Scaling of Entropic Shear Rigidity

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The scaling of shear modulus near the gelation-vulcanization transition is explored heuristically and analytically. It is found that in a dense melt the effective chains of the infinite cluster have sizes that scale *sublinearly* with their contour length. Consequently, each chain contributes $k_B T$ to the rigidity, which leads to a shear-modulus exponent $d\nu$. In contrast, in phantom elastic networks the scaling is *linear* in the contour length, yielding an exponent identical to that of the random resistor network conductivity, as predicted by de Gennes. For nondense systems, the exponent should cross over to $d\nu$ when the percolation correlation length is much larger than the density-fluctuation length.

Introduction.—Gelation and vulcanization are continuous phase transitions from liquids to random solids, caused by the introduction of chemical (i.e., permanent) cross-links; see, e.g., Ref. [1]. It is by now well established that the *geometrical* aspects of these transitions are correctly described by percolation theory [1–3]. Qualitatively speaking, both transitions—gelation-vulcanization and percolation—are controlled by the emergence and structure of an infinite cluster at the critical point.

The elastic and thermodynamic properties of gels near the critical point are not as well established. Of these, the most controversial is the scaling behavior of the static shear modulus μ, which is defined in the following way. Consider a spatially homogeneous, volume-preserving shear deformation Λ [4], with $\det\Lambda = 1$. Under such a deformation, the increase in the free energy of a gel is, to leading order, given by [5]

$$\delta F = V\mu(\mathrm{Tr}\,\mathbf{g} - d), \qquad \mathbf{g} \equiv \Lambda^T \cdot \Lambda, \qquad (1)$$

where $\mathbf{g}$ is the metric tensor and d is the spatial dimensionality. The shear modulus is expected, on general grounds, to obey a scaling law near the critical point,

$$\mu = \mu_0 \Theta(-r)|r|^f, \qquad (2)$$

where the control parameter r measures (minus the) deviation of the cross-link density from criticality (i.e., $r < 0$ in the solid phase), and Θ is the unit step function.

Values reported for the exponent f, from either experiments or computer simulations, are rather scattered, and seem to suggest four different universality classes [6]. For systems with *entropic* elasticity, which is the focus of this Letter, values of f usually fall into one of two classes. First, most numerical simulations [7] involving phantom networks, as well as many gelation experiments, suggest that f has the same value as the conductivity exponent t (≈ 1.9 in three dimensions) of random resistor networks, supporting a conjecture of de Gennes [1]. A second class of experiments, as well as some simulations, support the scaling result $f = d\nu$ (≈ 2.6 for three dimensions),

where ν is the percolation correlation-length exponent, as proposed in Ref. [8]. The argument for the latter exponent is in the spirit of the classical theory of rubber elasticity (see, e.g., Ref. [5]), in which the elastic modulus acquires a contribution of $k_B T$ per effective chain. The purpose of this Letter is to use heuristic and analytical methods to outline a resolution of the long-standing apparent contradiction between the two plausible arguments, mentioned above, as well as the inconsistency across experimental and simulational data.

Heuristic reasoning.—Let us first consider gelation in a dense system with strong interparticle repulsions, and let the system be near the critical point. Then the characteristic length scale for density fluctuations ξ_{den} is much smaller than the percolation correlation length ξ_{perc} (beyond which the infinite cluster is effectively homogeneous). Now let us invoke the "nodes-links-blobs" picture [9,10], in which the incipient infinite cluster is a network of effective chains, connected to one another at effective vertices, called nodes. For our purposes, it is adequate to treat the effective chains as quasi-one-dimensional objects having some average thickness. The end-to-end displacement of these effective chains has a certain distribution with a characteristic length scale, which is presumably identical to the percolation correlation length ξ_{perc}. In the absence of external stress, we expect these chains to exhibit a type of random walk [11], owing to thermal fluctuations. Therefore, the end-to-end displacements should scale *sublinearly* with the contour length. In the language of polymer physics, *every effective chain constitutes a single "thermal blob"*; see Fig. 1 and Ref. [12]. Under a small shear deformation, each chain is slightly stretched or compressed, thus contributing $k_B T$ to the shear modulus. As there are roughly ξ_{perc}^{-d} effective chains per unit volume, the shear modulus should scale as $k_B T \xi_{\mathrm{perc}}^{-d} \sim |r|^{d\nu}$, near the critical point. We note that the shear modulus has dimensions of energy per unit volume; hence, this scaling is also mandated by dimensional analysis, provided that ξ_{perc} is the only important length scale near the transition.
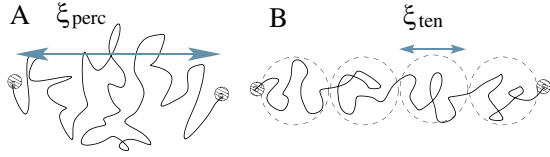
FIG. 1 (color online).   The infinite cluster is a network of effective chains: (a) In a dense melt each effective chain is one single thermal blob with typical size ξ_{perc}, and contributes $k_B T$ to the shear rigidity. (b) In a phantom network each chain is sequence of "tension blobs" (dashed circles), each of size ξ_{ten}. Each tension blob contributes $k_B T$ to the shear rigidity.

Let us now consider typical numerical simulations of phantom networks, i.e., systems without interparticle repulsions. The crucial observation, made above, that the equilibrium conformations of the effective chains are unstretched random walks (i.e., "thermal blobs") with typical size ξ_{perc} now breaks down for the following reason. In such simulations, the sol fraction (i.e., the finite clusters) are usually removed completely, as they do not interact with the gel fraction. The resulting gel is very sparse and tends to collapse so as to maximize the entropy. To prevent this, the system size is usually fixed during shear deformation. Consequently, long effective chains are *strongly stretched.* The conformation of the infinite cluster is such that the net *entropic* force at each node vanishes; i.e., the cluster is *statistically* in mechanical equilibrium. Therefore, the mean tension S carried by each chain has the same order of magnitude. As shown in Fig. 1(b), S defines a length scale, $\xi_{\text{ten}} \equiv k_B T / S$, beyond which chain conformations are dominated by tension, and are thus effectively straight. By contrast, within ξ_{ten} thermal fluctuations dominate, so that chain conformations are random walks. ξ_{ten} is, by definition, the typical size of a "tension blob" [13] for a polymer under tension S. Near the critical point, ξ_{ten} is much smaller than ξ_{perc}, which diverges as $|r|^{-\nu}$. It follows that the number of tension blobs on each chain, as well as the chain's end-to-end displacement, scales *linearly* with its contour length in a phantom network. Under a shear deformation, every tension blob contributes $k_B T$ to the overall shear rigidity [13]. Therefore, a typical chain, comprising many tension blobs, contributes a term to the total shear rigidity that is *proportional to its contour length.* This should be contrasted with the case of melt, in which every chain contributes $k_B T$, *independent of its contour length.* In a coarse-grained description, we may replace every tension blob by a *mechanical* spring of natural length zero and force constant $k_B T / \xi_{\text{ten}}^2$, without changing the elasticity. The resulting model is a randomly diluted network of *mechanical* springs of zero natural length *at zero temperature,* which can be mapped into the randomly diluted resistance network model [14]. In this mapping, the coordinates of nodes are mapped into voltages, and the shear modulus into the conductivity. Therefore the shear modulus of a randomly diluted entropic phantom network is equivalent to the conductivity of a random resistor net-

work, as de Gennes conjectured and many numerical simulations have supported.

Analytical reasoning.—We have extended the Landau theory for the elasticity of vulcanized matter [2] to the case of tunable repulsive interactions [15]. The relevant order parameter is the $(1 + n)$-fold replicated particle density distribution, less its expectation value in the liquid phase:

$$\Omega(\hat{x}) \equiv \Omega(\mathbf{x}^0, \mathbf{x}^1, \ldots, \mathbf{x}^n) \tag{3}$$

$$= \sum_{j=1}^{N} [\delta(\mathbf{x}^0 - \mathbf{c}_j)\langle\delta(\mathbf{x}^1 - \mathbf{c}_j)\rangle \cdots \langle\delta(\mathbf{x}^n - \mathbf{c}_j)\rangle] - \frac{N}{V^{1+n}}.$$

Here, $\hat{x}$ is shorthand for $(1 + n)$ d-dimensional vectors $(\mathbf{x}^0, \mathbf{x}^1, \ldots, \mathbf{x}^n)$; $\mathbf{c}_j$ labels the position of the jth particle in the system, $\langle\rangle$ denotes a thermal average over the measurement ensemble [16], and [ ] denotes the average over the cross-linking realization (i.e., the quenched disorder), as well as the thermal fluctuations of the preparation ensemble. Ω can be interpreted as giving the joint probability density function (PDF) that a particle is located at $\mathbf{x}^0$ in the preparation state and is later found at positions $\mathbf{x}^1, \ldots, \mathbf{x}^n$ in n independent measurements in the measurement state. $\Omega(\hat{x})$ encodes a great deal of information about random solid state. In particular, the particle density fluctuations of the preparation and measurement states are, respectively, given by

$$\Omega^0(\mathbf{x}) = \sum_{j=1}^{N} [\delta(\mathbf{x} - \mathbf{c}_j)] - N/V, \tag{4a}$$

$$\Omega^\alpha(\mathbf{x}) = \sum_{j=1}^{N} [\langle\delta(\mathbf{x} - \mathbf{c}_j)\rangle] - N/V, \tag{4b}$$

$$\Omega^\alpha(\mathbf{x}^\alpha) \equiv \int \prod_{\beta(\neq\alpha)=0}^{n} d\mathbf{x}_\beta \Omega(\hat{x}). \tag{4c}$$

In the liquid phase, all particles are delocalized, i.e., $\langle\delta(\mathbf{x}^\alpha - \mathbf{c}_j)\rangle \equiv V^{-1}$ for all j. This ensures that the order parameter $\Omega(\hat{x})$ vanishes identically. In the gel phase, however, a certain fraction of particles belongs to an infinite cluster and is localized. If such a particle were at position $\mathbf{x}^0$ in the preparation state, it would fluctuate around the same point in the measurement state (*modulo* a global translation and rotation that are common to the system as a whole). This is captured by a nonzero expectation value of the joint PDF (3) in the gel phase.

The Landau free energy functional comprises one part concerning localization and another describing density fluctuations. The localization part accounts for the effects of cross-links, and is given by

$$H_X = \int d\hat{x} \left\{ \frac{r}{2}\Omega^2 + \frac{K_0}{2}(\nabla^0\Omega)^2 + \frac{K}{2}\sum_{\alpha=1}^{n}(\nabla^\alpha\Omega)^2 - \frac{v}{3!}\Omega^3 \right\}, \tag{5}$$

where ∇^0 and ∇^α are, respectively, derivatives with respect to $\mathbf{x}^0$ and $\mathbf{x}^\alpha$. The parameter r controls the cross-

link density and drives the transition to the random solid state, whereas K_0 and K, respectively, measure the stretchability of polymer chains in the preparation and measurement states (the larger the K's, the softer the chains). The free energy cost for density fluctuations depends only on one-replica quantities, $\Omega^\alpha(\mathbf{x}^\alpha)$, and is

$$H_D = \frac{B_0}{2}\int d\mathbf{x}^0 \Omega^0(\mathbf{x}^0)^2 + \frac{B}{2}\sum_{\alpha=1}^{n}\int d\mathbf{x}^\alpha \Omega^\alpha(\mathbf{x}^\alpha)^2, \quad (6)$$

where the non-negative parameters B_0 and B are, respectively, the compressibilities of the system in the preparation and measurement states. A large value of B_0 would ensure that the system is cross-linked in a state with almost uniform density profile, i.e., vanishingly small fluctuations in Ω^0. On the other hand, B characterizes the repulsive interactions between particles in the measurement state. In a typical vulcanization experiment on a concentrated solution or melt, both B_0 and B are large, so that the density remains essentially uniform across the transition. It is important, however, to realize that B_0 and B are separately adjustable (as are K_0 and K), e.g., via tuning the solvent quality before and after cross-linking. For gelation, the network formation process commonly lasts for an extended period. As a result, B may differ from B_0, even by a large factor (e.g., due to correlations built up during the course of the chemical reaction), even if all external physical conditions remain unchanged.

In strong contrast, in typical numerical simulations of phantom systems, all polymers (or particles) are ascribed to lattice sites, and then cross-links are randomly introduced, connecting some neighboring particles. After removing the sol part, the system is allowed to relax at nonzero temperature, with intracluster repulsion completely ignored. This corresponds to a large positive value for B_0 but a *vanishing* value of B. As we shall soon see, it is this *qualitative* difference between B_0 and B that is responsible for conductivitylike scaling of the shear modulus in phantom networks.

To study the elastic properties, we consider deforming the system *after* cross-links have been introduced. As shown in Fig. 2, this amounts to making an affine change Λ of the boundaries for measurement replicas (1 through n), leaving the preparation replica intact. It is convenient to then make the linear coordinate transformation

$$\mathbf{c}^\alpha \to \Lambda \cdot \mathbf{c}^\alpha, \qquad \mathbf{x}^\alpha \to \Lambda \cdot \mathbf{x}^\alpha, \qquad \text{for } 1 \le \alpha \le n, \quad (7)$$

which restores the original boundary conditions for the n measurement replicas. Under this transformation, H_D of Eq. (6), is unchanged, provided we redefine B appropriately. As for H_X, Eq. (5), we find that all terms are invariant under the transformation (in the $n \to 0$ limit), except for the term with coefficient K, which becomes

$$\frac{K}{2}\sum_{\alpha=1}^{n}(\nabla^\alpha\Omega)^2 \to \frac{K}{2}\sum_{a,b=1}^{d}g_{ab}^{-1}\sum_{\alpha=1}^{n}\nabla_a^\alpha\Omega\nabla_b^\alpha\Omega, \quad (8)$$

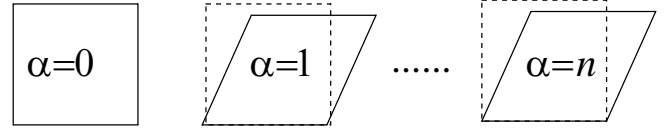where $\mathbf{g}$ is the metric tensor defined in Eq. (1).

FIG. 2.   Shear deformation (full vs dotted lines) is applied to measurement but not preparation replicas. After the coordinate transformation, the original boundaries are recovered at the cost of introducing a nontrivial metric tensor.

The effects of fluctuations, both thermal and quenched, are studied by averaging over all order-parameter configurations. Then the disordered-averaged physical free energy $[F]$ is related to the $(1+n)$-fold replicated partition function Z_{1+n} by

$$[F] = -\lim_{n\to 0}\partial_n \ln Z_{1+n} = -\lim_{n\to 0}\partial_n \ln \int D\Omega e^{-H_{1+n}},$$

where H_{1+n} ($\equiv H_D + H_X$) is the full effective [18] Hamiltonian; see Ref. [19].

A renormalization-group (RG) analysis of the full model, described by H_{1+n}, will be presented in a future publication [15]. Here, we present results for only two limiting cases: (a) $B_0 = B = +\infty$, i.e., vulcanization in an incompressible polymer melt; and (b) $B_0 = +\infty$ but $B = 0$, i.e., phantom networks. We apply a momentum-shell RG transformation, thus integrating out short length-scale fluctuations recursively, while rescaling the order-parameter field Ω and spatial coordinates such that K_0 and K remain unity. The renormalizations of r and v are independent of B and $\mathbf{g}$, i.e., the parameters describing the measurement ensemble. To one-loop order

$$\frac{dr}{dl} = r\left(2 + \frac{1}{6}v^2\right) + \frac{v^2}{2}, \qquad \frac{dv}{dl} = \frac{1}{2}\epsilon v - \frac{7}{4}v^3, \quad (9)$$

where $\epsilon \equiv 6 - d$. For $d < 6$ there is a nontrivial fixed point at $(r^*, v^{*2}) = (\epsilon/14, 2\epsilon/7)$. Correspondingly, the critical exponents (η, ν) are given by $(-\frac{1}{21}\epsilon, \frac{1}{2} + \frac{5}{84}\epsilon)$, which agree with results from the ϵ expansion for the percolation transition [20].

The flow of $\mathbf{g}$ determines the elastic properties. Expressing $\mathbf{g}$ as $g\tilde{\mathbf{g}}$, where $\tilde{\mathbf{g}}$ has unit determinant [so that $g^d = \det(\mathbf{g})$] we find that, regardless of the value of B, $\tilde{\mathbf{g}}$ does not flow. Therefore, renormalization of the metric $\mathbf{g}$ is completely controlled by its determinant. For $B = B_0 = +\infty$, we find the flow equation

$$\frac{dg}{dl} = \frac{2}{3}v^2(1 - g^3)g. \quad (10)$$

For $d < 6$, $v^2 \to v^{*2} = 2\epsilon/7 > 0$; hence g flows to unity. Qualitatively, this implies a symmetry between the preparation and measurement ensembles. It also suggests that the correlation length ξ_{perc} is the only relevant length scale, in agreement with the preceding heuristic argument that, in a dense melt, each effective chain constitutes a single thermal blob of typical size ξ_{perc}. Near the fixed point, the singular part of the free energy (i.e., the

elastic free energy) has the scaling form

$$f_s = |r|^{d\nu}\psi_1(\mathbf{g}^*) = |r|^{d\nu}\psi_1(\tilde{\mathbf{g}}). \tag{11}$$

As the shear modulus is given by an appropriate derivative of f_s with respect to $\mathbf{g}$ [cf. Eq. (1)], we immediately see that it scales as $|r|^{d\nu}$.

For the second case, viz., $(B_0, B) = (+\infty, 0)$, we find

$$\frac{dg}{dl} = \frac{2}{3}v^2 g \to \frac{4}{21}\epsilon g. \tag{12}$$

Now g, and also the metric tensor $\mathbf{g}$, are *relevant* near the percolation fixed point, with a positive crossover exponent ϕ_g of $4\epsilon/21$, echoing our heuristic argument that effective chains are strongly stretched in a phantom network. In general, the singular part of free energy should then have the scaling form

$$f_s = |r|^{d\nu}\psi_2(\mathbf{g}/|r|^{\phi_g}). \tag{13}$$

For a pure shear with $\det(\mathbf{g}) \equiv 1$, this f_s must agree with Eq. (1), up to a constant independent of $\mathbf{g}$. Therefore the shear-modulus exponent is given by $d\nu - \phi_g = 3 - \frac{5}{21}\epsilon$, which, to the same order in ϵ, is identical to the conductivity exponent of a random resistor network [20].

This equivalence between critical exponents of phantom elastic networks and random resistor networks should, in fact, hold to all orders in ϵ. To see this analytically, we note that setting $(B_0, B) = (\infty, 0)$ in H_D is equivalent to setting $B_0 = B = 0$, *together with the hard constraint* $\Omega^0(\mathbf{x}) \equiv 0$, which explicitly excludes configurations having nonzero density fluctuations in the preparation ensemble. The resulting model then becomes formally identical to the Harris-Lubensky formulation of the random resistor network problem [20], with the nd $(\to 0)$ coordinates associated with the measurement ensembles $(\mathbf{x}^1, \ldots, \mathbf{x}^n)$ mapped onto the D $(\to 0)$ replicated voltages ϑ, provided the stated limits are taken. Thus, the pair of systems are governed by identical RG equations and, hence, critical exponents.

Having established the two limiting cases, $B = \infty$ and $B = 0$, it is natural to ask which one is the more stable. As B, like r, has naive dimension 2, it is always relevant near six dimensions. Therefore, if we keep B_0 large and tune B to be small, the shear-modulus exponent should cross over—from the conductivity one, t, to the incompressible system one, $d\nu$—when $|r|$ becomes smaller than B. This can be readily realized in a numerical simulation, if one were to retain the sol part of the system and turn on a small repulsion. In principle, this crossover might also be observed in gelation experiments on nondense solutions, provided $|r|$ is sufficiently small.

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