order-parameter correlator and its physical significance.** Both above and below six dimensions, the critical exponents \( \nu, \eta \) and \( \beta \) of the VT, computed above, have identical values (at least to first order in \( \varepsilon \)) to their physical counterparts in percolation theory (as computed, e.g., via the Potts field theory \[14\]). To establish this correspondence, we now explore the physical content of the order parameter correlator \[15\]. (We remark that the identification of the VT \( \beta \) with the \( \beta \) of percolation is evident.)

To proceed, let us consider the construct

\[
C_t(r-r') = \left[ \frac{V}{N} \sum_{j,j'=1}^N \int_0^1 ds ds' \langle \delta(d) (r - c_j(s)) \delta(d) (r' - c_{j'}(s')) \rangle \langle e^{-it(\varepsilon(c_j(s)-r)} e^{it(\varepsilon(c_{j'}(s')-r')} \right] \quad \text{(7a)}
\]

\[
= \frac{N}{V} \sum_{k} e^{i(k+\mathbf{t}) \cdot (r-r')} \left[ \frac{1}{N^2} \sum_{j,j'=1}^N \int_0^1 ds ds' \langle e^{-ik(c_j(s)-c_{j'}(s'))} \rangle \langle e^{-it(\varepsilon(c_j(s)-c_{j'}(s')))} \rangle \right], \quad \text{(7b)}
\]

where the term in the second line that is delimited by square brackets is the microscopic counterpart of the correlator of a typical component of the order parameter, i.e., \( \langle \Omega(0, \ldots, 0, \mathbf{k}, \mathbf{t}) \rangle^* \Omega(0, \ldots, 0, \mathbf{k}, \mathbf{t}) \rangle^S \). The first thermal average in Eq. (7a) accounts for the likelihood that monomers \( j, s \) and \( j', s' \) are respectively to be found around \( r \) and \( r' \); the second describes the correlation between the respective fluctuations of monomer \( j, s \) about \( r \) and monomer \( j', s' \) about \( r' \).

The small-\( t \) limit of \( C_t(r-r') \) addresses the connectedness of clusters of mutually crosslinked macro-molecules \[16\]. To substantiate this claim, we examine Eq. (7a), and consider the contribution to \( C_t(r-r') \) from pairs of monomers that are in the same cluster and pairs that are in different clusters. (We assume that the system has only short-range interactions.) For a generic pair of monomers that are in the same cluster, we expect that \( \langle \exp(it \cdot (c_j(s) - c_{j'}(s'))) \rangle \sim 1 \), and that (for \( |r-r'| \lesssim R_g \)) \( \langle \delta(d) (r - c_j(s)) \delta(d) (r' - c_{j'}(s')) \rangle \sim V^{-1} R_g^{-d} \). Then the total intra-cluster contribution to \( C_t(r-r') \) is at least of order \( (N/V)^2 R_g^{-d} \). On the other hand, a similar analysis shows that the total inter-cluster contribution is at most of order \( (N/V)^d V^{-1} \). Therefore, the intra-cluster contribution dominates \( C_t(r-r') \) in the thermodynamic limit. (This is also true in the case of generic \( t \), and thus we can always ignore the inter-cluster contribution.) In other words, in the small-\( t \) limit, a pair of monomers located at \( r \) and \( r' \) contribute unity to \( C_t(r-r') \) if they are on the same cluster and contribute zero otherwise.

This limit of \( C_t(r-r') \) plays the same role as the pair-connectedness function defined in (the on-lattice version of) percolation theory \[17\]. For \( t = 0 \), \( C_t(r-r') \) is simply \( (V/N) \times \) the real-space density-density correlator, and is not of central relevance at the VT.

In the case of general \( t \), \( C_t(r-r') \) addresses the question: If a monomer near \( r \) is localized on the scale \( t^{-1} \) (or more strongly), how likely is a monomer near \( r' \) to be localized on the same scale (or more strongly)? From Eq. (7a) we see that \( t^{-1} \) serves as a cutoff to the range of the correlator, so that all pairs of monomers that are relatively localized on a length-scale much larger than \( 1/t \) do not contribute to \( C_t(r-r') \).

Given \( C_t(r-r') \), we can build a divergent susceptibility by integrating \( C_t(r-r') \) over space and passing to the \( t \to 0 \) limit:

\[
\lim_{t \to 0} \int \frac{d^dr \cdot d^d r'}{V} C_t(r-r') \sim \quad \text{(8)}
\]

\[
N \lim_{n \to 0} \langle \Omega(0, \ldots, 0, \mathbf{t}, \mathbf{-t}) \rangle^* \Omega(0, \ldots, 0, \mathbf{t}, \mathbf{-t}) \rangle^S \sim (-\tau)^{-\gamma}.
\]

This quantity is measure of the spatial extent over which pairs of monomers are relatively localized, no matter how weakly, and thus diverges at the VT.

**Concluding remarks.** As we have seen, the VT exponents obtained by the \( \varepsilon \) expansion turn out to be numerically equal to those characterizing physically analogous quantities in percolation theory, at least to first order in \( \varepsilon \). This equality between exponents seems reasonable, in view of the intimate relationship between percolation
theory and the connectivity of the system of crosslinked macromolecules. Such a connection has long been recognized, and supports the use of percolative approaches as models of certain aspects of the VT. 

A convenient formulation of the percolative approach is via the Potts model in its one-state limit. It is therefore worth considering similarities and differences between the minimal model of VT, Eq. (1), and the minimal field theory for the Potts model. Both have a cubic interaction and both involve an $n \to 0$ limit. Despite the similarities, however, there exist many differences: (i) The Potts field theory has a multiplet of $n$ real fields on $d$-dimensional space; the VT field theory has a real singlet field living on $(n + 1)d$-dimensional space. (ii) The Potts field theory emerges from a setting involving a single ensemble, whereas the VT field theory describes a physical problem in which two distinct ensembles (thermal and disorder) play essential roles. As such, the vulcanization field theory is a more natural and direct approach, in the sense that it is capable of providing a unified theory of both the transition and the structure of the solid state. (iii) The symmetry structures are different: most strikingly, the nature of the spontaneous symmetry breaking is different. The percolation transition (in its Potts representation) involves the spontaneous breaking of the $(n \to 0)$ limit of a discrete $(n + 1)$-fold permutation symmetry. By contrast, the VT involves the spontaneous breaking of the $(n \to 0)$ limit of the continuous symmetry of relative translations and rotations of the $n + 1$ replicas; the permutation symmetry remains intact in the amorphous solid state, as does the symmetry of common translations and rotations of replicated space. The fact that the critical exponents near the upper critical dimension are the same for both theories (at least to order $\varepsilon$) despite these apparent distinctions can be reconciled by delineating between three logically distinct physical properties pertaining to amorphous solidification transition: (i) macroscopic network formation; (ii) changes in the nature of thermal motion—i.e. random localization; and (iii) the acquisition of rigidity. Within mean-field theory (and hence above six spatial dimensions), these three properties go hand-in-hand, emerging simultaneously at the VT. At and below six dimensions they appear to continue to go hand-in-hand (although we have not yet investigated the issue of rigidity beyond mean-field theory) until one reaches two dimensions, where (as we shall discuss shortly) we believe this broad picture changes. Thus, in higher dimensions it appears that when both ensembles are incorporated the disorder fluctuations play a more important role than the thermal fluctuations.

This brings up the interesting issue of the nature of the VT at the neighborhood of two dimensions—the lower critical dimension of the VT. (The ideas reported in this paragraph result from an ongoing collaboration with H. E. Castillo.) Indeed, there is a conventional percolation transition in two dimensions, whereas the thermal fluctuations are expected to destroy the random localization. It is tempting to speculate [13] that in two dimensions an anomalous type of VT happens simultaneously with percolation transition: As the constraint-density is tuned from below to above its critical value, the order parameter would remain zero, whereas its correlations would change from decaying exponentially to decaying algebraically: one would have a quasi-amorphous solid state—the random analog of a two-dimensional solid [20].

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By small $|t|$ we mean $R_g \ll |t|^{-1} \ll V^{-1/3}$, with $R_g$ being the radius of gyration for the largest cluster.

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