CHARACTERISTIC POWER LAWS AND DIMENSIONALITY OF DYNAMIC PROCESSES
IN CONDENSED POLYMER SYSTEMS AS SEEN BY NMR TECHNIQUES

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Power laws of frequency or molecular weight are discussed for
nuclear magnetic relaxation times (T_1 and T_2) and transport coefficients
(self-diffusion coefficient and zero-shear viscosity). It is shown that these
techniques are suitable to derive information concerning the type, the dimen-
sionality and the rates of diverse processes relevant for condensed polymer
systems. Modifications of the defect diffusion and the reptation models are
discussed, which turned out to be necessary for a description of experimental
data of non-crystalline chain systems. Nuclear magnetic relaxation of polymer
melts reveals the existence of several characteristic molecular weights which
indicate transitions between limiting cases of the dynamics connected with
three fluctuation components. NMR and transport coefficient data can be des-
cribed in a consistent way.

1. Introduction

The occurrence of definite processes, their connection to certain

limiting cases and their general features such as the dimensionality is often

indicated by peculiar exponents, if characteristic power laws are valid. In

these cases the discussion and the fit of an excess of free parameters can be

avoided and the interpretation of experiments is less susceptible for ambi-

guities. Polymers normally form systems hardly accessible to ab initio treat-

ments. One therefore tends to restrict oneself to the discussion of such

scaling laws.

In this paper the time correlation function $G(\tau)$ and the spectral

density $I(\omega)$ of microscopic fluctuations play an outstanding role. These

functions more or less directly determine the properties of nuclear magnetic

relaxation and transport quantities. The type of $I(\omega)$ can be derived from NMR

relaxation experiments. Power laws of the frequency therefore are of special interest. Furthermore, molecular fluctuations may strongly depend on the molecular weight, which thus yields the base of a second class of relevant power laws.

A didactic example (though with a negative issue) illustrating the way of the argument presented in the following is the tentative application of the laws valid for particles dissolved in low-molecular fluids to polymer melts. The Stokes-Einstein-relation states that the self-diffusion coefficient D of dissolved particles should be inversely proportional to the viscosity of the surrounding medium $D \sim \eta_0^{-1}$. Moreover, the BPP-model [1, chap. 8] predicts proportionalities between the viscosity and the nuclear magnetic relaxation rates in the extreme-narrowing case: T_1^{-1}, $T_2^{-1} \sim \eta_0$. Thus, all these quantities are expected to be intimately related to each other and they should behave in an equivalent manner if one corrects for the varying particle "radii". The actual behaviour of polymer melts, however, is completely different as concerns the molecular weight dependence (Table I). Hence, certainly not contrary to expectations, the simple Stokes-Einstein-BPP-concept is ruled out for polymer melts.

In the subsequent sections we will first discuss the general influence of the dimensionality of diverse mechanisms in polymer systems to nuclear magnetic relaxation. Low-dimensional processes are often connected with non-Poissonian statistics of segment reorientations. As an example we will discuss the class of defect diffusion models. Then we will depict how reptative displacements compare with Rouse-like translations in polymer melts. Finally, we will oppose NMR-relaxation data to the rheological behaviour of polymeric liquids.

Table I. Comparison of the molecular weight dependences of dynamic quantities in polyethylene melts at 200°C. T_1 has been measured at 30 kHz. The molecular weight dependence of the free volume is included [2].

	$3*10^2 < M_w < 4*10^3$	$4*10^3 < M_w < 1.4*10^4$	$1.4*10^4 < M_w < 7*10^4$	$7*10^4 < M_w < 10^6$
T_1^{-1}	–	$\sim M_w^{1.9}$	$\sim M_w^{0.1}$	–
T_2^{-1}	$\sim M_w^{0.6}$	$\sim M_w^{1.9}$	$\sim M_w^{1.9}$	$\sim M_w^{0.4}$
η_0	$\sim M_w^{1.7}$	$\sim M_w^{3.4}$	$\sim M_w^{3.4}$	$\sim M_w^{3.4}$
D^{-1}	$\sim M_w^{2}$	$\sim M_w^{2}$	$\sim M_w^{2}$	–

2. Dimensionality and NMR relaxation

The probability laws for random walks or more generally for diffusive particle displacements strongly depend on the dimensionality of the process [3]. The time dependence of the probability for a certain displacement Δr typically is

$$P(\Delta r, t) = \frac{1}{(4\pi Dt)^{x/2}} \exp\left(- \frac{\Delta r^2}{4Dt}\right) \tag{1}$$

where D is the diffusion coefficient and x = 1, 2, 3 depending on the dimensionality. Therefore, one expects that the spectral density connected with such motions reflects the dimensionality and, hence, the frequency dependence of the spin-lattice relaxation time T_1 should be an indicator of it. In order to establish the power laws characteristic for the dimensionalities, one must first render an account of whether the interaction between the spins is modulated mainly by translations (affecting the inter-particle distance) or predominantly by molecular reorientations (virtually leaving inter-molecular distances constant).

A typical example of the first type is the relaxation of nuclei mainly relaxed by conduction electrons, the displacement of which is of a diffusive nature according to scattering by Coulomb repulsions [4]. Another possibility is the displacement of electronic spins connected with migrating solitons [5,6]. In the limit of small magnetic resonance frequencies (both of electronic spins and nuclei) compared with the inverse correlation time of the spin-interaction one expects (for infinite systems) [5]

$$T_1 \sim \omega^{1/2}, \tag{2a}$$

if the electronic motion is restricted to one dimension,

$$T_1 \sim (\ln \omega^{-1})^{-1} \,, \tag{2b}$$

in two dimensions, and

$$T_1 = const, $$

for unrestricted displacements. In infinite one- and two-dimensional systems no low-frequency plateau of $T_1(\omega)$ is expected in contrast to the three-dimensional case. This principal difference is connected with Polya's theorem [3] which states a reduced probability that the diffusing particle ever returns to its initial position for three dimensions only. The experimental verification of Eq. 2a, e.g. for polyacetylene led to the conclusion that this material shows a highly one-dimensional migration mechanism of the electronic spins [6]. This, of course, does not prove the soliton concept frequently assumed in this context.

In the limit of high frequencies, the power laws indicate whether the diffusion process is continuous or stepwise rather than the dimensionality. In the former case one expects

$$T_1 \sim \omega^{3/2} \,, \tag{3a}$$

in the latter

$$T_1 \sim \omega^2 \,. \tag{3b}$$

If the couplings are modulated by reorientations rather than by distance variations, there are again situations in which the dimensionality plays a role. We refer to the class of "defect diffusion" models for molecular re-orientations. The arrival of a structural defect is entailed to the reorientation of an interacting spin pair. Thus, the diffusion properties of the defects are relevant and their dimensionality is mirrored by the relaxation behaviour. The relation to dimensionality is, however, less direct than in the case of translational modulation of spin interaction. It is not the translation of defects which intrinsically modulates the coupling. Rather the statistics of defect arrivals is relevant, and additional properties enter such as defect concentration, lifetime, mutual hindrance and so on. A number of model cases has been treated in ref. 7.

A third mechanism, the dimensionality of which potentially influences spin-lattice relaxation, is the (immaterial) spin-diffusion. If there are rapidly relaxing centers (paramagnetic species, mobile groups, quadrupole

nuclei) dispersed in a slowly relaxing matrix, Zeeman energy can be trans-
ported to the relaxation sinks by the mutual flips between neighbouring spins
[1]. It is persuasive that the degree of anisotropy of the spin-spin coupling
defines the dimensionality of the transport paths and, therefore, the effect-
ivity and the properties of this relaxation mechanism. The systems of inte-
rest here, however, are no good candidates for studies of the dimensionality
on this basis, albeit spin diffusion in solid-like materials is ubiquitous.

3. Defect diffusion versus Poisson-processes

A structural defect, e.g. a rotational isomer, which shortens a
polymer chain by a certain amount, can be stabilized by the matrix. If the
chain is considered to be confined in a rigid tube, the annihilation of a
defect in the center part of the chain would require the cooperative displa-
cement of a large chain section. Thus, it is more persuasive to assume diffu-
sive defect motions along the chain. In a dilute polymer solution, on the
other hand, the term "defect diffusion" would be out of place because of the
absence of any stabilizing matrix.

In the following we consider diffusing defects stable at least in
the time scale of spin-lattice relaxation. Then the statistics of defect arri-
val at a certain reference position at time $t > 0$ depends on the defect dis-
tribution for instance at time 0 (i.e. in the past). In other words, the mere
knowledge of the interaction state at a certain time does not permit to de-
termine the probability for a future interaction state, and the fluctuation
of the interaction states is of a non-Markovian nature [3]. Non-Markovian
modulations of the interaction state normally are connected with spectral den-
sities which extremely deviate from Lorentzian frequency distributions. Defect
diffusion therefore should reveal itself in special shapes of the T_1 dis-
persion [7].

In real polymer systems, defect diffusion is limited to finite dis-
tances. The limitations can arise from the chain length, from barriers given
by the chemical structure or - if there is a mutual hindrance - out of the
free mean diffusion path length between neighbouring defects. The finiteness
of the possible diffusion paths further effects the characteristic power laws
of this class of processes. While the finiteness of the system in the case

of diffusive electron-spin motions (eqs. 2a and 2b) appears to be not restrictive in the frequency range considered, the limitations of diffusing defects must be expected to be much more effective. The consequence in any case is the appearance of low-frequency plateaus in the T_1-dispersion [7].

The γ-process of the amorphous parts of solid polyethylene for instance can be interpreted by the diffusion of rotational isomers along the chains. One expects and finds, however, that the free diffusion paths of defects are limited to a few bond lengths [2]. Hence, the shape of the T_1-dispersion curve in this case is not very strongly deviating from that for a Poissonian modulation of the spin interaction.

Thus, in order to verify the defect diffusion features in a more pronounced way, one has to consider a system which provides longer free diffusion paths. An example of this type is formed by lipid bilayers as e.g. dipalmitoyl phosphatidyl choline (DPPC) in the gel phase below the subtransition [8]. Here, we have alkyl-chain lamellae bordered by polar headgroup-layers. The "alkyl-G-process" observed in this system can perfectly be described by one-dimensional diffusion of isolated defects along the alkyl chains ([9] and Fig. 1) where diffusion paths are limited by the two terminal headgroups.

The comparison with the curve shape for Lorentzian spectral densities clearly shows the pronounced non-Poissonian character (Fig. 1). Three limits can be distinguished [9]

$$T_1 \sim \omega^{3/2} \quad \text{for } \omega\tau_b \gg 1,$$
$$T_1 \sim \omega^{1/2} \quad \text{for } \omega\tau_b \ll 1 \ll \omega\tau_d, \tag{4}$$
$$\text{and} \quad T_1 = \text{const for } \omega\tau_d \ll 1,$$

where τ_b is the mean "holding time" of a distortion by a defect at a reference segment and τ_d is the mean defect diffusion time over the whole distance d from headgroup to headgroup. The proportionality $T_1 \sim \omega^{1/2}$ is characteristic for one-dimensional diffusion of isolated defects. The low-frequency plateau indicates the limitation of the diffusion paths by d. Denoting the defect diffusion coefficient by D_d one has

$$\tau_d = \frac{d^2}{2D_d} \ . \tag{5}$$

The exponent 3/2 in Eq. 4 reminds of the continuous diffusion process assumed.
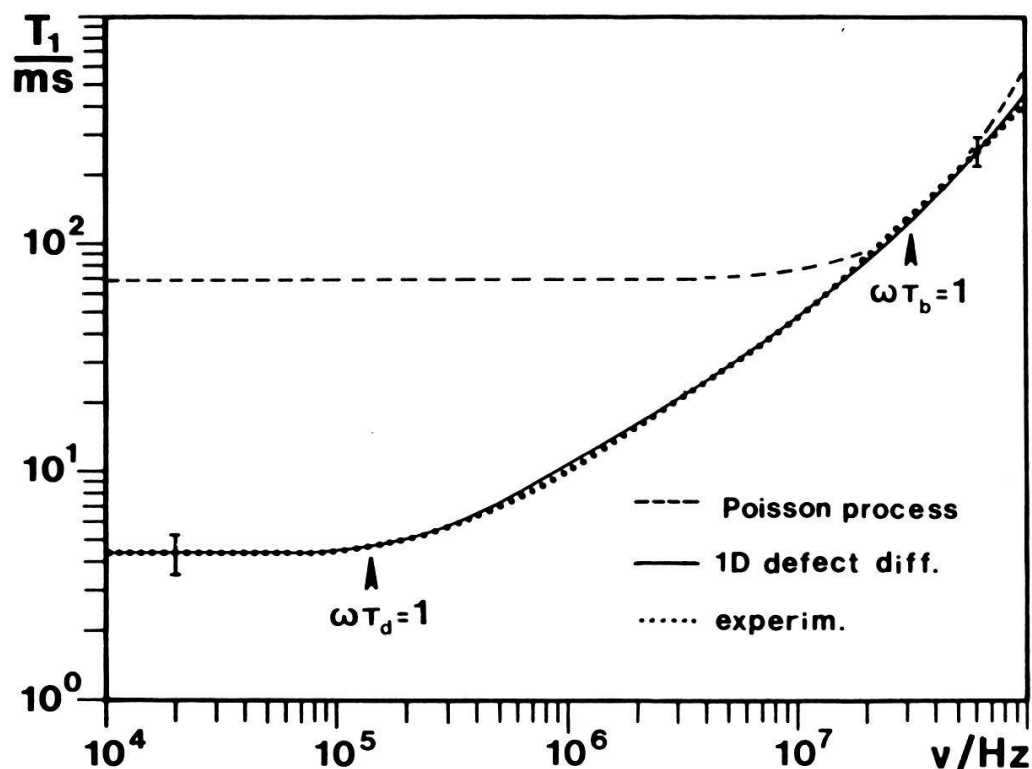
Fig. 1: Comparison of the proton T_1-dispersion of a defect diffusion and a Poisson-process. The experimental curve represents the proton spin-lattice relaxation times of the alkyl-chains of dipalmitoylphosphatidylcholine (DPPC) bilayers annealed at $0^{\circ}C$ for about three days. The data have been reproduced in three independent experiments (different samples, different field-cycling devices, different annealing periods up to several days). The theoretical curve for one-dimensional defect diffusion limited by the polar head-groups (9) has been calculated for $\tau_d = 1.1 \times 10^{-6}$ s (mean diffusion time over the headgroup distance) and $\tau_b = 4.9 \times 10^{-9}$ s (mean time a defect needs to pass a reference segment). The curve for the Poisson-process (Lorentzian spectral density) has been positioned such that the T_1-minima of the T_1 versus correlation time plots of the two models would coincide and fit to experimental data (10).

One-dimensional defect diffusion is always a possible candidate for fluctuations in polymer chains underlying topological restraints by a matrix of any kind. One should take this type of fluctuation into consideration even when the non-Poissonian character is less pronounced than in the example of Fig. 1.

4. Reptative versus Rouse-like displacements

The diffusive displacement of nuclei can be measured in two ways by NMR-techniques. Nuclear magnetic relaxation is sensitive to displacements having molecular reorientations as a consequence (apart from intermolecular interactions). In a rather direct way larger displacements can also be detected by the NMR field-gradient technique for the determination of self-diffusion coefficients. Both methods have been applied to polymer melts in Ref. 2.

Virtually, two types of displacements are discussed in context with polymer chains in the bulk state. Rouse-like displacements are expected in the free-draining limit, while reptative displacements (finally as a consequence of material transport by diffusing defects) are expected in the limit of entangled behaviour [11-13]. Strictly speaking the two types of chain displacements should exclude each other. Nevertheless, there are clear experimental hints to both views. The contradictory situation to which one is generally confronted with polymer melts with molecular weights above the critical value is summarized in Table II.

The reptation model is especially supported by the molecular weight dependence of the center-of-mass self-diffusion coefficient ([14,15], Fig. 2)

$$D \sim M^{-2.0 \pm 0.1} \tag{6}$$

instead of the law expected for Rouse-like displacements

$$D \sim M^{-1} \tag{7}$$

Also, crack-healing experiments [18] are in favour of this mechanism. Furthermore, the molecular weight dependence of the zero-shear viscosity [11-13]

$$\eta_0 \sim M^{3.4 \pm 0.1} \tag{8}$$

is well approached (compare also Ref. 17) while the Rouse-model predicts

$$\eta_0 \sim M. \tag{9}$$

The Rouse-relations 7 and 9 are usually accepted only for molecular weights below the critical value (after separation of the molecular weight dependent free-volume effects [19]).

Reptation intrinsically is a one-dimensional process. Segments are displaced on a curvilinear path within the coiled tube so that the translational displacement is correlated with the reorientation of segments [22]. As long as a segment remains confined in the initial and stationary tube, one

TABLE II. Dynamic model features in relation to experimental findings (D self-diffusion coefficient of the center of mass, η_0 zero-shear viscosity, S_{coh} dynamical structure factor for coherent neutron scattering, T_1, T_2 proton relaxation times, M_{trans} transverse magnetization, M_m matrix molecular weight, M_c, M_{BC}, M_{AB} characteristic molecular weights).

Characteristics of chain dynamics ($M > M_c$)	Pro	Contra
a) Strictly reptative displacements	D(M) (14, 15)	b)
b) Strictly Rouse-like displacements	$S_{coh}(q,t)$ (16)	a)
c) Matrix-independent tube renewal[+]	$M_{trans}(t,M_m)$ (2)	b)
d) Contour-length fluctuation	$\eta_0(M)$ (17), $T_{1,2}(M)$, M_c (2)	a), b)
e) Three-component behaviour	$T_1(\nu,M)$, $T_2(M)$, M_c, M_{BC}, M_{AB} (2)	a), b)

[+]free-volume effects not considered; $M < M_m$

therefore expects special power laws for the frequency dependence of T_1. If τ_ℓ is the mean diffusion time, a segment needs to diffuse over the orientation correlation length of the tube, one expects and finds [2, 21]

$$T_1 \sim \omega^{1/2} \tau_\ell^{-1/2} \tag{10}$$

for the limit $\omega\tau_\ell \ll 1$. Eq. 10 is at variance with the Gennes' original predication [23]

$$T_1 \sim \omega^{3/4} . \tag{11}$$

The reason is that we have assumed a one-dimensional diffusion process with curvilinear mean square displacements obeying the linear Einstein relationship $<s^2> \sim t$. (The problem is then equivalent to that of Eq. 2a.). Obviously, the frequency dependence Eq. 10 is more appropriate to the experimental finding (Fig. 3). Thus, the mean-square displacement laws, $<r^2> \sim t^{1/4}$ in three dimensions or $<s^2> \sim t^{1/2}$ in curvilinear coordinates, are not compatible with the T_1-dispersion result. In other words, the time scale $t < T_d$ (T_d equilibration time of the defect "gas" [23]) is not relevant for T_1 though the frequencies are relatively high. Nevertheless, the reptation model in a more general sense is supported.

On the other hand, astonishingly enough and, at the first sight, harassing any intuition, coherent neutron scattering experiments are in clear favour of Rouse-like displacements [16]. The adherents of this type of dynamics, however, predict a cross-over to reptative behaviour for short chains
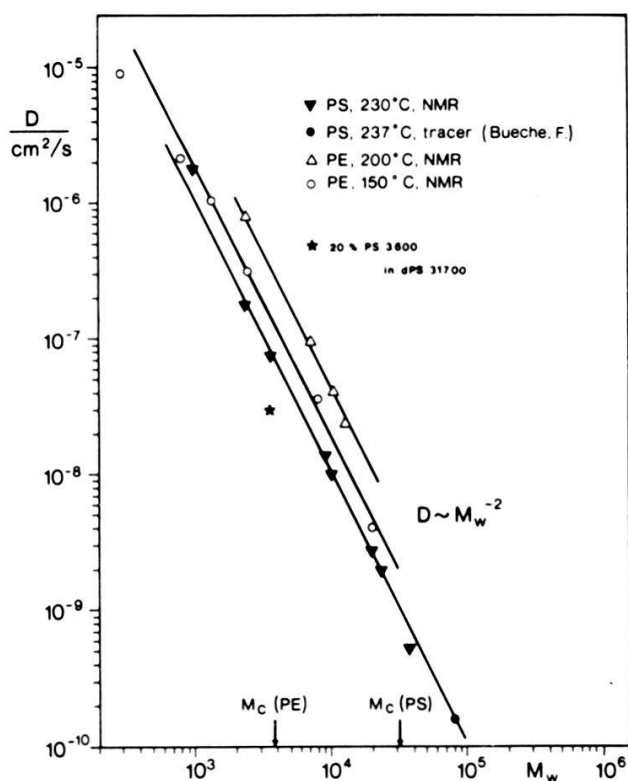
Fig. 2: Molecular weight dependence of (weight average) center of mass self-diffusion coefficients in polymer melts (linear polyethylene (PE) and atactic polystyrene (PS)) measured by a NMR field-gradient technique [15]. For $M_w < M_c$ the molecular weight dependence of the free volume enters as revealed by the reduced diffusion coefficient of PS 3600 in a matrix of deuterated PS 31700.

dissolved in a long-chain matrix [20]. Such a transition could not be verified with transverse proton relaxation experiments with short undeuterated chains dissolved in a deuterated matrix (Fig. 4). No matrix effect beyond the influence of the slightly reduced free volume and the diminution in the inter-chain dipolar interaction could be found. The conclusion is that a matrix-independent displacement mechanism must exist which combines both reptative and Rouse-like features.

The crucial point in the following will be that the equilibration time T_d of the defect gas which plays the central role in de Gennes' treatment [23] must be so short that it becomes irrelevant for experiments. How can that be imagined? The answer will be a kind of "decoupling" of different chain
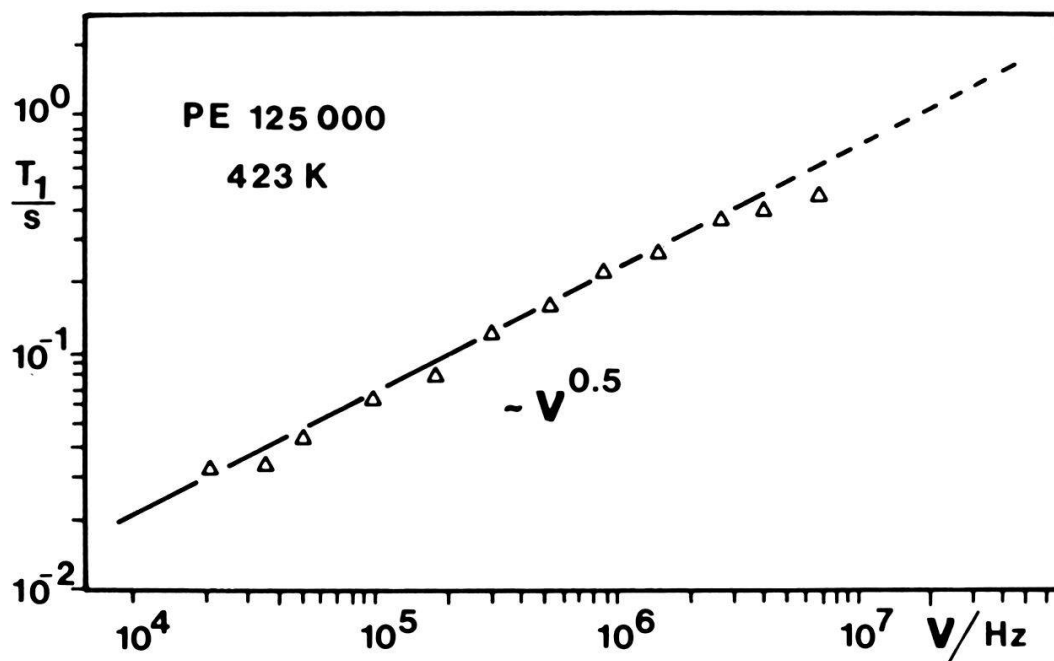
Fig. 3: Frequency dependence of the proton spin-lattice relaxation time of linear polyethylene. The experimental conditions are such that component B dominates (see section 5).

sections by what we call "folds" (lateral extensions able to fluctuate so that they play the same role as chain ends with respect to defect gas equilibration). A chain subdivided by such folds is expected to have a much shorter equilibration time T_d because of the reduced chain length effective for this process. In the time scale $T_d < t < \tau_r^r$ (τ_r^r tube renewal time), however, a Rouse-like displacement behaviour $<r^2> \sim t^{1/2}$ is expected in three dimensions, and this is exactly what one concludes from the T_1-dispersion experiment (vide supra).
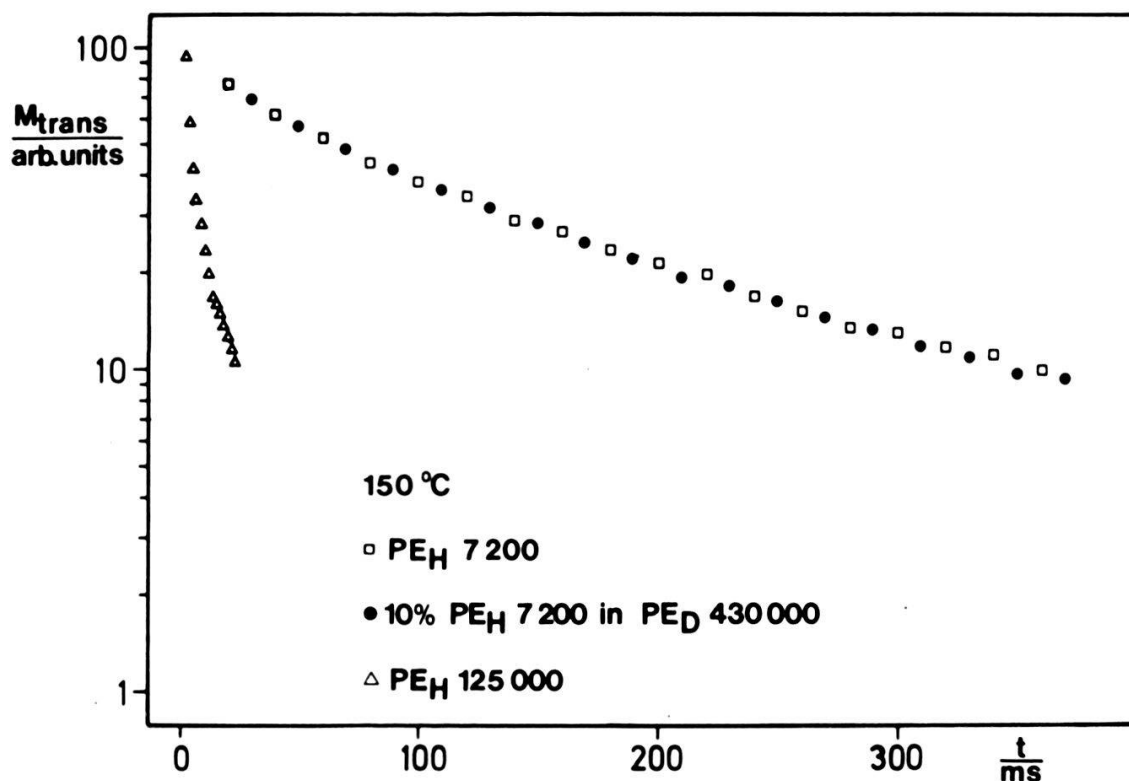
Fig. 4: Transverse proton relaxation curves for PE 7200 pure and dissolved in a matrix of deuterated high molecular weight chains. In order to indicate the sensitivity of the technique, data for pure PE 125000 are also plotted.

5. NMR versus rheological polymer melt data

As already mentioned in the introduction, there are extreme deviations in the behaviour of the nuclear magnetic relaxation times and the zero-shear viscosity both above and below the critical molecular weight M_c (Table I). Generally, the relaxation rates show a molecular weight dependence much weaker than that of the zero-shear viscosity. The explanation of this discrepancy is that nuclear magnetic relaxation is influenced by several dynamic components in a combined way [2]. A multi-component behaviour may also be the key to a compromise between reptative and Rouse-like displacements as required by the experiments listed in Table II.

Depending on the chain length, the frequency and in principle also on the temperature, the nuclear magnetic relaxation times permit us to distin-

guish local i.e. molecular weight independent from global processes. The local
processes (component A) are of a strongly anisotropic nature so that a residual
orientation correlation of the segments is maintained permitting the observa-
tion of the global processes. Defining a suitable tube on the basis of the
degree of this anisotropy leads to the conclusion that the diameter should be
in the order of at most a few mean nearest neighbour distances [2]. Reptative
displacements in such a tube lead to two further processes: component B refers
to the reorientation by diffusion around bends of the tube and is characterized
by Eq. 10. As a one-dimensional mechanism, its correlation function decays
extremely slowly and the final loss of correlation will therefore be provided
by the competitive tube renewal process or component C. The memory to the initial
tube conformation is erased as soon as the chain threads into a new tube either
by reptative displacements [13] or by contour-length fluctuation [17].

Contour-length fluctuation is a process which leads to a picture
combining both reptative and Rouse-like features. Lateral and in principle un-
limited and virtually matrix independent displacements in the form of unen-
tangled chain extensions ("folds") may account for Rouse-like features. The
fluctuation of folds leads to the fluctuation of the contour length which means
the tube length reduced by the length stored in folds. As such lateral exten-
sions can shrink again and vanish completely without distorting the matrix,
the segments displaced in this way keep the full memory of the topological
restraints due to entanglements. Thus, the properties expected in connection
with a "tube" are virtually maintained as long as motions of the chain as a
whole are considered.

From the three components, C will be the only one which is relevant
for the zero-shear viscosity η_0 [24]. Nuclear magnetic relaxation, on the other
hand, in principle depends on all three components [2]. It is for instance
essential that at molecular weights or frequencies at which tube renewal plays
a role, the time constant τ_r of component C only enters as a geometric average
with the time constant τ_ℓ of component B. The effective NMR correlation time
of the chain orientation is then

$$\tau_c = (\tau_r \, \tau_\ell)^{\frac{1}{2}} \quad . \tag{12}$$

Note that τ_c has the quality of an "equilibration" time of the distribution of
local chain orientations. The mixed-component behaviour reveals itself in a

molecular weight dependence much weaker than that of η_0 (Table I) both above and - notabene - below M_c.

The three-component expressions of the nuclear magnetic relaxation times imply diverse limiting cases, which can be reached by the appropriate choice of the molecular weight and other experimental parameters. The time constants of the three components best fitting to the experimental data, e.g. of polyethylene melts are [2]

$$\tau_s = \chi_s \ M_w^{0.0 \pm 0.1} \qquad \text{(component A)}, \cdot \qquad \text{(13a)}$$

$$\tau_\ell = \chi_\ell \ M_w^{0.5 \pm 0.3} \qquad \text{(component B)}, \qquad \text{(13b)}$$

$$\tau_r^c = \chi_r^c \ M_w^{1.7 \pm 0.3} \qquad \text{(component C, } M_w < M_c\text{)}, \qquad \text{(13c)}$$

$$\tau_r^r = \chi_r^r \ M_w^{3.0 \pm 0.3} \qquad \text{(component C, } M_w > M_c\text{)}. \qquad \text{(13d)}$$

Rough orders of magnitude of the proportionality factors at melt temperatures are $\chi_s \approx 10^{-10}$ s, $\chi_\ell \approx 10^{-10}$ s, $\chi_r^c \approx 10^{-13}$ s and $\chi_r^r \approx 10^{-18}$ s.

The molecular weight dependence of the time parameters lead to clear transitions between the limiting cases mentioned above. There are three characteristic molecular weights (M_c, M_{BC}, M_{AB}) which can be attributed to these transitions. In fig. 5 two of them are shown for polyethylene. These two characteristic molecular weights could also be resolved for polystyrene using ^{13}C transverse relaxation of the quaternary carbon [25].

The (frequency independent) value of M_c indicates the transition between the two types of tube renewal (via contour length fluctuation and via reptation). It virtually coincides with the critical molecular weight defined in rheology [12], so that nuclear magnetic relaxation proves to be sensitive to the motions relevant for the viscous behaviour. The competitive nature of the two types of tube renewal which had to be assumed in the interpretation of the M_c-transition of the NMR-data [2], also makes it plausible that the dynamics does not show any abrupt change.

At higher molecular weights, a (frequency-dependent) transition occurs at M_{BC} which is interpreted as a cross-over to a regime where component B determines the relaxation behaviour. Finally, at high molecular weights and
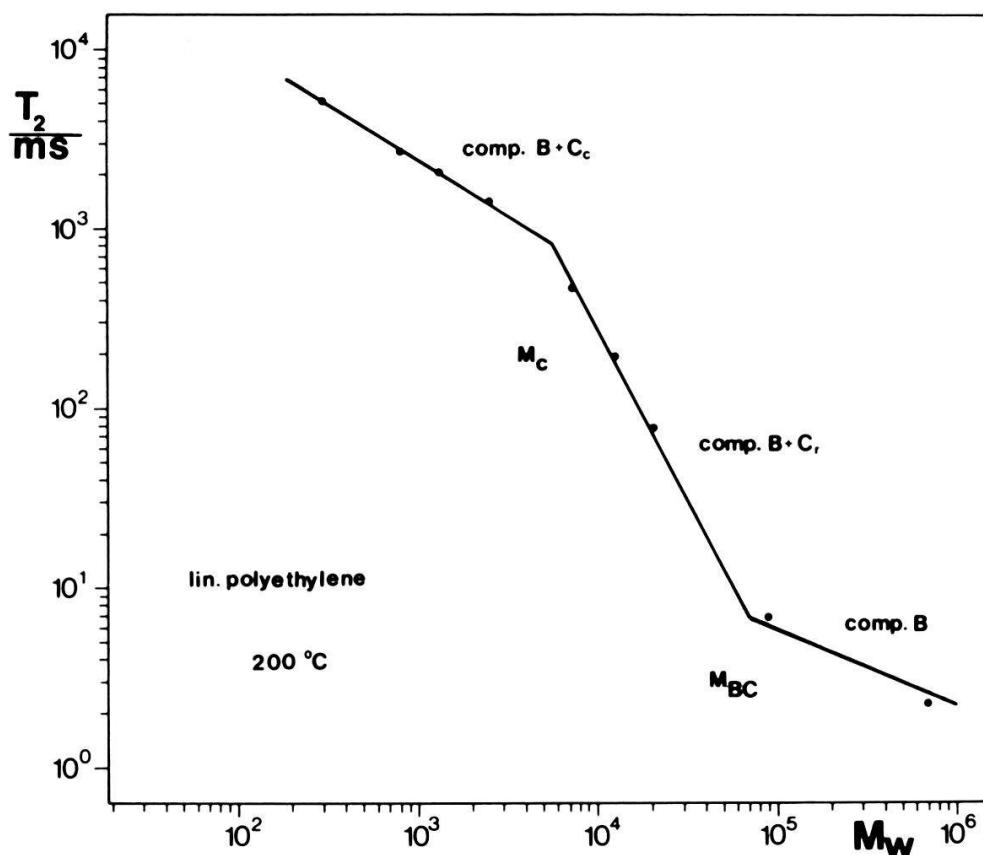
Fig. 5: Molecular weight dependence of the transverse proton relaxation times of linear polyethylene.

high frequencies the local and therefore molecular weight independent component A becomes relevant. The corresponding transition is characterized by M_{AB}. Fig. 6 shows the corresponding data for polyethylene [26].

The description of chain fluctuations on the basis of the three components permits to explain the NMR-relaxation features [2]. It is thus possible to extract the empirical M-dependences for component C alone from the NMR-data. As η_0 solely depends on this component, one can predict the characteristic laws for η_0 above and below M_c in this way. It turned out that the results compare favourably with direct rheological data, so that the discrepancies displayed in Table I are shown to be of an apparent nature.
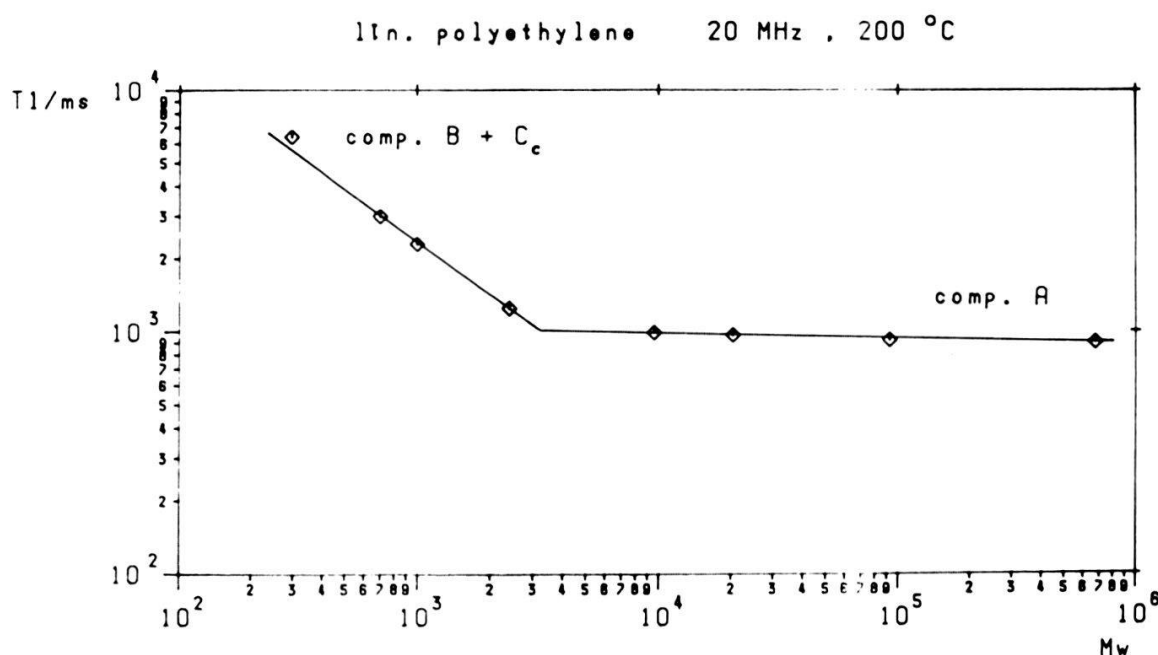
Fig. 6: Molecular weight dependence of the proton spin-lattice relaxation times of linear polyethylene. The plateau ($M_w > M_{AB}$) is governed by component A. At low molecular weights the common influence of components B and C_c is visible.

6. Discussion and concluding remarks

In this work, characteristic power laws have been used to deduce and construct a picture of polymer dynamics. The three-component concept forms the general frame to be filled with the experimental information. The conclusions to a certain degree have a cogent nature as can be seen with the following attempt to explain the molecular weight dependence of T_2 of polyethylene melts (Table I and Fig. 5) in an alternative manner.

Let us hypothetically assume that there are three processes I, II and III specifically relevant for the three power laws of T_2 (Table I). One is then tempted to attribute three correlation times τ_I, τ_{II}, τ_{III} to these processes. Consequently, these parameters should directly reflect the M_w-dependences of the relaxation times. Thus

$$\tau_I \sim M_w^{0.6} \sim T_2^{-1} \quad (M_w < M_c) \tag{14a}$$

$$\tau_{II} \quad \sim \quad M_w^{1.9} \sim T_2^{-1} \quad (M_c < M_w < M_{BC}) \tag{14b}$$

$$\tau_{III} \quad \sim \quad M_w^{0.4} \sim T_2^{-1} \quad (M_{BC} < M_w < M_{AB}) \tag{14c}$$

In the literature one indeed finds a law fitting to Eq. 14b within the experimental error. According to de Gennes [23], the equilibration time T_d for the defect concentration is proportional to M^2. T_d in an unspecified manner might reveal itself in Eq. 14b. τ_{III} could then be due to a process of a more local nature and τ_I could represent any mixed behaviour only valid for $M < M_c$. Thus, a very different picture would arise because for instance tube renewal in any form nowhere enters.

However, the range where τ_{III} would determine T_1 is connected with a frequency dependence $T_1 \sim \nu^{0.5}$ (Fig. 3). Hence the correlation function of process III must be non-exponential. From this one would expect that in the regime of process II, it still should have a strong influence, and a mixed behaviour similar to Eq. 12 should arise in contrast to a combination of processes with purely exponential correlation functions.

There are additional arguments against a hypothetical process on the basis of de Gennes' T_d mechanism as an interpretation of the proportionality Eq. 14b. In this regime one finds frequency independent spin-lattice relaxation times while de Gennes [23] predicts $T_1 \sim \nu^{3/4}$.

The time scale relevant for the T_2-values is $t > 10^{-4}$ s as is demonstrated, e.g. by the fact that M_{BC} (T_2) > M_{BC}(T_1 at 30 kHz) [2]. The mean displacements in this time scale can be calculated by the aid of the experimental self-diffusion coefficients [15]. They even exceed the coil diameter at low molecular weights, so that the regime II cannot solely be governed by the intra-coil displacements expected for the hypothetical T_d mechanism [23]. The M_{BC}-value directly indicates the limit below which the displacements become relevant for tube renewal. In this view it must be considered as a result rather than an interpretation that the tube renewal time τ_r^r (Eq. 13d) affects the relaxation data in a form corresponding to Eq. 12.

To summarize, it has been outlined how diverse NMR-techniques permit to set up laws characteristic for type and dimensionality of dynamic processes in polymer systems. On the basis of a set of power laws it has been possible to derive a picture of the dynamics in polymer systems which accounts

for various experimental facts known from other methods. The three-component concept reveals the apparent nature of several discrepancies appearing in comparisons of the behaviour of different dynamic quantities. The combined discussion of the relaxation times (T_1, T_2) and the transport coefficients (D, η_0) shows that these techniques provide partly complementary and partly overlapping information.

References

[1]   A. Abragam, The principles of nuclear magnetism, Oxford University Press, Oxford (1961).

[2]   R. Kimmich and R. Bachus, Colloid Polymer Sci. 260 (1982) 911.

[3]   W. Feller, An introduction to probability theory and its applications, 3rd edition, John Wiley, New York (1968) and S. Chandrasekhar, Rev. Mod. Phys. 15 (1943) 1.

[4]   F. Devreux, Phys. Rev. B13 (1976) 4651.

[5]   F. Devreux and M. Nechtschein in S. Barišic et al. (Ed.), Quasi one-dimensional conduction I, Lecture notes in Physics 95, Springer-Verlag, Berlin (1979).

[6]   M. Nechtschein, F. Devreux, R.L. Greene, T.C. Clarke and G.B. Street, Phys. Rev. Letters 44 (1980) 356.

[7]   R. Kimmich and G. Voigt, Z. Naturforsch. 33a (1978) 1294.

[8]   S.C. Chen, J.M. Sturtevant and B.J. Gaffney, Proc. Natl. Acad. Sci. USA 77 (1980) 5060.

[9]   R. Kimmich, G. Schnur and A. Scheuermann, Chem. Phys. Lipids 32 (1983) 271.

[10]   R. Kimmich and G. Voigt, Chem. Phys. Letters 62 (1979) 181.

[11]   R.T. Bailey, A.M. North and R.A. Pethrick, Molecular motion in high polymers, Clarendon Press, Oxford (1981).

[12]   J.D. Ferry, Viscoelastic properties of polymers, John Wiley, New York (1980).

[13]   P.G. de Gennes, Scaling concepts in polymer physics, Cornell University Press, Ithaca (1979).

[14]   J. Klein, Contemp. Phys. 20 (1979) 611.

[15]   R. Bachus and R. Kimmich, Polymer 24 (1983) 964.

[16]   D. Richter. A. Baumgaertner, K. Binder, B. Ewen and J.B. Hayter, Phys. Rev. Letters 47 (1981) 109.

[17]   M. Doi, J. Polymer Sci., Polymer Letters Edn. 19 (1981) 265.

[18]   K. Jud, H.H. Kausch and J.G. Williams, J. Materials Sci. 16 (1981) 204.

[19]   F.R. Eirich (Ed.), Rheology, Vol. 1, Academic Press, New York (1956).

[20]   K. Kremer, Macromolecules 16 (1983) 1632.

[21]   R. Kimmich, Polymer 16 (1975) 851.

[22]   Note that this mechanism can only be observed if the residual orientation correlation left over by the local processes is finite. Fits led to residual correlations in the order of percent which is much more than one expects for the Doi-Edwards tube diameter [11-13]. We therefore speak of a "tight tube" which then is assumed to have additional degrees

of fluctuation freedom [2]. All types of tube discussed in the litera-
ture are a matter of definition, of course.

[23] P.G. de Gennes, J. Chem. Phys. $\underline{55}$ (1971) 572.

[24] M. Doi, Chem. Phys. Letters $\underline{26}$ (1974) 269.

[25] R. Kimmich, E. Rosskopf, G. Schnur and K.-H. Spohn, Macromolecules, in press.

[26] The magnitude of the component A correlation time τ_S of polyethylene is
such that up to frequencies of the order of 10^7 Hz the extreme narrowing
condition $\omega\tau_S < 1$ is fulfilled and all limiting cases defined in Ref. 2
are relevant. In the special situation of polystyrene, however, rather
the opposite extreme is true for $\nu > 10^7$ Hz as can be concluded from the
observed frequency dependence T_1. The conclusions concerning the domi-
nance of component A are the same in both cases.