

Elasticity near the vulcanization transition

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Signatures of the vulcanization transition—amorphous solidification induced by the random cross-linking of macromolecules—include the random localization of a fraction of the particles and the emergence of a nonzero static shear modulus. A semimicroscopic statistical-mechanical theory is presented of the latter signature, which accounts for both thermal fluctuations and quenched disorder. It is found (i) that the shear modulus grows continuously from zero at the transition, and does so with the classical exponent, i.e., with the third power of the excess cross-link density and, quite surprisingly, (ii) that near the transition the external stresses do not spoil the spherical symmetry of the localization clouds of the particles. [S1063-651X(98)0907-5]

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INTRODUCTION

When a sufficient density of randomly located cross-links is imposed on a system of flexible linear macromolecules, an equilibrium phase transition (known as the vulcanization transition) occurs. At this transition a liquid state is replaced by an amorphous solid state. This transition has two main equilibrium signatures: (i) a nonzero fraction of the monomers become localized around random mean positions and with random localization lengths (structure); and (ii) the system, as a whole, acquires a nonzero static shear modulus (response). The former signature has been discussed previously; the purpose of the present Rapid Communication is to address the latter signature. Specifically, our aim is to develop a statistical-mechanical theory of the elastic properties of the amorphous solid state in the vicinity of the vulcanization transition. This theory incorporates both annealed (i.e., thermally equilibrating) and quenched random (i.e., cross-link specifying) variables. Its primary conclusions are (a) that the amorphous solid [in the sense of signature (i)] state emerging at the vulcanization transition is indeed a solid [in the sense of signature (ii)]; (b) that the shear modulus vanishes continuously as the transition is approached, and does so with the third power of the excess cross-link density (i.e., the amount by which the cross-link density exceeds its critical value); and (c) that the shearing of the container associated with elastic deformations does *not* lead to a shearing of the probability clouds associated with the thermal fluctuations of localized particles about their mean positions.

The elastic properties of vulcanized matter and related chemically bonded systems, especially those near the amorphous solidification transition, have received considerable attention to date. Notable approaches include the classical ones [1], in which it was argued that near the transition the elastic entropy in the solid phase (and consequently the static shear modulus E) grows as the third power of the excess cross-link density ϵ , i.e., $E \sim \epsilon^t$ with $t=3$. Subsequently, it was proposed that the amorphous solidification transition of polymer systems be identified with a percolation process [2,3]. Thus, the exponent t was identified with the critical exponent μ for percolation of conductivity (with $\mu \approx 2.0$ in three spatial dimensions). Subsequently it was observed that the elasticity percolation exponent for a random network is substantially

higher than μ when the forces are central [4].

More microscopically oriented approaches to the elastic properties of vulcanized matter have also been made, in which macromolecular degrees of freedom feature explicitly. Among these are the “phantom network” [5] and “affine network” [6] approaches, as well as the comprehensive discussion of rubber elasticity by Deam and Edwards [7] and others [8]. These approaches focus on the well-cross-linked regime rather than the lightly cross-linked regime near the vulcanization transition [9].

Experimentally, the exponent t has been addressed for several systems (although mostly for gelation rather than vulcanization); the results vary from $t \approx 2$ [10] to $t \approx 3$ [11]. This wide discrepancy is not understood.

Stimulating though they certainly are, it must be recognized that neither the classical [12,13,1] nor the percolation [2,3] approaches to the physics of vulcanized matter explicitly include both crucial ingredients: *thermal fluctuations* and *quenched disorder*. In recent years, an approach to the vulcanization transition has been developed [14–17] that takes into account both of these ingredients in the context of a semimicroscopic model for flexible, randomly cross-linked macromolecules. This approach is very much inspired by the work of Edwards and collaborators [7,18], as well as by concepts from the field of spin glasses. Emerging from this more recent approach has been a detailed picture of the *structure* of the amorphous solid state near to the vulcanization transition, including, in particular, an explicit form for the distribution of localization lengths. What has not yet been elucidated using this approach is the second signature of the vulcanization transition, namely the emergence of static *response* to shear deformations. This issue is the focus of the present Rapid Communication.

MODEL

At the heart of the theory of the *structure* of the amorphous solid state [17] is the analysis, employing the techniques of replica statistical mechanics, of a semimicroscopic model of N macromolecules subject to random cross-linking constraints. This analysis leads to an order parameter $\Omega_{\hat{k}}$ appropriate for diagnosing the amorphous solid state, as well as a Landau free energy $\mathcal{F}_n(\{\Omega_{\hat{k}}\})$ in terms of this order

parameter. A detailed review of this theory has been given in Ref. [17]. The order parameter is defined via

$$\Omega_{\hat{\mathbf{k}}} \equiv \left\langle \frac{1}{N} \sum_{i=1}^N \int_0^1 ds \exp[i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)] \right\rangle_{n+1}^P. \quad (1)$$

Here, hatted vectors denote replicated collections of vectors, viz., $\hat{\mathbf{v}} \equiv \{\mathbf{v}^0, \mathbf{v}^1, \dots, \mathbf{v}^n\}$; their scalar product is $\hat{\mathbf{v}} \cdot \hat{\mathbf{w}} \equiv \sum_{\alpha=0}^n \mathbf{v}^\alpha \cdot \mathbf{w}^\alpha$, and the trajectories $\{\hat{\mathbf{c}}(s)\}_{i=1}^N$ are the semi-microscopic configurations of the replicated macromolecules (where $0 \leq s \leq 1$ is the arclength in units of the total arclength). $\langle \rangle_{n+1}^P$ denotes an average for an effective pure (i.e., disorder-free) system of $n+1$ coupled replicas of the original system. To model the disorder we make the Deam-Edwards assumption [7] that the statistics of the cross-links is determined by the instantaneous correlations of the uncross-linked system. This leads to the need to work with the $n \rightarrow 0$ limit of systems of $n+1$ (as opposed to n) replicas. The additional replica, labeled by $\alpha=0$, represents the degrees of freedom of the original system before cross-linking, or, equivalently, describes the cross-link distribution. Consequently, any external strain applied to the system *after* the permanent constraints have been created will affect replicas $\alpha=1, \dots, n$, but not replica $\alpha=0$ [7]. Thus, the order parameter measures the correlations between the positions of individual particles before and after the deformation is applied.

In the saddle-point approximation [19], the disorder-averaged free energy f (per particle) in a d -dimensional system is obtained by minimizing the replicated free-energy functional $\mathcal{F}_n(\{\Omega_{\hat{\mathbf{k}}}\})$ [20]:

$$f = d \lim_{n \rightarrow 0} \min_{\{\Omega_{\hat{\mathbf{k}}}\}} \mathcal{F}_n(\{\Omega_{\hat{\mathbf{k}}}\}). \quad (2)$$

As discussed in detail in Ref. [17], the minimization in Eq. (2) yields the liquid–amorphous–solid phase transition at a certain critical value of the cross-link density. We parametrize the excess cross-link density beyond this critical value by the control parameter ϵ . As the transition is continuous (i.e., near the critical point the gel fraction is small and the typical localization length of localized particles is large), $\mathcal{F}_n(\{\Omega_{\hat{\mathbf{k}}}\})$ can be expanded in powers of the order parameter and gradients, with only low orders needing to be retained [21]:

$$\begin{aligned} nd\mathcal{F}_n(\{\Omega_{\hat{\mathbf{k}}}\}) = & \sum_{\hat{\mathbf{k}}} (-\epsilon + \frac{1}{2}|\hat{\mathbf{k}}|^2) |\Omega_{\hat{\mathbf{k}}}|^2 \\ & - \sum_{\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2, \hat{\mathbf{k}}_3} \Omega_{\hat{\mathbf{k}}_1} \Omega_{\hat{\mathbf{k}}_2} \Omega_{\hat{\mathbf{k}}_3} \delta_{\hat{\mathbf{k}}_1 + \hat{\mathbf{k}}_2 + \hat{\mathbf{k}}_3, \hat{\mathbf{0}}}. \end{aligned} \quad (3)$$

The symbol \sum denotes a sum over replicated wave vectors that contain at least two nonzero component vectors \mathbf{k}^α [22]. The saddle-point equation for the free-energy functional near the transition is exactly solved by the following hypothesis [16,17]:

$$\Omega_{\hat{\mathbf{k}}} = (1-q) \delta_{\hat{\mathbf{k}}, \hat{\mathbf{0}}} + q \delta_{\sum_{\alpha=0}^n \mathbf{k}^\alpha, \hat{\mathbf{0}}} W^u(\hat{\mathbf{k}}), \quad (4a)$$

$$W^u(\hat{\mathbf{k}}) \equiv \int_0^\infty d\tau p(\tau) e^{-\hat{\mathbf{k}}^2/2\tau}. \quad (4b)$$

The physical motivation for this hypothesis comes from a picture in which a fraction q of the monomers are localized around random mean positions $\mathbf{b}_i(s)$ about which they execute harmonic thermal fluctuations over random localization lengths $\xi_i(s)$. Furthermore, the mean positions are assumed to be homogeneously distributed over the sample, and the localization lengths are characterized by the statistical distribution $2\xi^{-3}p(\xi^{-2})$. Thus, delocalized and localized particles are, respectively, represented by the first and second terms on the right-hand side of Eq. (4a). The δ factor in the second term comes from the homogeneity of the distribution of mean positions. The function $W^u(\hat{\mathbf{k}})$, which we refer to as the *continuous part* of the order parameter, encodes all the information about thermal fluctuations (the superscript u standing for ‘‘unstrained’’). The hypothesis [(4a) and (4b)] satisfies the saddle-point equations provided that [16,17]

$$0 = -2q\epsilon + 3q^2, \quad (5a)$$

$$\frac{\theta^2}{2} \frac{d\pi}{d\theta} = (1-\theta)\pi(\theta) - \int_0^\theta d\theta' \pi(\theta') \pi(\theta - \theta'), \quad (5b)$$

where $\pi(\theta)$ is an ϵ -independent scaling function such that $p(\xi^{-2}) = (2/\epsilon)\pi(2/\epsilon\xi^2)$, and satisfies the boundary condition $\int_0^\infty d\theta \pi(\theta) = 1$. Equation (5a) determines the localized fraction q ; for $\epsilon \leq 0$ we obtain $q=0$ (i.e., the liquid phase, which has a vanishing static shear modulus); for $\epsilon > 0$ we obtain $q = 2\epsilon/3$, corresponding to the amorphous solid state, which is the state on which we shall focus from now on.

RESPONSE TO SHEAR STRAIN

We now set about determining the free-energy cost associated with making static shear deformations of the system. To do this, we consider the effect of changing the shape of the container (on which we have imposed periodic boundary conditions). We characterize the deformation by the $(d \times d)$ matrix \mathbf{S} , which describes the change in position of any point \mathbf{b} at the boundary of the system as follows: $\mathbf{b} \rightarrow \mathbf{S} \cdot \mathbf{b}$. For example, for $d=3$ and for a deformation in which the x , y , and z Cartesian components of the position vector are, respectively, elongated by the factors λ_x , λ_y , and λ_z , the matrix \mathbf{S} has the form $\text{diag}(\lambda_x, \lambda_y, \lambda_z)$. As we are concerned with the free-energy cost of pure shear strains, we shall assume that the deformation leaves the volume V of the system unchanged, i.e., $\text{Det } \mathbf{S} = 1$. For considering infinitesimal strains, it is convenient to define the (symmetric) strain tensor $\mathbf{J} \equiv \frac{1}{2}(\mathbf{S} + \mathbf{S}^T) - \mathbf{I}$. Here \mathbf{S}^T is the transpose of \mathbf{S} and \mathbf{I} is the identity matrix. As $\text{Det } \mathbf{S} = 1$, we have $\text{Tr } \mathbf{J} = 0$, to first order in the deformation.

Before taking the thermodynamic limit, the system is finite in extent, so that the Fourier representation of any function of position consists of a superposition of plane waves with discrete wave vectors. In particular, the order parameter

(which is a function in replicated Fourier space) is only defined for a discrete set of points. Now, under strain the boundaries in position space are displaced and, as a consequence, the discretization in replicated Fourier space changes. As mentioned above, any external strain that is applied to the system after the permanent constraints have been created will affect replicas $\alpha=1, \dots, n$, but not replica $\alpha=0$ [7]. Therefore, the change in the discretization of the wave vectors occurs only for $\alpha=1, \dots, n$, but not for $\alpha=0$. For convenience, we shall use the symbols R^u and R^s to denote the sets of allowed replicated wave vectors corresponding, respectively, to the unstrained and strained systems.

Conceptually, there are two sources for the change in free energy [Eq. (2)] under deformation: the change in the expression for the free-energy functional itself, and the consequent change in the value of the order parameter that solves the saddle-point equation. The free-energy functional for the strained system $\mathcal{F}_n^s(\{\Omega_{\hat{\mathbf{k}}}\})$ is obtained by repeating, step-by-step, the construction of the free-energy functional for the unstrained system $\mathcal{F}_n(\{\Omega_{\hat{\mathbf{k}}}\})$. The result [23] is that the coefficient in front of each term is unaltered, the only change being the replacement of each sum $\sum_{\hat{\mathbf{k}}}$ over the old set of discrete replicated wave vectors (i.e., $\hat{\mathbf{k}} \in R^u$) by a sum over the new set of discrete replicated wave vectors $\sum_{\hat{\mathbf{k}} \in R^s}$. As a result, the saddle-point equation for the strained system becomes

$$0 = 2(-\epsilon + \frac{1}{2}|\hat{\mathbf{k}}|^2)\Omega_{\hat{\mathbf{k}}} - 3 \sum_{\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2 \in R^s} \Omega_{\hat{\mathbf{k}}_1} \Omega_{\hat{\mathbf{k}}_2} \delta_{\hat{\mathbf{k}}_1 + \hat{\mathbf{k}}_2, \hat{\mathbf{k}}}. \quad (6)$$

We now obtain the order parameter for the strained system by making a physically motivated hypothesis similar to the one made for the unstrained system. First, for each localized monomer in the unstrained system we envision that its old mean position $\mathbf{b}_i(s)$ is displaced to a new mean position $\mathbf{S} \cdot \mathbf{b}_i(s) + \mathbf{r}_i(s)$, where $\mathbf{S} \cdot \mathbf{b}_i(s)$ is the affine displacement of the old position [6] and $\mathbf{r}_i(s)$ is a random additional displacement, which we take to be uncorrelated with $\mathbf{b}_i(s)$. With the assumption that (as in the unstrained system) there is no correlation between the extent (including shape) of the thermal fluctuations of a monomer about its mean position and the mean position itself, we arrive at the hypothesis

$$\Omega_{\hat{\mathbf{k}}} = (1-q) \delta_{\hat{\mathbf{k}}, \hat{\mathbf{0}}} + q \delta_{\hat{\mathbf{k}}, \hat{\mathbf{0}}} + \mathbf{S}^T \cdot \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{0} W^s(\hat{\mathbf{k}}), \quad (7)$$

where $W^s(\hat{\mathbf{k}})$ is the continuous part of the order parameter in the strained system. Now, to construct a form for $W^s(\hat{\mathbf{k}})$ we consider a conjecture for the form of $\langle e^{i\mathbf{k} \cdot \mathbf{c}_i(s)} \rangle_\chi^s$ [i.e., the thermal expectation values of the Fourier-transformed individual particle densities in the strained (s) system for a specific disorder realization χ]:

$$\exp[i\mathbf{k} \cdot \{\mathbf{S} \cdot \mathbf{b}_i(s) + \mathbf{r}_i(s)\}] \exp[-\xi_i^2(s) \mathbf{k} \cdot \{\mathbf{I} + \eta_i(s) \mathbf{J}\} \cdot \mathbf{k} / 2]. \quad (8)$$

We expect the Gaussian probability cloud to be isotropic, except for a correction due to the distortion. For infinitesimal distortions, this correction should be proportional to \mathbf{J} and have a random magnitude $\eta_i(s)$. For example, if $\eta_i(s) = 2$, then the probability cloud would have been affinely dis-

torted. On the other hand, if $\eta_i(s) = 0$, then the probability cloud would remain spherical. Assuming further that the random displacement $\mathbf{r}_i(s)$ also has a probability distribution shaped by a combination of \mathbf{I} and \mathbf{J} , and expanding to lowest nontrivial order in the deformation [24], we obtain the hypothesis

$$W^s(\hat{\mathbf{k}}) = q \int_0^\infty d\theta e^{-\hat{\mathbf{k}}^2 / \epsilon \theta} \left[\pi(\theta) - \frac{\varpi(\theta)}{\epsilon} \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{J} \cdot \mathbf{k}^\alpha \right]. \quad (9)$$

Here, $\varpi(\theta)$ is a second scaling function, which describes the change in the continuous part of the order parameter due to the deformation.

An alternative motivation for the form of $W^s(\hat{\mathbf{k}})$ is as follows. Let us assume that for small strains $W^s(\hat{\mathbf{k}})$ is unchanged under simultaneous rotations of \mathbf{S} and $\hat{\mathbf{k}}$. As it is only a function of $\hat{\mathbf{k}}^2$ this property certainly holds for $W^u(\hat{\mathbf{k}})$, and it therefore also holds for the difference between $W^s(\hat{\mathbf{k}})$ and $W^u(\hat{\mathbf{k}})$. To first order in \mathbf{J} this difference can only contain the following terms: (i) a linear function of $\sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{J} \cdot \mathbf{k}^\alpha$ and (ii) a product of an invariant linear function of \mathbf{J} with an invariant function of $\hat{\mathbf{k}}$. The only quantity linear in \mathbf{J} and invariant under rotations is $\text{Tr} \mathbf{J}$, which is zero for infinitesimal shear strains, as mentioned above. Thus we recover Eq. (9).

By inserting the hypothesis given by Eqs. (7) and (9) into the saddle-point condition (6), we recover Eqs. (5a) and (5b) for q and $\pi(\theta)$, together with the condition

$$\frac{\theta^2}{2} \frac{d\varpi}{d\theta} = (1-\theta)\varpi(\theta) - \frac{2}{\theta^2} \int_0^\theta d\theta' \theta'^2 \varpi(\theta') \pi(\theta - \theta'). \quad (10)$$

The boundary condition $\lim_{\theta \rightarrow \infty} \theta^2 \varpi(\theta) = 0$ stems from the fact that, by Eq. (1), $\lim_{|\hat{\mathbf{k}}| \rightarrow \infty} \Omega_{\hat{\mathbf{k}}} = 0$. The only solution of Eq. (10) that satisfies the boundary condition is the null function $\varpi(\theta) \equiv 0$ [25]. This result implies the first (and, *a priori*, the most surprising) result of this Rapid Communication: the continuous part of the order parameter *does not change* to first order in the strain, i.e., $W^s(\hat{\mathbf{k}}) = W^u(\hat{\mathbf{k}})$. This conclusion is consistent with the phantom network picture [5,9]. It also suggests that $W^s(\hat{\mathbf{k}}) = W^u(\hat{\mathbf{k}})$ for finite (and not merely infinitesimal) deformations, and indeed the resulting order-parameter hypothesis turns out to satisfy the saddle-point equation for arbitrarily strained systems.

We now have all the ingredients necessary to compute the change in the free energy, to leading order in ϵ , due to the deformation of the system:

$$\Delta f = d \lim_{n \rightarrow 0} [\mathcal{F}_n^s(\{\Omega_{\hat{\mathbf{k}}}^s\}) - \mathcal{F}_n^u(\{\Omega_{\hat{\mathbf{k}}}^u\})] = \frac{2\epsilon^3}{27} \text{Tr}(\mathbf{S} \cdot \mathbf{S}^T - \mathbf{I}),$$

where $\Omega_{\hat{\mathbf{k}}}^s$ and $\Omega_{\hat{\mathbf{k}}}^u$ are, respectively, the saddle-point values of the order parameter for the strained and unstrained systems. Thus we can extract the value of the static shear modulus for the amorphous solid state near the solidification transition (with physical units restored): $E = k_B T N C \epsilon^3$, where

k_B is Boltzmann's constant, T is the temperature, and C is a model-dependent positive constant. Hence, we see that the static shear modulus near the vulcanization transition is characterized by the exponent $t=3$, in agreement with the classical result [1,2]. A simple scaling argument, viz., that the modulus should scale as two powers of the order parameter (q^2) and two powers of the gradient (ξ_{typ}^{-2}), leads to the same value for t .

CONCLUDING REMARKS

We have presented a microscopic derivation of the static elastic response of a system of randomly cross-linked macromolecules near the amorphous solidification transition. In the picture that emerges, it is seen that (i) the amorphous solid state, which was previously shown to be characterized structurally by the localization of a nonzero fraction of particles, is also characterized by having a nonzero static shear modulus; (ii) the static shear modulus scales as the third

power of the excess cross-link density (beyond its value at the transition) [26]; and (iii) the form of localization that is exhibited by the particles is left unchanged by the strain. It is, however, not implausible that strain-induced changes would emerge from a more detailed analysis of the effects of the excluded-volume interaction, at least at higher cross-link densities. Being dependent only on the form of the free-energy functional [27,21], and not any specific semimicroscopic model, the approach to elasticity described here should be generally applicable not only to systems of randomly cross-linked flexible macromolecules, but also to other equilibrium amorphous solid forming systems.

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- [1] J. Scanlan, *J. Polym. Sci.* **43**, 501 (1960); L. C. Case, *ibid.* **45**, 397 (1960); M. Gordon and S. B. Ross-Murphy, *Pure Appl. Chem.* **43**, 1 (1975).
- [2] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- [3] P. G. de Gennes, *J. Phys. (France)* **37**, L1 (1976); **36**, 1049 (1975); D. Stauffer, *J. Chem. Soc., Faraday Trans. II* **72**, 1354 (1976).
- [4] S. Feng and P. N. Sen, *Phys. Rev. Lett.* **52**, 216 (1984).
- [5] H. M. James and E. Guth, *J. Chem. Phys.* **15**, 669 (1947).
- [6] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1971).
- [7] R. T. Deam and S. F. Edwards, *Philos. Trans. R. Soc. London, Ser. A* **280**, 317 (1976).
- [8] S. V. Panyukov, *Zh. Eksp. Teor. Fiz.* **103**, 1644 (1993) [*Sov. Phys. JETP* **76**, 808 (1993)].
- [9] See, e.g., J. E. Mark and B. Erman, *Rubberlike Elasticity, a Molecular Primer* (John Wiley, New York, 1988).
- [10] M. Adam *et al.*, *Pure Appl. Chem.* **53**, 1489 (1981); C. Allain and L. Salomé, *Polym. Commun.* **28**, 109 (1987); *Macromolecules* **20**, 2957 (1987); M. A. V. Axelos and M. Kolb, *Phys. Rev. Lett.* **64**, 1457 (1990).
- [11] M. Adam *et al.*, *Pure Appl. Chem.* **53**, 1489 (1981); M. Adam, M. Delsanti, and D. Durand, *Macromolecules* **18**, 2285 (1985); B. Gauthier-Manuel *et al.*, *J. Phys. (France)* **47**, 869 (1987); T. Woignier *et al.*, *ibid.* **49**, 289 (1988).
- [12] P. J. Flory, *J. Am. Chem. Soc.* **63**, 3083 (1941); **63**, 3091 (1941); **63**, 3096 (1941).
- [13] W. H. Stockmayer, *J. Chem. Phys.* **11**, 45 (1943).
- [14] P. M. Goldbart and N. Goldenfeld, *Phys. Rev. Lett.* **58**, 2676 (1987); *Macromolecules* **22**, 948 (1989); *Phys. Rev. A* **39**, 1402 (1989); **39**, 1412 (1989).
- [15] P. M. Goldbart and A. Zippelius, *Phys. Rev. Lett.* **71**, 2256 (1993).
- [16] H. E. Castillo, P. M. Goldbart, and A. Zippelius, *Europhys. Lett.* **28**, 519 (1994).
- [17] P. M. Goldbart, H. E. Castillo, and A. Zippelius, *Adv. Phys.* **45**, 393 (1996).
- [18] R. C. Ball and S. F. Edwards, *Macromolecules* **13**, 748 (1980); R. C. Ball, Ph.D. thesis, Cambridge University, 1980 (unpublished).
- [19] In the vulcanization of polymer melts, the width of the critical region, in which mean-field theory fails, vanishes in the limit of long macromolecules for $d \geq 3$ [2].
- [20] The complete expression for the free-energy functional for any cross-link density is given in Eq. (5.12b) of Ref. [17].
- [21] This form for $\mathcal{F}_n(\{\Omega_{\mathbf{k}}\})$ can be obtained either from a semimicroscopic model, as envisioned here, or via an argument involving symmetries and the continuity of the transition in the context of a Landau theory [27].
- [22] This condition reflects the fact that no crystalline order (or any other kind of macroscopic inhomogeneity) appears in the vicinity of the amorphous solidification transition. Consequently, $\Omega_{\mathbf{k}}=0$ for \mathbf{k} of the form $\{0, \dots, 0, \mathbf{q}, 0, \dots, 0\}$.
- [23] The construction of the free energy for the undeformed case is presented in detail in Ref. [17], Secs. 4 and 5. The only step affected by the displacement of the boundaries is the expansion of the constraints in real space as a sum in replicated Fourier space [c.f. Eq. (5.1b) in Ref. [17]]: $\prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}^\alpha) = \sum_{\hat{\mathbf{p}} \in R^u} e^{i\hat{\mathbf{p}} \cdot \hat{\mathbf{c}}} / V^{n+1} \rightarrow \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}^\alpha) = \sum_{\hat{\mathbf{p}} \in R^s} e^{i\hat{\mathbf{p}} \cdot \hat{\mathbf{c}}} / V^{n+1}$. The only consequence of this change is the replacement of $\sum_{\hat{\mathbf{p}} \in R^u}$ by $\sum_{\hat{\mathbf{p}} \in R^s}$ in the final expression for $\mathcal{F}_n^s(\{\Omega_{\mathbf{k}}^s\})$.
- [24] The shear modulus is determined by an expansion of the free energy to quadratic order in the deformation. Thus, only terms to linear order are needed in W^s .
- [25] To see this, one introduces $g(\theta) \equiv \theta^2 e^{2/\theta} \varpi(\theta)$, studies the resulting equation for $g(\theta)$, and analyzes the limit $\theta \rightarrow \infty$.
- [26] It is unclear why the *ad hoc* strategy for computing the shear modulus used, e.g., by Huthmann *et al.* [*Phys. Rev. E* **54**, 3943 (1996)] gives a too large value for t .
- [27] W. Peng, H. E. Castillo, P. M. Goldbart, and A. Zippelius, *Phys. Rev. B* **57**, 839 (1998); e-print cond-mat/9709250 (unpublished).