On the nature of the slow modes appearing in quasi-elastic light scattering by semi-dilute polymer solutions

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(Reçu le 28 novembre 1979, accepté le 22 février 1980)

Résumé. — Cet article décrit trois séries d’expériences de diffusion quasi élastique de la lumière par des solutions semi-diluées de polymère. En variant la concentration, la masse moléculaire et la nature des polymères, ainsi que l’intervalle de temps entre la préparation des solutions et le moment de l’expérience, nous sommes en mesure d’écarter certaines hypothèses sur les modes lents et de proposer une interprétation qualitative de leur origine.

Abstract. — We describe three series of experiments of quasi-elastic light scattering by semi-dilute solutions of polymers. By varying parameters such as the concentration, molecular mass, polymer structure, and the time interval between the solution preparation and the time of measurement, we are able to rule out a number of hypothesis about slow modes and to propose a qualitative interpretation of their origin.

Following the first papers of Pecora [1, 2] predicting that the spectrum of scattered light by long polymers should be composed of a large number of modes, a number of experimental papers [3-10] appeared, some reporting, the existence of several modes and some reporting the absence of several modes.

From an experimental point of view, it can be said that the autocorrelation function of scattered light contains more than one mode if it cannot be fitted by a single exponential variation plus a base line. In the beginning, experimentalists looked for the modes due to internal relaxation processes predicted by Pecora, which have a smaller time constant than the translational mode. In fact, even for relatively low concentrations, long polymers also have a tendency to show interactions among chains which give rise to additional modes. De Gennes [11, 12, 13] et al. described the theoretical aspects of these semi-dilute solutions.

Experiments were carried out based on several systems in different experimental conditions. Some showed the existence of several modes, others did not. Experimental data were then analysed in terms of a single mode or of two modes. Today following the work undertaken by de Gennes and the publications on semi-dilute solution [11-14], measurements on single modes or on fast modes (i.e. the modes of smaller relaxation time) are well understood [15, 16, 18, 19, 22]. This is not the case for the existence and the properties of slow modes about which conflicting explanations are proposed [5-10, 17, 18, 19]. A possible reason for this situation may be the fact that in most cases the relevant parameters have not been varied.

The purpose of this paper is to report three series of experiments which allow a number of proposed interpretations of slow modes to be ruled out. After a rapid description of the experimental methods and the data analysis, we describe each series of experiments from which specific conclusions can be drawn. Finally, we propose a model consistent with all the existing experimental evidence.

The experimental apparatus is standard [20]. A laser beam illuminates a polymer solution and the scattered light is detected by a photomultiplier. We used homodyne detection and a digital autocorrelator.

Experiments were done with three different systems. Polyadenilic acid in saline water is the system currently studied in our laboratory. Poly A is a polyelectrolyte and belongs to a series of systems (polynucleotides in saline water) in which slow modes have been reported. We also tested polystyrene in ethyl acetate with which experiments were done by Munch et al. [22]. Finally, we tested polystyrene in benzene, a polymer in a good solvent, for which slow modes have never been reported [15, 16, 22].

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Data analysis varies with experiments [21]. In cases, like ours, where the autocorrelation function involves more than one time scale, a two mode analysis is performed. Let us stress that by a direct examination of the correlation function, we observed two widely separated time scales. Since we were working with homodyne detection, we fitted the experimental correlation function with a squared sum of two exponentials

\[ A(t) = A + (B e^{-t/\tau_1} + C e^{-t/\tau_2})^2 \]

where \( \tau_1 > \tau_2 \), \( \tau_1 \) is referred to as the slow mode and \( \tau_2 \) as the fast mode.

Since the two time scales are so widely separated, the two exponentials fit (as opposed to a cumulant analysis for instance) is used by all authors. In all our experiments, we verified that both relaxation times varied as the inverse square of the scattering wave-vector. All the results concerning the relaxation times were then plotted in terms of diffusion constants, \( D \), defined by

\[ \frac{1}{\tau} = D q^2 . \]

Before discussing our own results, let us summarize the previous results which differ widely according to the systems. In polystyrene-benzene slow modes have never been reported [15, 16]. Apart from a single, but important exception [22], slow modes are only reported in polynucleotides (but not in every case). The studies on polynucleotides are numerous [5-10, 17-19]. In most cases, the polymer under study is DNA. The different varieties of molecular masses, concentrations, salinity, temperature... make the comparison between data difficult, but a review by Lee [17] and others shows the following tendencies:

- The amplitude of the slow mode increases with concentration.
- For low molecular masses, slow modes are not reported.
- If the length of the polymer is increased, the time constant of the slow mode increases (but this conclusion is reached from analysis of data where the solution differs not only by the molecular mass of DNA but also by temperature, polymer and NaCl concentrations).

From our previous experiments on polyadenilic acid in saline water, we agreed with the two first conclusions.

Finally, one should note the observation of a slow mode in a rather different system, polystyrene in ethyl acetate by Munch et al. [22].

Let us now report on our recent, more systematic experiments. As stated above, experimental techniques are rather standard. Sample preparation and characterization of Poly A are described in references [18] and [19].

1. Influence of the molecular mass of the polymer.

In the first series of experiments on Poly A, we measured both diffusion coefficients and the ratio of the corresponding amplitudes as a function of polymer concentration for three different molecular masses: 240 000, 420 000 and 760 000.

Figure 1 shows the fast diffusion coefficient \( D_r \) as a function of polymer concentration. Two regions of different behaviour are apparent. At low concentration, \( D_r \) depends on the polymer molecular mass (and not on concentration). \( D_r \) is related to translational diffusion of individual chains. At high concentration, one observes a diffusion coefficient which depends on the concentration (and not on the molecular mass). This is the well-known semi-dilute behaviour described by de Gennes [13] and observed by M. Adam et al. [16] on polystyrene in benzene.

In the semi-dilute regime, polymer chains are entangled. Their arrangement is roughly that of a fluctuating lattice of parameter \( \xi \). On a short time scale (like \( \tau_2 \)), one observes concentration fluctuations of this pseudo-lattice. The dynamics of this mode is given by [13]

\[ 1/\tau_2 = D(\xi) q^2 . \]

This pseudo-lattice description has been very helpful in interpreting the experimental data from neutron scattering [11] (static properties of the chains) and light scattering [16] (dynamical properties), at least as far as the fast modes are concerned. We then use the same description for the interpretation of slow modes.

Figure 2 shows the variation of the diffusion coefficient of the slow mode with concentration and figure 3 the variation of its amplitude as compared to that of the fast mode. First of all, the region of observation of slow modes is more limited than that of the fast mode. At low concentrations, the amplitude
of the slow mode decreases, while at high concentration, its relaxation time is too long to give reliable data. Moreover, we observed, at this stage, slow modes only in the samples of larger molecular mass.

We thus have significant results mainly in the semi-dilute region above a critical concentration $C^*$. De Gennes definition of $C^*$ is $C^* R_G^2 = 1$ where $R_G$ is the radius of gyration of an isolated chain. An experimental measurement of $C^*$ is the intersection of the two straight lines defining the behaviour of the fast mode in figure 1. The important observation is that the diffusion constant depends only on the concentration and not on the molecular mass. The same behaviour is observed for the ratio of the amplitude of the slow mode to that of the rapid mode in figure 3. This implies that the slow mode cannot be assigned to the motion of an individual chain: in such a case, the physical parameters defining the slow mode, its relaxation time and amplitude, would strongly depend on the molecular mass of the chain (see for instance the predictions of de Gennes [12, 13] for a reptation mode).

2. Influence of the quality of the solvent. — The second series of experiments were done with different systems, polystyrene of molecular mass 1,800,000 in ethyl acetate and in benzene. Figures 4, 5 and 6 show for these systems the same type of behaviour as for polyadenilic acid in saline water (respectively Figs. 1, 2 and 3). This is the first observation of slow mode in the polystyrene benzene system. In previous experiments [16], slow modes were not reported. This could be understood because their amplitude is weaker than for the polystyrene ethyl acetate. Furthermore, we were searching for slow modes. Thus the existence of slow modes appears as a general feature of semi-dilute solution, but their amplitude is smaller for polymers in good solvent. It can neither be attributed to any biological character of the chains, nor to their polyelectrolyte or semi-rigid character.
3. Influence of the time elapsed since the sample preparation. — In the last series of experiments, we prepared two concentrated solutions (11 g/l) of polyadenilic acid of different molecular masses 240 000 and 760 000 in salted water. At time $t = 0$, we diluted 12 times the two solutions, which then remained at 25 °C for a number of days. The first striking feature is the apparition of a slow mode for the light mass polymers. We said above that in usual conditions such light mass polymers do not show any slow mode. Usual conditions, in fact, are relative to our previous experiments where the cells containing the solutions remain a few weeks before the experiments are started. We then made a series of measurements for a number of days following the day of dilution. Figure 7 shows the decrease of the $B/C$ ratio with time (in the same time, only the rapid mode of the light fraction show any significant change; all the other relaxation times remain constant). From this time behaviour, we are able to understand that the slow mode is related to a structure which is not stable. When the concentrations and molecular masses are large, the evolution of this structure takes a time which is large compared to the laboratory standards (let us recall that Poly A is sufficiently stable for scientific observations over a period of about one year). Thus, slow modes were generally reported for large masses and large concentrations. On the other hand for small masses and/or smaller concentrations, the structure evolves rapidly and slow modes disappear. This is the reason why slow modes were not reported for light chains.

We also observed the decrease in the amplitude of the slow mode with time with the polystyrene solutions.

4. Conclusion. — Any model concerning the microscopic origin of the slow modes should take into account the following two experimental evidences:

— Since the physical parameters of the slow mode depend upon concentration and not upon molecular masses, the slow mode should be related to the chains pseudo-lattice.

— The decrease of the amplitude of the slow mode with time implies that it is due to the defects of the pseudo-lattice. The pseudo-lattice, which is very imperfect after dilution, rearranges itself by processes similar to reptation over this very long time scale which depends upon molecular mass.

We then propose the following scheme:

In the lyophilized state or in a concentrated solution, the polymers are arranged with a large number of entanglements. By dilution, the polymer chaos swells, but this process is not homothetic. If the chains were from the beginning in a pseudo-lattice which is perfect from a topological point of view (like a brass structure for instance), an homothetic swelling could occur. Of course, this is not the case. Because the number of entanglements is larger in the concentrated solution, the swelling process pulls the chains, but some parts of them remain blocked by the entanglements. This phenomenon is similar to that which is observed when one tries to disentangle a long rope by first loosening the knots. One is left with parts of the rope which are relatively free, separated by loosened knots which do not slide easily. In the same way, in the semi-dilute solution, regions exist where the polymer chains are well swollen, while, because of some entanglements, knots of higher concentration in polymer also exist. These long life time knots have a translational diffusion motion giving rise to the slow mode. Their cancellation under osmotic pressure action is of course a long process which involves reptation. Of course, polymers in good solvents are more easily swollen and have a least tendency to give knots. This explains the difficulties encountered in the observation of slow modes in polystyrene benzene solutions.

Acknowledgments. — We thank Dr. E. Geissler for helpful discussions.
References