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► **To cite this version:**

F. Brochard. Polymer networks swollen by a homopolymer solution. Journal de Physique, 1981, 42 (3), pp.505-511. 10.1051/jphys:01981004203050500 . jpa-00209036

HAL Id: jpa-00209036

<https://hal.science/jpa-00209036>

Submitted on 4 Feb 2008

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Classification

Physics Abstracts

64.75 — 62.20F — 61.40K

Polymer networks swollen by a homopolymer solution

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(Reçu le 3 juin 1980, révisé le 20 novembre, accepté le 1^{er} décembre 1980)

Résumé. — On étudie la configuration de réseaux polymériques (N monomères entre noeuds, fraction en volume φ_N) en équilibre avec une solution du même polymère (P monomères par chaîne mobile, fraction en volume φ_P^{ext}). En fonction de P/N et de φ_P^{ext} , on trouve trois régimes :

— Non miscible, gonflé (SUM) : les chaînes mobiles ne pénètrent pas. La concentration à l'intérieur du gel φ_P^{int} est exponentiellement petite. La distance entre noeuds adjacents du réseau varie comme $N^{3/5}$.

— Miscible, gonflé (SM) : les chaînes mobiles pénètrent la région occupée par le gel, mais le gel est encore gonflé ($R \sim N^{3/5}/P^{1/5}$).

— Miscible, idéal (IM) : ici aussi, les chaînes mobiles pénètrent le gel. Les interactions de type volume exclu entre monomères du gel sont fortement écrantées. Le gel doit atteindre un état final similaire à celui qu'il aurait en solvant θ .

Dans les cas de miscibilité, lorsqu'on part d'un gel gonflé mis en contact avec une solution de polymère, l'état final est atteint seulement après un temps très long : il pourrait être observé cependant sur des particules de gel de quelques microns.

Tous ces résultats ne sont plus valables si le gel est chimiquement différent des chaînes mobiles. Le simple fait que les noeuds du gel soient de nature chimique différente des chaînes peut suffire à expulser les chaînes mobiles du gel.

Abstract. — We study the conformation of a polymer network (N monomers between crosslinks, volume fraction φ_N) in contact with a solution of the same polymer (P monomers per mobile chain, volume fraction φ_P^{ext}). As a function of P/N and φ_P^{ext} , we find three regimes :

— Swollen unmixed (SUM) : the free chains do not penetrate. The internal concentration φ_P^{int} is exponentially small in the region occupied by the gel. The distance between crosslinks varies as $N^{3/5}$.

— Swollen mixed (SM) : the mobile chains *penetrate* the region occupied by the gel but the gel is still swollen ($R \sim N^{3/5}/P^{1/5}$).

— Ideal mixed (IM) : here again, the mobile chains penetrate the gel. The excluded volume interactions between monomers of the gel are strongly screened out. The gel is expected to reach a final state similar to what would be found in a θ solvent.

In all the mixed cases, when starting from a swollen gel in contact with a polymer solution, the final state is reached only at very long times : it could be observed however on small gel particles immersed in the solvent mixture or with one labelled chain (N monomers) in a solution of P chains.

All these results cease to be valid if the gel is even slightly chemically different from the mobile chains. In that case, the mobile chains are expelled out and the gel deswells as the concentration of the external polymer solution increases.

1. Introduction. — We study the partition of flexible polymer chains (« P chains ») between a swollen gel and a bulk solution with the same solvent. It is of some interest to find out when it is possible to introduce mobile macromolecules inside a gel :

a) problems of this type are met in « reptation » studies where the aim is to investigate the motion of a free chain trapped in a permanent network ;

b) the « penetrated » state of the gel may also be a useful intermediate in the fabrication of interpenetrating polymer networks (IPN) : a network of polymer 1 is swollen by a solution of polymer 2, which is then crosslinked.

Common belief has been that the mobile chains do *not* penetrate into the gel, even if they are compatible with the crosslinked chains. Experimentally it is often

hard to discriminate between a *thermodynamic* obstacle and a *kinetic* obstacle. In all cases, the chains reptate only slowly inside the gel. We want to discuss here the thermodynamic aspects of penetration and osmotic deswelling on a highly simplified case. We consider a gel of well calibrated chains (N monomers/chain). The free chains (P monomers/chain) are assumed to be chemically *identical* to the crosslinked chains. Finally the solvent is taken to be very good and for simplicity we choose the athermal limit ($\chi_{sp} = 0$, where χ is the Flory interaction parameter).

Up to this point, there is a close analogy between our problem and the question of grafted polymer chains exposed to polymer solutions, which has been analysed recently by De Gennes⁽¹⁾. The grafted chains correspond to the gel. However, the gel case is different in some aspects :

a) the gel is isotropic ;

b) the mechanical properties, and the swelling behaviour of a network, depend on the *detailed conditions of the gel preparation*. We assume here that the network has been prepared by crosslinking the polymer in solution, with a good solvent, in the « semi-dilute » regime. In this way entanglements trapped between crosslinks are not too frequent [3]. For this case, the unperturbed state (defined by the extension of the chains between crosslinks in the absence of excluded volume effects) corresponds to $R_0 = N^{1/2} a$. If the network had been prepared from a polymer melt the unperturbed distance between crosslinks would be different ($R_{unpert} \rightarrow N^{1/3} a$). The properties of this second type of gels are more complex because of the large number of entanglements trapped between crosslinks.

All our discussion is only *qualitative* and we neglect precise numerical coefficients.

Let us start by a simplified re-derivation of the Flory scheme adapted for a calibrated gel swollen by a pure good solvent (no P chains).

Using a lattice model, the free energy per site may be written as :

$$\frac{F_s}{T} = (1 - \varphi_N) \text{Log} (1 - \varphi_N) + 3Q \frac{\varphi_N}{N} \left(\frac{1}{2} \frac{R^2}{R_0^2} + \text{Log} \frac{R_0}{R} \right) + \chi_{12} \varphi_N (1 - \varphi_N) \quad (1)$$

where φ_N is the volume fraction occupied by the network. The first term is the entropy of mixing, the second term the classical elastic energy [1] which opposes gel extension and compression. R measures the distance between crosslinks and is related to φ_N through the packing conditions

$$\frac{\varphi_N}{N} \frac{R^3}{a^3} = f. \quad (2)$$

Note that equation (2) does *not* imply an affine deformation of the gel, but it does assume that first neighbouring crosslinks are connected crosslinks. Steric hindrance does not allow the approach of distant crosslinks. f is a numerical coefficient, which depends upon the functionality of the gel. (The compression term, using (2), has a striking similarity to the translational entropy for a collection of N chains ($\varphi_N/N \cdot \log \varphi_N$.) The last term is the interaction term. We take the solvent to be athermal ($\chi_{12} = 0$).

For simplicity, we set $Q = f = 1$.

The degree of swelling, specified by the value of φ_N , is derived from the equality of the chemical potential of the solvent inside and outside the gel :

$$\pi = - \frac{\partial(F\Omega)}{\partial\Omega} = \varphi_N^2 \frac{\partial(F/\varphi_N)}{\partial\varphi_N} = 0 \quad (3)$$

where Ω is the total volume of the gel.

Using equation (1) and expanding F at low polymer fraction, this gives :

$$\frac{1}{2} \varphi_N^2 - \frac{\varphi_N^{1/3}}{N^{4/3}} + \frac{\varphi_N}{N} = 0. \quad (4)$$

The gel is swollen because of the repulsion between monomers. The last term is negligible and the network adjusts its concentration to the value :

$$\varphi_N = \varphi_N^* = N^{-4/5}, \quad \text{i.e. } R = N^{3/5} a \quad (5)$$

where φ_N^* is the threshold concentration between the dilute and the semi-dilute regime of a solution of free chains N . These classical results have been confirmed by macroscopic measurements, and more recently by light scattering experiments on calibrated gels [3].

Let us now extend the Flory model of the swelling to gels in equilibrium with a homopolymer solution. It is helpful to start with the case of a *gel plus a polymer melt*. We will see that the behaviour of the gel plus a polymer solution is closely related to this case.

As pointed in reference [2], mean field theory correctly gives the equilibrium degree of swelling because of a favourable cancellation between two approximations. However when we want to derive energies rather than sizes, the mean field theory is not quite correct. This remark applies for instance to the calculation of the elastic modulus of the gel. To include these corrections, we proceed as follows :

— all the formulae of the text are given in the Flory-Huggins theory ;

— all the final results which have to be renormalized by scaling are indicated by the mark (+ SC) (+ SC = plus scaling correction) ;

— in the last section, 4, we give improved scaling arguments for problems of this type.

2. Gel immersed in a polymer melt. — We want to find out the effects of a polymer melt on a network of the same chemical species. We shall show that these

(¹) Macromolecules, to be published.

effects are strongly dependent on the size of the mobile chains (P monomers/chain).

Of course we already know the answer for the extreme case $P = 1$, recalled in the introduction. The gel is swollen and $\varphi_N = \varphi_N^* = N^{-4/5}$. We now extend the derivation to all P . In the Flory lattice model, the free energy (per site) may be written as :

$$\frac{F_s}{T} = \frac{1}{P} (1 - \varphi_N) \text{Log} (1 - \varphi_N) + \frac{3 \varphi_N}{N} \left[\frac{1}{2} \frac{R^2}{R_0^2} + \text{Log} \frac{R_0}{R} \right] + \chi_{12} \varphi_N (1 - \varphi_N). \quad (6)$$

The only difference from the expression of equation (1) is the factor $1/P$ in the entropy of mixing term.

The equilibrium of the gel again corresponds to zero osmotic pressure :

$$\pi = \varphi_N^2 \frac{\partial F / \varphi_N}{\partial \varphi_N} = 0. \quad (7)$$

In the limit $\varphi \ll 1$, equation (7) gives

$$\frac{1}{2P} \varphi_N^2 - \frac{\varphi_N^{1/3}}{N^{4/3}} + \frac{\varphi_N}{N} = 0. \quad (8)$$

Following the language of Edwards [5], we may say that the φ_N^2/P term corresponds to an excluded volume interaction between monomers of the gel ; this interaction is « screened » by the mobile chains ($\varphi_N^2 \rightarrow \varphi_N^2/P$). Equation (8) leads to two regimes, depending upon the value of P with respect to $P_c = \sqrt{N}$.

a) MIXED SWOLLEN REGIME ($P < N^{1/2}$). — The entropic term is dominant. The chains are swollen and we find :

$$\varphi_N^{5/3} = \frac{P}{N^{4/3}}, \quad R = \frac{N^{3/5}}{P^{1/5}} a. \quad (9)$$

When P increases the gel becomes less swollen.

b) MIXED IDEAL REGIME ($P \geq N^{1/2}$). — At larger P values, the excluded volume interaction is completely screened and the free energy is controlled entirely by the elastic term :

$$\left. \begin{aligned} R &= R_0 = N^{1/2} a \\ \varphi_N &\cong N^{-1/2} \end{aligned} \right] \quad (10)$$

Conclusion. — The melt penetrates the gel. The similarity of a gel to a solution of free chains with N monomers is maintained for the case of a gel immersed in a polymer melt. The distance between crosslinks corresponds to the end to end radius of the free chain (N monomer/chain) in a melt of chains with P monomers per chain (9-10).

Remark. — If the crosslinks are significantly different from the monomers as regards polarization, etc., the athermal hypothesis is not absolutely valid.

We must include an average interaction term $\chi_{12} = \chi_{cm}/N$ (χ_{cm} measuring the crosslink-monomer interaction). The excluded volume term becomes $\left(\frac{1}{2P} - \chi_{12} \right) \varphi_N^2$. If $\chi_{12} > 0$ and $P > \frac{1}{2\chi_{12}} \left(= \frac{N}{2\chi_{cm}} \right)$, we expect a collapse of the gel and no penetration.

3. Gel immersed in a polymer solution. — We now study the behaviour of a gel in equilibrium with a solution of the same polymer (P monomers/mobile chain). The volume fraction of P chains in the external solution is φ_P^{ext} . The volume fraction of P chains inside the gel is φ_P^{int} .

3.1 CONDITIONS FOR EQUILIBRIUM. — The equilibrium of a gel swollen by a one component fluid is always defined by a condition of zero osmotic pressure ($\Pi = 0$).

The equilibrium of a gel immersed in a binary mixture is defined by two equations : 1) the equality of the chemical potential of the solvent inside and outside the gel ; 2) the equality of the chemical potential of the mobile chains. For the case of an incompressible fluid, it is however much more convenient to use an « exchange » chemical potential, associated with the free energy required to exchange a P chain by solvent molecules, keeping the volume constant.

The free energy of the gel is entirely specified by the two variables φ_N , the volume fraction of the gel, and φ_P^{int} , the volume fraction of the mobile chains in the gel. The value of φ_N fixes the volume Ω occupied by the gel ($\Omega \varphi_N = N^0 N$, the total number of monomers). We can write the total free energy of the gel as :

$$F_{gel} = \Omega F_s(\varphi_N, \varphi_P^{int}). \quad (11)$$

The variation of F_{gel} can be expressed as :

$$dF_{gel} = - \Pi^{int} d\Omega + \mu_P^{int} dN_P \quad (12)$$

where μ_P is the exchange chemical potential of the mobile chains

$$\mu_P^{int} = \left. \frac{\partial F_{gel}}{\partial N_P} \right]_{\Omega = \text{const.}} = \frac{\partial F_s}{\partial \varphi_P}(\varphi_N, \varphi_P^{int}) \quad (13)$$

and Π is the osmotic pressure

$$\Pi^{int} = - \left. \frac{\partial F_{gel}}{\partial \Omega} \right]_{N_P = \Omega \varphi_P^{int} = \text{const.}} \quad (14)$$

Using (1) and the requirement $\Omega \varphi_N = N^0 N = \text{const.}$ we find :

$$\Pi = - F_s(\varphi_N, \varphi_P^{int}) - \Omega \frac{\partial F_s}{\partial \varphi_N} \frac{\partial \varphi_N}{\partial \Omega} - \Omega \frac{\partial F_s}{\partial \varphi_P^{int}} \frac{\partial \varphi_P^{int}}{\partial \Omega}.$$

Setting $\mu_N = \partial F / \partial \varphi_N$, we recover the classical result :

$$\Pi = - F_s(\varphi, \varphi_P) + \mu_N \varphi_N + \mu_P \varphi_P^{int}. \quad (15)$$

For the external solution, the free energy (per site) F'_s involves one variable, the volume fraction φ_P^{ext} of the polymer :

$$F_{\text{sol}} = (V - \Omega) F'_s(\varphi_P^{\text{ext}}). \quad (16)$$

Then :

$$dF_{\text{sol}} = \Pi^{\text{ext}} d\Omega + \mu_P^{\text{ext}} dN'_P$$

with

$$\Pi^{\text{ext}} = -F'_s(\varphi_P^{\text{ext}}) + \mu_P^{\text{ext}} \varphi_P^{\text{ext}} \quad (17)$$

where

$$\mu_P^{\text{ext}} = \frac{\partial F'_s(\varphi_P^{\text{ext}})}{\partial \varphi_P}. \quad (18)$$

The requirement $dF_{\text{total}} = dF_{\text{gel}} + dF_{\text{sol}} = 0$ with the condition $N_P + N'_P = \text{const.}$ leads to the two equilibrium conditions :

$$\begin{cases} \Pi^{\text{int}} = \Pi^{\text{ext}} & (\text{Eqs. (15, 17)}) \\ \mu_P^{\text{int}} = \mu_P^{\text{ext}} & (\text{Eqs. (13, 18)}) \end{cases} \quad (19) \quad (20)$$

3.2 THE FLORY LATTICE MODEL. — The free energy $F_s(\varphi_N, \varphi_P)$ in the mean field theory of Flory is given by :

$$F_s = \frac{\varphi_P^{\text{int}}}{P} \text{Log } \varphi_P^{\text{int}} + (1 - \varphi_N - \varphi_P^{\text{int}}) \text{Log} (1 - \varphi_N - \varphi_P^{\text{int}}) + F_{\text{el}} \quad (21)$$

with

$$F_{\text{el}} = \frac{3 \varphi_N}{N} \left(\frac{R^2}{2 R_0^2} + \text{Log} \frac{R_0}{R} \right).$$

The first two terms represent the translational free energy of the free chains and the solvent.

The last term is the elastic term. R_0 is the ideal size $R_0 = N^{1/2} a$.

We calculate the volume fractions, φ_N of the gel and φ_P^{int} of the mobile chains in the gel, as functions of the volume fraction φ_P^{ext} of the outside solution by the two conditions (9, 10).

The equation : $\mu_P^{\text{int}} = \mu_P^{\text{ext}}$ leads to :

$$\frac{1}{P} \text{Log} \frac{\varphi_P^{\text{int}}}{\varphi_P^{\text{ext}}} = \varphi_P^{\text{ext}} - (\varphi_P^{\text{int}} + \varphi_N) \quad (22)$$

and $\Pi^{\text{int}} = \Pi^{\text{ext}}$ leads to :

$$\frac{1}{2} [(\varphi_N + \varphi_P^{\text{int}})^2 - (\varphi_P^{\text{ext}})^2] + \frac{\varphi_P^{\text{int}} - \varphi_P^{\text{ext}}}{P} + \Pi_{\text{el}} = 0$$

with

$$\begin{aligned} \Pi_{\text{el}} &= -F_{\text{el}} + \varphi_N \frac{\partial F_{\text{el}}}{\partial \varphi_N} + \varphi_P \frac{\partial F_{\text{el}}}{\partial \varphi_P} \\ \Pi_{\text{el}} &= \frac{\varphi_N}{N} - \varphi_N^{1/3} N^{-4/3}. \end{aligned} \quad (23)$$

The discussion of equations (22-23), to be given below, leads to mixed and unmixed regimes (represented on figure 1).

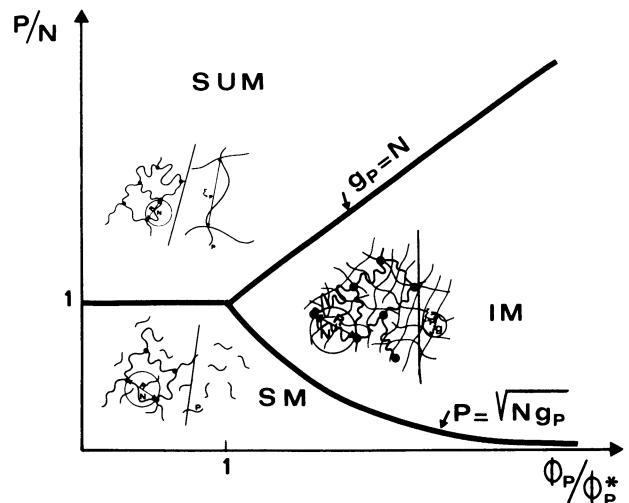


Fig. 1. — The three regimes of a gel swollen by an homopolymer P solution in the scaling theory.

P = number of monomers per free chain.

N = number of monomers between crosslinks.

φ_P^{ext} = volume fraction of P chains in the bulk solution.

φ_P^* = $P^{-4/3}$, threshold between the dilute D and the semi-dilute SD regime.

g_P = number of correlated monomers in the SD regime ($g_P = \varphi_P^{\text{ext}-5/4}$).

SUM = swollen unmixed : no penetration of the P chain.

SM = swollen mixed : penetration of P chains. Here the P chains are too small to screen the repulsion between monomers of the network.

IM = ideal mixed : final state similar to a gel in a θ solvent : penetration of long P chains and screening of the network monomers repulsions.

The border lines are not phase separation lines but cross-over lines : in the SUM region, the fraction of P chains is exponentially small for large P/N values ($\varphi_P \sim e^{-P/N}$) but it is of order one on the border line.

3.3 DISCUSSION OF THE DIFFERENT REGIMES. —

3.3.1 Unmixed regime (UM) [$\varphi_P^{\text{ext}} < \varphi_N^*$; $P\varphi_N > 1$ (+ SC : $P > N$)]. — In the limit $\varphi_P^{\text{int}} \ll \varphi_P^{\text{ext}}$, the partition coefficient derived from equation (22) is :

$$\frac{\varphi_P^{\text{int}}}{\varphi_P^{\text{ext}}} = e^{-P[\varphi_N - \varphi_P^{\text{ext}}]} \cong e^{-P\varphi_N} (+ \text{SC} : e^{-P/N}). \quad (24)$$

The volume fraction of the network is essentially the volume for swelling by the pure solvent

$$\varphi_N \cong \varphi_N^*. \quad (25)$$

The UM regime appears for $\varphi_P^{\text{ext}} < \varphi_N^*$ and $P\varphi_N^* > 1$. This last requirement is modified by scaling corrections to $P > N$ (see part 3).

3.3.2 Mixed regimes. — The mixed regimes are defined by $\varphi_P^{\text{int}} \cong \varphi_P^{\text{ext}}$. Expanding equations (23-24) as a function of the difference ($\varphi_P^{\text{int}} - \varphi_P^{\text{ext}}$) gives

$$\left[\frac{1}{P\varphi_P^{\text{ext}}} + 1 \right] [\varphi_P^{\text{int}} - \varphi_P^{\text{ext}}] - \frac{1}{2P\varphi_P^{\text{ext}2}} (\varphi_P^{\text{int}} - \varphi_P^{\text{ext}})^2 = -\varphi_N \quad (26)$$

$$\frac{(\varphi_P^{\text{int}} - \varphi_P^{\text{ext}})^2}{2P\varphi_P^{\text{ext}}} + \frac{1}{2} [\varphi_N + \varphi_P^{\text{int}} - \varphi_P^{\text{ext}}]^2 + \Pi_{el} = 0. \quad (27)$$

1) $P\varphi_P < 1$; $P\varphi_N < 1$ (+ SC : $\varphi_P < \varphi_P^*$, $P < N$).
In the limit $P\varphi_P < 1$, $P\varphi_N < N$, equations (26, 27) become :

$$\varphi_P^{\text{ext}} - \varphi_P^{\text{int}} = \varphi_N \varphi_P^{\text{ext}} P \quad (28)$$

$$\frac{1}{2} [1 - P\varphi_P^{\text{ext}}] \varphi_N^2 + \frac{\varphi_N}{N} - \varphi_N^{1/3} N^{-4/3} = 0. \quad (29)$$

The total monomer concentration φ is slightly larger in the gel region than outside. The distance between crosslinks obeys the Flory law :

$$R \sim N^{3/5} a (1 - P\varphi_P^{\text{ext}})^{1/5}$$

$$\varphi \simeq \varphi^*(N).$$

The free chains penetrate the gel and lead to a very small deswelling of the crosslinked chains.

2) $P\varphi_P^{\text{ext}} > 1$ (+ SC : $\varphi_P^{\text{ext}} > \varphi_P^*$, $\varphi_P^{\text{ext}} > \varphi_N^*$ (i.e. $\xi_P < R = N^{3/5} a$).

The bulk solution is semi-dilute. It forms a mesh of size $\xi_P < P^{3/5} a$. Under these conditions, we find that the overall monomer concentration is practically uniform

$$\varphi_P^{\text{int}} - \varphi_P^{\text{ext}} = -\varphi_N. \quad (30)$$

The swelling of the gel is given by :

$$\frac{\varphi_N^2}{2P\varphi_P^{\text{ext}}} + \frac{\varphi_N}{N} - \varphi_N^{1/3} N^{-4/3} = 0. \quad (31)$$

As for the case of a gel in a melt, the excluded volume between monomers is screened by the P chains. Depending upon P and φ_P^{ext} , we expect either a swollen or an ideal behaviour. The frontier between these two situations is given by the equality :

$$\frac{\varphi_N^2}{P\varphi_P^{\text{ext}}} = \frac{\varphi_N}{N} = \frac{\varphi_N^{1/3}}{N^{4/3}} \quad (32)$$

i.e. $\varphi_P^{\text{ext}} P > N^{1/2}$ (+ SC : $\frac{P}{g_P} > \sqrt{\frac{N}{g_P}}$, where $g_P = \left(\frac{\xi_P}{a}\right)^{5/3}$).

a) *Swollen behaviour (SM).*

The MS regime is limited by the frontier $\varphi_P^{\text{ext}} P = N^{1/2}$ (on figure 1, the frontier, corrected by scaling, corresponds to $\frac{P}{g_P} = \sqrt{\frac{N}{g_P}}$). For $P\varphi_P^{\text{ext}} < N^{1/2}$, the chains are swollen :

$$R = \frac{N^{3/5} a}{2(P\varphi_P^{\text{ext}})^{1/5}} \quad (33)$$

$$\left[+ \text{SC} : R = \left(\frac{N}{g_P}\right)^{3/5} \xi_P \left(\frac{P}{g_P}\right)^{1/5} = \frac{N^{3/5} a}{P^{1/5} \varphi_P^{1/4}} \right].$$

b) *Ideal behaviour (IM).*

For longer chains $P\varphi_P^{\text{ext}} > N^{1/2}$, the excluded volume interaction is screened. The chains become ideal :

$$R = R_0 \quad (34)$$

$$\left[+ \text{SC} : R = R_0(\varphi_P) = \left(\frac{N}{g}\right)^{1/2} \xi_P = \frac{N^{1/2} a}{\varphi_P^{1/8}} \right].$$

This is the only regime where P chains larger than N chains penetrate the gel.

This regime is similar to the case of a gel swollen in a θ solvent. It differs by the existence of two elastic moduli

— E_g associated with gel deformation [1] $E_g = kT/R^3$

— E_p associated with monomer concentration fluctuations [2] $E_p = kT/\xi_P^3$.

4. **Scaling corrections.** — The Flory theory works because of the cancellation of two strong approximations :

1) Correlation between monomers are ignored. The inclusion of correlation leads to a smaller repulsive energy

$$\varphi^2 \rightarrow \varphi^{2.25}. \quad (35)$$

2) The non ideality of the chains leads to a smaller elastic energy of distortion :

$$F_{el} = 3 \frac{\varphi_N}{N} \left(\frac{R^2}{2R_F^2(\varphi)} + \log \frac{R_F(\varphi)}{R} \right). \quad (36)$$

For a network immersed in a pure solvent or in a dilute solution of polymer P , R_F is the swollen size of a chain of N units, in a medium where local correlations are fixed by the size of the solvent molecules which we write as $P_F = N^{3/5} a$. If the network is swollen by a semi-dilute solution of the P chains and if the P chains are dominant ($\varphi_P^{\text{int}} \gg \varphi_N$), the P chains impose a certain correlation length [2]

$$\xi_P = a\varphi^{-3/4} \cong a\varphi_P^{-3/4}.$$

Because the local correlations are dominated by the P chains, the network chain has to be swollen at a scale ξ_P and $R_F(\varphi_P)$ is the end to end radius of an ideal chain of blobs of size ξ_P , each containing g_P monomers

($g_P^{3/5} a = \xi_P$). This gives $R_F(\varphi) = \sqrt{\frac{N}{g_P}} \xi_P(\varphi_P^{\text{int}})$.

Including these two corrections, the two equations governing the partitioning of the P chains and the swelling of the gel are

$$\frac{1}{P} \text{Log} \frac{\varphi_P^{\text{int}}}{\varphi_P^{\text{ext}}} = \left[\varphi_P^{\text{ext} 1.25} - (\varphi_P + \varphi_N)^{1.25} \right] \frac{2.25}{2} \quad (37)$$

$$\frac{1.25}{2} \left[(\varphi_N + \varphi_P^{\text{int}})^{2.25} - \varphi_P^{\text{ext} 2.25} \right] + \frac{\varphi_P^{\text{int}} - \varphi_P^{\text{ext}}}{P} + \Pi_{\text{el}} \quad (38)$$

with

$$\Pi_{\text{el}} = \frac{5}{8} \left[\frac{\varphi_N}{N} - \varphi_N^{1/3} N^{-23/15} f(\varphi_P) \right].$$

If the chains are excluded from the gel, $R_F = N^{3/5} a$, and $f(\varphi_P) = 1$. If the P chains are dominant and *semi-dilute* ($\varphi_P^{\text{int}} > \varphi_N$, $\varphi_P^{\text{int}} > \varphi_P^*$), then $R_F = \sqrt{\frac{N}{g_P}} \xi_P$ and $f(\varphi_P) = \left(\frac{\varphi_P}{\varphi_P^*} \right)^{1/4}$.

DISCUSSION OF THE DIFFERENT REGIMES. — 1) *Unmixed regimes.* — In the limit $\varphi_P^{\text{int}} \ll \varphi_P^{\text{ext}}$, the partition coefficient derived from (37) is

$$\frac{\varphi_P^{\text{int}}}{\varphi_P^{\text{ext}}} \simeq e^{-P[\varphi_N^{1.25} - \varphi_P^{\text{ext} 1.25}]} \quad (39)$$

We do not have penetration if $\varphi_P^{\text{ext}} < \varphi_P^*$. In that limit, equation (38) leads to $\varphi_N = \varphi_P^*$. We find for the partition coefficient

$$\frac{\varphi_P^{\text{int}}}{\varphi_P^{\text{ext}}} \simeq e^{-P/N} \quad (40)$$

This is the partition coefficient of a chain of P monomers confined in a tube of diameter R_F .

Conclusion. — The unmixed regime appears for long mobile chains ($P > N$) and dilute external concentration ($\varphi_P^{\text{ext}} < \varphi_P^*$, i.e. $g_P > N$).

2) *Mixed regime.* — We suppose $\varphi_P^{\text{ext}} > \varphi_P^*$ and that the P chains are semi-dilute ($\varphi_P^{\text{ext}} > \varphi_P^*$). In this limit, the logarithmic term in equation (37) is negligible and $\varphi_P^{\text{ext}} \simeq \varphi_P^{\text{int}} + \varphi_N$. Keeping the higher order terms, equation (38) becomes :

$$\Pi_{\text{el}} + \frac{\varphi_N^2}{2P\varphi_P} = 0 \quad (41)$$

with

$$\Pi_{\text{el}} = \frac{\varphi_N}{N} - \varphi_N^{1/3} N^{-4/3} \varphi_P^{1/4}.$$

The frontier between swollen and ideal behaviour is given by the equality of the three terms :

$$\frac{\varphi_N}{N} = \varphi_N^{1/3} N^{-4/3} \varphi_P^{1/4} = \varphi_N^2 / 2P\varphi_P \quad (42)$$

$$\text{i.e. } \varphi_P^{\text{ext} 5/8} P = N^{1/2} \text{ or } \frac{P}{g_P} = \sqrt{\frac{N}{g_P}}.$$

Swollen regime : $\frac{P}{g_P} < \frac{N}{g_P}$.

In that limit, equation (41) leads to :

$$R = \left(\frac{N}{g_P} \right)^{3/5} \xi_P / \left(\frac{P}{g_P} \right)^{1/5} = \frac{N^{3/5} a}{P^{1/5} \varphi_P^{1/4}} \quad (43)$$

Ideal regime : $\frac{P}{g_P} > \sqrt{N/g_P}$.

In that limit, $\Pi_{\text{el}} \simeq 0$ and $R = \sqrt{\frac{N}{g_P}} \xi_P$.

Conclusion. — The limits between different regimes have to be corrected by scaling. Some other results are modified too :

— The partition coefficient in the unmixed regime.

— The swelling of the gel in the mixed « semi-dilute » regime (i.e. $\varphi_P^{\text{int}} > \varphi_P^*$).

The results which are correctly derived from the mean field theory are :

— the swelling in the unmixed regime,

— the swelling in the mixed « dilute » regime (i.e. $\varphi_P^{\text{int}} < \varphi_P^*$).

5. Conclusion. — We have studied the partition of polymer chains between a bulk solution and a homopolymer gel. As a function of the volume fraction φ_P of the polymer in the bulk solution, we have three situations :

— Unmixed regime (SUM) : $R \sim N^{3/5}$, $\varphi_P = 0$.

— Swollen mixed regime (SM) : $R \sim N^{3/5}$, $\varphi_P^{\text{int}} \simeq \varphi_P^{\text{ext}}$.

— Ideal mixed regime (IM) : $R \sim N^{1/2}$, $\varphi_P^{\text{int}} \simeq \varphi_P^{\text{ext}}$.

— In the unmixed regime, the mobile chains do not penetrate the gel because the confinement energy of a chain trapped in the gel is very large ($F \sim kT \frac{P}{N}$).

This F must be compared to equivalent parameters for one P chain in the bulk solution : namely kT if the bulk solution is dilute, or $kT \frac{P}{g_P}$ if the bulk solution is SD, and $g_P \gg N$.

— In the mixed swollen regime, the chains are small ($P < N$) and they penetrate freely into the gel.

— In the ideal mixed regime, the P chains in the network are dominant and sufficiently large to screen out excluded volume effects. This is the *only* regime where very long chains ($\frac{P}{N} > 1$) can be introduced into

the gel. This regime is not easily observed, because it may require a long time to reach the final state (if P is large). There are two possible ways to introduce long chains into a gel. We could immerse the gel in a concentrated solution of the P chains. In a first stage, the solvent, which is much more mobile, is expelled (« osmotic deswelling »). In a second stage, the P chains diffuse into the gel. This must be a slow process because : (a) the diffusion constant of the P chains by

reptation is very small [2] ($D_P \sim P^{-2}$); (b) the osmotic pressure difference driving the process is small. We can also swell the gel with the P monomers, and polymerize them later in the gel to obtain P chains. Here also however the time to reach the final equilibrium states is probably long.

In practice the best way to prove the existence of the ideal mixed state would be to use small gel particles. Denoting the particle diameter by B , the diffusion times for the P chains are of order $\tau = B^2/D_{SD}$ where D_{SD} is the self-diffusion coefficient of the P chains in the network of the N chains and the other P chains forming a transient network. Because of the osmotic equilibrium ($\varphi_N + \varphi_P^{int} = \varphi_P^{ext}$), D_{SD} is equal to the self-diffusion coefficient in the external solution. According to reference [2], $D_{SD} = \frac{kT}{6\pi\eta_s a} \left(\frac{g_P}{P}\right)^2$, where g_P is the number of monomers between transient crosslinks ($g_P = \varphi_P^{-5/4}$). For

$$g_P/P = 0.1 \quad \text{and} \quad \frac{T}{6\pi\eta_s a} \cong 10^{-7} \text{ cm}^2/\text{s},$$

this corresponds to $D_{SD} = 10^{-9} \text{ cm}^2/\text{s}$. For $B = 10 \mu$, this gives a diffusion time of order 20 min.

These results can be tested even by taking only one single chain ! The equilibrium equations are identical for a gel and one single chain (N monomers) in a monopolymer solution.

Last but not least, we have also shown in paragraph 2 that a slight difference in chemical nature between the gel and the free chain leads to a collapse of the gel and to no penetration of the free chain. The crosslinks are often chemically different. This may be sufficient to expel the mobile chains from the gel.

Note added in proof. — I am grateful to S. Candau, L. Leibler and P. G. de Gennes for various discussions relating to this problem. A recent preprint by Bastide, Candau and Leibler describes experiments on osmotic deswelling showing no penetration by the mobile chains. They interpret this by a Flory-Huggins calculation similar to mine, but with one crucial difference : they do not include the term $\log(R_0/R)$ which limits the gel compression. My belief is that this term *must* be included, and that the absence of penetration should be interpreted differently — through kinetic effects or through an incompatibility (χ_{12}) between the nodes and the mobile chains.

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