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THEORY OF X-RAY SCATTERING BY LIQUID MACROMOLECULES WITH HEAVY ATOM LABELS

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Résumé. — On calcule l'intensité de diffusion des rayons X par une phase liquide pure formée de macromolécules marquées par des atomes lourds I, soit à une extrémité (cas A), soit aux deux extrémités (cas B). Dans le cas A, on trouve une corrélation non triviale entre atomes I, due aux répulsions de volume exclu entre chaînes porteuses. Dans le cas B, cet effet entre en compétition avec la corrélation directe entre paires I portées par une même chaîne. Au total, quoique les chaînes individuelles soient essentiellement gaussiennes, la fonction de corrélation I I est très différente d'une gaussienne. On discute aussi brièvement les complications qui surgissent si les atomes lourds I ont tendance à s'associer.

Abstract. — The present paper discusses pure liquid phases of long chain molecules each of them carrying heavy atoms « I » either at one end (case A) or at both ends (case B). For case A we find a non trivial I I correlation, due to the repulsion between carrier chains. For case B, the above effect competes against the direct correlation between I I pairs belonging to the same coil. Thus, although each coil is essentially gaussian, the overall I I correlation function is very different from a gaussian. Complications due to possible specific associations between the heavy atoms are also discussed.

I. Introduction. — In molten polymers the end-to-end length distribution for one chain is expected to be gaussian [1]. An attractive method to check this amounts to attach heavy atoms (which we call I atoms in what follows) to both ends of the chains, and to study the resulting scattering intensity versus angle [2] and [3]. However, to measure directly the correlation between I atoms belonging to the same chain, the following requirements must be satisfied :

(a) The scattering must be dominated by the I atoms.

(b) The labeled chains must represent only a small fraction f of the total chain population : if not, correlations between I atoms belonging to different chains become very important.

The conflicting requirements (a) and (b) make this experiment rather difficult. We propose here a slightly different approach, where all chains are labeled (f = 1). Then, correlations between different chains are indeed important, but we show here that they may be calculated with reasonable accuracy ; thus, an experiment of this type could provide a useful check of our ideas on coil shapes in concentrated polymers.

II. Random phase approximation. — We start with the following model : all the chains are identical flexible coils, with N monomer units (To define the position of a monomer along the chain, we use an index i running from 1 to N). The average squared and to end distances for one chain is $R^2 = N\sigma^2$. In order to describe the interactions between monomers with a minimal set of parameters, we may for instance, as in the Flory-Huggins theory [1], think of our coils as inscribed on a lattice : since we are discussing a pure polymer melt, each site of the lattice is occupied by one, and only one monomer. More generally, we may define our model by saying that the interactions between submits are simply replaced by a condition of constant monomer density. If $\rho_i(r)$ is the concentration of monomers (i) at point r, we impose the constraint

$$\sum_{i=1}^{N} \rho_i(r) = \rho = C^e .$$

(II.1)

On the other hand the individual $\rho_i$ will show local fluctuations (on the scale of $\mathcal{R}$), and it is these fluctuations which will be detected by the X-ray scattering experiment when the (i th) monomer is labeled by a heavy atom. Thus we are interested in correlation functions of the form

$$< \rho_i(r) \rho_j(r') > = < \rho_i > < \rho_j > = k_B T \chi_{ij}(r - r')$$

(II.2)

where the symbol $< >$ denotes a thermal average, and $< \rho_i > = < \rho_j > = \rho/N$.

According to a theorem by Yvon (for classical systems) [4] the functions $\chi_{ij}$ may be interpreted as response functions, and defined in the following way : if
the monomers of rank \( j \) are submitted to a small external potential \( U_j(r') \), the concentration of the \( (i) \) monomers is shifted by

\[
\delta \rho_i(r) = - \sum_{j=1}^{w} \int \text{d}r' \, \chi_{ij}(r - r') \, U_j(r') . \tag{II.3}
\]

It often is convenient to obtain the \( \chi_{ij} \)'s first, and then deduce the correlation function \( P_{ii} \) by eq. (II.2).

Here we shall derive the \( \chi_{ij} \)'s by a random phase approximation, very similar in spirit to that of ref. [5]. Let us first define a « bare » response function \( \chi_{ij}^0 \); this would be obtained if we switched off the interactions between monomers (still keeping the same value of \( R^2 \)).

\( \chi_{ij}^0 \) is proportional to the pair correlation function \( P_{ii}^0 \) for two monomers on an ideal coil, and is given by:

\[
\chi_{ij}^0(r) = \frac{\rho}{Nk_B T} P_{ii}^0(r)
\]

where \( \delta U \) is an effective potential describing the effect of the interactions between monomers. We shall obtain \( \delta U \) from the condition (II.1). It is convenient at this stage to introduce Fourier transforms :

\[
\delta \rho_i(r) = \sum_j \int \text{d}r' \, \chi_{ij}^0(r - r') \{ U_j(r') + \delta U(r') \} \tag{II.5}
\]

where \( \delta U \) is an effective potential describing the effect of the interactions between monomers. We shall obtain \( \delta U \) from the condition (II.1). It is convenient at this stage to introduce Fourier transforms :

\[
\delta \rho_i(q) = \int \delta \rho_i(r) \, e^{iq \cdot r} \, \text{d}r , \text{ etc...} \tag{II.6}
\]

Then

\[
\delta \rho_i(q) = - \sum_j \chi_{ij}^0(q) \{ U_j(q) + \delta U(q) \} . \tag{II.7}
\]

The condition (II.1) may be rewritten as

\[
\sum_i \delta \rho_i(q) = 0 \tag{II.8}
\]

from which we get

\[
\delta U(q) = - \frac{\sum_i \chi_{ij}^0(q) \, U_j(q)}{\sum_i \chi_{ij}^0(q)} . \tag{II.9}
\]

Inserting this result into eq. (II.5) we obtain an explicit expression of \( \delta \rho_i \) in terms of the \( U_j \)'s i. e. a response function

\[
\chi_{ij}(q) = \chi_{ij}^0(q) - \frac{\sum_i \chi_{ij}^0(q) \, \chi_{ij}^0(q)}{\sum_i \chi_{ij}^0(q)} . \tag{II.10}
\]

The first term in eq. (II.10) represents the direct correlation between monomers \( (i) \) and \( (j) \) on the same chain, while the second term is an effect of the repulsion between chains. We may now return to the X-ray problem : if \( x_i \) is the scattering amplitude for the \( i \)-th monomer, the scattering intensity for a scattering wave vector \( q = \frac{4 \pi}{\lambda} \, \sin \frac{\theta}{2} \) is from eq. (II.2) proportional to :

\[
S(q) = k_B T \sum_{ij} \chi_{ij}(q) \, x_j . \tag{II.11}
\]

We shall now discuss some simple applications of this formula :

- **Case A** : each chain labeled at one end
  \[
  x_1 = a \quad x_2 = x_3 = \cdots = x_N = b .
  \]

- **Case B** : chains labeled at both ends
  \[
  x_1 = x_N = a \quad x_2 = x_3 = \cdots = x_{N-1} = b .
  \]

**III. Explicit formula for the scattering intensity.**

- Let us first write down explicitly the dependence on \( q \) of the various response functions occurring in eqs. (II.10) and (II.11). The bare response function \( \chi_{ij}(q) \) is a gaussian :

\[
\chi_{ij}(q) = \frac{\rho}{N k_B T} \exp \left\{ - \alpha |i - j| \right\} \tag{III.1}
\]

Another function of interest is [6]

\[
\sum_{i_k} \chi_{ik}^0(q) = \frac{\rho}{N k_B T a} \{ 2 - e^{-a} - e^{-q(N-i)} \} . \tag{III.2}
\]

We also require the double sum

\[
\sum_{i_k} \chi_{ik}^0(q) = \frac{\rho N}{k_B T f_B(x)} \tag{III.3}
\]

where

\[
f_B(x) = \frac{2}{x} \left\{ 1 - \frac{1}{x} (1 - e^{-x}) \right\} \tag{III.4}
\]

\[
x = N \alpha = \frac{N q^2 \sigma^2}{6} = \frac{q^2 R^2}{6} .
\]

\( f_B(x) \) is the function, first calculated by Debye [7], which gives the scattering intensity for a single ideal coil. Collecting there results, we arrive at the following formula for chains with one labeled end (case A).

\[
S_A(q) = \frac{\rho (a - b)^2}{N} \left\{ 1 - \frac{(1 - e^{-x})^2}{2(x - 1 + e^{-x})} \right\} . \tag{III.5}
\]
A plot of $S(q)$ is given in figure (1). The first term in the bracket corresponds to individual scattering by I atoms. The second term describes the «correlation hole» surrounding one I atom and due to the repulsion between coils. The radius of the «hole» is essentially $R$. Returning to a space representation we may write

$$< \rho_1(0) \rho_1(r) > - \left( \frac{\rho}{N} \right)^2 = \frac{\rho}{N} \{ \delta(r) - h(r) \} \quad (\text{III.6})$$

where the «hole function» $h(r)$ is the Fourier transform of the second term in the bracket of eq. (III.5). For $r \gg R$ $h(r)$ goes to 0 more or less like a gaussian, but for $r \ll R$ $h(r)$ is very different from a gaussian (in fact for $\sigma \ll r \ll R$ $h(r)$ is proportional to $1/R^2 r$).

Note that $S(q=0)=0$, or that:

$$\int dr h(r) = 1. \quad (\text{III.7})$$

In our model the scattering intensity $S(q)$ vanishes at small angles ($q \to 0$) there are no long-wavelength fluctuations of the heavy atom concentration. Each I atom is linked to $N-1$ other monomers in a coil of finite size ($\sim R$). In any large volume $\Omega$ (of lateral size $\Omega^{1/3} \gg R$) the number of I atoms is thus $v_I = \rho \Omega/N$. The monomer concentration $\rho$ is fixed in our model: thus $v_I$ may not fluctuate.

To conclude on case A: eq. (III.6) shows that even with chains labeled at one end only, it is possible to measure the r.m.s. chain length $R$, since this gives the size of the correlation hole.

Let us now turn to case B (both ends labeled). Then eqs. (II.10) and (II.11) lead to

$$S_B(q) = \frac{2 \rho(a-b)^2}{N} \left( 1 + e^{-x} - \frac{(1-e^{-x})^2}{x - 1 + e^{-x}} \right). \quad (\text{III.8})$$

The first term in the bracket corresponds to the individual scattering by I atoms. The second term expresses the direct (gaussian) correlation between two I atoms belonging to the same chain. The last term is the correlation hole effect. A plot of $S_B(q)$ is shown on figure (2). Again this type of experiment should allow for a measurement of $R$.

IV. Effects of specific associations between the heavy atoms. — Our description of sections II and III assumed «ideal» labels: for instance, if we were dealing with a simple hydrocarbon chain, the terminal atom I was assumed to be entirely equivalent to a methyl group, as regards its interactions with the surroundings. In fact the experiments of Brady and coworkers on aliphatic chains ($N \sim 10$ to $20$) with iodine labels suggest the existence of some specific associations between I atoms [3]. There effects are rather complex in general, and we shall discuss them only when the following conditions are realised:

(a) All chains are labeled at one end and one end only (case A).

(b) The I-I excess interactions may be described by a single coefficient $w$ [8]. This is correct (since the I concentration is low, $\sim 1/N$) provided that the I atoms do not build up real clusters involving more than two partners.

We thus add to our model an effective interaction energy of the form:

$$E_{int} = \int dr \frac{1}{2} k_B T \rho_1^2(r) \quad (\text{IV.1})$$

where $w$ has the dimensions of a volume, and may be positive (repulsion between I atoms) or negative (attraction). This implies that we add in eq. (II.5) an extra potential acting only on the first unit of each chain:

$$\delta U_1(r) = k_B T w \delta \rho_1(r). \quad (\text{IV.2})$$
This leads to a new set of response functions $\tilde{X}_{ij}$. In particular the function of interest here is

$$
\tilde{X}_{11}(q) = \frac{X_{11}(q)}{1 + k_BT \omega X_{11}(q)} \quad (IV.3)
$$

where $X_{11}(q)$ has been defined in eq. (II.10) and includes the effects of the overall incompressibility. This leads to a scattering intensity

$$
\tilde{S}_A(q) = \frac{\rho(a - b)^2}{N} \frac{1 - h(q)}{1 + \mu - \mu h(q)}, \quad (IV.4)
$$

Here $\mu = wP/N$ and:

$$
h(q) = \frac{(1 - e^{-qR})^2}{2(x - 1 + e^{-qR})}
$$

is the Fourier transform of the « hole function » defined in eq. (III.6).

These formulas are meaningful only when $\mu > -1$. In fact for $\mu = -1$, $\tilde{S}_A(q)$ diverges at large $q$ values: this instability suggests a transition towards an ordered phase (however, since $\mu = -1$ corresponds to a very strong I-I attraction, a correct description of the transition would require a much more detailed knowledge of the forces between clustered I atoms).

The form of $\tilde{S}_A(q)$ predicted by eq. (IV.4) is a monotonously increasing function of $q$, going from 0 at small $q$'s ($qR < 1$) to a limit at large $q$'s ($qR > 1$). Thus, we expect no interesting short range order peak in the region $qR \sim 1$. However, there are reasons to expect a peak when the I-I interaction is attractive, and of finite range $d$ (instead of being the point interaction of eq. IV.1). $\mu$ is then replaced by a function $\rho(q)$ which is essentially the Fourier transform of the I-I interaction, and which goes to 0 for $qR \geq 1$. Inserting this into (IV.4), and assuming $d < R$, one finds a maximum for $\tilde{S}_A(q)$ at $q \sim 1/d$.

V. Conclusions. — When there is no specific association between label atoms, we can make reasonably accurate predictions on the X-ray scattering by labeled polymer melts. The main interest of the calculation is that it applies to a system where all chains are labeled ($f = 1$): the signals then are much easier to extract than in the cases which have been studied up to now ($f \sim 0.1$).

Our calculations would also apply to very viscous polymers or to glasses: here, deviations from our simple laws could be induced by various external perturbations such as stresses (leading to an ellipsoidal correlation hole ?) and might be of some interest.

The major source of worry is in possible associations between I atoms: such associations are strongly suggested by the results of Brady and coworkers on C$_{10}$ chains labeled at one end with iodine, and dispersed in non-labeled C$_{10}$ chains [3] ($f \sim 0.1$). Our calculations cover only the case $f = 1$. Assuming flexible chains and weak I-I attractions, we do not find a short range order peak in the regard $qR = 1$, i.e. for distances comparable to the coil size. This discrepancy may reflect some rigidity of the chains, or a very strong I-I interaction leading to a different mesomorphic phase. Both effects might be attenuated by choosing longer chains.

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References

[6] In the summation leading to eqs. (III.2) (III.3) we replace sums over an index $k$ by integration $\int \text{d}k$ ; this is correct provided that $N \gg 1$ and $qk_0 \ll 1$.
[8] In general we would need free coefficients $w_{II}, w_{IC}, w_{CC}$ to describe the couplings between heavy atoms (I) and non labeled monomers (C). But with the additional constraint of an overall constant concentration (eq. II.1) the number of required parameters drops down to one.