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Viscoelasticity near the sol-gel transition

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Measurements of viscoelastic properties near the sol-gel transition demonstrate that viscoelastic phenomena are described by power laws. To describe these phenomena, we derive the distribution of relaxation times for branched polymers, both in the reaction bath and in the dilute solution. From this spectrum we can compute viscoelastic properties such as the shear relaxation modulus $G(t)$ and the complex shear modulus $G(\omega)$. Near the gel point we find $G(t)\sim t^{-\Delta}$, with Δ a universal exponent, for times that are small compared to a divergent time τ_z: For longer times the decay is a stretched exponential. The exponent Δ is found to be sensitive to dilution. Likewise, the storage and loss parts of the complex shear modulus are found to scale as ω^{Δ}. These results for the dynamics lead to a theory for the critical growth of the equilibrium shear modulus E above the gel point, and the divergence of the steady-state creep compliance J_e^0 above the gel point. Finally, we discuss the concentration dependence of the viscosity of a solution of branched polymers.

I. INTRODUCTION

In the last several years rheologists have become increasingly interested in measuring the viscoelastic properties of chemical gels near the sol-gel transition.[1-5] For experimental reasons, the complex shear modulus $G(\omega)$, which describes storage and dissipation in an oscillating strain field of constant amplitude,[6] is usually measured, with the result that *at the gel point* both the storage G' and loss G'' parts of the modulus are power laws in frequency, $G'\sim G''\sim\omega^{\Delta}$. By a Fourier transform it can then be shown that the shear relaxation modulus,[6] which describes the relaxation of stress after a constant shear strain, must decay as $G(t)\sim t^{-\Delta}$, and by a Laplace transform it can be shown that the spectrum of relaxation times[6] scales as $H(\tau)d\ln\tau\sim\tau^{-\Delta}d\ln\tau$. Clearly, the determination of the *viscoelastic exponent* Δ, a principle goal of this paper, is a central theoretical problem in the dynamics of the incipient gel.

The decay of thermally induced fluctuations in the undiluted incipient gel is a closely related subject. Quasielastic light-scattering measurements have recently shown that the relaxation of concentration fluctuations is described by the power-law time decay[7] $S(q,t)\sim t^{-\phi}$. The function $S(q,t)$ has *two* associated divergent relaxation times: an average decay time $\langle\tau\rangle$ and a typical ($\sim$longest) decay time τ_z. Slightly beneath the gel point $S(q,t)$ is described by a power-law time decay until $t\cong\tau_z$: for larger times a stretched exponential decay is found. This basic framework is shared by the time-dependent viscoelastic functions.

A theory for the quasielastic light-scattering exponent ϕ was developed in terms of translational diffusion of the branched polymers in the reaction bath. The percolation model was used to describe the statistical properties of the branched polymer ensemble, and by using the concept of a length-scale-dependent viscosity, good agreement was found between theory and experiment.

In this paper the percolation-based theory used to explain the relaxation of concentration fluctuations is extended to the problem of viscoelasticity. Both the reaction bath and dilute solutions are considered. We first compute the relaxation times of the internal modes of a single, branched polymer and then obtain macroscopic properties by summing over the percolation cluster size distribution. For the reaction bath this yields the expression $\Delta=d\nu/(d\nu+k)$, where d is the spatial dimension, ν is the correlation length exponent, and k is the viscosity exponent. In dilute solutions the viscoelastic exponent is found to be the ratio of the fractal dimensions of swollen and unswollen clusters.

Although the main goal of this paper is viscoelasticity, some interesting results are found for time-independent properties, such as the elastic modulus, steady-state creep compliance, and the viscosity. For example, by taking strong and weak limits of the hydrodynamic interactions, and using Flory-type arguments for certain fractal dimensions, we are able to set the limits $0\leq k/\nu\leq(6-d)/2$ on the viscosity exponent k. This demonstrates that in the mean-field theory of gelation ($d=6$) the bulk viscosity diverges at most logarithmically.

Above the gel point it is shown that the equilibrium shear modulus E grows as the density of correlation volumes ("blobs") $E\sim kT/\xi^d$, where kT is the thermal energy. Likewise, it is found that the equilibrium steady-state creep compliance J_e^0, which diverges *beneath* the gel point, is the counterpart to the modulus, so $J_e^0\sim1/E$. This simple relation derives from the fact that each of these quantities involves a storage of energy. That the storage of energy is related to the density of blobs may be regarded as a statement of equipartition—in a unit shear deformation an energy kT is stored per correlation volume. This result disagrees with the analogy between the shear modulus of a gel and the growth of conductivity in a random resistor network.

Finally, the concentration dependence of the viscosity of a solution of branched polymers is discussed. The result bears a close analogy to entangled linear chain melts: The viscosity is found to be a power of the number of *concentration blobs* in a typical branched polymer.

II. PERCOLATION AND LATTICE ANIMALS

Before discussing the dynamics it is helpful to review the percolation model of branched polymers. For a thorough review one can consult several excellent articles.[8-10] In the bond-percolation model monomers occupying sites on a d-dimensional lattice are randomly bonded with probability p. When p is small only a few dimers and trimers are formed, but as p increases, very large connected clusters (branched polymers) appear. At a critical bond probability (extent of reaction) p_c an infinite cluster appears and certain average cluster sizes diverge to infinity. Thus $p=p_c$ marks the transition from the sol (finite branched polymers) to the gel (infinite network). Beyond p_c the very largest clusters become attached to the infinite cluster to form a network, within which are embedded finite clusters: The average size of these clusters decreases as p approaches 1. Near the sol-gel transition the percolation model is analogous to a continuous phase transition, in that many quantities diverge as powers of $\epsilon=|p-p_c|$. For example, as the gel point is approached from below, the viscosity diverges as $\eta\sim\epsilon^{-k}$ and above the gel point the elastic shear modulus of the infinite network increases as $E\sim\epsilon^{z}$.

In the following we will make frequent use of standard percolation results. The percolation cluster size distribution is given by[8] $N(m)=m^{-\tau}\exp(-m/M_z)$, where M_z is the mass of a typical cluster and $\tau=1+d/D$ is an exponent that is a bit larger than 2. The exponent $D\cong 2.52$ $(d=3)$ is the fractal dimension of a cluster smaller than M_z and so relates the mass of a cluster to its radius via $R^{D}\sim m$. Thus the distribution decays very slowly until $m\sim M_z$ where the algebraic decay is nearly truncated by the exponential.[8] The *z-average* cluster mass

$$M_z\equiv\sum m^3N(m)/\sum m^2N(m)$$

diverges like $M_z\sim\epsilon^{-D\nu}$: The radius of a cluster of mass M_z is called the correlation length ξ. Since $\xi^{D}\sim M_z\sim\epsilon^{-D\nu}$ we surmise that the correlation length diverges as $\xi\sim\epsilon^{-\nu}$. Three-dimensional simulations give $\nu\cong 0.89$.

In six dimensions the percolation model is equivalent to the mean-field theory of gelation developed by Flory and Stockmayer on the Bethe lattice.[11-13] The mean-field exponents have the values $D=4$ and $\nu=\frac{1}{2}$. It is often interesting and useful to make comparison to the mean-field theory of branched polymers.

In addition to these standard percolation results, we will repeatedly make use of the Flory-type formulas for the fractal dimension of branched polymers in the reaction bath and in good solvents, given by Isaacson and Lubensky[14] and de Gennes.[15] In the reaction bath, two-body interactions between monomers on a cluster are *screened* by intervening clusters. Due to this screening clusters are somewhat compact, having the percolation dimension, which is approximately[14] $D=(d+2)/2$ $(d\leq 6)$. However, when branched polymers are diluted with a good solvent, two-body interactions within a cluster are unscreened, and excluded volume interactions are strong. The fractal dimension D_s of these swollen clusters is then given by the *lattice-animal* model,[8] with[15] $D_s=2(d+2)/5$ $(d\leq 8)$. Lattice animals are the ensemble of all possible branched polymers, each occurring with equal probability, whereas percolation clusters are exponentially weighted by their surface sites—a low probability results from a large surface. Therefore, in three dimensions it is predicted that the fractal dimension of a *single*-branched polymer decreases from 2.5 to 2 upon dilution.

Finally, we note that in the reaction bath clusters larger than the correlation length have the lattice-animal fractal dimension D_s.[16] This is due to the fact that very large, exponentially rare clusters see the surrounding distribution of percolation clusters as a small solvent. This point is important when we discuss very-long-time relaxation phenomena.

III. RELAXATION TIMES

To compute the relaxation times for either a solution or melt of branched polymers it is helpful to consider first the dynamics of a single cluster. A single cluster has many degrees of freedom, including translational and rotational diffusion, and internal diffusive modes that define the shape of a cluster. A normal-mode analysis must take into account the connectivity of the cluster, excluded volume interactions between monomers on the cluster, and *hydrodynamic* interactions between monomers. Detailed normal-mode calculations for linear polymers were first published by Kirkwood and Riseman,[17] Rouse,[18] and Zimm[19] in several elegant papers; however, the complexity of the percolation model has prevented direct calculations for branched polymers.

The work on linear polymers can be summarized by recognizing that the Brownian dynamics of these chains obeys a dynamical self-similarity: If the relaxation times of a polymer chain are scaled by $\tau_R\sim R^2/D_t$, the time it takes a polymer to diffuse its own radius, then the long-time part of the nondimensioned relaxation time spectrum is scale independent. Thus just as R is the only length scale in a self-similar object, τ_R is the only time scale for the dynamics. For example, the rotational diffusion coefficient of any Brownian object is given by $\theta^{-1}\sim R^2/D_t$. This implies that regardless of the size of the object, it will on average rotate through the same angle during the time it takes it to diffuse a distance equal to its own radius. Trajectories are thus statistically equivalent when scaled by this time.

The assumption of self-similar Brownian dynamics leads to the following expression for the relaxation times of a single flexible polymer (linear or branched) of m monomers:

$$\tau_j\sim j^{-\alpha}\tau_R,\quad 1\leq j\leq m \tag{1}$$

where j is a mode index. The exponent α can be determined by expressing the cluster diffusion coefficient as $D_t\sim R^{-b}$ and noting that the relaxation of short-wavelength modes should be independent of the cluster size m, i.e., $\tau_m \sim m^{-\alpha}\tau_R \sim m^0$. This gives

$$\tau_j \sim (j/m)^{-(2+b)/D}\tau_0, \quad 1 \le j \le m \tag{2}$$

where D is the fractal dimension of the cluster and τ_0 is the relaxation time of the fastest mode, approximately the time it takes a polymer-entrained monomer to diffuse a distance equal to its own radius.

If a sudden shear deformation is applied to a macroscopic polymeric sample, the polymers will initially deform affinely and then will slowly approach their equilibrium conformations, thereby relaxing the stress. According to the Boltzmann superposition principle,[6] the shear relaxation modulus $G_m(t)$ of a single cluster can be expressed as an *unweighted* sum of the relaxations of all its normal modes. For times slower than the monomer diffusion time τ_0 and faster than the polymer diffusion time τ_R this gives the power-law decay

$$G_m(t) = \int_1^m \exp(-t/\tau_j)dj \sim m/t^{D/(2+b)}, \qquad \tau_0 \le t \le \tau_R . \tag{3}$$

To demonstrate the utility of this approach, it is instructive to apply Eq. (3) to linear polymers. We consider linear polymers in good solvents, described by the statistics of self-avoiding walks ($D=\frac{5}{3}$ for $d=3$), and linear polymers in θ solvents, which in $d=3$ are described by random walks ($D=2$). In each of these cases the hydrodynamic interactions between monomers on a chain can be strong or weak.

If hydrodynamic interactions are strong (Zimm model) the diffusion coefficient is given by the Stokes-Einstein formula $D_t \sim kT/\eta_0 R^{d-2}$ ($b=d-2$). Using Eq. (3) we then obtain $G_m(t) \sim m/t^{D/d}$, which gives the well-known θ-solvent prediction[6] $G_m(t) \sim m/t^{2/3}$ and the good solvent prediction[20,21] $G_m(t) \sim m/t^{5/9}$. On the other hand, if hydrodynamic interactions are negligible (Rouse model) the friction of the chain against the solvent is just the sum of the monomer frictions ζ_0, giving $D_t \sim kT/\zeta_0 m$ ($b=D$) and $G_m(t) \sim m/t^{D/(2+D)}$. For the θ chain this gives the celebrated Rouse result[6] $G_m(t) \sim m/t^{1/2}$, and in good solvents this gives $G_m(t) \sim m/t^{5/11}$. It is widely believed that an unentangled linear polymer melt[6,22] is a physical realization of the Rouse model, due to the screening of both excluded volume and hydrodynamic interactions. Thus the above formulation of the relaxation times reproduces several well-known results.

In the field of viscoelasticity it is customary to express results in terms of a logarithmic spectrum of relaxation times,[6] $H(\tau)d\ln\tau$. In this formulation the *single*-cluster spectrum, Eq. (2), can be written

$$H_m(\tau) = \frac{m}{\tau^{D/(2+b)}} f(\tau/\tau_R) . \tag{4}$$

In this continuous representation the function $f(\tau/\tau_R)$ truncates the spectrum of relaxation times at the longest time τ_R. Although the detailed nature of $f(x)$ is unknown, for $x<1$ we expect $f(x)=1$, whereas for $x \gg 1$, $f(x)$ should decay much faster than a power law (e.g., exponentially). In terms of $H_m(t)$ the single-cluster shear relaxation modulus is

$$G_m(t) = \int_{\ln\tau_0}^{\infty} H_m(\tau)e^{-t/\tau}d\ln\tau . \tag{5}$$

We will now apply this to branched polymers.

IV. A BRANCHED POLYMER

The relaxation time spectrum for a single, branched polymer can be obtained from an understanding of diffusion in the reaction bath. To understand diffusion we must first digress to consider the structure of the incipient gel, as described by percolation. The incipient gel is a *self-similar distribution* of fractal clusters of all sizes, from monomers to the infinite cluster. In order that all clusters see a scale-independent environment, the average separation distance S between clusters of radius $R \pm d\ln R$ must be proportional to R. By using $S \sim 1/N(R)^{1/d} \sim R$ we obtain the self-similar distribution $N(R)d\ln R \sim R^{-d}d\ln R$. From the fractal relation $R^D \sim m$ the well-known *hyperscaling* relation[8] $N(m)dm \sim m^{-1-d/D}dm$ is obtained for the mass distribution at the gel point. As we have mentioned, away from the gel point the distribution is only self-similar for clusters smaller than M_z: For larger clusters the self-similarity is truncated by an exponential cutoff[8] giving

$$N(m)dm \sim m^{-1-d/D}\exp(-m/M_z)dm ,$$

or equivalently,

$$N(R)d\ln R \sim R^{-d}\exp[-(R/\xi)^D]d\ln R .$$

Consider a cluster of radius R attempting to diffuse in the incipient gel. Since branched polymers of comparable size cannot overlap, it is reasonable to describe the diffusion as Stokes-Einstein, but in a medium with a *size-dependent* viscosity[7,23] (i.e., the viscosity depends on the cluster size). In other words, the diffusion coefficient of a cluster of radius R is expected to be proportional to that of a sphere of radius R. On the time scale on which this cluster relaxes (moves a distance proportional to R) smaller clusters will have already relaxed, but much larger clusters will appear nearly stationary. Thus the smaller clusters form a fluid with a finite viscosity, embedded in a medium of essentially immobile clusters which form a tortuous system of caverns through which the cluster must diffuse. From self-similarity we recognize that the tortuosity is the same for all clusters, and simply reduces the diffusion coefficient by some fixed, radius-independent amount. Thus the central issue is the viscosity $\eta(R)$ of the fluid of clusters of radius less than R. Noting that the cutoff in the size distribution is the correlation length ξ (the typical cluster radius), a fluid of viscosity $\eta(R)$ will be observed $\epsilon \sim R^{-1/\nu}$ beneath the gel point, where $\xi \sim \epsilon^{-\nu}$. Beneath the gel point the bulk viscosity diverges like $\eta \sim \epsilon^{-k}$, so the viscosity felt by a probe of radius R scales like $\eta(R) \sim R^{k/\nu}$. Using the Stokes-Einstein formula $D_t(R) = kT/6\pi\eta R$ for the diffusion coefficient then gives $D_t(R) \sim 1/R^{1+k/\nu}$. In d dimensions this becomes $D_t \sim 1/R^{d-2+k/\nu}$.

We can obtain the same result if we assume that a probe larger than the correlation length feels the bulk viscosity η_b, and a probe smaller than the correlation length feels a finite viscosity, i.e., *independent* of η since η diverges. This formulation leads to the scaling relation $\eta(R) \sim \eta_b h(R/\xi) \sim \eta_b^0$ for $R < \xi$. Using $\eta_b \sim \xi^{k/\nu}$ then gives $\eta(R) \sim R^{k/\nu}$ for $R < \xi$.

Physically it seems reasonable to interpret the term $R^{k/\nu}$ as representing the screening of hydrodynamic interactions. If the reaction bath corresponds to a Rouse model, where hydrodynamic interactions between monomers on a cluster are *completely* screened by smaller clusters, we recall that the diffusion coefficient should be $D_t \sim kT/\zeta_0 m \sim 1/R^D$, where ζ_0 is a monomeric friction factor. In this case $D = d - 2 + k/\nu$. However, since the assumption of complete hydrodynamic screening is unjustified we should expect the reaction bath to be between the Rouse and Zimm limits, so $d - 2 \le d - 2 + k/\nu \le D$. Using the percolation estimate $D \cong (d+2)/2$ then gives $0 \le k/\nu \le (6-d)/2$. This inequality demonstrates that in the mean-field limit ($d = 6$) k must vanish, and the viscosity must diverge at most logarithmically,[9] i.e., $\eta \sim \ln(1/\epsilon)$. The experimental limits are $0 \le k \le 1.35$.

For a single branched polymer in the reaction bath the result for the diffusion coefficient leads to $b = d - 2 + k/\nu$. The spectrum of relaxation times is then

$$H_m(\tau) = \frac{m}{\tau^{D\nu/(d\nu+K)}} f(\tau/\tau_R) \quad \text{(reaction bath)} \tag{6}$$

with the longest relaxation time scaling as $\tau_R \sim m^{(d\nu+k)/D\nu}\tau_0$. Using Eq. (5), the shear relaxation modulus of a single branched polymer (not the macroscopic sample) immersed in the reaction bath is

$$G_m(t) \sim \frac{m}{t^{D\nu/(d\nu+k)}}, \quad \tau_0 < t < \tau_R \quad \text{(reaction bath)}\ . \tag{7a}$$

If the branched polymers are diluted into a good solvent the clusters swell ($D \to D_s$) and hydrodynamic interactions are unscreened. Using the Stokes-Einstein relation $D_t \sim 1/R^{d-2}$ and $\tau_R \sim m^{d/D_s}\tau_0$ gives the following result, which would apply to a fractionated dilute solution of branched polymers:

$$G_m(t) \sim m/t^{D_s/d}, \quad \tau_0 < t < \tau_R \quad \text{(dilute solution)}\ . \tag{7b}$$

The lattice-animal dimension $D_s = 2$ gives $G_m(t) \sim m/t^{2/3}$ for a *monodisperse* solution of branched polymers in a good solvent.

V. THE POLYDISPERSE ENSEMBLE

In order to compute macroscopic properties, it is necessary to sum over the distribution of clusters. The spectrum of relaxation times is

$$H(\tau) = \sum_m N(m) H_m(\tau)\ ,$$

and by using our expression for $N(m)$ we obtain

$$H(\tau) = (1/\tau^{d\delta/D}) F(\tau/\tau_z)\ , \tag{8}$$

where δ is the single-cluster viscoelastic exponent. $F(x)$ again plays the role of a cutoff function that truncates the power-law decay of the distribution of relaxation times at $\tau = \tau_z \sim \xi^2/D_t(\xi)$, the longest relaxation time for a cluster the size of the correlation length (a physical interpretation of this time will be given later). Using $\delta = D\nu/(d\nu+k)$ (reaction bath) and $\delta = D_s/d$ (dilute solution) we obtain

$$H(\tau) = \frac{1}{\tau^{d\nu/(d\nu+k)}} F(\tau/\tau_z) \quad \text{(reaction bath)} \tag{9a}$$

$$= \frac{1}{\tau^{D_s/D}} F(\tau/\tau_z) \quad \text{(dilute solution)} \tag{9b}$$

with $\tau_z \sim \epsilon^{-d\nu-k}$ for the reaction bath and $\tau_z \sim \epsilon^{-d\nu(D/D_s)}$ in dilute solution. Equation (9a) contains the prediction $\Delta = d\nu/(d\nu+k)$ for the viscoelastic exponent of the reaction bath. Later we will show that this value of the viscoelastic exponent is consistent with a sum rule of viscoelasticity.

A Laplace transform of $H(\tau)$ gives the experimental predictions

$$G(t) \sim \frac{1}{t^{d\nu/(d\nu+k)}}, \quad \tau_0 \le t \le \tau_z \quad \text{(reaction bath)} \tag{10a}$$

$$\sim \frac{1}{t^{D_s/D}}, \quad \tau_0 \le t \le \tau_z \quad \text{(dilute solution)}\ . \tag{10b}$$

Likewise, a Fourier transform of the shear relaxation modulus gives the storage and loss parts of the complex modulus

$$G'(\omega) \sim G''(\omega) \sim \omega^{d\nu/(d\nu+k)}, \quad \tau_0^{-1} > \omega > \tau_z^{-1} \quad \text{(reaction bath)}\ , \tag{11a}$$

$$G'(\omega) \sim G''(\omega) \sim \omega^{D_s/D}, \quad \tau_0^{-1} > \omega > \tau_z^{-1} \quad \text{(dilute solution)}\ . \tag{11b}$$

Using the inequality $0 \le k/\nu \le (6-d)/2$ for the viscosity exponent, we can establish the inequality $2d/(d+6) \le \Delta \le 1$ for the viscoelastic exponent of the reaction bath. Experimentally, this gives $\frac{2}{3} \le \Delta \le 1$, whereas in the mean-field limit $\Delta = 1$ (we will show that the mean-field value must be 1 in order for the viscosity to diverge logarithmically).

VI. STRETCHED EXPONENTIAL TAIL OF $G(t)$

If we are somewhat beneath the gel point, the decay of $G(t)$ will no longer be a power law for times larger than τ_z. At these very large times only the exponentially rare clusters, with $m \gg M_z$ will still contribute to the decay. As we have mentioned, simulations of percolation show that these exponentially rare clusters are lattice animals,[16] with a fractal dimension of 2 ($d = 3$). Since these clusters are much larger than the correlation length they should feel the bulk viscosity, and so should have a diffusion constant proportional to $kT/\eta_b R^{d-2}$. Thus the long-time tail of $G(t)$ may be described by the relaxation of the Zimm modes of the exponentially distributed lattice animals.

If we first sum over the discrete internal modes of a single-lattice animal we obtain a long-time decay for a single cluster that is proportional to e^{-t/τ_R}, where $\tau_R \sim m^{d/D_s}$. Averaging this over the distribution of cluster sizes and using the method of steepest descents gives

$$G(t) \sim \exp[-(t/\tau_z)^{D_s/(d+D_s)}] . \tag{12a}$$

Thus for $d=3$ we predict a stretched exponential tail with an exponent of $D_s/(D_s+d)=\frac{2}{5}$. We mention a final caveat, however. If the cutoff function for the distribution of relaxation times of a single cluster is slower than we have assumed from summing over discrete modes, then the observed exponent for the stretched exponential may be smaller than 0.4.

Although it cannot be rigorously justified, a useful form for fitting data taken for the reaction bath might be

$$G(t) \sim \frac{1}{t^{d\nu/(d\nu+k)}} \exp[-(t/\tau_z)^{D_s/(d+D_s)}] . \tag{12b}$$

We emphasize that this is merely a simple way of connecting the short- and long-time behaviors of the relaxation function. Finally, it is noteworthy that the stretched exponential tail applies to the case of dilute clusters as well.

VII. VISCOSITY AND EQUILIBRIUM MODULUS

The theory of viscoelasticity provides an important check on our calculation of the dynamic exponent Δ. The integral of the shear relaxation modulus, which is the arithmetic average relaxation time $\langle \tau \rangle$, is the zero-frequency viscosity η.[6] Thus we must have $\langle \tau \rangle \sim \epsilon^{-k}$ in order for our theory to make sense. A direct calculation demonstrates that this is indeed the case,

$$\langle \tau \rangle \equiv \int_0^\infty G(t)dt \sim \int_0^{\tau_z} t^{-\Delta} dt \sim \epsilon^{-k} . \tag{13}$$

This result justifies our initial assumption that the dynamics of a single cluster is scaled by the single relaxation time R^2/D_t.

At this point we have identified two divergent relaxation times relevant to the viscoelasticity of branched polymers: the arithmetic average, or bulk viscosity, given by $\langle \tau \rangle \sim \epsilon^{-k}$, and the terminal (longest) relaxation time τ_z, defined by

$$\tau_z \equiv \frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt} \sim \epsilon^{-d\nu-k} . \tag{14}$$

This multiplicity of divergent time scales has already been noted in quasielastic light-scattering measurements from gels.[7] From the theory of rheology we recognize Eq. (14) as the expression for ηJ_e^0, where J_e^0 is the steady-state creep compliance.[6] The relations $\langle \tau \rangle \sim \eta$ and $\tau_z \sim \eta J_e^0$ can then be solved to obtain $J_e^0 \sim \tau_z / \langle \tau \rangle \sim \epsilon^{-d\nu}$, a result with a striking physical interpretation, as we will now discuss.

The scaling behavior of the longest relaxation time in the pregel reaction bath can also be derived by examining the high- and low-frequency limits of the complex shear modulus $|G^*|$. The following scaling argument was developed by Clerc *et al.*[24] in the context of electrical networks, and applied to gels by Daoud[25] (who applied this argument to the spectrum of relaxation times) and Winter.[26] At low frequencies, $|G^*|$ by definition is equal to $\eta\omega$, and at high frequencies, we have shown that $|G^*| \sim \omega^\Delta$. Therefore $1/\tau_z$ can be defined as the frequency where these two limiting behaviors meet. This gives $\tau_z \sim \epsilon^{-k/(1-\Delta)}$ and, with $\Delta = d\nu/(d\nu+k)$, we again see that $\tau_z \sim \epsilon^{-\nu d - k}$. The scaling behavior of the longest relaxation time in the postgel reaction bath τ_z^* is found similarly. Here, though, the low-frequency limit of $|G^*|$ is E, the equilibrium modulus, which results in $\tau_z^* \sim \epsilon^{-z/\Delta}$. If we assume that τ_z and τ_z^* scale with ϵ in the same manner, then $k/(1-\Delta) = z/\Delta$ or $\Delta = z/(z+k)$.

This scaling result is in the same form as our prediction $\Delta = d\nu/(d\nu+k)$, leading to the identification of $d\nu$ as the elastic modulus exponent z. Recalling our result for J_e^0, we recognize that the elastic modulus scales as $1/J_e^0$ (note that these quantities are defined on opposite sides of the gel point). Apparently, this is due to the fact that each of these quantities involves a storage of energy: E is the energy stored in the gel, and $1/J_e^0$ is the energy stored in the sol in a creep experiment. In any case, we observe that the equilibrium steady-state creep compliance is the critical point counterpart to the equilibrium shear modulus.

The exponent $d\nu$ has a simple physical interpretation. First, if the modulus is determined solely by entropy, then the thermodynamic theory of elasticity tells us the modulus should be proportional to T, the temperature. Noting that the modulus is an energy density and noting that $E \sim \epsilon^{d\nu} \sim \xi^{-d}$ gives

$$E \sim \frac{1}{J_e^0} \sim \frac{kT}{\xi^d} . \tag{15}$$

Thus the elastic shear modulus is proportional to the density of *correlation* blobs in the gel. The situation is analogous to semidilute linear polymer solutions, where the *osmotic* modulus is proportional to the density of *concentration* blobs.[22] Equation (15) may be thought of as a statement of equipartition of energy: In a unit shear deformation an energy kT is stored per correlation volume at equilibrium.

On the other hand, we can use the scaling relation[8] $d\nu = D\nu + \beta$ (where β is the gel fraction exponent $G \sim \epsilon^\beta$) to obtain $E \sim kTG/M_z$. This shows a clear analogy to the original Flory theory[27] of rubber elasticity, where the modulus was found to be proportional to the density of *elastically effective* chains. In this interpretation the gel fraction may be regarded as the elastically effective portion of the network and the mass of a typical cluster is the size of an elastically effective unit.

Numerically $d\nu$ is insensitive to dimension, for example, $d\nu = \frac{8}{3}$ $(d=2)$, $d\nu \cong 2.67$ $(d=3)$, and $d\nu = 3$ in the mean-field limit. This value of z is in good agreement with experimental measurements,[28–31] which tend to give $z \cong 3$, but is larger than the value of $z \cong 1.94$ (Ref. 32) obtained by making an analogy between elasticity and the growth of the conductivity in a random resistor network (in the mean-field limit both theories give $z = 3$).

Finally, we relate the viscosity beneath the gel point to the shear elastic modulus above the gel point. From our result $\tau_z \sim \epsilon^{-d\nu - k}$ this is

$$\eta \sim \tau_z E \ . \tag{16}$$

Once again, there is a relation to entangled, semidilute, monodisperse, linear polymer solutions[22] if τ_z is taken to be the terminal relaxation time of a linear polymer chain and E is the plateau modulus. In the Rouse approximation the viscosity scales as $\eta \sim E^{-(6-d)/2d}$, which in $d = 3$ is the inverse root of the modulus.

VIII. CONCENTRATION DEPENDENCE OF THE VISCOSITY

In the case of a dilute solution of polydisperse branched polymers in a good solvent a few interesting remarks can be made. At infinite dilution the intrinsic viscosity can be computed by integrating the shear relaxation modulus

$$[\eta] \sim \int_0^{\tau_z} t^{-D_s/D} dt \sim M_z^{d(D_s^{-1} - D^{-1})} \sim \epsilon^{-dD\nu(D_s^{-1} - D^{-1})} \ . \tag{17}$$

Note that the result depends critically on whether or not the fractal dimension of a branched polymer changes upon dilution. If the fractal dimension D_s of a cluster in a good solvent is equal to that in the reaction bath D, then the intrinsic viscosity diverges only logarithmically, $[\eta] \sim \ln(1/\epsilon)$. However, if the Flory-type theories of swelling are correct, then using $D_s = 2$, $D = 2.5$, and $\nu = .89$ we obtain $[\eta] \sim M_z^{3/10} \sim M_w^{3/8} \sim \epsilon^{-2/3}$. Thus the divergence of the intrinsic viscosity is a very sensitive test of the swelling hypothesis. This result for the intrinsic viscosity has been obtained by Daoud *et al.*[33] directly, without recourse to the viscoelastic functions.

The concentration dependence of the viscosity can be obtained from the result for the intrinsic viscosity. In dilute solutions the viscosity can be expanded as $\eta = \eta_0(1 + c[\eta] + \cdots)$, where η_0 is the solvent viscosity. The intrinsic viscosity is a specific volume, so when the concentration of chains approaches $C^* \sim 1/[\eta]$, the solution is *semidilute*, i.e., branched polymers just fill the entire volume of the solution. (Note that the semidilute crossover concentration goes to zero as the gel point is approached.) If we quench a chemically gelling solution before it gels and dilute that solution to C^* the viscosity should be independent of the average molecular weight of the branched polymers. Thus for $C \gg C^*$ we write the scaling relation $\eta \sim (C/C^*)^x \sim (C[\eta])^x$. If we use $[\eta] \sim \epsilon^{-L}$ $[L = dD\nu(D_s^{-1} - D^{-1})]$, then from the constraint $\eta \sim \epsilon^{-k}$ $(C = 1)$ we obtain the concentration dependence

$$\eta \sim (C[\eta])^{k/L}, \quad C \gg [\eta]^{-1} \ . \tag{18}$$

Once again we can use the Flory-type arguments for the fractal dimensions $[D = (d+2)/2,\ D_s = 2(d+2)/5]$, along with the Rouse and Zimm limits for k to obtain the inequality $0 \le k/L \le 2(6-d)/d$. In the Rouse limit this gives the experimental prediction $\eta \sim C^2 M_w^{3/4}$.

Before leaving this topic we should point out a formulation of the viscosity problem that illustrates another connection to scaling in semidilute monodisperse linear polymer solutions. Percolation is a random model, so there are no spatial correlations larger than a monomer. However, when a solvent is added this introduces a spatial correlation length[34] ξ_s. In analogy with linear polymer solutions[22] we define a concentration blob as a domain of size ξ_s. On length scales smaller than ξ_s clusters are swollen and correlations within a cluster are described by the fractal dimension D_s, and on larger length scales single-cluster correlations are described by the dimension D. Since the spatial correlation length depends on a power of the concentration we can write a scaling law of the form $\eta \sim \epsilon^{-k}/\xi_s^x$, which applies when $\xi_s \ll \xi^{D/D_s}$, where ξ^{D/D_s} is the correlation length *at infinite dilution*. The result $x = kD_s/\nu D$ can then be obtained by applying the constraint that at $\xi_s = \xi^{D/D_s}$ (i.e., $C = C^*$) the viscosity is molecular weight independent, so $\eta \sim \epsilon^0$.

The viscosity can now be expressed in terms of our two length scales as $\eta \sim (\xi^D/\xi_s^{D_s})^{k/D\nu}$. This has a simple physical interpretation: ξ^D is just M_z, the mass of a typical cluster, and $\xi_s^{D_s} = g$, the mass within a concentration blob. The ratio M_z/g is the number of concentration blobs within a *typical* cluster N_{blob}. Thus the viscosity depends on this single parameter through

$$\eta \sim N_{\text{blob}}^{k/D\nu} \ . \tag{19}$$

Once again we have a striking analogy to entangled linear polymer solutions, where the viscosity is a power of the number of concentration blobs.[22] This result has the correct limiting behaviors: at C^*, $N_{\text{blob}} = 1$, and the viscosity is independent of ϵ; at $C = 1$, $N_{\text{blob}} \sim M_z$ so $\eta \sim \epsilon^{-k}$. Finally, if we once again take the Rouse limit with $D = (d+2)/2$ we find $\eta \sim N_{\text{blob}}^{(6-d)/(d+2)}$; this gives $\eta \sim N_{\text{blob}}^{3/5}$ in $d = 3$ and a logarithmic divergence in the mean-field limit.

IX. DISCUSSION

We will now summarize some of the experimental and theoretical work in the literature. We will start with the elastic modulus, then discuss the viscosity, and finish with the viscoelastic properties.

de Gennes developed a clever analogy between gelation and electrical networks. Using a scalar form of the elasticity de Gennes was able to show that the elastic modulus of a gel should scale as the growth of conductivity in a random resistor-insulator network.[22] Computer simulations of resistor networks give[32] $z = 1.94 \pm 0.1$, in disagreement with our prediction $z = d\nu = 2.67 \pm 0.01$. In the mean-field limit, however, both of these theories give $z = 3$. The resistor analogy has been criticized since it is necessary to assume a form of the elasticity that is not rotationally invariant. By including a bond-bending term in the network energy Kantor and Webman[35] have obtained the estimate $z \geq d\nu + 1 = 3.67 \pm 0.01$.

There are several experimental studies of the elasticity of gels. In 1979 Gordon *et al.*[28] studied triacetic acid decamethylene glycol–benzene polycondensates and found mean-field behavior ($z = 3$). Early studies by Adam *et al.*[29,30] gave $z = 2.1 \pm 0.3$ for radical copolymerization and 3.2 ± 0.6 for polycondensation. More refined measurements by Adam *et al.*[31] gave 3.2 ± 0.5 for polycondensation. These studies have led Adam to question the universality of the mechanical properties, although some of the difficulties may be due to defining the width of the critical regime.

Finally, Adam *et al.*[31] noticed an interesting feature of gels: When polycondensate gels were prepared by end linking high-molecular-weight polymers, no clear scaling of the modulus was observed near p_c. Perhaps when long chains are gelled one suppresses the critical behavior to a small, experimentally inaccessible regime near the critical point.

de Gennes has also proposed an analogy between the divergence of the viscosity and the divergence in the conductivity in a random superconductor-resistor network.[36] Simulations of superconductivity show that this analogy gives the prediction[37] $k = 0.75 \pm 0.04$. We recall that our limits on k are $0 \leq k \leq 1.35$. Experimental measurements by Adam *et al.*[29,30] on both polycondensates and on radical copolymerization gave $k = 0.78 \pm 0.05$. Later work by Adam *et al.*[31] on polycondensates gave $k = 0.8 \pm 0.1$. However, measurements by Colby *et al.*[38] on silica gels gave $k = 1.3 \pm 0.2$ and Martin *et al.*[7] obtained $k = 1.5 \pm 0.2$ from an *indirect* interpretation of quasielastic light-scattering data. Finally, Martin *et al.*[39] found $k = 1.4 \pm 0.2$ for epoxy resins. Although the situation is uncertain, several of these results are close to the upper limit of k, suggesting a Rouse melt.

This now brings us to the more complex discussion of the viscoelastic exponent Δ. If the de Gennes values of the exponents z and k, obtained from simulations, are substituted into $D = z/(z+k)$, we obtain $\Delta = 0.72 \pm 0.02$. This number is within the limits we have obtained, $0.66 \leq \Delta \leq 1$. The first experimental work to illustrate the scaling of the viscoelastic properties near the gel point was published by Chambon and Winter.[1] These studies demonstrated that in end-linked polydimethylsiloxane gels the viscoelastic exponent is 0.5. These gels were called stoichiometric, since they had sufficient cross linker to end link every chain in the solution. This means these gels had much more cross linker than that necessary to form a gel. When the amount of cross linker was reduced, a larger value of $\Delta = 0.58$ was observed.[2] These studies were somewhat complicated by the fact that these gels were made of long polydisperse interlinking chains, of weight-average molecular weight 22 000. Long chains have the effect of reducing the critical regime and of introducing relaxation times for the interlinking chains themselves. These interlinking chain modes taken alone give a power decay in $G(t)$ with an exponent of 0.5.

Chambon and Winter[3] also studied polyurethanes with much shorter interlinking chains ($M_n = 454$, 965, and 2018). With excess cross linker (at the gel point) it was again found that $\Delta = 0.5$. However, it was found that when the cross-linker density was reduced to just that necessary to form a gel, the value $\Delta = .66$ was obtained.[4] Durand *et al.*[5] also studied polyurethanes with low amounts of cross linker and found $\Delta = 0.70 \pm 0.02$. On the other hand, Martin *et al.*[39] studied epoxy resins (diglycidyl ether of bisphenol A, cross linker diethanolamine) and found $\Delta = 0.70 \pm 0.05$, but in this case there *was* an excess of cross linker at the gel point.

Thus in some systems with excess cross linker at the gel point a low value of $\Delta = 0.5$ is found, but with low amounts of cross linker the dynamical exponent appears to be approximately $\frac{2}{3}$. One point should be clarified: In the experimental literature gels are called stoichiometric if there is sufficient cross linker that in the *fully cured rubber* all cross linker is exhausted. This gives an excess of unreacted cross linker at the gel point. This should be distinguished from the case where only sufficient cross linker is introduced to form a gel. In this case the cross linker is fully reacted at the gel point, so we will refer to this as *stoichiometric* at the *gel point.* In the following it is useful to think of the cross linkers as occupying sites on a lattice, with the interlinking chains forming the bonds. Thus if the system is stoichiometric at the gel point, the cross linkers (with their range of interaction given by the radius of the interlinking chains) barely site percolate.

In the presence of excess cross linker at the gel point, certain complications can occur. For example, it is known that making end-linked polyurethanes with isocyanates causes the rapid formation of difunctional bonds, giving a bath of long linear polymers, that then slowly cross link to form a gel. This occurs because of a large activation energy to form a third bond at the isocyanate. Thus in the presence of an excess of cross linker it is possible to form very long linear chains before the isocyanates bridge a third time to form a gel. These long interlinking linear chains would contribute Rouse modes to the relaxation and at nonvanishing frequency would tend to reduce Δ to 0.5. Additionally, in some polyurethanes there is a significant incompatibility between the cross linker and the chains. In the presence of large amounts of cross linker this can cause microphase separation into isocyanate-rich domains, which then form *physical* cross links. Thus it would seem that it is best to minimize the amount of cross linker in order to make comparisons to the percolation theory.

On the other hand, if the amount of cross linker is reduced to be stoichiometric at the gel point, linear chain formation is suppressed, and the system closely resembles percolation. This is simply because no difunction cross links remain in the fully reacted system. Thus the possibility of interfering Rouse modes is suppressed, and the experimental results are closer to the percolation model given here.

X. CONCLUSIONS

From the initial assumption that the relaxation times in a single-branched polymer can be scaled by the longest time, R^2/D_t, we have been able to derive a theory for the viscoelasticity and mechanical properties of a gel near the sol-gel transition. The viscoelastic functions are found to be the power laws $G(t) \sim t^{-\Delta}$, $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$, and $H(\tau) \sim \tau^{-\Delta}$, where $\Delta = d\nu/(d\nu + k)$. Two divergent relaxation times are found near the gel point. The average relaxation time $\langle \tau \rangle$ scales as the viscosity, and the longest relaxation time τ_z scales as the viscosity times the steady-state creep compliance J_e^0. We set the bounds $1 \geq \Delta \geq 2d/(d+6)$ on the viscoelasticity exponent. Experiments often give numbers close to the lower bound of this estimate.

It is predicted that below the gel point the long-time tail of $G(t)$ should be described by a stretched exponential with an exponent of $D_s/(D_s + d)$. Using the swollen percolation dimension of 2 ($d = 3$) we obtain the prediction $\ln G(t) \sim -(t/\tau_z)^{0.4}$ for $t \gg \tau_z$.

The exponent $d\nu$ describes the growth of the elastic shear modulus, so E is just the density of correlation blobs kT/ξ^d. Numerically this is $E \sim \epsilon^{2.7}$, which is in good agreement with experimental data, that typically give an exponent near 3. We observe that the inverse equilibrium steady-state creep compliance is the critical point counterpart of E, and so diverges with the same exponent on the opposite side of the critical point. It is found that the viscosity and modulus are related through $\eta \sim \tau_z E$ although these divergences occur on opposite sides of the critical point.

We set limits on the viscosity divergence: The exponent k has the bounds $0 \leq k/\nu \leq (6-d)/2$. In three dimensions this is $0 \leq k \leq 1.35$ and in the mean-field limit ($d = 6$) $k = 0$. Thus the viscosity does not diverge in the mean-field theory. The latter conclusion is also found in the superconducting network analogy of de Gennes. Again, experimental data support these limits, with some of the data being near the upper limit. This would imply that a branched polymer melt is a Rouse fluid.

Finally, it is predicted that the viscosity varies as $\eta \sim C^2 M_w^{3/4}$, where C is the concentration of a semidilute branched-polymer solution. We note that this viscosity can be expressed as a power of the number of concentration blobs in a typical cluster, in analogy with semidilute linear polymer solutions. We expect to see quite a bit of experimental work emerging in this area in the future, so the value and limitations of this scaling approach should become apparent.

Note added in proof. By an alternate method Cates[40] has established the limits $0.62 \leq \Delta \leq 1$.

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