Critical Properties of Viscoelasticity of Gels and Elastic Percolation Networks

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Two superelastic percolation models are proposed to explain the observed behavior of the viscosity η of gels near the gel point. The elastic moduli G of one model diverge at the percolation threshold p_c with a critical exponent τ given by $\tau=\nu-\beta_p/2$, where ν and β_p are the critical exponents of percolation correlation length and the strength of the infinite cluster, respectively. We propose that this system can model the behavior of η in the Zimm limit. In the second model, which we propose to be appropriate for the Rouse limit, G diverge at p_c with an exponent $\tau'=2\tau$. Large-scale simulations confirm these scaling laws. The experimentally observed deviations from these scaling laws are also discussed.

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The viscoelastic properties of gels are of great practical importance, and have received considerable experimental and theoretical attention.[1,2] The gelling solution *at* the sol-gel transition has unique and unusual properties: Its viscosity η is infinite, whereas all of its elastic moduli G are zero. The original treatment of this phenomenon by Flory[3] is in fact a complete solution of the percolation problem[4] on the Bethe lattice. Stauffer[5] and de Gennes[1,6] emphasized the importance of deviations from Flory's solution, and proposed to replace it by the more general percolation models on finite-dimensional lattices. In particular, de Gennes[6] proposed that, close to the gel point (GP), the elastic moduli of the gel and the viscosity of the sol are directly related to the conductivity σ of a percolation network of random resistors, and of random superconductors, respectively. Consider a percolation network in which a fraction p of bonds has a conductance a, while the rest of the bonds have a conductance b. If $a=1$ and $b=0$, then, near the percolation threshold p_c, one has $\sigma\sim\epsilon^{\mu}$, whereas if $a=\infty$ and $b=1$, $\sigma\sim\epsilon^{-s}$, where $\epsilon=|p-p_c|$. de Gennes's suggestions are equivalent to saying that, near the GP, G vanish according to a power law characterized by the exponent μ, whereas η diverges with the exponent s. The most recent experimental data[7-9] indicate that G vanish with an exponent in the range 3.5–3.8, whereas for three-dimensional (3D) systems,[10] $\mu\simeq 2$. To explain the behavior of G, percolation models have been suggested[11-14] in which each bond of the network is an elastic element which can be stretched and bent. Simulation of this model in 3D has shown that,[15] near p_c, the elastic moduli of the system vanish with an exponent $f\simeq 3.8$, in good agreement with the experimental data, and in fact it has been proposed[16] that $f=\mu+2\nu$, where ν is the exponent of percolation correlation length $\xi\sim\epsilon^{-\nu}$, and $\nu(d=3)\simeq 0.88$. However, the situation for η is not clear yet. Experimental measurements indicate that near the GP, η diverges with an exponent k, the value of which is either[17-19] in the range 1.3–1.5, or is[20,21] mostly in the range 0.6–0.8 (there are some data indicating deviations from the latter range; this is discussed below), whereas for 3D systems,[22] $s\simeq 0.735$. While some scaling theories have been advanced,[17,18,23] no appropriate model has been proposed to predict the peculiar behavior of η and k. In this Letter we propose two percolation models to explain the behavior of the viscosity exponent k, relate k to the percolation exponents, perform large-scale computer simulations to test the models, and compare our results with the experimental data.

To begin with, we contend that the behavior of σ in percolation networks has no relation with that of η near the GP because, in general, the rotation and deformation of finite polymers in local viscous shears should make k smaller than s. Such deformations and rotational motions also make the field equations for σ totally different from those for η. Indeed, η is related to a tensor quantity (complex shear modulus), whereas σ is a scalar quantity and, therefore, there is no reason to believe that η and σ should have the same scaling behavior. As an alternative view, we propose that the behavior of η near the GP is similar to that of the shear modulus κ of an appropriate elastic percolation network (EPN), to be defined below, near p_c. Consider an EPN in which the elastic energy E is given by[11-14]

$$E=\frac{\alpha}{2}\sum_{\langle ij\rangle}[(\mathbf{u}_i-\mathbf{u}_j)\cdot\mathbf{r}_{ij}]^2 g_{ij}+\frac{\beta}{2}\sum_{\langle jik\rangle}(\delta\theta_{jik})^2 g_{ij}g_{ik}\,, \qquad (1)$$

where $\mathbf{u}_i$ is the displacement of site i, $\mathbf{r}_{ij}$ is a unit vector from i to j, and g_{ij} is a random variable which takes the values a and b with probabilities p and $1-p$, respectively. Here $\langle jik\rangle$ indicates that the sum is over all triplets in which the bonds ji and ik form an angle whose vertex is at site i, α and β are the stretching-force and bond-bending-force constants, respectively, and $\delta\theta_{jik}$ is the change of angle between bonds ji and ik. In the limit of $a=\infty$ and $b=1$, one obtains[24] a *superelastic* percolation network (SEPN) in which κ diverges[24,25] according to the power law

$$\kappa\sim(p-p_c)^{-\tau}. \qquad (2)$$

Theoretical considerations[26] indicate that for 2D and 3D systems, $\tau<s$, although published numerical results[24,25,27] for $\tau(d=2)$ do not consistently confirm this prediction; no estimate of $\tau(d=3)$ has yet been reported.

To relate the critical properties of κ to η, we consider

two limiting cases. The first case is the so-called Zimm limit,[1,28] in which there are strong hydrodynamic interactions between monomers and also the polymers of various sizes. Since there are large polymers (clusters) near the GP, the strong hydrodynamic interaction hinders diffusion of the polymers in the reaction bath and, therefore, there is no significant polymer movement. Thus the behavior of the system in this limit may be described by a static percolation network. However, contrary to the previous suggestions[6,23] which invoke an analogy between η and σ, we propose that, in this limit, η is analogous to the shear modulus of a static SEPN whose energy is given by Eq. (1) and, therefore, $k=\tau$. We now estimate τ by large-scale Monte Carlo calculations.

To estimate τ we use finite-size scaling analysis (FSSA) according to which, for a percolation network of linear dimension L at p_c, one has

$$\kappa \sim L^x[1+a_1 g_1(L)+a_2 g_2(L)], \tag{3}$$

where $x=\tau/\nu$. Here $g_1(L)$ and $g_2(L)$ are, respectively, the leading nonanalytical and analytical corrections to scaling, which are important for small to moderate values of L. To calculate κ we minimize E with respect to $\mathbf{u}_i$ and solve the resulting set of linear equations for $\mathbf{u}_i$'s by the adaptive accelerated Jacobi-conjugate gradient method. Calculations were done on a simple-cubic network at $p_c \simeq 0.249$, and the statistics of the simulations are given in Table I. The results, which were fitted to Eq. (3), are shown in Fig. 1. Various forms for $g_1(L)$ and $g_2(L)$ were tried in order to find the most accurate fit to the data, which we found to be provided by $g_1(L)=(\ln L)^{-1}$ and $g_2(L)=L^{-1}$. From Fig. 1 we obtain $\tau/\nu \simeq 0.74 \pm 0.04$, which means that

$$\tau \simeq 0.65 \pm 0.03 . \tag{4}$$

This value of τ is consistent with those experimental data for k which are[17-19] mostly in the range 0.6–0.8 (see also below).

Two points are worth discussing here. According to Eq. (4), $\tau < s$, which is consistent with the theoretical predictions.[26] The second point concerns the relation between τ and the standard percolation exponents. Several authors[23,29,30] have used scaling arguments, some of which[23,29] are based on the analogy between the conductivity of superconducting percolation networks and η, and have derived the following relation for s:

$$s=\nu-\beta_p/2 , \tag{5}$$

TABLE I. Number of realizations for each network size L for simulations at p_c for the Zimm limit.

L	6	9	12	15	18	20			
Cubic network	800	400	200	160	135	90			
L	15	20	25	30	35	40	50	60	70
Square network	1500	1000	800	600	500	300	300	200	100

where β_p is the critical exponent of the strength $P(p)$ of the infinite cluster near p_c; $P(p) \sim \epsilon^{\beta_p}$. Since $\beta_p(d=3) \simeq 0.43$, Eq. (5) predicts that $s \simeq 0.66$, in disagreement with the latest simulation estimate of Normand and Herrmann,[22] $s \simeq 0.735 \pm 0.004$. Moreover, since $\nu(d=2)=\frac{4}{3}$ and $\beta_p(d=2)=\frac{5}{36}$, Eq. (5) predicts that $s=\frac{91}{72} \simeq 1.26$, whereas simulations[22] yield $s \simeq 1.297 \pm 0.03$. On the other hand, if we use Eq. (5) to estimate τ (i.e., invoke an analogy between κ and η instead of σ and η), we find that $\tau(d=3) \simeq 0.66$, in complete agreement with (4). To further test the validity of Eq. (5) for estimating τ, we also determined τ for 2D networks. We used a square lattice, determined κ at $p_c=0.5$, and estimated τ using FSSA. The statistics of the simulations are presented in Table I, and the results are shown in Fig. 2. We found again that $g_1(L)=(\ln L)^{-1}$ and $g_2(L)=L^{-1}$. From Fig. 2 we obtain $\tau/\nu \simeq 0.92 \pm 0.03$, which means that

$$\tau \simeq 1.24 \pm 0.03 \tag{6}$$

which again agrees with $\tau=\nu-\beta_p/2$. Moreover, Eq. (5) predicts that for 1D systems $\tau=1$ (exact), and for $d \geq 6$, which represents the mean-field limit for the percolation problem, one has $\tau=0$ (i.e., κ diverges logarithmically), which agrees with the exact solution of the problem on a Bethe lattice. Note the small difference between τ and s in 2D. Previous estimates[24,25,27] of τ in 2D could not detect this small difference, presumably because finite-size effects were ignored in these works. According to Limat,[26] the eccentricity of elastic percolation clusters, which measures the strength of a coupling effect between displacements and rotations, tends to rigidify the clusters, giving rise to the difference between τ and s. Therefore, we propose that for the Zimm limit $k=\tau$

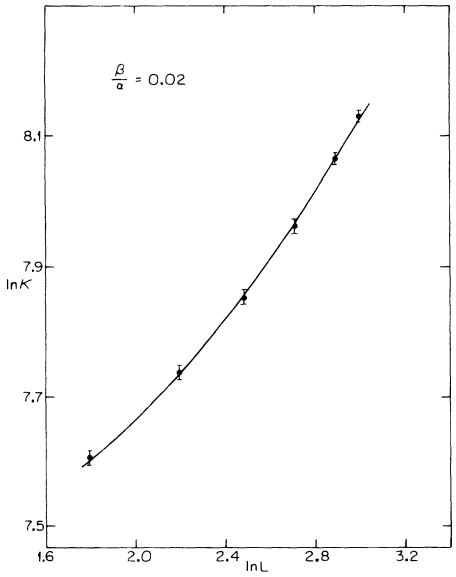

FIG. 1. Variations of the shear modulus κ of the static superelastic network with the linear size L of the network at the bond percolation threshold p_c of the simple-cubic network.

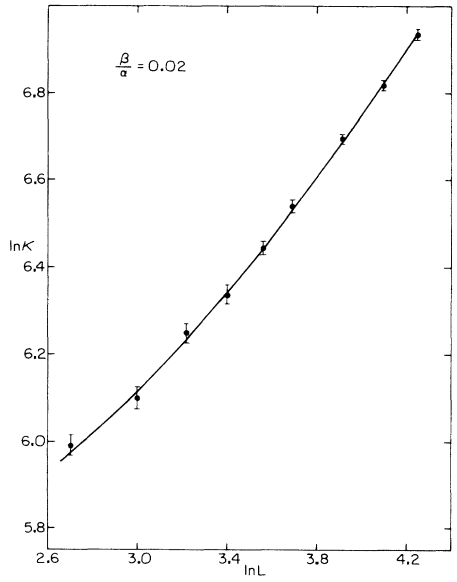

FIG. 2. Variations of κ of the static superelastic network with the linear size L at p_c of the square network.

where, for $1 \leq d \leq 6$,

$$\tau = \nu - \beta_p/2 . \quad (7)$$

Consider now the Rouse limit,[28] which is the opposite of the Zimm limit. In this case there are no hydrodynamic interactions between the various polymers present in the reaction bath. Polymers of comparable size cannot overlap but, because of the absence of any interaction, they can diffuse essentially freely throughout the reaction bath. Diffusion of a given cluster can be described by the Stokes-Einstein formula, but in a medium with a *size-dependent* viscosity.[17,18] A polymer larger than the correlation length feels the bulk viscosity, and the smaller polymers have a finite viscosity. For this case it has been shown that[18]

$$k = 2\nu - \beta_p , \quad (8)$$

which had also been conjectured earlier[31] based on various analyses. We now propose a SEPN for the Rouse limit, in which κ diverges at p_c with an exponent $\tau' = k$, where k is given by Eq. (8). Similar to the Zimm limit, we consider a SEPN below p_c, in which a fraction p of bonds are totally rigid ($g_{ij} = \infty$). Below p_c there is a large (but finite) rigid cluster, whose radius of gyration R is comparable to ξ, and for which κ depends on R. There is also a wide distribution of smaller rigid clusters which represent polymers of various sizes. Similar to the Zimm limit, the bonds with $g_{ij} = 1$ represent the sol phase. Since in the Rouse limit the absence of hydrodynamic interactions between the polymers allows the polymers to diffuse in the reaction bath, we similarly allow the rigid clusters to diffuse in the network (in the Zimm limit they were fixed). Each time two rigid clusters touch one another, they temporarily form a larger rigid cluster which can be broken up again at a later time. The motion of the rigid clusters in the network is similar to the diffusion of the polymers in the reaction bath in the Rouse limit. This is a dynamic network in which the rearrangement of the rigid clusters gives rise to an efficient transmission of force and stress throughout the network. As a result, as p_c is approached from below, the elastic moduli of the network increase and eventually diverge at p_c. Because of this efficiency, the divergence of the elastic moduli of this dynamic network is even stronger than those of the static SEPN considered for the Zimm limit, in the sense of being characterized by a critical exponent $\tau' > \tau$. We now show, by Monte Carlo simulations, that the exponent τ' is the same as k given by Eq. (8).

To estimate τ' we generate, for a given $p < p_c$, a SEPN of size L. At each time step, a randomly selected fraction of rigid clusters are moved, with equal probability, in one of the principal directions of the lattice. Two rigid clusters cannot overlap. We then calculate κ, move another randomly selected fraction of rigid clusters, determine κ again, and so on. Computations are carried out for enough steps until κ achieves an essentially constant value. We then generate another realization of the network, repeat the computations, and average the results over all realizations. In principle, calculations can be carried out at $p = p_c$ and for various sizes L, and τ' can be estimated using FSSA. However, this requires a very large amount of computer time. Instead, we used a square network with $L = 200$, and calculated κ for $p = 0.47$, 0.48, 0.485, 0.49, and 0.495, averaged over 50 realizations. The results are presented in Fig. 3, from which we obtain

$$\tau' \simeq 2.50 \pm 0.15 . \quad (9)$$

For 2D systems Eq. (8) predicts that $k = \frac{91}{36} \simeq 2.53$, in excellent agreement with τ'. Thus, if we use Eq. (8) to estimate τ' for 3D systems, we obtain $\tau' \simeq 1.33$, completely consistent with the experimental data[17-19] in the range 1.3–1.5, which also supports the validity of the model. Equations (7) and (8) then lead to upper and lower bounds for k. Since the Zimm and Rouse limits represent two opposite systems, one has

$$\nu - \beta_p/2 \leq k \leq 2\nu - \beta_p . \quad (10)$$

Moreover, most experimental data are either close to the Zimm or the Rouse limit.

We should remark about some experimentally observed deviations of k from the exponents τ and τ'. Experimental determination of k (and f) involves measuring the complex shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ at a frequency ω, where G' and G'' are the storage and loss shear moduli, respectively. At the GP, G' and G'' are predicted[10,17-21] to scale with ω as $G' \sim G'' \sim \omega^{\Delta}$, where $\Delta = f/(f+k)$. Strictly speaking, the scaling laws proposed here are valid only in the limit of $\omega \to 0$, whereas in practice it is highly difficult to achieve such a limit and, therefore, the reported values of k are sometimes larger than τ. However, we believe that the difference between k and τ (or τ') is a transient effect and recent, more precise,[32,33] measurements of k clearly

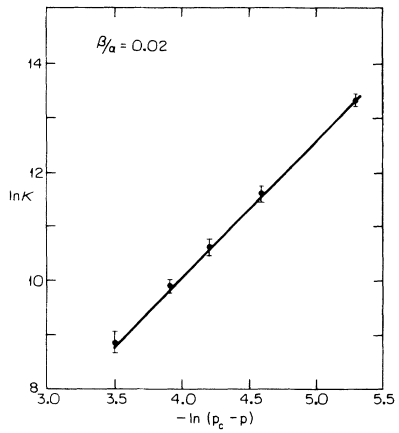

FIG. 3. Variations of κ of the dynamic superelastic percolation network with the fraction p of rigid bonds in the square network.

show a trend towards lower values closer to τ or τ'. We should also mention that Martin and co-workers[17,18] have proposed that $f=vd$. They also contend that this relation is derived based on a percolation model. However, the predictions of this relation, originally suggested by Daoud and Coniglio,[34] do not agree with those of EPNs. For example, it predicts that $f(d=3)\simeq 2.64$, as compared with[15] $f\simeq 3.8$ for EPNs. We shall discuss this in more detail in a future paper.[35]

In summary, we have proposed two SEPNs for modeling of the divergence of the viscosity of gels near the GP. The first model is a static SEPN which may model η in the Zimm limit, with a critical exponent τ given by $\tau=\nu-\beta_p/2$. The second model is a dynamic SEPN in which κ diverges with an exponent $\tau'=2\tau$. This model may be used to study η in the Rouse limit. Our results presented here and elsewhere[15,35] provide a fairly complete description of viscoelastic properties of gels near the GP. We should mention that there are some experimental data that indicate $f\simeq\mu$ and $k\simeq s$. We believe such systems are still described by an EPN or a SEPN (instead of a resistor network[6]) because the analogy between σ and G, or η and σ, is inappropriate. However, the elastic energy of a gel system for which $f\simeq\mu$ does not have to be the same as in Eq. (1). For example, for an EPN with a Born Hamiltonian[35] $f=\mu$. As argued by Alexander,[36] an EPN with a Born Hamiltonian may be the appropriate model for describing gels which are under external or internal stress. Thus, for those gels for which $f\simeq\mu$ and $k\simeq s$, we must still use an EPN or a SEPN, except that the elastic energy of the system may be described by the Born model.

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