Defect Diffusion Models in NMR and Dielectric Relaxation

Rainer Kimmich and Gerhard Voigt

Sektion Kernresonanzspektroskopie, Universität Ulm

The effect of diffusing defects such as vacancies, displacements, torsions, and rotational isomers on the nmr and dielectric relaxation behaviour is treated under various aspects. The influences of the dimensionality of the diffusion process, of the mutual hindrance, of the defect concentration, of the defect length and of the mean lifetime are derived and discussed.

1. Introduction

Defect diffusion has proven to be a good tool in many cases to solve the problem arising when molecular motions are not describable by exponential correlation functions i.e. as Poisson processes. Thus a series of models and applications can be found in literature [1—6] concerning continuous or step-wise diffusion mechanism with and without restriction.

On the other hand there is the possibility to use distributions of correlation times in order to describe the deviations from exponential correlation functions found with the majority of disordered and amorphous substances. It should be stressed that such formal distributions are only justified in heterogeneous samples where we have a real distribution of differently relaxing components. For homogeneous materials there is no alternative way than to consider a single correlation function derived from the special type of molecular motion. An experimental distinction between both situations is possible in nmr relaxation provided that no rapid material exchange or spin diffusion occurs as for instance in solids with a diluted species of observable nuclei. In this case any heterogeneity is revealed by nonexponential relaxation curves.

In the following we want to develop further the defect diffusion models, previously given in literature, so that applications to practical cases in physics of amorphous substances and related fields become possible.

2. Definitions

Under the usual conditions the longitudinal nmr relaxation rate is given for a homogeneous sample with spins $1/2$ by *

$$\frac{1}{T_1} = \frac{9}{8} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \sum_{\text{pairs}} [I^{(1)}(\omega_{\mathrm{L}}) + I^{(2)}(2\omega_{\mathrm{L}})]. \quad (1)$$

The sum, which will be omitted below, runs over all interacting pairs a reference nucleus participates. The intensity functions $I^{(l)}(\omega_{\mathrm{L}})$ are the Fourier transforms of the unnormalized autocorrelation functions $G^{(l)}(\tau)$ of the dipolar interaction functions $F^{(l)}$. In the following we shall use the normalized correlation function in the form

$$\begin{aligned}
G_n(\tau) &= \frac{G^{(l)}(\tau) - G^{(l)}(\infty)}{G^{(l)}(0) - G^{(l)}(\infty)} \\
&= \frac{\langle F^{(l)}(0) F^{(-l)}(\tau) \rangle - |\langle F^{(l)} \rangle|^2}{\langle |F^{(l)}|^2 \rangle - |\langle F^{(l)} \rangle|^2}
\end{aligned} \quad (2)$$

where $l = 1, 2$ and

$$F^{(\pm 1)} = r^{-3} \cos\theta \sin\theta \exp(\pm i\,\varphi);$$
$$F^{(\pm 2)} = r^{-3} \sin^2\theta \exp(\pm i\,2\varphi).$$

$r,\ \varphi,\ \theta$ are the spherical co-ordinates of the spin-spin-vector. Notice that $G_n(\tau)$ is no more dependent on the type of the dipolar interaction functions $F^{(l)}$. The normalized intensity function $I_n(\omega)$ is then given by the Fourier transform of $G_n(\tau)$. $G^{(l)}(0) - G^{(l)}(\infty)$ will be abbreviated below by $\sigma^{(l)}$.

For diluted electric dipoles Eq. (2) represents also the correlation function of the dipole orientation with respect to the electric field strength. In the following we shall use the expression for the complex dielectric constant ε derived by Glarum [7, 8], though the discussion about the relation between microscopic and macroscopic correlation properties is still going on [9]. All solutions of the problem base, however, on the molecular correlation function, so that the final evaluation formula can be derived from it.

* All symbols have the usual meaning if not stated otherwise, but have to be taken in SI-units.
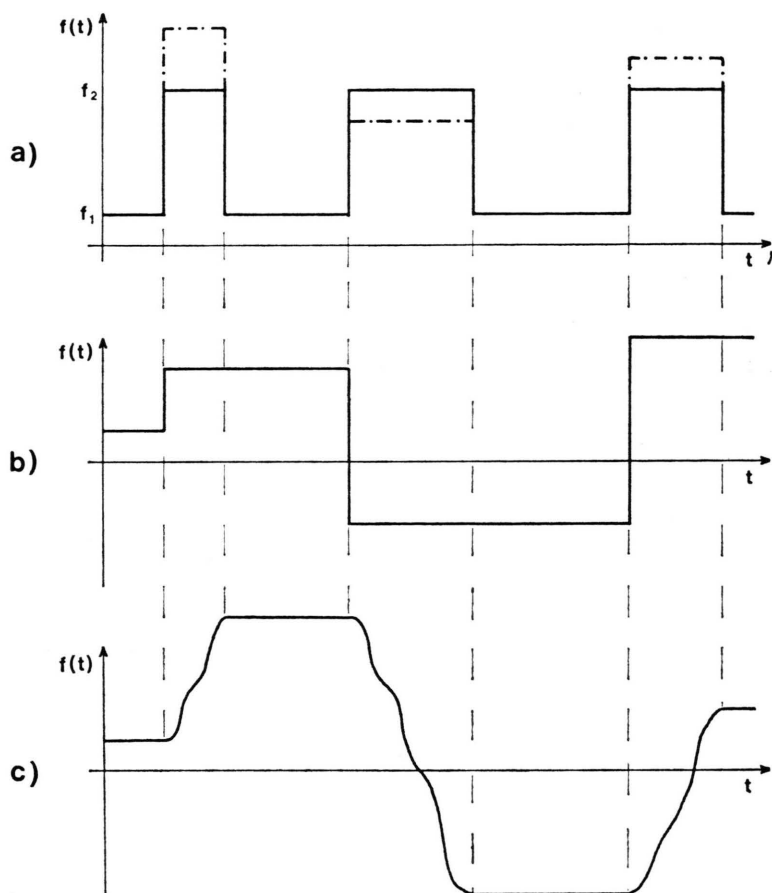
Fig. 1. Schematic representation of the types of fluctuation connected with the different models. The fluctuation at a reference position within the system is assumed to be described by a function $f(t)$. The time dependence of this function is caused by defects diffusing across the reference position.

(a) Defects with restoring capability: The reference position is passed by defects which leave the initial state after passage. The distortion amplitude can be stochastic or — in the simplest case — constant. Both the arrival and the departure of a defect are relevant. Distortion pulses of varying lengths are relevant. Distortion pulses of varying lengths are the consequence.

(b) Defects without restoring capability: Merely the arrival of a defect is relevant. The state, abruptly changed by the defect in an uncorrelated manner, is kept constant until the next arrival of a defect. Thus the extension of the defect has no influence.

(c) Defects without restoring capability causing smoothly increasing distortions: The fluctuating function $f(t)$ is smoothly changed during the passage of a defect rather than abruptly. Thus the width of the defects has a certain degree of influence.

Identifying $G_n(\tau)$ with the normalized correlation function of the dipole orientation,

$$G_n(\tau) = \frac{\Gamma(\tau) - \Gamma(\infty)}{\Gamma(0) - \Gamma(\infty)} \qquad (3)$$

with

$$\Gamma(\tau) = \langle \cos\theta(\tau)\cos\theta(0) \rangle$$

(θ is the angle between the electric dipole moment and the local electric field strength), Glarum's formula can be written as

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)} = -\mathscr{L}\left\{ \frac{dG_n(\tau)}{d\tau} \right\}$$
$$= 1 + i\,\omega\,\mathscr{L}\{G_n(\tau)\}, \qquad (4)$$

$\mathscr{L}$ indicates the Laplace transform with respect to the variable $s = -i\omega$. The simple form of Eq. (4) holds for samples with negligible local field effect, i.e. especially for diluted polar substances. Otherwise Eq. (4) has to be modified slightly [7, 8].

3. Basic Models, Correlation Functions and Probabilities

In the following we shall distinguish on the one hand defects which restore the initial state after having passed the reference position and, on the other hand, defects which leave a state uncorrelated to the initial state. In the second case only the next arrival of a defect provides a further change of the state.

The first model is appropriate for ordered materials with local defects so that the state at a reference position is determined either by a defect or — in the absence of a defect — by the ordered environment. The simplest case is a two-state model defining only one defect state (Figure 1a). This model will be used for convenience. In a certain sense we have here to deal with a pulse model as described in Reference [10]. In that paper it has been shown that the stochastic variation of the

pulse amplitude does not influence the intensity spectrum. Therefore the treatment of the present model with two states should not cause any loss of generality.

The second model should be applicable to materials with a weak influence of the environmental structure. Then only the arrival of a defect is relevant. It will cause (and leave) a state uncorrelated to the initial situation as schematically shown in Fig. 1 b and c.

The calculation of G_n according to Eq. (2) or (3) requires a series of averages. For this purpose we define the following probabilities *.

$$p(i) \equiv \text{a priori probability to find the state no. } i;$$

$P_c(i, j, \tau) \equiv$ conditional probability that the state j will be present after a time τ if the system was initially in a state i.

Then the probability that we have initially a state i and that a state j is found after the period τ is given by

$$P(i, 0 \,|\, j, \tau) = p(i) \, P_c(i, j, \tau). \tag{5}$$

Normalization requires for the two-state model

$$\begin{aligned} P_c(1, 1, \tau) &= 1 - P_c(1, 2, \tau), \\ P_c(2, 2, \tau) &= 1 - P_c(2, 1, \tau), \\ p(1) &= 1 - p(2). \end{aligned} \tag{6}$$

The continuity of defect flow is fulfilled if

$$P(i, 0 \,|\, j, \tau) = P(j, 0 \,|\, i, \tau) \quad (i \neq j). \tag{7}$$

In terms of these definitions, Eq. (2) or (3) yield generally by expressing the averages as weighted sums

$$G_n(\tau) = \frac{P(i, 0 \,|\, i, \tau) - P(i, 0 \,|\, i, \infty)}{P(i, 0 \,|\, i, 0) - P(i, 0 \,|\, i, \infty)} \tag{8a}$$

where i stands for the initial state.

As $P(i, 0 \,|\, i, \infty) = [p(i)]^2$ and $P(i, 0 \,|\, i, 0) = p(i)$ Eq. (8a) can be rewritten in the form

$$G_n(\tau) = \frac{P_c(i, i, \tau) - p(i)}{1 - p(i)}. \tag{8b}$$

Alternatively, we can express $G_n(\tau)$ by the probability that any change occurs during τ, leading for the two-state model to

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* Probabilities refering to the reference particle are designated by the letter p, those refering to defects by the letter q.

$$G_n(\tau) = 1 - \frac{P(i, 0 \,|\, j, \tau)}{P(i, 0 \,|\, j, \infty)} \tag{9}$$

with

$$\begin{aligned} P(i, 0 \,|\, j, \tau) &= p(1) \, P_c(1, 2, \tau) \\ &= p(2) \, P_c(2, 1, \tau) \end{aligned}$$

and

$$P(i, 0 \,|\, j, \infty) = p(1) \, p(2) \quad (i \neq j).$$

The second type of ansatz assumes that the first arrival of a defect suffices to destroy completely the correlation to the initial state. We define with $\tilde{P}(\tau)$ the probability that at least one defect has reached at least once the reference molecule within τ. If $\tilde{P}(\infty) = 1$ we obtain for the normalized correlation function

$$G_n(\tau) = 1 - \tilde{P}(\tau) = P(i, 0 \,|\, i, \tau) \tag{10}$$

i.e. the probability that no change has occurred. For this type of ansatz a treatment with „absorbing walls" is appropriate [1, 2, 6].

In the following we will distinguish diffusion models according to the dimensionality and the limitation to a restricted area. In contrast to previous studies [3, 4] we will assume continuous diffusion models.

4. One-Dimensional, Unlimited Defect Diffusion

4.1. Correlation Function for the Two-state Model

We assume defects having an infinite lifetime and being able to penetrate each other without any hindrance. We designate the unperturbed state by „1" and the defect state by „2". If ϱ_1 is the number of defects per unit length and b is the length of a defect, then the a priori probability to meet no defect between $-b/2 \leqq x \leqq b/2$, i.e. that the reference particle at the origin is unperturbed, is given by

$$p(1) = e^{-\varrho_1 b}. \tag{11}$$

The probability that the final state is the same as initially, i.e. the probability that none of the defects in the system influences the reference particle after an interval τ is then

$$P_c(1, 1, \tau) = \Big\langle \prod_l [1 - P_c{}^l(1, 2, \tau)] \Big\rangle.$$

$P_c{}^l(1, 2, \tau)$ is the probability the lth defect influences the reference particle at time τ. The average concerns all possible initial arrangements of the

defects. As the defects are assumed to move independently we may write

$$P_c(1, 1, \tau) = \prod_l [1 - \langle P_c{}^l(1, 2, \tau) \rangle]$$

$$= \lim_{n \to \infty} [1 - \langle P_c{}^l(1, 2, \tau) \rangle]^n . \quad (12)$$

The limes takes into account the infinity of the system. The average $\langle P_c{}^l(1, 2, \tau) \rangle$ is of course the same for all defects and can be calculated by taking into account all initial positions of a defect outside of $-b/2 \leqq x \leqq b/2$:

$$\langle P_c{}^l(1, 2, \tau) \rangle = \frac{2}{n \, l_0} \int_{b/2}^{\infty} q_1(x', \tau) \, \mathrm{d}x' \quad (13)$$

l_0 is the mean nearest defect distance, $n \, l_0$ the total length of the system. $\mathrm{d}x'/n \, l_0$ is consequently the probability that a specific defect lies initially between x' and $x' + \mathrm{d}x'$. $q_1(x', \tau)$ is the probability that the defect diffuses from this initial position to the reference region $-b/2 \leqq x \leqq b/2$.

By the use of the solution of the one-dimensional diffusion equation we obtain

$$q_1(x', \tau) = \int_{x'-b/2}^{x'+b/2} \frac{1}{2 \sqrt{\pi D \tau}} \times \exp(- x''^2/4 D \tau) \, \mathrm{d}x'' , \quad (14)$$

where D is the diffusion coefficient of the defects. Combining Eq. (13) and (14) yields

$$\langle P_c{}^l(1, 2, \tau) \rangle = \frac{2}{n \, l_0} \int_{b/2}^{\infty} q_1(x', \tau) \, \mathrm{d}x'$$

$$= \frac{1}{n \, l_0} \int_{b/2}^{\infty} \left[\mathrm{erf}\left(\frac{x' + b/2}{2 \sqrt{D \tau}}\right) - \mathrm{erf}\left(\frac{x' - b/2}{2 \sqrt{D \tau}}\right) \right] \mathrm{d}x'$$

$$= \frac{1}{n \, l_0} \lim_{\xi \to \infty} \left[\int_{b}^{\xi + b/2} \mathrm{erf}\left(\frac{\bar{x}}{2 \sqrt{D \tau}}\right) \mathrm{d}\bar{x} - \int_{0}^{\xi - b/2} \mathrm{erf}\left(\frac{\tilde{x}}{2 \sqrt{D \tau}}\right) \mathrm{d}\tilde{x} \right] \quad (15)$$

where we have used the error function defined by

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, \mathrm{d}t .$$

The integral of this function is [11]

$$\int \mathrm{erf}(a \, x) \, \mathrm{d}x = x \, \mathrm{erf}(a \, x) + \frac{e^{-a^2 x^2}}{a \sqrt{\pi}} + \mathrm{const.}$$

Thus it follows from Eq. (8b), (12) and (15)

$$G_n(\tau) = \frac{\exp\left\{ - \dfrac{b}{l_0} \left[1 + \sqrt{\dfrac{2 \tau}{\pi \tau_b}} \left(1 - \exp\left\{ - \dfrac{\tau_b}{2 \tau} \right\} \right) - \mathrm{erf} \sqrt{\dfrac{\tau_b}{2 \tau}} \right] \right\} - p(1)}{1 - p(1)} \quad (16\mathrm{a})$$

with $\tau_b = b^2/2 D$ and $p(1) = \exp(- b/l_0)$.

In the limit $b \ll l_0$ i.e. for low defect concentrations, we may write in linear approximation

$$G_n(\tau) = \mathrm{erf}\left(\sqrt{\frac{\tau_b}{2 \tau}} \right) - \sqrt{\frac{2 \tau}{\pi \tau_b}} \left(1 - \exp\left\{ - \frac{\tau_b}{2 \tau} \right\} \right) . \quad (16\mathrm{b})$$

The condition $b \ll l_0$ is rather uncritical as can be shown by a numerical test. It is remarkable that this limiting expression doesn't depend any more on the defect density. Merely the unnormalized correlation function, i.e. the absolute values of the relaxation sizes, are shifted by the defect density.

This behaviour corresponds to that found by Noack et al. [10] for a random pulse model by use of Campbell's theorem. As illustrated in Fig. 1a, we have here a similar situation apart from the fact that all time dependences are diffusion controled. Campbell's theorem states that the spectrum of a Poisson-like pulse sequence is dominated by the spectrum of the individual pulse shape rather than by the mean pulse rate. In the defect-diffusion model the „pulse-rate" is determined by the defect concentration, so that a complete analogy exists.

4.2. Nuclear Magnetic Relaxation

The Fourier transform of Eq. (16b) yields the normalized intensity function

$$I_n(\omega) = \tau_b{}^{-1/2} \omega^{-3/2} (1 - e^{-\sqrt{\omega \tau_b}} [\cos \sqrt{\omega \tau_b} + \sin \sqrt{\omega \tau_b}]) \quad (17)$$

with $\tau_b = b^2/2D$. For the longitudinal relaxation rate we make use of the fact that even for anisotropic motions [3] the following relation is frequently valid

$$\langle |F^{(2)}|^2 \rangle - |\langle F^{(2)} \rangle|^2$$
$$\approx 4 \left(\langle |F^{(1)}|^2 \rangle - |\langle F^{(1)} \rangle|^2 \right) \qquad (18)$$
$$\equiv 4\,\sigma^{(1)}(\varrho_1)$$

so that for a two-spin 1/2 ensemble

$$\frac{1}{T_1} = \frac{9}{8}\,\gamma^4 \hbar^2 \left(\frac{\mu_0}{4\pi}\right)^2 \sigma^{(1)}(\varrho_1)\,[I_n(\omega) + 4\,I_n(2\,\omega)]. \qquad (19)$$

$\sigma^{(1)}(\varrho_1)$ is the mean square deviation of $F^{(1)}$. The dependence on the defect concentration enters merely by this quantity. For $\varrho_1 b \ll 1$ it holds $\sigma^{(1)}(\varrho_1) \sim \varrho_1$.

For $\omega\tau_b \ll 1$ we find the limit

$$1/T_1 \sim \sqrt{\tau_b/\omega} \qquad (20\,\mathrm{a})$$

while for $\omega\tau_b \gg 1$

$$1/T_1 \sim \tau_b^{-1/2}\,\omega^{-3/2}. \qquad (20\,\mathrm{b})$$

Thus we have obtained analogous limits as Hunt and Powles [2] for the nearest neighbour approximation. The $\omega^{-3/2}$-slope of Eq. (20b) is related with the continuous diffusion assumed above. For stepwise defect diffusion one would expect a final ω^{-2}-slope [3]. A T_1-minimum occurs for $\omega\tau_b \approx 1.4$. Notice that τ_b is the mean diffusion time for a mean

square displacement b^2. Figure 2 and 3 show plots of the behaviour of Equation (19).

4.3. Dielectric Relaxation

We combine Eq. (16b) with Equation (4). For this purpose we use the Laplace transform [12]

$$\mathscr{L}\{G_n(\tau)\}$$
$$= \frac{1}{i\,\omega}\left[\frac{1 - e^{-\sqrt{\omega\tau_b}}(\cos\sqrt{\omega\,\tau_b} - \sin\sqrt{\omega\,\tau_b})}{2\sqrt{\omega\,\tau_b}} - 1 \right.$$
$$\left. + i\,\frac{1 - e^{-\sqrt{\omega\tau_b}}(\cos\sqrt{\omega\,\tau_b} + \sin\sqrt{\omega\,\tau_b})}{2\sqrt{\omega\,\tau_b}} \right] \qquad (21)$$

leading finally to

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)}$$
$$= \frac{1}{\sqrt{\omega\,\tau_b}}\left[e^{-\sqrt{\omega\tau_b}}\sin\sqrt{\omega\,\tau_b} + \frac{1+i}{2} \right. \qquad (22)$$
$$\times\left. (1 - e^{-\sqrt{\omega\tau_b}}\{\cos\sqrt{\omega\,\tau_b} + \sin\sqrt{\omega\,\tau_b}\}) \right].$$

The limiting behaviour of this formula at low and high frequencies is plotted in Figures 2 and 3.

4.4. Total Correlation Loss

We turn now to the second type of ansatz as illustrated in Figure 1b. The arrival of a defect shall cause a sudden change leaving a state uncorrelated to the initial one. On this basis Bordewijk [6] has
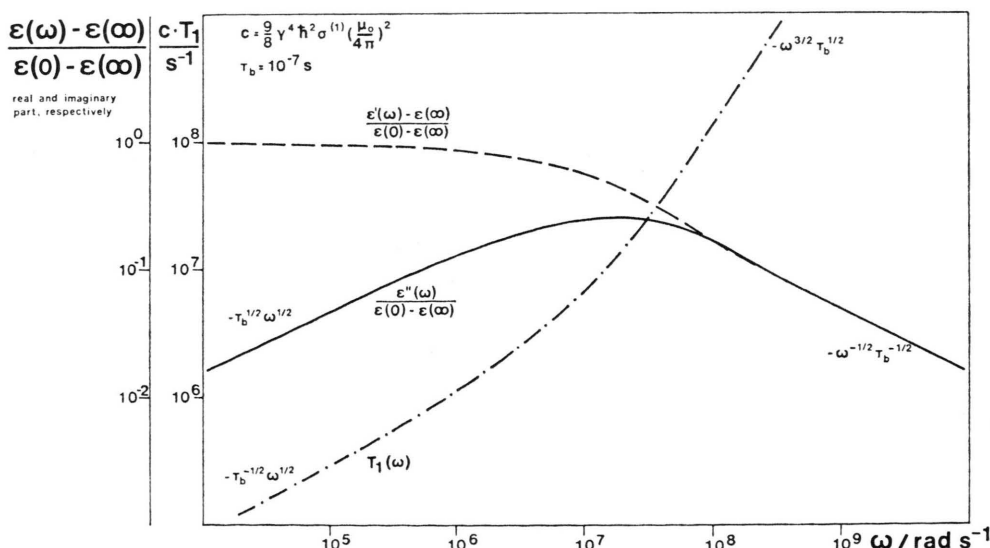

Fig. 2. Frequency dependence of *nmr* and dielectric relaxation quantities for *unlimited one-dimensional* diffusion of defects with restoring capability.
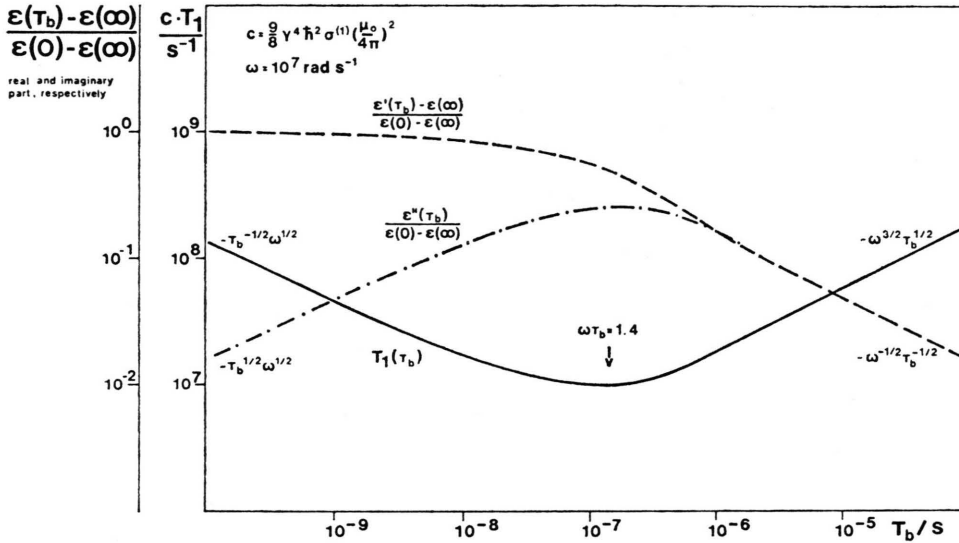
Fig. 3. NMR and dielectric relaxation quantities in dependence on τ_b for *unlimited one-dimensional* diffusion of defects with restoring capability.

derived an expression compatible with the empirical formula of Williams and Watts [13]

$$G_n(\tau) = \exp[-(\tau/\tau_l)^{1/2}] \qquad (23)$$

with $\tau_l = \pi l_0^2 (16 D)^{-1}$. The intensity function is then

$$I_n(\omega) = \sqrt{\frac{2\pi}{\tau_l}} \frac{1}{\omega^{3/2}} \{\cos(\alpha)[\tfrac{1}{2} - C_2(\alpha) \qquad (24)$$
$$+ \sin(\alpha)[\tfrac{1}{2} - S_2(\alpha)]\}$$

with $\alpha = (4\omega\tau_l)^{-1}$. C_2 and S_2 are the Fresnel-integrals

$$C_2(x) = \frac{1}{\sqrt{2\pi}} \int_0^x \frac{\cos t}{\sqrt{t}} \, dt,$$

$$S_2(x) = \frac{1}{\sqrt{2\pi}} \int_0^x \frac{\sin t}{\sqrt{t}} \, dt,$$

which are tabulated for instance in Reference [14]. The limiting behaviour for

$$\omega\,\tau_l \gg 1 \quad \text{is} \quad I_n \sim \tau_l^{-1/2}\,\omega^{-3/2}.$$

The dielectric relaxation behaviour is discussed in Reference [13].

The abrupt loss of the correlation at the arrival might be somewhat unrealistic. We want therefore to add a short discussion of defects causing a smoothly increasing distortion (Figure 1 c).

We consider a reference particle at $x = 0$. When this position is reached, the total correlation to the initial state is assumed to be lost. As we don't know the details of this distance dependent distortion, we simply use the rate of the first arrival of the defect at a position x averaged over $-b/2 \leqq x \leqq +b/2$.

An alternative interpretation of this picture would be the assumption that a reference particle at $x = 0$ can suddenly lose the correlation to the initial state at any position of the defect within $-b/2 \leqq x \leqq b/2$. An example could be a vacancy which gives an atom the chance to jump in it over a certain range of distance.

The probability that a defect passes a distance $|x' - x|$ between τ and $\tau + d\tau$ for the first time is [15]

$$\dot{q}_1(x', x, \tau)\,d\tau = \frac{|x - x'|}{2(\pi D)^{1/2}\tau^{3/2}}$$
$$\cdot \exp(-(x - x')^2/4 D\,\tau)\,d\tau$$

where x' is the position of the „absorbing wall" and x is the initial co-ordinate of the defect. The average over the positions of the „absorbing walls" yields

$$\dot{q}_1(x, \tau) = \frac{1}{2b(\pi D)^{1/2}\tau^{3/2}} \int_{-b/2}^{b/2} |x - x'|$$
$$\cdot \exp(-(x - x')^2/4 D\,\tau)\,dx' \qquad (25)$$
$$= \frac{D^{1/2}}{b(\pi\tau)^{1/2}} [\exp(-(|x| - b/2)^2/4 D\,\tau)$$
$$- \exp(-(|x| + b/2)^2/4 D\,\tau)].$$

The average over all initial positions x of the defect $-a/2 \leq x \leq -b/2$ and $b/2 \leq x \leq a/2$ leads to

$$\dot{q}_1(\tau) = \frac{2D}{ab} \left[\mathrm{erf}\left(\frac{a-b}{4\sqrt{D\tau}}\right) - \mathrm{erf}\left(\frac{a+b}{4\sqrt{D\tau}}\right) \right.$$
$$\left. + \mathrm{erf}\left(\frac{b}{2\sqrt{D\tau}}\right) \right] \qquad (26)$$

where a is the length of the total system. As $a \gg b$ we may write

$$\dot{q}_1(\tau) = \frac{2D}{ab} \, \mathrm{erf}\left(\frac{b}{2\sqrt{D\tau}}\right) \qquad (27)$$

so that

$$q_1(t) = \frac{D}{ab} \int_0^t \mathrm{erf}\left(\frac{b}{2\sqrt{D\tau}}\right) \mathrm{d}\tau$$

or by substitution

$$q_1(t) = \frac{b}{4a} \int_0^{4Dt/b^2} \mathrm{erf}(u^{-1/2}) \, \mathrm{d}u \, .$$

The probability that none of n defects has touched the reference region is then

$$[1 - q_1(t)]^n \, .$$

Recognizing that $a = n l_0$ and that n is a large number, leads to

$$G_n(t) = \lim_{n\to\infty} \left[1 - \frac{1}{n} \frac{b}{4 l_0} \int_0^{4Dt/b^2} \mathrm{erf}(u^{-1/2}) \, \mathrm{d}u \right]^n$$
$$= \exp\left\{ - \frac{b}{4 l_0} \int_0^{4Dt/b^2} \mathrm{erf}(u^{-1/2}) \, \mathrm{d}u \right\} \, .$$

For $t \lesssim b^2/4D$ we can use the approximation

$$G_n(t) = 1 - \frac{b}{4 l_0} \int_0^{4Dt/b^2} \mathrm{erf}(u^{-1/2}) \, \mathrm{d}u \, . \qquad (28)$$

The intensity function can then directly be derived from Eq. (28) by the aid of the Laplace-transform

$$\mathscr{L}\{G_n(t)\} = \frac{D}{b l_0} \frac{\exp\left(-\sqrt{\dfrac{b^2 s}{D}} - 1\right)}{s^2} \qquad (29)$$

with $s = -i\omega$. The intensity function is then

$$I_n(\omega) = 2 \, \mathrm{Re}\{\mathscr{L}\{G_n(t)\}\} \qquad (30)$$
$$= \frac{2D}{b l_0} \frac{1}{\omega^2} \left[1 - \exp\left(-\sqrt{\frac{b^2\omega}{2D}}\right) \cos\sqrt{\frac{b^2\omega}{2D}} \right] .$$

For $b \ll \sqrt{2D/\omega}$ we derive from Eq. (30) the limit for $\omega\tau_l \gg 1$ of Eq. (24) as it must be.

5. Three-Dimensional, Unlimited Defect Diffusion

5.1. Correlation Function

In the three-dimensional case Eq. (13) has to be modified in a way that the integral covers the whole space except a small sphere of radius $a/2$ around the reference point. The defects are now considered to be extended over a sphere of diameter a.

The average probability that the lth defect influences the reference particle after a period τ is then quite analogous to Eq. (13)

$$\langle P_c^l(1,2,\tau)\rangle = \frac{1}{n V_0} \int_{r'>a/2} q_3(r',\tau) \, \mathrm{d}^3 r' \, . \quad (31)$$

V_0 is the mean free volume per defect, $n V_0$ the sample volume, $q_3(r',\tau)$ is the probability that a defect, initially in a distance r' is finally near the reference point within a sphere of radius $a/2$. According to Ref. [15] it holds

$$q_3(r',\tau) = \frac{1}{(4\pi D\tau)^{3/2}} \int_{\substack{r'-a/2 \\ \leq r'' \leq \\ r'+a/2}} e^{-r''^2/4D\tau} \, \mathrm{d}^3 r'' \, . \qquad (32)$$

The integration concerns all final positions of the defect affecting the reference position.

So far we have assumed that the perturbation can occur with spherical symmetry around the defect position. The reference point would thus be influenced by all defects located within a sphere of radius $a/2$ [Eq. (32)]. This leads however to a rather complicated form of the integral in Equation (32). The problem can be avoided by the use of a considerably simplifying approximation, which fortunately leads to no severe alteration of the final result.

The integration in Eq. (32) can be performed by integrating over all curved infinitesimally thin slices described by the perturbation volume around the reference position and, on the other hand, by the spherical shell of thickness $\mathrm{d}r''$ with a radius r'' around the initial defect position (Figure 4). For a spherical shape of the perturbation region the volume element thus would be

$$\mathrm{d}^3 r'' = \pi \frac{r''}{r'} \left[\frac{a^2}{4} - (r' - r'')^2 \right] \mathrm{d}r'' \, . \qquad (33)$$

Instead of this we approximate for simplicity the perturbation volume by a virtually conical shape (Fig. 4), so that the same volume results. The
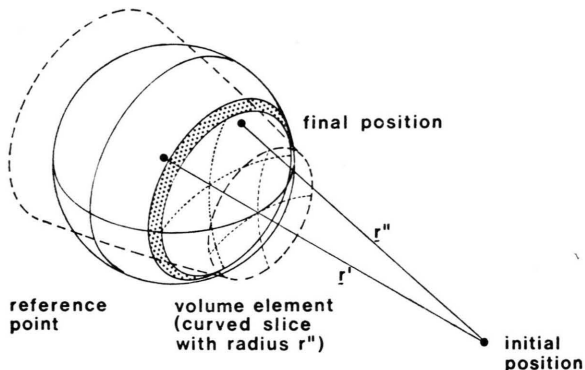
Fig. 4. Illustration of the approximative volume element used in Section 5.1. The reference point in the center of the indicated volumes (r') is influenced by all defects entering these volumes (r''). The volume elements both for the spherical and for the conical shape have to be considered as curved slices of thickness dr'' and with a radius of curvature r''.

volume element is now

$$d^3 r'' = \frac{\pi}{6} a^2 \frac{r''}{r'} dr'' . \tag{34}$$

$\frac{\pi}{6} a^2$ can be considered as the mean perturbation cross section of the defects. A numerical control of this approximation is given below.

Equation (32) then becomes

$$q_3(r', \tau) = \frac{a^2}{48 \pi^{1/2} (D\tau)^{3/2} r'} \int_{r'-a/2}^{r'+a/2} r'' e^{-r''^2/4D\tau} dr''$$
$$= \frac{a^2}{24 (\pi D \tau)^{1/2} r'} \left[\exp\left(-\frac{(r' - a/2)^2}{4 D \tau} \right) \right.$$
$$\left. - \exp\left(-\frac{(r' + a/2)^2}{4 D \tau} \right) \right]. \tag{35}$$

Together with Eq. (31) we derive

$$\langle P_c^l(1, 2, \tau) \rangle = \lim_{\varepsilon \to \infty} \frac{4\pi}{n V_0} \int_{a/2+\varepsilon}^{\infty} r'^2 q_3(r', \tau) dr'$$
$$= \frac{1}{n V_0} \left\{ \frac{a^2 \sqrt{\pi D \tau}}{3} [1 - e^{-a^2/4 D\tau}] \right.$$
$$+ \frac{\pi a^3}{6} \left[1 - \frac{1}{2} \operatorname{erf}\left(\frac{a}{\sqrt{4 D \tau}} \right) \right.$$
$$\left. \left. - \frac{1}{2} \lim_{\varepsilon \to \infty} \operatorname{erf}\left(\frac{\varepsilon}{\sqrt{4 D \tau}} \right) \right] \right\}. \tag{36}$$

Inserting Eq. (36) in Eq. (12) and (8b) yields

for $\tau > 0$ and $G_n(0) = 1$. $V = \pi a^3/6$ is the volume of a defect; $V_0 = \varrho_3^{-1}$ is the volume per defect; $p(1) = \exp\{- V/V_0\}$; $\tau_a = a^2/6D$. As $V \gg V_0$ we may use the linear approximation

$$G_n(\tau) = \frac{1}{2} \operatorname{erf} \sqrt{\frac{3 \tau_a}{2 \tau}} - \sqrt{\frac{2 \tau}{3 \pi \tau_a}}$$
$$\cdot \left(1 - \exp\left\{ -\frac{3 \tau_a}{2 \tau} \right\} \right) \tag{37b}$$
for $\tau > 0$ and $G_n(0) = 1$.

The condition $V \gg V_0$ is again rather uncritical. The deviations numerically found between Eq. (37a) and Eq. (37b) are even for $V = 2 V_0$ only about 20%. This function has a similar form as in the one-dimensional case [Eq. (16)]. The discontinuity at $\tau = 0$ is due to the approximation Equation (34). The numerical integration leads to a correlation function with a smooth initial part while the final decay becomes more and more identical to the approximated function. Figure 5 shows that the effect of this discontinuity on the relaxation behaviour is a small shift of the curves which can easily be corrected. It is again remarkable that the normalized correlation function doesn't depend on the defect concentration, which merely influences the absolute value of the relaxation rates but not the frequency or temperature dependence.

5.2. Nuclear Magnetic Relaxation

Together with the Fourier transform of Eq. (37b) we obtain

$$\frac{1}{T_1} = \frac{9}{8} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \sigma^{(1)} [I_n(\omega) + 4 I_n(2 \omega)]$$

with

$$I_n(\omega) = (3 \tau_a)^{-1/2} \omega^{-3/2} [1 - \exp(-\sqrt{3 \omega \tau_a})$$
$$\times (\cos \sqrt{3 \omega \tau_a} \tag{38a}$$
$$+ \sin \sqrt{3 \omega \tau_a} \{1 + \sqrt{3 \omega \tau_a}\})] .$$

The discussion of the one-dimensional case (Section 4.2) can be transferred to Eq. (38a) which shows the same qualitative behaviour except for the limit $\omega \tau_a \ll 1$, for which the frequency depen-

$$G_n(\tau) = \frac{\exp\left\{ -\frac{V}{V_0} \left[1 + \sqrt{\frac{2 \tau}{3 \pi \tau_a}} \left(1 - \exp\left\{ -\frac{3 \tau_a}{2 \tau} \right\} \right) - \frac{1}{2} \operatorname{erf} \sqrt{\frac{3 \tau_a}{2 \tau}} \right] \right\} - p(1)}{1 - p(1)} \tag{37a}$$
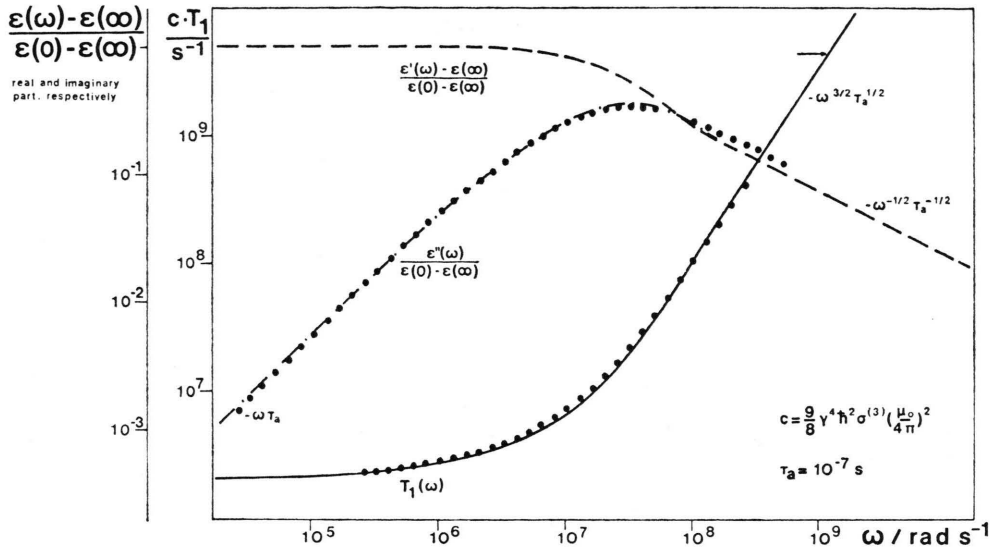
Fig. 5. Frequency dependence of *nmr* and dielectric relaxation quantities for *unlimited three-dimensional* diffusion of defects with restoring capability. The points have been calculated numerically by the use of the correct volume element Equation (33). The lines represent the approximative results obtained from Eq. (38a) and (39a), respectively, which have been corrected by the substitution of ω by $0.6\,\omega$ as indicated by the arrow [Eq. (38b) and (39b), respectively]. The correction symbol has been omitted for simplicity. The deviations are less than the experimental errors usually found.

dence vanishes. All remarkable features are given in Fig. 5 and 6. The numerical integration using the exact volume element Eq. (33) leads to merely shifted curves. Thus a correction of Eq. (38a) is possible by the substition of ω by $0.6\,\omega$:

$$I_n^{corr}(\omega) = I_n(0.6\,\omega) \,. \tag{38b}$$

5.3. Dielectric Relaxation

The stepwise initial decay of the correlation function Eq. (37b) makes again no physical sense because it is a consequence of the approximation Equation (34). Thus we use only the smoothly decaying part of the correlation function, which has
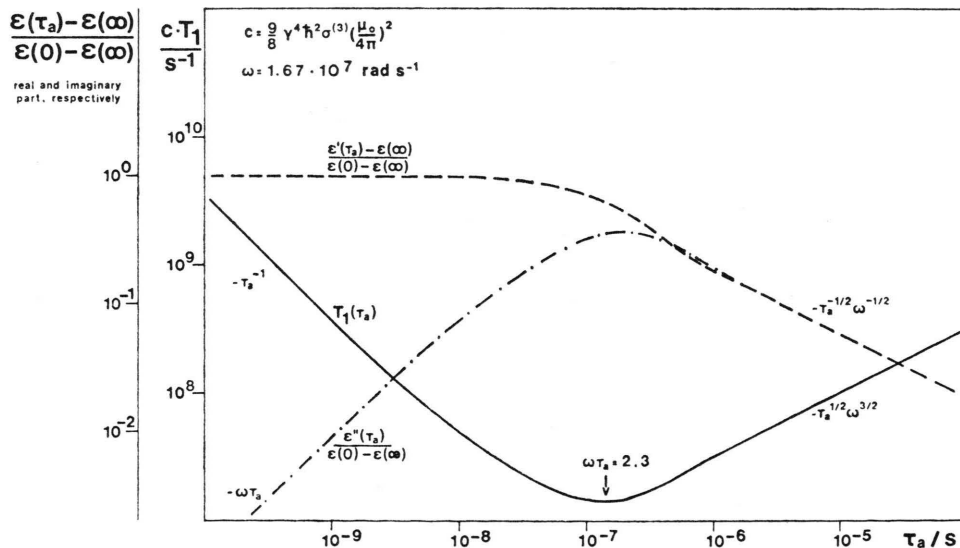

Fig. 6. NMR and dielectric relaxation quantities in dependence on τ_a for *unlimited three-dimensional* diffusion of defects with restoring capability. The correction formulae (38b) and (39b), respectively, have been applied omitting the correction symbol.

to be renormalized according to the requirements of Equation (4). It follows

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)} = \frac{1}{\sqrt{3\omega\tau_a}} [1 - \exp(-\sqrt{3\omega\tau_a})$$
$$\times \{\cos\sqrt{3\omega\tau_a}(1 + \sqrt{3\omega\tau_a}) - \sin\sqrt{3\omega\tau_a}\}$$
$$+ i(1 - \exp(-\sqrt{3\omega\tau_a})\{\cos\sqrt{3\omega\tau_a}$$
$$+ \sin\sqrt{3\omega\tau_a}(1 + \sqrt{3\omega\tau_a})\})] . \qquad (39a)$$

The numerical test proves again that this result represents the actual behaviour of the model with satisfying accuracy, especially if the curves are shifted according to the correction formula

$$\varepsilon_{corr}(\omega) = \varepsilon(0.6\,\omega) . \qquad (39b)$$

6. Limited Defect Diffusion

6.1. The Problem

So far we have considered non-interacting defects which diffuse independently from each other. In cases where this assumption is not justified we have to deal with a „many-particle problem". Especially in the one-dimensional case and, for high defect densities, in three dimensions we can no more neglect „collisions" between defects. An altered diffusion behaviour is the consequence.

It is clear that an exact analytical treatment can not be envisaged. There are however two ways to overcome the difficulties:

(i) The time development of the system can be simulated with the aid of a Monte-Carlo calculation. Previously we have chosen this way for the derivation of the correlation function in molten polymers, assuming a one-dimensional system [16]. An extension to three dimensions is principally possible, though it may be a problem of the available computer time.

(ii) It can be tried to simplify the system in such a way that an analytical treatment becomes possible and that the essential features of the processes are still included. Thus we have previously treated the one-dimensional diffusion of a single defect between reflecting walls, which might represent the neighbouring defects or barriers arising from the structure of the system [4, 5].

The second method has certainly the advantage of yielding analytical expressions, though it is restricted to the one-dimensional case. In three dimensions the effect of defect collisions is, however, less severe. There are no „reflexions" in the sense mentioned above. We expect essentially a reduction of the effective diffusion constant while the time dependence of the diffusion process is qualitatively the same as in the case without interaction between the defects. Therefore we will only discuss diffusion in one dimension according to the treatment given in Reference [5].
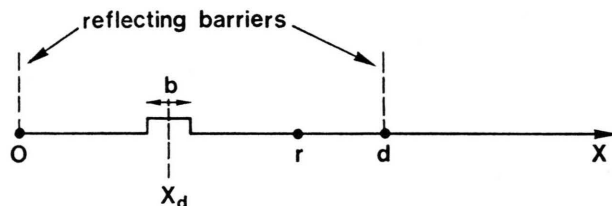

Fig. 7. Schematic representation of the problem to be dealt with in the case of limited defect diffusion.

We consider a model situation as represented in Figure 7. The probability that the interaction state is changed after a period τ is given by

$$P(i, 0\,|\,j, \tau) = \frac{1}{d(d-b)} \int_{b/2}^{d-b/2} \int_{\substack{x_i \geq r+b/2 \\ x_i \leq r-b/2}} \int_{r-b/2}^{r+b/2}$$
$$\cdot P_c(x_i, x_f, \tau)\,dx_f\,dx_i\,dr \qquad (40)$$

with the probability that the defect diffuses from x_i to x_f in the time interval τ

$$P_c(x_i, x_f, \tau)\,dx_f = \sum_{n=-\infty}^{\infty} [q(2\,n\,d - (x_i - x_f), \tau)$$
$$+ q(2\,n\,d - (x_i + x_f), \tau)]\,dx_f \qquad (41)$$

[$q(x, \tau)$ is given by the integrand of Equation (14)]. The sum comprises all diffusion pathways produced by the „method of images" [17]. Equation (40) includes the averages over all final positions of the defect except those near the reference point, all initial positions in the range

$$r - b/2 \leq x_i \leq r + b/2 ,$$

and, finally, over all positions of the reference point. Exactly spoken the latter average should be performed afterwards with the whole relaxation rates according to the assumption of rapid spin diffusion in the nmr case. Thus we have in principle to

deal with different ensembles for each value of r. Formally this average can however be performed at this stage.

The required relaxation sizes have been calculated in Reference [5]. The results can be expressed either in rather lengthy real expressions or in short complex formulae. Both representations require a computer evaluation in order to plot the analytical behaviour. In the following we'll discuss some approximative expressions. This will be performed by defining two characteristic time constants, namely $\tau_d = d^2/2D$ and $\tau_b = b^2/2D$. The exact formulae can be found in Reference [5].

6.2. Nuclear Magnetic Relaxation

a) $\omega \tau_d \ll 1$:

(This limit includes $\omega \tau_b \ll 1$.) The use of Eq. (18) and (19) leads to the frequency independent formulae

$$\frac{1}{T_1} \approx \frac{15}{4} \gamma^4 \hbar^2 \left(\frac{\mu_0}{4\pi}\right)^2 \sigma^{(1)} \sqrt{\tau_b \tau_d}$$
$$\cdot \left(1 - \frac{\sqrt{\tau_b \tau_d}}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2}\right). \quad (42)$$

b) $\omega \tau_b \ll 1 \ll \omega \tau_d$:

$$\frac{1}{T_1} \approx \frac{9}{8} \gamma^4 \hbar^2 \left(\frac{\mu_0}{4\pi}\right)^2 \sigma^{(1)} \sqrt{\tau_b \tau_d}$$
$$\cdot \frac{\sqrt{\tau_d} - 2\sqrt{\tau_b}}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2} \frac{(1 + 2\sqrt{2})}{\omega^{1/2}}. \quad (43)$$

c) $\omega \tau_b \gg 1$:

(This limit includes $\omega \tau_d \gg 1$).

$$\frac{1}{T_1} \approx \frac{9}{8} \gamma^4 \hbar^2 \left(\frac{\mu_0}{4\pi}\right)^2 \sigma^{(1)} \sqrt{\frac{\tau_d}{\tau_b}}$$
$$\cdot \frac{1 + \sqrt{2}}{\sqrt{\tau_d} - \sqrt{\tau_b}} \frac{1}{\omega^{3/2}}. \quad (44)$$

The temperature dependence of T_1 shows a minimum for $\omega \tau_b = 1.2$ ($\tau_d \gg \tau_b$) as indicated in Figure 8.

6.3. Dielectric Relaxation

a) $\omega \tau_d \ll 1$:

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)} = 1 + i \frac{\omega}{3} \left(\sqrt{\tau_b \tau_d}\right.$$
$$\left. - \frac{\tau_b \tau_d}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2}\right). \quad (45)$$

b) $\omega \tau_b \ll 1 \ll \omega \tau_d$:

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)} = \frac{1}{2} \frac{\sqrt{\tau_d}}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2}$$
$$\cdot [2\sqrt{\tau_d} - 3\sqrt{\tau_b} - \sqrt{\omega}(\sqrt{\tau_d \tau_b}$$
$$- 2\tau_b) + i\sqrt{\omega}(\sqrt{\tau_d \tau_b} - 2\tau_b)]. \quad (46)$$

c) $\omega \tau_b \gg 1$:

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon(0) - \varepsilon(\infty)} = (1 + i) \frac{1}{2}$$
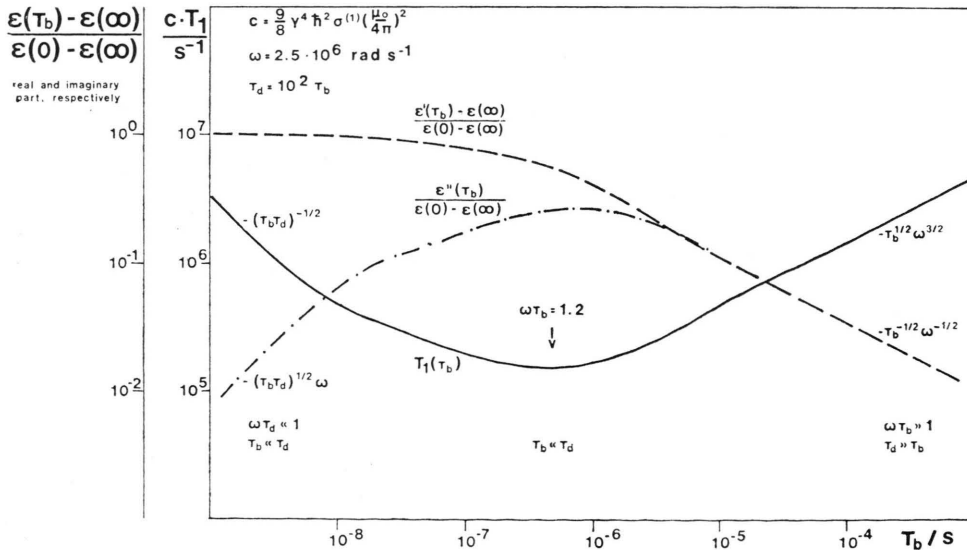$$\cdot \frac{\sqrt{\tau_d}}{\sqrt{\tau_b \tau_d} - \tau_b} \frac{1}{\omega^{1/2}}. \quad (47)$$

Fig. 8. NMR and dielectric relaxation quantities in dependence on τ_b for *limited one-dimensional* defect diffusion where we have assumed $\tau_d = 10^2 \tau_b$.
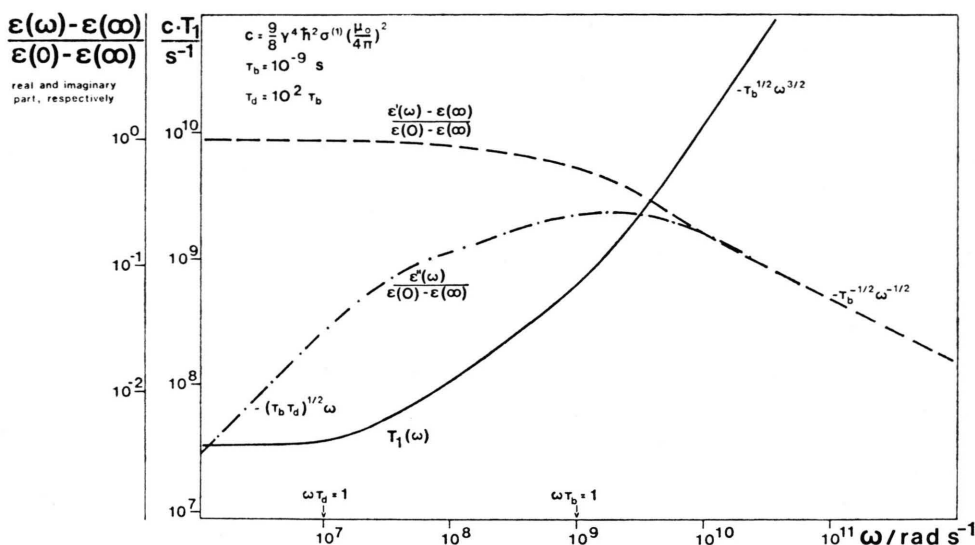
Fig. 9. Frequency dependence of nmr and dielectric relaxation quantities for *limited one-dimensional* defect diffusion. Notice that the ratio $\tau_d : \tau_b = 10^2$ is too small to show fully the intermediate behaviour given in Equation (43) and (46).

Figure 9 shows a plot of the whole frequency dependence.

7. Discussion

In this paper we have reviewed defect diffusion models basing on different assumptions. The most elementary distinction concerns the type of the diffusion processes. We have here assumed that the defects diffuse continuously, though the thermal activation suggests a stepwise character. Denoting the mean step time by τ_s, we can consider the present calculation to be valid in any case for $\omega \tau_s \ll 1$. Previously the possibly stepwise diffusion could be taken into account in some special models [3, 4]. From these investigations we conclude that the only consequence of the stepwise character would arise in the limit $\omega \tau_s \gg 1$ for which the proportionality $T_1 \sim \omega^2$ has been calculated.

Secondly we have distinguished certain degrees of restrictions of the defect diffusion, caused by the interaction between defects. In the three-dimensional case, our argument was, that no principally different behaviour — except an alteration of the effective diffusion constant — should be expected. In the one-dimensional case, however, the limitation of the diffusion paths severely influences the relaxation for $\omega \tau_b \ll 1$, while the limit $\omega \tau_b \gg 1$ is unaffected. The decision, which degree of mutual hindrance of the defects has to be assumed, depends

on the type of the considered defect. Extended torsions in polymer chains, for instance, are expected to penetrate each other without essential hindrance. The same holds for diffusing vacancies in any kind of material. A stronger hindrance is expected for dislocations in solids and localized defects in polymer chains. The energetics of these defects suggest more or less a hard-core behaviour.

The type of the defects and of the material defines also the dimensionality of the diffusion process. The decision of the dimensionality is quite important for the relaxation behaviour in the limit $\omega \tau_a \ll 1$ or $\omega \tau_b \ll 1$, respectively, while in the opposite limits the behaviour is identical.

An important question is the dependence on the defect concentration. It is an essential statement of this study that unlimited diffusion can lead to normalized correlation functions independent on the defect concentration as discussed in Section 4.1. A concentration dependence appears, on the other hand, for Bordewijk's model and for the restricted diffusion case via τ_d.

Comparing the diverse defect diffusion models presented in literature, one should be aware of the following. In previous calculations the nearest neighbour approximation has been used [1—3]. Taking into account only the nearest neighbours is however somewhat inconsistent with the assumption of unrestricted diffusion as outlined in Section 6. If no mutual hindrance of the defects is assumed,

the treatment should include in any case *all* defects in the system]6].

Finally we want to discuss the assumption of an infinite lifetime of the defects or a lifetime long compared with the relevant diffusion times, a quite essential feature of the whole formalism. What would happen if annihilation and creation of defects would be allowed at any place within the sample with the same probability and in a time scale shorter than the relevant diffusion times τ_x? Clearly, the resulting behaviour approaches that of a Poisson process, i.e. an exponential correlation function analogous to that derived in Sect. 3.1 of Reference [3]. For mean lifetimes $\tau_0 \gg \tau_x$ the formalism presented above is appropriate. In the intermediate range and for finite systems, there remains the possibility to apply the matrix method described in Reference [4].

Applications of the models given above are possible for all kinds of more or less disordered systems. Thus a first discussion of defect diffusion in amorphous polyethylene is given in Reference [18]. The diffusion of vacancies in crystalline materials on the other hand can be treated by refering directly to the symmetry properties as demonstrated in Ref. [19, 20] and in subsequent papers.

[1] S. H. Glarum, J. Chem. Phys. **33**, 639 (1960).
[2] B. I. Hunt, and J. G. Powles, Proc. Phys. Soc. London 88, 513 (1966).
[3] R. Kimmich, Colloid & Polymer Sci. **252**, 786 (1974).
[4] R. Kimmich, and A. Peters, J. Magn. Resonance 19, 144 (1975).
[5] R. Kimmich, Z. Naturforsch. **31 a**, 693 (1976).
[6] P. Bordewijk, Chem. Phys. Letters **32**, 592 (1975).
[7] S. H. Glarum, Mol. Phys. **24**, 1327 (1972); J. Chem. Phys. **33**, 1371 (1960).
[8] R. H. Cole, J. Chem. Phys. **42**, 637 (1965).
[9] D. Kivelson and P. Madden, Mol. Phys. **30**, 1749 (1975).
[10] F. Noack, G. J. Krüger, W. Müller-Warmuth, and R. van Steenwinkel, Z. Naturforsch. **22 a**, 2102 (1967).
[11] I. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series and Products, Academic Press, New York 1965.
[12] G. E. Roberts and H. Kaufman, Table of Laplace Transforms, W. B. Saunders & Co., Philadelphia 1966

and F. Oberhettinger, Tabellen zur Fourier Transformation, Springer-Verlag, Berlin 1957.
[13] C. Williams, D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).
[14] M. Abramowitz and J. A. Stegun, Handbook of Mathematical Functions, National Bureau of Standards, Washington 1964.
[15] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[16] R. Kimmich, and W. Doster, J. Polymer Sci. Polymer Physics Edition **14**, 1671 (1976).
[17] W. Feller, An Introduction to Probability Theory and its Applications, Wiley New York 1968.
[18] G. Voigt, and R. Kimmich, Chem. Phys. Letters **56**, 275 (1978) and Proceedings of the European Conference on NMR of Macromolecules, Sassari, 1978.
[19] H. C. Torrey, Phys. Rev. **92**, 962 (1953).
[20] M. Eisenstadt and A. G. Redfield, Phys. Rev. **132**, 635 (1963).