Vulcanization and the random solid state it yields: A statistical mechanical perspective[1,2]

Paul M. Goldbart and Weiqun Peng

Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, U.S.A.

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, known as the vulcanization transition, to a random solid state. In this random solid state, particles are permanently but randomly localized, 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 established techniques of equilibrium statistical mechanics.

The aims of this paper are two-fold: First, the briefest sketch will be given of aspects of the mean-field theory of the vulcanization transition and the emergent random solid state. (These aspects have been reviewed elsewhere rather recently.) Second, a more detailed account will be given of various new results on the vulcanization transition beyond mean-field theory.

INTRODUCTION

The vulcanization transition (VT) is an equilibrium phase transition from a liquid state of matter to an amorphous solid state. This transition occurs when a sufficiently large density of permanent random constraints (e.g. chemical crosslinks)—the quenched randomness—is introduced to connect the constituents (e.g. linear, flexible macromolecules), whose spatial coordinates constitute the thermally fluctuating—the annealed—variables of the system.

A rather detailed description of the VT has emerged over the past few years within the context of a mean-field approximation [1–5]. At the heart of this description is a carefully crafted order parameter together with a minimal model

1) Work supported by the U.S. National Science Foundation via grant DMR99-75187. The contributions of several collaborators, including N. D. Goldenfeld, A. Zippelius, H. E. Castillo and K. A. Shakhnovich are gratefully acknowledged.

2) To appear in the Proceedings of the King's College (London) Conference on *Disordered and Complex Systems*, U.K., July 10-14, 2000.

(i.e. a Landau-Wilson effective free energy) that governs the equilibrium behavior of the order parameter.

In what follows, we shall begin by outlining the basic ingredients (order parameter, minimal model, etc.) of the theory of the VT. Then, as it has already been summarized several times (see, e.g., Refs. [1,5]), we shall very briefly sketch the mean-field level picture of the VT. We shall then turn to our main purpose: to discuss recent results concerning critical fluctuations near the VT [6]. The reader may notice that, in contrast with the oral version of this paper, the present version focuses more on recent developments concerning critical fluctuations and less on mean-field aspects of the theory of vulcanized matter.

MODELING THE VULCANIZATION TRANSITION

Order parameter. The appropriate order parameter for the VT, capable *inter alia* of distinguishing between the liquid and amorphous solid states, is the following function of the $n+1$ wave vectors $\{\mathbf{k}^0, \mathbf{k}^2, \cdots, \mathbf{k}^n\}$:

$$\Big[\frac{1}{N}\sum_{j=1}^{N}\int_0^1 ds\,\langle e^{i\mathbf{k}^0\cdot\mathbf{c}_j(s)}\rangle_\chi \cdots \langle e^{i\mathbf{k}^n\cdot\mathbf{c}_j(s)}\rangle_\chi\Big]. \tag{1}$$

Here, N is the total number of macromolecules in the system, $\mathbf{c}_j(s)$ (with $j = 1,\ldots,N$ and $0 \leq s \leq 1$) is the position in d-dimensional space of the monomer at fractional arc-length s along the j^{th} macromolecule, $\langle\cdots\rangle_\chi$ denotes a thermal average for a particular realization χ of the quenched disorder (i.e. the crosslinking), and $[\cdots]$ represents a suitable averaging over this quenched disorder. This form of order parameter is motivated by the order parameter employed in the context of spin glasses: the repeated thermal average detects the existence of static *random* density fluctuations (see, e.g., Ref. [1]). 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, although this symmetry does become *spontaneously* broken at the VT, albeit in a hidden way, detectable only via this refined order parameter.

Minimal model. This describes the relative free-energy cost of order-parameter configurations. It can be ascertained by (i) invoking the replica trick to incorporate the consequences of the permanent random constraints, and (ii) making the Deam and Edwards assumption [7] about the statistics of constraint realizations (i.e. that the statistics of the disorder is determined by the instantaneous correlations of the unconstrained system). Thus we are led to the need to work with the $n \to 0$ limit of systems of $n+1$ (rather than the usual n) replicas, the additional replica, labeled by $\alpha = 0$, describing the constraint distribution.

The minimal model can be determined within the spirit of Landau approach to continuous phase transitions, i.e., from from the transformation properties of the order parameter and the symmetries of the effective free energy, along with the assumptions of the analyticity of the effective free energy and the continuity of the transition [2]. (It can also be derived from a variety of semi-microscopic models.) Either scheme leads to the following minimal model, which takes the form of a cubic field theory involving the order-parameter field $\Omega(\hat{k})$ which lives on $(n+1)$-fold replicated d-dimensional space [8]:

$$f \propto \lim_{n\to 0} n^{-1} \ln[Z^n]\,, \qquad\qquad [Z^n] \propto \int \overline{\mathcal{D}}^{\dagger}\Omega \,\exp(-\mathcal{S}_n), \tag{2a}$$

$$\mathcal{S}_n = N \sum_{\hat{k}\in\mathrm{HRS}} \Big(- a\tau + \frac{b}{2}|\hat{k}|^2\Big)|\Omega(\hat{k})|^2 - Ng \sum_{\hat{k}_1,\hat{k}_2,\hat{k}_3\in\mathrm{HRS}} \Omega(\hat{k}_1)\,\Omega(\hat{k}_2)\,\Omega(\hat{k}_3)\,\delta_{\hat{k}_1+\hat{k}_2+\hat{k}_3,\hat{0}}\,, \tag{2b}$$

where the reduced control parameter τ measures the density of random constraints. Averages weighted by $\exp\left(-\mathcal{S}_n\right)$ will be denoted $\langle\cdots\rangle^{S}$. The coefficients a, b and g are phenomenological coefficients which encode the microscopic details of the system. We use the symbol $\hat{k}$ to denote the replicated wave vector $\{\mathbf{k}^0, \mathbf{k}^1, \ldots, \mathbf{k}^n\}$, and define the extended scalar product $\hat{k}\cdot\hat{c}$ by $\mathbf{k}^0\cdot\mathbf{c}^0 + \mathbf{k}^1\cdot\mathbf{c}^1 + \cdots + \mathbf{k}^n\cdot\mathbf{c}^n$. The symbol $\hat{k}\in$ HRS indicates that a summation over replicated wave vectors is restricted to those wave vectors containing *at least two nonzero component-vectors* $\mathbf{k}^{\alpha}$. (We say that such wave vectors lie in the higher-replica-sector, i.e., the HRS.) This HRS condition reflects the fact that no crystalline order (or any other kind of macroscopic inhomogeneity) appears in the vicinity of the VT; it determines the symmetry of the effective free energy and, thus, plays a crucial role.

CONCLUSIONS AT THE MEAN-FIELD LEVEL

Let us give the briefest sketch of the mean-field theory of the VT and the emergent random solid state.

(i) The order parameter encodes a great deal of statistical information about the microstructure of the random solid state, including the fraction of monomers that are localized and the statistical distribution of localization lengths (i.e. RMS position fluctuations of the localized monomers). The localized fraction grows continuously and linearly with the excess crosslink density (i.e. the amount by which the crosslink density exceeds its critical value). For all near-critical crosslink densities, the distribution of localization lengths has a *universal mean-field scaling form*, so that the distributions, when suitably plotted, should collapse on to a single master-curve determined once and for all by the theory. As discussed, e.g., in Refs. [2,5], these features are all borne out by extensive molecular dynamics computer simulations of three-dimensional, off-lattice, interacting, macromolecular systems, due to Barsky and Plischke [9].

(ii) By explicitly bounding the eigenvalues of the appropriate Hessian matrix from below, the field-theory saddle-point corresponding to the random solid state has been shown to be stable with respect to all small fluctuations (up to the expected Goldstone mode associated with the breaking of translational symmetry) [3].

(iii) By examining the increase in free energy associated with changing the shape of the system at fixed volume, the elastic properties of the random solid state have been determined. In particular, it has been shown that at the mean-field level the shear modulus becomes nonzero as the random solid state is entered, and grows continuously, with the third power of the excess crosslink density [4].

VULCANIZATION BEYOND MEAN-FIELD THEORY

We now turn to our main purpose: to outline certain recent results concerning critical fluctuations near the VT. A detailed account can be found in Ref. [6].
Ginzburg criterion. Let us begin by estimating the range of reduced crosslink densities $\delta\tau$ within which the effects of order-parameter fluctuations are relatively strong. This is accomplished by following the conventional strategy of computing the loop expansion for the 2-point vertex function to one-loop order. (In the present setting the loop expansion amounts to an expansion in the inverse monomer density.) This 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 randomly crosslinked macromolecular systems (see, e.g., Ref. [1]) and, hence, find the following form of the Ginzburg criterion: for $d < 6$, fluctuations cannot be neglected for values of τ satisfying

$$|\tau| \lesssim (L/\ell)^{-\frac{d-2}{6-d}} \left(\varphi/g^2\right)^{-\frac{2}{6-d}} . \tag{3}$$

Here, L is the arc-length of each macromolecule, ℓ the persistence length, and $\varphi \equiv (N/V)(L/\ell)\ell^d$ is the volume fraction. Equation (3) indicates that the fluctuation-dominated regime is narrower for longer macromolecules and for higher densities (provided $2 < d < 6$). Such dependence on the degree of polymerization L/ℓ is precisely that argued for by de Gennes on the basis of a percolation picture [10].
Expanding around six dimensions. Let us now mention the results that emerge from the $\varepsilon(\equiv 6-d)$ expansion calculation. The procedure is standard, but turns out to be rather non-trivial to implement, owing to the constraint that the critically fluctuating fields reside in the higher replica sector only.

As reported in detail in Ref. [6], we consider the order parameter correlator $\langle\Omega(\hat{k})\,\Omega(-\hat{k})\rangle^S$, which obeys the homogeneity relation $\langle\Omega(\hat{k})\,\Omega(-\hat{k})\rangle^S \sim |\hat{k}|^{-2+\eta}\, g(|\hat{k}|\,|\tau|^{-\nu})$ [in which $g(x) \sim x^{2-\eta}$ for $x \to +0$ and approaches a constant value for large x]. For this correlator we find that: (i) For ε negative (i.e. for $d > 6$) there is only the *Gaussian* fixed point, for which the exponents take on their classical values: $\nu^{-1} = 2$ and $\eta = 0$. (ii) For ε positive (i.e. $d < 6$), in addition to the Gaussian fixed point, a new fixed point—the *Wilson-Fisher* fixed point—emerges, and controls the critical behavior. The critical exponents are (to first order in ε) $\nu^{-1} = 2 - (5\varepsilon/21)$ and $\eta = -\varepsilon/21$.

A standard scaling argument [albeit with the subtlety associated with that fact that the theory does not contain $\Omega(\hat{0})$] leads us to the critical exponent β for the gel fraction. We find that for $d > 6$ we have $\beta = 1$, and for $d < 6$ we have $\beta = \nu(d+2-\eta)/2 = 1-\varepsilon/7$. In fact, under the (not unreasonable) assumption that in the random solid state the scale of the fluctuation correlation length is the same as that of the localization length, we can go further and propose a general scaling hypothesis for the (singular part of) $\langle\Omega(\hat{k})\rangle^S$, namely $\langle\Omega(\hat{k})\rangle^S \propto \tau^\beta\, w(\hat{k}^2\tau^{-2\nu})$, which is supported by the mean-field result [2].

Both above and below six dimensions, the critical exponents are identical (at least to first order in ε) to those in percolation theory, as computed via the Potts field theory [12,13]. In order to be sure that identical exponents arising in both theories describe physically analogous quantities, we discuss, in next section, the physical content of the VT order-parameter correlator along with its relationship with the correlation function of percolation theory.

ORDER-PARAMETER CORRELATOR AND ITS PHYSICAL SIGNIFICANCE

In order to explore the physical content of the order parameter correlator [14], we examine the construction $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}') \equiv$

$$\left[\frac{V}{N}\sum_{j,j'=1}^{N}\int_0^1 ds\, ds' \langle \delta^{(d)}(\mathbf{r}-\mathbf{c}_j(s))\,\delta^{(d)}(\mathbf{r}'-\mathbf{c}_{j'}(s'))\,\rangle \langle e^{-i\mathbf{t}\cdot(\mathbf{c}_j(s)-\mathbf{r})}\, e^{i\mathbf{t}\cdot(\mathbf{c}_{j'}(s')-\mathbf{r}')}\rangle\right] \quad (4a)$$

$$= \frac{N}{V}\sum_{\mathbf{k}} \mathrm{e}^{i(\mathbf{k}+\mathbf{t})\cdot(\mathbf{r}-\mathbf{r}')}\left[\frac{1}{N^2}\sum_{j,j'=1}^{N}\int_0^1 ds\, ds'\, \langle \mathrm{e}^{-i\mathbf{k}\cdot(\mathbf{c}_j(s)-\mathbf{c}_{j'}(s'))}\rangle_\chi \langle \mathrm{e}^{-i\mathbf{t}\cdot(\mathbf{c}_j(s)-\mathbf{c}_{j'}(s'))}\rangle_\chi\right]. \quad (4b)$$

(The two versions are simply related by Fourier representations of the delta functions.) Note that, in the second line, the expression involving the square brackets is precisely the microscopic prototype of a typical order-parameter correlator $\langle \Omega(\mathbf{0},\mathbf{k},\mathbf{t},\mathbf{0},\ldots,\mathbf{0})^*\,\Omega(\mathbf{0},\mathbf{k},\mathbf{t},\mathbf{0},\ldots,\mathbf{0})\rangle^S$. What about the meaning of $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$? The first expectation value in Eq. (4a) accounts for the likelihood that monomers (j,s) and (j',s') will respectively be found around $\mathbf{r}$ and $\mathbf{r}'$; the second describes the correlation between the respective fluctuations of monomer (j,s) about $\mathbf{r}$ and monomer (j',s') about $\mathbf{r}'$.

In the case that $\mathbf{t}=\mathbf{0}$, the quantity $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$ is simply (V/N times) the real-space density-density correlator, and is not of central relevance at the VT. The small-$\mathbf{t}$ limit of $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$ addresses the connectedness of clusters formed from crosslinked macromolecules, and can be shown [6] to be almost exactly the pair-connectedness function defined in (the on-lattice version of) percolation theory [13]. In the case of general $\mathbf{t}$, $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$ addresses the question: If a monomer near $\mathbf{r}$ is localized on the scale t^{-1} (or more strongly), how likely is a monomer near $\mathbf{r}'$ to be localized on the same scale (or more strongly)? From Eq. (4a) we see $1/t$ serves as a cutoff to the range of correlation, so that all pairs of monomers that are relatively localized at a length-scale much larger than $1/t$ do not contribute to $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$.

Given $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$, by integrating $C_{\mathbf{t}}(\mathbf{r}-\mathbf{r}')$ over space and passing to the $\mathbf{t}\to\mathbf{0}$ limit we can build a divergent susceptibility: $\lim_{\mathbf{t}\to\mathbf{0}}\int d^d r\, C_{\mathbf{t}}(\mathbf{r})$

$$\sim N \lim_{\mathbf{t}\to\mathbf{0}} \lim_{n\to 0} \left\langle \Omega(\mathbf{0},\mathbf{t},-\mathbf{t},\mathbf{0},\ldots,\mathbf{0})^{*}\,\Omega(\mathbf{0},\mathbf{t},-\mathbf{t},\mathbf{0},\ldots,\mathbf{0})\right\rangle^{\mathrm{S}} \sim (-\tau)^{-\gamma}. \tag{5}$$

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 exponents describing the VT obtained via the ε expansion turn out to be numerically equal to those characterizing physically analogous quantities in percolation theory, at least to first order in ε. This equality between exponents seems reasonable, in view of the intimate relationship between percolation theory and the *connectivity* of the system of crosslinked macromolecules. This connection has long been realized, and supports the use of percolative approaches as models of certain aspects of the VT [11,13].

An essential ingredient of the percolative approaches is the Potts model in its one-state limit. It is therefore worth considering similarities and differences between the minimal model of the VT [i.e. Eq. (2b)] and the minimal field theory for the Potts model. Both have a cubic interaction term and both involve $n\to 0$ limits. But, despite the similarities, 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 represents a setting involving a *single* ensemble, whereas the VT field theory describes a physical situation in which *two* distinct ensembles (thermal and disorder) play essential roles. As such, the vulcanization field theory is a natural approach, in the sense that it provides a unified theory of both the transition regime and the structure of the solid state. (iii) The symmetry structures are different. More importantly, 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 fact that the critical exponents near the upper critical dimension are the same for both theories (at least to order ε) despite these apparent distinctions can be understood by delineating between three logically distinct physical properties pertaining to randomly crosslinked macromolecular systems: (i) macroscopic network formation; (ii) the change in nature of thermal motion—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, we believe, this broad picture will change [6,15]. Thus, at least in higher dimensions, it appears that, when both ensembles are considered, disorder fluctuations play a more important role than do thermal fluctuations, as far as the percolative aspects of the critical phenomenon are concerned.

We conclude by simply mentioning that the concepts and strategies featuring in the present discussion of randomly crosslinked macromolecular systems can also be applied to systems such as chemical gels, in which low molecular weight objects (rather than macromolecules) are permanently covalently bonded together at random. These issues are discussed in detail in Refs. [16,17].

REFERENCES

1. For a detailed review, see P. M. Goldbart, H. E. Castillo and A. Zippelius, Adv. Phys. **45**, 393 (1996).
2. W. Peng, H. E. Castillo, P. M. Goldbart, A. Zippelius, Phys. Rev. B **57**, 839 (1998).
3. H. E. Castillo, P. M. Goldbart and A. Zippelius, Phys. Rev. B **60**, 14702 (1999).
4. H. E. Castillo and P. M. Goldbart, Phys. Rev. E **58**, R24 (1998); cond-mat/9909054, Phys. Rev. E (in press, 2000).
5. P. M. Goldbart, J. Phys. Cond. Mat. **12**, 6585 (2000).
6. W. Peng and P. M. Goldbart, Phys. Rev. E **61**, 3339 (2000).
7. R. T. Deam and S. F. Edwards, Phil. Trans. R. Soc. **280A**, 317 (1976).
8. The measure $\overline{\mathcal{D}}^{\dagger}\Omega$ indicates that we integrate $\Omega(\hat{k})$ with $\hat{k} \in$ HRS and with $\hat{k}$ restricted to a half-space via an additional condition $\hat{k} \cdot \hat{m} > 0$ for some suitable unit $(n+1)d$-vector $\hat{m}$. This is due to the fact that $Q(-\hat{k}) = Q(\hat{k})^*$.
9. S. J. Barsky and M. Plischke, Phys. Rev. E **53**, 871 (1996); S. J. Barsky, Ph.D. Thesis, Simon Fraser University, Canada (unpublished, 1996); S. J. Barsky and M. Plischke (unpublished, 1997).
10. P. G. de Gennes, J. Physique Lett. **38**, L355 (1977); see also Ref. [11].
11. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
12. A. B. Harris, T. C. Lubensky, W. K. Holcomb and C. Dasgupta, Phys. Rev. Lett. **35**, 327 (1975); and **35**, 1397 (E).
13. See, e.g., T. C. Lubensky, pp. 405-475, in *Ill-Condensed Matter* (Les Houches XXXI, 1978), edited by R. Balian, R. Maynard and G. Toulouse (North Holland: Amsterdam, 1979); and reference therein.
14. Some initial considerations of these issues were given in A. Zippelius and P. M. Goldbart, pp. 357-389, *Spin Glasses and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1998).
15. H. E. Castillo, P. M. Goldbart and W. Peng, work in progress (2000).
16. P. M. Goldbart and A. Zippelius, Europhys. Lett. **27**, 599 (1994).
17. K. A. Shakhnovich and P. M. Goldbart, Phys. Rev. B **60**, 3862 (1999).