Consequences of Restricted Defect Diffusion on NMR and Dielectric Relaxation

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Nuclear magnetic and dielectric relaxation formulas are given for a model of limited diffusion of defects. The limitation is introduced by the assumption of fixed reflecting barriers on both sides of the defect. The diffusion process is assumed to be one-dimensional and continuous. The effect of the finite length of the defects is included in the presented treatment.

1. Introduction

Defect-diffusion has been considered by several authors as a mechanism for dielectric and nmr relaxation in diverse systems [1–5]. The following discussion predominantly concerns polymers and related substances, i. e. we may restrict ourselves to the case of one-dimensional defect diffusion.

Glarum [1] and Hunt and Powles [2] have described dielectric or nmr relaxation on the basis of one-dimensional defect diffusion by assuming that the diffusion process is continuous and that only the nearest defect is relevant. Bordewijk [5] has taken into account not only the nearest but all defects in the system. He still assumes that there is no mutual influence of the defects and that the diffusion is continuous. In previous papers [3, 4], we have discussed the special case of the diffusion of kinks (e. g. gt$\bar{g}$-sequences) along polymer chains. The nmr relaxation due to nearest neighbour kinks has been treated on the basis of a stepwise diffusion process. In Ref. [4], we have considered defect diffusion restricted within two reflecting walls as a model situation for lipid bilayers.

We want now to extend the latter model in the limit of continuous diffusion of defects between two reflecting barriers to more general applications. Furthermore we include defects of finite length into our discussion. Models of defect diffusion, restricted in this way, could be relevant e. g. for alkane chain lamellae (lipids, paraffins), crystallites in polymers or highly branched polymers. Assuming that defects in polymers cannot permeate each other, the following treatment even could be a rough model for polymer chains, containing defects in high concentration: Each defect possesses two neighbouring defects acting as reflecting barriers, though not static but surely restricting the diffusion of the considered defect to a narrower region than if they were absent.

2. General Relaxation Formulas

The longitudinal nmr relaxation rate is given by

$$\frac{1}{T_1} = \frac{9}{8}\,\gamma^4\,\hbar^2\,\big(I^{(1)}(\omega_\mathrm{L}) + I^{(2)}(\omega_\mathrm{L})\big) \tag{1}$$

$$= \frac{9}{4}\,\gamma^4\,\hbar^2\,\big(\mathrm{Re}\,\{\mathcal{L}^{(1)}\,\{G^{(1)}(\tau)\}\} + \mathrm{Re}\,\{\mathcal{L}^{(2)}\,\{G^{(2)}(\tau)\}\}\big)$$

where γ and $\hbar$ have the usual meaning. The intensity functions $I^{(i)}(\omega_\mathrm{L})$ are won from the correlation functions $G^{(i)}(\tau)$ by taking twice the real part of the Laplace transformation $\mathcal{L}^{(i)}\{\dots\}$ with respect to the circular frequencies ω_L and $2\,\omega_\mathrm{L}$, respectively. The normalized correlation functions $G_n{}^{(i)}(\tau)$ depend on the dipolar interaction functions $F^{(i)}$ (e. g. Ref. [6])

$$G_n{}^{(i)}(\tau) = \frac{\overline{F^{(i)}(0)\,F^{(-i)}(\tau)} - |\overline{F^{(i)}}|^2}{\overline{|F^{(i)}|^2} - |\overline{F^{(i)}}|^2} \tag{2}$$

(the special form of these functions is provided to describe anisotropic motions). We express this ensemble average by introducing probabilities for the occurence of the diverse interaction states resulting in

$$G_n{}^{(i)}(\tau) = 1 - W(\tau)/W(\infty) \tag{3}$$

which can easily be verified. $W(\tau)$ is the probability that the reference proton is initially undisturbed but is disturbed by a defect after a period τ (or vice versa).

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For the complex dielectric constant ε the following expression is valid [7]

$$\frac{\varepsilon(\omega)-\varepsilon(\infty)}{\varepsilon(0)-\varepsilon(\infty)} = -\int_0^\infty \exp(i\,\omega\,\tau)\,\dot{G}_n(\tau)\,\mathrm{d}\tau = 1 + i\,\omega\,\mathcal{L}\{G_n(\tau)\} \tag{4}$$

where $G_n(\tau)$ is the normalized macroscopic correlation function

$$G_n(\tau) = \frac{\overline{P(0)P(\tau)} - \overline{P}^2}{\overline{P^2} - \overline{P}^2} \tag{5}$$

of the polarization components parallel to the electric field. $G_n(\tau)$ can be expressed as sums of dipole autocorrelation and dipole crosscorrelation functions. It is usually assumed that the dipole component of a certain dipole at time τ depends not on the dipole component of a second dipole at time 0. Taking this assumption as an approximation, valid for dipoles not too close together, we may write

$$G_n(\tau) \approx \Phi_n(\tau) = 1 - W(\tau)/W(\infty) \tag{6}$$

$\Phi(\tau)$ is the microscopic dipole correlation function for the dipole components parallel to the electric field.

Thus, the common problem in the calculation of Eqs. (1) and (4) is the knowledge of the probability $W(\tau)$.

3. The Probability $W(\tau)$

We have defined $W(\tau)$ as the probability that the reference proton or dipole is initially undisturbed and is disturbed by a defect after a period τ or vice versa. This probability can be split into a product of the a priori probability p_i for the initial state and the conditional probability P_c for the alteration of this initial state

$$W(\tau) = p_\mathrm{i}\,P_\mathrm{c}(\tau) \quad \text{and} \quad W(\infty) = p_\mathrm{i}(1-p_\mathrm{i})\,. \tag{7}$$

In the following, we consider the defect state as the initial situation. Then we may write

$$p_\mathrm{i} = b/d \tag{8}$$

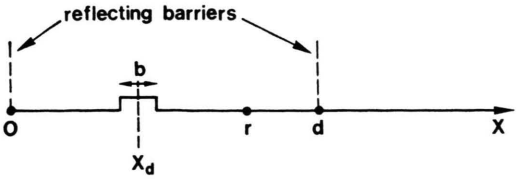

Fig. 1. Schematic representation of the problem treated in this paper: Diffusion of a defect of length b between two reflecting walls at $x=0$ and $x=d$. $x=r$ is the position of the reference particle.

where b is the width of the defect and d is the distance of the reflecting barriers on both sides of the considered defect (Figure 1). Dessignating the probability that the defect is situated between x_f and $x_\mathrm{f}+\mathrm{d}x_\mathrm{f}$ after a period τ after starting at position x_i by $P_\mathrm{c}{}^\mathrm{d}(x_\mathrm{i},x_\mathrm{f},\tau)\,\mathrm{d}x_\mathrm{f}$, we obtain for $P_\mathrm{c}(\tau)$ the expression

$$P_\mathrm{c}(\tau) = \frac{1}{d-b}\int_{b/2}^{d-b/2} \frac{1}{b}\int_{r-b/2}^{r+b/2} \left[\int_{r+b/2}^{d} P_\mathrm{c}{}^\mathrm{d}(x_\mathrm{i},x_\mathrm{f},\tau)\,\mathrm{d}x_\mathrm{f} + \int_0^{r-b/2} P_\mathrm{c}{}^\mathrm{d}(x_\mathrm{i},x_\mathrm{f},\tau)\,\mathrm{d}x_\mathrm{f}\right]\mathrm{d}x_\mathrm{i}\,\mathrm{d}r\,. \tag{9}$$

The brackets contain two integrals over all final defect positions not covering the reference particle. The outer integrals average this expression over all initial defect positions and all positions of the reference particle, respectively. Here, we have assumed that the middle of the defect is reflected at positions 0 and d (Figure 1). Strictly speaking, reference particles just near the reflecting walls should be treated separately. At least for $b \ll d$, however, their influence will be negligible.

Analogously to our previous treatment [4], we find

$$P_\mathrm{c}{}^\mathrm{d}(x_\mathrm{i},x_\mathrm{f},\tau)\,\mathrm{d}x_\mathrm{f} = \sum_{n=-\infty}^{\infty}\left[\eta(2\,n\,d - |x_\mathrm{i}-x_\mathrm{f}|,\tau) + \eta(2\,n\,d - (x_\mathrm{i}+x_\mathrm{f}),\tau)\right]\mathrm{d}x_\mathrm{f}\,. \tag{10}$$

$\eta(x,\tau)\,\mathrm{d}x$ is the probability that the defect diffuses from 0 to $x\ldots x+\mathrm{d}x$ during τ in the absence of reflecting barriers. This function is given in the continuous diffusion limit by [8]

$$\eta(x,\tau)\,\mathrm{d}x = \frac{1}{2\sqrt{\pi D \tau}}\exp\{-x^2/4\,D\,\tau\}\,\mathrm{d}x \tag{11}$$

(D is the diffusion coefficient of the defect).

Using a special type Theta-function, defined by

$$\theta_4(\bar\nu\,|\,\bar x) = \frac{1}{\sqrt{\pi\,\bar x}}\sum_{n=-\infty}^{+\infty}\exp\left\{-\frac{1}{\bar x}\,[\bar\nu + n + \tfrac{1}{2}]^2\right\}, \tag{12}$$

we abbreviate Eq. (10) in the form

$$P_\mathrm{c}{}^\mathrm{d}(x_\mathrm{i},x_\mathrm{f},\tau)\,\mathrm{d}x_\mathrm{f} = \frac{1}{2\,d}\left[\theta_4\left(\frac{|x_\mathrm{i}-x_\mathrm{f}|}{2\,d} - \frac{1}{2}\,\middle|\,\frac{D\,\tau}{d^2}\right) + \theta_4\left(\frac{x_\mathrm{i}+x_\mathrm{f}}{2\,d} - \frac{1}{2}\,\middle|\,\frac{D\,\tau}{d^2}\right)\right]\mathrm{d}x_\mathrm{f}\,. \tag{13}$$

Both in Eqs. (1) and (4), we need the Laplace transform of the correlation function, i. e. of the

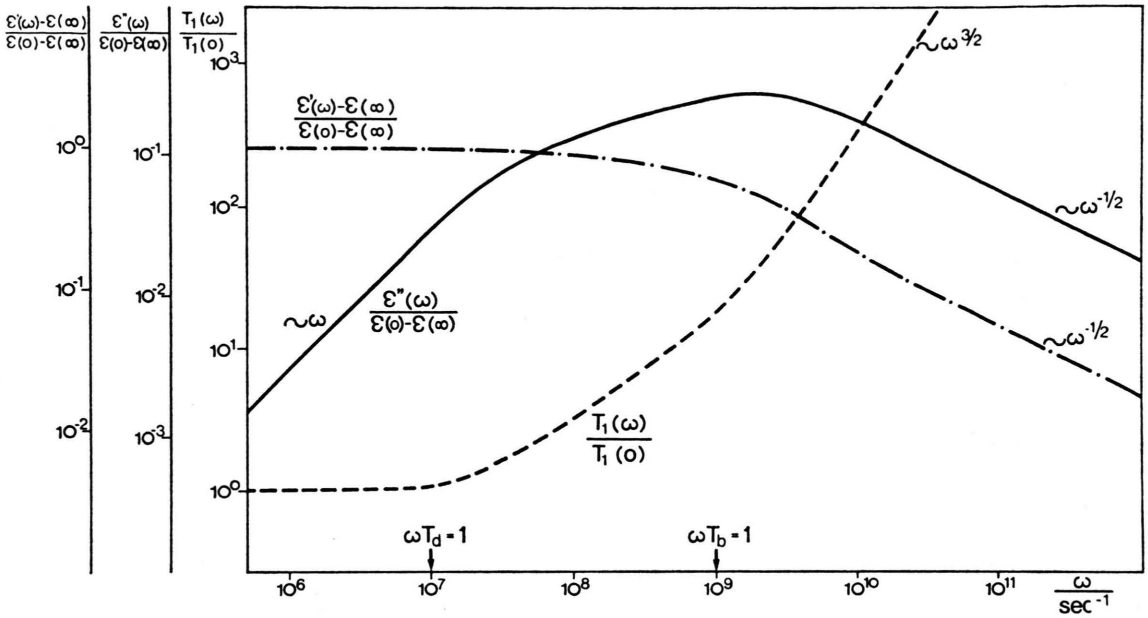

Fig. 2. Frequency dependence of nmr and dielectric relaxation sizes.

probability $W(\tau)$. By exchanging this transformation with the integrations in Eq. (9), we find for $\omega > 0$ [9, 10]

$$\mathcal{L}\{W(\tau)\} = \frac{1}{\sqrt{2\,\tau_d}}\,\frac{1}{S^{3/2}}\,[\mathrm{Sh}\,\sqrt{2\,\tau_b\,S} + \mathrm{cth}\,\sqrt{2\,\tau_d\,S}\,(1-\mathrm{ch}\,\sqrt{2\,\tau_b\,S})] + \frac{1}{4}\,\frac{1}{\tau_d - \sqrt{\tau_d\,\tau_b}}\,\frac{1}{S^2}\,[2\,\mathrm{ch}\,\sqrt{2\,\tau_b\,S} - 1 + \mathrm{cth}\,\sqrt{2\,\tau_d\,S}\,(\mathrm{Sh}\,\sqrt{8\,\tau_b\,S} - 2\,\mathrm{Sh}\,\sqrt{2\,\tau_b\,S}) - \mathrm{ch}\,\sqrt{8\,\tau_b\,S}] \tag{14}$$

with

$$S = -i\,\omega\,, \quad \tau_d = d^2/2\,D \quad \text{and} \quad \tau_b = b^2/2\,D\,.$$

This expression finally allows to calculate Eqs. (1) and (4). The separation of Eq. (14) into a real and an imaginary part will lengthen this equation considerably. An easy way for such a treatment is the use of the "Reduce" simplification procedure, created by Hearn [11]. It is more practicable, however, to leave Eq. (14) in this compact but complex form, which can conveniently be evaluated by a simple computer program (Figure 2). In order to show the analytical behaviour of the relaxation sizes, we give explicit expressions for the low- and high-frequency limits in the subsequent section.

4. Results

For the longitudinal nmr relaxation rate we make use of the fact that

$$\overline{|F^{(2)}|^2} - |\overline{F^{(2)}}|^2 \approx 4\,(\overline{|F^{(1)}|^2} - |\overline{F^{(1)}}|^2) \tag{15}$$

leading to

$$\frac{1}{T_1} = \frac{9}{8}\,\gamma^4\,\hbar^2\,(\overline{|F^{(1)}|^2} - |\overline{F^{(1)}}|^2)\,[I(\omega) + 4\,I(2\,\omega)] \tag{16}$$

with
$$I(\omega) = \frac{-2\,\mathrm{Re}\,\{\mathcal{L}\{W(\tau)\}\}}{W(\infty)}\,.$$

In the limit $\omega\,\tau_d \ll 1$ (which includes $\omega\,\tau_b \ll 1$) we find

$$I(\omega) \approx \tfrac{2}{3}\,\sqrt{\tau_b\,\tau_d}\left(1 - \frac{\sqrt{\tau_b\,\tau_d}}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2}\right) \tag{17}$$

i. e. a low frequency plateau.

The high frequency limit $\omega\,\tau_d \gg 1$ and $\omega\,\tau_b \gg 1$ leads to

$$I(\omega) \approx \sqrt{\frac{\tau_d}{\tau_b}}\,\frac{1}{\sqrt{\tau_d} - \sqrt{\tau_b}} \cdot \left(\frac{1}{\omega^{3/2}} - \frac{1}{2}\,\frac{1}{\omega^2}\,\frac{1}{\sqrt{\tau_d} - \sqrt{\tau_b}}\right). \tag{18}$$

At high frequencies, the same behaviour as for unlimited diffusion occurs [2], in contrast to all cases of stepwise diffusion [3, 4]. The low frequency behaviour coincides with the plateau found with limited stepwise diffusion[4], but deviates from all cases of unlimited diffusion[2,3].

For the complex dielectric constant we find from Eq. (4)

$$\frac{\varepsilon(\omega)-\varepsilon(\infty)}{\varepsilon(0)-\varepsilon(\infty)} = -i\,\omega\,\frac{\mathcal{L}\{W(\tau)\}}{W(\infty)} \tag{19}$$

leading to

$$\frac{\varepsilon(\omega)-\varepsilon(\infty)}{\varepsilon(0)-\varepsilon(\infty)} = 1+i\,\frac{\omega}{3}\left(\sqrt{\tau_b\,\tau_d}-\frac{\tau_b\,\tau_d}{(\sqrt{\tau_d}-\sqrt{\tau_b})^2}\right) \tag{20}$$

for $\omega\tau_d \ll 1$, and to

$$\frac{\varepsilon(\omega)-\varepsilon(\infty)}{\varepsilon(0)-\varepsilon(\infty)} = (1+i)\,\frac{1}{2}\,\frac{\sqrt{\tau_d}}{\sqrt{\tau_b\,\tau_d}-\tau_b}\,\frac{1}{\omega^{1/2}} \tag{21}$$

for $\omega\tau_b \gg 1$.

In Fig. 2, the frequency dependence of T_1 and ε is plotted. The dispersion behaviour can obviously be divided into three regions: a) $\omega \ll 1/\tau_d$, b) $1/\tau_d < \omega < 1/\tau_b$ and c) $\omega \gg 1/\tau_b$. The corresponding slopes are indicated in Figure 2.

5. Conclusion

The introduced limitation of one-dimensional defect diffusion causes a more realistic low frequency behaviour of relaxation sizes than unlimited diffusion. A possible distribution of the distance of the reflecting barriers, however, might be necessary in some applications. The presented treatment probably includes the essential effect of mutual hindrance of defects, though we have assumed that the reflecting barriers are fixed obstacles. This assumption causes however no strong change of the results, because multiple reflexions contribute less the longer the total diffusion pathway. In amorphous polymers, the presented, somewhat abstract situation corresponds to chains, almost saturated with defects, so that there is only a narrow distribution of free diffusion lengths around a certain mean value. The results correspond to the frequently observed effects of broadened dispersion regions of relaxation sizes and flat T_1-minima. Thus, the given formulas might help to interprete relaxation measurements of appropriate systems.

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