Elastic Modulus and Equilibrium Swelling of Near-Critical Gels

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Received January 10, 1994®

ABSTRACT: Scaling ideas are used to predict the modulus G_0 of gels, just above the point of incipient gel formation, in the reaction bath as a function of the proximity to the gel point ϵ. The concentration dependence of the modulus when the gel is diluted in a good solvent is also calculated and used to predict the maximum swelling Q, obtained from the gel swollen at equilibrium with pure solvent. The Ginzburg criterion separates the critical ($\epsilon < \epsilon_G$) and mean-field ($\epsilon > \epsilon_G$) percolation regimes. We derive a new criterion for entanglement ϵ_E, which leads us to expect three regimes of behavior. Close to the gel point (for $\epsilon < \epsilon_G$) critical percolation applies to an unentangled gel: $G_0 \sim \epsilon^{2.6}$ and $Q \sim \epsilon^{-1.1}$. For $\epsilon_G < \epsilon < \epsilon_E$ we predict a mean-field unentangled regime with $G_0 \sim \epsilon^3$ and $Q \sim \epsilon^{-8/5}$. For $\epsilon > \epsilon_E$ entanglements raise the modulus and restrict the swelling of the mean-field gels, with $G_0 \sim \epsilon^{14/3}$ and $Q \sim \epsilon^{-13/5}$.

1. Introduction

The modulus and equilibrium swelling of gels have been studied for over 50 years.[1-3] We start with two crucial early ideas: (1) The modulus arises from the energy stored by elastically active strands.[1,2] (2) Swelling equilibrium is determined by minimizing a free energy with osmotic and elastic contributions.[1,3] These ideas are combined with modern notions about semidilute solutions, entanglement formation, and percolation to calculate the modulus of gels in the reaction bath. For unentangled gels (section 2) this leads to predictions in the critical and mean-field regimes that are already known in the literature.[4-7] In section 3 we derive a new criterion for trapped entanglements between network strands and a new prediction for the modulus of entangled gels.

Following ideas of Panyukov,[8] we derive the concentration dependence of modulus and equilibrium swelling for unentangled mean-field gels in section 4. We then briefly discuss the prediction of Daoud et al.[9] for the swelling of (unentangled) critical gels in section 5. In section 6 we derive new predictions for the concentration dependence of modulus and equilibrium swelling for entangled gels. We discuss some common features in section 7.

2. Modulus of Unentangled Gels in Their Preparation State

We consider gels made by cross-linking precursor chains of N monomers at the reaction volume fraction ϕ_0 in a good solvent. We assume this reaction to be instantaneous, so that no microphase separation occurs.[10] We restrict ourselves to cross-linking extents that result in many blobs between cross-links[11] so that both before and after reaction, the precursor chains are random walks of blobs of size ξ_0, each blob comprising a linear chain of g_0 monomers of size b. The standard scaling for good-solvent semidilute solution applies.[10]

$$\xi_0 \cong b\phi_0^{-3/4} \tag{1}$$

$$g_0 \cong \phi_0^{-5/4} \tag{2}$$

The end-to-end distance of the starting chains is determined as a random walk of these blobs.

$$R_0 \cong \xi_0(N/g_0)^{1/2} \cong bN^{1/2}\phi_0^{-1/8} \tag{3}$$

The reaction is assumed to occur randomly and is stopped at an extent of reaction p beyond the gel point ($\epsilon \equiv (p-p_c)/p_c > 0$, where p_c is the critical extent of reaction at the gel point). Well beyond the gel point, the size of a gel strand (correlation length of the gel) R_0^*, the number of monomers in the (branched) gel strand N^*, and the gel fraction P_{gel} are known from mean-field percolation theory.[12]

$$R_0^* \cong R_0\epsilon^{-1/2} \tag{4}$$

$$N^* \cong N\epsilon^{-2} \tag{5}$$

$$P_{gel} \cong \epsilon \tag{6}$$

Strictly speaking, R_0 and N should be the (average) size and number of monomers in linear sections between branch points in the network. However, for scaling relations near the gel point, the distinction between precursor chains and linear sections between branch points is unimportant.

At $\epsilon \cong 1$, essentially all polymers have attached to the gel ($P_{gel} \cong 1$; see eq 6). In this paper we consider near-critical gels, meaning that $0 < \epsilon < 1$. Beyond $\epsilon \cong 1$, the properties of networks are discussed in our companion paper.[13]

As with other phase transitions, closer to the gel point the mean-field theory no longer applies. The Ginzburg criterion[14] has been calculated as the point ϵ_G where mean-field theory becomes inconsistent with itself.

$$\epsilon_G \cong (N/g_0)^{-1/3} \cong N^{-1/3}\phi_0^{-5/12} \tag{7}$$

For $\epsilon < \epsilon_G$ critical percolation theory is valid, while $\epsilon > \epsilon_G$ is the mean-field regime. It is useful to define R_G, N_G, and P_G as the size of the gel strand, the number of monomers in the gel strand, and the gel fraction, respectively, at the Ginzburg point ϵ_G.

$$R_G \cong R_0\epsilon_G^{-1/2} \tag{8}$$

$$N_G \cong N\epsilon_G^{-2} \tag{9}$$

$$P_G \cong \epsilon_G \tag{10}$$

In the critical regime, mean-field statistics effectively apply up to the length scale R_G and critical statistics apply

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® Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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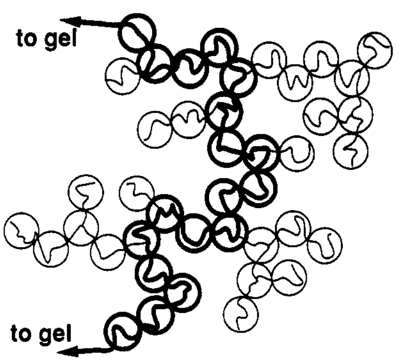

Figure 1. Schematic representation of a gel strand showing backbone (thick chain) and appendages (thin chain). Blobs are denoted as circles.

Table 1. Critical Exponent Predictions[12,15]

	ν	σ	β	τ	c	$\beta + 1/\sigma$
critical percolation	0.88	0.46	0.43	2.2	1.3_4	2.6
mean-field percolation	$^1/_2$	$^1/_2$	1	$^5/_2$	2	3

on larger length scales. This results in power laws analogous to eqs 4–6 with different exponents and prefactors in powers of ϵ_G that ensure crossover between the two regimes at the Ginzburg point.

$$R_0^* \cong R_G(\epsilon/\epsilon_G)^{-\nu} \cong R_0{\epsilon_G}^{\nu-1/2}\epsilon^{-\nu} \qquad (11)$$

$$N^* \cong N_G(\epsilon/\epsilon_G)^{-1/\sigma} \cong N{\epsilon_G}^{1/\sigma-2}\epsilon^{-1/\sigma} \qquad (12)$$

$$P_{\text{gel}} \cong P_G(\epsilon/\epsilon_G)^{\beta} \cong {\epsilon_G}^{1-\beta}\epsilon^{\beta} \qquad (13)$$

Here, ν, $1/\sigma$, and β are critical exponents (see Table 1). Note that throughout the paper we use the rational values of mean-field exponents and use Greek letters to denote critical exponents.

We divide the gel strand of N^* monomers into a backbone of N_{bb} monomers and $N^* - N_{\text{bb}}$ appendage monomers, as depicted in Figure 1. This separation is necessary because only the backbone bears stress at steady state and thus contributes to the modulus. Backbone monomers can be easily distinguished from appendage monomers, as the backbone monomers are connected to the infinite gel structure by at least two independent paths,[16] while appendage monomers are only connected to gel by one path (see Figure 1). The backbone is a fractal object.

$$N_{\text{bb}} \cong N\begin{cases}(R_G/R_0)^2(R_0^*/R_G)^c & \epsilon < \epsilon_G\\ (R_0^*/R_0)^2 & \epsilon > \epsilon_G\end{cases} \cong N\begin{cases}{\epsilon_G}^{\nu c-1}\epsilon^{-\nu c} & \epsilon < \epsilon_G\\ \epsilon^{-1} & \epsilon > \epsilon_G\end{cases} \qquad (14)$$

The connectivity exponent c is also denoted $d_{\min}$ or d_{chem} in the fractal literature.[12,17] Its value is known for both critical percolation and mean-field (see Table 1). We have used the mean-field value of $c = 2$ in eq 14 ($c = 2$ means the backbone is a simple random walk). The volume fraction of backbone ${\phi_0}^{\text{bb}}$ is

$${\phi_0}^{\text{bb}} \cong P_{\text{gel}}\phi_0 N_{\text{bb}}/N^* \cong \phi_0\begin{cases}{\epsilon_G}^2(\epsilon/\epsilon_G)^{\beta-\nu c+1/\sigma} & \epsilon < \epsilon_G\\ \epsilon^2 & \epsilon > \epsilon_G\end{cases} \qquad (15)$$

For unentangled backbones, the modulus in the reaction bath is simply the number density of backbones times kT, because each backbone can store kT of elastic energy.

$$G_0 \cong \frac{{\phi_0}^{\text{bb}}}{b^3N_{\text{bb}}}kT \cong \frac{\phi_0 kT}{b^3N}\begin{cases}{\epsilon_G}^{3-\beta-1/\sigma}\epsilon^{\beta+1/\sigma} & \epsilon < \epsilon_G\\ \epsilon^3 & \epsilon > \epsilon_G\end{cases} \qquad (16)$$

Note that[12] $\beta + 1/\sigma = (\tau - 1)/\sigma$, which is exactly 3 for mean-field and roughly 2.6 for critical percolation (see Table 1). These results for the growth of modulus beyond the gel point have been derived previously in the literature[4–7] and are quite consistent with experiments on chemical gels prepared by step growth processes.[18–20] Gordon[18] reports $G \sim \epsilon^{3.1}$, Adam[19] observes $G \sim \epsilon^{3.2\pm0.5}$, and we[20] have recently found $G \sim \epsilon^{3.0\pm0.7}$. The modulus predicted by eq 16 is independent of the fractal dimension of the backbone because there is one backbone per network strand (${\phi_0}^{\text{bb}}/N_{\text{bb}} \cong P_{\text{gel}}\phi_0/N^*$).

3. Modulus of Entangled Gels in Their Preparation State

In certain circumstances, the backbones of network strands can entangle with one another. Such entanglements are permanently trapped when the network is formed and thus contribute to the modulus.[21] Appendages can form entanglements with backbones, other appendages, or sol species, but all appendage entanglements are temporary in that they can disentangle by arm-retraction processes and thus do not contribute to the terminal modulus.

Since backbones do not overlap in the critical percolation regime, we only need to consider entanglement effects in the mean-field regime. The mesh size of trapped entanglements between backbones (tube diameter) requires careful consideration. We define an entanglement strand backbone as the (linear) section of a backbone between trapped entanglements. Since we are in good solvent, if all monomers were parts of backbones, the backbone tube diameter would be given by the standard good-solvent scaling result[10] $a' \cong a_1\xi_0/b \cong a_1\phi_0^{-3/4}$, where a_1 is the tube diameter in a melt of long chains (at $\phi_0 = 1$). However, a' counts both permanent and temporary entanglements. Actually, only a small fraction of monomers are parts of the linear backbones, so we must develop a new criterion for permanent (trapped) entanglements.

Depending on reaction bath concentration, precursor chain length, and extent of reaction, the section of gel strand making up an entanglement strand can be either linear or branched. The key simplifying aspect is that the fractal dimension of the backbone for $\epsilon > \epsilon_G$ is always 2 on length scales larger than the screening length,[22] because excluded volume is screened. The situation is analogous to a linear chain in a Θ solvent, with ξ_0 the effective monomer size, the number of blobs in the backbone N_{bb}/g_0 being the effective degree of polymerization, and blobs of sol and appendage monomers being effective Θ solvent. The renormalized volume fraction of chains is ${\phi_0}^{\text{bb}}/\phi_0$, and we apply the standard Θ-solvent scaling for entanglement,[23] which assumes a fixed number of binary contacts per volume ${a_0}^3$ determine an entanglement.

$$a_0 \cong \frac{a_1}{b}\xi_0\left(\frac{\phi_0}{{\phi_0}^{\text{bb}}}\right)^{2/3} \cong \frac{a_1}{b}\xi_0\epsilon^{-4/3} \qquad (17)$$

The second result was obtained from the mean-field case of eq 15.

For entanglement to be important, the tube diameter must be smaller than the size of a gel strand ($a_0 < R_0^*$).

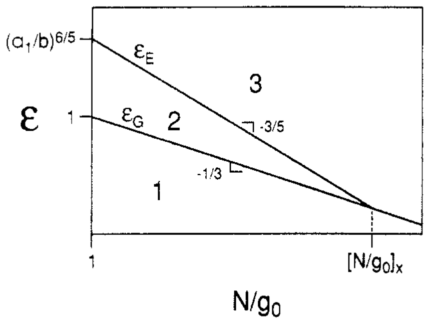

Figure 2. Phase diagram for the preparation state modulus in the parameter space of relative extent of reaction and number of blobs in the precursor chain. The solid lines are eqs 7 and 18, which separate the three regimes: (1) unentangled critical gels, (2) unentangled mean-field gels, and (3) entangled mean-field gels. Scales are logarithmic.

From the above we can write this criterion as $\epsilon > \epsilon_{\mathrm{E}}$.

$$\epsilon_{\mathrm{E}} \cong \left(\frac{a_1}{b}\right)^{6/5}\left(\frac{N}{g_0}\right)^{-3/5} \cong \left(\frac{a_1}{b}\right)^{6/5}{\epsilon_{\mathrm{G}}}^{9/5} \qquad (18)$$

Note that the ratio a_1/b is typically 5, so $\epsilon_{\mathrm{E}} > \epsilon_{\mathrm{G}}$ if the number of blobs per precursor chain is less than $[N/g_0]_x \cong 10^3$. Such chains are rather long—usually $N/g_0 < [N/g_0]_x$—and thus there is an unentangled mean-field regime with $\epsilon_{\mathrm{G}} < \epsilon < \epsilon_{\mathrm{E}}$. Experiments[24] indicate that there is a prefactor of order 0.1 in eq 7 ($\epsilon_{\mathrm{G}} \cong 0.1(N/g_0)^{-1/3}$), making $\epsilon_{\mathrm{E}} > \epsilon_{\mathrm{G}}$ for even longer chains (for $N/g_0 < [N/g]_x \cong 10^7$). Figure 2 plots eqs 7 and 18 in the parameter space of ϵ and N/g_0, which is then divided into three regimes.

(1) For $\epsilon < \epsilon_{\mathrm{G}}$ the gels are unentangled with critical percolation statistics and the modulus $G \sim \epsilon^{2.6}$. (2) For $\epsilon_{\mathrm{G}} < \epsilon < \epsilon_{\mathrm{E}}$ the gels are again unentangled, but with mean-field statistics, and $G \sim \epsilon^3$. (3) For $\epsilon > \max\{\epsilon_{\mathrm{E}},\epsilon_{\mathrm{G}}\}$ we again have mean-field statistics, but the gels have trapped entanglements along their backbones. The number of monomers in an entanglement strand backbone is determined as a random walk of blobs.

$$N_{\mathrm{e}} \cong g_0(a_0/\xi_0)^2 \cong \phi_0 {a_0}^2 \xi_0 b^{-3} \cong (a_1/b)^2 {\phi_0}^{-5/4} \epsilon^{-8/3} \qquad (19)$$

Simple algebra shows that $N_{\mathrm{e}} = N_{\mathrm{bb}}$ (eq 14) at $\epsilon = \epsilon_{\mathrm{E}}$. The entanglement-dominated modulus is simply kT per entanglement strand.

$$G_0 \cong \frac{{\phi_0}^{\mathrm{bb}}}{b^3 N_{\mathrm{e}}} kT \cong \frac{kT}{{a_0}^2 \xi_0}\epsilon^2 \cong \frac{kT}{{a_1}^2 b}{\phi_0}^{9/4}\epsilon^{14/3} \qquad \epsilon > \max\{\epsilon_{\mathrm{E}},\epsilon_{\mathrm{G}}\} \quad (20)$$

We show modulus predictions for gels in their state of preparation in Figure 3 for four examples. All are cross-linked without solvent ($\phi_0 = 1$) using chain lengths of N = 1, 10, 100, and 1000. For $N = 100$ (solid curve), $\epsilon_{\mathrm{G}} \cong 0.22$ and $\epsilon_{\mathrm{E}} \cong 0.44$, so all three possible regimes are present. (1) As the reaction proceeds beyond the gel point, the modulus initially increases slowly ($G \sim \epsilon^{2.6}$, eq 16 with $\epsilon < \epsilon_{\mathrm{G}}$), as the network strands of critical percolation do not overlap. (2) Beyond the Ginzburg point but below the entanglement threshold ($\epsilon_{\mathrm{G}} < \epsilon < \epsilon_{\mathrm{E}}$), the network strands overlap and mean-field statistics apply, resulting in a slightly stronger modulus scaling ($G \sim \epsilon^3$, eq 16 with $\epsilon > \epsilon_{\mathrm{G}}$). (3) Beyond the entanglement threshold, the modulus is determined by trapped entanglements between backbones and increases much faster ($G \sim \epsilon^{14/3}$, eq 20). Entanglements are formed between network strand backbones much faster than the strands themselves are formed because overlap of strands increases with reaction extent.[25]

More typical are examples with fewer than three regimes. For $N = 1$ (dash–dotted curve), $\epsilon_{\mathrm{G}} \cong 1$ and the entire near-critical region ($\epsilon < 1$) falls in the critical percolation regime, with modulus scaling as $G_0 \sim \epsilon^{2.6}$. For $N = 10$ (dashed curve), $\epsilon_{\mathrm{G}} \cong 0.46$ and $\epsilon_{\mathrm{E}} > 1$, so there are two regimes (critical and mean-field unentangled) with the modulus scaling as $G \sim \epsilon^{2.6}$ for $\epsilon < \epsilon_{\mathrm{G}}$ and $G \sim \epsilon^3$ for $\epsilon > \epsilon_{\mathrm{G}}$. For $N = 1000$, $\epsilon_{\mathrm{G}} \cong \epsilon_{\mathrm{E}} \cong 0.10$ and the only two regimes are critical (with $G \sim \epsilon^{2.6}$) and mean-field entangled (with $G \sim \epsilon^{14/3}$).

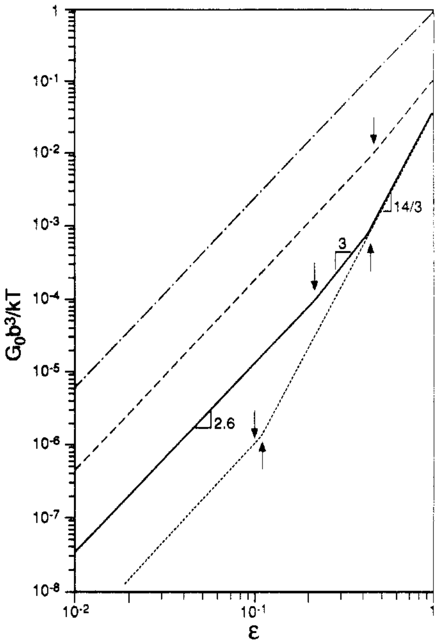

Figure 3. Normalized modulus in the reaction bath as a function of relative extent of reaction (cross-linked at $\phi_0 = 1$) for four different chain lengths: $N = 1000$ (dotted line), $N = 100$ (solid line), $N = 10$ (dashed line), and ($N = 1$) (dash–dotted line). Ginzburg points ϵ_{G} are shown as down-pointing arrows, and entanglement points ϵ_{E} are shown as up-pointing arrows. $N_{\mathrm{e}} \cong (a_1/b)^2 = 25$.

4. Swelling of Unentangled Mean-Field Gels: $\epsilon_{\mathrm{G}} < \epsilon < \epsilon_{\mathrm{E}}$

We consider the swelling of gels, prepared as described in section 2, with the sol fraction removed and good solvent added to make a polymer volume fraction ϕ. The free energy of swollen gels has two contributions:[3] an osmotic part F_{os} promoting swelling and an elastic part F_{el} restricting swelling. The osmotic free energy term is kT per blob[10] of size ξ.

$$F_{\mathrm{os}} \cong \frac{b^3 kT}{\xi^3} \qquad (21)$$

Following Panyukov,[8] the elastic free energy term is kT per strand times the quadratic Hookean stretching of the strand relative to its Gaussian state.[13]

$$F_{\mathrm{el}} \cong b^3 kT \nu_x \left(\frac{\lambda {R_0}^*}{R^*}\right)^2 \qquad (22)$$

Here, ν_x is the number density of network strands, λ is the linear expansion factor ($\lambda = (P_{\mathrm{gel}}\phi_0/\phi)^{1/3} \cong (\phi_0\epsilon/\phi)^{1/3}$ assuming cross-links move affinely during swelling), and R^* is the Gaussian size that unconnected strands (of N^* monomers) would have at volume fraction ϕ. As discussed in ref 13, eq 22 is essentially Hooke's law applied to each network strand, with spring constant kT/R^{*2}. The Gaussian unconnected strand size R^* is used because that is the fluctuation size arising from kT of thermal energy.[13]

The number of monomers in a backbone (N_{bb}) and the volume fraction of monomers in the gel that are parts of backbones (ϕ^{bb}/ϕ) do not change on swelling.

$$\frac{\phi^{\mathrm{bb}}}{\phi} = \frac{{\phi_0}^{\mathrm{bb}}}{P_{\mathrm{gel}}\phi_0} \cong \epsilon \tag{23}$$

This leads to the following expression for the number density of swollen network strands.

$$\nu_{\mathrm{x}} = \frac{\phi^{\mathrm{bb}}}{b^3 N_{\mathrm{bb}}} \cong \frac{\phi}{b^3 N}\epsilon^2 \tag{24}$$

To determine R^*, we must consider unconnected network strands at concentrations lower than the preparation state, where one must be careful to determine whether the blobs are still linear or branched. For $\phi > N^{-4/5}$ (the overlap concentration[10] for the linear strands), swollen blobs are made up of linear chains (i.e., linear blobs of size $\xi < R$, with g monomers per blob and $g < N$). The standard good-solvent semidilute solution results apply to the statistics of linear blobs.[10]

$$\xi \cong b\phi^{-3/4} \qquad g \cong \phi^{-5/4} \qquad \phi > N^{-4/5} \tag{25}$$

Beyond ξ, there are linear chains of blobs up to the length scale R, the swollen size of the primary chains.

$$R \cong \xi(N/g)^{1/2} \cong bN^{1/2}\phi^{-1/8} \qquad \phi > N^{-4/5} \tag{26}$$

The Gaussian unconnected strand size is then determined from the mean-field statistics of a branched polymer (a fractal of dimension $D = 4$ beyond the size of a linear chain R).

$$R^* \cong R(N^*/N)^{1/4} \cong b(N^*N)^{1/4}\phi^{-1/8} \qquad \phi > N^{-4/5} \tag{27}$$

On the other hand, if $\phi < N^{-4/5}$, swelling occurs to such an extent that there are many branch points inside a blob (i.e., branched blobs of size $\xi > R$) and the size of a primary chain is $R \cong bN^{3/5}$. The blob is made up of a branched assembly of g/N self-avoiding primary chains.

$$\xi \cong R(g/N)^{1/2} \qquad \phi < N^{-4/5} \tag{28}$$

The number of monomers in a blob, g, is still $\phi(\xi/b)^3$, because blobs are space-filling. Equation 28 leads to new relations for the size of a branched blob and the number of monomers in it.

$$\xi \cong bN^{-1/5}\phi^{-1} \qquad g \cong N^{-3/5}\phi^{-2} \qquad \phi < N^{-4/5} \tag{29}$$

The unconnected Gaussian strand size is once again determined by the mean-field statistics of a randomly branched fractal (with the primary unit being a branched blob of size ξ).

$$R^* \cong \xi(N^*/g)^{1/4} \cong bN^{*1/4}N^{-1/20}\phi^{-1/2} \qquad \phi < N^{-4/5} \tag{30}$$

As concentration is lowered, the blob size increases until the overlap concentration of the Gaussian strands is reached (where $g = N^*$ and $\xi = R^*$). Concentrations lower than the overlap concentration are not important in network swelling,[26] and it will turn out that $\xi \le R^*$ always.

Substituting the two values of R^* into eq 22 yields two regimes of behavior for the elastic part of the free energy, and hence the modulus G, of mean-field unentangled swollen gels.

$$G \cong \frac{F_{\mathrm{el}}}{b^3} \cong \frac{kT}{b^3}{\phi_0}^{5/12}\epsilon^{8/3}\begin{cases} N^{-2/5}\phi^{4/3} & \phi < N^{-4/5} \\ N^{-1}\phi^{7/12} & \phi > N^{-4/5} \end{cases} \tag{31}$$

Note that the crossover between the two regimes is smooth. The concentration exponent $^7/_{12}$ is also found for gels with $\epsilon > 1$,[13] but the exponent of $^4/_3$ is unique to near-critical gels. However, the pronounced swelling required to get into a regime of branched blobs for mean-field gels is only possible at very low concentrations (if at all), so the linear blob regime (with $G \sim \phi^{7/12}$) applies over most of the attainable concentration range for mean-field gels.

The equilibrium swelling Q is defined as the volume of the swollen gel in equilibrium with pure solvent divided by the volume of the dry gel (with sol phase and solvent removed), so Q is the reciprocal of the volume fraction ϕ in the fully swollen state. Q is determined by minimizing the total free energy with respect to concentration, and both branched and linear blobs give the same result.

$$Q \cong N^{3/5}{\phi_0}^{-1/4}\epsilon^{-8/5} \tag{32}$$

This result for equilibrium swelling of mean-field gels was originally derived by Panyukov.[8]

5. Swelling of Critical Gels: $\epsilon < \epsilon_G$

In the critical regime, permanent entanglements are not expected to be important[27] (because network strands do not overlap in the preparation state). Excluded volume in the preparation state is neither fully screened nor fully effective, and clusters of a given size are just at overlap, as discussed by Cates.[28] Since the affine assumption requires no disinterpenetration of strands on swelling, we expect critical gel strands to be at their overlap concentration in the fully swollen state as well. Thus the c^* theorem[10] predictions for swelling of critical gels[9] are identical to the affine predictions summarized below.

As in the mean-field gels, the concentration dependence of modulus for critical gels has different regimes of behavior depending on whether the blobs are linear or branched. The calculation of modulus proceeds in exactly the same manner as in section 4 (using eq 22) but using critical relations instead of the mean-field ones. This results in the following expression for the concentration dependence of modulus of critical gels.

$$G \cong \frac{F_{\mathrm{el}}}{b^3} \cong \frac{kT}{b^3}{\phi_0}^{5/12}\epsilon^{8/3}\left(\frac{\epsilon}{\epsilon_{\mathrm{G}}}\right)^{5/6\sigma}\begin{cases} N^{-2/5}\phi^{4/3} & \phi < N^{-4/5} \\ N^{-1}\phi^{7/12} & \phi > N^{-4/5} \end{cases} \tag{33}$$

For critical percolation, $G \sim \epsilon^{1.8}$. Note that the crossovers to the mean-field result (eq 31) are smooth, and both mean-field and critical have the same ϕ dependences for the modulus.

For the fully swollen state (in equilibrium with pure solvent) *the blobs are always branched*[29] in the critical regime. The osmotic free energy term is determined as kT per branched blob by combining eqs 21 and 29.

$$F_{\mathrm{os}}/kT \cong N^{3/5}\phi^3 \tag{34}$$

As in section 4, the equilibrium swelling Q is determined from minimization of the total free energy.

$$Q \cong N^{4/5}{\epsilon_{\mathrm{G}}}^{-1}\left(\frac{\epsilon}{\epsilon_{\mathrm{G}}}\right)^{-1/2\sigma} \qquad \epsilon < \epsilon_{\mathrm{G}} \tag{35}$$

For critical percolation $\sigma \cong 0.46$ (see Table 1), $Q \sim \epsilon^{-1.1}$, consistent with the predictions of Daoud et al.[9] and Panyukov.[8] Note that eqs 32 and 35 crossover smoothly at the Ginzburg point ϵ_{G}, where the equilibrium swelling is $Q_{\mathrm{G}} \cong N^{4/5}{\epsilon_{\mathrm{G}}}^{-1}$.

6. Swelling of Entangled Gels: $\epsilon > \epsilon_E$

Gels that have trapped entanglements in their preparation state (see section 3) will *maintain these trapped* entanglements when swollen. We derive the concentration-dependent modulus and equilibrium swelling of entangled gels in the same manner as in section 4, with entanglement strands being the effective network strands, as they were for the modulus in the preparation state (section 3), assuming the ends of entanglement strands are displaced affinely upon swelling. The elastic free energy term is similar to eq 22.

$$F_{\mathrm{el}} \cong b^3 kT \nu_{\mathrm{e}} \left(\frac{\lambda a_0}{a}\right)^2 \qquad (36)$$

Here, ν_{e} is the number density of entanglement strands (analogous to ν_{x}) and a is the Gaussian size of these entanglement strands at volume fraction ϕ, if they were unconnected (analogous to R^*). The number density of entanglement strands at any swelling concentration ϕ is

$$\nu_{\mathrm{e}} = \frac{\phi^{\mathrm{bb}}}{b^3 N_{\mathrm{e}}} \cong \frac{\phi\epsilon}{b^3 N_{\mathrm{e}}} \qquad (37)$$

Here, N_{e} is the number of monomers in the linear backbone of an entanglement strand (eq 19), and ϕ_{bb} is the volume fraction of backbones (eq 23). The Gaussian size of an unconnected entanglement strand a, like the Gaussian size of an unconnected network strand R^* in section 4, depends on whether the blobs are linear or branched. Whether the entanglement strand itself is linear or branched is of no consequence because the backbone of the entanglement strand is always a random walk of blobs. The calculation is fully analogous to section 4, and we merely give the result here.

$$a \cong bN_{\mathrm{e}}^{1/2} \begin{cases} N^{-3/10}\phi^{-1/2} & \phi < N^{-4/5} \\ \phi^{-1/8} & \phi > N^{-4/5} \end{cases} \qquad (38)$$

Simple algebra can show that $a = R^*$ (eqs 27 and 30) at the entanglement threshold $\epsilon = \epsilon_{\mathrm{E}}$ (using eqs 17–19). The elastic free energy, and hence the modulus, is obtained by substituting eqs 17, 37, and 38 into eq 36.

$$G \cong \frac{F_{\mathrm{el}}}{b^3} \cong \frac{kT}{b^3}\phi_0^{5/12}\epsilon^{8/3}\left(\frac{\epsilon}{\epsilon_{\mathrm{E}}}\right)^{5/3} \begin{cases} N^{-2/5}\phi^{4/3} & \phi < N^{-4/5} \\ N^{-1}\phi^{7/12} & \phi > N^{-4/5} \end{cases} \qquad (39)$$

As expected, this crosses over to eq 31 at the entanglement threshold ϵ_{E}.

The equilibrium swelling is determined by minimizing the total free energy, with the osmotic part being given by eq 21, keeping in mind that the blobs can be either linear (eq 25) or branched (eq 29).

$$Q \cong N^{3/5}\phi_0^{-1/4}\epsilon^{-8/5}\left(\frac{\epsilon}{\epsilon_{\mathrm{E}}}\right)^{-1} \cong \left(\frac{a_1}{b}\right)^{6/5}\phi_0^{-1}\epsilon^{-13/5} \qquad (40)$$

Note that this crosses over smoothly with eq 32 for the swelling of entangled mean-field gels at $\epsilon = \epsilon_{\mathrm{E}}$. Figure 4 shows the equilibrium swelling predictions for the four near-critical gel examples of Figure 3 (cross-linked at $\phi_0 = 1$). For $N = 100$ (solid curve) all three regimes of the phase diagram (Figure 2) are important ($\epsilon_{\mathrm{G}} \cong 0.22$ and $\epsilon_{\mathrm{E}} \cong 0.44$). (1) For $\epsilon < \epsilon_{\mathrm{G}}$ we have the critical regime (eq 35) with extensive gel swelling, where $Q \sim \epsilon^{-1/2\sigma}$ ($1/2\sigma \cong 1.1$). (2) For unentangled mean-field gels ($\epsilon_{\mathrm{G}} < \epsilon < \epsilon_{\mathrm{E}}$) swelling is smaller and given by eq 32, $Q \sim \epsilon^{-8/5}$. (3) Entangled gels ($\epsilon > \epsilon_{\mathrm{E}}$) swell even less, with $Q \sim \epsilon^{-13/5}$ (eq 40).

As with the reaction bath modulus (Figure 3), the other examples have fewer than three regimes. For $N = 1$ critical percolation is valid and $Q \sim \epsilon^{1.1}$. For $N = 10$ there are critical and mean-field unentangled regimes. For $N = 1000$ there are critical and mean-field entangled regimes.

The only experimental data for swelling of near-critical gels are for the polyester system of ref 24. This system is known to be in the crossover between critical and classical regimes (the apparent $\tau = 2.35 \pm 0.03$), and the modulus[20] is consistent with the predictions for unentangled gels ($G \sim \epsilon^{3.0\pm0.7}$). In Figure 5 we plot the equilibrium swelling data of ref 24 against the mass of the largest sol molecule (determined as M_{max}, the molecular weight corresponding to the peak in the light scattering detector in a size exclusion chromatography experiment). Least-squares regression (solid line) determines $Q \sim M_{\mathrm{max}}^{0.60\pm0.05}$. Since $M_{\mathrm{max}} \sim \epsilon^{-1/\sigma}$ and $0.46 \leq \sigma \leq 0.50$ (see Table 1), we can conclude that $Q \sim \epsilon^{-1.25\pm0.15}$ (95% confidence intervals). This is in excellent agreement with the scaling theory expectation for unentangled gels in the crossover between critical percolation ($Q \sim \epsilon^{-1.1}$) and mean-field ($Q \sim \epsilon^{-1.6}$).

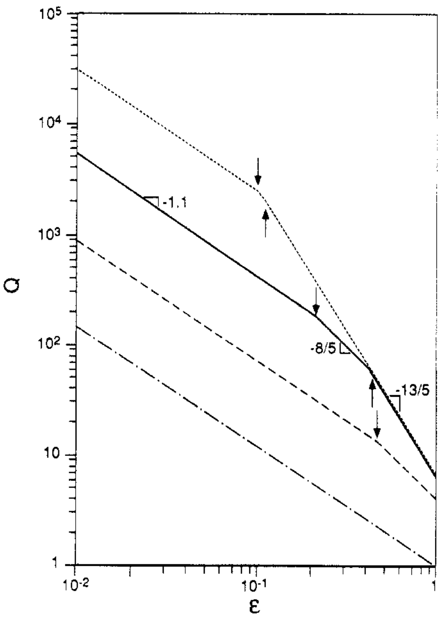

Figure 4. Equilibrium swelling ratio as a function of relative extent of reaction for $\phi_0 = 1$ with four different chain lengths: $N = 1000$ (dotted line), $N = 100$ (solid line), $N = 10$ (dashed line), and $N = 1$ (dash–dotted line). Ginzburg points ϵ_{G} are shown as down-pointing arrows, and entanglement points ϵ_{E} are shown as up-pointing arrows. $N_{\mathrm{e}} \cong (a_1/b)^2 = 25$.

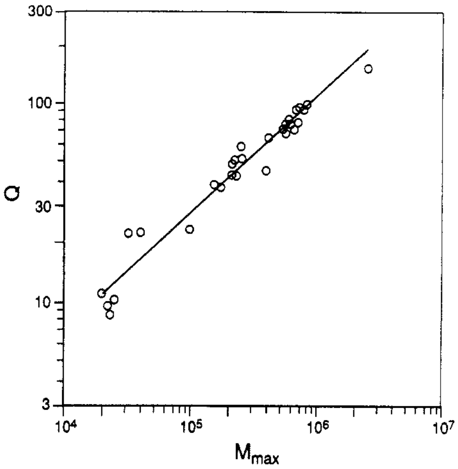

Figure 5. Equilibrium swelling as a function of largest molecular weight of the sol fraction for near-critical polyester gels (data from ref 24). Line is least-squares regression (see text).

In Figure 6 we plot the concentration dependence of modulus (in good solvent) for three near-critical gels with their sol fraction removed. The three examples are made in the melt ($\phi_0 = 1$) with $N = 100$, with the reaction stopped at three extents: $\epsilon = 0.1 < \epsilon_{\mathrm{G}}$, $\epsilon_{\mathrm{G}} < \epsilon = 0.3 < \epsilon_{\mathrm{E}}$, and $\epsilon = 1 > \epsilon_{\mathrm{E}}$. At $\epsilon = 0.1$ (dashed curve) the gel is in the critical regime and there are two concentration regimes for the modulus (eq 33). For $\phi > N^{-4/5}$ the blobs are linear with $G \sim \phi^{7/12}$, and for $\phi < N^{-4/5}$ the blobs are branched with $G \sim \phi^{4/3}$. At $\epsilon = 0.3$ (solid curve) the gel is in the mean-field unentangled regime, which again shows the two concentration regimes of branched and linear blobs (eq 31). At $\epsilon = 1$ (dotted curve) we have an entangled gel, with

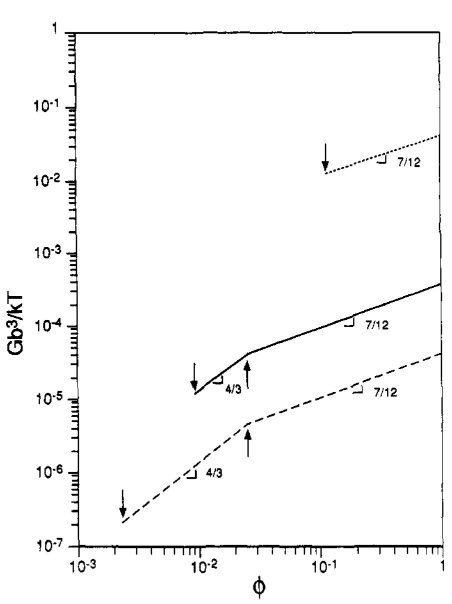

Figure 6. Concentration dependence of modulus for three near-critical gels in good solvent with the sol fraction removed. All three were prepared with $N = 100$, $N_e \cong (a_1/b)^2 = 25$, and $\phi_0 = 1$ but stopped at different extents of reaction: $\epsilon = 0.1$ (dashed curve), $\epsilon = 0.3$ (solid curve), and $\epsilon = 1$ (dotted curve). The fully swollen state ($\phi = Q^{-1}$) is indicated by down-pointing arrows. The overlap concentration of the linear chains ($\phi \cong N^{-4/5}$) is indicated by up-pointing arrows.

modulus given by eq 39, but swelling does not occur to a sufficient extent to get branched blobs ($Q < N^{4/5}$), so there is only one concentration regime (with linear blobs) and $G \sim \phi^{7/12}$. One should note that while it is possible for an entangled gel to be able to swell to a sufficient extent to get branched blobs, this scenario is rare. In most cases entangled gels should only exhibit one concentration regime (as shown in Figure 6).

7. Discussion

For both entangled and unentangled cases, at relative extents of reaction near unity (i.e., $\epsilon \cong 1$), the reaction bath modulus, the concentration-dependent modulus, and the equilibrium swelling predictions in mean-field cross over to those predicted in ref 13. For $\epsilon > 1$, the gels are no longer "near-critical", as the gel fraction is roughly unity. Thus ϵ dependence is only meaningful for $\epsilon < 1$. When $\epsilon_E > 1$ (see Figure 2) only two regimes occur in the near-critical range (dashed curves in Figures 3 and 4). Similarly, when $\epsilon_G = \epsilon_E$ (large N/g_0 in Figure 2), only two regimes occur (dotted curves in Figures 3 and 4).

For cases with $\epsilon_E > 1$, entanglement effects are *never* important (even in the regime of $\epsilon > 1$) because at $\epsilon = 1$ the network already has a strand length $N^* \cong N$ that is smaller than the entanglement spacing. When $\epsilon_E < 1$, all gels at a given ϕ_0 with $\epsilon = 1$ have the same modulus in the reaction bath (eq 20 with $\epsilon = 1$) and the same equilibrium swelling (eq 40 with $\epsilon = 1$) because both are dominated by trapped entanglements. The shortest network strands with entanglement domination at $\epsilon = 1$ occur when $\epsilon_E = 1$, corresponding to $N = N_e$ (given by eq 19). For $\epsilon_E < 1$, $N > N_e$ at $\epsilon = 1$, and entanglements continue to dominate well into the $\epsilon > 1$ regime as discussed in ref 13.

There is a simple relation between the equilibrium swelling and the modulus in the fully swollen state, because gels swell until the osmotic and elastic contributions to the free energy are equal.

$$G|_{\phi=1/Q} \cong \frac{kT}{b^3}\begin{cases} N^{3/5}Q^{-3} & Q > N^{4/5} \\ Q^{-9/4} & Q < N^{4/5} \end{cases} \tag{41}$$

The relation between swollen modulus and equilibrium swelling is independent of N if the blobs are linear ($Q < N^{4/5}$). The crossover to branched blobs occurs well inside the mean-field regime, and no change in behavior occurs at the Ginzburg point. Thus the relation between swollen modulus and equilibrium swelling is only sensitive to the state of the blobs at swelling equilibrium, and not the preparation state of the gel. This is because at swelling equilibrium, the modulus can be determined entirely from the osmotic part of the free energy, which is only sensitive to the state of the blobs (see eq 21).

There is also a simple relation between the dry modulus of the gel fraction (at $\phi = 1$ with the sol fraction removed) and the equilibrium swelling.

$$G|_{\phi=1} \cong \frac{kT}{b^3}Q^{-5/3} \tag{42}$$

This relation should be valid, provided that the deswelling of the network caused by removal of the sol fraction and any solvent in the reaction bath is not too severe. As discussed in ref 13, severe deswelling can cause changes in the configurations of network strands and thus alter the modulus prediction. However, if deswelling is not too severe, eq 42 should hold for any network (even for $\epsilon > 1$)[13] with the main assumption being affine displacement of junctions during swelling.

Moduli of swollen gels always have weaker ϵ dependences than the preparation state moduli. Comparison of these states is not trivial because the sol fraction is only present in the preparation state, and swelling can greatly alter the configuration of the network strands. For unentangled gels one may write the following expression for the ratio of preparation state modulus and modulus of a partially swollen gel (with the sol fraction removed).

$$\frac{G_0}{G} \cong \left(\frac{P_{\rm gel}\phi_0}{\phi}\right)^{1/3}\left(\frac{R^*}{R_0^*}\right)^2 \tag{43}$$

The first bracketed term in eq 43 is a simple affine concentration effect ($P_{\rm gel}\phi_0$ is the volume fraction of gel in the preparation state, and ϕ is the gel volume fraction in solution). The second term accounts for the difference between the preparation state strand size and the Gaussian strand size at volume fraction ϕ (for entangled gels eq 43 applies with a and a_0 replacing R^* and R_0^*). In mean-field, R^* and R_0^* have identical ϵ dependences, and thus the only ϵ dependence in eq 43 enters in the gel fraction ($G_0/G \sim P_{\rm gel}^{1/3} \sim \epsilon^{1/3}$ for both entangled and unentangled mean field). In the critical regime, $R_0^* \sim \epsilon^{-\nu}$, $R^* \sim N^{*1/4} \sim \epsilon^{-1/4\sigma}$, and $P_{\rm gel} \sim \epsilon^{\beta}$, making the ratio considerably more complicated ($G_0/G \sim \epsilon^{\beta+1/6\sigma}$).

8. Conclusions

The main new physics in this paper concerns entanglement trapping during the preparation of networks near the gel point. We assume that there are the same number of entanglements in gels as there are in semidilute solutions of long linear chains at the same concentration. We divide these entanglements into those that are permanently trapped (involving only backbones of network strands) and temporary ones (involving appendages and/or sol). We argue that the criterion for trapped entanglement formation is analogous to solutions of linear polymers in a Θ solvent and use a scaling conjecture that seems to be in good agreement with experiments on modulus and viscosity of semidilute Θ solutions.[23] We have envisaged the backbone blobs as forming the effective chain, with appendage blobs and sol blobs acting as effective Θ solvent (see Figure 1). Historically,[21] the trapping efficiency is described by the entanglement trapping factor T_e, with modulus being the sum of unentangled and entangled contributions (thereby representing the entanglement crossover as well).

$$G_0 \cong \nu kT + G_N{}^\circ T_e \qquad (44)$$

The first term is the affine prediction for the modulus without entanglement (eq 16) where ν is the number density of strands ($\nu = \phi_0{}^{bb}/(b^3 N_{bb})$). The second term is the contribution from entanglements, where $G_N{}^\circ$ is the plateau modulus of a solution of linear chains at volume fraction ϕ_0. The plateau modulus is given by standard scaling in good solvent[10] ($G_N{}^\circ \cong kT\phi_0{}^{9/4}/[a_1{}^2 b]$), so comparing with eq 20, we find our prediction for the trapping factor.

$$T_e \cong \begin{cases} \epsilon^{14/3} & \epsilon < 1 \\ 1 & \epsilon > 1 \end{cases} \qquad (45)$$

For $\epsilon > 1$, essentially all entanglements are trapped ones (this case is discussed in the accompanying paper[13]). Complete trapping at $\epsilon \cong 1$ is also evident in eq 17 for the (trapped) tube diameter because $a_0 \cong (a_1/b)\xi_0$ when all entanglements are trapped.

We predict three regimes of behavior for modulus in the reaction bath and equilibrium swelling. Close to the gel point critical percolation applies. Beyond the Ginzburg point, there is a regime where mean-field percolation applies and entanglements are not yet important (provided that the network strands are not too long). Further from the gel point, entanglements become important. The situation is quite analogous to semidilute Θ solutions of linear chains that are not too long, where there is a regime of semidilute-unentangled behavior separating the regimes of dilute solutions and entangled solutions.[23,30] For very long chains, these intermediate regimes disappear in both problems, but real polymers are not usually so long.

The unentangled predictions for modulus in the reaction bath[4-7] and swelling[8,9] appear to be quite consistent with available experiments.[18-20,24] The entangled predictions are new and need experimental testing. We hope this work will motivate new experiments on near-critical gels made from long-chain polymers, which should exhibit entanglement effects even for $\epsilon > 1$.

Acknowledgment. We thank S. V. Panyukov for discussions that led to profound changes in an earlier version of the manuscript.

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