

HETEROGENEOUS SOLIDS AND THE MICRO/MACRO CONNECTION: STRUCTURE AND ELASTICITY IN ARCHITECTURALLY COMPLEX MEDIA AS EMERGENT COLLECTIVE PHENOMENA

Paul M. Goldbart

*Department of Physics and Institute for Condensed Matter Theory,
University of Illinois at Urbana-Champaign, USA*

Launched before the atomic hypothesis took hold, elasticity theory is a spectacular achievement. A continuum-level description, it provides a powerful toolkit for determining how architecturally simple solids such as crystals respond macroscopically to stress, whilst encoding microscopic, atomic-realm details parsimoniously, via a few parameters. Solids that are architecturally complex at the atomic level—such as vulcanized rubber, gels and glasses—are commonly addressed using elasticity theory, too. However, their microscopic-level irregularity raises new issues, not only of elasticity but also of structure: How do the elastic ‘constants’ of such media fluctuate across a sample? Do such media strain non-affinely in response to stresses? Are there regional variations in the position-fluctuations of the atoms? More generally, can the structure and elasticity of architecturally complex solids be viewed as emergent collective phenomena, determinable from their underlying microscopic thermal motion and characterizable by some suitable continuum theory?

Keywords: Elasticity; Emergent phenomena; Heterogeneity; Random solids; Statistical mechanics; Vulcanized matter

INTRODUCTORY REMARKS

In this note, I sketch the essential elements of a microscopic approach to the physical properties of architecturally complex media—pioneered by Sam Edwards in the mid-1970s [1]—and the modern, continuum-based notions of structure and elasticity fathered by the Edwards approach [2, 5]. At the heart of this microscopic approach is an extension of statistical mechanics that enables the handling of architecturally complex media, with their two distinct classes of microscopic random variables: (i) the (equilibrating) atomic coordinates, and (ii) the (fixed) descriptors

Received 29 July 2009; accepted 2 October 2009.

This paper accompanies an invited lecture given at the 8th International Congress on Thermal Stresses, held at the University of Illinois at Urbana-Champaign, June 1–4, 2009.

This work was supported by NSF DMR 06-05816 and 09-06780. I gratefully acknowledge the contributions of my collaborators—especially Nigel Goldenfeld, Annette Zippelius, and the current and former members of my research group—to the issues sketched here.

Address correspondence to Paul M. Goldbart, Department of Physics and Institute for Condensed Matter Theory, University of Illinois at Urbana-Champaign, 61801, USA. E-mail: goldbart@icmt.illinois.edu

of the architectural complexity. Edwards' bold extension hints at a continuum theory for architecturally complex media whose mathematical form would, I believe, be hard to divine without Edwards' microscopic intervention. In particular, the basic fields of this continuum theory inhabit a strange world, depending on a *continuously tunable* number of copies of the three-dimensional position-vector. This curious tunability has the virtue of permitting the encoding and determination of detailed information about the emergent, spatially heterogeneous structure and elasticity of complex solids. This information embodies the physical notion that the structure and elasticity of complex solids should be characterized not by 'constant' parameters but by *statistical distributions*.

ARCHITECTURALLY SIMPLICITY VS. ARCHITECTURAL COMPLEXITY

Let us reflect on two representative types of medium. On the one hand, consider a collection of many copper atoms. Because its chemical make-up is completely specified via a small amount of information—the type and number of atoms—we term such a system *architecturally simple*. On the other hand, consider a collection of many, long, flexible macromolecules that originally are identical to one another but subsequently are cross-linked via some chemical process that bonds randomly selected atoms on randomly selected macromolecules, essentially permanently—vulcanized rubber. Let the number of these bonds be large (e.g., comparable to the number of macromolecules). In addition to providing the type and number of the macromolecules, a complete specification of the chemical make-up of the system requires the provision of the large, random information set specifying which macromolecules are connected to one another and where on them the connections reside. For this reason, we term such systems *architecturally complex*; we shall be concerned with such systems, the physical features of theirs that arise from this complexity, and the conceptual and technical challenges that their determination present.

What features do we have in mind? As we discuss further, the introduction of a sufficiently large number of cross-links changes the equilibrium state of a system of macromolecules: from a liquid, readily relaxing to accommodate static, macroscopic alterations in the shape (but not the volume) of the sample; to a solid, responding to shape-altering strains by developing persistent stresses that would, for all time, restore the shape held at the time of cross-linking. But this *random solidness* is not, at least in any elementary way, foreshadowed by the microscopic structure of the medium. In contrast with crystalline media, for which (at least in three and more dimensions of space) rigidity is accompanied by the reduction of the (large) continuous translational invariance of the particle density to the smaller (but still constructive) discrete translation invariance of the crystal lattice, the random solidity of architecturally complex media is not associated with the emergence of spatial regularity. Instead, the ordering can be thought of as taking place in the *time domain*: cross-linking 'traps in,' at least to some degree, the random configuration of the atoms present at the time of cross-linking. Thus, snapshots of atom locations taken today or tomorrow will both reveal random structure, with spatial organization only at the shortest length-scales. But in snapshots of liquids, today's and tomorrow's randomness will be essentially uncorrelated, whereas in random solids they will be correlated, all the more so if the cross-linking is strong.

Thus, the random solid is characterized via the permanence of its random spatial structure, and we shall need to ascertain how to characterize such states. Their randomness necessarily brings heterogeneity: distinct regions of the medium are distinct environments, and the behavior of the atoms inhabiting them will reflect this, e.g., via their RMS thermal (or quantal) fluctuations, which will be distributed statistically. Moreover, in the absence of any surviving symmetry (such as a crystalline lattice), how the medium responds internally to a simple, externally imposed shape-deformation is no longer stringently constrained by symmetry. Instead, some regions will be more strongly displaced and others less so, in a random way that results from a competition amongst the complex architectural elements. (This is the phenomenon of non-affine response.) The entire sample is a single unit cell containing roughly Avogadro's number of particles.

So we see that, at least in settings such as vulcanized media, architectural complexity is not a mere detail. Rather, it is the essence of the matter, fundamental both in *driving* the formation of the random solid state and in *determining* its emergent structure and properties.

WHAT DOES STATISTICAL MECHANICS SEEK TO ACCOMPLISH?

Imagine that we are in possession of a complete understanding of the atoms or molecules that constitute our system, including the collection of possible conformations that they may adopt and the interactions between the constituents. As a practical matter, such information may be beyond reach, but let us not worry about that. We would like to use the Gibbs formulation of equilibrium statistical mechanics to develop a picture of the structure and elastic response of the random solid state that sufficient cross-linking induces, along with the characteristics of the cross-linking-triggered phase transition from the liquid state to this state. This entails—*inter alia*—computing the partition function of the canonical ensemble (as we are primarily concerned with systems at a prescribed temperature T). To do this, we need a scheme for delineating the accessible configurations and computing their energies. The energy aspect is not unusual, so I shall not dwell on it; but the delineation of the accessible configuration is, if (as we shall) we choose to idealize the consequence of each of the cross-links as a *holonomic constraint* that eliminates configurations in which any cross-linked pair of atoms fail to remain essentially 'touching' one another. Thus, we need a scheme for doing statistical mechanics in the presence of many random constraints; this is what Edwards created and I now sketch.

Consider a system whose configurations \mathcal{C} can, in the absence of the constraints, range over some set Σ , and let configuration \mathcal{C} have energy $\mathcal{E}(\mathcal{C})$. Then, according to Gibbs, the thermodynamic properties are contained in the free energy \mathcal{F} , obtained via the canonical partition function \mathcal{Z} according to $e^{-\mathcal{F}/T} = \mathcal{Z} = \sum_{\mathcal{C} \in \Sigma} e^{-\mathcal{E}(\mathcal{C})/T}$ where we have chosen units in which Boltzmann's constant is unity. Now consider the impact of a large, random set of constraints, which we denote by χ . Let $\Delta(\mathcal{C}, \chi)$ be a 'filter' that is unity for configurations \mathcal{C} obeying the constraints χ and vanishes for those that do not. Now the thermodynamic properties are contained in the constraint-dependent free energy $F(\chi)$, obtained via

the constraint-dependent canonical partition function $Z(\chi)$:

$$e^{-F(\chi)/T} = Z(\chi) = \sum_{\mathcal{C} \in \Sigma} e^{-\mathcal{E}(\mathcal{C})/T} \Delta(\mathcal{C}, \chi) \quad (1)$$

Computing \mathcal{F} is hard enough; computing $F(\chi)$, in the presence of the random variables determining χ , is out of the question for situations of interest. What proves instructive, instead, is to regard the set χ as being *stochastic* (e.g., by envisaging a random process that gives rise to the constraints), to build a probability measure on χ , and then to take suitable averages, which we denoted by $[\dots]$. Viewed from the standpoint of mathematical expedience, averaging $Z(\chi)$ to produce $[Z]$ would seem wise, in view of the location of Δ in Eq. (1). But this would not produce a quantity of much physical significance because the summation over configurations \mathcal{C} would then occur on the same footing as the one over the constraints χ , and this would describe a physically inappropriate situation—one in which, rather than being persistent, the constraints would explore their possible values *simultaneously* with the configurations. This is not what is happening in the envisaged experiments. Instead, they are correctly captured via the mathematically less expedient quantity

$$[F] = -T[\ln Z] = -T \left[\ln \sum_{\mathcal{C} \in \Sigma} e^{-\mathcal{E}(\mathcal{C})/T} \Delta(\mathcal{C}, \chi) \right] \quad (2)$$

which describes the (constraint-averaged or, more generally, disorder-averaged) properties of a system in thermal equilibrium *in the presence of permanent random constraints or disorder*. The problem is the logarithm. Even in the unlikely event that the configuration sum in Eq. (2) could be computed despite the presence of the vast number of random variables characterizing χ , taking the logarithm and then disorder averaging is surely beyond hope.

The bold remedy invoked by Edwards is known as the *replica technique*, and it goes as follows. Recall the mathematical identity: $\lim_{n \rightarrow 0} (z^n - 1)/n = \ln z$. Apply it to the logarithm in Eq. (2) to obtain

$$\begin{aligned} [F] &= -T \left[\lim_{n \rightarrow 0} \frac{1}{n} (Z(\chi)^n - 1) \right] \\ &= -T \left[\lim_{n \rightarrow 0} \frac{1}{n} \left(\sum_{\mathcal{C}^1, \dots, \mathcal{C}^n \in \Sigma} e^{-\frac{1}{T} \sum_{v=1}^n \mathcal{E}(\mathcal{C}^v)} \prod_{v=1}^n \Delta(\mathcal{C}^v, \chi) - 1 \right) \right] \end{aligned} \quad (3)$$

where we have subtly represented a non-integral power as an n -fold product of summations over configurations \mathcal{C}^v of *replicas* of the original system. Next, interchange averaging over constraints χ and summing over configurations, to get

$$[F] = -T \lim_{n \rightarrow 0} \frac{1}{n} \left(\sum_{\mathcal{C}^1, \dots, \mathcal{C}^n \in \Sigma} e^{-\frac{1}{T} \sum_{v=1}^n \mathcal{E}(\mathcal{C}^v) + \ln[\prod_{v=1}^n \Delta(\mathcal{C}^v, \chi)]} - 1 \right) \quad (4)$$

where we have admittedly been cavalier about interchanging the order of taking averages and limits.

Let me spell out the upshot of these formal manipulations. At the price of having to deal with not 1 but n replicas of the original system (and to

negotiate the $n \rightarrow 0$ limit) we have arrived at a formulation that no longer involves random constraints. This is not to say there are no *consequences* of the random constraints. On the contrary, the effective scheme for computing the energies of the configurations of the replicated system now reads $\sum_{v=1}^n \mathcal{E}(\mathcal{C}^v) - T \ln[\prod_{v=1}^n \Delta(\mathcal{C}^v, \chi)]$, in which averaging over the randomness has generated a *coupling amongst the replicas*, whose form and strength that depends on the statistics of the constraints and which will play *the leading role* in the developments to be described. Although this replica strategy has been used for decades, it still has a maverick air to it: the random constraints are gone, and in their place lie replicas coupled to one another.

It is worth noting that there are other, perhaps more physical, ways of introducing replicas, which come to light once one sees the kinds of mathematical detectors (known as order parameters) that are useful in the setting of random solids [4] and other systems, such as spin glasses [8], that undergo phase transitions to ‘randomly frozen’ states. But the key point I wish to stress here is this: the configurations of the original system involve the coordinates of the many constituent particles, each in three dimensions, and they give rise, say, to physical fields describing densities that ‘live’ on three-dimensional space, just as the displacement, strain, and stress fields of conventional elasticity theory do. Now that we have arrived at a formulation involving replicas, it is not unreasonable for the fields that enter to ‘live’ on n -fold replicated three-dimensional space, which is $3n$ dimensional, in the $n \rightarrow 0$ limit. In fact, the measure on the constraints χ , mentioned after Eq. (1), which accounts for the natural correlations amongst them, has the intriguing consequence of increasing the number of replicas by unity, so that the fields to be explored have arguments that number in the neighborhood not of $3n|_{n \rightarrow 0}$ but rather of $3n|_{n \rightarrow 1}$. Hence the remarks in Introductory Remarks about a strange world inhabited by the fields describing complex media.

NECESSITY AS THE MOTHER OF INVENTION: FIELDS AS DETECTORS

We have found ourselves with a strategy for computing—in principle—the disorder average of the free energy of an architecturally complex medium, formulated in terms of an architecturally simple but replicated medium. This is still a many-body problem with interactions playing an essential, so just solving it directly (e.g., computing the partition function) is unlikely to be a viable option. So, what routes *are* open? In my opinion, the most profitable path is the development of a *statistical field theory*. This would have us eliminating the microscopic freedoms (e.g., the coordinates of the replicas of the particles) in favor of a continuous field (e.g., a collective coordinate) Ω whose arguments ($\mathbf{r}^0, \mathbf{r}^1, \dots, \mathbf{r}^n$) are these replicated coordinates—just as one might exchange the coordinates of the particles in a simple fluid for a density field. Then the computation of the disorder-averaged free energy takes the form of a *functional integral* over the collective coordinates (see, e.g., Ref. [3]),

$$\sum_{\mathcal{C}^1, \dots, \mathcal{C}^n \in \Sigma} e^{-\sum_{v=1}^n \mathcal{E}(\mathcal{C}^v)/T + \ln[\prod_{v=1}^n \Delta(\mathcal{C}^v, \chi)]} \sim \int \mathcal{D}\Omega e^{-\mathcal{H}(\Omega)/T} \quad (5)$$

for which one must construct the *effective Hamiltonian* $\mathcal{H}(\Omega)$ governing the statistics of the field Ω . Amongst the virtues of this route are that it keeps the *symmetry*

structure of the theory at center-stage, it lends itself to natural and systematically improvable schemes of analysis via well-established methods, and it empowers one to focus on the long-distance aspects of the physics, which are the aspects that one expects to be generic (and thus more lucrative). These virtues are especially valuable when analyzing continuous phase transitions, of which the liquid-to-random-solid transition, triggered by cross-linking, is an example—albeit a rather exotic one.

Although introduced formally, so as to arrive at a field-theoretic formulation, the field Ω turns out to have a physical interpretation that precisely meets our needs. It is the *detector* or *order parameter* that serves to distinguish between the candidate equilibrium states of the system: liquid, crystalline solid, and random solid. Its expectation value, weighted by $\exp(-\mathcal{H}/T)$ (and Fourier transformed on all arguments so that $\mathbf{r}^v \rightarrow \mathbf{k}^v$) can be shown to have the following meaning:

$$\langle \Omega(\mathbf{0}, \mathbf{k}^1, \dots, \mathbf{k}^n) \rangle_{\mathcal{H}} = \left[\frac{1}{P} \sum_{p=1}^P \langle e^{-i\mathbf{k}^1 \cdot \mathbf{r}_p^1} \rangle \dots \langle e^{-i\mathbf{k}^n \cdot \mathbf{r}_p^n} \rangle \right]$$

Here, p ($=1, \dots, P$) is an index running over the particles, and $\langle \dots \rangle$ denotes an equilibrium expectation value. How does the advertised state-detection come about? Try playing with this object for the situation in which all particles are delocalized, as in the liquid state; you should find $\prod_{v=1}^n \delta_{\mathbf{0}, \mathbf{k}^v}$. Now try this for the random solid state, i.e., when some fraction Q of the particles are localized at random positions (i.e., with no crystallinity) and with random localization lengths ξ distributed according to \mathcal{P} ; you should find the qualitatively distinct result

$$(1 - Q) \prod_{v=1}^n \delta_{\mathbf{0}, \mathbf{k}^v} + Q \delta_{\mathbf{0}, \sum_{v=1}^n \mathbf{k}^v} \int d\xi \mathcal{P}(\xi) e^{-\xi^2 \sum_{v=1}^n |\mathbf{k}^v|^2 / 2}$$

A crystalline state would give yet a third qualitative form. Try it. These forms can be examined from the perspective of spontaneous symmetry breakdown: the notion that cross-linking (or some other correlating agent) can induce the equilibrium states of the system less symmetric than the liquid state. If we could compute the expectation value $\langle \Omega \rangle_{\mathcal{H}}$ and, in addition, the correlators of the fluctuations of Ω about its expectation value, we would be able to extract Q and \mathcal{P} and a considerable amount of additional information about the random solid state. Can we do this?

COMPUTING THE INFORMATION CONVEYED BY THE DETECTOR

An exact computation of the expectation value of Ω and its fluctuation correlators is not feasible. These quantities can, however, be computed in certain regimes and at certain levels of approximation. Amongst the computations that can be done is a Landau-style mean-field computation (see [9]) of $\langle \Omega \rangle_{\mathcal{H}}$ and the disorder-averaged free energy $[F]$. These follow from constructing an approximation to \mathcal{H} , whose structure is stringently controlled by symmetries and length-scales, and then by treating the functional integral in Eq. (5) at the saddle-point level (i.e., maximizing the integrand and neglecting fluctuations). Here is not the setting for discussing the details; I just mention that results emerge for $\langle \Omega \rangle_{\mathcal{H}}$ and $[F]$, and hence for *structural* characteristics of the random solid state, such as Q and \mathcal{P} . Hence, one

begins to have a picture of the *structure* of the solid state of architecturally complex media, characterized by the collective localization of particles about randomly distributed centers of localization, as well as by spatial heterogeneity in the position fluctuations of the constituents about their centers, quantified by the distribution \mathcal{P} . More accurate computations of $\langle \Omega \rangle_{\mathcal{P}}$ and the fluctuation correlators, incorporating the effects of phonon-like fluctuations, will be mentioned in Goldstone Excitations and Emergent Rigidity.

Going beyond mean-field theory, renormalization-group based computations of correlators (and physical interpretations of them) have also been accomplished in the liquid state, as the constraint density is increased towards the critical value at which the random solidification transition occurs, and also precisely at the transition point [6].

The computation of $\langle \Omega \rangle_{\mathcal{P}}$, just discussed, gives us an image of the emergent solidness of architecturally complex media in terms of *structure*. But what about solidness in terms of *response*, e.g., to forces that would deform the macroscopic shape of the system [7, 10]? This is, after all, the version of solidness that is most familiar to us.

GOLDSTONE EXCITATIONS AND EMERGENT RIGIDITY

If a phase transition is accompanied by spontaneous symmetry breakdown (SSB), and if it is a *continuous* symmetry that breaks, then a general route for understanding the implications of SSB for rigidity presents itself, via a circle ideas named for their originator in the high-energy physics context: Goldstone. The essential point is that SSB implies that degenerate families of equilibrium states exist, continuously connected to one another by the ‘lost parts’ of the symmetry. As a result, a family of low-energy excitations—the Goldstone branch—must exist. They amount to states that, locally, are equilibrium states, but which particular member of the family is realized, locally, varies slowly across the system. In general, such excitations are characterized by a ‘generalized stiffness,’ which reflects their kinship with the elasticity of solids, for which the lost symmetry is that of continuous translations and the Goldstone branch of excitations are the acoustic phonons. For random solids this program can be traced through, and a generalized stiffness can be obtained. What is not *a priori* evident is that the generalized stiffness has anything to do with the elastic shear modulus, but the identification can be made [10], so that the *microscopic* approach yields *macroscopic* elasticity, both form and strength.

Unlike crystalline media, for architecturally complex media there is more to the story. One can go further and construct the *interactions* between the Goldstone excitations, but now the interpretation is subtler and more revealing [7]. A delicate argument shows that these interactions describe the *elastic heterogeneity* of the random solid state, i.e., they furnish a statistical characterization of the correlations amongst the random spatial variations of the local elastic parameters and stress that occur when these quantities are sampled over realizations of the medium. Thus, we see that the replica theory is informing us not only about *structure and its heterogeneity* but also about *elasticity, its heterogeneity, and its correlations*.

As is to be expected, Goldstone fluctuations have an especially strong impact in two spatial dimension [10]. There, they have the effect of ‘unlocalizing’ the

particles, albeit weakly, and restoring the symmetry that the mean-field analysis suggests is broken, and yet leaving the system rigid. This setting is not so extreme: it can be realized by macromolecules confined to the interface between two fluids, and has the virtue of emphasizing the logical distinction between localization and rigidity.

WHAT OTHER TOPICS MIGHT HAVE BEEN DISCUSSED

These include connections with percolation ideas which, at least intuitively, seem closely related to random solidification, even though they allow for only one class of random variables (not two: equilibrating and fixed), they admit no concept of particle motion or its qualitative changes brought about by the transition, and they cannot describe emergent rigidity, let alone its heterogeneity. Nevertheless, it has been shown that the theory of random solidification *contains* percolation theory, in the sense that—as well as yielding localization, rigidity and heterogeneity—it gives percolation theory's answers to percolation theory questions [6]. I might also have discussed recent applications to systems containing additional, internal freedoms, such as cross-linked polymer blends [11] and liquid crystalline elastomers [12]. However, for reasons of space I shall have to omit them.

REFERENCES

1. R. T. Deam and S. F. Edwards, The Theory of Rubber Elasticity, *Phil. Trans R. Soc. Lond. Ser. A*, vol. 280, pp. 317–353, 1976.
2. For early reviews, see Refs. [3, 4].
3. P. M. Goldbart, H. E. Castillo, and A. Zippelius, Randomly Crosslinked Macromolecular Systems: Vulcanisation Transition and Properties of the Amorphous Solid State, *Adv. Phys.*, vol. 45, pp. 393–468, 1996.
4. P. M. Goldbart, Random Solids and Random Solidification: What Can Be Learned by Exploring Systems Obeying Permanent Random Constraints? *J. Phys. Cond. Mat.*, vol. 12, pp. 6585–6599, 2000.
5. Owing to space limitations, I am able to cite here only a small fraction of the relevant literature. The papers that *are* cited here, especially Refs. [3, 4, 6, 7], refer to many of the papers that ought to have been cited here.
6. W. Peng and P. M. Goldbart, Renormalization-Group Approach to the Vulcanization Transition, *Phys. Rev. E*, vol. 61, pp. 3339–3357, 2000.
7. X. Mao, P. M. Goldbart, X. Xing, and A. Zippelius, Soft Random Solids and their Heterogeneous Elasticity, *Phys. Rev. E*, vol. 80, pp. 031140/1–35, 2009.
8. S. F. Edwards and P. W. Anderson, Theory of Spin Glasses, *J. Phys. F*, vol. 5, pp. 965–974, 1975.
9. W. Peng, H. E. Castillo, P. M. Goldbart, and A. Zippelius, Universality and its Origins at the Amorphous Solidification Transition, *Phys. Rev. B*, vol. 57, pp. 839–847, 1998.
10. P. M. Goldbart, S. Mukhopadhyay and A. Zippelius, Goldstone-Type Fluctuations and their Implications for the Amorphous Solid State, *Phys. Rev. B*, vol. 70, pp. 184201/1–21, 2004.
11. C. Wald, P. M. Goldbart, and A. Zippelius, Glassy Correlations and Microstructures in Randomly Crosslinked Homopolymer Blends, *J. Chem. Phys.*, vol. 124, pp. 214905/1–18, 2006.
12. X. Xing, S. Pfahl, S. Mukhopadhyay, P. M. Goldbart, and A. Zippelius, Nematic Elastomers: From a Microscopic Model to Macroscopic Elasticity Theory, *Phys. Rev. E*, vol. 77, pp. 051802/1–10, 2008.