

Intermediate swelling of gels

A. Johner, M. Daoud

▶ To cite this version:

A. Johner, M. Daoud. Intermediate swelling of gels. Journal de Physique, 1989, 50 (15), pp.2147-2159. 10.1051/jphys:0198900500150214700. jpa-00211051

HAL Id: jpa-00211051 https://hal.science/jpa-00211051

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Classification Physics Abstracts 64.60A — 82.70G

Intermediate swelling of gels

A. Johner (1) and M. Daoud (2)

- (1) C.R.M., 6 Rue Boussingault, 67083 Strasbourg Cedex, France
- (2) Laboratoire Léon Brillouin (*), C.E.N. Saclay, 91191 Gif/Yvette Cedex, France

(Reçu le 16 mars 1989, accepté le 24 avril 1989)

Résumé. — Nous étudions le gonflement intermédiaire de gels au voisinage du seuil de gélation. Nous considérons aussi bien des gels faits de petits éléments multifonctionnels que des macromolécules linéaires vulcanisées. Nous analysons d'abord minutieusement la structure des gels dans le bain de réaction. Nous trouvons que des blobs branchés idéaux sont présents même dans le cas de vulcanisats critiques. Le gonflement de gels vulcanisés se fait en deux étapes successives. Dans le cas classique, elles correspondent à la désinterpénétration des différents réseaux présents dans le bain de réaction, puis au gonflement progressif des blobs idéaux. Nous discutons la conformation des gels à toutes les échelles de distances pour les différents régimes en concentration.

Abstract. — We consider the intermediate swelling of gels close to the gelation threshold. We treat both gels made of small polyfunctional units and vulcanized linear macromolecules. We first analyze carefully, within a Flory approximation, the structure of the gels in the reaction bath. We find that ideal branched blobs are present even in critical vulcanizates. For vulcanized gels, swelling includes two successive stages. In the classical case, these correspond to the disinterpenetration of the various networks that are present in the reaction bath, then to the gradual swelling of the ideal blobs. We discuss the conformation of the gel at all distance scales in the various concentration regimes.

1. Introduction.

A very large attention has been payed recently to static [1-12] and dynamic [13-18] properties of branched polymers and gels close to the gelation threshold. Most of these studies were concerned with the swelling of very large but finite macromolecules below the threshold, or with strong gels [19, 40, 41], far above it. The swelling of tenuous gels close to the threshold was considered theoretically [20] in the limit of the maximum swelling, when the sol is extracted from the solution and the gel has reached its swelling equilibrium. Recently

^(*) Laboratoire commun C.N.R.S.-C.E.A.

however, N.M.R. experiments by Cohen-Addad and coworkers [21] provided information about the intermediate swelling of such gels. Among others, it was clearly shown that two distinct steps are present in the case of vulcanized gels, made of cross-linked linear polymers. The main purpose of the present paper to discuss the intermediate swelling of these vulcanized gels and more specifically to understand the origin of these two steps in the swelling. This will lead us to consider the conformation of gels at all length scales in various concentration ranges.

Polymerization of small polyfunctional units is usually [43] well described by percolation [22-24] in its critical [25] version. On the other hand, vulcanization of linear chains in a melt is also well described by percolation. In this case however, its mean field — or Flory-Stockmayer — [26-28] version is valid most of the time. The reason for such different behaviors was analyzed first by de Gennes [29]. He related them to the fluctuations in connectivity that are small in the case of vulcanization of linear polymers in a melt, and more generally when any reacting species may interact with a large number of others [42]. Another argument was given subsequently [20], based on a Flory type of analysis. In the latter approach, which we will use below, one considers the free energy of a typical polymer, and more precisely its interaction part F_i . The latter is due to the excluded volume interaction that is present between any two monomers in an actual solution. Depending on the relative value of such interaction energy with respect to the thermal energy $k_{\rm B} T$, critical or mean field percolation is valid. An important fact that was missed when such analysis was performed [20] is the eventual existence of ideal (Flory-Stockmayer) blobs when the overall behavior of typical polymers is critical. As we will show, the presence of such blobs is crucial when one wishes to understand how two distinct steps are present, as was observed by Cohen-Addad et al. in their N.M.R. experiments.

In the following we will first recall the Flory analysis for gelation and vulcanization. In addition to the known results, we will carry out a detailed discussion of the (local) overlap in vulcanized gels : the striking fact is that even the critical vulcanized gels involve overlaping ideal branched blobs. In section 3, we recall the results for the fully swollen state [20] and study the intermediate regimes. We find a single range for gels made of small multifunctional units. Two swelling regimes are present for both critical and classical vulcanized gels. In the first one, at high concentrations, there is disinterpenetration of the linear chains. In the second regime, for lower concentrations, swelling of the branched parts only is involved. As we will show, after disinterpenetration, the classical gel swells at local scales while larger scales are involved in the critical case. Swelling of gels made of small polyfunctional units occurs in a single step : only one network is present.

An important assumption we will make is that upon swelling, entanglement effects are not important. Although this is a crude assumption [44], we believe it to be not too restrictive in the vicinity of the gelation threshold that we are considering. Farther from the threshold, trapped entanglements become important, and one would have to estimate their influence.

Finally in all the following we will equivalently use any of the expressions mean field, classical, Flory-Stockmayer, and ideal for the same physical situations.

2. Initial state : the reaction bath.

In this section we recall the main results for a gel in the reaction bath within a Flory theory [30, 31]. The free energy for a large typical polymer is

$$F = \frac{R_{\rm i}^2}{R_0^2} + \frac{v}{N_{\rm w}} \frac{N^2}{R_{\rm i}^3}$$
(1)

N° 15

The first term is the elastic contribution where it is assumed that the elastic constant is inversely proportional to the square of the ideal (classical) radius $R_0 \cdot R_i$ is the actual radius or mesh size, to be determined. The second term is the interaction energy F_i , with v the excluded volume parameter. The presence of the weight average molecular weight N_w reflects the Edwards screening [32, 33] of the interactions, due to the presence of smaller polymers inside the large ones. N is the mass of the large clusters, and there is a relation between N_w and N. In the Flory theory, the classical expression for this relation is assumed :

$$N_{\rm w} \sim N^{1/2}$$
 (2)

and the ideal radius is

$$R_0 \sim N^{1/4} \ell$$
 (3)

 ℓ is the length of a monomer.

Minimizing the free energy with respect to R_i and taking equations (2) and (3) into account, we find the fractal dimension of the gel in the reaction bath. For small polyfunctional precursors, the monomer is also the unit in the percolation problem, and the interaction free energy is large. Thus in this case we get a critical gel and

$$N \sim R_{\rm i}^{D_{\rm p}} \tag{4a}$$

with

$$D_{\rm p} = 5/2 \tag{4b}$$

For the vulcanization of long linear chains in a melt, the situation is quite different. Now the unit in the percolation problem is a polymer chain with weight Z and radius $Z^{1/2} \ell$. Thus, using mean field exponents, the classical Flory-Stockmayer results may be written in the following form [20]:

$$N_{\rm w} \sim \left(\frac{N}{Z}\right)^{1/2} Z \tag{5}$$

$$R_{\rm i} \sim \left(\frac{N}{Z}\right)^{1/4} Z^{1/2} \ell \tag{6}$$

Inserting relations (5) and (6) in the interaction part F_i of the free energy given in equation (1), we find

$$F_{\rm i} \sim \left(\frac{N}{Z}\right)^{3/4} Z^{-1/2} \tag{7}$$

Near the percolation threshold N diverges and the interaction energy is large. Thus the problem is critical. On the other hand, far enough from the gelation point, N is smaller, so that the free energy is smaller and the problem becomes classical. The crossover size between these limits is

$$N^* \sim Z^{5/3}$$
 (8)

Finally, N is related to the distance ε to the percolation threshold. In the Flory-Stockmayer limit we have

$$N \sim \varepsilon^{-2} Z \tag{9}$$

JOURNAL DE PHYSIQUE

Using relations (8') and (9) we recover de Gennes' result [29]: for $\varepsilon \ge \varepsilon^*$, with

$$\varepsilon^* \sim Z^{-1/3} \tag{8'}$$

the dimensionless interaction energy F_i is smaller than unity and the problem is classical : the Flory-Stockmayer approach is valid. This implies that the fractal dimension is $D_0 = 4$. In the opposite case, $\varepsilon \ll \varepsilon^*$, interactions are relevant and the problem is critical : the fractal dimension of the largest polymers (and of the gel) is given by relation (4b), and critical exponents are needed for overall properties. It is interesting however to consider smaller polymers or local properties of the gel. Using relations (6) and (8') and generalizing equation (7) to smaller parts made of g monomers, the interaction energy of a smaller part is

$$F'_{\rm i} = (g/Z)^{3/4} Z^{-1/2} \tag{7'}$$

The latter relation shows that even when the energy of a large polymer is large, the situation may be inverted if we consider smaller scales. More precisely, one realizes that there is a crossover size g_{id} . For larger scales the interaction energy is large and the behavior is governed by relation (4b). For smaller scales the interaction energy becomes small, and the behavior is ideal. We are thus led to introduce ideal blobs, made of g_{id} monomers. Equating the local free energy, relation (7'), to unity gives the size of the ideal blob. We get

$$g_{\rm id} \sim Z^{5/3} \tag{10}$$

Note that at the cross-over between classical and critical vulcanization, $\varepsilon = \varepsilon^*$, the ideal blob has the typical mesh size.

The situation in the reaction bath may be summarized as follows :

- For small polyfunctional units, the problem is critical, and the characteristic length of the gel (the mesh size) is

$$R_{\rm i} \sim N^{2/5} \,\ell \tag{11}$$

— For vulcanization in a melt, and for scales larger than the radius $R_{\rm L} \sim Z^{1/2} \ell$ of a linear chain, two cases may be met : For gels made not too close to the gelation threshold, when $\varepsilon \gg \varepsilon^*$, the problem is classical and the Flory-Stockmayer theory is valid. The mesh size is

$$R_{\rm i} \sim \left(\frac{N}{Z}\right)^{1/4} R_{\rm L} \sim N^{1/4} Z^{1/4} \ell \tag{12}$$

Close to the threshold, when $\varepsilon \ll \varepsilon^*$, the problem is critical but we are led to introduce a second length χ_{id} corresponding to a local ideal blob. Using (10) and (12) we get

$$\chi_{\rm id} \sim Z^{2/3} \,\ell \tag{13}$$

The overall behavior is governed by equation (4b) if we take the ideal blob as unit :

$$R_{\rm i} \sim (N/g_{\rm id})^{2/5} \chi_{\rm id} \sim N^{2/5} \ell$$
 (14)

Thus the vulcanized gel does not look critical at all length scales, but only at large ones. For small distances, it is dense. Such crossover has important implications regarding the interpenetration of the networks in the critical case that we discuss below. Finally we note that at ε^* , the ideal blob becomes of the order of the mesh size, and that relations (12) to (14) merge.

N° 15

The *interpenetration* of the networks was mentioned first by Bastide *et al.* [34] and further discussed in reference [20]; we wish here to make a further step. For small polyfunctional units, it is known [35] that only one [45] infinite network is present. In the classical case, several networks are interpenetrating [36, 37]. Following reference [20] we estimate their number by comparing the gel fraction G and the density ρ of one of them. In the mean field case we have

$$G \sim \left(\frac{N}{Z}\right)^{-1/2} \tag{15}$$

and, using equation (6),

$$\rho \sim \frac{N}{R_i^3} \sim \left(\frac{N}{Z}\right)^{1/4} Z^{-1/2} \tag{16}$$

Thus the number n of nodes per unit volume is

$$n = G/\rho \sim \left(\frac{N}{Z}\right)^{-3/4} Z^{1/2} \tag{17}$$

Relation (17) gives the number of interpenetrating networks in the classical case and crosses over to the critical value, unity, at ε^* , when relation (8') is satisfied.

Note that for critical vulcanization, although there is no interpenetration for large scales, as mentioned above, because of the existence of the ideal blobs, there is local interpenetration. Combining relations (6) and (17) and generalizing to smaller masses and distances, we find for a mass g or a distance r:

$$n(g) \sim \left(\frac{g}{Z}\right)^{-3/4} Z^{1/2} \sim \left(\frac{r}{\chi_{\rm id}}\right)^{-3}$$
(18)

crossing-over to unity for large masses in the critical case. For small masses, on the contrary, it becomes larger than one. Setting n = 1 leads to the ideal blob size g_{id} , relation (10).

3. Final state : the swollen gel.

3.1 EQUILIBRIUM SWELLING. — Upon addition of a good solvent, the gel swells. In all the following, we will always assume that the initial state is the gel in its reaction bath. We review first the known results concerning the equilibrium swelling, at concentration C_e , when the gel cannot absorb solvent anymore. The basic hypothesis in these results is that there are no trapped entanglements that act as cross-links. We argue that this assumption is not too strong because we are considering the vicinity of the gelation threshold. The breaking down of this assumption as one goes farther from the threshold, into the stronger gel limit is still an open question.

In a Flory approximation, the swelling of the gel corresponds to a change in the fractal dimension [20] from its value in the bath to the fractal dimension of a dilute branched polymer, $D_s = 2$. The latter value is related to the absence of screening in the swollen state. In the mean field case, in addition to this change in the fractal dimension, one has also to take into account the disinterpenetration of the different networks. Let R_f be the mesh size in the swollen state. Thus we have

for the small polyfunctional unit case, and

$$R_{\rm f} \sim \left(\frac{N}{Z}\right)^{1/2} Z^{3/5} \ell \tag{20}$$

for the vulcanization case.

Recalling that the concentration in the reaction bath is of order unity, and calling R_i the initial mesh size, in the reaction bath, that was considered above, the equilibrium concentration C_e is

$$C_{\rm e} \sim \left(\frac{R_{\rm i}}{R_{\rm f}}\right)^3 \sim N^{-3/10}$$
 (21)

$$\sim N^{-3/10} Z^{-3/10}$$
 (22)

in the polyfunctional unit and critical vulcanization cases respectively, and

$$C_{\rm e} \sim n \left(\frac{R_{\rm i}}{R_{\rm f}}\right)^3 \sim Z^{-4/5} \tag{23}$$

for the classical vulcanization case, where the factor *n* takes into account the disinterpenetration of the networks. Note that relation (23) corresponds to the overlap concentration $C_{\rm L}^*$ of the linear chains. Note also that for critical vulcanizates the equilibrium concentration, relation (22), is smaller than $C_{\rm L}^*$: the C * theorem [22] breaks down in the critical case. Using relations (6) and (9) we note that relations (22) and (23) merge for $\varepsilon = \varepsilon^*$ as they should.

In order to study the intermediate swelling, we will first consider the more direct case of polyfunctional units before considering the vulcanization cases.

3.2 INTERMEDIATE SWELLING OF POLYFUNCTIONAL UNITS. — Let C be the final concentration, after addition of some (good) solvent. Because the initial concentration in the reaction bath is of order unity, we have

$$C \sim \left(\frac{R_{\rm i}}{R_{\rm f}}\right)^3 \tag{24}$$

Using (11) we get

$$R_{\rm f} \sim N^{2/5} C^{-1/3} \ell \tag{25}$$

Note that the fractal dimension for the overall behavior is unchanged, and that we recover the fractal dimension of swollen polymers $D_s = 2$ only at the equilibrium concentration, relation (21). Swelling is merely related here to a change in the fractal dimension at a local scale ξ_b . This corresponds to a swollen blob made of g_b monomers such that

$$\boldsymbol{\xi}_{\mathrm{b}} \sim \boldsymbol{g}_{\mathrm{b}}^{1/2} \boldsymbol{\ell} \tag{26}$$

Then the swollen gel has the same structure as the one it had in the rection bath if we take the blob as unit :

$$R_{\rm f} \sim \left(\frac{N}{g_{\rm b}}\right)^{2/5} \xi_{\rm b} \tag{27}$$

Combining equations (25) to (27) we get

$$\xi_{\rm b} \sim C^{-5/3}$$
 (28)

and

$$g_{\rm b} \sim C^{-10/3}$$
 (29)

Thus the structure of the final gel is swollen, with fractal dimension 2, for scales smaller than the blob size, and is the same as in the reaction bath for larger scales. Note that the blob size is the same as in a semi-dilute solution of randomly branched polymers [38]. For these intermediate concentrations there is no difference between the sol and the gel structures. The different distance scales are summarized in figure 1.

Let us now turn to the less direct case of a classical vulcanized gel.



Fig. 1. — The different length scales for an intermediate concentration, $C_e \ll C \ll 1$, of a gel made of small polyfunctional units. The blob size ξ_b increases from the monomer size ℓ to the mesh size R_f when concentration decreases from 1 to C_e .

3.3 INTERMEDIATE SWELLING OF A CLASSICAL VULCANIZATE. — The main difference with the previous case is that in the case of vulcanizates, upon addition of a small amount of solvent, linear blobs are present in a first step. In a second step, when more solvent is added, the blobs are blanched. One realizes easily that during the first stage, linear chains disentangle [22, 39] and thus that there is a gradual disinterpenetration of the different networks that are present in the reaction bath. As we will see, the second state is similar to what was discussed in the previous section.

3.3.1 Disinterpenetration. — As mentioned just above, for high concentrations, when a small amount of solvent is added, a swollen linear blob is present. This is identical to the one in a semi-dilute solution of linear polymers. Let g_L , ξ_L and R_L be respectively the number of monomers and radii of the linear blob and chain. We know [22, 39]

$$g_{\rm L} \sim C^{-5/4}$$
 (30)

$$\xi_{\rm I} \sim C^{-3/4}$$
 (31)

$$R_{\rm I} \sim Z^{1/2} \, C^{-1/8} \tag{32}$$

The characteristic mesh size is merely changed because the chain radius is. Thus relation (12) becomes

$$R_{\rm f} \sim \left(\frac{N}{Z}\right)^{1/4} R_{\rm L} \sim N^{1/4} Z^{1/4} C^{-1/8}$$
(33)

Because of the local swelling of the linear chains, we also know that the linear polymers disentangle. This is due to the fact that we have now to take the linear blob as statistical unit instead of the actual monomer. This implies a disinterpenetration of the networks that we evaluate by generalizing equation (18). Taking the linear blob made of $g_{\rm L}$ monomers as unit, the latter becomes :

$$n_{\rm f} \sim \left(\frac{N}{Z}\right)^{-3/4} \left(\frac{Z}{g_{\rm L}}\right)^{1/2} \tag{18'}$$

Inserting (30) in (18'), it is possible to determine the cross-over concentration C_1 when n_f becomes of the order of unity. We find

$$C_1 \sim \left(\frac{N}{Z}\right)^{6/5} Z^{-4/5}$$
 (34)

For concentrations smaller than C_1 , the gel is disinterpenetrated. Above C_1 there is still interpenetration; but upon addition of solvent, the gel disinterpenetrates gradually at the short scales corresponding to the linear blob. Finally, one may calculate the swelling ratio Q which is the ratio of the final to initial volumes of the gel.

$$Q = \frac{V_{\rm f}}{V_i}$$

This is the product of a disinterpenetration and a swelling parts.

$$Q = \frac{n}{n_{\rm f}} \left(\frac{R_{\rm f}}{R}\right)^3 \sim C^{-1} \tag{35}$$

as it should.

It is important to note that for intermediate swelling, as in the reaction bath, interpenetration is a decreasing function of distance. Interpolating relation (18') for intermediate distances and using relation (33) we find at intermediate scales instead of relation (18), for $R_{\rm L} \ll r \ll R_{\rm f}$:

$$n_{\rm f}(r) \sim \left(\frac{r}{R_{\rm L}}\right)^{-3} \left(\frac{Z}{g_{\rm L}}\right)^{1/2}$$
 (36)

3.3.2 Swelling. — At C_1 the various networks have completely disinterpenetrated, so that if one adds more solvent the only remaining process is the swelling of these networks. This is achieved by a change in the fractal dimension of the gel, which goes from its initial value $D_0 = 4$, valid both in the reaction bath and in the high concentration regime, $C > C_1$, that we discussed above, to the swollen value $D_s = 2$, as discussed in section 3.1. It is important to realize that although the various networks are disentangled at large scales, they are not at smaller scales, in the same way as discussed in section 1 for critical vulcanizates. This is related to the existence of ideal blobs with radius χ_{id} inside which the interactions are still smaller than the thermal energy. Thus a second length is present, in addition to the mesh size R_f . Both lengths may be calculated by assuming the following scaling relation :

$$L = N^{1/4} Z^{1/4} C^{-1/8} f_{R, \gamma} (C/C_1)$$
(37)

where the first term in the right hand side is the mesh size in the high concentration range, relation (33), and C_1 is given by relation (34). $f_{R,\chi}(x)$ are unknown functions with known asymptotic behaviors. In the high concentration regime, they are analytic whereas for small values of their arguments we assume that they behave as power laws.

$$f(x) \sim x^a \qquad (x \ll 1) \tag{38}$$

The exponents a for R_f and χ_{id} are estimated by imposing that R_f behaves as $N^{1/2}$ and that χ_{id} is independent of N. We find

$$\chi_{\rm id} \sim Z^{2/3} C^{1/12} \tag{39}$$

$$R_{\rm f} \sim \left(\frac{N}{Z}\right)^{1/2} Z^{1/3} C^{-1/3} \tag{40}$$

The reader may check that in this low concentration regime, the structure of the gel is made of a swollen arrangement of ideal blobs. Upon addition of solvent, the size of the ideal blob decreases from the mesh size R_i in the reaction bath, $C \sim 1$, until it vanishes when it reaches its minimum value, which corresponds to the initial linear chain, relation (32), at the equilibrium concentration C_e , equation (23). Finally one may also check that the swelling ratio $Q \sim C^{-1}$ of the final to initial volumes is the product of a concentration dependent swelling part and a constant disinterpenetration part. The latter part is constant because in this concentration range the networks are already disentangled at large scales, as discussed above, so that the final state always corresponds to $n_f = 1$:

$$Q \sim \frac{V_{\rm f}}{V_{\rm i}} \sim n \left(\frac{R_{\rm f}}{R_{\rm i}}\right)^3 \tag{41}$$

with n the initial number of entangled networks in the reaction bath, relation (18). Note the difference between relations (36) and (41) about the final interpenetration. The various swelling regimes of a classical vulcanized gel are summarized in figure 2.



Fig. 2. — Length scales for intermediate concentrations of a classical vulcanizate. (2a), $C_1 \ll C \ll 1$, corresponds to the disinterpenetration of the networks because of local swelling of the linear chains. At C_1 disinterpenetration is complete at large scales. (2b) For $C_e \ll C \ll C_1$, there is an ideal blob and swelling of the branched part at large scales. This ideal blob with size χ_{id} shrinks when concentration decreases an disappears at C_e . Note that C_e is of the order of the overlap concentration C_L^* of the linear chains.

3.4 INTERMEDIATE SWELLING OF A CRITICAL VULCANIZATE. — The main difference between these gels and the classical ones that we just discussed is that the former do not overlap in the reaction bath a least on large scales, whereas the latter overlap strongly, as discussed in section 1. Thus starting from the reaction bath, if one adds a good solvent in small amount, swelling is related to the local swelling of the linear chains, without any change in the fractal dimension of the gel itself. Because there is no disengagement, the final mesh size may

be calculated directly from the knowledge of the swelling ratio Q which in the present case is simply the ratio of final to initial volumes of the unit cell:

$$Q = C^{-1} \sim \left(\frac{R_{\rm f}}{R_{\rm i}}\right)^3 \tag{42}$$

Combining equations (42) and (14), we get

$$R_{\rm f} \sim N^{2/5} C^{-1/3} \tag{43}$$

Let us now turn to the more local properties. As we will see two concentration regimes are also present in this case.

3.4.1 The high concentration range $(C \ge C_1^*)$. — On a local scale, as we just mentioned, there is a swelling of the linear chains. There results a linear blob with radius ξ_L and a radius R_L for the chain given by equations (31) and (32) respectively. Because of this local disentanglement of the linear chains, the number of monomers g_{id} in the ideal branched blob, equation (13), also changes. This number as well as the radius χ_{id} may be calculated by observing that the present regime is similar to the reaction bath if we take the linear blob, made of g_L monomers and with radius ξ_L as unit. Thus equation (13) has to be replaced by

$$\frac{g_{\rm id}}{Z} \sim \left(\frac{Z}{g_{\rm L}}\right)^{2/3} \tag{44}$$

and

$$\chi_{\rm id} \sim \left(\frac{g_{\rm id}}{Z}\right)^{1/4} R_{\rm L} \tag{45}$$

Using (30) to (32), we find

$$\chi_{\rm id} \sim Z^{2/3} C^{1/12} \tag{46}$$

We note that at the overlap concentration $C_{L}^{*} \sim Z^{-4/5}$ of the linear chain, this ideal blob disappears by merging with the linear chains.

At still larger distances, $\chi_{id} \ll r \ll R_f$, the structure of the gel is made of swollen branched blobs (see Fig. 3). The presence of such blobs may be understood easily by direct comparison



Fig. 3. — Length scales for intermediate concentrations of a critical vulcanizate. For $1 \ge C \ge C_L^*$, figure 3a, the ideal blob swells in the same way as in figure 2b, leading to both an ideal and a swollen blobs. For $C_L^* \ll C \ll C_e$, figure 3b, no ideal part is left. The structure is made of swollen blobs and is the same as in figure 1.

with the case of semi-dilute solutions of linear chains. Moreover, it is easy to check, using relations (43) to (46), that consistency cannot be achieved, and that an extra distance scale is needed. Let g_b and ξ_b be respectively the number of monomers and the radius of the swollen branched blob. Then we have

$$R_{\rm f} \sim \left(\frac{N}{g_{\rm b}}\right)^{2/5} \xi_{\rm b} \tag{47}$$

with

$$\xi_{\rm b} \sim \left(\frac{g_{\rm b}}{g_{\rm id}}\right)^{1/2} \chi_{\rm id} \tag{47'}$$

Using relations (43) to (47), we find

$$g_{\rm b} \sim Z^{5/3}$$
 (48a)

and

$$\xi_{\rm b} \sim Z^{2/3} \, C^{-1/3} \tag{48b}$$

Note that in this concentration range the number g_b of monomers in the swollen branched blob remains constant and that at this scale, swelling is the same as for the ideal case, section $c\beta$ [note the similarity between equations (40) and 48)]. Thus in this regime one encounters successively, for increasing distances, the swollen linear blob, the linear chain, the ideal branched and the swollen branched blobs, as shown in figure 3a. As mentioned above, at the overlap concentration C_L^* of linear chains, the firts three ones merge, and only the last two ones remain for concentrations less than C_L^* .

3.4.2 The low concentration regime. — An important difference between the critical vulcanizates and the other two cases that we considered before is that in the present case the equilibrium concentration C_e , relation (22), is less than the overlap concentration C_L^* of the linear chains, relation (23). For concentrations below the latter concentration, as we saw above, the local structures have merged into the linear swollen chain, with radius $R_L \sim Z^{3/5} \ell$. Because there is no disinterpenetration, relation (43) is still valid for the mesh size. This allows us to evaluate directly the size g_b and radius ξ_b of the swollen branched blob :

$$\xi_{\rm b} \sim \left(\frac{g_{\rm b}}{Z}\right)^{1/2} Z^{3/5} \tag{49}$$

Using relations (43), (47) and (49), we get

$$\xi_{\rm b} \sim Z^{-2/5} C^{-5/3} \tag{50}$$

Swelling in this concentration range is very similar to the small polyfunctional unit case discussed in section (3.2). Note that relation (50) crosses over smoothly to (48b) for $C \sim C_{\rm L}^*$ and to the mesh size $R_{\rm f}$, equation (20) for the equilibrium concentration $C_{\rm e}$, relation (22).

4. Conclusion.

We have discussed within a Flory approximation the intermediate swelling that occurs upon progressive addition of a good solvent to a tenuous gel in its reaction bath. The discussion was carried out for « critical » gels made of small polyfunctional units or vulcanized gels very close to the gelation threshold and for « classical » vulcanizates. In order to treat the latter cases, we had to come back to the structure of cross-linked linear chains. In this case we showed that ideal branched blobs are present even for the critical case of vulcanization. This is very important, especially when gelation is performed in the presence of a solvent, so that the critical region, where the classical theory is believed to fail, is wide. The present paper was concerned only with the case of vulcanization in the bulk, but generalization to semi-dilute solution of linear chains is straightforward. A very important hypothesis in this work is that we assume that the entanglement effects are not important [44]. Although this is a strong assumption, we argue that it should hold close to the gelation threshold. Our results may be summarized as follows :

— in the case of small polyfunctional units, swelling occurs locally. As a consequence, swollen branched blobs are present. This is very similar to what happens in a semi dilute solution of linear chains;

— for vulcanization, two steps are involved, as was recently observed experimentally by Cohen-Addad *et al.* These are not identical for the classical and critical cases ;

— in the classical case several networks are interpenetrated in the reaction bath. Swelling includes their disinterpenetration in a first stage, down to a concentration C_1 , equation (33). Further swelling, between C_1 and the equilibrium concentration C_L^* , corresponds to a progressive swelling of the ideal blobs that are present. Note that in this regime the local blobs are ideal whereas the large scale behavior is swollen. The maximum swelling corresponds to the overlap concentration C_L^* of the linear chains. At this concentration the ideal behavior is no longer presentt;

— for critical vulcanizates, although there is only one infinite network, ideal branched blobs, with Flory-Stockmayer behavior, are present in the reaction bath. The equilibrium swelling concentration C_e in this case is smaller than the overlap concentration C_L^* of the linear chains. Again two regimes are present. For concentrations higher than C_L^* , swelling is related to the gradual disappearance of the ideal blobs upon addition of solvent and to the presence of swollen branched blobs. In this range, the number of monomers in the latter is constant. When solvent is added, the size of the ideal blobs shrinks, until no more ideal behavior is present, at C_L^* . In the lower concentration range, for $C_e \ll C \ll C_L^*$, there is a second regime with no ideal blobs. Swelling corresponds to the gradual increase of the size of the swollen branched blobs, which reach the mesh size at C_e .

Acknowledgments.

The authors are much indebted to J. P. Cohen-Addad, J. P. Cotton, G. Jannink and A. Schmitt for very stimulating discussions.

References

- [1] CANDAU S., BASTIDE J., DELSANTI M., Adv. Pol. Sci. 44 (1982) 27.
- [2] RICHARDS R. W., DAVIDSON N. S., Macromolecules 19 (1986) 1381.
- [3] LUMPKIN O. J., DEJARDIN P., ZIMM B. H., Biopolymers 24 (1985) 1573.
- [4] LEIBLER L., SCHOSSELER F., Phys. Rev. Lett. 55 (1985) 1110.
- [5] ADAM M., DELSANTI M., MUNCH J. P., DURAND D., J. Phys. France (1987) 1809.
- [6] MARTIN J. E., KEEFER K. D., Phys. Rev. A 34 (1986) 4988.

- [7] BOUCHAUD E., DELSANTI M., ADAM M., DAOUD M., DURAND M., J. Phys. France 47 (1986) 1273.
- [8] CABANE B., DUBOIS M., DUPLESSIS R., J. Phys. France 48 (1987) 2131.
- [9] ALLAIN C., SALOME L., Macromolecules 20 (1987) 2958.
- [10] GEISSLER E., HORKAY F., HECHT A. M., ZRINYI M., to be published.
- [11] PATTON E. V., WESSON J. A., RUBINSTEIN M., WILSON J. C., OPPENHEIMER L. E., to be published.
- [12] BRIBER R. M., BAUER B. J., Macromolecules 21 (1988) 3296.
- [13] MATSUO E. S., TANAKA T., J. Chem. Phys. 89 (1988) 1695.
- [14] GEFEN Y., AHARONY A., ALEXANDER, Phys. Rev. lett. 50 (1983) 77.
- [15] DAOUD M., J. Phys. A 21 (1988) L973.
- [16] MARTIN J. E., ADOLF D., WILCOXON J. P., Phys. Rev. Lett. 61 (1988) 2620.
- [17] DELSANTI M., ADAM M., MUNCH J. P., DURAND D. Universalities in Condensed Matter Physics, Springer Proc. Phys. (1988).
- [18] RUBINSTEIN M., COLBY R. H., GILLMOR J. R., to be published.
- [19] BASTIDE J., LEIBLER L., Macromolecules 21 (1988) 2647.
- [20] DAOUD M., BOUCHAUD E., JANNINK G., Macromolecules 19 (1986) 1955.
- [21] COHEN-ADDAD J. P., SCHMIT C., J. Pol. Sci, Pol. Lett. 25 (1987) 487.
 SCHMIT C., COHEN-ADDAD J. P., Macromolecules, to be published;
 SCHMIT C., Thesis (1988), available on request from Laboratoire de Spectrometrie Physique, U.S.M.G., F38042 St Martin d'Heres cedex.
- [22] DE GENNES P. G., Scaling concepts in Polymer physics (Cornell Un. Press, Ithaca, N.Y. 1979.
- [23] STAUFFER D., CONIGLIO A., ADAM M., Adv. Pol. Sci. 44 (1982) 103.
- [24] BASTIDE J., Thesis (1985), available on request at C.R.M., 6 rue Boussingault, 67083 Strasbourg cedex.
- [25] STANLEY H. E., Introduction to phase transitions and critical phenomena (Oxford Un. Press, Oxford, U.K.) 1982.
- [26] STOCKMAYER W. H., J. Chem. Phys. 11 (1943) 45.
- [27] FLORY P. J., Principles of polymer chemistry (Cornell Un. Press, Ithaca, N.Y.) 1953.
- [28] GORDON M., ROSS-MURPHY S. B., Pure Apll. Chem. 43 (1975) 1.
- [29] DE GENNES P. G., J. Phys. Lett. France 38 (1977) 355.
- [30] DE GENNES, C. R. Acad. Sci. France 291 (1980) 17.
- [31] ISAACSON J., LUBENSKY T. C., J. Phys. Lett. France 42 (1981) 175.
- [32] EDWARDS S. F., Proc. Phys. Soc. 88 (1966) 265.
- [33] DE GENNES P. G., J. Pol. Sci. Pol. Symp. 61 (1977) 313.
- [34] BASTIDE J., PICOT C., CANDAU S. J., J. Macrom. Sci. B 19 (1981) 13.
- [35] STAUFFER D., Introduction to percolation theory, Taylor and Francis (1985).
- [36] CONIGLIO A., Physics of finely divided matter, Springer Proc. Phys. 5 (1985) 84.
- [37] ALEXANDER, S., Physics of finely divided matter, Springer Proc. Phys. 5 (1985) 162.
- [38] DAOUD M., LEIBLER L., Macromolecules 21 (1988) 1497.
- [39] DES CLOIZEAUX J., JANNINK G., Les polymères en solution (Ed. de Physique, Les Ulis) 1987.
- [40] BASTIDE J., CANDAU S. J., LEIBLER L., Macromolecules 14 (1981) 719.
- [41] BROCHARD F., J. Phys. France 42 (1981) 505.
- [42] DAOUD M., J. Phys. Lett. France 40 (1979) 201.
- [43] With some exceptions, see for instance HERRMANN H. J., LANDAU D. P. and STAUFFER D., Phys. Rev. Lett. 49 (1982) 412.
- [44] See however KANTOR Y., HASSOLD G. N., Phys. Rev. Lett. 60 (1988) 1457.
- [45] NEWMANN C. M., SCHULMAN L. S., J. Stat. Phys. 26 (1981) 613.

N° 15