Amorphous Solid State of Vulcanized Macromolecules: A Variational Approach

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We present a microscopic theory of the transition to and properties of the amorphous solid state of a system of vulcanized (i.e., randomly crosslinked) macromolecules. Our approach invokes a variational hypothesis for the random static density fluctuations characterizing this solid state. The variational parameter is the inverse monomer localization length, which is zero in the liquid state and increases continuously as the mean number of crosslinks exceeds a critical value. The emergent solid is a homogeneous isotropic elastic medium, whose elastic moduli we compute near the transition.

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Introduction.—Vulcanization, i.e., the introduction of a sufficient number of permanent crosslinks at random into a melt or solution of macromolecules, causes the equilibrium state of the system to undergo a thermodynamic phase transition from a liquid state to an amorphous solid state—the so-called rubbery state. In the liquid state, the macromolecules will, given sufficient time, wander throughout the container, and the system will respond viscously to an external static shear stress. By contrast, in the solid state at least a finite fraction of the macromolecules will spontaneously become localized in space, their monomers retaining forever a statistical association with a certain mean location. Because of the random nature of the crosslinks, this solid will be an amorphous one. It will respond rigidly to an external static shear stress by undergoing a static shear deformation. Typical instantaneous microscopic configurations would not distinguish this amorphous solid state from the liquid state, although the correlations found in long temporal sequences of configurations would.

The purpose of this Letter is to develop a statistical mechanical theory of the equilibrium state of a system of randomly crosslinked macromolecules. We focus, in particular, on the so-called vulcanization transition, and on the elastic properties of the resulting rubbery state. The theory addresses both solutions of macromolecules, for which collapse of the network is prevented by the presence of a good solvent, and melts.

Our investigation is based on the model of randomly crosslinked macromolecules pioneered by Edwards and co-workers [1, 2]. We adopt the spirit of Ref. [3], and construct a Ginzburg-Landau free energy in terms of the local static density fluctuations, which result from the random localization of the macromolecules and emerge at the transition to mark the onset of solidification. At the heart of the present approach is a variational hypothesis for the local static density fluctuations: we assume that in the solid state the monomers are localized at random spatial positions about which they exhibit Gaussian fluctuations characterized by a single length scale ξ that is finite, whereas in the liquid state ξ is infinite. The free energy is computed as a function of ξ, and the physical value of ξ is selected so as to make the free energy stationary.

The principal results of this Letter are as follows. First, we find a continuous transition from the liquid state, in which $\xi^{-1} = 0$, to the solid state, in which ξ^{-1} grows continuously from zero, as the mean number of crosslinks $[M]$ is increased beyond a critical value M_c. For $0 \leq ([M] - M_c)/M_c \ll 1$ we find $\xi^{-1} \sim \left([M]/M_c - 1\right)^{1/2}$. Second, we construct the free-energy cost associated with static elastic distortions of the equilibrium state, and show that the liquid is a compressible fluid, with zero shear modulus, whereas the solid is a homogeneous isotropic elastic medium, compressible *and resistant to shear.* We find that the shear modulus S behaves as $S \sim \xi^{-4} \sim \left([M]/M_c - 1\right)^2$ near the transition, whereas the bulk modulus acquires a singular contribution equal to $2/d$ times the shear modulus (in d dimensions).

Model and order parameter.—We consider a system of N identical macromolecules of arclength L and persistence length l, moving in a d-dimensional (hyper)-cubic volume V. The macromolecules are labeled by the index $i = 1, \ldots, N$, and the location in space of the monomer an arclength distance s from a certain end of chain i is given by the (d-dimensional) vector $\mathbf{c}_i(s)$ (with $0 \leq s \leq L$). In the absence of interactions the rms end-to-end distance of a single macromolecule is $\sqrt{lL}$. We consider the thermodynamic limit: $N, V \to \infty$ with N/V and $\sqrt{lL}$ fixed and finite. To ease the notation, we introduce dimensionless vectors, volumes, and arc lengths: $\mathbf{c} \to \mathbf{c}/(lL/d)^{1/2}$, $V \to V/(lL/d)^{d/2}$, and $s \to s/L$. Also, we adopt units of energy such that $k_B T = 1$.

We model the system using the Edwards Hamiltonian [4–6] which, in the units we have adopted, is

$$H = \frac{1}{2}\sum_{i=1}^{N}\int_0^1 ds \left|\frac{d\mathbf{c}_i(s)}{ds}\right|^2 + \frac{\lambda^2}{2}\sum_{i,i'=1}^{N}\int_0^1 ds \int_0^1 ds'\, \delta(\mathbf{c}_i(s) - \mathbf{c}_{i'}(s')), \qquad (1)$$

where λ^2 characterizes the effect of the (repulsive) excluded-volume interaction between monomers and $\delta(\mathbf{c})$ is the d-dimensional Dirac delta function. We suppose that permanent crosslinks are introduced between a ran-

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dom number M of randomly selected pairs of monomers, i.e., monomer s_e on chain i_e is crosslinked to monomer s'_e on chain i'_e (with $e = 1, \ldots, M$). These constraints, which enforce certain pairs of monomers to occupy common spatial locations, do not break translational symmetry, and play the role of quenched random variables. The partition function $Z(\{i_e, s_e; i'_e, s'_e\}_{e=1}^{M})$ for the system of macromolecules constrained by M random crosslinks, relative to the partition function of the uncrosslinked system, is then given by

$$Z(\{i_e, s_e; i'_e, s'_e\}_{e=1}^{M}) = \left\langle \prod_{e=1}^{M} \delta(\mathbf{c}_{i_e}(s_e) - \mathbf{c}_{i'_e}(s'_e)) \right\rangle_1^E .$$

The product of delta functions enforces the constraints imposed by the crosslinks, and the angle brackets denote normalized averaging with respect to the Edwards Hamiltonian: $\langle \cdots \rangle_1^E \equiv \int \mathcal{D}\mathbf{c}\, e^{-H} \cdots / \int \mathcal{D}\mathbf{c}\, e^{-H}$, where $\mathcal{D}\mathbf{c}$ indicates functional integration over all configurations of the macromolecules.

To model a realistic vulcanization process, in which crosslinks are introduced in the liquid state, we assume that all pairs of monomers that happen (at some particular instant) to be nearby are, with a certain probability, crosslinked. The statistics of such a crosslinking process reflect correlations in the underlying liquid state. An appropriate crosslink distribution $\mathcal{P}$ can then be constructed, following the elegant strategy of Deam and Edwards [1], by choosing $\mathcal{P}_M(\{i_e, s_e; i'_e, s'_e\}_{e=1}^{M})$ to be proportional to

$$\frac{1}{M!}\left(\frac{\mu^2 V}{2N}\right)^M \left\langle \prod_{e=1}^{M} \delta(\mathbf{c}_{i_e}(s_e) - \mathbf{c}_{i'_e}(s'_e)) \right\rangle_1^E . \qquad (2)$$

We allow the number of crosslinks to fluctuate in a manner controlled by the parameter μ^2. All that we shall need to know about μ^2 is that the mean number of crosslinks per macromolecule $[M]/N$ is a smooth, monotonically increasing function of μ^2 that can, in principle, be determined using the distribution $\mathcal{P}$.

To calculate the average of the free energy over the crosslink distribution we use the replica technique [3, 7]. Given the crosslink distribution $\mathcal{P}$, we adopt the unusual strategy of simultaneously computing the partition function and the crosslink distribution [1, 2]. The crosslink distribution can then be regarded as being generated by an additional replica, so that the disorder-averaged free energy per macromolecule is given by $f \equiv \lim_{n\to 0} f_n$, where $-Nnf_n = \{[Z^n] - 1\}/n = \{\mathcal{Z}_{n+1} - \mathcal{Z}_1\}/\mathcal{Z}_1$. Averaging over the disorder is denoted by $[\cdots]$, and

$$\mathcal{Z}_{n+1} \equiv \left\langle \exp\left(\frac{\mu^2 V}{2N} \sum_{i,i'=1}^{N} \int_0^1 ds\, ds' \prod_{\alpha=0}^{n} \delta(\mathbf{c}_i^\alpha(s) - \mathbf{c}_{i'}^\alpha(s'))\right)\right\rangle_{n+1}^E .$$

Here, n-fold replicated variables $\{\mathbf{c}^1, \ldots, \mathbf{c}^n\}$ have been introduced, along with one additional replica, $\mathbf{c}^0$, which generates the crosslink distribution. It will be convenient to collect together $(n+1)$-fold replicated d-dimensional vectors, such as $\mathbf{c}^\alpha$, by introducing the notation $\hat{\mathbf{c}} \equiv \{\mathbf{c}^0, \ldots, \mathbf{c}^n\}$. Introducing an appropriate order-parameter field Ω we can formulate the problem in terms of a Ginzburg-Landau free energy per macromolecule

$$nf_n\{\Omega\} = \frac{\mu^2}{2V^n} \overline{\sum_{\hat{\mathbf{k}}}} |\Omega_{\hat{\mathbf{k}}}|^2 - \ln\left\langle \exp\left(\frac{\mu^2}{2V^n} \overline{\sum_{\hat{\mathbf{k}}}} \int_0^1 ds\, e^{-i\hat{\mathbf{k}}\cdot\hat{\mathbf{c}}(s)}\, \Omega_{\hat{\mathbf{k}}} + \text{c.c.}\right)\right\rangle_{n+1}^W . \qquad (3)$$

The angle brackets $\langle \cdots \rangle_{n+1}^W$ denote averaging with respect to the $(n+1)$-fold replicated Wiener measure. The expectation value $\langle \Omega \rangle$, taken with the Boltzmann weight $\exp(-Nnf_n\{\Omega\})$, is related to the disorder average of the static density fluctuations:

$$\langle \Omega_{\hat{\mathbf{k}}} \rangle = \frac{1}{N} \sum_{i=1}^{N} \int_0^1 ds \{\langle \exp[i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)] \rangle\}. \qquad (4)$$

When at least two of the $(n+1)$ component vectors in $\hat{\mathbf{k}}$ are nonzero then $\langle \Omega_{\hat{\mathbf{k}}} \rangle$ is the order parameter that distinguishes between liquid and amorphous solid states, detecting the emergence of random static density fluctuations. For example, assuming replica symmetry, $\langle \Omega_{\mathbf{0},\mathbf{k},-\mathbf{k},\mathbf{0},\ldots,\mathbf{0}} \rangle = N^{-1} \sum_i \int ds\, [\langle \exp i\mathbf{k} \cdot \mathbf{c}_i(s) \rangle \langle \exp -i\mathbf{k} \cdot \mathbf{c}_i(s) \rangle]$, and is nonzero in the amorphous solid state: it is the analog of the Edwards-Anderson order parameter for spin glasses [3]. When all but one of the component vectors in $\hat{\mathbf{k}}$ is zero then $\Omega_{\hat{\mathbf{k}}}$ is the density. The excluded-volume interaction together with the crosslinking constraints give rise to a contribution to the free energy from the density. We have not included this [as the overbar in Eq. (3) indicates] because we assume that the repulsive monomer-monomer interaction strongly suppresses density fluctuations and, in particular, stabilizes the system against crystallization or collapse.

Variational hypothesis.—We analyze the free energy, Eq. (3), at the saddle-point level by invoking a variational hypothesis for the saddle-point solution $\overline{\Omega}$. To motivate the form of our variational hypothesis, let us suppose that the amorphous solid state has the following characteristic properties: typical monomers are permanently localized at random noncrystalline locations $\mathbf{a}_i(s)$, and exhibit Gaussian fluctuations around these locations parametrized by the localization length ξ, so that $\langle e^{i\mathbf{k}\cdot\mathbf{c}_i(s)} \rangle = e^{i\mathbf{k}\cdot\mathbf{a}_i(s)} e^{-\xi^2 k^2/2}$. In the liquid state ξ is infinite, whereas in the solid state ξ remains finite. In an amorphous solid with these properties $\overline{\Omega}_{\mathbf{0},\mathbf{k}^1,\ldots,\mathbf{k}^n}$ is given by $\delta_{\mathbf{0},\mathbf{k}^1+\cdots+\mathbf{k}^n} \exp(-\frac{1}{2}\xi^2 \sum_{\alpha=1}^{n} |\mathbf{k}^\alpha|^2)$, in which the Kronecker delta function arises from the absence of crystallinity, and indicates that the solid state remains macroscopically translationally invariant, despite the spontaneous breaking of symmetry that has occurred microscopically through the localization of the monomers.

Guided by the form of $\overline{\Omega}$ obtained above, it is natural to hypothesize the variational form [8]

$$\overline{\Omega}_{\hat{\mathbf{k}}} = \delta_{\mathbf{0},\mathbf{k}^0+\cdots+\mathbf{k}^n}\, e^{-\xi^2\hat{\mathbf{k}}^2/2}, \tag{5}$$

where $\hat{\mathbf{k}}^2 \equiv \sum_{\alpha=0}^{n} |\mathbf{k}^\alpha|^2$, and to regard ξ^2 as a variational parameter with respect to which the free energy $f(\xi^2)$ should be made stationary. Close to the transition (i.e., for $\xi \gg 1$), and to within a μ-dependent constant, $f(\xi^2)$ is given by

$$\frac{2}{d}f(\xi^2) = [h(\mu^2) - \tfrac{1}{2}\mu^2]\ln\xi^2 + \tfrac{1}{6}h(\mu^2)\xi^{-2} + \mathcal{O}(\xi^{-4}),$$

where $h(x) \equiv e^{-x} - (1-x)$. The computation of terms of higher order in ξ^{-2} is straightforward but tedious.

We now demand that in the equilibrium state $f(\xi^2)$ be stationary with respect to ξ^2, so that $\partial f/\partial(\xi^2) = 0$, i.e.,

$$[h(\mu^2) - \tfrac{1}{2}\mu^2]\xi^{-2} - \tfrac{1}{12}\mu^2\xi^{-4} + \mathcal{O}(\xi^{-6}) = 0. \tag{6}$$

For $\mu^2 \le \mu_c^2 = 2h(\mu_c^2) \approx 1.59$, i.e., for a sufficiently small mean number of crosslinks per macromolecule, there is only one non-negative solution for ξ^2, viz., the liquid state $\xi^2 = \infty$. As μ^2 is increased beyond μ_c^2, so that the mean number of crosslinks is increased beyond a certain critical value, the $\xi^2 = \infty$ solution continues to exist but is no longer stable. However, a second non-negative solution appears, continuously bifurcating from the $\xi^2 = \infty$ solution and marking a continuous phase transition to the amorphous solid state. For $0 \le (\mu^2 - \mu_c^2) \ll 1$ this solution is given by $\xi^{-2} \approx 6\left(1 - \mu_c^{-2}\right)\left(\mu^2 - \mu_c^2\right)$. Thus the variational parameter ξ^{-1} is zero in the liquid state and grows continuously from zero beyond the transition to the solid state.

The formation of such a state, with monomers localized on semimicroscopic length scales, is only compatible with crosslink distributions that respect the connectivity of the macromolecules and the d-dimensional random network. Distributions that omit correlations between crosslinks [3] do not lead to the consistent picture presented in this paper, and instead lead to localization on length scales comparable with $V^{1/d}$ (see Ref. [9]).

The variational ansatz can be generalized to account for an arbitrary distribution of localization lengths. For an exponential distribution we have found that neither μ_c nor the singular μ dependence of ξ are changed. Work considering unrestricted distributions is in progress.

Elastic free energy.—The free energy, Eq. (3), is invariant under replica-dependent, spatially uniform translations of the monomers, i.e., $\mathbf{c}_i^\alpha(s) \to \mathbf{c}_i^\alpha(s) + \mathbf{u}^\alpha$ does not change f_n. Translational invariance is broken locally by the appearance of microscopic static density fluctuations, i.e., for a given monomer $\langle\exp[i\mathbf{k}\cdot\mathbf{c}_i(s)]\rangle \neq 0$, whereas macroscopic quantities remain homogeneous, e.g., $N^{-1}\sum_i \int ds\, \langle\exp[i\mathbf{k}\cdot\mathbf{c}_i(s)]\rangle = 0$. Hence, there is a manifold of degenerate solutions for the order parameter generated by these spatially uniform translations: $\overline{\Omega}_{\hat{\mathbf{k}}}\left(\{\mathbf{u}^\alpha\}\right) = e^{i\hat{\mathbf{k}}\cdot\hat{\mathbf{u}}}\,\overline{\Omega}_{\hat{\mathbf{k}}}\left(\{\mathbf{0}\}\right)$. Given the translational symmetry of the free energy, we expect low-energy excitations, i.e., phonons, for *almost uniform* displacements of the monomers.

To calculate the elastic free energy [10] within the variational approach we consider nonuniform displacements of the thermodynamic degrees of freedom: $\mathbf{c}_i^\alpha(s) \to \mathbf{c}_i^\alpha(s) + \mathbf{u}(\mathbf{c}_i^\alpha(s))$ for $\alpha = 1,\ldots,n$. (Recall that the $\alpha = 0$ replica is present to generate the crosslink distribution.) Under this transformation

$$\overline{\Omega}_{\hat{\mathbf{k}}} \to \Omega_{\hat{\mathbf{k}}} = \exp\left\{i\sum_{\alpha=1}^{n}\mathbf{k}^\alpha\cdot\mathbf{u}(\partial/\partial i\mathbf{p}^\alpha)\right\}\overline{\Omega}_{\hat{\mathbf{p}}}\Big|_{\hat{\mathbf{p}}=\hat{\mathbf{k}}}. \tag{7}$$

We have constructed the elastic free energy $\delta F\{\mathbf{u}\} \equiv N\left(f\{\Omega\} - f\{\overline{\Omega}\}\right)$ to second order in $\mathbf{u}$. For displacement fields $\mathbf{u}(\mathbf{r})$ varying on length scales much longer than the localization length ξ we find that the elastic free energy, with physical units restored, is given by

$$\delta F\{\mathbf{u}\} = \int d^d r\left[\frac{1}{2}B\left(u^{aa}\right)^2 + S\left(u^{ab} - \frac{1}{d}\delta^{ab}u^{cc}\right)^2\right]. \tag{8}$$

Here, $u^{ab} \equiv \frac{1}{2}\left(\partial^a u^b + \partial^b u^a\right)$ is the (linearized) strain field and Cartesian superscripts (over which summation is implied) range from 1 to d. To lowest nontrivial order in ξ^{-2} the bulk modulus B and shear modulus S are given by

$$B = \frac{Nk_BT}{V}\left\{1 - \frac{1}{2}\mu^2 - e^{-\mu^2} + \frac{2}{d}G(\mu^2)\left(lL/d\xi^2\right)^2\right\},$$

$$S = \frac{Nk_BT}{V}\,G(\mu^2)\left(lL/d\xi^2\right)^2,$$

$$G(x) \equiv e^{-x}\sum_{l=2}^{\infty}\frac{x^l}{l!}\,\frac{l-1}{l}\,\frac{2l^2+2l+3}{180}.$$

(Note that there is always an additional nonsingular μ-dependent contribution to the bulk modulus, associated with the uncrosslinked liquid, which is typically large.) Hence, we find that above the vulcanization transition randomly crosslinked macromolecules form a homogeneous isotropic elastic solid. The shear modulus of this solid vanishes continuously, as the transition to the liquid state is approached, in qualitative agreement with experiment [11–13]. We find $S \sim (\mu^2 - \mu_c^2)^t$, with $t = 2$, independent of d, in agreement with the naive mean-field estimate, which can be obtained using the Josephson relation [14]. A Ginzburg-type estimate [15] suggests that in $d = 3$ and for dense systems of long macromolecules (i.e., $L/l \gg 1$) mean-field results should be observed over a wide range of crosslink densities, failing only in a small interval $|\mu^2 - \mu_c^2|/\mu_c^2 \lesssim (L/l)^{-1/3}$ near the transition; this has been confirmed numerically [16].

Theoretical approaches were stimulated by the analogy between vulcanization and percolation [17]. This suggests that the conductivity and shear modulus exponents are the same, and are given by $t = 1 + (d-2)\nu$ (where ν is the correlation length exponent for percolation). This suggestion has not been confirmed by studies of random elastic networks [18] which, in general, yield larger exponents for the shear modulus. These network models are mechanical, and only consider geometrical fluctuations. In our system, by contrast, a large number of microstates is always compatible with the quenched random constraints. These fluctuations of the annealed variables must be treated by statistical mechanics: thus the rigidity of rubber is mainly an issue of entropy.

The shear modulus exponent t has been studied experimentally in the context of gelation (rather than vulcanization) with conflicting results: Ref. [11] gives $t \approx 2$, and Ref. [12] gives $t \approx 3$. The origin of this discrepancy is not currently understood.

We note that for displacement fields $\mathbf{u}(\mathbf{r})$ varying on length scales much smaller than the localization length ξ but still much larger than the radius of gyration $\sqrt{lL}$ we recover the elastic properties of the liquid state. It would be interesting to study this crossover in detail.

The structure of the elastic free energy, Eq. (8), is quite general, and does not depend on the specific details of our variational hypothesis for the order parameter, although the values of the elastic moduli do. A full solution to the problem of computing the elastic response would require: (i) the solution of the saddle-point equation; (ii) the construction of the effective elastic free energy; and (iii) the analysis of nonlinear interactions between fluctuations. As we have been unable to solve the saddle-point equation we have, instead of step (i), adopted our variational approach. We cannot exclude the possibility that our hypothesis leads to an overestimate of the critical mean number of crosslinks. Furthermore, the possibility of replica symmetry breaking should also be considered. We have accomplished step (ii) to the Gaussian level, within our variational framework; constructing the nonlinear terms is straightforward, and would provide the starting point for studying how the nonlinear interactions affect the singular behavior of the shear modulus.

Conclusions.—Our intention has been to develop a consistent picture of the transition to and nature of the rubbery (i.e., amorphous solid) state. With this aim in mind, we have examined the statistical mechanics of a system of randomly crosslinked macromolecules using a variational mean-field theory. We have found that the system undergoes a continuous transition from a liquid state to an equilibrium amorphous solid state. In this state, monomers are localized around randomly located mean positions: the solid remains translationally invariant at the macroscopic level, and there is no crystalline order. The monomers exhibit Gaussian fluctuations around their mean positions with a characteristic localization length that diverges at the transition to the liquid state. We have demonstrated that this solid is, macroscopically, a homogeneous isotropic elastic solid, and have calculated its linear elastic moduli, showing, in particular, that the shear modulus vanishes continuously at the transition.

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