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Continuum Model of Heterogeneous Gels: Formation and Elastic Properties

V.G. Oshmian ⁽¹⁾ and L. Benguigui ^(2,*)

⁽¹⁾ Institute of Chemical Physics, Russian Academy of Sciences, Kosygin Street 4, Moscow, Russia

⁽²⁾ Solid State Institute, Technion, Israel Institute of Technology, Haifa 32000, Israel

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Abstract. — A kinetic model of heterogeneous gel formation and a method to calculate gel stiffness are proposed, with application to the elastic properties of polyacrylamide gels. The model is based on assumptions about nucleation and growth of dense regions, governed by the concentration of monomer units (p_0) crosslink agent (c_0) and rate constants for chain propagation and curing. It is shown that at low c_0 the polymer and crosslink densities inside and outside an inclusion are almost the same and that the gel may be regarded as homogeneous. But the difference between densities increases sharply with c_0 , giving growth of heterogeneities. Calculation of the elastic modulus was performed using a self-consistent method. Stiffness grows with p_0 at fixed c_0 , but goes through a maximum as a function of c_0 at fixed p_0 . The theoretical analysis is in qualitative agreement with the experimental data.

1. Introduction

The elastic modulus E of a polymer networks under uniaxial tension may be described by the James and Guth approximate expression for the energy [1,2]:

$$F = \frac{1}{2} \left(\frac{1}{2} \Phi - 1 \right) N_c k T (l_1^2 + l_2^2 + l_3^2) \quad (1)$$

$$E = \frac{\partial^2 F}{\partial \lambda_i^2} = \left(\frac{1}{2} \Phi - 1 \right) N_c k T \quad (2)$$

where Φ is the crosslink functionality, N_c = crosslinks density, k = Boltzmann's constant, T = absolute temperature, l_i = deformation ratio in Cartesian directions $i = 1, 2, 3$. So, if the effect of entanglements is negligible, then the stiffness of the system is proportional to the crosslink density. If one identifies N_c with the crosslinking agent concentration c_0 , there is a linear $E - c_0$ dependence. But in reality not every molecule of the crosslinking agent forms an effective knot of the network, even in the case when it is incorporated into the chain. There are three reasons for this phenomenon: 1) the real crosslinking functionality may be less than

(*) Author for correspondence (e-mail: ssgilles@technunix.technion.ac.il)

Φ ; 2) some molecules from short branches or loops and so, the effective functionality is less than Φ ; 3) the crosslinking agent molecule disposes in sol fraction.

But one expects always a relationship between E and c_0 such that E is an increasing function of c_0 . Such is the case for several gels [3]. However the polyacrylamide gels are exception: $E(c_0)$ is not a monotonically increasing function but rather exhibits a maximum [4–6] at a polymer volume concentration p_0 of about 10%. For lower polymer concentration, E saturates when c_0 increases, and for larger p_0 , $E(c_0)$ increases with c_0 , but with an inflexion point [6]. It is the goal of this paper to propose an explanation of this behavior in connection with the inhomogeneities of these gels.

As it is well known, the problem of inhomogeneities in gels is very important [7]. The simple and naive picture is to see these inhomogeneous region as spherical domains with crosslink molecule and polymer densities larger than their mean values. Application of this model to polyacrylamide gels was made by Weiss *et al.* [8] and more recently by Cohen *et al.* [5]. This last group used the model to interpret their small angle X-ray scattering intensity, as the sum of a Gaussian (from which the mean size of the dense regions is obtained) and a Lorentzian (which permits extraction of the coherence length).

A less naive picture was proposed by Bastide *et al.* [9], in particular to explain the “butterfly” effect. The regions with higher crosslink density are seen as fractal objects. This model was used by Mendes *et al.* [10] to analyze gels for which the small angle neutron scattering intensity cannot be interpreted as the sum of a Gaussian and a Lorentzian.

In this paper, we shall adopt the first picture in spite of its naivety. We can consider the results of reference [5] as reasonable support for this approach. Our model consists of two basic steps. The first is to determine the size of the inhomogeneous regions (seen as spherical inclusions), and the density of the polymer and crosslink molecules in the inclusions and in the matrix, as functions of the mean polymer and crosslink molecule concentrations. The second step is the calculation of the Young modulus of this heterogeneous structure.

It is clear that the Young modulus of the inclusions will be larger than that of the matrix. In the model of Bastide *et al.*, it was supposed that the high crosslink density regions are undeformable, (*i.e.* their elastic modulus is infinite), tending to increase the total Young modulus of the gel. But this is associated with a decrease of the Young modulus of the matrix. It was proposed in reference [6] that these two opposing mechanisms may explain the maximum of E in the polyacrylamide gels. However, this implies so strong a depletion of the crosslink molecules in the matrix that it is very unlikely. We shall add a new ingredient to our model. It is based on the well known result that the introduction of crosslink molecules in a polymer in solution is limited and depends on the polymer concentration. The depletion process mentioned above (*i.e.* the fact that the polymer and crosslink densities are low in the matrix) may decrease the Young modulus of the matrix because its polymer density becomes too low to be able to accept all the crosslink molecules in the network. Thus, we expect that the polymer concentration in the matrix will decrease when the mean crosslink concentration increases. As shown below, this is one of the results of the model.

Before presenting the details of the model, we should mention the work of Schimmel and Heinrich [11]. They consider highly disperse gels of the network strands and they observe a decrease of the elastic modulus with increase of the molecular weight distribution. They interpret their result as the decrease of the effective number of active network junctions. We cannot exclude such a mechanism in the case of polyacrylamide gels. Nevertheless, we think that our model is well-adapted to the case of strong spatial fluctuations of the polymer and crosslink concentrations. Our suggestion is that such is the case for the polyacrylamide gels [12].

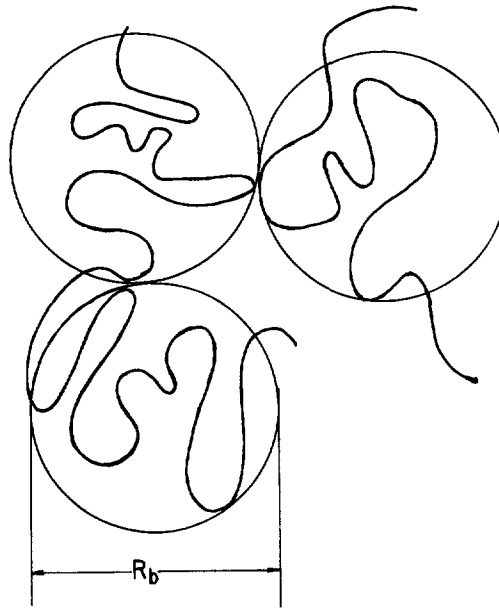


Fig. 1. — Blob picture of the polymer network.

The paper is organized as follows:

1. In order to understand the influence of the polymer concentration on E , we propose a determination of the effective crosslinked density c_{eff} . For the sake of the simplicity, we shall neglect the detail mechanism of the real crosslink functionality diminution.
2. A kinetic model of the nucleation of the inhomogeneities is presented: it permits us to determine the radius of the inhomogeneities as well as the crosslink molecule and polymer concentrations.
3. The third step is the calculation of E from the results of the self-consistent method used in the theory of composite materials. The gel is seen as a mixture of a soft matrix and stiff inclusions which are the spherical inhomogeneities.
4. A comparison of the results of the model is made with the experiments. We get good qualitative agreement.

2. Effective Crosslink Density

We begin by finding the effective crosslink density c_{eff} in a polymer network with concentrations c and p of crosslink molecules and monomer units. This network, with chemical and physical junctions, may be represented by a system of touching blobs (Fig. 1). The number of contact points of the blobs is the upper limit of the effective crosslink density c_{eff} .

The effective crosslink density c_{eff} cannot exceed the density of contact points c_{cp} between chains. Let us estimate the latter, following the scaling concepts of the de Gennes [13] and neglecting loops, short branches and sole fraction. Flory [14] obtained an elegant and sufficiently exact estimation of the linear macromolecule blob radius R_b in terms of the number N

of Kuhn segments in good solvent:

$$R_b \simeq aN^\nu, \quad \nu = 3/(d+2) \quad (3)$$

where d is the dimension of the space ($\nu = 3/5$ in the three-dimensional case). The representation proposed leads to the following scaling relations for the density of contact points and the monomer unit density:

$$c_{cp} \simeq \frac{1}{R_b^3} = a^{-3} N^{-9/5} \quad (4)$$

$$p \simeq \frac{N}{R_b^3} = a^{-3} N^{-4/5} \quad (5)$$

(4) and (5) give the correlation between the densities as

$$c_{cp} \simeq a^{15/4} p^{9/4} \quad (6)$$

and the chemical distance between neighbor contact points as

$$N \simeq p/c_{cp} \quad (7)$$

According to the results above, we have:

$$c_{\text{eff}} \leq \min(c, c_{cp}) = \min(c, a^{15/4} p^{9/4}) \quad (8)$$

Let us treat (8) as an equality and assume that every contact point is either an effective crosslink or an entanglement. Edwards and Vilgis [15] suggested an additive expression for the effective crosslink and entanglement contributions to the polymer-network free energy. However, in the present work, we do not take into account the entanglements because their introduction will not give a dramatic change in the results. The model is only qualitative at the present stage. So, we shall describe the stiffness of the homogeneous gel by (2) with (8) taken into account:

$$E = kT c_{\text{eff}} = kT \min(c, a^{15/4} p^{9/4}) \quad (9)$$

The expression (9) is one of the important results of this model. It shows (as expected) that one cannot introduce an unlimited number of crosslinks in a polymer network. One consequence of this relation is that one may observe saturation of the Young modulus with increasing crosslink content. When one considers the variation of c_{eff} as a function of c , for a given polymer concentration p , one has two regions. As long as $c < a^{15/4} p^{9/4}$, c_{eff} is equal to c . However, if $c > a^{15/4} p^{9/4}$, c_{eff} is constant and equal to $a^{15/4} p^{9/4}$. This means that there are not enough contact points for the crosslink molecules. Thus $c_{\text{eff}}(c)$ is linear for small c and tends to saturate. The saturation value of c_{eff} increases like $p^{9/4}$.

3. Kinetic Model of Inhomogeneities Formation

3.1. ESTIMATION OF THE POLYMER AND CROSSLINK CONCENTRATIONS INSIDE DENSE REGIONS. — As mentioned above, our starting point is the formation of dense spherical regions which represent the inhomogeneities. We begin by estimating the polymer and crosslink concentrations inside the inhomogeneities. We shall assume that further growth of a dense region occurs by accepting new monomers and crosslink molecules to its surface without change in the densities.

The following method for this density calculation is proposed. We use a simplified chemical model of polymer-network formation. It includes two kinds of reactions between monomer (MG) and curing agent (CAG) groups:

- i) Polymer chain propagation (MG+MG), rate constant k_p .
- ii) Polymer chains curing (MG+CAG), rate constant k_c .

Further we shall denote concentrations by small letters and corresponding amounts in the volume by large ones. Subscripts i or m refer to the region (inhomogeneity or matrix). Subscript 0 refers to the initial concentrations, (or to the mean values); p_0 and c_0 to monomer units and crosslink agents respectively. We shall distinguish between monomer units and crosslink molecules and their chemically active groups. It is assumed that a monomer unit has two active groups and that a crosslink agent molecule has four. $p_i, c_i, P_i, C_i, p_m, c_m, P_m, C_m$ are concentrations and numbers of molecules in the network inside the inhomogeneity (dense region) and the matrix (rare region), p_0, c_0, p and c are initial and current concentrations of active groups. (p and c do not have the same meaning as in the preceding section). In order to avoid any confusion one should keep in mind that, in any material balance equations for chemical groups we shall multiply quantities of monomer unit molecules by 2 and of crosslink agents by 4.

The kinetic equations for the increments ΔP_i of monomer units and ΔC_i crosslink molecules quantities per unit value of the interface area are of the form:

$$\Delta P_i = sp_0(k_p 0.5p_i + k_c 1.5c_i)\Delta t \quad (10a)$$

$$\Delta C_i = sc_0k_c 0.5p_i\Delta t \quad (10b)$$

The surface factor s , which has the dimension of a length, is introduced in order to take into account specific conditions for chemical reactions between p_i and p_0 , p_i and c_0 , c_i and p_0 on the interface. Coefficients $0.5 = (0 + 1)/2$ and $1.5 = (0 + 1 + 2 + 3)/4$ are chosen as mean values of chemically active groups on the surface of the network region. We assume that every contact point is an effective crosslink inside inhomogeneity. It makes possible to calculate the chemical distances N and N' between neighbor crosslinks inside the dense region and the new layer:

$$N = \frac{P_i}{c_i} \quad (11a)$$

$$N' = \frac{\Delta P_i}{\Delta C_i} = \frac{p_0(k_p p_i + 3c_i)}{c_0 k_c p_i} \quad (11b)$$

Estimates of the crosslink and polymer densities in the dense region may be obtained from the assumption:

$$N = N' = \frac{1}{2} \frac{k_p}{k_c} \frac{p_0}{c_0} + \sqrt{\frac{1}{4} \left(\frac{k_p}{k_c} \right)^2 \left(\frac{p_0}{c_0} \right)^2 + 3 \frac{p_0}{c_0}} \quad (12)$$

$$p_i = p'_i = a^{-3} N^{-4/5} \quad (13)$$

$$c_i = c'_i = a^{-3} N^{-9/5} \quad (14)$$

The average distance \bar{N} between neighbor contact points in the gel may be estimated as:

$$\bar{N} \simeq \frac{p_0}{c_0} \quad (15)$$

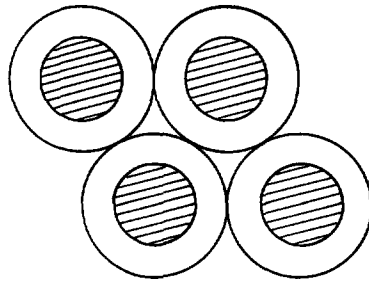


Fig. 2. — Shell model of a composite material made of stiff inclusions in a soft matrix.

The degree of heterogeneity is likely determined by the competition between two chemical reactions: chain propagation (constant k_p) and crosslinking (k_c). It is seen from (12), that if $k_p \gg k_c$ we shall have N of the order of \bar{N} but the active crosslink reaction ($k_p \ll k_c$) leads to the formation of dense regions: $N \simeq \sqrt{\bar{N}}$.

3.2. GROWTH AND FORMATION OF HOMOGENEITIES. — The polydisperse model [16], (Fig. 2) of composite materials is used for the description of gel's geometry and stiffness. It assumes that the dense regions are of the same (spherical) shape and are placed with their spherical shells (radius of every shell is proportional to the radius of internal dense region) without intersections (see Fig. 2). Each cell of this structure is similar to any other and may be analyzed separately.

The proposed continuum model of gel structure formation is based on the following points:

- i) Inhomogeneities nucleate at the beginning of the process. Their densities c_i and p_i are determined by (12–14) and remain constant further.
- ii) Propagation of dense regions occurs through their surface as mentioned above:

$$\frac{dP_i}{dt} = 4\pi R^2 s p (0.5k_p p_i + 1.5k_c c_i) \quad (16a)$$

$$\frac{dC_i}{dt} = 4\pi R^2 s (0.5k_c c p_i) \quad (16b)$$

In (16a) and (16b), R is the radius of the inclusion, P_i and C_i are respectively the monomers and the crosslink molecule quantities in the dense regions, and p and c are the concentrations of the active monomer and crosslink groups. Since p_i and c_i are taken constant, one has $(dP_i/dt) = (p_i/c_i)(dC_i/dt)$. This can be seen in the following way. By definition $(dP_i/dV) = p_i$ and $(dC_i/dV) = c_i$, when V is the volume of one inclusion. Equivalently, one can write $(dP_i/dt) = p_i(dV/dt)$ and $(dC_i/dt) = c_i(dV/dt)$. Eliminating (dV/dt) gives the relation

$$\frac{dP_i}{dt} = \frac{p_i}{c_i} \frac{dC_i}{dt} \quad (17)$$

This implies that the two equations (16a) and (16b) are not independent. The variation of P_i and C_i will be controlled by the slowest process given by equations (16a) and (16b):

$$\frac{dP_i}{dt} = \frac{1}{2}s p_i \min \left[p \left(k_p + \frac{3k_c c_i}{p_i} \right), \frac{ck_c p_i}{c_i} \right] 4\pi R^2 \quad (18a)$$

$$\frac{dC_i}{dt} = \frac{1}{2}s c_i \min \left[p \left(k_p + \frac{3k_c c_i}{p_i} \right), \frac{ck_c p_i}{c_i} \right] 4\pi R^2 \quad (18b)$$

From $P_i = 4\pi R^3 p_i / 3$ and equation (16a), one gets

$$\frac{dR}{dt} = \frac{1}{2}s \min \left[p \left(k_p + \frac{3k_c c_i}{p_i} \right), \frac{ck_c p_i}{c_i} \right] \quad (19)$$

iii) The matrix network is formed by polymerization in the bulk governed by the following kinetic equations:

$$\frac{dp_m}{dt} = k_p p^2 + \frac{1}{2} k_c p c \quad (20a)$$

$$\frac{dc_m}{dt} = \frac{1}{4} k_c p c \quad (20b)$$

where p_m is the concentration of chemically passive monomer units and c_m is the concentration of crosslink molecules in the matrix. Taking into account that $P_m = 4\pi(R_m^3 - R^3)p_m/3$, and $C_m = 4\pi(R_m^3 - R^3)c_m/3$, where R_m is the radius of the shell, one gets

$$\frac{dP_m}{dt} = \frac{3R^2}{R_m^3 - R^3} P_m \frac{dR}{dt} + \frac{4\pi}{3} (R_m^3 - R^3) p \left(k_p p + \frac{1}{2} k_c c \right) \quad (21a)$$

$$\frac{dC_m}{dt} = \frac{3R^2}{R_m^3 - R^3} C_m \frac{dR}{dt} + \frac{4\pi}{3} (R_m^3 - R^3) \frac{k_c p c}{4} \quad (21b)$$

iv) The active polymer concentration, p , and crosslink molecule concentration, c , are dispersed in the matrix region. Some of them belong to the network and the rest to the mobile monomer units and crosslink molecules. Material balance gives:

$$\frac{4\pi}{3} R_m^3 p_0 = \frac{4\pi}{3} R^3 (2p_i) + 2P_m + \frac{4\pi}{3} (R_m^3 - R^3) p \quad (22a)$$

$$\frac{4\pi}{3} R_m^3 c_0 = \frac{4\pi}{3} R^3 (4c_i) + 4C_m + \frac{4\pi}{3} (R_m^3 - R^3) c \quad (22b)$$

It is simpler to use reduced variables: $\bar{R} = R/R_m$, $\bar{P}_m = P_m/R_m^3$, $\bar{C}_m = C_m/R_m^3$, and $\bar{s} = s/R_m$. Such new variables do not change the concentrations, and we have the following system:

$$\frac{d\bar{R}}{dt} = \frac{1}{2}\bar{s} \min \left[p \left(k_p + \frac{3k_c c_i}{p_i} \right), \frac{ck_c p_i}{c_i} \right] \quad (23)$$

$$\frac{d\bar{P}_m}{dt} = \frac{3\bar{R}^2}{1 - \bar{R}^3} \bar{P}_m \frac{d\bar{R}}{dt} + \frac{4\pi}{3} (1 - \bar{R}^3) p \left(k_p p + \frac{1}{2} k_c c \right) \quad (24)$$

$$\frac{d\bar{C}_m}{dt} = \frac{3\bar{R}^2}{1 - \bar{R}^3} \bar{C}_m \frac{d\bar{R}}{dt} + \frac{4\pi}{3} (1 - \bar{R}^3) \frac{k_c p c}{4} \quad (25)$$

$$\frac{4\pi}{3} p_0 = \frac{4\pi}{3} \bar{R}^3 (2p_i) + 2\bar{P}_m + \frac{4\pi}{3} (1 - \bar{R}^3) p \quad (26)$$

$$\frac{4\pi}{3} c_0 = \frac{4\pi}{3} \bar{R}^3 (4c_i) + 4\bar{C}_m + \frac{4\pi}{3} (1 - \bar{R}^3) c \quad (27)$$

The equations (23–27) form a system which permits us to calculate the various quantities of interests \bar{P}_m , \bar{C}_m and \bar{R} . Since we are interested only in static results, we solve the system numerically in the time segment $0 \leq t \leq t_{\max}$, sufficiently long for stabilization of the structure: $d\bar{R}/dt = 0$, $p = 0$ or $c = 0$, and then the value of the quantity, $4\pi(1 - \bar{R}^3)p/3$ was added to \bar{P}_m instead further integration up to infinite time. The initial conditions are clearly zero for all the time dependent quantities (\bar{R} , \bar{P}_m , \bar{C}_m) and $p = p_0$, $c = c_0$.

4. Calculation of the Elastic Modulus

We cannot assume that the effective Young modulus of the gel will be the average of the Young moduli of the dense regions and of the matrix. This is possible only if they are not too different.

One of the many composite-stiffness theories may be applied for the calculation of the gel stiffness. We assume that both dense and rare regions are incompressible. Their elastic moduli E_i , E_m are described by (9); we use the self-consistent field approach [17], which coincides formally with the bottom Hashin-Shtrickman estimate [18]:

$$E = E_m \left(1 + \frac{\alpha_d(E_i - E_m)}{E_m + 4\alpha_r(E_i - E_m)} \right) \quad (28)$$

where $\alpha_d = \bar{R}^3$ and $\alpha_r = (1 - \bar{R}^3)$ are the dense inclusion and rare matrix volume contents.

In conclusion of this section it should be noted, that the above approach is restricted by the condition of matrix type composite structure, *i.e.* a region of low density and separation of dense inhomogeneities. Otherwise (as likely occurs at high polymer content) approximation (28) is not valid and the percolation approach [19] should be applied.

5. Results and Discussion

The peculiarities of polyacrylamide-gel mechanical behavior are revealed in reference [6]. At sufficiently low polymer content ($p \leq 18$ vol.%), the $E - c_0$ relationship passes through a maximum, shifted to larger E_{\max} and c_{\max} with increase of p_0 . For large polymer concentration (20 and more vol.%) the elastic moduli increase with crosslinking agent concentration. The curves have the same initial slope for $p_0 \leq 12$ vol.%, well described by the James and Guth theory [1, 2].

We shall explain how we used the model in order to calculate the Young modulus of the gel. First, we have to chose values of p_0 and of c_0 (mean value of the polymer and crosslink densities). In the first step we calculate the five basic quantities of the model: the polymer and crosslink densities in the dense regions (p_i and c_i) through equations (12), (13) and (14); the polymer and crosslink densities in the matrix (p_m and c_m) by solving the system of equations (23–27); the radius \bar{R} . For that we have to chose explicitly the parameters of the model. In a second step, we calculate E_i and E_m with the help of equation (9), taking $k_B T = 1$ for the sake of simplicity. Finally, E_{eff} is calculated by equation (28).

The parameters of the model are:

- i) The rate constants k_p and k_c ;
- ii) The constant a in equation (3);
- iii) The coefficient s (Eq. (10)). This coefficient has the dimension of a length and it can be seen as the thickness of the active layer at the surface of the dense region.
- iv) Radius of the shell R_m . s and R_m enter only through their ratio \bar{s} .

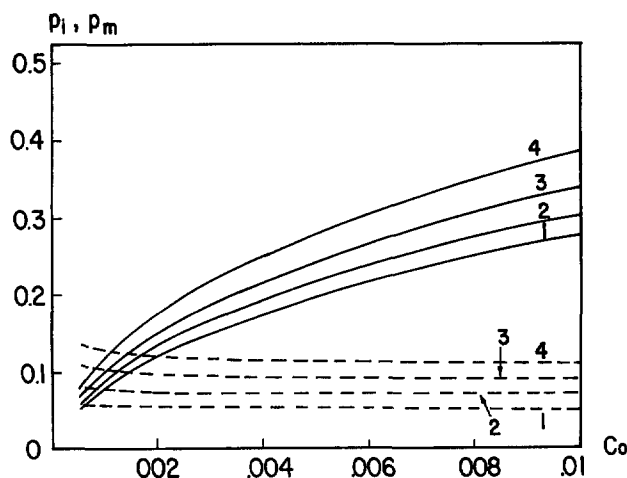


Fig. 3. — Variation of the polymer densities p_i inside the heterogeneities and p_m inside the rare matrix as function of c_0 : 1. $p_0 = 0.06$; 2. $p_0 = 0.08$; 3. $p_0 = 0.10$; 4. $p_0 = 0.12$. — p_i ; - - - p_m .

The choice of the parameters was made in order to get good qualitative agreement. Since we are not interested in the dynamics of the process, only the ratio k_c/k_p is important; we varied it between 1.25 and 5. \bar{s} is clearly much smaller than 1, but its exact value does not have a strong influence on the results. The last parameter a is also a characteristic length of order of some angstroms [9]; a cannot be taken too small because we found in some cases unphysical results. p_0 and c_0 are expressed in relative volume, instead of a number of molecules by unit volume and we translated the value of a in these units for the case of the polyacrylamide gels. If a is taken to one, this corresponds to a length of 5 Å.

We consider now the variation of the concentration p_i and c_i inside the heterogeneities, and p_m and c_m in the matrix as functions of p_0 and c_0 , the mean concentrations. The general trends are the following: p_i and c_i increase with p_0 and c_0 . c_m increases with c_0 and depends very weakly on p_0 . Finally, p_m decreases if c_0 increases but increases with p_0 . However, we have $p_m > p_i$ for low c_0 and $p_m < p_i$ for larger c_0 . Clearly, the model is meaningful if $p_m < p_i$. Thus we have to choose k_c/k_p relatively large. This reduces the region where $p_m < p_i$ to the lowest values of c_0 (≤ 0.005).

In Figure 3, we show the variation of p_i and p_m versus c_0 , for several values of p_0 and in Figure 4, we show the variation of c_i and c_m , for the following values of the parameters: $k_p = 2$, $k_c = 10$, $\bar{s} = 0.06$ and $a = 0.9$. We note that c_i is larger than c_m by one order of magnitude.

The decrease of p_m when c_0 increases is an important feature of the model. Because of equation (9), it means that the matrix will not always be able to include all the crosslink molecules. Consequently, it results a decrease of E_m when c_0 increases.

The dependence of \bar{R} with p_0 and c_0 is as follows (Fig. 5): it increases with p_0 but decreases if c_0 increases. In some cases (small p_0), \bar{R} exhibits a minimum. We have to recall that \bar{R} is the size of the inhomogeneities relatively to their mean distance. If \bar{R} decreases, it can be because of the diminution of their size or an increase in their distance, or both. At the present time, there are no experimental results of \bar{R} as we defined it (in Ref. [5], the absolute size R is given).

In Figure 6, we show the effective crosslink density $c_{\text{eff}}(m)$ in the matrix, as defined by (8). The Young modulus E_m of the matrix is directly proportional to $c_{\text{eff}}(m)$.

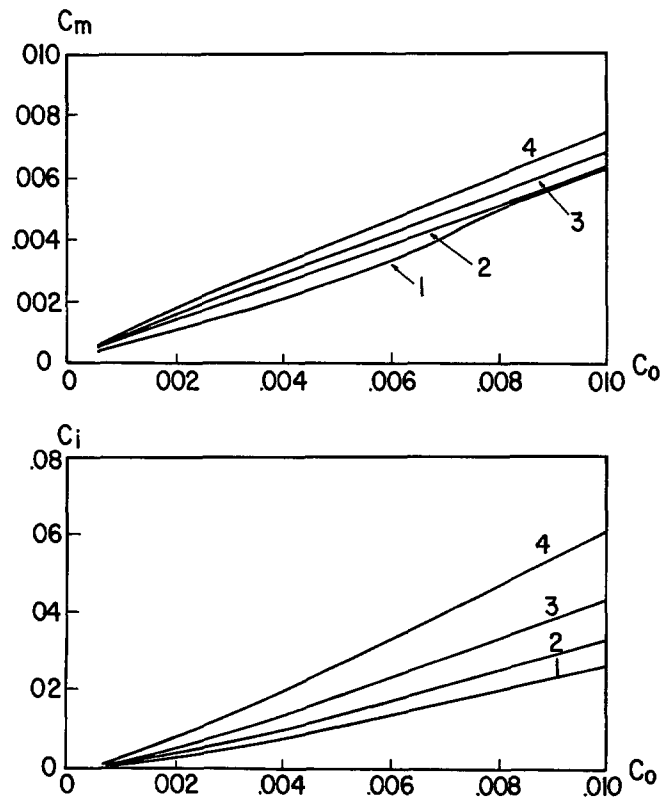


Fig. 4. — Variation of the crosslink molecule densities c_i in the heterogeneities and c_m inside the rare matrix as functions of c_0 . 1, 2, 3, 4, as in Figure 3.

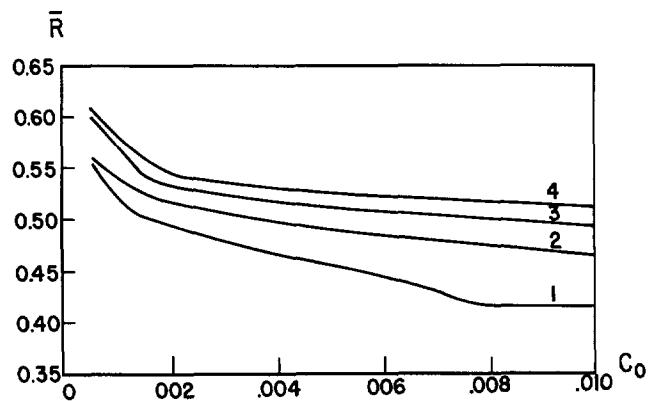


Fig. 5. — Radius of heterogeneity *versus* c_0 for different p_0 . 1, 2, 3, 4 as in Figure 3.

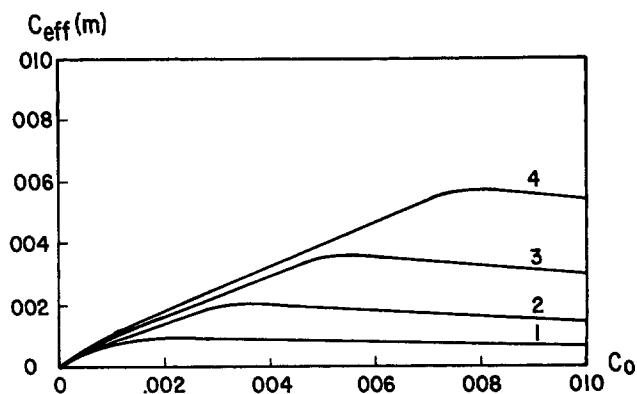


Fig. 6. — Effective crosslink density in the matrix as a function of c_0 . 1, 2, 3, 4 as in Figure 3.

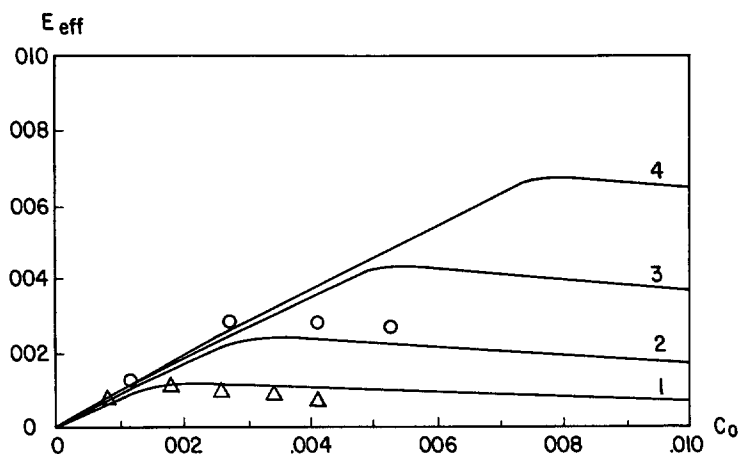


Fig. 7. — Young modulus of the gel as a function of c_0 . The shape of the curves is in qualitative agreement with the experiments. 1, 2, 3, 4 as in Figure 3. Experimental results: (Δ) for $p_0 = 0.08$, (\circ) for $p_0 = 0.13$.

$c_{\text{eff}}(m)$ as a function of c_0 is characterized by a break in the slope. This can be easily understood considering equation (8). As long as $c_0 < a^{15/4} p_m^{9/4}$, $c_{\text{eff}}(m) = c_0$ and increases with c_0 . But, if $c_0 > a^{15/4} p_m^{9/4}$, $c_{\text{eff}}(m) = a^{15/4} p_m^{9/4}$ which is a slowly decreasing function of c_0 .

The effective Young elastic modulus is calculated with the help of (28) where E_i is taken equal to c_i and E_m to $c_{\text{eff}}(m)$ (Fig. 7). E_{eff} is very similar to $c_{\text{eff}}(m)$ although in the inhomogeneities c_i is much larger than $c_{\text{eff}}(m)$. This is because in (28) the influence of the heterogeneities is important only for value of \bar{R} near 1. We indicate also the experimental results for $p_0 = 8\%$ and 13% . One can see that the model reproduces well the dependence of E_{eff} with c_0 . However, the calculated values are larger than the experimental ones.

The important result of the paper is the variation of $c_{\text{eff}}(m)$ with c_0 . To understand physically this behavior, we have to recall that for low c_0 , $p_m \approx p_i$ and the system can be seen as homogeneous, and $c_{\text{eff}}(m) \sim c_0$. However, for larger c_0 , the quantities c_m and p_m will be

such that $c_{\text{eff}}(m)$ will be controlled only by p_m which decreases with c_0 . The formation of the heterogeneities implies that the matrix has a low polymer concentration which gives a low value of $c_{\text{eff}}(m)$. The exact value of the Young modulus in the heterogeneities has almost no influence on the results contrary to what was postulated in reference [6].

We are well aware that our approach is a simplification by the following reasons. First, the system is very probably heterogeneous at many scale, when we suppose that the heterogeneities are spherical with the same radius R . For this reason, we prefer to consider R as a mean value of the radius of gyration of the heterogeneities, as in the experiments presented in reference [5]. Secondly, the heterogeneities may have more complicated shape. However, one can propose that the growth of the heterogeneous regions takes place in an analogous manner as in Eden model. In this model, aggregates are compact with a constant density, with a shape near a sphere, as we postulated.

For these two main reasons, we cannot expect more than a good qualitative agreement with the experiments. We do not mention the possibility of percolation of the heterogeneities because this point have been already discussed in reference [6].

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