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Quasielastic Light Scattering (QELS) in Semi-Dilute Polymer Solutions A Comparison of "Slow-Mode" Diffusion with Self-Diffusion from FT-Pulsed Field Gradient NMR

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Summary

Quasielastic light scattering measurements and pulsed field gradient NMR measurements have been made on poly(ethylene oxide) fractions in semi-dilute solutions. Similar measurements have been made on polystyrene in chloroform and toluene. Through suitable choice of sampling times, the QELS experiments allowed analysis of the "fast" and "slow" modes of relaxation in terms of the corresponding diffusion coefficients and their relative amplitudes. Comparison of the slow mode with self-diffusion shows that the former is between one and two orders of magnitude slower than self-diffusion which contrasts with a number of recent reports. Furthermore, the proportion of fast to slow modes is highly sensitive to temperature and concentration. It is concluded that the slow mode must involve a concerted pseudogel motion sensitive to polymer-polymer friction.

Introduction

In recent communications dealing with QELS measurement on semi-dilute solutions, observations have been made of the presence of "fast" and "slow" modes. (CHU & NOSE, 1980, NISHIO & WADA, 1980, MATHIEZ et al., 1980). The former workers suggest that the fast mode is related to pseudogel motions (i.e. internal motion or flexing of segments of overlapping polymer chains) while the slow mode is associated with the translational diffusion coefficient of the entire coil. It was noted, however, (NISHIO & WADA, 1980, MATHIEZ et al., 1980) that the contribution of the slow mode increased with concentration and also, perhaps significantly, that the relative amplitude of the slow mode increases with decreasing solvent quality (MATHIEZ et al., 1980).

More recently there have been similar observations (AMIS et al, 1981, AMIS & HAN, 1982) and an identification of the slow and fast modes (i.e. exponential decays differing by several orders of magnitude) with self-diffusion (D^*) and cooperative diffusion (D_c), respectively. However, the argument used for the equivalence of the slow relaxation with self-diffusion is at best tenuous since it rests on the qualitative observation that diffusion becomes slower as concentration increases (NISHIO & WADA, 1980) and the identity of the value of the concentration dependence with that predicted by the reptation model for self-diffusion (de GENNES, 1976, 1979).

We have chosen to further examine this postulated identity by making an experimental comparison of the diffusion coefficients deduced from analysis of the slow decay process with those obtained using pulsed-field-gradient NMR (PFG-NMR). The latter measurement yields unambiguously, the self-diffusion coefficient.

Experimental

Quasielastic light scattering

The experimental arrangement has been described previously (ROOTS and NYSTRÖM, 1982) and the main features only are summarized here.

The light source was a Coherent Radiation model CR-4 argon ion laser containing a quartz etalon frequency-stabilizer in the cavity to ensure single-mode operation at 488 nm. The detector system comprised an ITT FW 130 photomultiplier, the output of which was digitized by a Nuclear Enterprises amplifier/discriminator system. A Langley-Ford 128-channel autocorrelator was used to generate the full autocorrelation function of the scattered intensity. The correlator was interfaced to a Luxor ABC-computer, programmed to calculate the normalized full photon counting time correlation function and the data stored on floppy discs. The measurements were made at 25°C except where otherwise specified. The solutions, in D_2O/H_2O (50:50) and, in case of polystyrene, in chloroform ($CDCl_3$) and toluene were continuosly filtered through a 0.22 µm Millipore filter in a closed-circuit flow-cell assembly.

Fourier-transform pulsed field gradient NMR

All measurements were made on protons at 99.6 MHz using an internal D_2O lock on a standard JEOL FX-100 Fourier transform NMR spectrometer. The measurements procedure currently employed has recently been described in detail (STILBS, 1982). Due to the favourably long transverse relaxation time (T_2) for PEO, the field gradient pulses could be spaced as widely as 240 msec. thus allowing longer durations (δ) of the gradient pulses. Under these conditions, the water signal is completely absent from the spectra and the lower range of accessible diffusion coefficients lay between 10^{-11} and 10^{-12} $m^2 s^{-1}$ and the experimental uncertainty was, respectively $\pm 1.5\%$ and $\pm 13\%$ at these values.

Polymers:

Narrow distribution poly(ethylene oxide) (PEO) fractions were obtained from Toya Soda Ltd., Tokyo, Japan. The following data were supplied:

Type	$\bar{M}_w$/ $g\,mol^{-1}$	$\bar{M}_w/\bar{M}_n$	$[\eta]$ $dl\,g^{-1}$
SE-8	73000	1.02	0.930
SE-15	148000	1.04	1.51
SE-30	278000	1.05	2.35

Polystyrene (M=110000; $\bar{M}_w/\bar{M}_n<1.06$) was obtained from Pressure Chemical Co., Pittsburgh, Pa, (lot no. 4b).

Solvent and Solutions

Deuterium oxide (99.8% D) and chloroform (99.6% D) were purchased from Stohler Isotope Chemicals, Innerberg, Switzerland. Measurements (PEO) were made in D_2O/H_2O (50:50) for lock purposes in the NMR experiments. Measurements on polystyrene were made in chloroform ($CDCl_3$) and in toluene (Merck, puriss).

All solutions were prepared by weighing and corrections made for moisture content.

Data Treatment

The full photon counting time autocorrelation function was analyzed by the method of cumulants. Thus:

$$\ln|g^{(2)}(\tau) - 1| \text{ versus } \tau$$

was fitted with appropriate weighting in a linear regression program to a second order equation. The first coefficient equals $(-2\bar{\Gamma})$ and the second (μ_2) where $\bar{\Gamma}$ is the average decay rate and its variance is $\mu_2/\bar{\Gamma}^2$.

The intensity correlation function was in most cases clearly the sum of two exponential functions, where the gamma values were in the ratio of approximately 100:1. It was thus necessary to make two experiments on each solution using sampling times differing by a factor $>$100. The sampling time was chosen so that the 120 channels covered 2-5 relaxation times in the observed exponential process. With the slow process it was necessary to discard the data for the shortest correlation times; thus the first ten points were rejected. From the intercepts of the cumulant treatment, the relative proportions of the fast and slow components could be estimated. These are designated A_f and A_s.

Results and Discussion

PEO/water system - diffusion coefficients

Examples of autocorrelation data for short- and long-time measurements on a semi-dilute solution of PEO 150000 in water are shown in Figs 1(a, b) as exponential and semi-log plots of $|g^{(2)}(\tau)-1|$ vs channel number (τ/T). These data were obtained at a scattering angle of 90^o. The measurements were also repeated at 68^o and 112^o and, when the angular factor was used, the same relaxation coefficient was found for the fast (and slow) processes, irrespective of angle.

Similar data were obtained for PEO fractions of mol.mass 73000 and 280000. The results are shown in Figs 2a, b and c for the three samples. Included in these Figures are also data for the dilute region (mutual diffusion) and self-diffusion coefficients obtained using pulsed field gradient NMR. At infinite dilution for each fraction these latter data coincide with the values extrapolated from the QELS data in dilute solution. As the concentration is increased, the mutual diffusion coefficient increases linearly with concentration (Fig. 4) and then flattens off as hydrodynamic friction becomes more important; see the discussion in ref. 10 (PATTERSON et al, 1980). These data yield $D \sim C^{0.47}$ in comparison with a predicted exponent of 0.75 (de GENNES 1976 1979).

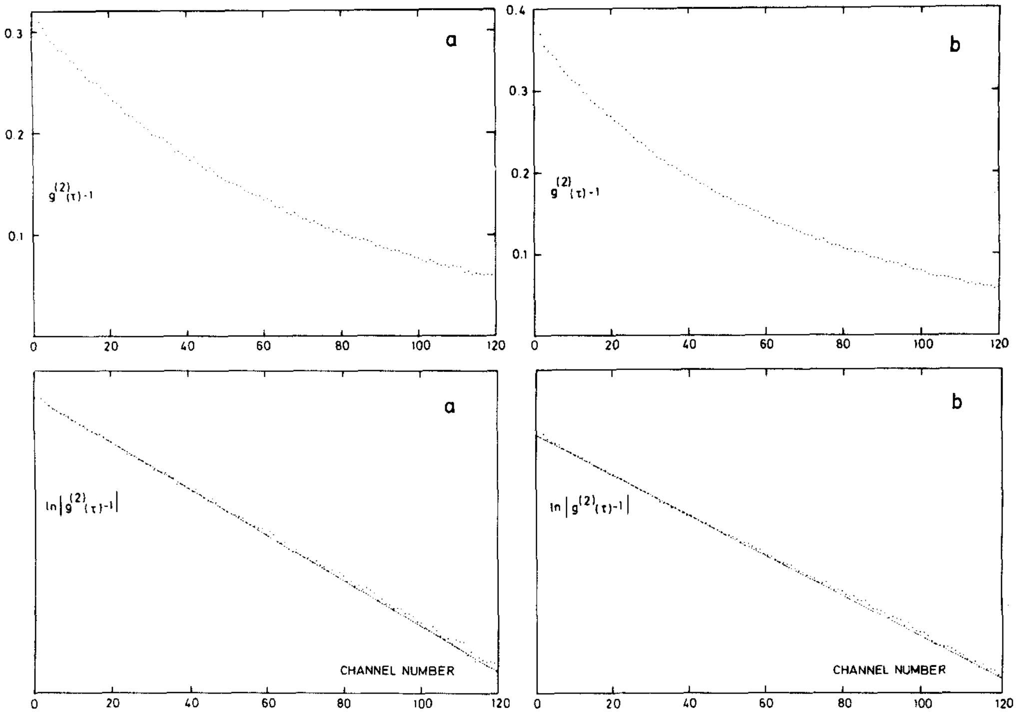
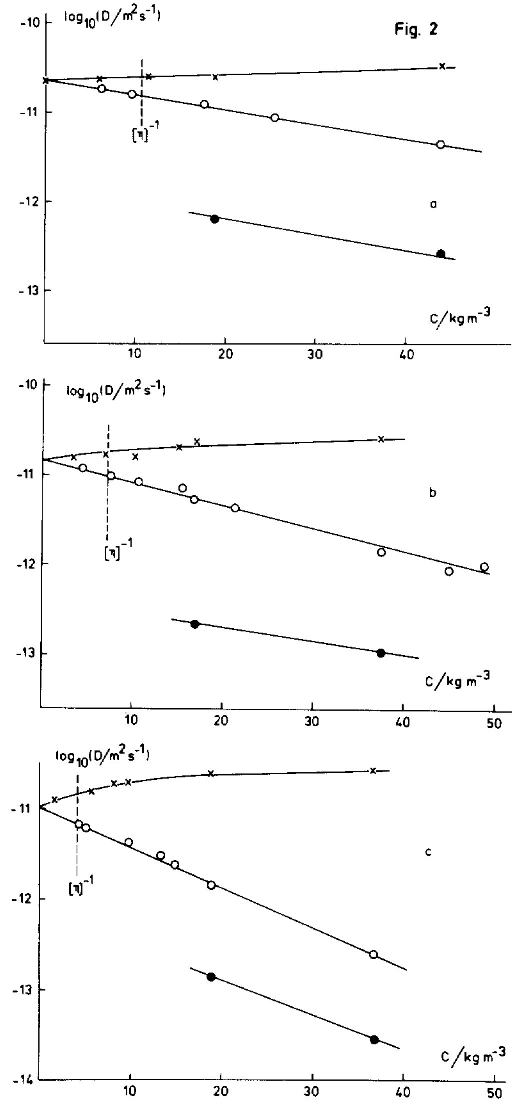


Fig. 1. Plots of normalized autocorrelation function at two sampling times for PEO 150000 at a concentration of 17 kg m^{-3} using the method of cumulants (a) 0.5 µs/channel: (b) 100 µs/ channel. At the bottom are the the respective semi-logarithmic plots of the same data.

Comparison of Figs 2a, b and c shows that in the semi-dilute region the cooperative diffusion coefficient (D_c) (QELS) is approximately independent of the molar mass in accordance with what has been predicted and found experimentally (MUNCH et al., 1977).

Two features are noteworthy:

1. A simple exponential decay of the self-diffusion coefficient, D*, with concentration has been noted in previous communications (MOSELEY, 1980, BROWN and STILBS, 1982, BROWN et al., 1982) and is also apparent in Fig. 2. Such is not consistent with de Gennes predictions (de GENNES, 1976, 1979) where D* is postulated to be independent of concentration up to C* and then to subsequently decrease according to a power law $D \sim C^{-1.75}$. This suggests that some re-appraisal of the concentration dependence of the self-diffusion coefficient is called for.
2. The slow decay process corresponds to, or is a quantity equivalent to, diffusion coefficients which are about two orders of magnitude lower than those for the fast decay and between 1 and two orders of magnitude smaller than the self-diffusion coefficients (PFG-NMR). We thus disagree with previous workers (AMIS et al, 1981, AMIS and HAN, 1982) who identify thw slow decay with self-diffusion in the semi-dilute region. It is noted here that the present data lie in the region $q \cdot R_g < 1$ and $C/C^* > 1$ i.e. in the regime, according to ref. 6.



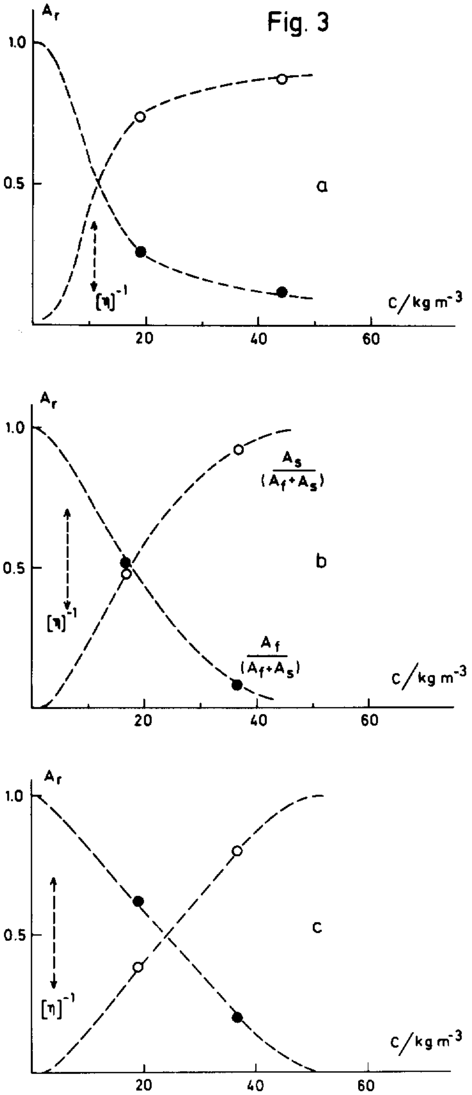


Fig. 2. Semi-log plots of D versus C for PEO fractions in aqueous solution. Top: PEO 73000, centre PEO 150000, bottom PEO 278000. (X "fast-mode" QELS; ⊙ PFG-NMR; ● "slow-mode" QELS).

Fig. 3. Relative amplitudes of fast and slow modes for PEO in aqueous solution. Top: PEO 73000, centre PEO 150000; bottom PEO 278000. The dashed lines are intended only as a visual aid.

(de GENNES, 1976), where centre of mass translational diffusion is observed. Their observation that the slow mode relaxation (diffusion coefficient) decreases with increasing concentration is not in itself a ground for its identification with self-diffusion but only serves to indicate that the slow mode must involve some concerted motion of a number of segments in such a way that polymer-polymer frictional interactions are brought into play. This is, of course, in contradistinction to the fast mode characterizing the flexing of the individual segments of correlation length, ξ.

Polystyrene - diffusion coefficients

Similar conclusions to these above under point 2 may be derived from the data for polystyrene. It is consistently the case that the slow decay is between 2 and 3 orders of magnitude smaller than the fast decay process. The slow decay is slower by about 2 orders of magnitude than self-diffusion data for the same polystyrene fraction obtained by two independent techniques; PFG-NMR (CALLAGHAN and PINDER, 1981) and forced Rayleigh scattering (HERVET et al, 1979). This comparison is shown in Table 1. Even allowing for the small differences in concentration and solvent viscosity, it is clear that the slow relaxation is much slower than that corresponding to self diffusion.

Table 1. Comparison of diffusion coefficients from "slow-mode" relaxation and for self-diffusion of polystyrene (110000).

PS 110000		
	A.	Slow decay process
$C = 22.5$ kg m^{-3} (chloroform, $\eta_o = 0.54$) 22°C		$D_s = 5.2 \cdot 10^{-13} m^2 s^{-1}$ (PRESENT WORK) ($A_r = 0.09$) (fast mode $6.1 \cdot 10^{-11}$; $A_r = 0.91$)
$C = 28.7$ kg m^{-3} (toluene, $\eta_o = 0.655$) 10°C		$D_s = 1.4 \cdot 10^{-13} m^2 s^{-1}$ (PRESENT WORK) ($A_r = 0.93$) (fast mode $2.3 \cdot 10^{-11}$; $A_r = 0.07$)
	B.	Self-diffusion
$C = 20$ kg m^{-3} (benzene, $\eta_o = 0.608$) 25°C		$D^* = 3.2 \cdot 10^{-11} m^2 s^{-1}$ (CALLAGHAN and PINDER, 1981) (PFG NMR)
$C = 21$ kg m^{-3} (benzene, 25°C)		$D^* = 2.9 \cdot 10^{-11} m^2 s^{-1}$ (HERVET et al, 1979) (Forced Rayleigh Scattering)

Similarly, it may be estimated from the diagrams in ref. 5 (AMIS and HAN, 1982) that their diffusion coefficients characterizing the slow decay for PS 110000 are of the same magnitude as those describing the slow process in the present communication and are consequently much smaller than self-diffusion.

Relative amplitudes of modes (A_r)

The relative amplitude is $A_r = \frac{A_f}{(A_f+A_s)}$ or $\frac{A_s}{(A_f+A_s)}$ where A_f

and A_s are described under DATA TREATMENT. It may be noted that no difficulty was experienced in separating the fast and slow modes using our method of analysis. These data are shown in Fig. 3 for PEO fractions in water as a function of concentration.

It is seen that the transition from fast to slow modes commences in each case at a concentration exceeding C* (defined here as $1/[\eta]$) and occurs over a relatively narrow interval in concentration.

Comparing Figs 3a, b anc c, it may be noted that at a given concentration, for example 20 kg m^{-3}, the relative amplitude of the slow component is greater the lower the molar mass. This suggests that the frequency of occurrence of chain ends is important in determining the transition fast-slow.

A_r is shown as a function of temperature for PS 110000/ toluene in Fig. 5, where it is seen that above about 22 °C virtually all relaxation is in the form of the fast mode, whereas at 10 °C about 90% is in the form of the slow mode.

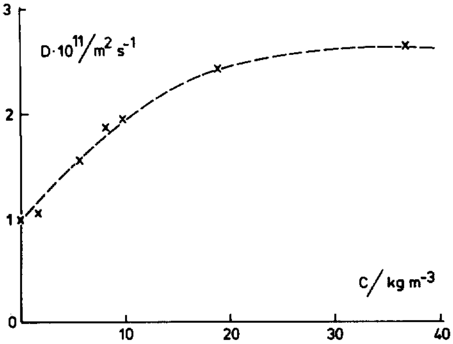


Fig. 4.

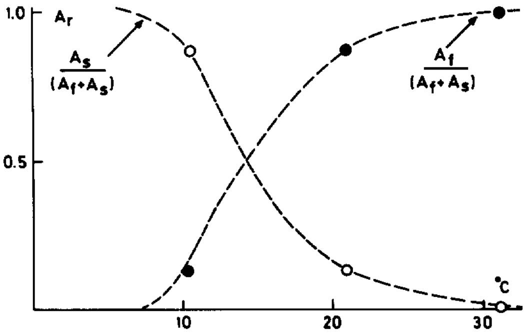


Fig. 5.

Fig. 4. Diffusion coefficients (QELS) for PEO 278000 vs concentration in aqueous solution.

Fig. 5. Relative amplitudes of fast and slow modes for PS 110000 in toluene as a function of temperature (C=50.2 kg m^{-3}).

It may be noted that these conclusions harmonize with the earlier observations (NISHIO and WADA, 1980, and MATHIEZ et al, 1980) of the dependence of the slow mode amplitude on concentration and solvent quality. These findings are in themselves convincing evidence that the slow mode derives from a concerted pseudogel relaxation rather than self-diffusion since a fast-slow transition as noted here is obviously not a feature of centre of mass translation but instead a reflection of a change in the state of the system.

There appears to be a consensus that, in the semi-dilute region, the fast mode corresponds to cooperative diffusion characterizing the motion of segments defined by the average distance between entanglements points (ξ).

Although in the semi-dilute region we do not identify the slow relaxation mode as self-diffusion, an alternative source is not readily assigned. There are various types of pseudogel and internal motion in addition to those associated with the lifetime of the transient entanglements in the network. A possibility is the motion of slow-moving supramolecular entities. A slow-relaxation could also have a trivial explanation, e.g. arise from the presence of dust in the system. The results are not in keeping with such an explanation. The temperature dependence of the slow-mode amplitude for PS/ toluene (Fig. 5) cannot be explained in this way. Neither are the concentration dependences of the amplitudes in Fig. 3 (where the slow mode becomes the dominant feature at the higher concentration) consistent with the presence of a dust contamination.

The dynamics of entangled chains are as yet incompletely understood and a substantial experimental base is still required for their elucidation.

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