



SMALL ANGLE SCATTERING AND POLYMERS

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ABSTRACT

The determination of polymer structure is a problem of interest for both statistical physics and industrial applications. The average polymer structure is defined. Then, it is shown why small angle scattering, associated with isotopic substitution, is very well suited to the measurement of the chain conformation. The corresponding example is the old, but pedagogic, measurement of the chain form factor in the polymer melt. The powerful contrast variation method is illustrated by a recent determination of the concentration profile of a polymer interface.

1. Introduction

Using a wavelength λ of about 10\AA , small angle neutron scattering (SANS) is well suited to the dimensions of polymers. Thus it is an excellent technique allowing [1] to determine the conformation, i.e. the average structure, of polymers in different environments. The parameters obtained are the molecular weight, the radius of gyration and the persistence length of the polymer and more generally its form. They are obtained from polymer solutions using similar procedures as those of light or X-ray techniques [2-5]. But neutron is the scattering radiation that allows a labelling method keeping unchanged the chemical properties of the labelled moieties: **the isotopic substitution**.

As a peculiar case, SANS is the only technique allowing to determine the conformation of one chain inside different polymeric materials by using deuteration as a labelling method. This is an important result since plastic material is essential element of human life. The possibility to vary the coherent scattering lengths of the solvent simplifies the determination of the partial structure functions of complex solutions. These possibilities are at the origin of the success of SANS in the polymer field. The aim of this lecture is to show how.

2. Basis of the polymer conformation [6-8]

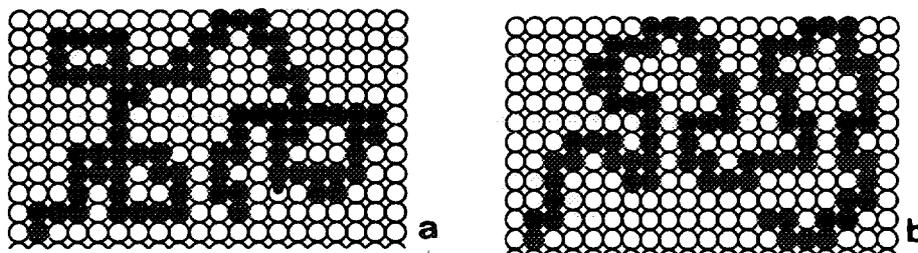


Fig. 1 - Schematic representation of polymer conformations on a lattice of step ℓ . Fig. 1a represents a random walk, Fig. 1b a self avoiding walk or a polymer with excluded volume.

A polymer is a linear succession of N , chemically bound, identical units each of length ℓ . The easiest model to describe the polymer conformation is a random walk e.g. there is no correlation between two successive monomers (see Fig. 1a). As a consequence, the mean quadratic distance R between the polymer ends is:

$$R^2 = N\ell^2 = 6R_g^2 \quad (1)$$

where R_g is the radius of gyration of the chain (the inertial moment of the polymer divided by its mass). Typical values of these parameters are: $N \sim 5000$ that corresponds to a molecular weight $M \sim 500000$ and $\ell \sim 3 \text{ \AA}$. The size of a solvent molecule is similar to ℓ . The length scale is given by ℓ and by the global size of the chain $R_g \sim (5000 \cdot 10/6)^{1/2} \sim 100 \text{ \AA}$.

The number of configurations that a chain can adopt is z^N . z is the number of neighbours of each monomer extremity; $z = 3$ in the square lattice of Fig. 1 or for a carbon-carbon bond. This number is usually greater than 10^{1000} . Then the polymer entropy is very high and originates the basic random coil behaviour of the chain. The conformation of polymers, in a given environment (a solution, a network, an interface, a flow...), is submitted to the competition of the constraint of this environment and of the entropy which strongly leads the polymer to adopt a random coil conformation. For a real chain, the constraint is the impossibility to have two monomers far along the chain at the same position whereas it was the case for an ideal chain. This steric phenomenon, called the excluded volume effect, leads to an important swelling of the chain that clearly appears in dilute polymer solutions (see Fig. 1b). It occurs in good solvents where the pair interaction between monomers is repulsive. Nevertheless, it is possible to find [6] a temperature Θ corresponding to a compensation between interactions monomer-monomer and monomer-solvent. At this Flory temperature, the ideal chain conformation is observed. Thus the random walk model is not so far from reality.

The polymer conformation is well defined if the conditional probability $g_1(\mathbf{r})$ of having two repetitive units at a distance \mathbf{r} is known. It is convenient to write $g_1(\mathbf{r})$ with the formalism of Van Hove [9], since this formalism is well suited to show how to extract the polymer conformation from a scattering experiment. Following Van Hove, the pair correlation function $g_1(\mathbf{r})$ is expressed as a function of the density $\rho(\mathbf{r})$ of the chain repetitive units of which positions are \mathbf{r}_i ($i = 1 \dots N$).

$$\rho(\mathbf{r}) = \sum_1^N \delta(\mathbf{r} - \mathbf{r}_i) \quad g_1(\mathbf{r}) = \langle \rho(\mathbf{0}) \rho(\mathbf{r}) \rangle \quad (2)$$

where $\delta(\mathbf{r})$ is the distribution function of Dirac, $\int_V \delta(\mathbf{r}) d_3r = 1$.

The determination of $g_1(r)$ is a non trivial statistical problem which needs the dichotomy between theoretical predictions and experimental measurements. Note, in particular, that the second moment of $g_1(r)$ is proportional to R_g^2 ,

$$R_g^2 = \frac{1}{2N^2} \sum_{i,j} \langle (r_i - r_j)^2 \rangle = \frac{1}{N} \sum_i \langle s_i^2 \rangle \quad (3)$$

where s_i is the monomer position relatively to the centre of gravity G of the chain (see Fig. 2), $\sum_i s_i = 0$.

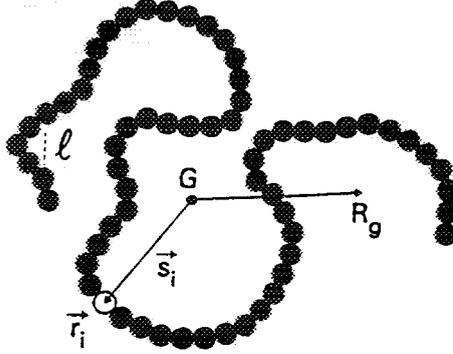


Fig. 2 - Representation of a polymer where the statistical length ℓ involves a few number of monomers. G is the centre of gravity of the chain and R_g its radius of gyration.

In the intermediate range, $\ell \ll r \ll R_g$, the variation of $g_1(r)$ gives information concerning the form of the polymer. For instance, $g_1(r) \sim r^{-1}$ characterizes a gaussian coil (a random walk), $g_1(r) \sim r^{-4/3}$ corresponds to a self avoiding walk whereas $g_1(r) \sim r^{-2}$ labels a rigid rod (de Gennes [7] p.37).

3. The SANS cross section and the contrast notion

Let us consider a solution of n polymers each having N monomers. Since the domain of distances of interest was shown lying in between 3 and 500Å, the scattering vector range of Q needed for a SANS experiment varies from 0.1 to 10^{-3} \AA^{-1} . At this small angle scale, the structure factors of the solution molecules are reduced to unity. Thus the monomers and the solvent molecules can be considered as scattering points of which coherent scattering length b_i is the sum of the coherent scattering lengths of their atoms. Thus the intensity scattered by the solution writes:

$$I(Q) = \sum_{i,j} b_i b_j \langle \exp(iQ(r_i - r_j)) \rangle = \sum_{i,j} b_i b_j S_{ij}(Q) \quad (4)$$

where the scattering functions $S_{ij}(Q)$ are the partial structure factors. For the polymer solution, $I(Q)$ is:

$$I(Q) = b_p^2 S_{pp}(Q) + 2b_p b_s S_{ps}(Q) + b_s^2 S_{ss}(Q) \quad (5)$$

where the indexes p and s characterize the monomers and the solvent molecules respectively. Eq. 4 and 5 are general and valid even for wide Q values. Nevertheless it is difficult to extract the polymer response, $S_{pp}(Q)$, from the measurement of $I(Q)$. Fortunately in the Q range of SANS, the incompressibility of the sample is a constraint which simplifies [10] these equations by introducing the contrast notion.

3.1. Isothermal compressibility and the contrast notion

Let us consider first a system of identical scatterers, a solvent or a polymer melt for instance, in a volume V . The average number of scatterers (a solvent molecule or a monomer) is $\langle n \rangle$, each has a partial volume $v_s = V/\langle n \rangle$ and a scattering length b_s . A

general thermodynamical expression [11] relates the extrapolation of $I(Q)$ to zero Q value to the isothermal compressibility χ_T :

$$I(0) = b_s^2 S(0) = b_s^2 \langle n \rangle / v_s k T \chi_T \quad (6)$$

Where k is the Boltzmann constant and T the temperature. In practice, the thermodynamical limit is already reached [10] for Q values below Q^* ,

$$I(Q) \cong I(0) \quad ; \quad Q < Q^* \quad (7)$$

The value of Q^* is rather large, about 0.6 \AA^{-1} . Note that the Q range of interest for polymer studies ($Q\ell < 1$) lies also below Q^* . Moreover, far from a critical temperature, these systems are considered as incompressible ($\chi_T \sim 0$) since the density fluctuations are negligible relatively to the concentration fluctuations. Thus the intensity scattered by a melt of polymers of one species is quasi-zero, in the range $Q\ell < 1$. It is only due to the very weak density fluctuations of monomers. It is the origin of the transparency of materials made with amorphous (flexible) polymers such as polystyrene or Plexiglas (polymethylmetacrylate). **The incompressibility hypothesis is the basic point of the notion of contrast in small angle scattering experiments.**

Let us consider, now, a mixture of scatterers of $\alpha = 1 \dots m$ different chemical species. The parameters are the mean number $\langle n_\alpha \rangle$, v_α the partial molecular volume and the scattering length b_α . Here the sample scatters the following intensity:

$$I(Q) = \sum_{\alpha, \beta} b_\alpha b_\beta S_{\alpha\beta}(Q) \quad (8)$$

The extension of the thermodynamical limit [11] writes:

$$\langle n_\beta \rangle k T \chi_T = \sum_{\alpha} v_\alpha S_{\alpha\beta}(0) \cong \sum_{\alpha} v_\alpha S_{\alpha\beta}(Q) \quad ; \quad Q < Q^* \quad (9)$$

The combination of Eq. 8 and 9 allows to eliminate one component, $m = 1$ for instance. Then, using $\chi_T = 0$, Eq. 8 becomes:

$$I(Q) = \sum_{\alpha, \beta} k_\alpha k_\beta S_{\alpha\beta}(Q) \quad , \quad k_\alpha = b_\alpha - b_1(v_\alpha/v_1) \quad Q < Q^* \quad (10)$$

where k_α is the contrast length of the species α relatively to the species 1. In the following the condition, $Q < Q^*$, of the incompressibility will be considered as fulfilled.

Applying this result to the polymer solution, the scattering intensity writes:

$$I(Q) = k_p^2 S_{pp}(Q) \quad ; \quad k_p = b_p - b_s(v_p/v_s) \quad (11)$$

It gives directly the monomer-monomer scattering function, the solvent molecules having not to be taken into account.

Let us now give a few numerical examples of the k_p value for polystyrene, $(C_8H_8)_N$, in different solvents as the carbon disulphide, CS_2 , or the benzene, C_6H_6 , deuterated or not. The usual rules for the calculation of k_p are: the partial molecular volume of a molecule is deduced from the bulk density of the species; the isotopic substitution does not change the volume of the labelled molecule. Table I gives these values that the reader may verify using the more recent table of coherent scattering lengths [12].

Table I - Values of the contrast length for H and D polystyrene chains in different solvents

k_p (10^{-12} cm)	CS_2	C_6H_6	C_6D_6
- C_8H_8 -	0.319	0.396	- 6.518
- C_8D_8 -	8.647	8.724	1.810

In Table I, the striking result derives from the intensity scattered by H chains in CS_2 that is proportional to $0.1 (k_p^2)$. Whereas the same polymer, but deuterated, in the same solvent scatters an intensity 700 times greater! This example shows why isotopic

substitution is an excellent method of labelling since it keeps unchanged the electronic shells of atoms and thus the chemical properties of the labelled molecules.

With polymers, using deuteration of the chains or of the solvent molecules, it is possible to improve the contrast of SANS and to study the conformation of chains in rather dilute solutions (10^{-3} gcm^{-3}). This conformation can also be determined as a function of the concentration of the solution by using mixtures of H and D polymers [13]. This until the polymer melt as described further.

3.2. The form factor and the distinct scattering function

Coming back to the polymer solution of volume V, Eq. 11 gives :

$$I(Q) = k_p^2 S_T(Q) = k_p^2 \sum_{\alpha, \beta}^{n, n} \sum_{i, j}^{N, N} \langle \exp(iQ(\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta)) \rangle \quad (12)$$

where \mathbf{r}_i^α is the position of the i^{th} monomer of the chain α ($\alpha = 1, \dots, n$), each with N monomers. The total scattering function $S_T(Q)$ can be split in an intra-polymer scattering function $S_1(Q)$, the form factor, and an inter-polymer scattering function $S_2(Q)$:

$$\begin{aligned} S_T(Q) &= nS_1(Q) + n^2S_2(Q) \\ S_1(Q) &= \sum_{i, j} \langle e^{iQ(\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha)} \rangle = \int e^{iQ\mathbf{r}} g_1(\mathbf{r}) d\mathbf{r} \\ S_2(Q) &= n^{-2} \sum_{\alpha, \alpha \neq \beta} \sum_{i, j} \langle e^{iQ(\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta)} \rangle \end{aligned} \quad (13)$$

$S_1(Q)$ is the Fourier transform of the pair correlation function $g_1(\mathbf{r})$ which characterizes the polymer conformation as discussed in section 2. Even in the simple case of a binary system, $S_1(Q)$ is not easily obtained: the experiment has to separate the functions $S_1(Q)$ and $S_2(Q)$ in Eq. 13. Such a procedure has been early developed by Zimm [14] for light scattering experiment. The determinations of the molecular weight and of the radius of gyration of polymers in dilute solution are usually obtained from extrapolations to zero concentration of data obtained with light, X-ray or neutron experiments [1].

3.3. Conformation in the polymer melt : The 50/50 theorem.

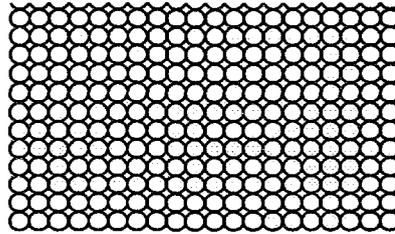


Fig. 3 - A melt of polymer is a liquid-like structure.

A melt of polymers is a liquid like structure of monomers (see Fig. 3) of density $\rho_m = n_m N/V$. In this case, there is no concentration fluctuations and very weak density fluctuations. The system, as already discussed in section 3, can be considered as incompressible and does not scatter:

$$S_T(Q) = \frac{n_m N^2}{V} kT \chi_T \approx 0 \quad ; \quad Q < Q^* \quad (14)$$

Therefore there is a compensation between the intra- and the inter-chain fluctuations of monomer positions that is written from Eq. 13 and 14 :

$$S_1(Q, n_m) = - n_m S_2(Q, n_m) \quad (15)$$

Thus a scattering experiment by a polymer melt cannot give the chain conformation.

Nevertheless, this problem can be solved using a labelling method (see Fig. 4) which creates, artificially, concentration fluctuations due to the contrast of the polymer with itself. For photon scattering experiments, as photons interact with the electronic shells of atoms, the labelling of a polymer needs to change the atoms and therefore the chemical species of monomers. But a mixture of polymers of different chemical species leads, generally, to a phase separation since the threshold of miscibility of two polymers varies as the inverse of the molecular weight or N (see ref. [7] p.106). Consequently to label a polymer is very difficult with light or X-ray techniques. Whereas the neutrons, which essentially interact [15,16] with the nuclei of atoms, allow to label the atoms using the isotopic substitution which keeps unchanged the electronic shells. Moreover the substitution proton (H) deuteron (D), rather easy to obtain, gives one of the highest values of contrast [12]. These are, also, fundamental reasons of the use of small angle scattering (SANS) in the polymer field.

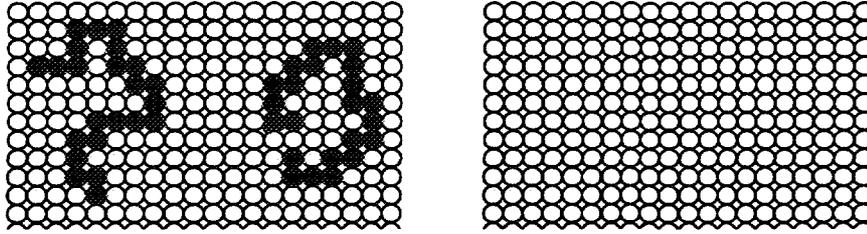


Fig.4 - Schematic representation of a polymer melt with and without labelled chains.

Let us write the intensity of a solution of xn labelled polymers (noted D) of contrast length k_D and $(1-x)n$ unlabelled ones (H, k_H), both having the same number of monomers. Assuming a totally random spatial distribution of labelled and unlabelled polymers, Eq.10 becomes:

$$I(Q) = k_D^2 S_{DD}(Q) + 2k_D k_H S_{DH}(Q) + k_H^2 S_{HH}(Q) \quad (16a)$$

where

$$\begin{aligned} S_{DD}(Q) &= xnS_1(Q, n) + x^2 n^2 S_2(Q, n) \\ S_{DH}(Q) &= x(1-x)n^2 S_2(Q, n) \\ S_{HH}(Q) &= (1-x)nS_1(Q, n) + (1-x)^2 n^2 S_2(Q, n) \end{aligned} \quad (16b)$$

Finally $I(Q)$ is given by:

$$I(Q) = \langle k^2(x) \rangle n S_1(Q, n) + \langle k(x) \rangle^2 n^2 S_2(Q, n) \quad (17)$$

where

$$\langle k^2(x) \rangle = xk_D^2 + (1-x)k_H^2 \quad \text{and} \quad \langle k(x) \rangle = xk_D + (1-x)k_H \quad (18)$$

The total scattering function $S_T(Q, n)$ can be introduced in Eq. 17; this leads to use the mean square deviation of $k(x)$:

$$\langle k^2(x) \rangle - \langle k(x) \rangle^2 = (k_D - k_H)^2 = (b_D - b_H)^2$$

which only depends of the scattering lengths of the scatterers. Eq. 17 becomes:

$$I(Q) = x(1-x)(b_D - b_H)^2 n S_1(Q, n) + \langle k(x) \rangle^2 S_T(Q, n) \quad (19)$$

In the melt, using the incompressibility, $S_T(Q, n_m) \sim 0$, Eq. 14, Eq. 19 becomes :

$$I(Q) = (b_D - b_H)^2 x(1-x) n_m S_1(Q) \quad (20)$$

This result, early predicted by des Cloizeaux [17], shows that the scattering intensity gives directly $S_1(Q)$ without any extrapolation of the concentration x of labelled polymers. It is often called the 50-50 theorem since the scattering intensity is maximum for $x = 0.50$. It has been experimentally verified [18] with amorphous polymers. For these polymers, the quenched melt, sometimes, presents some voids of which contrast is greater with D polymers than with H polymers. In order to minimize the spurious central

scattering of such voids, it is often better [18b] to use a concentration of deuterated chains smaller, $x \sim 0.20$, than the optimum one (0.50). On the contrary, with liquid crystalline polymers [19], probably due to their liquid character, such voids are not important and all the experiments made used samples with one half of partially D polymers.

4. From the form factor to the chain conformation

In the previous section, it is shown that SANS by a melt of H and D polymers gives an intensity directly proportional to the form factor of one chain. Now, we want to discuss how the chain conformation can be determined from this form factor.

The intensity $i(Q)$, per unit volume of sample, writes (see Eq. 12 and 20) :

$$i(Q) = I(Q)/V = (A/N)S_1(Q) = ANP(Q) \quad (21)$$

where $A = k_p^2 \rho$ for a polymer in solution and ρ is the monomer concentration ($\rho = nN/V$) or $A = (b_D - b_H)^2 x(1-x)\rho_m$ for a polymer melt containing x percent of deuterated chains; ρ_m is the number of monomers per unit volume. $P(Q)$ is the form factor (normalized at unity, $P(0) = 1$) which writes :

$$P(Q) = N^{-2} \sum_{i,j}^{N,N} \left\langle e^{iQ(r_i - r_j)} \right\rangle \quad (22)$$

As a general principle, it can roughly be said that in a scattering experiment Q acts as the magnification of a microscope. Depending on the Q values, are explored the scales from the radius of gyration R_g of the chain to that of the statistical unit ℓ .

For small Q values, $QR_g < 1$, the Guinier range, the SANS experiment allows to determine R_g or the global chain size. The form of the polymer is obtained in the intermediate Q range, $(4R_g)^{-1} < Q < \ell^{-1}$, where the correlations between monomers intervene. In this range the form of the polymer is deduced [7] from the characteristic exponent α of the $Q^{-\alpha}$ dependence of $P(Q)$, as it is developed, in the following, in the cases of oriented and unoriented polymers.

4.1. Case of unoriented samples

If the polymer can adopt all the orientations in space as it is the case for isotropic particles or for unoriented samples, the orientation average leads to write $P(Q)$ as [2]:

$$P(Q) = N^{-2} \sum_{i,j}^{N,N} \left\langle \frac{\sin(Qr_{ij})}{Qr_{ij}} \right\rangle \quad (23)$$

where r_{ij} is the module of the vector $r_i - r_j$.

At small Q values, the expansion of $P(Q)$ gives [2]:

$$i(Q) \approx AN(1 - Q^2 R_g^2 / 3); \quad QR_g \ll 1 \quad (24)$$

where R_g is the radius of gyration of the polymer, already defined (see Eq. 3), which gives its global size. The experimental value of R_g is deduced from the slope of the straight line $i^{-1}(Q)$ versus Q^2 in the so called Zimm representation [14]:

$$\frac{A}{i(Q)} = \frac{1}{N}(1 + Q^2 R_g^2 / 3); \quad QR_g \ll 1 \quad (25)$$

This representation was adopted for polymers because it is valid until $QR_g \sim 1$ and greater if the polymers have a little polydispersity (see ref. 1 p.189). From the linear extrapolation to zero Q value, the number N of monomers (or the chain molecular weight $M = Nm$, m is the molecular weight of the repetitive unit) can be measured. Such

a determination of N needs absolute SANS measurements [10, 20] which are, always, very useful.

The whole form factor allows to determine the chain conformation. The procedure consists to fit the experimental data with models of $P(Q)$. The more usual are the following [1,2,21]:

The ideal chain: It is the basic conformation of linear polymers, that of a random walk of N steps of length ℓ . Its form factor is the Debye function [22]:

$$P(Q) = \frac{2}{X^2} (e^{-X} - 1 + X) ; X = Q^2 R_g^2 = Q^2 \frac{N\ell^2}{6} \quad (26)$$

In the intermediate Q range, $(4R_g)^{-1} < Q < \ell^{-1}$, the Q^{-2} variation of $P(Q)$, $i(Q) \cong 12A/Q^2\ell^2$, is a well-known characteristic of Gaussian polymers.

The self avoiding walk: There is no analytic function of the form factor of the chain with excluded volume effect. Nevertheless the variation of R_g as a function of N and the intermediate behaviour of $P(Q)$ are known [7,8]:

$$R_g^2 \sim N^{2\nu} ; P(Q) \sim Q^{-1/\nu} \quad (27)$$

The value of ν is 0.588. The ν change from 0.500 to 0.588 characterizes the swelling of the chain due to the excluded volume effects.

The rod of length L , without thickness, has the following form factor [1,2]

$$P(Q) = \frac{1}{X} \int_0^{X/2} \frac{\sin u}{u} du - \frac{\sin^2 X}{X^2} ; X = \frac{QL}{2} ; R_g^2 = \frac{L^2}{12} \quad (28)$$

In the intermediate Q range, $4QL > 1$, the Q^{-1} variation of $P(Q)$, $\sim \pi/QL$, is another signature of a rigid rod.

The wormlike chain corresponds to a more realistic model of a polymer chain. It is a Gaussian chain which evolves continuously to a rigid rod when decreasing the distance below the persistence length l_p . Two parameters define the chain: its contour length L and l_p . The form factor of such a chain is not a simple function [23-25]. The simplest expression is obtained from the amalgamation [26] of three functions, within an error bar of 1.5%, thus much lower than the experimental ones [26]; it is valid only for $L \geq 10l_p$. These functions are:

$$P_1(Q) = \frac{\pi}{QL} + \frac{2}{3Q^2 l_p L} ; Ql_p \geq 4$$

$$Q^2 l_p L P_2(Q) = 6 + 0.5470(Ql_p)^2 - 0.01569(Ql_p)^3 - 0.002816(Ql_p)^4 ; 2 < Ql_p < 4$$

$$P_3(Q) = \frac{2}{x^2} (e^{-x} - 1 + x) + \frac{2}{15u} \left[4 + \frac{7}{x} - \left(11 + \frac{7}{x} \right) e^{-x} \right] ; x = Q^2 l_p L / 3 ; u = L / l_p ; Ql_p \leq 2 \quad (29)$$

$P_1(Q)$ is the asymptotic form given by des Cloizeaux [23], $P_2(Q)$ is an approximation, better than $4 \cdot 10^{-3}$, of the tabulated data also given by des Cloizeaux in ref.23. $P_3(Q)$ is the approximation of Sharp and Bloomfield [24] for finite chains, valid only for small Q values $Ql_p \leq 2$. The radius of gyration of this chain is [27]:

$$R_g^2 = l_p^2 \left(\frac{u}{3} - 1 + \frac{2}{u} - \frac{2}{u^2} (1 - e^{-u}) \right) \quad (30)$$

When $u=L/l_p$ tends towards infinite, R_g^2 tends to $Ll_p/3$, thus the statistical unit of the wormlike chain is $\ell = 2l_p$.

The sphere of radius R. This model can be useful to analysis the form factor of a collapsed polymer.

$$P(Q) = \frac{9}{X^6} (\sin X - X \cos X)^2 \quad ; \quad X = QR \quad ; \quad R_g^2 = 3R^2/5 \quad (31)$$

In the intermediate range, if the polydispersity of the sphere sizes has a sufficient value to level the oscillations of $P(Q)$, $P(Q)$ has a Q^{-4} variation characteristic of the sharp interfaces. This result is a particular case of the well known Porod law [28]:

$$i(Q) = 2\pi(k_1/v_1 - k_2/v_2)^2 (S/V)Q^{-4} \quad (32)$$

which allows to determine the area per unit volume S/V of a sharp interface between media 1 and 2 .

4.2. Case of oriented samples

Let us consider the case of anisotropic polymers as stretched polymers or liquid crystalline polymers. The preferential directions are those parallel and perpendicular to the stretching direction or to the nematic director.

At small Q values, the expansion of the form factor $P(Q_x)$, Eq. 22, in any direction x , can be written:

$$P(Q_x) \approx 1 - Q^2 R_x^2 \quad ; \quad Q^2 R_x^2 \ll 1 \quad (33)$$

R_x is called [29] the inertial mean distance in the x direction and is defined by:

$$R_x^2 = \frac{1}{N} \int s^2 n(s) ds \quad ; \quad N = \int n(s) ds \quad (34)$$

where $n(s)$ is the number of monomers between two planes normal to this direction and at distances $x=s$ and $x=s+ds$ of the centre of gravity G of the polymer. $n(s)$ is also the number of intersections of the polymer with such a plane, see Fig. 5. For an isotropic model, the radius of gyration is given by:

$$R_g^2 = R_x^2 + R_y^2 + R_z^2 = 3R_x^2 \quad (35)$$

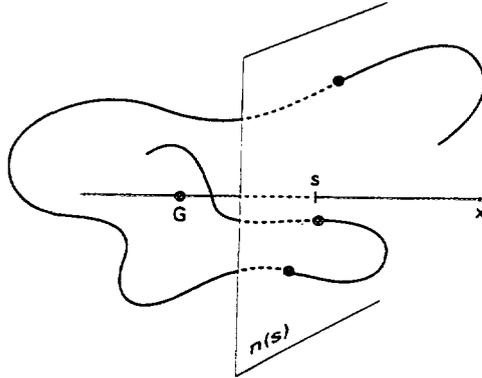


Fig. 5 - The inertial quadratic mean distance R_x^2 is the second moment of $n(s)$ the number of intersections of the polymer with the plane normal to the direction x at a distance s of the centre of gravity G of the polymer. From ref. 19.

The whole form factor can also be used, here, to fit the data with a model in any direction. A simple model is that of a cylinder (length $2H$ and radius R) of which form factor is:

$$P_\alpha(Q) = \left(\frac{\sin(QH \cos \alpha)}{QH \cos \alpha} \frac{2J_1(QR \sin \alpha)}{QR \sin \alpha} \right)^2 \quad (36)$$

where α is the angle between the cylinder axis and the scattering vector \mathbf{Q} and $J_1(x)$ the Bessel function of the first order. The inertial mean distance in the α direction is:

$$R_\alpha^2 = \frac{4H^2 \cos^2 \alpha}{12} + \frac{R^2 \sin^2 \alpha}{4} ; \quad Q(2H \text{ or } R) \ll 1 \quad (37)$$

Other form factors of simple models are given in the book of Feigin and Svergun (ref. 21 p. 93). The effects of the length distribution of the chain, the polydispersity, are discussed elsewhere [1,19,30].

5. The polymer conformation in the melt

Before the SANS experiments, the conformation of polymers in their melt was unknown. As the chains are rather globular in dilute solution, somebodies thought that increasing the concentration has for effect to condense the chains on themselves, each keeping its individuality. The supporters of the globular form underevaluated the viscoelastic properties of polymers wich is an indication of the existence of entanglements. The latter was taken into account by a Flory's prediction [6] assuming an ideal conformation of chains. That corresponds to interpenetrating chains. Others thought that local alignments of polymers occured, see Fig. 6.

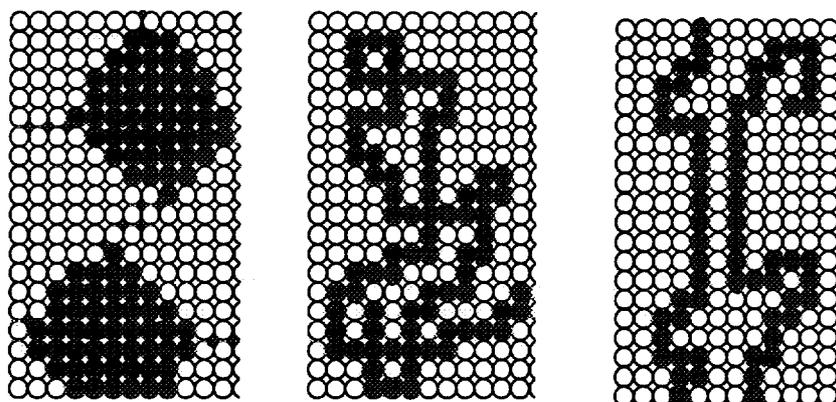


Fig. 6 - Before SANS, the three possible conformations of polymer chain in the melt: a globular form, a Gaussian conformation (the chains are interpenetrated) and the existence of partial chain alignments.

This problem was solved with the development of the SANS technique, at the beginning of seventies, when the possibilities of the deuteration in this field were achieved. The first experiments were made in Europe using only a small amount of D polymers dispersed in a matrix of H polymers. The 50-50 theorem was not yet recognized! The results obtained with chains of polymethylmethacrylate (Plexiglas) [31], polyethylene [32] and polystyrene [17,33] were consistent. They will be discussed now in the light of the polystyrene case [17], a standard of flexible amorphous polymer.

Fig. 7a shows the raw data. The upper curve is obtained with an H polystyrene containing $2 \cdot 10^{-2}$ of deuterated chains of similar molecular weight ($M_w \sim 21\ 000$). The lower curve is the intensity scattered by a test sample made with only H polymers; it has not to give a coherent signal. Both set of data shown in Fig. 7 are typical of the SANS technique.

The central scattering of the lower curve results from defects of the collimation of the incident beam. Its flat part is rather high; it is due to the incoherent background of

the numerous protons of the sample. Notice that this background is proportional to the solid angle $\Delta\Omega$ defined by the detector of the spectrometer. In SANS, $\Delta\Omega = s/D^2$ (s is the detector area and D the detector-sample distance), $\Delta\Omega$ has a very small value, typically $3 \cdot 10^{-5}$. Thus the background due to protons is not a real problem as it is claimed in the case of wide angle neutron experiments.

With a low D monomer concentration ρ and a weak number of monomers ($N \sim 200$), the coherent intensity, proportional to ρN , is particularly weak in this example. Nevertheless the intensity resulting from the difference between the two curves in Fig. 7a is tractable as it appears clearly in Fig. 7b.

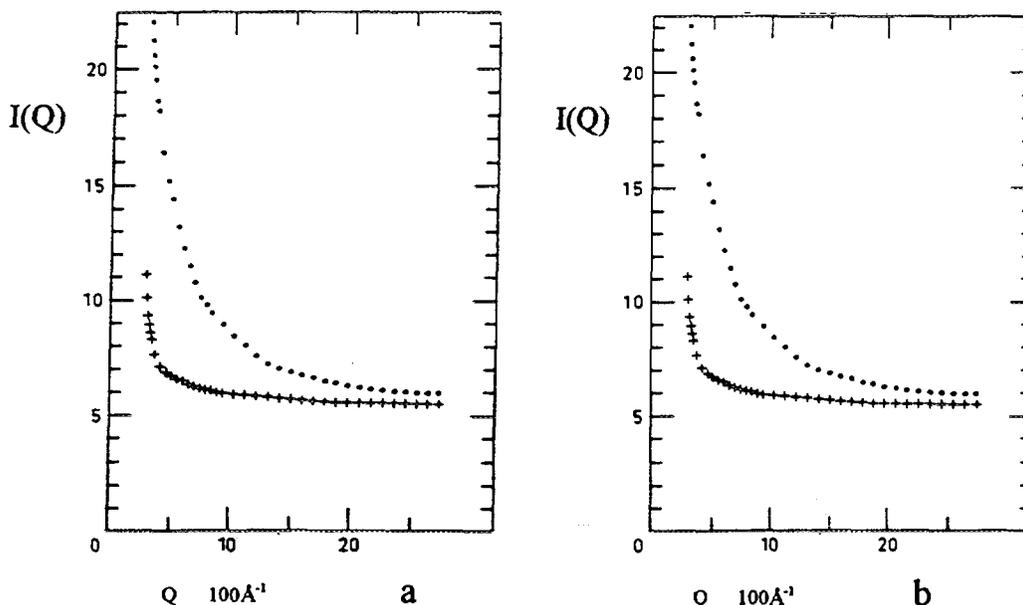


Fig. 7a - Raw data of the intensity as a function of the scattering vector Q . The lower curve is that scattered by a melt of H polystyrene chains, it is the background. The upper curve corresponds to a similar sample where 2 percent of D polystyrene are dispersed. The molecular weight of D chains (21 000) is similar to that of the H chains (20 000).

Fig. 7b - Form factor of the D chain as a function of Q . The data results directly from the difference between those of Fig. 7a. In spite of the particularly weak coherent scattering of these samples, the intensity is rather good. The full line is a fit with the Debye function (Eq. 26). The data of Fig. 7a and 7b are those of ref. 17.

5.1. Conformation deduced from the radius of gyration

Following Eq. 20, the curve of Fig. 7b is proportional to the form factor of the short polystyrene chain. From the slope of the Zimm representation, $I^1(Q)$ versus Q^2 , the value of the radius of gyration, $R_g = 38\text{\AA}$, is obtained. Here the chain is too short to study the intermediate Q range since this domain, $QR_g > 4$, corresponds to dimensions well inside that ℓ of the monomer ($\ell = 18\text{\AA}$ [26,35]). Thus the correlations between monomers cannot be reached in this way. It is sad since the value of the radius of gyration gives only a number that is the global size but nothing about the form. Nevertheless the indication concerning the form can be obtained from the variation of R_g as a function of N (or the molecular weight M) but it needs more samples. If the polymer is globular, its size has to vary as $N^{1/3}$ (Eq. 31), this variation becomes $N^{1/2}$ for an ideal chain (Eq. 26) and N^1 for a rod (Eq. 28).

The experiments [17] were made using samples with eight different molecular weights lying in between 20 000 and 1 100 000. The R_g values obtained in the melt were

compared to those obtained in a good solvent CS_2 and in a Θ solvent (H polystyrene in D cyclohexane at 30°C). The results are shown in Fig. 8. In the good solvent the exponent 0.6 is in good agreement with that of 0.588 predicted by modern theories [7,8] for a self avoiding walk. In the Θ solvent and in the melt, the polymer sizes are similar and the slope of 0.5 is in very good agreement with a Gaussian conformation of polymers in their melts.

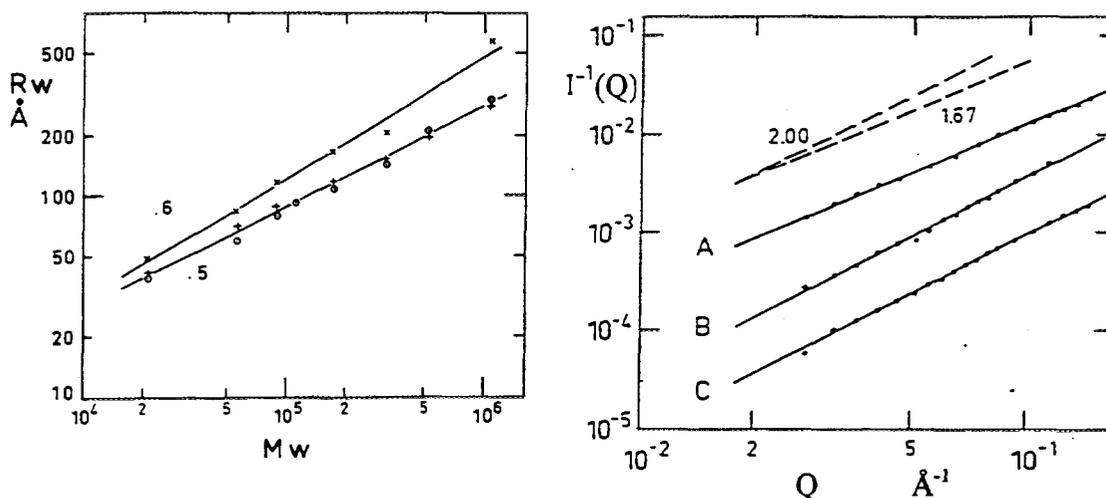


Fig. 8 - Log log plot of the radius of gyration of a polystyrene chain versus the molecular weight. Different environments were used: a good solvent CS_2 (x), a Θ solvent and in its melt (\odot). The data obtained in the melt and in the Θ solvent are very similar with a slope of 0.5. These data are those of ref. 17.

Fig. 9 - Log log plot of the inverse scattered intensity as a function of the scattering vector Q . The data are obtained from polymers in different environments: in a good solvent CS_2 (A), a Θ solvent (B) and in the melt (C). The data obtained in the melt and in the Θ solvent have the same slope of value 2.0. These data are those of ref. 35.

5.2. Conformation obtained in the intermediate range

In the intermediate Q range, see section 4, the chain conformation is deduced from the exponent α of the Q^α dependence of the form factor $P(Q)$, thus **with only one scattering curve**. If the chain is globular $\alpha = 4$, for a Gaussian chain $\alpha = 2$ and for a rigid rod $\alpha = 1$. As the Q range obtained with SANS is rather limited, it is useful to vary also the length of the polymer as a function of the searched parameters. If this parameter is the radius of gyration, its determination is easiest with short chains. Whereas the best polymer allowing to reach the intermediate range is the longest one. Thus the experiment in the intermediate range was made [35] with polystyrene chains of molecular weights greater than $1.1 \cdot 10^6$. The result is shown in Fig. 9.

The intensities determined in the limit of the large Q range, $QR_g > 4$, correspond to the form factor since the interactions are negligible in this domain [1,36]. Thus in good solvent the $Q^{-1.67 \pm 0.06}$ variation corresponds to a self avoiding walk with $\nu = 0.59 \pm 0.02$ (see Eq. 27), in good agreement with the modern predictions [7,8]. The Q exponent was [35] 2.06 ± 0.08 in the Θ solvent and 2.01 ± 0.08 in the melt.

Thus in the melt a polymer has a Gaussian conformation. This was also been verified by fitting the whole form factor with the Debye function, Eq.26. It is realized, Fig. 7b, for the smaller chain, because both Q ranges ($QR_g > 1$ and < 1) are reached. The absence of excluded volume effects for a chain in its melt means [7] that there is a

compensation of interactions between monomers belonging to the same chain and those between monomers belonging to distinct chains (having the same length).

6. Polymer interfaces and the contrast variation method

The stability of colloids is often obtained by coating the particles with polymers, see Fig. 10. Thus the repulsive interaction between polymers avoids the particle aggregation. It is of current interest to determine the structure of the polymer layer. SANS is a good technique of which capacities, in this field, are far to be totally explored.

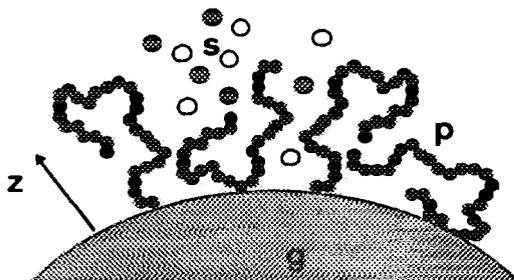


Fig. 10 - Schematic representation of polymers (p) coating a particle (g) in a mixture of labelled and unlabelled molecules of solvent.

The SANS intensity by unit volume $i(Q)$ of such a system of volume V writes:

$$I(Q) = V i(Q) = k_p^2 S_{pp}(Q) + 2 k_p k_g S_{pg}(Q) + k_g^2 S_{gg}(Q) \quad (38)$$

In order to separate the partial structure factors, it is very useful to vary continuously the scattering length of the solvent and thus the contrast length values. This method, describes now, was early introduced by Stuhrmann [37].

6.1. The contrast variation method

The contrast variation method consists in using for the solvent a mixture containing a ratio y (volume per volume) of labelled molecules of scattering length b_{sD} and $(1-y)$ of unlabelled molecules (b_{sH}). Under these conditions and because the isotopic labelling does not change the partial molar volume of the molecules, the mean scattering length $b_s(y)$ of the solvent molecule and the contrast length of the scatterers of species α are written:

$$b_s(y) = y b_{sD} + (1-y) b_{sH} ; k_\alpha(y) = b_\alpha - b_s(y) \cdot v_\alpha / v_s$$

This method is very useful for organic solvents, since the substitution of protons ($b_{sH} = -0.374 \cdot 10^{-12}$ cm) by deuterons ($b_{sD} = +0.667 \cdot 10^{-12}$ cm) leads to changes of the corresponding contrast lengths which can reach a range in between 1 to 9. The corresponding scattered intensities have variations from 1 to 80, thus of sufficient amplitudes to be clearly separated even if the variation of y is limited from 0 to 1.

Two specific values of y , the solvent proportion of labelled molecules, are of interest: y_p , for which $k_p(y_p) = 0$, the solvent matches the polymer, and y_g , $k_g(y_g) = 0$, which kills the grain: a contrast matching experiment can give directly one of the partial structure factors. In the opposite case, three measurements made with three samples, each prepared with a different y value, allow to determine $S_{gg}(Q)$, $S_{gp}(Q)$ and $S_{pp}(Q)$. It will be shown in the following, how this method, first introduced by the Bristol group [38] and developed by Auvray [39], was used to determine the concentration profile of polymers adsorbed or grafted on particles. Until these works, only the specular reflection of neutrons or X-rays was recognized to reach this aim [40].

6.2. Determination of a layer concentration profile [39]

Let us consider the colloidal solution represented in Fig. 10. The solid grain g has a sharp interface and a large radius of curvature R . The thickness of the polymer layer is h . The Q range of interest for the SANS experiment lies in the neighbourhood of $Qh \sim 1$ in order to analyse the polymer layer. Now the basic assumption is that R is much greater than h , thus at the observed Q scale the solid surface can be considered as a plane. Under this condition, $i(Q)$ is proportional to the form factor of the colloid and writes:

$$i(Q) = k_p^2 \rho S_{pp}^1(Q) + 2 k_p k_g \rho S_{pg}^1(Q) + k_g^2 \rho S_{gg}^1(Q) \quad (39)$$

where ρ is the number of colloids by unit volume of solution. The index 1 recalls that the interactions between colloids are negligible in the Q range $QR \gg 1$.

The solid-solid partial form factor is given by the Porod law (Eq. 32):

$$\rho S_{gg}^1(Q) = \frac{2\pi S}{v_g^2 V} Q^{-4} \quad ; \quad QR \gg 1$$

The cross term, $S_{gp}^1(Q)$ is proportional to the Fourier transform $\langle \rho_g(\mathbf{0}) \rho_p(\mathbf{r}) \rangle$. It is written [39a] by considering the specific symmetry of the system i.e. the invariance of the structure of the polymer layer by translation along the surface and its isotropy in the directions parallel to it. Thus the local monomer concentration $\rho_p(\mathbf{r})$ is given by:

$$\rho_p(\mathbf{r}) = \langle \rho_p(z) \rangle + \delta \rho_p(\mathbf{r}) = c(z) + \delta \rho_p(\mathbf{r})$$

where $c(z)$ is the mean concentration of the polymer layer at a distance z of the solid surface (see Fig. 10) and the cross term is:

$$\rho S_{gp}^1(Q) = \frac{2\pi S}{v_p v_g} Q^{-3} \int_0^\infty dz. c(z) \sin Qz \quad ; \quad QR \gg 1 \quad (40)$$

It is of peculiar interest since it gives directly the sine-Fourier transform of the monomer concentration profile $c(z)$.

The monomer-monomer scattering function is separated in two terms:

$$\rho S_{pp}^1(Q) = \frac{2\pi S}{v_p^2 V} Q^{-2} \left| \int_0^\infty dz. c(z) e^{iQz} \right|^2 + \rho \tilde{S}_{pp}^1(Q) \quad ; \quad QR \gg 1 \quad (41)$$

where $\rho \tilde{S}_{pp}^1(Q)$ corresponds to the intensity scattered by the pair correlation function of concentration fluctuations inside the layers. The latter is predominant at large Q values $Qh \gg 1$.

The striking result is the possibility to determine $c(z)$ from the cross term by using the contrast variation. Relatively to the specular reflection which gives only the density profile involving the solvent molecules, the SANS determination of the concentration profile is easier to interpret. Another advantage derives from the quantity of interface that is greater in the bulk of SANS samples. It is well illustrated in the case of polymer layers coated inside porous medium for instance.

6.3. Example of the determination of a polymer brushes [41]

The polymer brushes are formed by grafting a polymer extremity on a wall with a high grafting density (see Fig. 11). The concentration profile was theoretically predicted to be a step function [42] or a parabolic profile [43]. The step profile is: $c(z) = c_s$ if $0 < z < h$ and $c(z) = 0$ elsewhere. This leads [41] to the following scattering function for the cross term:

$$\rho S_{gp}^1(Q) = -\frac{2\pi S}{v_p v_g} Q^{-4} c_s (1 - \cos Qh) \quad (42)$$

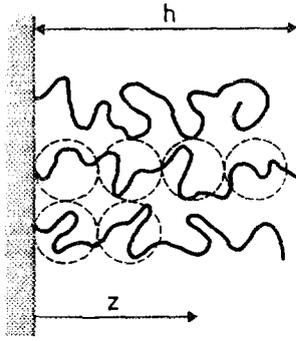


Fig. 11 - Schematic representation of a brush of polymers grafted on solid particle. h is the thickness of the layer and z the distance to the wall. The model is that of a rod of blobs with excluded volume [42].

The parabolic profile is: $c(z)=c_s [1-(z/h)^2]$, the corresponding scattering function is:

$$\rho S_{gp}^1(Q) = -\frac{4\pi}{v_p v_g} \frac{S}{V} Q^{-4} c_s \left[1 - \frac{2}{Qh} \sin Qh + \frac{2}{(Qh)^2} (1 - \cos Qh) \right] \quad (43)$$

The experiment [41] was made using a deuterated polymer chain ($M_w=69000$) grafted on a porous silica (mean pore diameter of about 3000\AA and $2.5\text{ m}^2/\text{cm}^3$ of specific area). The grafting density was $5.98\text{ mg}/\text{m}^2$. The solvent is a good solvent of polystyrene, the dichloromethane CH_2Cl_2 . A ratio $y_g=90\%$ of CD_2Cl_2 in the solvent matches the scattering length of the silica. The cross term ρS_{gp}^1 was determined from others measurement made with $y=100$ and 50% . The fit of experimental data with Eq. 43 is shown in Fig. 12.

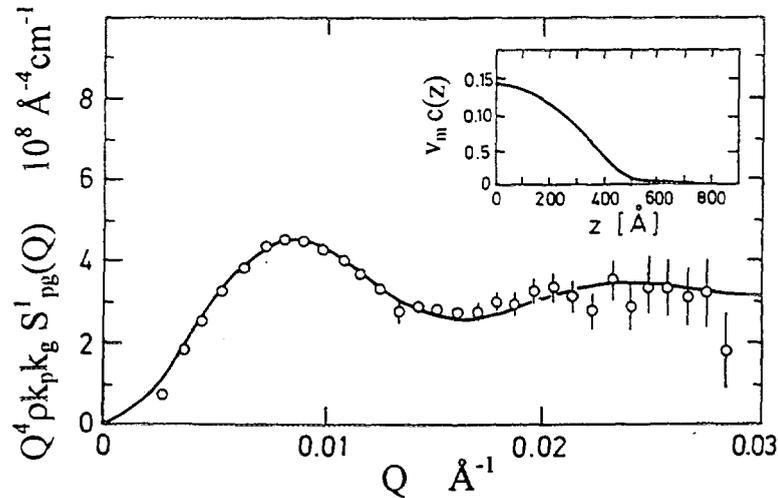


Fig. 12 - Plot of the cross term polymer particle, $Q^4 \rho k_p k_g S_{pg}^1$ versus the scattering vector Q . The full line is a calculated curve using the parabolic profile $c(z)$ shown in the inset as a function of the distance to the wall z .

The quality of the fit proves that the profile is parabolic since the step profile gives a very different function. This result was simultaneously obtained by neutron reflectometry [44]. The reader will find in ref. 41b a detailed discussion about the determination of $c(z)$ from the term S_{pp}^1 and the sensitivity of the SANS technique for such a determination.

7. Discussion

The aim of this introductory course was to demonstrate that SANS is the main tool in order to determine the polymer conformations. It has been shown how to create

a contrast by the deuteration of a polymer in its melt and how to simplify the study of a binary system with the contrast variation method. It is difficult to discuss all the numerous SANS possibilities in the polymer field. Nevertheless two methods, recently developed to study the concentrated solutions, have to be mentioned. One is the ZAC (zero average contrast) method [45] which allows to measure directly the chain form factor from a mixture of H and D polymers in a mixture of H and D solvents. The other is the TIS (Triple Isotopic Substitution) method [46] which gives the form factor of labelled moieties of a macromolecule dispersed in a complex solution. The latter is useful for block copolymers. A survey of these possibilities is given elsewhere [47].

At last, **the difficulties of the isotopic substitution have to be raised.** Until now, the isotopic substitution was assumed to have no action on the labelled scatterers i. e. there was no correlation between the position of an atom and its isotopic species. It is true for the solvent molecules. For instance, preferential adsorption is not encountered with a mixture of deuterated and undeuterated ones. It is not true with polymers for which it is well known [1,3,7] that interaction between H and D monomers exists but is weak. The formalism developed by de Gennes (section IV in ref. 7) for the polymer blends has to be applied in the melt. If χ is the Flory parameter of the interaction between monomers of different species, assuming $N_D=N_H$, Eq. 20 becomes :

$$\frac{(b_D - b_H)^2 n_m}{I(Q)} = \frac{1}{xS_{ID}(Q)} + \frac{1}{(1-x)S_{IH}(Q)} - 2\chi \quad (44)$$

In the general case the spinodal decomposition occurs when $I(0)$ diverges :

$$\frac{1}{xN_D} + \frac{1}{(1-x)N_H} - 2\chi = 0 \quad (45)$$

(this avoids negative intensity values for the larger χ values). Thus the higher is the molecular weight the higher is the probability to have a phase separation. For isotopic blend of polystyrene, the χ value is weak, about $2 \cdot 10^{-4}$.

Another difficulty for the SANS workers is the transesterification [48]. It is a random scission and recombination of carboxyl groups (C=O)O in each monomer of polyester induced by heating. But the recombinations do not necessarily occur with the arms of the originate polymer chain. Thus starting with a mixture of totally protonated and deuterated polymers, then proceeding to a careful annealing in order to eliminate voids, as final sample a very homogeneous melt of D polymers, partially D polymers and totally H polymers is obtained. The data scattered by such a sample are, to day, quite impossible to analyse.

Finally deuteration can introduce changes that can be important in the neighbouring of a transition temperature. For instance the heavy ice occurs at 4°C and not at 0°C as for H₂O or the concentration from which surfactant molecules are beginning to aggregate is different in H₂O or in D₂O. For polymers, it is known [1] that the crystallisation temperatures or the Flory temperature Θ depend on the isotopic species. The effects of these small temperature variations, a few degrees relatively to about 300K, have to be studied before starting any SANS experiment.

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