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Gel-like modes of polymer solutions in « θ » solvents

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Résumé. — Une solution de polymère forme un gel transitoire, qui se renouvelle en un temps caractéristique T_r . En bon solvant, la taille l de la maille du filet est identique à la longueur de corrélation ξ des fluctuations de concentration c . Mais en solvant « θ », où les interactions entre paires s'annulent, l est inférieure à ξ . Il faut deux modules élastiques E pour décrire les propriétés dynamiques : 1) à basse fréquence, $E = E_0 = kT/\xi^3 \sim c^3$ est petit ; 2) à haute fréquence, $E = E_{\text{gel}} = kTc^2$ et $E_{\text{gel}} \gg E_0$. Dès que $q > q_g$, on observe deux modes, le mode rapide étant le mode de gel. Bien que ce mode contribue peu à l'intensité diffusée, il domine la pente à l'origine du facteur de structure $S_q(t)$ ($t \rightarrow 0$). On calcule le coefficient de diffusion relatif au mode de gel dans les trois gammes de vecteur d'onde :

- a) régime « multichaînes » ($q_g < q < 1/\xi$). On trouve $D_g \simeq kT/6 \pi \eta_s a$;
- b) régime « chaîne isolée enchevêtrée » ($\xi^{-1} < q < l^{-1}$), $D_g(q) \sim 1/q$;
- c) régime « chaîne idéale désenchevêtrée » ($q > l^{-1}$), $D_g \sim q$.

Les régimes de b) et c) ne pourraient être observés que dans des expériences aux neutrons. Mais le passage de a) vers b) pourrait expliquer certains résultats de battements de photon sur le PS dans le cyclohexane.

Abstract. — A polymer solution forms a transient network of lifetime T_r . In good solvents, the mesh size l is identical to the correlation length ξ for the fluctuations of the monomer concentration c . But in « θ » solvents (where the pair interaction vanishes), l is much smaller than ξ . The dynamics involve then two quantitatively very different elastic moduli E : 1) at low frequencies, $E = E_0 = kT/\xi^3 \sim c^3$ is small ; 2) at higher frequencies, $E = E_{\text{gel}} \simeq kTc^2$ and $E_{\text{gel}} \gg E_0$. This leads to two modes in photon-beat experiments at wave vectors q larger than a certain value q_g , the high frequency mode being the gel mode. Although this gives only a small fraction of the total scattered light, it still dominates the slope of the dynamical structure factor $S(q, t)$ at small times. We investigate the corresponding diffusion coefficient D_g in the three regimes :

- a) « many chain » regime ($q_g < q < 1/\xi$), $D_g \simeq kT/6 \pi \eta_s a$ is very high (a is a monomer size and η_s the solvent viscosity) ;
- b) entangled « single chain » regime ($\xi^{-1} < q < l^{-1}$), $D_g(q) \sim 1/q$;
- c) disentangled « single chain » regime ($ql > 1$), $D_g \sim q$.

The regimes b) and c) could be observed only in neutron experiments. But the cross-over from a) to b) could explain certain photon-beat results on PS in cyclohexane.

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1. Introduction. — The understanding of polymer solutions in good solvents is based on the existence of one coherence length ξ ($\xi \sim c^{-3/4}$) which measures :

- the screening of the monomer-monomer interactions ;
- the screening of the hydrodynamic interactions ;
- and finally the distance between entanglements.

The dynamical behaviour of these solutions can also be derived by scaling assumptions (Ref. [5]) : at small wavelengths ($k\xi > 1$), one recovers the modes of one isolated chain ; at large wavelengths, the solution may be described either as a transient gel (with a rubber like elastic modulus E_g) or through its osmotic pressure π , giving rise to an osmotic elastic modulus $E_0 = c \frac{\partial \pi}{\partial c}$. Both E_0 and E_g scale as kT/ξ^3 . This leads

to a cooperative diffusion coefficient $D = kT/6\pi\eta_s\xi$ holding for both « osmotic » and « gel-like » modes.

In θ solvents (where the effective monomer-monomer interaction cancels out), the correlation length ξ ($\xi \sim c^{-1}$) is not related to the distance between entanglements. This has been pointed out in reference [1]. The θ solution is represented schematically in figure 1. At distances smaller than ξ , the pair correlation function is dominated by the self correlation function of one ideal isolated chain. But in θ solvents, as shown in reference [1], a chain is self-entangled [3, 4, 1] and forms a micro gel of mesh size $l = \sqrt{\xi}a$ and the density of cross-links is proportional to c^2 . We expect, then, two elastic moduli which oppose concentration fluctuations :

1) at low frequency, the osmotic modulus $E_0 = kT/\xi^3 \sim c^3$;

2) at $\omega T_r > 1$, the rubber modulus $E_g = f k T c^2 - E_g$ is proportional to the density of cross-links (c^2). The factor f measures the efficiency of the knots. In a melt, $f \sim 10^{-2}$. In a semi-dilute solution, $f \sim 1$

in good solvents [7]. We do not know the value of f in « θ » solvents.

For the dynamical properties, the « blobs » of size ξ behave as hydrodynamic units : the screening of the back-flow interactions is entirely controlled by the static pair correlation function [5], of range ξ .

In the present paper, after a brief reminder on good solvents, we study the relaxation of concentration fluctuations δc_q at a wave vector q in θ solvents.

We find 4 regimes : a) very low frequencies (obtained for q below a certain limit q_g) where all gel effects drop out ; b) many chain gel $q_g < q < 1/\xi$; c) single « self-entangled » chain $1/\xi < q < 1/l$; d) non-entangled ideal chain $ql > 1$.

At $\omega T_r > 1$, an additional slow relaxation mode complicates the dynamics. We calculate the structure factor $S(q, \omega)$ and its Fourier transform $S(q, t)$ to see the weight of the gel-like mode and how to measure it.

2. The two-fluid model [6]. — The motion of the monomers with a local velocity \mathbf{r} is ruled by the balance between the viscous and the elastic force :

$$\frac{c}{\mu} \mathbf{r} = E \nabla^2 \mathbf{r} . \quad (1)$$

We shall discuss now the values of the mobility μ and the elastic modulus E as a function of the wave vector q and the frequency ω of the concentration fluctuation.

2.1 MOBILITY. — a) *Hydrodynamic regime* ($q\xi < 1$). — μ is related to the pair correlation function $g(r) = \frac{1}{c} (c(r) c(0) - c^2)$ by a Kubo formula [5, 1]

$$\mu = \int \frac{g(r) d_3 \mathbf{r}}{6 \pi \eta_s r} \sim \frac{g}{6 \pi \eta_s \xi} \sim c^{-1/2} \quad \text{good solvent} \quad (2)$$

$$\sim c^{-1} \quad \text{« } \theta \text{ » solvent}$$

where $g = \int g(r) d_3 \mathbf{r}$ is the number of monomers per blob of size ξ . Equation (2) means that a blob behaves hydrodynamically as an impenetrable sphere ($\mu_{\text{blob}} = \mu/g = 1/6 \pi \eta_s \xi$). The results (2) fit the experimental data [8] well.

b) *Non-hydrodynamic regime* ($q\xi > 1$). — If the wave vector of the concentration fluctuation is larger than ξ , the blob picture breaks down. The dynamic screening length is given by q^{-1} because only part of the coils of size q^{-1} move cooperatively. This can be quantitatively deduced from the Kubo formula for μ extended to large q [3] :

$$\mu(q) = \int \frac{g(r) e^{i \mathbf{q} \cdot \mathbf{r}}}{6 \pi \eta_s r} d_3 \mathbf{r} \sim \frac{g_q \times q}{6 \pi \eta_s} \sim q^{-2/3} \quad \text{good solvent}$$

$$\sim q^{-1} \quad \text{« } \theta \text{ » solvent.} \quad (3)$$

Then, at large q , the blob picture can still be maintained, but the size of the blob is (q^{-1}) instead of (ξ)

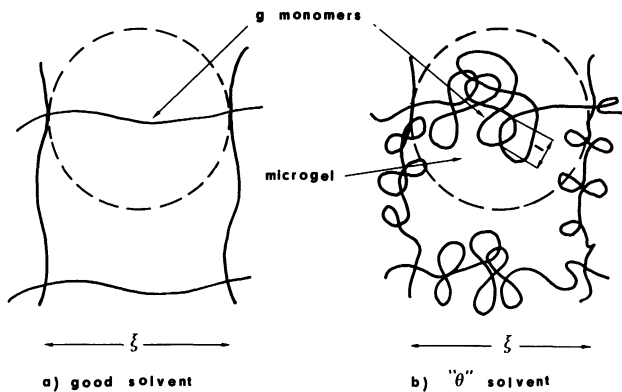


Fig. 1. — Conformations in semi-dilute polymer solutions. a) Good solvents ; b) « θ » solvents. ξ is the correlation length. In a « blob » of size ξ , one expects a « single chain » behaviour. In good solvents, ξ is also the distance between cross-links. In « θ solvents », because the chains are self-entangled, the distance between cross-links l is smaller than ξ .

and the number of monomers per blob is $g_q (g_q^{\nu_F} a = q^{-1})$, where ν_F is the Flory exponent).

2.2 ELASTIC MODULUS. — a) In the hydrodynamic limit ($q\xi < 1$, $\omega T_r < 1$), E is the osmotic rigidity related to the Fourier Transform of $g(r)$:

$$E_0 = \frac{ckT}{g_q(q=0)} = \frac{ckT}{g}. \quad (4)$$

b) At high frequency ($\omega T_r > 1$) and small q ($ql < 1$), E is dominated by the rubber modulus. If ν is the density of cross-links and « fv » the number of efficient knots :

$$E_g = kTfv, \quad \nu = \frac{c}{g} \quad \text{good solvent} \\ \nu = c^2 a^3 \quad \text{« } \theta \text{ » solvent.} \quad (5)$$

To cover the cases (a) and (b), one has to take in equation (1) :

$$E = E_0 + E_g \frac{i\omega T_r}{1 + i\omega T_r}. \quad (6)$$

c) At high q ($ql > 1$), we recover the case of a single non-entangled chain. The coils can be pictured as a succession of blobs of size q^{-1} (containing g_q monomers) and E is proportional to the density of these blobs :

$$E_{\text{self}} = \frac{ckT}{g_q}. \quad (7)$$

3. Eigenmodes. — Let us analyse a fluctuation $\delta r_x = \delta r_0 e^{iqx} e^{-i/\tau_q}$. The dispersion relation derived from equation (1) is :

$$\frac{1}{\tau_q} = \frac{\mu(q) E(q, \omega)}{c} q^2 = D_q q^2. \quad (8)$$

3.1 DISCUSSION OF D_q IN GOOD SOLVENTS. —

a) *Hydrodynamic range* ($q\xi < 1, \omega T_r < 1$). — Taking $\mu = g/6 \pi \eta_s \xi$ and $E_0 = ckT/g$, we find :

$$D_s = \frac{kT}{6 \pi \eta_s \xi} \sim c^{0.75}. \quad (9)$$

b) *Gel-like mode* ($q\xi < 1, \omega T_r > 1$). — In a good solvent, $E_g \sim E_0$ and result (9) is not modified

$$D_g = \frac{kT}{6 \pi \eta_s \xi} \sim c^{0.75}. \quad (10)$$

c) « *Self-chain* » mode ($q\xi > 1, \omega T_r > 1$). — Taking $\mu_q = g_q q/6 \pi \eta$ and $E_q = ckT/g_q$, one gets :

$$D_{\text{self}} = kTq. \quad (11)$$

Results (9), (10), (11) fit the experimental data [9] rather well.

3.2 DISCUSSION OF D_q IN θ SOLVENTS. — We have more cases because of the existence of the two lengths l and ξ .

a) *Hydrodynamic regime* ($q\xi < 1, \omega T_r < 1$). — Taking $\mu = g/6 \pi \eta_s \xi$ and $E_0 = ckT/g$ (Eq. 4) we find a « slow » cooperative diffusion coefficient :

$$D_s = \frac{kT}{6 \pi \eta_s \xi} \sim c. \quad (12)$$

b) *Interchain « gel-like » mode* ($q\xi < 1, \omega T_r > 1$). — With $\mu = g/6 \pi \eta_s \xi$ and $E_g = f k T c^2$ (Eq. 5) we expect a large diffusion coefficient :

$$D_g = f \frac{kT}{6 \pi \eta_s a} \quad (13)$$

independent of c ! We show in the next sections that this mode dominates the initial slope of $S_q(t)$ as soon as $q > q_g$ ($D_g q_g^2 T_r = 1$). Below q_g one observes $D_s \sim c$ and above q_g , $D_g = \text{const.}$ It may explain experimental data on PS in toluene [10]. (For large chains, D_g is found to be independent of c .)

c) *Single chain « gel-like » mode* ($\xi^{-1} < q < l^{-1}$). — For $q\xi > 1$, μ becomes dependent upon q (as shown by Eq. 3), whereas $E = E_g$ is unmodified because we look at scale larger than l . It leads to :

$$D_g(q) = \frac{kT}{6 \pi \eta_s q a^2} c a^3. \quad (14)$$

Then $D_g(q)$ is a decreasing function of q for $l^{-1} < q < \xi^{-1}$ as shown in figure 2. This unusual result has also been observed by inelastic neutron scattering [10].

d) *Single « non-entangled » ideal chain regime* ($ql > 1$). — For $ql > 1$, we recover the dynamics of a single ideal chain [6]. With $\mu_q = g_q q/\eta_s$ and $E_q = ckT/g_q$ we find the expected result :

$$D_q = \frac{kT}{\eta_s} q \quad (15)$$

leading to a characteristic frequency $\omega_q = \frac{kT}{\eta_s} q^3$.

For $ql = 1$ we do have a cross-over with regime (c) as shown in figure 2.

4. Observation through the short time limit of correlation functions. — By inelastic light scattering or neutron scattering, one measures either :

$$S(q, t) = \int \langle \delta c(0) \delta c(rt) \rangle e^{iqr} dr \quad (16)$$

or

$$S(q, \omega) = \frac{1}{2\pi} \int S(q, t) e^{-i\omega t} dt. \quad (17)$$

To find the contribution of the gel-like mode to $S(q, \omega)$, we follow the approach of reference [1].

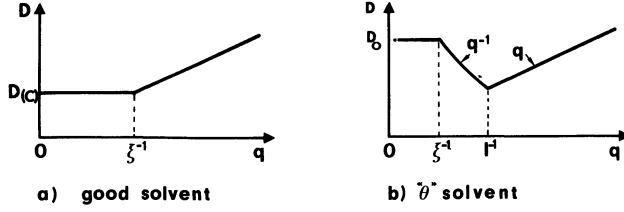


Fig. 2. — Cooperative diffusion coefficient D_{coop} of polymer solutions corresponding to the gel-like mode. a) In a « good solvent », one expects two regimes : $q\xi < 1$ (multichains) and $q\xi > 1$ (single chain). b) In a « θ solvent », we predict three regimes :

- $q > \xi^{-1} = \text{multichains } (D = D_0 \text{ is independent upon } q)$;
- $\xi^{-1} < q < l^{-1} = \text{single « entangled » chain}$;
- $q > l^{-1} = \text{ideal non-entangled single chain}$.

The gel-like regime is observed only for $q > q_g$ (Eq. 25). For $q < q_g$, $D_{\text{coop}} : 1)$ depends upon c ($D_{\text{coop}} \sim c$); 2) is much smaller than D_0 .

A general theorem relates $S(q, \omega)$ to the response function of the motion of the polymer to an external force $F_{\text{ex}}(q, \omega)$. In the presence of F_{ex} equation (1) becomes :

$$\frac{c}{\mu} \ddot{\mathbf{r}} = \left(E_0 + E_g \frac{i\omega T_r}{1 + i\omega T_r} \right) \nabla^2 \mathbf{r} + F_{\text{ex}}(q, \omega) \quad (18)$$

leading to :

$$\mathbf{r} = \chi(q, \omega) F_{\text{ex}} \quad (19)$$

with

$$\frac{1}{\chi(q, \omega)} = i\omega \frac{c}{\mu} + E_0 q^2 + E_g q^2 \frac{i\omega T_r}{1 + i\omega T_r}. \quad (20)$$

The poles of χ give two relaxation modes :

a slow hydrodynamic mode :

$$s_1 = \frac{D_s q^2}{1 + T_r D_g q^2} \quad (21)$$

where D_s and D_g are given by equations (12), (13);

a « fast » mode :

$$s_2 = \frac{1}{T_r} + D_g q^2 \quad (22)$$

$S(q, \omega)$ is related to $\chi(q, \omega)$ by :

$$S(q, \omega) = -T \frac{c}{\pi\omega} q^2 \text{Im } \chi(q, \omega).$$

Inserting (20) in (22) leads to :

$$S(q, \omega) = \frac{\mu T q^2}{s_2 - s_1} \left(\frac{1}{\pi} \frac{s_2}{\omega^2 + s_2^2} \left(1 - \frac{1}{T_r s_2} \right) + \frac{s_1}{\pi(\omega^2 + s_1^2)} \left(\frac{1}{s_1 T_r} - 1 \right) \right) \quad (23)$$

If \mathcal{A}_1 is the total intensity scattered by the slow mode and \mathcal{A}_2 the contribution of the gel-like mode, one has :

$$\mathcal{A}_1 \sim \frac{1}{s_1 T_r} - 1 = \frac{1 + D_g q^2 T_r}{D_g q^2 T_r} \quad (24)$$

$$\mathcal{A}_2 \sim 1 - \frac{1}{s_2 T_r} = \frac{D_g q^2 T_r}{1 + D_g q^2 T_r}. \quad (24bis)$$

$\mathcal{A}_1/\mathcal{A}_2 \rightarrow \infty$ as $q \rightarrow 0$ and $\mathcal{A}_1/\mathcal{A}_2 \rightarrow E_g/E_0$ as soon as $q > q_g$, with q_g given by :

$$D_g q_g^2 T_r = 1 \quad (25)$$

q_g [12] is a threshold wave vector separating two dynamical behaviours as seen from equations (21), (24) ($q_g^{-1} \sim \xi(N/g)^{3/2}$ may be large : with $N = 10^4$, $g = 10^2$, $q_g^{-1} \sim 10 \mu$).

For $q < q_g$, a fluctuation of concentration $\delta c_q = \delta c_0 e^{iqr}$ relaxes with a single frequency : the solvent moves through the chain very slowly and the chains can disentangle during a diffusion time $(D_s q^2)^{-1}$.

For $q > q_g$, the concentration fluctuation is relaxed by two processes. First, the solvent moves through the chain but now the chains do not have time to disentangle ; this first motion stops as the osmotic pressure equilibrates the elastic stress. In a second stage, the stress is relaxed viscously with the characteristic time proportional to T_r . Whatever the range of q , the slow mode dominates $S(q, \omega)$. The gel-like mode rather difficult to extract [2], as first pointed out by us [1].

On the other hand, the gel-like mode can be easily studied from $S(q, t)$.

The Fourier Transform of $S(q, \omega)$ (Eq. 22) is :

$$S(q, t) = \mathcal{A}_1 \left(e^{-s_1 t} + \frac{\mathcal{A}_2}{\mathcal{A}_1} e^{-s_2 t} \right).$$

In the gel regime, $q > q_g$, $s_1 = D_s/D_g T_r$, $s_2 = D_g q^2$ and $\mathcal{A}_2/\mathcal{A}_1 = D_s/D_g$.

Even if $\mathcal{A}_2 < \mathcal{A}_1$, the times scale of the two modes are so different that the slope at time $t \rightarrow 0$ is controlled by the fast mode :

$$\frac{d}{dt} S(q, t) = -\mathcal{A}_1 \left(s_1 + \frac{\mathcal{A}_2}{\mathcal{A}_1} s_2 \right).$$

The contribution of the two modes are comparable for $q \simeq q_g$ but the fast mode dominates the small-times behaviour as soon as $q > q_g$.

5. Conclusion. — By the study of the slope of $S(q, t)$ at small times by light or neutron scattering, it is possible to measure the osmotic diffusion coefficient at small q and the gel diffusion coefficient D_g for $q > q_g$. Our new result is that the variation of D_g as a function of $q = D_g$ is first constant, decreases and then increases linearly at $ql > 1$.

Experimentally, a second, slow mode appears for

$q > q_g$. From reference [1], we are led to predict a q -independent relaxation rate for this slow mode ($1/\tau_{\text{slow}} = E_0/E_g T_r$). Recent NBS experiments [9] give a very different result ($1/\tau = D_{\text{self}} q^2$) where D_{self} is very close to the self-diffusion coefficient of one polymer chain creeping through the others

$$\left(D_{\text{self}} \sim \frac{Na^2}{T_r} \right).$$

This q^2 behaviour is not explained in our model and may be due to polydispersity effects [11].

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