a local scale (sizes comparable to the distance between crosslinks) segregation may take place, but this is expected to require higher reaction rates, and should occur at a point B' below B. These "microphase separations" are very important in practical fabrications of gels, but are still poorly understood.

(iii) At high concentrations $\phi > \phi_{c*}$ our model gives instant gelation: clearly in this regime, a more detailed model allowing for contact without reaction is required.

To summarize: a gelation process in the presence of solvent always brings in a trend towards segregation of the gelating species. However, by a suitable choice of the concentration in the reaction bath, one can still observe a well-defined sol–gel transition. The critical exponents observed in this case may still be of the percolation type. The latter statement has been proven more formally in one case = quasi equilibrium with mixtures of linear chains and crosslinking agents in a athermal solvent.*

V.3. Gels in Good Solvents

We now focus on gels which are well beyond the gelation threshold. We assume that they have been prepared in good solvents, and that, at the moment of study, they are also in good solvents. This is the best situation if we wish to avoid segregation effects and the resulting heterogeneities. Also, for simplicity, we focus our attention on calibrated gels, where the number $N$ of monomers between adjacent crosslinks is well defined. The classic picture for these gels is from Flory and is very successful. We present it here in different language.

V.3.1. The $c*$ theorem

Let us start with a solution of chains (polymerization index $N$) in a good solvent (excluded volume parameter $v = a^3 (1 - 2\chi) > 0$). The chains repel each other, and this is reflected in the existence of a positive osmotic pressure $\Pi$.

We now begin to attach the chains together, for example by reaction of the chain ends with certain $z$-functional molecules ($z$ being equal to 3, 4, etc.), and we let them choose their density. They would like to separate from each other as much as possible; however, each coil must remain in contact with its neighbors because of the crosslinks. The net result is shown in Fig. V.15.

\[ c = k(z) c^* = k(z) N^{-4/5} a^{-3/5} \]  

(V.25)

where $k(z)$ is a constant number, of order unity, depending on the functionality $z$ of the crosslinks and on the preparation conditions.

Eq. (V.25) summarizes the Flory theory of gels. Changing the chemical nature of the solvent amounts to changing the excluded volume parameter $v$; if $v$ increases (better solvent), $c^*$ decreases (swelling). Eq. (V.25) has been confirmed by macroscopic measurements on many gel systems. Experimentally, it is important to wait long enough to choose a correct equilibration of the solvent. Since we cannot stir the system, concentrations are equilibrated only slowly by diffusion processes. Equilibration times are of order $L^2/D$ where $L$ is a sample size and $D$ is a diffusion coefficient. Typical values of $D$ are in the range $10^{-6}$ to $10^{-7}$ cm$^2$/sec, and the resulting times are around one day.

V.3.2. Pair correlations in the gel

In its original derivation of equations similar to eq. (V.25) Flory assumed gaussian statistics for the chains plus a mean field estimate for the repulsive energies. His theory is successful; the scientific community has

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naturally concluded that the chains in a swollen gel are gaussian to a very good approximation. This is entirely wrong for the following reason.

Flory's calculation is quite similar to his discussion of a single chain in a good solvent, which we analyzed in Section I.3. In this case we saw that an excellent result came from a cancellation between two serious approximations—one related to the use of gaussian statistics, and one due to the neglect of correlations between chains. The same cancellation occurs for swollen gels, and the success of the theory does not tell us that the chains are gaussian.

The correct structure of pair correlations in the gel can be read from Fig. V.16. At short distances, the correlation function

$$g(r) = \frac{1}{c} \langle c(o) c(r) \rangle - c^2$$

is dominated entirely by correlations inside one chain and follows the Edwards law [eq. (I.31)]. It is only when $g(r)$ goes down to values of the order $c = kc^*$ that the existence of a gel phase affects the correlation. This crossover point corresponds to $r$ values comparable with the single coil size $R_F$ (given by eq. (IV.49)). At larger distances density fluctuations are limited by the macroscopic rigidity of the gel, and $g(r)$ decays rapidly in space.

The latter statement can be made more precise from a generalized form of elastic theory at long wavelengths, corresponding to the free energy (per cm$^3$)

$$F = \frac{1}{2} E \left( \frac{\delta c}{c} \right)^2 + \frac{1}{2} L \left[ \nabla \left( \frac{\delta c}{c} \right) \right]^2 + \text{higher gradient terms (V.26)}$$

where $\delta c$ is the local change in concentration, $E$ is the bulk rigidity, and $L$ represents a higher order correction (usually ignored in continuous elasticity). Since the only characteristic length available is $R_F$, scaling means that

$$L \approx E R_F^2$$

Going to Fourier transforms, eq. (V.26) gives a sum of terms for different wave vectors $q$

$$F = \frac{1}{2} \sum_q \left( \frac{\delta c_q}{c} \right)^2 (E + Lq^2)$$

Applying the equipartition theorem to each mode $q$, we get

$$\frac{1}{c^2} \langle (\delta c^2_q) \rangle = \frac{T}{E + Lq^2} \quad (qR_F < 1)$$

Note that eq. (V.28) applies only for $qR_F \ll 1$ because eq. (V.26) assumes slow spatial variations. Returning to real space, we can transform eq. (V.28) into

$$g(r) = \frac{c^*}{4\pi L r} \exp \left[ - \left( \frac{E}{L} \right)^{1/2} \right] \quad (r > R_F)$$

$$g(r) \approx \frac{N}{R_F^2 r} \exp \left[ - \text{constant} \left( \frac{r}{R_F} \right) \right]$$

The scaling form of the coefficient in eq. (V.30) has been obtained separately from the requirement that at $r = R_F$, the correlation function $g(r)$ must be comparable with the average concentration $c$ ($\sim c^*$). Thus a byproduct of our discussion is to give (by comparison between eqs. V.30 and V.29) the scaling form of the elastic moduli:

$$E \approx \frac{L}{R_F^2} \approx \frac{c^*}{N} T \equiv \frac{c T}{N}$$

The whole picture subtended by Fig. V.15 may be simply stated in terms of suitable "blobs." To each chain ($N$ monomers) we associate a blob of size $R_F$. The blobs are essentially closely packed (the exact packing depending on the functionality of the gel and on the conditions of
Inside one blob, the \textit{correlations are of the excluded volume type}—i.e., the blobs are not gaussian. Neighboring blobs are coupled by elastic forces; using eq. (1.45) to predict the spring constant of one blob, we may easily redervative eq. (V.31).

This picture can be tested in principle by various scattering measurements. Neutron data on gels have been taken by the Strasbourg group, \textsuperscript{35} However, the main emphasis has been on a different type of measurement where a certain part of the gel structure is \textit{labeled}; in particular it is comparatively easy to deuterate the crosslinks and to measure the correlation between them. The resulting diffraction pattern is very similar to diffraction by an \textit{amorphous solid}; the crosslinks maintain a certain average distance (or order \(R_p\)), and this gives rise to a diffuse peak (at \(q \sim 1/R_p\)) in the scattering pattern. Two crosslinks cannot come very close together; this would imply a large overlap between two neighboring blobs and an energy which would then become quite large.

Under the stimulation of H. Benoit, similar experiments with labeled centers were also made with \textit{solutions} of star-shaped polymers which have the same geometry and the same concentration\textsuperscript{35} (Fig. V.17). The scattering patterns for both situations are of the same type. This is not surprising since both systems are at \(c = c^*\) and are very similar to a dense fluid of hard spheres.

V.3.3. Elasticity of swollen gels

We have seen in eq. (V.31) that the bulk modulus \(E\) of the gel should scale like \((c/N)T\). A similar scaling law should also hold for the shear modulus, which is more easily accessible to experiment. (In what follows, since we are interested only in scaling properties, we use the same symbol \(E\) for both.) It is possible to test eq. (V.31) by varying either the quality of the solvent (i.e., \(v\)) or the length of the chain (i.e., \(N\)). Recall that \(c, v,\) and \(N\) are always linked by the \(c^*\) theorem [eq. (V.25)].

For a given solvent (fixed \(v\)) it is often convenient to eliminate \(N\) between eqs. (V.31) and (V.25), obtaining

\[ E \equiv T c^{2.25} (v^{14} a^{1.5}) \]  
(V.32)

Thus, the elastic modulus should scale like the power 2.25 of concentration. Recent elastic data of Belkebir-Mran\textsuperscript{36} have been reanalyzed along these lines.\textsuperscript{38} They do show exponents which are close to 2.25 if the comparison is made at \textit{fixed functionality} \(z\) (the numerical coefficient in eq. V.32 depends on \(z\)).

For a fixed \(N\) and a solvent of variable quality, the elastic modulus should scale linearly with concentration \((E \equiv cT/N)\). This is also well confirmed.

The above discussion was restricted to linear elasticity—i.e., to the regime where the relationship between stress (\(\sigma\)) and deformation (\(\lambda\)) is of the form

\[ \sigma = E(\lambda - 1) \]  
(V.33)

(We define \(\lambda\) for longitudinal deformations as the ratio of the extended length of the sample to the length at rest.) This is obtained when \(\sigma \ll E\).

The opposite limit \(\sigma \gg E\) would be of great interest. Unfortunately, gels usually break at low \(\sigma\) values, and these strong deformations are difficult to study. However, they are important because the stress is then sensitive to the non-gaussian character of the individual chains. Section I.4 showed that swollen chains have a nonlinear relationship between force and elongation; this should show up in \(\sigma(\lambda)\). The prediction is\textsuperscript{37}

\[ \sigma = E \lambda^{5.72} \quad \text{(real gel; } \sigma \gg E) \]  
(V.34)

for longitudinal extension at constant \(c^*\).\textsuperscript{*} Compare this with the law for gaussian chains

\[ \sigma = E \lambda^2 \quad \text{(gaussian; } \sigma \gg E) \]  
(V.35)

Some readers may be surprised by the occurrence of a quadratic law [eq. (V.35)] for gaussian chains which have a linear spring behavior. The reason is simple. When we extend our sample very much, its lateral dimensions decrease, and \(\sigma\) (which is a force per unit area of cross-section) increases by one extra power of \(\lambda\). The really interesting feature is the difference between eq. (V.34) and eq. (V.35), which reflects the Fisher-Pincus scaling law for swollen chains in strong extension [eq.

\*Since the experiment must be done relatively fast, the gel cannot change its solvent content during elongation.