Nuclear spin relaxation and intermolecular interactions

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1. Introduction

In order to specify what kind of information about intermolecular interactions can be obtained by nuclear spin relaxation, we consider a suitable microscopic representation of a liquid. For reasons which will become clear below, this article is entirely confined to the treatment of the liquid phase. The molecular or microscopic picture of a liquid may be considered to be a system consisting of very many mass points being separated in space. Thus, if there are $N$ mass points, we have at each instant $N$ positions $\mathbf{r}_i$ which are all different from each other. These positions are changing with time and thus $\frac{d\mathbf{r}_i}{dt} \neq 0$, which means that each mass point is also characterized by an instantaneous velocity.

Generally, the motion of the mass points, $\mathbf{r}_i(t)$, is uncorrelated, that is, if $\mathbf{r}_i(t) - \mathbf{r}_i(0)$ represents the displacement vector of the $i$th mass point after a time $t$, then the displacement vector of another mass point $j$, $\mathbf{r}_j(t) - \mathbf{r}_j(0)$, may have any value. Thus the change with time of the vector pointing from one mass point to the other, $\mathbf{r}_j - \mathbf{r}_i$, can be described as an ordinary relative random diffusion process. However, for certain pairs of mass points $i,j$ we observe correlations of the motion, the most important forms of correlations are those for which $|\mathbf{r}_i - \mathbf{r}_j|$ remains unchanged with time, or in other words, the distance between two mass points—apart from vibrational motions—is a constant quantity. Of course, such correlations are characteristic for intramolecular vectors connecting two atoms.

Furthermore, the mass points have another property, they are 'named mass points' in the sense that they represent a certain chemical substance, or, briefly expressed, they have a well defined position $\mathbb{R}_j$ in the two-dimensional coordinate system which is called the periodic table of the elements. In contrast to the positions in ordinary space, $\mathbf{r}_i$, the mass points may have partly the same positions $\mathbb{R}_j$ in the element space, even more than this, in a liquid element all mass points are at the same $\mathbb{R}_j$. For all systems of "reasonable" composition, and those are the systems to be treated here, the number of occupied positions $\mathbb{R}_j$ in element space is small $\leq 10$, say.

Now we consider a molecule as being a set of 'named' mass points. As will be seen below, it is not a simple matter to define a molecule in a liquid on a microscopic level. However let us postulate that the molecule is well defined by some macroscopic analytical or chemical operation. Here it is sufficient to require that within the molecule at least partly there exist strict distance and possibly also angular correlations between the mass points (atoms) which allow the construction of a three-dimensional coordinate system in the molecule. This means that at least partly the representation of the molecule as a rigid body is possible. Let us now consider a pair of molecules. Then
we will find that the origin of the coordinate system of the second molecule is located at
\( r \equiv r_{12} \) with respect to the coordinate system in the first molecule. Let the relative
orientation of the two molecules (rigid body coordinate systems) be given by the set of
three Eulerian angles, \( \Omega \). Then the potential energy in vacuo of this pair as a function of \( r \)
and \( \Omega \),

\[
E = E(r, \Omega),
\]

we denote by the intermolecular interaction energy. It should be emphasized that this
concept refers to the isolated pair of molecules, thus the operational definition of
\( E(r, \Omega) \) involves the separation of the molecular pair from the bulk of the liquid and
transferring it into the extremely diluted gas phase. Furthermore, we have already
indicated that in many cases the molecule is not a rigid body, it may exist in several
conformations, then we would have an intermolecular interaction energy

\[
E = E(r, \Omega, \alpha),
\]

where \( \alpha \) characterizes any appropriate internal degree of freedom which is virtually
independent of \( r \) and \( \Omega \).

A special form of intermolecular interaction is the H-bond. For the treatment to be
given below it is convenient to present a definition of the H-bond here. We select from
the totality of molecules those which contain an H atom being separated by \( \approx 1 \) Å from
one of the atoms O, N, F (C only in exceptional cases, e.g. CCl\(_3\)H). Then again, formally
(1) or (1a) constitute what we call a hydrogen bond. The classification of an
intermolecular interaction to be a H-bond may also be confined to a certain range or
interval of \( r \) and \( \Omega \), which would more strongly emphasize the character of a bond, but
this is merely a matter of convention. Now, if we have an H-bond, \( E(r, \Omega) \) has some
particular features. We quote four which seem to be the most important ones. (1)
\( E(r, \Omega) \) certainly contains some electrostatic admixtures, the one of lowest multipole
character being the electric dipole-dipole interaction. (2) If we choose the zero of \( E(r, \Omega) \)
at very large separation, then the minimum value of \( E(r, \Omega) \) is lower than that found for
other molecules of comparable mass and composition. (3) The separation of the
minimum for the potential energy from the hydrogen atom is particularly small, such
that the distance between the oxygen or corresponding other atoms is \( \leq 3.4 \) Å and
\( \geq 1.7 \) Å. (4) finally, the H-bond has the following peculiarity: Assume for a moment that
all other atoms apart from those H's having a distance \( \approx 1 \) Å from O, N, or F constitute
a rigid molecule. Let the intramolecular positions of one of these atoms be \( r_{1i}, i = 1, 2 \),
where \( i = 1, 2 \) means: in the first and second molecule, respectively. Then we may
investigate the potential energy function

\[
E^* = E^*(r, \Omega, r_{11}, r_{12}),
\]

\( i.e. \) we take the potential energy as a function of \( r, \Omega, \) and the two atomic positions \( r_{11},
\)
\( r_{12} \). The result will be that the dependence of \( E^* \) on \( r_{11} \) and \( r_{12} \) is virtually independent
of \( r \) and \( \Omega \). Next we select the H-atoms adjacent to the N, O, or F, let their
intramolecular positions be \( r_{H1}, r_{H2} \) (if there is only one such H-atom per molecule,
otherwise we have to add one more index). We investigate again the potential energy

\[
E^* = E^*(r, \Omega, r_{H1}, r_{H2}),
\]

and we will find that the dependence of \( E^* \) on the two positions \( r_{H1}, r_{H2} \) varies strongly
when another set of variables \( r, \Omega \) is chosen. In particular, for certain configurations
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\[
\left( \frac{\partial E^*}{\partial r_{hi}} \right)_{r,\Omega, T} \to \text{comparatively small.} \tag{3}
\]

The region of \( r \) and \( \Omega \) for which (3) is valid defines the H-bond in a narrower sense.

The following two things will have become clear from the description of the liquid system given so far:

1. We wish to apply nuclear spin relaxation with the aim of obtaining information about \( E = E(r, \Omega) \).
2. \( E = E(r, \Omega) \) is a continuous function in six-dimensional space, so it will certainly not be possible to get complete information about \( E(r, \Omega) \), the information has to be a truncated one. Moreover, as we have seen, \( E = E(r, \Omega) \) is defined as a property of an isolated molecule pair \textit{in vacuo}, it raises the question of which of the properties of \( E(r, \Omega) \) is preserved if we merge the pair of molecules in the bulk of the liquid, the object of our experimental procedures.

A rigorous and general answer to the latter question cannot be given. However, in principle the answer should come from the calculation of configurational distribution functions. To characterize the situation, let us return to the assembly of named point masses representing the microscopic picture of the liquid. It is a postulate of the atomistic description of matter that—at least in classical systems—a microscopic observer can perform measurements of the positions \( r_i \) of the particles. From our knowledge of the nature of the system we can, in principle, make predictions of the probability that the microscopic observer finds certain positions. These predictions involve the laws of classical mechanics together with the particular reasoning of statistical mechanics. It is fairly clear that the probability of finding any mass point (atom) of kind \( k \) at a given position \( r \) is \( N_k/V \cdot dr \) where \( N_k \) is the total number of particles of type \( k \) and \( V \) is the volume of the system. One sees that this probability is independent of the system. However, if we ask what the probability is of finding a second atom at \( r \) relative to the first one, it can only be independent of \( r \) if the atoms considered are far apart. At smaller separations, the probability \( p(r)dr \) is distance dependent. Furthermore, as we saw when the molecules can be considered to be rigid bodies or partly rigid bodies, then a pair of molecules is not only characterized by the vector \( r \) pointing from the origin of one intramolecular coordinate system to that in the other one, the relative orientation has also to be given. Then we may ask what is the probability density \( p(r, \Omega) \) for the microscopic observer of finding a pair of molecules being characterized by the set of quantities \( r \) and \( \Omega \). For this probability density we can formally write:

\[
p(r, \Omega) = \frac{N}{V 8\pi^2} \exp \left[ -\tilde{E}(r, \Omega, T)/kT \right], \tag{4}
\]

where \( N \) is the total number of molecules in the system, the probability distribution of which we wish to predict or to study. The exponent is dimensionless, thus the quantity \( \tilde{E}(r, \Omega, T) \) must be of the dimension of energy. Since in general the left-hand side of (4) is unknown, \( E(r, \Omega, T) \) represents nothing more than a transcription of the unknown function \( p(r, \Omega) \) into the function \( \tilde{E}(r, \Omega, T) \), consequently \( \tilde{E}(r, \Omega, T) \) is also an unknown function. \( \tilde{E}(r, \Omega, T) \) is designated as the potential of mean generalized forces for reasons which cannot be explained in detail here. The question arises: what is the relation between \( E(r, \Omega) \) as given by (1) and \( \tilde{E}(r, \Omega, T) \) occurring in (4)? It is obvious that \( \tilde{E}(r, \Omega, T) \) is some kind of superposition of all the effective interactions in the liquid to
yield the occurrence probability for a certain pair of configurations. The superposition involves the temperature because in some way the relevant distributions are governed by the temperature. In contrast to this, \( E(r, \Omega) \) does not contain a temperature dependence, it is defined in connection with one isolated particle pair in vacuo where the temperature has no physical meaning. Now, the only possibility for us to make any progress at all towards the aim we have envisaged is to set

\[
E(r, \Omega) \approx \tilde{E}(r, \Omega, T)
\]

(5)

In general the justification of this approximation may be very doubtful, there may be cases where \( E(r, \Omega) \) is much larger than \( \tilde{E}(r, \Omega, T) \), perhaps twice as large, this will probably be the case if we have fairly long range intermolecular interactions, as in the presence of hydrogen bonds as we have already mentioned. In principle, of course, within the framework of statistical mechanics \( \tilde{E}(r, \Omega, T) \) should be fully determined by \( E(r, \Omega) \), however, the relevant equations connecting these two quantities, even if we postulate that they are known, are mathematically very complicated. As will be shown below, as approximate as it may ever be, (5) represents the first link between the intermolecular interaction energy and the nuclear magnetic relaxation process.

The information contained in (4) can be reduced by an averaging procedure with respect to the orientation. We once again consider the atom \( k \) which is one of the constituents of the molecule in question. Assume that we have a particular pair configuration in which the intermolecular distance between the atoms \( k \) is \( r_{kk} \). Now we average over all orientations \( \Omega \) and \( r \) values which are compatible with \( r_{kk} \). This averaging procedure must also be done for all directions of \( r_{kk} \) with respect to the intramolecular reference system. The result is the \( k-k \) atomic pair distribution function

\[
p(r_{kk}) = N_k \exp \left[ -\frac{\tilde{E}(r_{kk}, T)}{kT} \right]
\]

(6)

a quantity which is well-known, in particular from the evaluation of x-ray, neutron, and electron scattering experiments. It gives the probability density of finding the atom \( k \) at a distance \( r_{kk} \) anywhere around the reference atom \( k \). A typical representation of \( p(r_{kk}) \) is given in figure 1 (see e.g. Egelstaff 1967; Hansen and McDonald 1976; Kohler 1972; Croxton 1975). Now in the light of (6) the intermolecular interaction

![Figure 1](image_url)

Figure 1. A typical atomic pair distribution function given in the number density scale.
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energy seems to be smeared out spherically symmetric around the reference atom. Clearly in such a situation the intermolecular interaction energy seems to be a quantity which only depends on the mutual separation of the atom in question. It should be noted that in x-ray and electron scattering experiments—apart from other fundamental problems—difficulties occur when there are several atoms of kind \( k \) in the molecule, then the requirement that (6) tells us something about the intermolecular interactions is no longer fulfilled. In nuclear magnetic relaxation experiments the situation is more favourable because the isotopic substitution techniques can be applied in many cases to distinguish between inter- and intramolecular interactions. In a more restricted sense isotope substitution is also helpful in performing and analyzing suitable neutron scattering measurements (see e.g. Enderby and Neilson 1979). Details of the isotope substitution method will be given below. Thus in a quite general sense, for the nuclear spin relaxation studies to be described here (6) is a fairly basic relation, however, in order to be connected with direct experimental results it has to undergo a further averaging process, thus the information available is much more limited as will become clear below.

In order to proceed further, at the moment it is convenient to consider (6) as an intermediate result to which we shall return later and go back once again to the microscopic model of the liquid as being a system of 'named' mass points in which certain configurational and motional correlations exist.

We have now to direct our attention to the fact that some of the mass points may have an intrinsic angular momentum, the nuclear spin, and connected with it a magnetic moment. Whether the atom has a nuclear moment or not depends on the particular isotopic species which it represents. So far we did not mention the electronic cloud surrounding the mass points. Indeed, for the most important physical facts we are going to describe, it suffices to consider the atoms as being simple named mass points, referring to the nuclear spin variable; and certain further specification of the isotopic individuum in some cases is necessary, however, for other types of experiments where we need to take into account the electron cloud indirectly because it may produce an electric field gradient at the nuclear site. If the nucleus has a spin \( I > \frac{1}{2} \), it will also have an electric quadrupole moment which interacts with the electric field gradient. Only quite occasionally we shall meet a situation where the electron cloud as well has an intrinsic angular momentum, the electron spin—again this spin is connected with a magnetic moment.

The sum of all nuclear magnetic moments, of course, is a macroscopic property of the liquid and thus it must be an observable, otherwise there would be no reason to speak of the nuclear magnetic moments. If we refer the sum of all these nuclear moments to unit volume, we have the nuclear magnetization \( \mathbf{M} \) of the liquid in question. It is clear that in ordinary thermodynamic equilibrium the observable mean value of the magnetization is zero. However, in the presence of an external magnetic field the nuclear magnetization does not vanish and if we apply external magnetic fields which are time dependent, then in general the nuclear magnetization will also vary with time; thus we obtain for the three components of the nuclear magnetization

\[
\frac{dM_x}{dt} \neq 0, \quad \frac{dM_y}{dt} \neq 0, \quad \frac{dM_z}{dt} \neq 0.
\]

These observable quantities, under suitable conditions are characterized by certain macroscopic kinetic parameters \( 1/T_1 \) and \( 1/T_2 \) being intrinsic properties of the system.
and which as a consequence are the object of the experimental investigations yielding
the desired information about the intermolecular interaction relevant for the liquid in
question. $1/T_1$ and $1/T_2$ are called the longitudinal and transversal relaxation rates,
respectively, and describe the change with time of the components of \( \mathcal{M} \) in the case that
the external magnetic field is independent of the time (Abragam 1961; Farrar and
Becker 1971; Slichter 1980). Then if at any instant we have $\mathcal{M}_z, \mathcal{M}_y, \mathcal{M}_x \neq 0$, $1/T_1$ and
$1/T_2$ are defined by the relations

$$
\frac{d\mathcal{M}_z}{dt} = \frac{1}{T_1} (\mathcal{M}_z^0 - \mathcal{M}_z),
$$

$$
\frac{d\mathcal{M}_x}{dt} = -\frac{1}{T_2} \mathcal{M}_x, \quad \frac{d\mathcal{M}_y}{dt} = -\frac{1}{T_2} \mathcal{M}_y,
$$

where $\mathcal{M}_z^0$ is the equilibrium magnetization in the presence of the static field, the two
equations containing $1/T_2$ are referring to the transverse components of $\mathcal{M}$ measured in
a coordinate system which rotates with the nuclear magnetic resonance frequency.

Now let us return to (6). It may be seen that $p_{kk}(r)$, or more generally, $p(r)$, does not
contain the time, it is an equilibrium property which of course is time independent. On
the other hand, the macroscopic quantity $\mathcal{M}$ we are observing is a time dependent
quantity, it is the movement towards equilibrium with which we are concerned. Thus it
is natural to expect that the observables $d\mathcal{M}_i/dt$, $i = x, y, z$, are not primarily
determined by the time independent $p(r)$. There must be some internal microscopic
motion which causes or produces the macroscopic change with time. In fact, it is the
motion of the mass points carrying the nuclear magnets which makes $d\mathcal{M}_i/dt \neq 0$, and
in particular, it is the fluctuating nuclear magnetic interaction energy (or quadrupole
interaction energy) between the mass points which is important. From this insight it will
be immediately clear that the only thing which is relevant for us is the relative motion of
a given mass point with respect to another one, of course then the total effect comes
from the superposition of all the fluctuating pair interactions.

It is important to clarify the term 'interaction energy' here, because it occurs in two
different senses. First we have the intermolecular interaction $E = E(r, \Omega)$ between the
molecules which causes the particular structure of the liquid. Then secondly we have the
interaction energy between the nuclear magnets (or between the nuclear quadrupole
moments and the electric field gradients) which we may denote by $V(r)$ where now the
vector $r$ connects the two nuclei—or the reference nucleus with a representative site of
the source of the field gradient. $V(r)$ does not at all influence the structure of the liquid
because we have $V(r) \ll E(r, \Omega)$. Thus the interaction energy $V(r)$ is essentially applied
to probe the intermolecular energy we wish to study. After these introducing remarks it
will be understandable that the microscopic quantity we need in order to link it with the
macroscopic observable is the motion of one mass point relative to the other one, and
this property is described by the quantity $\mathcal{P}(r_0, r, t)$ which is the microscopic density
self-correlation function of atom 2 relative to the atom 1. Expressed in another way,
$\mathcal{P}(r_0, r, t)$ is the probability density of finding at time $t = 0$ a given atom—here
numbered as atom 2—at $r_0$ relative to another atom—here numbered as atom 1—and
of finding the same atom 2 at time $t = t$ at $r$ relative to atom 1. It is clear that in general
$\mathcal{P}(r_0, r, t)$ as a full function of the three variables $r_0, r$, and $t$ is not available, this is the
same situation as we had found it for the two time-independent probability distribution
functions we have discussed so far. However, for the readers convenience, it should be
stated that one limiting form of \( \mathcal{P}(r_0, r, t) \) which can immediately be written down is
\[
\mathcal{P}(r_0, r, t) = c' \left[ 4\pi(D_1 + D_2) t \right]^{-3/2} \exp \left[ -\frac{(r - r_0)^2}{4(D_1 + D_2) t} \right],
\]
(9) if \( r_0 \) is very large compared with the radius \( r^*_2 \) of the second coordination sphere of atom 1. \( r^*_2 \) is defined by the location of the second minimum of the 1-2 pair distribution function, \( c' \) is the number density of the atom 1 and \( D_1 \) and \( D_2 \) are the self-diffusion coefficients of the molecules carrying the atom 1 and 2, respectively, and the factor of \( c' \) in (9) is the appropriate solution of the ordinary diffusion equation.

From the inspection of (9) it is directly suggested that in the general case we may write for \( \mathcal{P}(r_0, r, t) \)
\[
\mathcal{P}(r_0, r, t) = p(r_0) P(r_0, r, t),
\]
(10) where \( p(r_0) \) is very often called the 'propagator', it is the joint probability density of finding at time \( t \) atom 2 at \( r \) relative to atom 1 if it is known that at \( t = 0 \) the relative location of 2 was \( r_0 \), \( p(r_0) \) is the radial pair distribution function with respect to the pair of atoms 1 and 2 and is exactly the quantity we have given as (6). There we had considered the special case that the vector \( r \) connects two atoms of kind \( k \), here the atoms 1 and 2 may be of any kind, either different or the same; the subscript 0 was not needed in (6) because time did not enter the picture. If we are not explicitly interested in the time development, we shall again omit the subscript 0 in the following.

The macroscopic movement of the nuclear magnetization of course must involve a time integral over \( \mathcal{P}(r_0, r, t) \), moreover due to the nature of the system, we can only be concerned with an integration over all pair configurations, thus an expression
\[
\int_0^\infty \left( \int p(r_0) P(r_0, r, t) \, dr_0 \, dr \right) Dt,
\]
enters the microscopic theory. Finally, as was already mentioned, the nuclear interaction \( V(r) \) must also occur in the expression determining the time dependence of the magnetization, thus we arrive at the expression
\[
\int_0^\infty \exp \left( -i\omega t \right) \left\{ \int p(r_0) V(r_0) V(r) P(r_0, r, t) \, dr_0 \, dr \right\} dt,
\]
(11) where \( \omega \) is the nuclear magnetic resonance frequency, the factor \( e^{-i\omega t} \) reminds us that we have to do with a resonance phenomenon in which in some way transitions from one state to another are of importance. As will be seen below, expressions of the type (11) have to be evaluated in order to get information about \( p(r_0) \) from spin relaxation data. Indeed, the reader will agree that the access to the intermolecular interactions via the study of nuclear magnetic relaxation is only a very indirect one. And one fact which we have not mentioned yet should not be overlooked, namely, that the propagator \( P(r_0, r, t) \) is also determined by the same intermolecular potential \( E(r, \Omega) \) which determines \( p(r) \). Thus, in order to obtain the very limited information about \( p(r) \), in the ideal case it is supposed that \( P(r_0, r, t) \) which is determined by the same intermolecular forces, is already known. This is of course a presupposition which is never fulfilled.

At the end of the introduction it should be mentioned that the translational motion can directly be studied by an NMR technique. Spin-echo methods (Abragam 1961) allow the measurement of the self-diffusion coefficient. The dephasing of transversal magnetization firstly depends on 'natural' relaxation processes. In addition a specific
molecule moves from one particular geometric locus inside the sample to a different one by translational motion. If both loci have a different value of the magnetic field, the dephasing processes are different. With a known magnetic field gradient over the sample region this second process enables a direct evaluation of $D$. These are the quantities occurring in (9), both the single values $D_1$ and $D_2$ can be measured in favourable cases. The value of $D$ of one special chemical system can be discussed by comparing it with the $D$ of a suitably chosen reference state. Intermolecular interactions result in characteristic changes. To give an example we expect a slowing-down of the translational motion for a system forming higher aggregates. The determination of $D$ will be a great aid in the interpretation of the nuclear magnetic relaxation rates.

Two final comments should be added. There is, in general, no other method which in a clear cut way gives better information about $E(r, \Omega)$ or $E(r)$ in molecular liquids. Secondly, in solids $P(r_0, r, t)$ or $r \neq r_0$ in most cases is a very small quantity, therefore the methods of description and evaluation we present in this article do not apply to solid state NMR investigations. In the solid the intermolecular interactions are manifested by the respective distances in the crystal structure (Schuster et al 1976) or by the kind of the vibrational motion (Anderson et al 1973). If there are molecular motions in the solid leading to nuclear magnetic relaxation processes, then these motions mostly are also determined by intramolecular forces, only in a few cases does the whole molecule perform a rotational motion and thus reflect intermolecular interaction alone (see e.g. Walker 1980). Although solid state NMR can yield certain information about intermolecular forces, for reasons of room the respective topics will be omitted in this article (Mehring 1976; Spiel 1978b; Owens et al 1979).

2. The intermolecular relaxation rate

2.1 Some introductory remarks

We have considered a system consisting of $N$ molecules, each of them carrying $n$ nuclear (or electron) spins. Then the total relaxation rate $1/T_1$ of the nuclear spin system is caused by the magnetic interaction of each of the nuclei with $n-1$ nuclei in the same molecule and $(N-1)n$ nuclei in other molecules. $1/T_1$ is defined by (7). Thus, in general $1/T_1$ has to be separated into two contributions denoted as intra- and intermolecular relaxation rates, $(1/T_1)_{\text{intra}}$ and $(1/T_1)_{\text{inter}}$ (Abragam 1961; Hertz 1967a)

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}}. \quad (12)$$

According to the programme given in the introduction, the systems under consideration will be liquids in all cases. It was already indicated that the denotations intramolecular and intermolecular are not without problems, this requires a definition of a 'molecule' in the liquid phase. In the gaseous phase a molecule may be defined by the respective equations of state, as e.g. by the relation $pV = (m/M)RT$. In the liquid state intermolecular interactions may cause correlations termed by chemists as complex formation or as association. Indeed, a wide range of degrees of association is observed in liquids and liquid mixtures and the concept of a molecule may require a careful definition. In favourable cases (12) itself may be used as a definition of the molecule, the result may be different from the usual concept adopted by chemists. In such a case the classification will be justified by the finding that correlated motions of the various spins
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during an observation time of the order of \(10^{-11}\) s yield a perfect prediction of \((1/T_1)_{\text{intra}}\).

However, in general one classifies the interactions due to the geometry of the ordinary chemical molecules. Nevertheless, the existence and the treatment of intermolecular correlations is a problem which makes the understanding and interpretation of intermolecular contributions to nuclear magnetic relaxation in liquids difficult and which has not been accorded proper attention in the literature in many cases.

Being concerned with intermolecular relaxation contributions one is usually faced with the magnetic dipole-dipole interaction as the relaxation mechanism. Indeed, in the present chapter only this interaction will be considered as the relaxation producing mechanism. Relaxation by spin-rotation and chemical shift anisotropy are usually considered typically intramolecular processes. This is true if the relaxing nucleus is part of a molecule. However, it has been shown recently that if the relaxing nucleus is located in a monoatomic ion, intermolecular spin-rotation and chemical shift anisotropy may determine \(1/T_1\) (Schwartz 1976). There is also some evidence for such contributions to the relaxation of OH protons in the first hydration sphere of ions (Langer and Hertz 1977; Gill et al 1976).

If the relaxing nucleus possesses spin \(I > 1/2\) the relaxation process is usually dominated by quadrupolar interaction. Also in this case \(1/T_1\) may be governed by intermolecular interactions, if the nucleus is located within a monoatomic ion or an ion exhibiting spherical symmetry around the nucleus (Hertz 1973a, b; Weingärtner and Hertz 1977). For the latter topics the reader is referred to review articles recently published by various authors (Lindman and Forsén 1976, 1978; Wehrli 1979).

2.2 Some basic equations

According to the basic theory, the intermolecular relaxation rate \((1/T_1)_{\text{inter}}\) (as also the intramolecular one) is given by a linear combination of a number of spectral densities \(J(\omega)\) (Abragam 1961; Hertz 1973b)

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = K \sum_i J(\omega_i).
\]

The summation is over a set of frequencies \(\omega_i\) given by the theory and \(K\) is a constant involving the nuclear properties of the interacting system. The frequencies \(\omega_i\) are certain linear combinations of the nuclear magnetic resonance frequencies of the interacting nuclei. Let us treat here systems consisting of like spins \(I\), the extension to systems of unlike spins being more complicated (Abragam 1961) details need not be considered, the final formulas to be used show only minor modifications. Then \((1/T_1)_{\text{inter}}\) is given by the relation

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{8\pi}{5} \gamma_i^2 h^2 I(I+1) \left\{ J(\omega) + 4J(2\omega) \right\},
\]

\(\gamma_i\) is the gyromagnetic ratio of the spin \(I\), \(J(\omega)\) is the Fourier transform of the time correlation function \(G(t)\) describing the time evolution of the magnetic dipole-dipole interaction which was denoted by \(V(r)\) in the introduction:

\[
J(\omega) = \int_0^\infty G(t) \exp(-i\omega t) \, dt,
\]
\[ G(t) = \frac{N \mathbb{V}_2^m(0)}{r^3(0)} \mathbb{V}_2^m(t), \]  

\( N \) is the number of interaction partners. The vector \( r \) connects the reference nucleus with its interaction partner, \( r(0) \) is the vector at \( t = 0 \). The functions \( \mathbb{V}_2^m(\theta, \phi) \) are the spherical harmonics of second degree and \( m \)th order, depending on the polar and azimuthal angles \( \theta \) and \( \phi \) of the vector \( r \) relative to the laboratory system, the \( z \)-direction is defined by the magnetic field. The interaction partners undergo diffusion relative to each other, so we have \( r = \{ \theta(t), \phi(t), r(t) \} \). Since in an isotropic system \( G(t) \) does not depend on \( m \) (Hubbard 1969) the superscripts \( m \) may be dropped. Next, we reformulate (16) as first introduced by Oppenheim and Bloom and by Abragam (Oppenheim and Bloom 1961; Abragam 1961) to give

\[ G(t) = 4\pi r_o^2 p(r_0) \frac{r^3}{r^3} P(r_0, r, t) dr_0 dr. \]  

\( 4\pi r_0^2 p(r_0) dr_0 \) is the probability of finding an interaction partner (spin \( I \)) within a spherical shell of volume \( 4\pi r_0^2 dr_0 \) around the reference nucleus selected at random. \( p(r_0) \) is the quantity we have already discussed, see (6). It will be seen that (15) and (17) together represent a verification of our statement that the expression (11) is of dominant importance to determine the intermolecular nuclear magnetic relaxation rate. A first coordination number with respect to the spin \( I \) may be defined via

\[ n_c = 4\pi \int_0^{r_1} p(r_0)r^2 dr_0, \]  

where \( r_1 \) defines the range of the first coordination sphere.

As already explained, the propagator \( P(r_0, r, t) \) in (17) determines the probability that at time \( t \) a particle is in the volume element \( dr \) at \( r \) relative to the reference nucleus, if we know that it was at \( r_0 \) at \( t = 0 \). Thus, the propagator involves the information on the dynamical behaviour of the system.

The fundamental importance of (17) for all further treatments requires some further comments. In (17) it has been assumed that the total correlation function is the sum of \( N \) independent correlation functions which implies that all cross terms between different particles are neglected. This results in the factor appearing before the integral in (17). To the authors' knowledge no treatment considering this and related problems of intermolecular nuclear magnetic interactions has been given as yet. However, it should be mentioned that other relaxation mechanisms, in particular quadrupolar interaction, are markedly influenced by such higher-particle correlations (Hertz 1973b).

Furthermore, it seems to be worth to recall the exact meaning of the propagator. By definition \( P(r_0, r, t) \) yields the information on the motion of a particle as seen from another one, i.e. it is not the 'absolute' translational motion, measured in the laboratory system. Thus, in a strict sense \( P(r_0, r, t) \) does not yield information on the self-diffusion process and \( (1/T_1)_{\text{inter}} \) cannot be used to determine the self-diffusion coefficient \( D \) as recently suggested (Burnett and Harmon 1972). Rather, one has to introduce a model which relates self-diffusion to relative diffusion. This fact distinguishes the dynamic information obtainable from \( (1/T_1)_{\text{inter}} \) from that available from quasielastic neutron scattering experiments and direct self-diffusion measurements. It is known from the theory of neutron scattering (Egelstaff 1967) that the intensity of the scattered neutrons
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is the twofold Fourier transform of the translational propagator of the scattering particle, the latter being denoted as self-contribution of the van Hove correlation function. Therefore, within this nomenclature the propagator occurring in the theory of intermolecular dipole-dipole relaxation may be considered as a ‘relative’ self-contribution of the van Hove correlation function.

2.3 Model propagators and pair distribution functions

We see from (14), (15), and (17) that, in order to predict \((1/T_1)_{\text{inter}}\), we need the knowledge of both, the pair distribution function and the propagator. Thus the standard procedure would be to assume a certain \(p(r_0)\), to derive from this the propagator \(P(r_0, r, t)\) by the aid of statistical mechanics and then to check by trial and error which \(p(r_0)\) gives the observed \((1/T_1)_{\text{inter}}\) as a function of the frequency \(\omega\) and the temperature. Another possibility would be to choose a model pair distribution function which is characterized by a set of constant parameters, and likewise also to construct a model propagator which is described by a set of parameters. The experimental \((1/T_1)_{\text{inter}}(\omega)\) then may be used to determine all these parameters. Both these methods have not been applied yet. And more than this, with two exceptions to be discussed below (Hwang and Freed 1975; Pumpernik and Azman 1975) no attempts have been made to use coupled expressions for \(p(r_0)\) and \(P(r_0, r, t)\). In view of this situation we have only to consider simple models depending on a small set of parameters either for the propagator or the pair distribution function. Then an approximation for \(P(r_0, r, t)\) may be used to obtain information on \(p(r_0)\) and vice versa.

Before proceeding further we may ask: Do we in certain cases have knowledge of \(p(r_0)\) in molecular liquids with which nuclear spin relaxation data can be compared? In fact, an order of magnitude estimate is always given by simple density considerations. Apart from this at present experimental information is scarce. Certain information on \(p(r_0)\) may be obtained from scattering experiments (Zeidler 1980; Bertagnolli and Hertz 1978) but the particular interest in nuclear magnetic relaxation is devoted to proton distributions which are hard to obtain if isotopic substitution by deuterons is not feasible. Some progress has been obtained in a recent study on neutron scattering in the proton-carrying liquid CHCl₃ (Bertagnolli and Chieux 1980). Apart from such measurements further approximate information may be obtained by molecular dynamics simulations which have the advantage that beyond the equilibrium properties information on the dynamical behaviour are also provided (McDonald 1978; Kushik and Berne 1978).

2.3a. Models neglecting pair correlation effects: At first, we consider the propagator for the free diffusion. Assume that at \(t = 0\) the nucleus is at \(r = 0\), then at a sufficiently long time we have (Abragam 1961)

\[
P(r_0, r, t) = (4\pi Dt)^{-3/2} \exp\left(-r^2/4Dt\right),
\]

which is the solution of the translational diffusion equation,

\[
\frac{\partial P(r, t)}{\partial t} = D \nabla^2 P(r, t).
\]

This Gaussian form of the propagator represents the long time limit in which all translational propagators must pass for sufficiently long times, when all dynamical detail is averaged out.
Next, we have to construct the relative propagator, entering into (17). The simplest choice is to convert the propagator in (19) to a relative one by replacing $D$ by $2D$ as e.g. suggested by Oppenheim and Bloom (1961). This procedure implies that the translational motion of the particles is totally uncorrelated. Likewise, one may define a relative diffusion coefficient for liquid mixtures of unlike species $A$, $B$ by $D_{\text{rel}} = 2\bar{D} = D_A + D_B$. In fact, from these arguments one sees that we have already the relative propagator in (9). As the simplest 'model' situation one may assume a random particle distribution up to a closest distance of approach $a$. Then $p(r_0)$ is given by the step function

$$p(r_0) = \begin{cases} 0 & \text{for } r < a \\ c' & \text{for } r \geq a' \end{cases}$$

where $c'$ is the number density of particles and $a$ is the distance of closest approach between two spins. A distribution according to (21) has been termed as 'force free model' (Hwang and Freed 1975). The distribution of (21) is shown in figure 2 together with two other very simple model distribution functions. Introduction of these functions into (15) and (17) yields the relations first derived by Pfeifer (1961):

$$J(\omega) = \frac{v}{D} f(x)$$

(22)

Figure 2. Three different possibilities to construct model atomic pair distribution functions. Type (c) depends on the steepness parameter $n$, here we have $n_1 > n_2 > n_3$. 
with
\[ f(x) = \frac{2}{x^5} \left[ \frac{x^2}{2} - 1 + \exp(-x) \left( \left( \frac{x^2}{2} - 1 \right) \sin x + \left( \frac{x^2}{2} + 2x - 1 \right) \cos x \right) \right] \]

and
\[ x = \left( \frac{a^2 \omega}{D} \right)^{1/2}, \]

where \( \nu \) takes account of the fact that the interaction partner may carry \( \nu \) spins.

Introduction of (22) in (14) allows an examination whether the propagator (19) is in principle correct by the observation of \((1/T_1)_{\text{inter}}(\omega)\). It should be recalled that in any case (22) involves the approximation (21).

At this point we should briefly consider the experimental situation. Due to the unavailability of sufficiently high magnetic fields the resonance frequencies \( \nu_1 = \omega/2\pi \) are limited to the order of some 100 MHz at the maximum for protons. However, for liquids of not very high viscosity i.e. diffusion constants in the order of some \( 10^{-5} \text{ cm}^2 \text{ sec}^{-1} \), the characteristic time constants \( \tau_c \) describing the decay of \( G(t) \) may be estimated by the relation \( \tau_c \approx a^2/3D \) (Hertz 1974), which are in the order of \( 10^{-11} \text{ sec} \). Thus we have \( \omega \tau_c \ll 1 \), this situation is termed the ‘extreme narrowing’ limit (Abragam 1961), now \( 1/T_1 \) measures only the zero-frequency behaviour of \( G(t) \), i.e.

\[ J(\omega) = J(0), \]

and the frequency dependence of \( 1/T_1(\omega) \) cannot be realized experimentally. One way out of this difficulty would be to work at much lower temperatures. Unfortunately for most liquids the transition to the solid phase precludes this possibility. Consequently the method to investigate \( P(r_0, r, t) \) is confined to those liquids (with molecules of moderate size) which can be cooled down sufficiently. Glycerol is a favourable example. In figure 3 we present the intermolecular proton relaxation rate as a function of \( t \) at two temperatures (Kintzinger and Zeidler 1973). The data have been fitted to (22) and partly to (26) to be given below. The resulting parameters are \( a = 2.5 \cdot 10^{-8} \text{ cm}, \alpha = 0 \) (see below) for \( T = 30^\circ \text{C} \) \( (D = 3.2 \cdot 10^{-18} \text{ cm}^2 \text{ sec}^{-1}) \) and \( a = 2.3 \cdot 10^{-8} \text{ cm}, \alpha = 0.003 \) (see below) at \( T = 13^\circ \text{C} \) \( (D = 6.5 \cdot 10^{-9} \text{ cm}^2 \text{ sec}^{-1}) \). The diffusion coefficients have been measured independently (Tomlinson 1972; Preissing et al. 1971). It may be seen from the figure that the quantitative fit is relatively poor, but qualitative agreement between theory and experiment is attained. There are fast processes which are not taken into account by (22).

In solutions containing paramagnetic particles the resonance frequency \( \omega_e \) of the electron spin acting as the interaction partner is about three orders of magnitude larger than in those systems where the interaction partner is a nuclear spin. Thus, even with liquids of normal fluidity we have \( \tau_c \omega_e \approx 1 \). Now the form (13) which is valid for the relaxation caused by unequal spins has to be applied, details need not be given here. Studies with solutions of paramagnetic particles have the very great advantage that the intermolecular relaxation rate is the primary experimental quantity, no tedious isotopic substitution experiments are needed (see below). Moreover, the concentration of the electron paramagnetic interaction partner usually is relatively low which facilitates the consideration of relative and collective motions somewhat. Indeed, numerous experimental studies have been performed with solutions of free radicals (see e.g. Dally and Müller-Warmuth 1977, 1978, 1980; Nientied et al 1981), also the electron-nucleus Overhauser effect has been utilized (Müller-Warmuth and Meise-Gresch 1983) which is
another technique to study the frequency dependence of the spectral density $J(\omega)$ as given by (15). It has been shown in these investigations that formulas of the type (13) give an approximate description of the experimental results. The order of magnitude of the self-diffusion coefficient which can be derived is correct, some typical deviations from the expected behaviour at high frequencies have been observed.

Before passing to the next type of approximation, we should mention a difficulty which is inherent in the reduction of the general distribution (4) to the atomic distribution function (6) and which indirectly was already mentioned. Apart from translational motions molecules may also perform rotational motions. Thus the short time behaviour of $P(r_0, r, t)$ may deviate from (19). The fluctuating dipolar interaction is only insensitive to such motion if the interacting nuclei reside in the centres of the molecules. Otherwise, the distance $a$ does not refer to an interaction situation with spherical symmetry and furthermore, there may be an additional modulation of the spin-spin interaction due to molecular reorientation. Propagators which represent a superposition of rotational and translational movements have been given by Sears (1967) and Zeidler (1971). A correction of $(1/T_I)_{\text{inter}}$ by the 'off-center' effect has been discussed by Hubbard (1963). The correction factor is given by an expansion in even powers of $s/r_s$, where $s$ denotes the distance between the spin and the molecular centre and $r_s$ denotes the effective radius of the molecular sphere. A typical situation with $s/r_s = 0.5$ yields an increase of $(1/T_I)_{\text{inter}}$ by 13%. The theory has later been generalized by Harmon (1978) accounting for jump diffusion processes and Zeidler (1975) accounting for pair correlation effects.
Next we consider the simplest improvement of the propagator \(19\). This is a two parameter representation of \(P(r_0, r, t)\) and is based on the pioneering work of Torrey (1953). Torrey has considered the following model: A molecule is bound in a potential well for a mean time \(\tau_0\), after which it leaves the respective site and makes a jump and comes to rest in another well with displacement \(r_1\). After one jump the probability of finding a given displacement \(r_1\) is

\[
P(r_1) = (\frac{3}{2} \pi \langle r_1^2 \rangle)^{-1} \exp \left[ -r_1 / (\frac{3}{2} \langle r_1^2 \rangle)^{1/2} \right],
\]

where \(\langle r_1^2 \rangle\) is the mean square displacement caused by one jump. Defining the self-diffusion coefficient \(D\) by the relation

\[
\langle r_1^2 \rangle = 6D\tau_0,
\]

and introducing a Poisson distribution of jumping times, the following expression for the propagator may be derived (Torrey 1953; Hertz 1974)

\[
P(r_0, r, t) = (2\pi)^{-3} \int_0^\infty \exp \left[ -2D \kappa^2 t/1 + \frac{\langle r_1^2 \rangle}{\sigma^2} \right] \times \exp \left[ -i\kappa (r - r_0) \right] d\kappa.
\]

It will be seen that this propagator is characterized by the two parameters \(D\) and \(\langle r_1^2 \rangle\). It is not an easy matter to state in which way this propagator is connected with the intermolecular interactions. The dependence of \(\tau_0\) on \(E\) is of the type

\[
\tau_0 = \tau_0^0 \exp \left( \frac{E}{kT} \right),
\]

where \(E\) is the effective potential depth, for the mean square path length \(\langle r_1^2 \rangle\) no simple answer can be given. Insertion of (21) and (25) in (17) yields the intermolecular relaxation rate \((I = 1/2, \text{equal spins})\)

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{3\pi}{5} \gamma^4 \hbar^2 c' \frac{a^3}{\alpha \omega} \left\{ f(\alpha, x) + 2f(\alpha, 2^{1/2}x) \right\}
\]

with

\[
f(\alpha, x) = \frac{2}{x^2} \left\{ u \left( 1 - \frac{1}{u^2 + v^2} \right) + \exp \left( -2v \right) \left[ u \left( 1 + \frac{1}{u^2 + v^2} + 2 \right) \right] \right\}
\]

\[
\cos (2u) + \exp \left( -2v \right) u \left( 1 - \frac{1}{u^2 + v^2} \right) \sin (2u)
\]

and

\[
u = \frac{1}{2} \left( q \left( 1 - q \right) \right)^{1/2}; \quad v = \frac{1}{2} \left( q \left( 1 + q \right) \right)^{1/2}; \quad q = \frac{\alpha x^2}{(1 + \alpha^2 x^4)^{1/2}};
\]

\[
\alpha = \langle r_1^2 \rangle / 12a^2; \quad x = \left( \frac{\omega a^2}{D} \right)^{1/2}; \quad c' = N/V.
\]

In the extreme narrowing situation, \(\tau_0 \omega \ll 1\), (26) simplifies to

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \pi^4 \hbar^2 c' \frac{a^3}{\alpha \tau_0} \left( 1 + \frac{12}{5} \frac{a^2}{\langle r_1^2 \rangle} \right)
\]
or, if one considers the case of unlike spins, one obtains

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{8}{9} \gamma_1^2 \gamma_2^2 \hbar^2 S(S+1) \frac{c'}{a^2} \tau_r \left( 1 + \frac{12a^2}{5 \langle r_1^2 \rangle} \right)
\]

(28)

with

\[
\tau_r = \frac{\langle r_1^2 \rangle}{6D}
\]

\[
D = \frac{1}{2} (D_I + D_S).
\]

Torrey's relations have often been used to interpret \((1/T_1)_{\text{inter}}\). As an example we refer again to the work of Kinzinger and Zeidler (1973). In connection with figure 3 we had already mentioned that a fitting procedure of the intermolecular relaxation rate to (26) yielded \(\alpha = 0.003\), thus the mean flight length characterizing a hypothetical jump has been found to be much smaller than the closest distance of approach. In such a situation, \(a^2/\langle r_1^2 \rangle \gg 1\), (27) and (28) pass to the relations

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{2}{3} \pi \gamma^4 \hbar^2 \frac{c'}{aD}; \quad I = \frac{1}{2}
\]

(29)

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{8}{9} \pi \gamma^4 \hbar^2 I (I+1) \frac{c'}{aD}; \quad \text{for any } I
\]

(29a)

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{4}{9} \pi \gamma^2 \gamma_2^2 \hbar^2 S(S+1) \frac{c'}{aD}
\]

(30)

It is clear that in the situation of extreme narrowing \(D\) and \(\tau_r\) cannot be determined separately. A general procedure is to determine \(D\) by independent self-diffusion measurements and then to calculate \(\tau_r\). However, even in the 'non-extreme narrowing' situation where the frequency dependence of \((1/T_1)_{\text{inter}}\) may be measured one should be cautious in determining dynamical details by this method. This can only be done if the effective observation time \(\tau_{\text{obs}} = (\hbar^2 D)^{-1}\) is smaller than the time constants describing the various elementary processes (Hertz 1974). Therefore, we have to find the smallest value of \(\tau_{\text{obs}}\) which enters into \((1/T_1)_{\text{inter}}\). \(G(t)\) has essentially decayed when the spherical harmonics have changed their sign. The smallest displacement which may cause such a behaviour is of the order of \(a\) and the corresponding observation time is of the order \(\tau_{\text{obs}} \approx a^2/D\) (Hertz 1974). Rewriting the exponential in (25) in a suitable form yields the result

\[
\exp \left[ -2t \left( \frac{\tau_{\text{obs}} + \langle r_1^2 \rangle/6D}{t_{\text{obs}}} \right) \right],
\]

which means that \(\langle r_1^2 \rangle\) or \(\tau_r\) can be observed only if \(\langle r_1^2 \rangle \gg a^2\). Whereas jump diffusion models for liquids have been under debate for a long time, it seems now to be accepted that mean square (free path) jump lengths of the order of molecular diameters do not occur, rather translational motions in liquids are well described by continuous or micro-step diffusion processes (Rahman and Stillinger 1971; Stillinger and Rahman 1974). Thus, the omission of jump diffusion does not seem to be the reason for the deficiency of (22), though inclusion of such effects may bring the theoretical prediction closer to the experimental findings.
2.3b Models taking into account pair correlation effects: We must expect that an important reason for the shortcoming of the above theories is the neglect of pair correlation effects. In fact, the intermolecular interactions in molecular liquids do cause deviations from random particle distribution leading to pair distribution functions of a general type as shown in figure 1. Already in 1957 it had been pointed out that a correct theory should include realistic models for \( p(r_0) \) (Seiden 1957). So various authors have introduced simple model distribution functions and then connected them with a continuous diffusion or Torrey’s model to describe the motional part (Harmon and Muller 1969; Krynicki 1966; Oppenheim and Bloom 1961; Göller et al 1972). However \( (1/T_1)'\text{inter} \) has turned out to be not very sensitive to weak maxima in \( p(r_0) \).

Considering the range of possible variation of \( p(r_0) \), the models discussed in §2.3a must be taken as a particular limiting case, i.e. we were concerned with systems of weak intermolecular interaction, as already mentioned above. Another limiting case is obtained if the intermolecular potential between the interaction partners has a deep minimum such that there is a tight binding between the molecules. In this case the intermolecular distances between the molecules will remain unchanged during the observation time of \( \approx 10^{-11} \) sec. Then \( p(r_0) \) can be approximated by a \( \delta \)-function and \( P(r_0, r, t) \) degenerates to a rotational propagator (Abragam 1961; Hertz 1973c)

\[
P(r_0, r, t) = \sum_{l,m} Y^m_l(\theta_0, \phi_0) Y^m_l(\theta, \phi) \exp \left[ -l(l+1)D_r t \right],
\]

where \( D_r \) is the rotational diffusion coefficient of the molecular system consisting of the associated particles. The rigorous application of this concept leads to the relations for intramolecular relaxation rates as derived by Abragam (1961). The application of (31) to systems with intermolecular binding will be given below.

Clearly, any real system lies between these two limiting cases. Thus, in principle a rotational contribution as given in (31) should in some way be combined with the translational propagator according to (19) or (25). Such a procedure has indeed been performed for electrolyte solutions in various versions (Kramer et al 1965; Hertz 1967c).

Up to now we only have considered the attractive part of the intermolecular potential to be the reason demanding the incorporation of configurational and notional correlations in the treatment. But even if the attractive forces are weak, there remains the repulsive part of the potential which has its simplest manifestation in the volume of the reference molecule not being accessible for the interaction partners. Moreover, if \( \bar{n} \) molecules have given positions, one is not entirely free to choose the position of the \( \bar{n} + 1 \)th molecule. Thus, rigorously the \( N \) spin-spin magnetic interaction pairs are not independent of one another. The corresponding contribution, termed as excluded volume effect, has been a long standing problem. Only recently two groups of workers have independently analyzed this effect. The idea of Hwang and Freed (1975) is to superimpose on the free diffusion a current directed such that the particles are driven away from the interaction partners. This desired property is obtained by deriving the propagator from the Smoluchowski equation which may be considered as a generalization of Fick’s law defining the propagator in (20):

\[
\frac{\partial P(r_0, r, t)}{\partial t} = D_{rel} \nabla \left( \nabla P(r_0, r, t) + \frac{1}{kT} P(r_0, r, t) \nabla E(r) \right)
\]

with the condition

\[
\lim_{t \to 0} P(r_0, r, t) = \delta(r_0 - r).
\]
Clearly (32) passes into the free diffusion limit if the second term on the right-hand side
of (32) becomes negligible, then at \( t > 0 \) the Gaussian form of the propagator is
obtained. However, in general, on the free diffusion the current

\[
-D_{\text{rel}} \frac{1}{kT} P(\mathbf{r}_0, \mathbf{r}, t) \nabla \tilde{E}(\mathbf{r})
\]

is superimposed which drives the particles away from each other.

The potential of mean force \( \tilde{E}(\mathbf{r}) \) is already well known to us, it is related to the pair
distribution function as given in (6). Three subcases have been treated. Only if \( p(\mathbf{r}_0) \) is
given by (11)—‘force-free-model’—an analytical solution is possible. We are mainly
interested in the extreme narrowing limit, then one obtains

\[
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{16\pi}{27} \gamma^4 \hbar^2 I (I + 1) \frac{c'}{aD} = 1,11 \left( \frac{1}{T_1} \right)_{\text{inter}}^{A^T}
\]

where \( (1/T_1)_{\text{inter}}^{A^T} \) stands for the Abragam-Torrey limit, (29a). In this case the effect of the
excluded volume does not influence \( (1/T_1)_{\text{inter}} \) very drastically. The two other pair
correlation functions considered by the authors are the hard sphere pair correlation
function based on the Percus-Yevick equation (Egelstaff 1967) and a hard sphere pair
correlation function obtained from computer simulation, but in these cases the
numerical efforts to get the solution are considerable.

At the same time Ayant et al (1975) have solved the translational diffusion equation
subject to the boundary condition at the surface of a hard sphere. This treatment
corresponds totally to the 'force-free model' discussed above and the results in both
papers are identical.

Summarizing at this stage we feel that the improvements of the Abragam-Torrey
theory on a more rigorous level, though of considerable interest for the understanding
of the underlying physical processes, do not yield a substantial improvement of
agreement between experimental results and theoretical predictions. Moreover in some
cases the computational efforts to be made are considerable. On the other side, as a
positive result of the many investigations dedicated to the intermolecular relaxation
rate as such—including temperature and frequency dependences—we should state that
it has been confirmed that the self-diffusion coefficient of the molecules carrying the
relaxing spins essentially gives the correct description of the motional processes
entering in the total mechanism of nuclear magnetic relaxation.

2.4 The simple approach for \( (1/T_1)_{\text{inter}} \) used in the Karlsruhe laboratory

All treatments so far mentioned turned out to be mathematically difficult because of the
particular functional dependence of the propagator on \( \mathbf{r}_0 \) and \( \mathbf{r} \). This is still the case if
we only treat the limiting case of extreme narrowing \( \omega \tau \ll 1 \), which as we had explained,
has the greatest practical importance due to the high fluidity of ordinary liquids. So, all
the formulas to be given in this section only refer to the situation of extreme narrowing.
In order to simplify the computation we may say that the decay of the correlation
function is caused primarily by the rotation of the vector connecting the reference
nucleus with the interaction partner. Superimposed on the rotational motion there is a
radial displacement of the molecule which also contributes to the decay of the
correlation function \( g(t) \), but the radial displacement does not change the sign of the
magnetic dipole interaction, thus it may be considered to be less effective. Finally we
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have to take into account the rotation of the individual molecule, the ‘tumbling’, both of
the reference and the partner molecule.

These arguments lead us to the use of the rotational propagator (31) alone in (17). Then, after integration over all orientations we obtain from (17)

\[ G(t) = 4\pi \exp \left( -t/\tau_c^* \right) \int_0^\infty p(r_0) r_0^2 \, dr_0/r_0^* \]

where \( \tau_c^* \) is the correlation time which governs the decay of \( G(t) \) and which now we have to consider. The time after which a partner molecule has moved from one side of the reference molecule to the other is

\[ \tau_r \approx (2r_m)^2/2 \cdot 2 \overline{D} = r_m^2/\overline{D}, \]

\( r_m = \) separation between the centre of masses of the reference and partner molecule. In order to take account of the relative motion we have taken 2\( \overline{D} \). We are interested in the correlation time of the spherical harmonics of second order, thus

\[ \tau_m = r_m^2/3\overline{D}. \]

Taking also into account the tumbling of the molecules and the fluctuation of the distance between the molecules one arrives at the estimate (Hertz 1974)

\[ \tau_c^* = a^2/3\overline{D}, \]

where, as before, \( a \) is the closest distance of approach between the two interacting nuclei.

Now any radial distribution function may be introduced in (34). Let us choose the two functions shown in figure 2. The distribution function \( c \) may be written as

\[ p(r_0) = \begin{cases} \frac{p_0}{(r_0 - r^*)^a} & \text{for } a \leq r_0 \leq b, \\ c' & \text{for } r_0 > b, \end{cases} \]

as before \( c' \) is the spin concentration in the bulk liquid, \( p_0 \) is given by the relation

\[ 4\pi \int_a^b p(r_0) r_0^2 \, dr_0 = n_c \]

where \( n_c \) is the first coordination number around the molecular group carrying the reference nucleus. For the parameters \( r^* \) and \( b \) we set:

\[ r^* = ka \]

\[ b = la \]

we set \( k = 0.9 \).

With this distribution function and with (34), (17), (15) and (14) \( (\omega = 0) \) one obtains the intermolecular relaxation rate (like spins, \( I = 1/2 \)) (Hertz and Rädle 1973)

\[ \left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{1}{2} \gamma^* \hbar^2 \frac{n_c}{a^2 \overline{D}} g(n, k, l) + \delta^*, \]
where the function $g(n, k, I)$ is depicted in figure 4. On the other hand, with the
distribution function $b$ of figure 2 the result is

$$
\left( \frac{1}{T_1} \right)_{\text{inter}} = \frac{1}{2} \gamma^4 \hbar^2 \frac{n_c}{a^4 D} + \delta^*,
$$

in both cases

$$
\delta^* = \frac{2 \pi}{3} \gamma^4 \hbar^2 \frac{C'}{b D}.
$$

Equation (37) contains three parameters: the steepness of the pair distribution function,
the depth of the attractive potential, characterized by $n$, the first coordination number $n_c$ of the group or molecule containing the relaxing nucleus, and $b$, the radius of the
second coordination sphere. It may be shown that satisfactory agreement between
experimental results and (39) can be achieved if the experimental diffusion coefficients
are used and if the parameters $n$, $n_c$ and $b$ are suitably chosen, see table 1.

It will be seen that (38) is just the Abragam-Torrey limiting formula given as (29), the
only difference is that now the numerical factor $3/5$ is replaced by the factor $2/3$, which is
an improvement. In fact, whereas the Torrey formula usually yields closest distances $a$
which are too small, (35), when applied alone, leads to more reasonable values of the
closest distance of approach. As will be demonstrated with a number of examples
below, for a wide range of common organic liquids closest distances of approach $a$
\(= 2.5 - 4 \text{Å} \) are obtained with (37).

\begin{figure}[h]
\centering
\includegraphics{figure4}
\caption{The quantity $g(n, k, I)$, characterizing the mean value of $1/r^6$, as a function of the
geometry parameter $I$ (see text). The parameter at the various curves is the steepness parameter
$n, k = 0.9$.}
\end{figure}
Table 1. Methyl halides: intermolecular relaxation rates, closest distances of approach between protons, potential steepness parameter \( n \), and some other structural and dynamic data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>((1/T_1)_{\text{inter}}) at 25°C (s(^{-1}))</th>
<th>(a(\text{A}))</th>
<th>(b(\text{A}))</th>
<th>(n)</th>
<th>(2r_M) ((\text{A}))(^{\text{iv}})</th>
<th>(D) (10(^{-5}) cm(^2) sec(^{-1}))</th>
<th>(E_A) (kJ/mol)</th>
<th>References(^{\text{x}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_3)</td>
<td>9·3 × 10(^{-3})</td>
<td>4·1</td>
<td>8</td>
<td>1·2</td>
<td>5·76</td>
<td>2·5</td>
<td>Caparelli et al (1976); Bender and Zeidler (1971)</td>
<td></td>
</tr>
<tr>
<td>CFCl(_3)</td>
<td>4·0 × 10(^{-3})(^{\text{i}})</td>
<td>4·5</td>
<td>10</td>
<td>1·0</td>
<td>6·04</td>
<td>2·65</td>
<td>9·08</td>
<td>Gillen and Griffith (1972)</td>
</tr>
<tr>
<td>CFB(_3)</td>
<td>1·75 × 10(^{-2})</td>
<td>4·5</td>
<td>10</td>
<td>1·7</td>
<td>6·12</td>
<td>0·8(^{\text{ii}})</td>
<td>12·4</td>
<td>Huang and Rogers (1978)</td>
</tr>
<tr>
<td>CH(_3)Cl</td>
<td>1·0 × 10(^{-2})</td>
<td>4·5</td>
<td>10</td>
<td>1·3</td>
<td>5·26</td>
<td>3·85</td>
<td>7·82</td>
<td>Sandhu (1978)</td>
</tr>
<tr>
<td>CH(_2)Br(_2)</td>
<td>1·8 × 10(^{-2})</td>
<td>4·5</td>
<td>12</td>
<td>1·2</td>
<td>5·54</td>
<td>1·55</td>
<td>9·12</td>
<td>Sandhu (1977); Sandhu (1969)</td>
</tr>
<tr>
<td>CH(_2)I(_2)</td>
<td>4·4 × 10(^{-2})</td>
<td>4·5</td>
<td>12</td>
<td>1·2</td>
<td>5·76</td>
<td>0·56</td>
<td>13·1</td>
<td>Sandhu and Peemoller (1976); Sandhu (1969)</td>
</tr>
<tr>
<td>CH(_3)Br</td>
<td>1·1 × 10(^{-2})</td>
<td>4·5</td>
<td>12</td>
<td>1·6</td>
<td>5·12</td>
<td>3·6(^{\text{iii}})</td>
<td>9·62</td>
<td>Lassigne and Wells (1977b)</td>
</tr>
<tr>
<td>CH(_3)I</td>
<td>1·6 × 10(^{-2})</td>
<td>4·5</td>
<td>10</td>
<td>1·3</td>
<td>5·32</td>
<td>3·5</td>
<td>100</td>
<td>Gillen et al (1971); Zeidler (1965)</td>
</tr>
</tbody>
</table>

\(^{\text{i}}\) Extrapolated from low temperature data; \(^{\text{ii}}\) estimated from viscosity data; \(^{\text{iii}}\) self-diffusion coefficient of C\(_2\)H\(_3\)Br (McLaughlin 1959); \(^{\text{iv}}\) molecular diameter as estimated from molar volume \(V_M\), filling factor 0·666; \(^{\text{v}}\) if two references are given then the second one refers to self-diffusion coefficients; the first coordination number with respect to the molecule has been taken to be \(n_c = 4\) in all cases.
3. Experimental results for pure liquids

3.1 Some general aspects

In a pure liquid a rigorous separation of \( (1/T_1)_{\text{inter}} \) from intramolecular contributions is only possible on performing isotopic substitution experiments (Bonera and Rigamonti 1965; Zeidler 1965). With this method one uses the fact that there may exist more than one isotope of an element exhibiting different gyromagnetic ratios. Such a procedure cannot be performed for all nuclei, but fortunately the isotope pair proton-deuteron allows such measurements.

On the other hand, in a number of liquids showing hydrogen bond formation the isotopic substitution method cannot be applied to the H-bond protons. This is a consequence of the delocalization of the respective proton which we have described in connection with the definition of the H-bond in §1. A method to suppress the exchange effect and to determine \( (1/T_1)_{\text{inter}} \) in favourable cases for H-bond protons as well (Goldammer and Zeidler 1969) has been reported. In the other systems in which proton relaxation is to be observed, and for the alkyl protons of H-bonded liquids, one has to measure \( 1/T_1 \) in a mixture of the normal molecule (containing a OD group for H-bonded liquids) with the fully deuterated molecule. Denoting the mole fraction of the proton containing species by \( x_H \), we have

\[
\frac{1}{T_1} = \left( \frac{1}{T_1} \right)_{\text{intra}} + \left( \frac{1}{T_1} \right)_{\text{inter}} [x_H + \varepsilon (1 - x_H)]
\]  

\[
\varepsilon = \frac{2 I_D (I_D + 1)}{3 I_H (I_H + 1)} = 0.042.
\]

Thus measurements at (at least two) different proton concentrations allow a separation of both contributions. Strictly (39) is only valid if both the normal and the deuterated liquid have the same viscosity, otherwise the difference must be taken into account by an appropriate correction.

Let us briefly discuss the various possibilities for application of (39). If the reference molecule carries more than one proton the intermolecular relaxation rate is usually less than 50% of the total contribution. On the other hand, the molecule often carries no equivalent magnetic nucleus apart from the reference one and the intramolecular contribution with respect to the partial nuclear magnetization considered vanishes. Thus \( 1/T_1 \) directly reflects \( (1/T_1)_{\text{inter}} \). Examples are the relaxation of OH protons in alkyl deuterated alcohols (Güner and Hertz 1972; Bender and Hertz 1977; Berg et al 1976), acids, or of formyl protons in HCOOD (Kratochwill and Hertz 1977) and HCOOND_2 (Leiter et al 1983). A reduction of \( (1/T_1)_{\text{intra}} \) has also been achieved using partially deuterated methyl groups in the compounds CD_2HOD (Gill et al 1976), CD_2HCN (Tokuhir 1979), and CD_2HCD_2COOH (Hertz and Radle 1973).

However, often mechanisms other than dipolar, and in particular spin rotation interaction, cannot be neglected. Thus the proton in CHCl_3 relaxes by intermolecular dipole-dipole and spin rotation interaction (Bender and Zeidler 1971). Since both contributions differ in the sign of the temperature dependence suitable measurements have been performed to separate the two mechanisms (Dinesh and Rodgers 1972). Regrettably, the respective results of Dinesh and Rodgers deviate remarkably from the results of the direct isotopic substitution experiment (Bender and Zeidler 1971).

Several other methods have been suggested in order to separate intra- and
intermolecular contributions. Instead of diluting in the deuterated analogue one may dilute the proton carrying species in a magnetically inert solvent such as CCl₄. However, in the latter case one is concerned with the problem that the correlation time describing the motion of the dissolved molecule differs from that in the pure state. Likewise, one may estimate \(1/T_1\)_{intra} via the deuteron relaxation rate. These procedures are of importance in those cases where proton exchange between the molecules does not allow the separation of \(1/T_1\)_{inter} via the usual isotopic dilution experiment.

3.2 Proton-proton distributions

The earlier work on (inter) molecular relaxation in liquids has been summarized by one of the present authors (Hertz 1967a). To the authors' knowledge no further review including intermolecular relaxation in liquids has been published since then. Most of the earlier data have been reported by Zeidler (1965) who performed the first systematic investigations using the isotopic substitution technique. It should be mentioned that meanwhile \(T_1\) for some systems have been reported which are slightly longer than the values obtained by Zeidler (1965). In this situation one is justified in assuming that the longer \(T_1\) results are the better ones since impure substances and unsuitable equipment have the tendency to shorten \(T_1\) values. The pertinent results of these studies in the light of intermolecular forces will be discussed below.

The following considerations refer only to such work where \(1/T_1\)_{inter} has been determined via the isotopic dilution experiment. Only in cases where such an experiment is not possible other methods are considered. There are numerous papers where intra- and intermolecular contributions have been determined by alternative methods or by an estimate of \(1/T_1\)_{intra}. Clearly, such methods cannot give substantial results on intermolecular relaxation rates.

3.2a Hydrocarbons: Only a small amount of work has been done. Harmon and Muller (1969) have studied the intermolecular proton relaxation rate in liquid ethane. Their conclusion that diffusion occurs via a jump process has recently been criticized by Hwang and Freed (1975) who have pointed out that the failure of the theoretical approach of the Torrey theory may be a consequence of other sources, in particular the 'excluded volume effect'. Data on proton relaxation in cyclohexane and benzene have been summarized by Zeidler (1965).

3.2b Methyl halides: This class of compounds may serve as model or representative compounds for small molecules without strongly specific interactions and without internal flexibility. Within this context there have been a large number of investigations on the dynamical behaviour of such molecules. However, though a lot of data on \(1/T_1\)_{inter} may be found in the respective papers the authors' main interest has been devoted to the intramolecular contributions.

A survey on the respective data on \(1/T_1\)_{inter} is given in table 1. In the second column the intermolecular relaxation rate is shown. Since the values at 298 K are partly taken from graphical representations or are interpolated from the original data, they may involve certain errors. The seventh column shows the corresponding self-diffusion coefficients.

The compound investigated most extensively is chloroform. This molecule provides a rather ideal example to check theories on intermolecular relaxation since it
contains only one proton and the deviation from spherical shape is still tolerable. At 298 K we have \((1/T_1)_{\text{inter}} = 9 \cdot 10^{-3} \text{ sec}^{-1}\), the self-diffusion coefficient is about \(2.5 \cdot 10^{-5} \text{ cm}^2/\text{sec}\) (Bender and Zeidler 1971). The Abragam-Torrey formula (29) yields a distance of closest approach between the protons of \(a = 2.6 \text{ Å}\). Models show that this value is far too small, i.e. the interaction constant works out to be too small. The Hubbard correction (Hubbard 1963) yields a variation of about 10% of the \((1/T_1)_{\text{inter}}\) value calculated from the Abragam-Torrey formula. Also the application of the relation by Hwang and Freed, accounting for the 'excluded volume' effect, yields no substantial improvement.

Let us consider the model evaluated by one of the present authors (HGH), see (37) and (38). For liquids without strong specific interactions the intermolecular potential is flat. In these cases \(g(n, k, l) \approx 0.3\) has proved to be a reasonable value. With \(b = 8 \text{ Å}\) the translational contribution due to the protons beyond the first coordination sphere yields \((1/T_1)_{\text{inter}} = 4.5 \cdot 10^{-3} \text{ sec}^{-1}\) = \(\delta^*\). With \(n = 1, 2\) and a first coordination number \(n_c = 4\) one derives from (37) and (38), \(a = 4.1 \text{ Å}\). From the density of the liquid one estimates a diameter of the chloroform molecule, \(d \approx 5.8 \text{ Å}\). Recent neutron scattering experiments on chloroform have yielded a first peak in the proton distribution at about \(4.3/\text{Å}\) which is also in good agreement with the above result (Bertagnolli 1981). Equations (37) and (38) have also been used for the evaluation of the closest distances of approach for other methyl halides collected in table 1.

For compounds of type \(\text{MeX}_2\text{H}_2\) the difficulty is that there are two protons in equal positions. This may cause a splitting of the first peak in the proton distribution. In principle one may account for this situation choosing a model pair distribution function which exhibits two peaks. However, since the protons are chemically equal it seems to be more appropriate to calculate an effective distance assuming a coordination number, \(v n_c\), where \(v\) is the number of equivalent protons and \(n_c\) is the first coordination number with respect to the molecules. Then the effective distance is an appropriate mean value; one should recall that it is not the algebraic mean, rather a \(1/r^6\) weighted value according to the particular form of (37) when it is rewritten in the form

\[
\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{1}{2} \gamma^* \hbar^2 g(n, k, l) \frac{v n_c}{a^6} \tau^* + \delta^*.
\]

It will be seen from the data summarized in table 1 that the figures obtained are physically reasonable. In particular, the potential steepness parameter \(n\) is close to unity in all cases which demonstrates that the intermolecular forces between these molecules are weak. Strictly speaking, our information refers to the H–H part of the intermolecular potential.

3.2c Nitriles: Proton intermolecular relaxation rates were determined by Zeidler (1965) at 25°C and by Woessner et al (1969) in the temperature range -40 to 70°C. \(^{13}\text{C}\)-\(^1\text{H}\) intermolecular relaxation rates of the nitrile carbon were evaluated by Leipert et al (1974) using an indirect procedure—experimentally separating the non-dipolar part with the help of double resonance techniques and subtracting the calculated intramolecular contribution from the dipolar relaxation rate. A direct method was used by Kratochwill (1978) measuring \(^{13}\text{C}\) relaxation rates in system \(\text{CD}_3\text{CN/CH}_3\text{CN}\). By combining \(^1\text{H}-^1\text{H}\) and \(^{13}\text{C}-^1\text{H}\) intermolecular dipolar relaxation rates and the self-diffusion coefficient the model molecular pair distribution function was evaluated. The distance of closest approach are \(a(\text{CH}_3-\text{CH}_3) = 4.3 \text{ Å}\) and \(a(\text{CN}-\text{CH}_3) = 3.5 \text{ Å}\), which
are nearly independent of temperature (a variation less than 0.1 Å was observed in the
temperature range -40 to 25°C). In the first coordination sphere the molecules are
arranged most probably with antiparallel orientation in accordance with a previous
x-ray investigation of liquid acetonitrile (Kratochwill et al 1973). Using the model
atomic pair distribution functions inherent in the detailed 'correlation cluster model' of
the x-ray investigation intermolecular relaxation rates were calculated, which were in
good agreement with the experimental values, eg at 25°C: \(1/T_1(\text{H}^{-1}\text{H})\)
= 1.88 \times 10^{-2} \text{ sec}^{-1} (expt: 1.80 \times 10^{-2} \text{ sec}^{-1}; Zeidler 1965) and
\(1/T_1(\text{\textsuperscript{13}C}^{-1}\text{H})\)
= 1.12 \times 10^{-3} \text{ sec}^{-1} (expt: 1.05 \times 10^{-3} \text{ sec}^{-1}; Kratochwill 1978).

4. The detection of association by the study of the \(A\) parameter

4.1 Association between equal molecules

The knowledge of the intermolecular relaxation rate can be used to detect molecular
association in liquid mixtures, the term association being understood as a configur-
ationally well defined concept. We are confining the treatment here to binary mixtures;
let us denote the two components as 1 and 2. We first consider a possible association
between particles of similar kind and begin with the definition of the first coordination
number of atom \(i\) with respect to such atoms \(i\) which are not members of the same
molecule. We note that the concept of a first coordination number never refers to a
sharply defined quantity, so we shall give here a number of possible definitions which
are more or less equivalent. This conceptual development will facilitate the understand-
ing of the more general definition to be presented. We begin with the most conventional
form in which we have already used in (18) and (37). The first intermolecular coordination
number of atom \(i\) with respect to another atom \(i\) is given by the expression

\[
n_{ii} = 4\pi \int_{r_i}^{r_i^*} p_{ii}(r) r^2 \, dr \quad i = 1, 2
\]

where \(r_i^*\) is the location of the first minimum of \(g_{ii}(r)\) (see figure 1), and \(g_{ii}\) is the atomic
pair correlation function of species \(i\). \(c_i\) is the corresponding number density. Thus we
have

\[
p_{ii}(r) = c_i g_{ii}(r).
\]

Now we rewrite (40) in the form

\[
n_{ii} = 4\pi c_i \int_{0}^{\infty} \delta_{ii}(r) g_{ii}(r) r^2 \, dr,
\]

where \(\delta_{ii}\) is a step function having the property

\[
\delta_{ii}(r) = 1 \quad \text{for} \quad 0 < r \leq r_i^*,
\]

and

\[
\delta_{ii}(r) = 0 \quad \text{for} \quad r > r_i^* \tag{43}
\]

Next we modify the function \(\delta(r)\) so that it is represented by a Gaussian function,

\[
\delta'(r) = \exp[-\alpha(r-a)^2], \quad r \geq a \tag{44}
\]
According to this defining function we have a modified kind of a first coordination number,

\[ n'_{ii} = 4\pi c'_i \int_a^\infty \delta'_i(r) g_{ii}(r) r^2 \, dr, \quad (45) \]

where \( a \) is a certain atom-atom distance which we may again call the closest distance of approach. The constant \( a \) characterizes the width of the region we wish to count as belonging to the first coordination sphere. At \( r' = a + (1/a)^{1/2} \) we have \( \delta'_i(r) = e^{-1} \), thus \( r' \) should be \( \approx r'_* \).

Finally, we may also define the first coordination sphere by the function

\[ \delta^*_i = a^6/r^6 \]

so that we have

\[ n^*_i = 4\pi c'_i a^6 \int_a^\infty \delta^*_i(r) g_{ii}(r) r^2 \, dr \]

\[ = 4\pi c'_i a^6 \int_a^\infty \frac{g_{ii}(r)}{r^6} r^2 \, dr, \quad (47) \]

where now we have \( \delta^*_i(r) = 1/e \) for \( r = a e^{1/6} = 1.16a \).

The next step is to introduce reduced first coordination numbers \( (n_{ii})_r, (n_{ii})_r, \) and \( (n^*_i)_r \) by the definitions

\[ (n_{ii})_r = n_{ii}/c'_i \]

\[ (n_{ii})_r = n_{ii}/c'_i \]

\[ (n^*_i)_r = n^*_i/c'_i. \]

(40a) (45a) (47a)

It will be seen that in the event that \( g_{ii}(r) \) is independent of the composition over the entire composition range, the reduced first coordination numbers are strictly constant quantities. Or, expressed in other words, in this situation the first coordination number of atom \( i \) with respect to \( i \) is proportional to the number density of \( i \). Thus we say, if in a given mixture \( g_{ii}(r) \) does not change with the composition, then there is no association in this system with respect to the atomic species \( i \). If, however, with decreasing concentration of component \( i \) the corresponding reduced first coordination number \( (n_{ii})_r \) increases, then we say that \( i-i \) intermolecular atomic association exists in the mixture. In terms of \( g_{ii}(r) \) this means that \( g_{ii}(r) \) changes its form such that the product \( \delta_{ii}(r) g_{ii}(r) \) becomes larger, i.e. \( g_{ii}(r) \) becomes larger in those regions where \( \delta_{ii}(r) \) is larger and this is in the close neighbourhood of the reference atom. This way of systematic description requires a designation for a situation which usually is not employed. Namely, we may also have the case that the reduced first coordination number \( (n_{ii})_r \) decreases if the concentration of \( i \) decreases. Now we say that on diluting the component \( i \), de-association with respect to atom \( i \) occurs in the mixture. It is clear that in this event the pair correlation function \( g_{ii}(r) \) changes its form such that in regions around the reference atom for which \( \delta_{ii}(r) \) is already small \( g_{ii}(r) \) increases whereas in the regions of direct contact \( g_{ii}(r) \) becomes smaller.

The results which we have obtained by these arguments have now to be introduced in the expressions for the intermolecular relaxation rate as given by (14). First we insert (47) in (34), the result is

\[ G(t) = \frac{n^*_i}{a^6} \exp\left[ -t/\tau^*_i \right]. \]
Nuclear spin relaxation and intermolecular interactions

If we put this expression in (15) and confine the treatment to the extreme narrowing, i.e. the zero frequency case, we obtain
\[
\left( \frac{1}{T_i} \right)_{\text{inter}} = \frac{1}{2} \gamma^* h^2 \frac{n_i^*}{a^4 D},
\]
where, as we did before, we have used (35) as an estimate for the correlation time \( \tau^* \). If we divide (48) by \( c'_i / D \) and take into account (47a), we obtain
\[
\left( \frac{1}{T_i} \right)_{\text{inter}} \cdot \frac{D}{c'_i} = \frac{1}{2} \gamma^* h^2 \frac{1}{a^4} (n_i^*),
\]
Now we denote the quantity on the left-hand side of (49) by \( A \), the association parameter,
\[
\left( \frac{1}{T_i} \right)_{\text{inter}} \cdot \frac{D}{c'_i} \equiv A
\]
and applying the formulations given above, we can make the following statement: If we are justified in assuming that the closest distance of approach, \( a \), is a constant quantity, then we have no association in the liquid mixture if \( A \) remains constant throughout the total composition range; there is association with respect to atom \( i \) if \( A \) increases with decreasing \( c'_i \), and in the case of a decreasing \( A \) as \( c'_i \) becomes smaller, de-association with respect to atom \( i \) occurs.

We may also apply the \( A \) parameter in connection with (37). Then we have
\[
A_{ii} = \left( \frac{1}{T_i} \right)_{\text{inter}} \frac{D}{c'_i} = \gamma^* h^2 \left[ \frac{g(n, k, l)}{2a^4} (n_i^*) + \frac{2 \pi}{3 b} \right],
\]
where the definition (40a) for the reduced first coordination number has been used. With (51) an observed increase of \( A \) cannot exclusively be identified as indicating an increase of the reduced first coordination number, rather a part of the effect has also be assigned to the factor \( g(n, k, l) \), so that apart from the additive constant term \( 2/3 \pi b \), the product \( g(n, k, l) (n_i^*) \) corresponds to the more general reduced first coordination number \( n_i^* \), occurring in (49). In principle it may be that also the closest distance of approach varies with decreasing concentration \( c'_i \). Then it is quite natural also to interpret a decrease of \( a \) as a higher degree of association and vice versa. In fact, a decrease of the distance of approach \( a \) causes an increase of \( A \), so that the statement that \( A \) is a tool to detect the occurrence of \( i-i \) association remains valid.

4.2 Some experimental results for equal particle association as identified through the \( A \) parameter

Before we quote some experimental results for the association parameter \( A \), a general remark should be made concerning the experimental uncertainty. As was explained above, the intermolecular relaxation rate is the difference between the total relaxation rate and the intramolecular relaxation rate. As \( c'_i \to 0 \) the intermolecular relaxation rates vanishes, whereas the intramolecular relaxation rate remains a finite quantity. Thus one is confronted with the experimental problem of measuring a quantity which is the small difference between two comparatively large numbers. The experimental results so far available have been obtained from primary measurements with an experimental uncertainty of the total and intramolecular relaxation rate which is at best
± 5%, this leads to results for the intermolecular relaxation rates which even at a moderate degree of dilution have a limit of error of ± 20%.

The most important type of intermolecular interaction where one would certainly expect an increase of $A$ with an increasing degree of dilution of the interacting molecules is the H-bond formation. And indeed, the effect in question here has been observed for the system ethanol/CCl$_4$ (Bender and Hertz 1977). Some data are depicted in figure 5. The increase of $A$ is strongest for the OH group, however for the CH$_2$ and CH$_3$ protons as well H–H association is detectable. It is interesting to note that in the solvent water, ethanol-ethanol association could not be observed (Hertz and Tutsch 1976). Methanol in the mixture with benzene has also been studied (Ansari and Kratochwill 1978), the association of the OH hydrogen can clearly be seen, the $A$ coefficient corresponding to the methyl hydrogen remains constant over the composition range. This is also the case for the methyl groups of methanol in the mixture with pyridine (Helm and Kratochwill 1978), however in this system the $A$ coefficient for OH decreases with decreasing alcohol concentration, thus, as has been explained above, we observe a de-association of the OH hydrogen in the solvent pyridine.

Let us now turn to the carboxylic acids. Here the first investigations pertinent to our association criterion were performed on aqueous mixtures with butyric, propionic and acetic acids (Hertz and Tutsch 1976). In these systems again the arguments given in the

![Figure 5. The association parameter $A$ for the various $^1$H atoms of ethanol (Et) and propionic acid (Prop) in their mixtures with CCl$_4$ as a function of the $^1$H number density. The other corresponding hydrogen atoms of the H-bonding molecules are deuterons.]
introduction in connection with (3) have to be applied. The displacement of a given OH proton from intramolecular bond partner oxygen requires little energy, this has the consequence that the acidic proton exchanges with those of the solvent water and thus for this proton no information about \( A \) can be obtained. However, by suitable isotopic substitution the methylene and methyl protons can be studied separately and in all cases association for the H atoms located in the various groups as defined above has been detected. Usually the systematic trend of the observations is such that for those CH protons closest to the carboxylic group the increase of \( A \) with decreasing acid concentration is strongest. Thus the methyl hydrogen of propionic acid shows only a fairly weak association effect. This, of course, means that the hydrocarbon parts of the acid molecules have an appreciable amount of freedom to move around the more tightly coupled carboxylic group, however it should be kept in mind that the so called hydrophobic interaction should introduce a tendency to bring the hydrocarbon parts of the molecule in contact (Franks 1975). It is clear that in the present system a short cut distinction, between what contribution of the observed association effect has to be attributed to the H-bonding in the carboxylic group and which to the hydrophobic interaction, cannot be made. But it has been found that \( \text{CH}_3 \) association in \( \text{H}_2\text{O} + \) butyric acid is stronger than \( \text{CH}_3 \) association in \( \text{H}_2\text{O} + \) propionic acid which is indeed a confirmation of the hypothesis of hydrophobic association: the larger the hydrocarbon part of the molecule, the stronger is the association.

There are quite a number of investigations dealing with mixtures of carboxylic acids with non-aqueous solvents, we quote the following systems: \( \text{CH}_3\text{CH}_2\text{COOH}/\text{CCI}_4 \) (Bender and Hertz 1977), \( \text{CH}_3\text{COOH}/\text{CCI}_4 \) (Berg et al 1976), \( \text{CH}_3\text{COOH}/\text{C}_6\text{H}_{12} \) (Capparelli et al 1978), \( \text{HCOOH}/\text{CCI}_3\text{H} \) (Kratochwill and Hertz 1977). In these solvents there is no exchange of the acid protons with the solvent protons, so that \( A \) can also be studied for the OH protons. In all cases the behaviour is as expected—there is a strong increase of \( A \) as the acid concentration decreases. It is interesting to note that in the solvent cyclohexane \( \text{CH}_3\text{CH}_2\text{COOH} \) association seems to be fairly weak, whereas in the system \( \text{CH}_3\text{COOH}/\text{CCI}_4 \) such an association has been observed (Capparelli et al 1978, Berg et al 1976). The association of the \( \text{CH}_3 \) group in \( \text{CCI}_4 \) solution has been interpreted as a folding of the acid dimers such that the two acid molecules which are connected via the H-bond do not form a planar arrangement as it is usually represented in the classical treatments, rather the two ‘methyl ends’ of the H-bonded ‘double molecule’ approach towards each other such that one gets a V-shaped molecular system. In the more inert solvent \( \text{C}_6\text{H}_{12} \), this degree of folding or bending of the double molecule is less. Apart from this particular observation the other \( A \) values so far available for the carboxylic acids give essentially qualitative information so that we refrain from a detailed discussion or comparison of these numbers.

Also for systems in which one of the components forms weak H-bonds or in which no H-bonding occurs, association has been detected. So it has been found that chloroform-chloroform association exists in the mixture of \( \text{CCI}_3\text{H} \) with acetone (Capparelli et al 1976) and with dioxane (Helm and Kratochwill 1978), the association was detected via an increasing \( A \) coefficient for the H atom of chloroform as \( C_{\text{CCI}_3\text{H}} \to 0 \). In the mixture dimethylformamide-benzene (DMF/\( \text{C}_6\text{H}_6 \) association of the DMF molecules has been observed as well (Hertz et al 1976). The behaviour of the \( A \) coefficient reflecting DMF-DMF association is shown in figure 6. It should be noted that in the systems we quoted for that component we did not mention that the \( A \) coefficient usually remains constant or shows small variation with the variation of the composition. Here association is
absent or it is so weak that the uncertainty of the experimental method in its present state does not allow any definite statement.

4.3 Association between unlike molecules as detected by the A coefficient

We are now going to discuss the association between unlike molecules in a binary mixture. The intermolecular relaxation rate of a proton (or set of protons) residing on the molecule of kind 1 and being caused by the magnetic dipole-dipole interaction with all or selected protons on molecule 2 has also been studied. Now we are interested in the quantity $n_{12}$, the first (intermolecular) coordination number of atom 1 with respect to atom 2. Here atom 1 means any atom of the molecule forming component 1 and likewise, atom 2 means any atom on molecule 2. The protons on a given molecule may be equivalent or not, depending on the special system, so if one defines a first coordination number $n_{12}$, one has to give the necessary specification in the corresponding case. Then we have

$$n_{12} = 4\pi c'_1 \int_0^{\infty} \delta_{12}(r) g_{12}(r) r^2 \, dr$$

where $\delta_{12}(r)$ is any one of the three defining functions we have introduced above. $g_{12}(r)$ is the pair correlation function between the (hydrogen) atoms 1 and 2. Of course, we have $g_{12}(r) = g_{21}(r)$, and since it is reasonable also to set $\delta_{12}(r) = \delta_{21}(r)$ we obtain the result

$$n_{21} = n_{12} \frac{c'_1}{c'_2}.$$
where \( n_{21} \) is the first coordination number of atom 2 with respect to atom 1

\[
n_{21} = 4\pi c'_1 \int_0^\infty \delta_{21}(r)g_{12}(r)r^2 \, dr.
\]

We see from these equations that the reduced first coordination numbers,

\[
n_{12}/c'_2 = n_{21}/c'_1 = (n_{12})_r = (n_{21})_r = 4\pi \int_0^\infty \delta_{12}(r)g_{12}(r)r^2 \, dr,
\]

are equal for both species 1 and 2.

Now if \( (n_{ij})_r \) increases with decreasing concentration of species \( j \), then we say that we have association of atom \( j \) with atom \( i \), and on the other hand, if \( (n_{ij})_r \) decreases with decreasing concentration of species \( j \), then we have association of atomic species \( i \) with atom \( j \). Of course, if \( (n_{ij})_r \) remains constant over the entire composition range, then \( i-j \) (or \( A-B \)) association is absent. In full correspondence to the arguments given above we may again define a \( A_{ij} \) parameter, so that we have

\[
A_{ij} = \left( \frac{1}{T_1} \right)_{i, \text{inter}} \frac{\bar{D}}{c'_j},
\]

where \( (1/T_1)_{i, \text{inter}} \) is the intermolecular relaxation rate of the nucleus \( i \) caused by the magnetic dipole-dipole interaction with the atomic species \( j \) on the molecule of the other mixture component. As above, \( \bar{D} \) is the mean self-diffusion coefficient of the two mixture components

\[
\bar{D} = \frac{1}{4}(D_1 + D_2),
\]

where \( D_1 \) and \( D_2 \) are the self-diffusion coefficients of molecules 1 and 2, respectively. In (52) the intermolecular relaxation rate is given by the expression

\[
\left( \frac{1}{T_1} \right)_{i, \text{inter}}^{(i)} = 3 \gamma_i^2 \gamma_j^2 \hbar^2 \frac{n_{ij}^*}{a^4 \bar{D}},
\]

which is almost the same as (48), \( \gamma^4 \) is replaced by the product of the squares of the two gyromagnetic ratios and (48) has been multiplied by the factor 2/3 because now we have the interaction between two unlike spins. The gyromagnetic ratios may be effectively equal if we are working with two nuclei of the same kind, however being non-equivalent due to the effect of the chemical shift. For unlike spins (37) may be modified in the same way

\[
\left( \frac{1}{T_1} \right)_{i, \text{inter}}^{(i)} = \frac{1}{3} \gamma_i^2 \gamma_j^2 \hbar^2 \frac{n_{ij}^*}{a^4 \bar{D}} \left[ \frac{n_{ij}^* + 4\pi c'_j}{a^4 + \frac{3}{b}} \right].
\]

Equations (53) and (54) both refer to a situation where the two interacting nuclei have a spin \( I = 1/2 \), in the more general case the formulas have to be multiplied by an appropriate factor \( 4S(S+1)/3 \) where \( S \) is the spin of the nucleus causing the relaxation effect.

Considering (52), (53) and (54) we get for the association coefficient \( A_{ij} \)

\[
A_{ij} = \frac{1}{3} \gamma_i^2 \gamma_j^2 \hbar^2 \frac{(n_{ij}^*)^b}{a^4}
\]

or

\[
A_{ij} = \frac{2}{3} \gamma_i^2 \gamma_j^2 \hbar^2 \left[ \frac{g(n, k, l)}{2a^4} (n_{ij})_r + \frac{2\pi}{3b} \right].
\]
Finally, it may easily be seen that we have

\[ A_{ji} = \frac{v_i}{v_j} A_{ij} \]

where \( v_i \) and \( v_j \) are the number of equivalent protons \( i \) and \( j \), respectively, on the two molecules which form the components of the binary mixture in question.

We now report on some liquid mixtures for which the association behaviour between unlike molecules (AB association) has been studied, the first point which is to be stated is that A-B association has usually been found to be much weaker than association between equal molecules. The first system to be studied was DMF-C\(_6\)H\(_6\), where no A-B association was found and \( A_{12} \) was found to be constant over the entire composition range (Hertz et al 1976), but later, in a recent investigation (Holz and Hertz 1981) the experimental results for the self-diffusion coefficients were improved and it turned out that there exists a weak association of DMF with benzene. The corresponding \( A \) parameter is also shown in figure 6. In the next study it was shown that chloroform is associated with acetone (Capparelli et al 1976), and interestingly, it turned out that dioxane is associated with chloroform (Helm and Kratochwill 1978), thus here we have the reverse association behaviour. Finally, there seems to exist a weak association of pyridine with methanol (Helm and Kratochwill 1978).

5. The study of the relative orientation of molecules in the liquid

We begin this chapter with a reconsideration of the association parameter \( A \) which we have introduced in the preceding chapter. Let us assume that again we have a binary mixture consisting of components 1 and 2. However now a special situation occurs, for instance, molecule 1 carries two different kinds of protons which are 'chemically non-equivalent'. We denote the two kinds of protons as \( I \) and \( S \) protons, respectively. The symbols \( I \) and \( S \) stand for a set of protons which among themselves are equivalent and which are considered to be located at two respective representative positions within the molecule. For example, if we consider the compound CH\(_3\)-CH\(_2\)Br, then the three methyl protons are the \( I \) spins, the representative point giving their effective position is close to the carbon atom. Likewise, we have two methylene spins \( S \), their effective position is at the centre of the vector connecting the two hydrogen atoms. In an exact sense, the effective position is given by the mean value of \( 1/r_i^6 \), where \( r_i \) is the intermolecular distance between a reference spin with which the magnetic dipole-dipole interaction occurs and the \( i \)th member of the set \( I \).

Now we perform a dilution experiment, that is, we study the quantity \( A_{II} \) as the concentration of the component 1 decreases. In order to obtain \( A_{II} \) alone in such an experiment, we replace the \( S \) proton spins by deuterons. Let us assume that \( A_{II} \) increases in this experiment, then we conclude that we have association with respect to the atomic species \( I \). In the next series of measurements we switch the \( I \) protons off by applying the deuteron substitution technique and we obtain the concentration dependence of \( A_{SS} \) in the same way by progressive dilution of component 1. Now it may occur that \( A_{SS} \) remains practically constant, whereas \( A_{II} \) definitely increases, as already mentioned.

What is the meaning of this experimental finding? In a first step of interpretation we assume that \( a_{II} \) and \( a_{SS} \), the closest distances of approach for spins \( I \) and \( S \), respectively, remain constant throughout the entire composition range. Then our measurements of
A II tell us that \( g_{II}(n_{II}, k, l) \) and \( (n_{II}) \), increase as will be seen from the equations (see (37))

\[
\left( \frac{1}{T_1} \right)_{\text{inter}}^{II} = \frac{\gamma^4 \hbar^2}{2 a_{II}^4 D} g_{II}(n, k, l) n_{II} + \delta_{II}^*,
\]

and

\[
A_{II} = \gamma^4 \hbar^2 \left[ \frac{1}{2 a_{II}^4} g_{II}(n, k, l) (n_{II}) + \frac{2}{3} \frac{\pi}{b} \right],
\]

however, \( g_{SS}(n, k, l) \) and \( (n_{SS}) \), which are given by the equations

\[
\left( \frac{1}{T_1} \right)_{\text{inter}}^{SS} = \frac{\gamma^4 \hbar^2}{2 a_{SS}^4 D} g_{SS}(n, k, l) n_{SS} + \delta_{SS}^*,
\]

\[
A_{SS} = \gamma^4 \hbar^2 \left[ \frac{1}{a_{SS}^4} g_{SS}(n, k, l) (n_{SS}) + \frac{2}{3} \frac{\pi}{b} \right],
\]

remain constant. \( n_{II} \) and \( n_{SS} \) are the first coordination numbers of spin I and S, respectively, with respect to the same type of proton (II and SS). Thus we see that there is a 'movement' of spin I towards the reference spin I as we dilute component I causing a crowding of I around the reference spin I relative to the mean I concentration in the mixture. There is no such crowding around the spin S with respect to S. We can now, of course, also describe the situation by saying that there is a rotation of the molecule I relative to the reference molecule 1, as we perform the dilution experiment. A rotation means that the relative orientation of the two 1 molecules is changing. Next we must emphasize that in general we do not know exactly whether the closest distances of approach remain constant or not. Our experimental finding may also be interpreted in such a manner that \( a_{SS} \) becomes larger and at the same time \( g_{SS}(n, k, l) \) becomes larger in a corresponding way was to leave \( A_{SS} \) constant, furthermore, \( a_{II} \) becomes smaller. Then it is even more evident that we are concerned with a rotation of the molecules relative to each other. It may also be argued in a similar way when we have only information about the A of one type of proton. Then, if we have reasons from any other source to state that the first coordination number with respect to any other point within the molecule, the 'centre of the molecule', say, remains constant, we can conclude that the increase of A gives evidence for a relative rotation or reorientation of 1 molecule as the dilution process is going on. Such a rotation has been postulated for chloroform-chloroform pairs in the mixture of chloroform with acetone (Capparelli et al 1976).

After the description of the concept of a rotation or reorientation of one molecule relative to the other one when the composition of a binary mixture is changed, the question arises, whether in a system with given composition—which is not supposed to change—the relative orientation of two molecules can be determined. What we have so far, are the two intermolecular relaxation rates \( (1/T_1)_{II} \) and \( (1/T_1)_{SS} \). Applying (37) we may derive the two closest distances of approach \( a_{II} \) and \( a_{SS} \). Of course, this demands the knowledge of the \( g(n, k, l) \) for the two respective atom-atom pair distribution functions. We recall that the parameter \( n \) described the steepness of the model atomic pair distribution function, and the steepness in turn is a measure for the strength and maximum depth of the effective intermolecular potential. For instance, if the S proton belongs to an OH group and the OH groups are coupled through an H-bond, then \( n \) will be a comparatively large number and consequently we have \( g(n, k, l) \approx 1 \) (see figure 4). On the other hand, if the spins I are the protons of a methyl group, then \( n \) will
be small and \( g \approx 0.4-0.5 \). Fortunately, the closest distance of approach \( a \) enters with the fourth power in the expression for the experimental quantity \( (1/T_1)_{\text{inter}} \) (see (37)) so that the final result one obtains for the closest distance of approach will only moderately be influenced even if \( g(n, k, l) \) and the first coordination number have a fairly wide range of uncertainty.

However, even if the two closest distances of approach, \( a_{\|} \) and \( a_{SS} \) are known, the problem of finding the relative orientation is not yet solved. This will be seen from figure 7. In this figure the molecule is schematically drawn as a rod, at the two ends of the rod the two spin sets \( I \) and \( S \) reside, let the length of the rod be \( r_{IS} \). Then we may construct two circles with the radii \( a_{\|} \) and \( a_{SS} \) around the two end points \( I \) and \( S \), respectively. We select any point on the circle with radius \( a_{\|} \). Let this point be the location of the spin \( I \) of the other molecule. Then that point on the circle with radius \( a_{SS} \) around \( S \) which has the distance \( r_{IS} \) from the original point on the circle \( a_{\|} \) gives a possible pair configuration leading to the pair of closest distances \( a_{\|} \) and \( a_{SS} \). The corresponding construction is shown in figure 7. It will be seen that there is an infinite number of pair partner rods all of which have the same occurrence probability. To fix the relative orientation of maximum occurrence probability we need more information. This additional information will be supplied by a third intermolecular relaxation rate. The next series of experiments is performed in such a way that the contribution \( (1/T_1)_{\text{inter}}^{IS} \) to the relaxation rate of spin \( I \) is determined which is caused by the intermolecular magnetic dipole-dipole interaction of spin \( S \) with spin \( I \). This may or may not require partial deuteration of the molecules investigated, depending on the kind of the system. In the same way, the contribution to the relaxation rate of spin \( S \) caused by the intermolecular dipole-dipole interaction with spin \( I \) may also be evaluated to obtain the relaxation rate \( (1/T_1)_{\text{inter}}^{SI} \). And, of course, taking into account the relative numbers of spins \( I \) and \( S \), the two results should be internally consistent. As before, the intermolecular relaxation rate \( (1/T_1)_{\text{inter}}^{IS} \) is given by the relaxation rate

\[
\left( \frac{1}{T_1} \right)_{\text{inter}}^{IS} = \frac{4\gamma_i^2\gamma_s^2\hbar^2}{3\hbar^2} S(S+1) \left[ \frac{n_{IS}}{Da_{IS}} g_{IS}(n, k, l) + \frac{\pi c_s^2}{3bD} \right] \tag{57}
\]

and the proper estimate of \( n_{IS} \) and \( g_{IS}(n, k, l) \) yields \( a_{IS} \), the closest distance of approach between the spins \( I \) and \( S \). Of course, we must have \( a_{IS} = a_{SI} \). If now the \( a_{IS} \) value is available, the further construction procedure is as shown in figure 8. One draws two circles with radius \( a_{IS} = a_{SI} \) around the locations of the two spins \( I \) and \( S \) on the

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**Figure 7.** A number of \( I-S \) rod-rod configurations, having all the same closest distances of approach \( a_{\|} \) and \( a_{SS} \).
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Figure 8. Circle construction to find two equivalent I-S rod-rod configurations of maximum occurrence probability, when the three closest distances of approach $a_{11}$, $a_{1S}$, and $a_{SS}$ are given.

reference rod. The point of intersection between the circles $a_{11}$ and $a_{SS}$ obviously is a possible location of the spin $S$ of the pair partner rod. Since for this partner rod the spin $I$, when it comes closest to the spin $I$ of the reference rod, must lie on the circle $a_{11}$, and at the same time it must have a distance $r_{1S}$ from the point of intersection $a_{51} a_{SS}$, and so the relative orientation of the two molecules are found as shown in figure 8. But there is another equivalent relative configuration, namely, the point of intersection between the $a_{1S}$ around $S$ and the circle $a_{11}$ is also a possible position of the spin $I$ of the pair partner rod. Again, the spin $S$ of the partner rod must lie on the circle $a_{SS}$ and a distance $r_{1S}$ apart from the point of intersection just mentioned. This gives the pair configuration which is indicated by the dashed arrow in figure 8. The model atomic pair distribution function as shown in figure 2 and written down as (36) has the property that the distance of closest approach is also the distance of maximum occurrence probability. As a consequence, the two equivalent rod configurations shown in figure 8 are also configurations of maximum occurrence probability. Of course, there is an infinite number of pair configurations which may also occur, however, their occurrence probability is smaller. A more detailed description of the method has been given elsewhere (Hertz 1976), only some further general aspects should be mentioned here.

According to the scheme of construction to find the pair configuration of maximum occurrence probability the corresponding distribution should have cylindrical symmetry around the axis of the reference rod $IS$. However, in many cases the shape of the molecules renders such a cylindrical symmetry impossible. There may, for instance, be a bromine atom below the line connecting the spins $I$ and $S$ in figure 8. This would lead us back to our example of the ethyl-bromide molecule. And in figure 8 it has been assumed that such an atom or a more bulky functional group is indeed present, and therefore the probability of finding the partner molecule below the rod in the same configuration as above the reference molecule, is zero.

In figures 9–14 we give a number of examples for pair configurations of maximum occurrence probability which have been derived from intermolecular nuclear magnetic relaxation rates. The relation of these pictures to the scope of this article, namely the study of intermolecular interactions, is given by the fact that any alteration of the pair configurations away from those shown in the figures require the delivery of work, ie the configurations shown should correspond to a minimum of effective potential energy. Finally, we mention that three dimensional pair configurations of maximum occurrence probability have also been worked out (Bender and Hertz 1977).
Figure 9. Pair configuration of maximum occurrence probability for \( \text{C}_2\text{H}_5\text{Br} \), as constructed from \( a_{11}, a_{1S}, \) and \( a_{SS} \). Here, by accident the two equivalent configurations shown in figure 8 are identical. Arrows pointing towards Br indicate electric dipoles in a schematic way (Hertz 1978).

Figure 10. Various pair configurations of maximum occurrence probability derived from figure 9 as a visualization. The picture is to be understood in the following way: the maximum probability assigned to the pair: a-central molecule refers to the situation where all other molecules may have any configuration relative to the central one. Likewise, if the pair b-central molecule is fixed, then the other molecules may have any configuration. The angle \( \gamma \) may always have any value in the range indicated. Configurations b and c are equivalent, pair partner d is so distant from the central molecule, that proton-proton interaction does not contribute to relaxation rate (Hertz 1978).
Figure 11. Various configurations of maximum occurrence probability for formic acid in the pure liquid. I and S are the formyl and carboxyl protons, respectively. We have presented a special case of a planar configuration and the small circles schematically indicate the carbonyl oxygen (Kratochwill and Hertz 1977).

Figure 12. (a) Configuration 3 corresponding to that given as no. 3 in figure 11 showing the real molecular skeleton, (b) Selection of chainlike structure according to x-ray data of liquid formic acid (Kratochwill and Hertz 1977; Geisenfelder and Zimmermann 1963).

6. The intramolecular relaxation rate as a tool to study intermolecular interactions

6.1 Some general remarks

We return to (10) where the microscopic density self-correlation function of atom 2 relative to atom 1 was written as a product of the pair distribution function \( p(r_0) \) and the propagator \( P(r_0, r, t) \). We had stated that \( p(r_0) \) and \( P(r_0, r, t) \) are both determined by the nature of the intermolecular forces. In a more general situation we can also say that both these quantities are determined by the interatomic forces. Here the most well known type of atomic interaction is the formation of a molecule. Now \( p(r_0) \) has an intramolecular contribution which is given by the structure of the rigid or partly rigid molecule. This part of \( p(r_0) \), when we disregard for a moment the atomic vibrations, should be a set of \( \delta \)-functions in a coordinate system fixed in the molecule. If the molecule is a rigid body, then in any case \( P(r_0, r, t) \) should also be a property of the rigid body, and as we shall see shortly, the time constant describing the evolution with time of \( P(r_0, r, t) \), will come out the longer, the larger is the rigid body, the molecule. Thus we see that partly \( P(r_0, r, t) \) is determined by an intramolecular feature of the molecule and
this contribution is not of direct interest to us. However, even if the molecular sizes and masses of two compounds are almost equal, it happens that the function $P(r_0, r, t)$ is markedly different. For instance, the molecules of ammonia and water are almost equal when mass and intramolecular distances are considered. Yet the quantity $P(r_0, r, t)$ which is a $\delta$-function at $t = 0$ in NH$_3$ spread out in rotational space (the spherical surface of unit radius) to become uniform ($= 1/4\pi$) after a much shorter time than it does in water. This particular feature, of course, is a manifestation of the intermolecular forces and in the present chapter we deal with those aspects of the intramolecular relaxation rate which, as we suppose, are a consequence of the intermolecular forces.

When we said that $P(r_0, r, t)$ changes from a $\delta$-function on a unit sphere to $P(r_0, r, t) = 1/4\pi$ as $t \to \infty$ we already implicitly stated that in the case of intramolecular motions the propagator is of purely rotational form. This must be so because within the molecule all the interaction distances apart from vibrations have constant values, so that only the orientation can change with time. In a polyatomic molecule there are many different vectors connecting two magnetically interacting nuclei. Now it is fairly evident that the rotational motion of the various vectors will be the same if the vectors are all physically indistinguishable due to the high symmetry of the molecule. If all vectors within the molecule show the same motion then we say that we have the situation of isotropic rotational motion. In other cases, the motion is different for the various vectors in the molecule, and we speak of an anisotropic rotational motion. In
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Figure 14. (a) Acetic acid dimer in a state of folding in the mixture with CCl₄ (Xₐcₐd 0-t). The experimental uncertainty is indicated by the two double arrows, (b) Molecular arrangement in pure acetic acid; molecules 2 and 3 are above and below molecule 1, respectively. This figure should be understood in the same way as explained in connection with the CH₃Br pairs in figure 10 (Berg et al 1976).

the present chapter which is more on an introductory level, we shall only treat the molecular motion as representing isotropic rotational diffusion even if the molecule has not the symmetry which necessarily demands isotropy of the motion. In the next chapter the emphasis will be on the anisotropic character of the rotational motion.

For the intramolecular magnetic dipole-dipole interaction between two spins, the time correlation function describing the change of the positional and rotational coordinates is

\[ G(t) = \frac{1}{4\pi r_0^6} \int Y_2(\Omega_0) Y_2(\Omega) P(\Omega_0, \Omega, t) d\Omega_0 d\Omega. \]  

(57)

It will be seen that this is essentially (17), however three modifications have been introduced: \( p(r_0) \) is replaced by \( 1/4\pi \), the probability density of finding a given orientation \( \Omega_0 \) of the spin-spin vector. \( \Omega_0 \) and \( \Omega \) are the orientations of the vector at \( t = 0 \) and \( t \geq 0 \), respectively, they are given by the pair of angles \( \theta \) and \( \phi \). Finally, the propagator is written in terms of orientation alone and \( r_0 \) is a constant quantity not changing with time. Then, if one introduces (57) in (15) and (14) and considers only the case of extreme narrowing, one obtains the result

\[ \left( \frac{1}{T_1} \right)_{\text{intra}} = \frac{3\gamma^4\hbar^2}{2r_0^6} \tau_e. \]  

(58)
The proton-proton distance $r_0$ is known from the geometry of the molecule, $\tau_c$ is the rotational correlation time, it is given by the expression

$$\tau_c = \int_0^\infty G(t) \, dt. \quad (59)$$

In order to get a clearer understanding of the concept of the rotational correlation time $\tau_c$, it is instructive to compare this quantity with the reorientation time $\tau_r$ of a molecule in the liquid. $\tau_r$ is the time after which the proton-proton vector has changed its direction by ca 180°. Actually, the strict definition of the reorientation time is somewhat different, but for the qualitative purpose which is the intention here, the description given suffices. The reorientation time of the molecule is approximately equal to the dielectric relaxation time (Hasted 1972). We can also say that the intersection point of a vector fixed in the molecule with the unit sphere performs an erratic motion. Now the elementary steps of the rotational path on the unit sphere may be very small, in this event we speak of micro-step diffusion, or they may be larger, implying free paths of 90°, say, in such cases we would speak of rotational jump diffusion. The motion we have to assign to molecules undergoing fairly strong intermolecular interactions is closer to the former type and in particular we may assume that for the reorientational motion of H-bonded molecules the micro-step process is generally the better description of reality.

In the case of micro-step rotational diffusion the valid relation is

$$\tau_c = \frac{1}{3} \tau_r. \quad (60)$$

As the rotational steps become larger, $\tau_c \to \tau_r$, but for the present article it is sufficient to identify the rotational correlation time as one third of the reorientation time of the molecule considered. We give a brief indication why the factor $1/3$ occurs in (63). In the situation of microstep rotational diffusion the propagator as given in (31) and used in (57) describes the motion of the vector. Due to the orthogonality relations of the spherical harmonics of the second degree in (16) all terms of (31) except the one belonging to $l = 2$ drop out. For the electric dipolar relaxation the $Y_2(t)$ are replaced by the spherical harmonics of first degree $Y_1(t)$, and consequently one is left only with terms corresponding to $l = 1$ after the averaging process. Now the respective correlation or reorientation time is given by the relation

$$\frac{1}{\tau_i} = l(l+1)D_r.$$ 

Thus we have $l(l+1) = 6$ and $l(l+1) = 2$ in the two cases and the ratio $\tau_c/\tau_r = 1/3$.

The molecule may contain several proton-proton vectors the relaxation contributions of which are observed simultaneously. Still let us assume that the motion is sufficiently isotropic. Then in a fair approximation the total observed intramolecular relaxation rate is given by the relation

$$\frac{1}{T_1} = \frac{1}{\nu} \sum_{i<j} \frac{2}{T_{ij}}. \quad (61)$$

$v$ is the number of like spins—here usually protons—in the molecule. $T_{ij}$ is the relaxation time one would calculate for the spin pair formed from spins $i$ and $j$ according to (58) and the sum includes all pairs of like spins in the molecule.

Equations (58) and (61) apply when the magnetic dipole-dipole interaction between two or more protons is the relaxation mechanism. The deuteron has spin $I = 1$ and thus
it possesses a nuclear quadrupole moment which interacts with the electric field at the position of the nucleus. The electric field gradient is connected with the electron cloud of the molecule. Usually the relaxation rate caused by quadrupole interaction dominates over the magnetic effect to be expected from the nucleus with spin $I > 1/2$, this is also true for the deuterons. From the theory one obtains the formula (Abragam 1961; Farrar and Becker 1971; Slichter 1980)

$$
\frac{1}{T_1} = \frac{3}{40} \frac{2I + 3}{I(I - 1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{eQ}{\hbar^2}\right)^2 q^2 \tau_c.
$$

Here $Q$ is the electric quadrupole moment, $e$ is the charge of the proton, $q$ is the maximum electric field gradient, $\eta$ is an asymmetry parameter of the electric field gradient which in most cases is neglected. $\tau_c$ is the same correlation time which appears in (58) and (61) if the rotational motion is isotropic. Use of (62) has the advantage that the experimental relaxation rate is the intramolecular relaxation rate $1/T_1 = (1/T_1)_{\text{intra}}$, it has the disadvantage that one has to know the quadrupole coupling constant $eQ/\hbar \cdot q$ in order to calculate $\tau_c$ which is not always an easy matter (Lucken 1969).

6.2 A model to connect the orientational correlation time with the intermolecular forces

As was already mentioned, H-bonding is the most important type of intermolecular interaction which can be studied by the intramolecular relaxation rate, as may be intuitively expected. A more detailed report about the various systems which have been studied has been given elsewhere (Hertz and Zeidler 1976), so here we shall only give a brief description of the basic ideas underlying the treatment and some representative experimental examples. For more detailed information the reader is referred to Hertz and Zeidler (1976). A molecule which is H-bonded to its neighbours has a longer rotational correlation time than a non-H-bonded molecule of comparable size and mass. Also the self-diffusion coefficient of such a molecule will be smaller. This is understandable because the rotational motion is determined by the angular dependence and the translational motion by the radial part of the intermolecular potential. Very often the depths of these potentials do not differ very much. Thus, all facts which we now describe as regarding rotational diffusion have their analogous in the translational form of motion which also gives us the justification to quote and discuss the self-diffusion coefficients when corresponding data are available. It has been briefly mentioned above that self-diffusion coefficients can also be obtained by the NMR method.

Our starting point is the well known Debye relation (Abragam 1961; Andrew 1956; Pople et al 1959).

$$
\tau_c = \frac{4\pi r^3 \eta}{3kT}.
$$

The radius of the molecule in question is $r$. We assume that the shape of the molecule does not deviate too much from a sphere. $\eta$ is the effective viscosity, it is usually smaller than the macroscopic viscosity of the liquid, it is often called the microviscosity, in itself it is not a well defined quantity. Here we define $\eta$ in terms of (63), that is, it connects the experimental quantity $\tau_c$ with the molecular radius $r$. This procedure implies that $r$ is sufficiently well-known; as we shall show shortly, this requirement confines the application of (63) to such liquids where we know that H-bonding is absent. Some
correlation times for such liquids are collected in table 2. It may be noted that in general \( \dot{\eta} \) will also depend on the size of the molecule, it will increase with increasing molecular radius \( r \). Thus, there are two sources for an increase of \( \tau_c \) when the molecule is large, a direct one, the \( r^3 \) effect, and the indirect one, the \( \dot{\eta} \)-effect which previously also we called the ‘background effect’ (Grüner and Hertz 1972).

Now let us, at the beginning, consider (63) as being valid for non-H-bonded molecule. Next imagine that for a given system the H-bonds are ‘switched on’. We observe that \( \tau_c \) becomes longer. The reason is clear, since a set of molecules which are connected by a certain arrangement of links or bonds now acts as if it were one larger molecule, in other words the radius \( r \) of the monomeric molecule has to be replaced by the radius \( r^* \) of the aggregate which of course is greater, \( r^* > r \). Now we can rewrite (63) to give

\[
\tau_c = \frac{4\pi (r^*)^3 \dot{\eta}^*}{3kT}
\]

(64)

\( \dot{\eta}^* \) is the microviscosity for the H-bonded liquid and since we said that \( \eta \) increases with increasing particle size, we get \( \dot{\eta}^* > \dot{\eta} \).

Next we ask: In what way is the effective radius \( r^* \) connected with the actual radii of the H-bonded aggregates? In the present situation the correlation time is usually of the order of \( 10^{-11} \) sec. Thus if the aggregate behaves like a stable molecule for a time longer than \( 10^{-11} \) sec, then with respect to the observation time implied in \( \tau_c \) it is indistinguishable from a stable molecule. Furthermore, in general we have an association equilibrium involving aggregates composed of varying numbers of particles \( n \). During the process of the relaxation of the nuclear magnetization, a given individual molecule for many times is a member of each aggregate of type \( n \). Under these conditions, as the theory shows (Zimmerman and Brittin 1957), the third power of the effective radius of the molecule, \( r^* \), equals the mean third power of the radius of the aggregate (see (67))

\[
(r^*)^3 = p_0 (\Delta E(\tau_c)) (r^*)^3 + p_1 (\Delta E(\tau_c)) r_1^3 + p_2 (\Delta E(\tau_c)) r_2^3 + \ldots
\]

(65)

\( p_1 \) is the probability that a given molecule is H-bonded to one neighbour, \( p_2 \) is the probability that it is bonded to two neighbours, and so on. Of course we have

\[
p_0 + p_1 + p_2 + \cdots = 1
\]

But as we pointed out, the validity of (65) is coupled to the condition that \( \tau_h \gg \tau_c \), i.e. the lifetime \( \tau_h \) in a given \( (n\text{-fold}) \) bound state must be longer than the correlation time \( \tau_c \) (Hertz 1970). We may write

\[
\tau_h = \tau_0 \exp \left( -\frac{\Delta E}{RT} \right)
\]

(66)

\( \tau_0 \approx 10^{-14} \) sec, thus for \( \tau_h \gg 10^{-11} \) sec we obtain \( \Delta E \leq -18.8 \text{ kJ/mole} \). Therefore, we have added the parentheses with \( (\Delta E(\tau_c)) \) at the \( p_i \)'s in order to give the correct classification of what we mean by the word aggregate. We note that the quantity \( \Delta E \) denotes the potential depth (i.e. it is a negative quantity) between two molecules in the presence of all the other molecules in the surrounding liquid, thus again it is an effective intermolecular potential. There may be aggregates for which \( \Delta E > \Delta E(\tau_c) \). These aggregates contribute to \( \dot{\eta}^* \), i.e. they are the reason that \( \dot{\eta}^* \) also becomes greater apart from a certain repulsive contribution when the H-bonds are formed, this is the background effect. The situation just described, \( \tau_h \gg \tau_c \) may be called the situation of slow exchange. Slow exchange means that the residence times in the various
### Table 2. Some rotational correlation times and self-diffusion coefficients for non-H-bonded and H-bonded molecules.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucleus observed</th>
<th>Temperature (°C)</th>
<th>(\langle 1/T_1 \rangle_{\text{intra}}) sec(^{-1})</th>
<th>(\tau_c) ((10^{-12}\ \text{sec}))</th>
<th>(D) ((10^{-5}\ \text{cm}^2\ \text{sec}^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)CD(_2)Br</td>
<td>(^1)H</td>
<td>25</td>
<td>0.032</td>
<td>0.67</td>
<td>3.9</td>
<td>Engelsmann et al (1974)</td>
</tr>
<tr>
<td>CD(_3)CH(_2)Br</td>
<td>(^1)H</td>
<td>25</td>
<td>0.020</td>
<td>0.84</td>
<td>3.9</td>
<td>Engelsmann et al (1974)</td>
</tr>
<tr>
<td>(CD(_3))(_2)CO</td>
<td>(^1)H</td>
<td>25</td>
<td>0.20</td>
<td>0.47</td>
<td></td>
<td>Zeidler (1965); O'Reilly and Peterson (1971); Goldammer and Hertz (1970)</td>
</tr>
<tr>
<td>(CH(_3))(_2)=CD(_2)</td>
<td>(^2)H</td>
<td>0</td>
<td>0.33</td>
<td>0.59</td>
<td>4.51</td>
<td>Mills and Hertz (1980)</td>
</tr>
<tr>
<td>(CH(_3))(_2)O</td>
<td>(^1)H</td>
<td>25</td>
<td>0.021</td>
<td>0.57</td>
<td>3.4</td>
<td>Zeidler (1965)</td>
</tr>
<tr>
<td>C(_2)D(_2)N</td>
<td>(^2)H</td>
<td>30</td>
<td>0.85</td>
<td>1.55</td>
<td></td>
<td>Zeidler (1965)</td>
</tr>
<tr>
<td></td>
<td>(^14)N</td>
<td>25</td>
<td>606</td>
<td>1.86</td>
<td>1.9</td>
<td>Kintzinger and Lehn (1971)</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>(^1)H</td>
<td>25</td>
<td>0.009</td>
<td>1.1</td>
<td>2.20</td>
<td>Holz and Hertz (1981)</td>
</tr>
<tr>
<td>C(_6)H(_12)</td>
<td>(^1)H</td>
<td>25</td>
<td>0.051</td>
<td>1.2</td>
<td>1.7</td>
<td>Zeidler (1965)</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>(^1)H</td>
<td>-71</td>
<td>0.064</td>
<td>0.66</td>
<td></td>
<td>Powles and Rhodes (1967)</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>(^13)C</td>
<td>35</td>
<td>0.027</td>
<td>0.43</td>
<td></td>
<td>Lyerla and Grant (1972)</td>
</tr>
<tr>
<td></td>
<td>(^17)O</td>
<td>25</td>
<td>240</td>
<td>4.3</td>
<td></td>
<td>Versmold and Yoon (1972)</td>
</tr>
<tr>
<td>CH(_3)OD</td>
<td>(^1)H</td>
<td>25</td>
<td>0.047</td>
<td>0.9</td>
<td>2.2</td>
<td>Goldammer and Zeidler (1969)</td>
</tr>
<tr>
<td></td>
<td>(^2)H</td>
<td>25</td>
<td>3.23</td>
<td></td>
<td>4.4</td>
<td>Hertz and Zeidler (1976)</td>
</tr>
<tr>
<td>C(_2)H(_2)OH</td>
<td>(^17)O</td>
<td>25</td>
<td>649</td>
<td>11.6</td>
<td></td>
<td>Versmold and Yoon (1972)</td>
</tr>
<tr>
<td>C(_2)H(_2)OD</td>
<td>(^1)H</td>
<td>25</td>
<td>0.107</td>
<td>2.2</td>
<td>1.1</td>
<td>Goldammer and Zeidler (1969)</td>
</tr>
<tr>
<td></td>
<td>(^2)H</td>
<td>25</td>
<td>7.14</td>
<td>9.8</td>
<td></td>
<td>Hertz and Zeidler (1976)</td>
</tr>
<tr>
<td>CD(_3)CH(_2)OH</td>
<td>(^2)H</td>
<td>25</td>
<td>1.06</td>
<td>2.6</td>
<td></td>
<td>Goldammer and Hertz (1970)</td>
</tr>
<tr>
<td>CH(_3)CD(_2)OH</td>
<td>(^2)H</td>
<td>25</td>
<td>0.862</td>
<td>2.1</td>
<td></td>
<td>Goldammer and Hertz (1970)</td>
</tr>
<tr>
<td>CH(_3)COOD</td>
<td>(^2)H</td>
<td>25</td>
<td>7.7</td>
<td>13.6</td>
<td>1.1</td>
<td>Berg et al (1976)</td>
</tr>
<tr>
<td></td>
<td>(^1)H</td>
<td>25</td>
<td>0.157</td>
<td>3.0</td>
<td></td>
<td>Goldammer and Zeidler (1969); Hertz and Tutsch (1976)</td>
</tr>
<tr>
<td>CD(_3)COOH</td>
<td>(^2)H</td>
<td>25</td>
<td>0.76</td>
<td>1.8</td>
<td></td>
<td>Goldammer and Zeidler (1969)</td>
</tr>
</tbody>
</table>
environments are much longer than the corresponding correlation times, thus we have slow exchange relative to the rotational correlation time which here acts as an effective observation time, although, in a stricter sense $T_1$ is the observation time. This is due to the fact that we only treat a zero frequency observation of the relaxation rate. The zero frequency relation for the intramolecular relaxation rate under the circumstances indicated is

$$\left( \frac{1}{T_1} \right)_{\text{intra}} = \frac{2\pi r_A^4 h^2 \hat{J}^*}{kT r_\delta^6} \left[ p_0(\Delta E(\tau_c)) (r^0)^3 + p_1(\Delta E(\tau_c)) r_1^{-3} + \ldots \right]$$

and in fact (67) gives the justification for the averaging relation (65) (Zimmerman and Brittin 1957).

Let us now consider a liquid with weaker H-bonding for which

$$p_n(\Delta E(\tau_c)) = 0, \quad \text{for all } n \neq 0.$$ 

Now we have no aggregates which are long-lived as compared with the rotational correlation time. But still there are aggregates in the liquid, formally association can always be assigned to the molecular structure of a liquid and it is entirely a matter of our convenience which number for $\Delta E$ we choose for our classification: bonded aggregate—non-bonded single molecule. Thus it is equally well a possibility to choose $\Delta E \sim -RT$ as a line of demarcation between the states 'free' and 'bonded'. Now the life time of the corresponding aggregates is $10^{-13} \leq \tau_a \leq 10^{-12} \text{ sec}$, this is approximately the time after which the angular velocity correlation function has decayed to zero which has the consequence that we are just at the border line of the time scale in which a rotational diffusion coefficient can be defined, and since the coupled particles move together, a common diffusion coefficient may also be defined, at least qualitatively. The same argument is also valid for the translational self-diffusion coefficient. If we now have stated that the life time of the aggregate is short, as indicated above, so that it is smaller, in the limit very much smaller than the rotational correlation time $\tau_c$, and during the time $\tau_c$ a given molecule often or very often has changed its surroundings: free, coupled to one neighbour, coupled to two neighbours, free, coupled to three neighbours, coupled to one neighbour, free and so on. We have the situation of fast exchange relative to the correlation time $\tau_c$. Again $\tau_c$ might act as the observation time via (58) and clearly we are unable to get any detailed dynamical information about the exchange process from a study of $\tau_c$. We have fast exchange and thus only the mean value of the dynamical processes can be studied.

It may be shown (Beckert and Pfeifer 1965; Anderson 1967; Hertz 1967b; Anderson and Fryer 1969) that under the conditions of fast exchange the interconnection between the effective radius $r^*$ occurring in (64) and the radii of the aggregates is given by the formula

$$(r^*)^{-1} = p_0(-RT)(r^0)^{-3} + p_1(-RT)r_1^{-3} + p_2(-RT)r_2^{-3} + \cdots,$$

thus,

$$\frac{1}{\tau_c} = \frac{3kT}{4\pi r_A^2 \hat{J}^*} \left[ p_0(-RT)(r^0)^{-3} + p_1(-RT)r_1^{-3} + \cdots \right].$$

All aggregates with $\Delta E > -RT$ contribute to the background effect $\hat{J}^*$. Together with a change of the repulsive contribution due to binding, they cause an increase of $\hat{J}^*$. In (68) and (69) we have again marked the probabilities by the boundary value $-RT$ which
Nuclear spin relaxation and intermolecular interactions

has been used to define the nature of the aggregates. We see from (69) that again $\tau_e$ becomes longer when H-bonds are present, but the connection between the effective radius and the aggregate size has changed. Now

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{2\pi\gamma^*\hbar^2}{kT}\delta_0^6 (p_0 (r^6)^{-3} + p_1 r_1^{-3} + p_2 r_2^{-3} + \cdots).$$

(70)

Usually the direct application of (67) and (70) presents the following difficulty: If the monomeric particle is of spherical shape, then in general the higher aggregates will more or less deviate from spherical shape. Thus, each term would have to be corrected for anisotropic motion. However, the main purpose of these equations is to show that in the case of slow exchange (with respect to the correlation time $\tau_e$) the correlation time is mostly influenced by the large aggregates whereas in the event of fast exchange it is mainly determined by the small aggregates.

6.3 Discussion of some experimental results

The interconnection between the rotational correlation time of a molecule as obtained from nuclear spin relaxation and H-bonding has been described fairly extensively in a previous review article (Hertz and Zeidler 1976), in which experimental results have also been presented and discussed. The number of new papers pertinent to this problem and appearing in the last four years is small. Thus it may suffice that in the present article we only give a brief summary of the experimental results, for more details the reader is referred to Hertz and Zeidler (1976). In the upper half of table 2 we present the rotational correlation times for a number of molecules in the corresponding pure liquid which do not form H-bonds. All these molecules are not spherical rigid bodies in the strict sense, however, they deviate as little as can be realized by the scheme of chemical bonding from such an ideal shape. Apart from ammonia these molecules have three to six heavy atoms, i.e., C, or O, or in one case Br. It will be seen that the correlation times (= 1/3 of the reorientation times) of these molecules range from 0.6 to 2 psec, the occurrence of internal motion in some of the examples should be noticed. The self-diffusion coefficient for these non-hydrogen bonded substances ranges from almost $2 \cdot 10^{-5}$ to almost $5 \cdot 10^{-5}$ cm$^2$ sec$^{-1}$.

In the lower part of table 2 a number of data are collected which refer to molecules which again contain two to five heavy atoms which, however, form H-bonds. Now the rotational correlation times of the 'molecules' are definitely longer, they range from 4 to 60 psec. This clearly is the effect of the H-bonds, effectively the molecules have become larger. There exists one complication which we have already indicated by setting the word 'molecule' in quotation marks. Indeed, the values for the rotational correlation times refer to the H-bonded parts of the molecule in all cases, i.e. the OH groups. The alkyl part shows internal rotation, so that the correlation time of the methyl or methylene protons are shorter. Yet, again, when compared with the internal rotation-modified data of the non-hydrogen-bonded molecules, the times are longer which is an indirect manifestation of the H-bonding.

What we have found for the rotational motion is also verified for the translational diffusion: the self-diffusion coefficients in the case of H-bonding are about half as large as in the normal liquids.

What is the kind of quantitative information that can be derived from these experimental results? As we already mentioned, the problem arises from the fact that by
the coupling of two spherical molecules with a bond we do not create a new spherical molecule. Thus, even if we can assign a suitable radius \( r^0 \) to the monomer this will not generally be possible for the dimer which will be more or less cigar-shaped. In this situation one can choose between two possibilities for proceeding further: One may have knowledge about the correlation time of a suitable model molecule for the dimer or trimer and so on. For example \((C_2H_5)_2CO\) (propyl acetate) has been taken as a model substance for the dimer of ethanol (Grüner and Hertz 1972). The other possibility is to estimate the correct values of \( r_1, r_2, \ldots \). An example is given in a paper by Weingärtner et al (1978), who studied the association between water and dimethyl formamide.

If we now have knowledge of suitable \( r^0, r_1, r_2, \ldots \) values then we can introduce these numbers in (67) or (70). The former equation is valid if the slow exchange limit represents the correct description, the latter section holds for the fast exchange situation (see the previous section). If the existence of aggregates containing many molecules cannot be excluded and still the increase of the relaxation rate relative to the monomeric state is not very great, then (70) is to be applied. This is the situation expected in pure water. In contrast to this, if in a given solution the occurrence of high aggregates is very unlikely and still an appreciable increase of the intramolecular relaxation rate with increasing H-bonding component has been observed, then the slow exchange formula certainly is the correct one. In this situation one can conclude that the potential depth of binding force is greater than the limiting energy necessary for a lifetime to be equal to the correlation time in question, i.e. \(-18.8 \text{ kJ/mole}\) in the case where we have a correlation time of the order of \(10^{-11}\) sec. This method has been applied to the mixture \(CCl_4\)-ethanol at comparatively low ethanol concentrations (Grüner and Hertz 1972). Probably at higher concentrations of methanol and ethanol the exchange becomes faster and it is doubtful whether (67) is still valid because in the pure liquid large aggregates would lead to very large proton relaxation rates which have not been observed. On the other hand, it has been found (Göller et al 1972) that the intermolecular \(\text{OH} \cdots \text{OH}\) relaxation rate in \(\text{CD}_3\text{OH}\) and \(\text{C}_2\text{D}_5\text{OH}\) can be calculated approximately correctly if one assumes that a proton-proton vector only performs rotational motion with a correlation time \(\approx 10^{-11}\) sec. Such a model would imply that the life-time of the dimer is about \(10^{-11}\) sec. i.e. it is not short compared to the correlation time. It should be emphasized that the method we have described so far has been applied only very rarely, and, particularly these days as owing to more modern equipment more reliable and precise experimental results can be obtained, a systematic application of the intramolecular relaxation method is strongly recommended.

As we already mentioned, the correct description of the dynamical situation in water is given by a fast or at least moderately fast exchange of the water molecule among aggregates containing two or more molecules. The residence time in a given state of aggregation is \(\approx 10^{-12}\) sec. The rotational—and translational—diffusion is close to a microstep diffusion, though it probably does not really represent the ideal form of microstep diffusion. It has been calculated from \(\tau_\alpha = 2.5\) psec, the rotational correlation time in pure liquid water (25°C), and from \(\tau_{\alpha 0} = 0.5\) psec, the estimated correlation time of monomeric water in an inert solvent, that the probability \(\omega_1^+\) of finding a water molecule (in pure liquid H_2O) attached to another one in the first coordination sphere for a time substantially longer than the decay time of angular velocity correlations, i.e. longer than \(10^{-13}\) sec, is \(\omega_1 \approx 0.7\). The corresponding probability for a second coordination sphere is \(\omega_2^+ \approx 0.25\) (Hertz 1970).
The $p_i$'s in (70) are suitable products of $\omega_i^+ + 1 - \omega_i^+$, $i = 1, 2$. Furthermore, again from the comparison of $\tau_i$ in pure water and $\tau_{\text{c}}$ for the unbound molecule, it has been estimated that the effective potential depth in liquid H$_2$O which couples two water molecules together for a time $\approx 10^{-12}$ sec is $\leq -9.6$ kJ/mole (Hertz 1971). This result demonstrates again that in a qualitative way numerical results for the effective intermolecular potential can be derived from the study of intramolecular nuclear spin relaxation rates.

7. Anisotropic motion and intermolecular interaction

7.1 Evaluation of spectral densities and effective correlation times

In the following two sections we discuss the anisotropic rotational motion of small, rigid molecules as studied by nuclear magnetic relaxation rates. First we introduce briefly the theoretical framework. Recent work has demonstrated that the measurement of cross-correlation (dipolar) relaxation terms in addition to the familiar autocorrelation terms can provide valuable new information (Redfield 1965). Therefore we quote here the formulas for dipolar relaxation in full generality—the meaning of the technical terms 'auto- and cross-correlation' will be explained in the text subsequently.

We give a series of experimental examples arranged logically in three subsections, symmetric top molecules, asymmetric top molecules which have been treated approximately as symmetric tumblers, and finally planar asymmetric top molecules where a complete analysis of motional anisotropy has been performed.

In the previous chapters it has been discussed thoroughly that the time correlation function of a perturbation, or its associated Fourier-transform, the spectral density, is the central quantity relating the microscopic behaviour and the measurable relaxation rate. We illustrate the evaluation of spectral densities here for dipolar relaxation, and for the sake of notational simplicity we consider only spins $1/2$. In the dipolar relaxation mechanism we have to deal with fluctuating magnetic moments associated with individual spin pairs residing on one molecule. Basic relaxation theory (Abragam 1961) shows that a time correlation function of the so-called 'lattice part' $\gamma^m_l (\Omega_{AB}(t))/r_{AB}(t)$ has to be calculated. $\gamma^m_l$ is the $m$th component of a spherical harmonic of degree two. $AB$ refers now to a spin pair $r_{AB}(t)$ is an internuclear vector with the orientation $\Omega_{AB}(t)$ and the magnitude $r_{AB}(t)$. For intramolecular relaxation we have obviously $r_{AB}(t) = r_{AB}(0)$ if the vector is between two nuclei in a rigid molecule. When evaluating the time correlation function one has to include correlations between $\gamma^m_l/r$ for $AB$ and $CD \neq AB$ pairs, see (71) below. The motional model used so far is the rotational diffusion model since it is the only one that allows the calculation of the time correlation function for asymmetric rotors for auto- and cross-correlation. To build a conceptual bridge to older work on the basis of the spherical rotor model effective correlation times may be conveniently introduced. For auto-correlation these $\tau_{\text{eff}}$'s are associated in a pictorial interpretation with the motion in time of one internuclear vector—in the spherical model the $\tau_{\text{eff}}$'s for all internuclear vectors in a rigid molecule are equal by definition. Cross-correlation 'effective correlation times' should be considered more as formal quantities; they may be $< 0$ and this obviously conflicts with the concept that the correlation time is a measure of the decay of the orientational correlation function.

Dipolar interaction (DO) is a tensor interaction of rank two. Likewise quadrupolar interaction (QF) is a tensor interaction of rank two. Effective correlation times defined
for QF are therefore identical to $\tau_{\text{eff}}$'s from DD, and in the practical evaluation of anisotropic motion one can use a combination of $\tau_{\text{eff}}$'s from DD and QF. To proceed we start with the time correlation function for dipolar interaction. $AB$ and $CD$ refer in the most general situation to two different spin pairs, $\mathbf{r}_{AB}(t)$ and $\mathbf{r}_{CD}(t)$ are the two internuclear vectors associated with them.

$$G(t) = N \frac{Y_{2}^{(m)}(\Omega_{AB}(0))}{r_{AB}^{3}(0)} \cdot \frac{Y_{2}^{(m)}(\Omega_{CD}(t))}{r_{CD}^{3}(t)}.$$  \hspace{1cm} (71)

$N$ is the normalization factor.

Here we have used the result that for correctly normalized lattice functions the correlation functions are independent of the component index $q$ of the spherical harmonics $Y_{2}^{(m)}$ (Hubbard 1969) $\Omega_{AB}$ are the two Eulerian angles that describe the orientation of the vector $\mathbf{r}_{AB}$ in the laboratory frame. If we separate the ensemble average over vibration and rotation (71) changes to

$$G(t) = N \langle \mathbf{r}_{AB}^{3}\rangle_{\text{vib}} \cdot \langle \mathbf{r}_{CD}^{3}\rangle_{\text{vib}} \cdot \langle Y_{2}(\Omega_{AB}(0)) Y_{2}(\Omega_{CD}(t)) \rangle_{\text{rot}}.$$  \hspace{1cm} (72)

(correctly not $r^{-3}$ but $(Y_{2}/r^{3})$ should be averaged, Diehl and Niederberger 1973).

Equation (71) is generally valid for dipole-dipole relaxation but (72) only for intramolecular relaxation if the magnitude of vectors $\mathbf{r}_{ij}$ is constant in time. Such a condition is met by internuclear vectors in a rigid molecule but generally not by vectors between a nucleus in a internally rotating group and a nucleus in the rigid ‘backbone’. Obviously only angular functions determine $G(t)$. Expressions of the form of (72) with $AB \neq CD$ occur naturally in the complete theoretical treatment. They are denoted as ‘cross-correlation’ terms whereas for $AB = CD$ we have ‘auto-correlation’ terms. To perform the average $\langle \cdots \rangle_{\text{rot}}$ in (72) we define the orientation of an internuclear vector $\mathbf{r}_{ij}$ in a molecule-fixed system. This is straightforward enough for rigid molecular systems. Complications because of additional degrees of freedom of internal rotation shall not be treated here (Woessner 1962a, b; Woessner et al 1969). A time dependent transformation connects the molecule-fixed with the laboratory system,

$$\langle Y_{2}^{(m)}(\Omega_{AB}(0)) Y_{2}^{(m)}(\Omega_{CD}(t)) \rangle_{\text{rot}}^{AB} = \sum_{n,n'} \langle D_{nm}^{(2)}(\Omega(0)) D_{n'm'}^{(2)}(\Omega(t)) \rangle_{\text{rot}}^{\text{mol}} Y_{2}^{(m)}(\Omega_{AB}^{\text{mol}}) Y_{2}^{(m)}(\Omega_{CD}^{\text{mol}}).$$  \hspace{1cm} (73)

$\Omega$ (without indices) are the Eulerian angles which relate the laboratory frame to the molecular frame, and $D_{nm}^{(2)}$ are elements of the Wigner rotation matrix. To evaluate the rot-average on the right-hand side of (73) one has to introduce a motional model. Microstep rotational diffusion is widely accepted (above all in the extreme-narrowing limit) and is also the only model that enables the calculation of cross-correlation terms. Hubbard (1970) and Huntress (1970) have first performed the (tedious) evaluation, and a recent reformulation has been given by Werbelow and Grant (1977). The full description contains the rotational diffusion-tensor or in its diagonal form the three rotational diffusion constants $D_{ii}, i = x, y, z$. Principal rotational correlation times are defined by

$$\tau_{ii} = \frac{1}{6D_{ii}}, \quad i = x, y, z.$$  \hspace{1cm} (74)

where the numerical factor 6 stems from having calculated tensor quantities of rank two (see also §6.1). Only if the molecule-fixed coordinate system, introduced above,
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coincides with the principal diffusional system the three constants $D_i$ give a correct description! (Here, of course, only the angular transformation is important, the origin of the centers is unimportant in the calculation of the correlation function. $\Omega_{A}^{\text{MOL}}$ is the orientation of an internuclear vector $r_{AB}$ with respect to any arbitrary coordinate system fixed in the molecule.) Otherwise nondiagonal elements $D_{ij}, i \neq j$ have to be included (Huntress 1970). The orientation of the principal diffusional axis system can be given by symmetry or its orientation to the molecular frame is an additional parameter. For molecules with symmetry $C_{2v}$ or greater, the inertial tensor diagonalizes also the diffusional tensor. The constants $D_{ij}$ are statistical parameters which describe the 'average' behaviour of a single molecule, and therefore, in the ensemble equivalent parts of a molecule experience equivalent interactions with the environment.

We give finally the result in the situation of extreme narrowing (experimental work has been almost exclusively in this limit):

$$ J = J_{AB,CD} = 0, 3 \left\langle r_{AB}^{-3} \right\rangle \cdot \left\langle r_{CD}^{-3} \right\rangle \tau_{AB,CD} $$

$$ \tau_{\text{eff}} = \tau_{AB,CD} $$

is the effective correlation time for the interaction of two spin pairs $AB$ and $CD$. The full and lengthy expressions for $\tau_{AB,CD}$ can be found in Vold and Vold (1978, eqs (35a)-(38d)). It is possible that other published tables (Vold et al 1977; Wright et al 1979) contain misprints. $\tau_{AB,CD}$ is a function of the orientation of the two vectors $r_{AB}$ and $r_{CD}$ (4 angles) and the diffusion constants $D_i, i = x, y, z$, in the principal diffusional axis system, i.e. the relative orientation of the diffusional axis system with respect to a molecular frame must be known. Three linear independent relaxation rates should allow the determination of the three coefficients $D_i$. The practical application has revealed that due to the complicated angular dependence of the effective correlation times on the diffusion constants a large numerical uncertainty of the $D_i$'s results, in particular if only auto-correlation terms $\tau_{ABAB}$ are used in the calculation of the diffusion constants. Recent work (Vold et al 1977; Vold and Vold 1978; Nery and Canet 1978; Stark et al 1979; Kratochwill et al 1979) has shown how this problem may be circumvented by including cross-correlation terms in the analysis.

Most of the experimental work has been done using simple models. For an isotropic model with

$$ D_r = D_{xx} = D_{yy} = D_{zz}, $$

we have

$$ \tau_{\text{eff}} = \tau_{AB,CD} = \frac{1}{6D_r}. $$

One relaxation rate is sufficient to determine $D_r$. For the symmetric rotor model (Woessner 1962a, b) we obtain with

$$ D_\parallel = D_{zz} \quad \text{and} \quad D_\perp = D_{xx} = D_{yy}, $$

$$ \tau_{\text{eff}} = \frac{A}{6D_\perp} + \frac{B}{5D_\perp + D_\parallel} + \frac{C}{2(D_\perp + 2D_\parallel)} $$

where

$$ A = \frac{1}{4} (3l^2 - 1)^2, $$

$$ B = 3l^2 (1 - l^2)^2, $$

$$ C = \frac{3}{4} (l^2 - 1)^2. $$
is the direction cosine between the internuclear vector and the axis which describes the parallel motion. Equations (76)–(80) are valid for auto-correlation terms, i.e. the conventional relaxation rates. $\tau_{\text{eff}}$ is then formally given by $\tau_{\text{eff}}$, and the time correlation function of one particular vector $\mathbf{r}_{\text{AB}}$ is considered. With the values of $\tau_{\text{eff}}$ we have the desired expressions for the longitudinal relaxation rate by substituting $\tau_{\text{eff}}$ in (58) and (62) by $\tau_{\text{eff}}$. According to (79) two (independent) relaxation rates allow the determination of the diffusion constants $D_\perp$ and $D_\parallel$.

For the sake of completeness and to illustrate the increased complexity we cite in table 3 expressions for effective correlation times in planar molecules. $\phi_{ij}$ is the azimuthal angle of the vector $\mathbf{r}_{ij}$ in the principal axis system. $\Delta_+$ and $\Delta_-$ are two redefined motional parameters (Vold et al. 1977). It is

$$\Delta_+ = \frac{D_{xx} + D_{yy}}{2D_{zz}}$$

(motional anisotropy)

and

$$\Delta_- = \frac{D_{xx} - D_{yy}}{D_{zz}}$$

(motional asymmetry)

For a determination of $\Delta_+$, $\Delta_-$ and $D_{zz}$ three effective correlation times are necessary, one of these has to be connected with a cross-correlation term ($J_{ABCD}$, $AB \neq CD$).

The symmetric diffusive rotor model, (79) and (80), seems to be most appealing for experimental verification. It contains basic features of anisotropic motion and for the experimental analysis only two relaxation rates (auto-correlation) are needed. A study of symmetric top molecules $ZX_3Y$ is of interest since for $C_3v$ symmetry the orientation of the diffusion tensor is given by symmetry. Widespread application for molecules with less than $C_3v$ symmetry has been dictated by practical reasons: it was often impossible to measure more than two independent relaxation rates. A very important class of chemical systems studied in this way are the planar aromatic six-membered rings. We consider monosubstituted benzenes as an example. Based on experimental results the ratio of ortho(meta)-/para-carbon relaxation rates constitute a convenient parameter to describe motional anisotropy:

$$\rho = \frac{1/2 \left[ (1/T_1)_{\text{intra(ortho)}} - (1/T_1)_{\text{intra(meta)}} \right]}{(1/T_1)_{\text{intra(para)}}}$$

Table 3. Effective correlation times for planar asymmetric tumblers.

<table>
<thead>
<tr>
<th>$\tau_{\text{eff}}$</th>
<th>$A = 1/2(1 - (1 - \Delta_+)/\Omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1 = 3/4 \sin 2\phi \sin 2\phi'$</td>
<td>$B = 1/2(1 - (1 - \Delta_+)/\Omega)$</td>
</tr>
<tr>
<td>$c_2 = 1/4 A + w_1 B + w_2 C$</td>
<td>$C = (3^{1/2}/2) \Delta_+/\Omega$</td>
</tr>
<tr>
<td>$c_3 = 1/4 A - w_1 A - w_2 C$</td>
<td>$w_1 = 3/4 \cos 2\phi \cos 2\phi'$</td>
</tr>
<tr>
<td>$\lambda_1 = 2D_{xx}(2 + \Delta_+)$</td>
<td>$w_2 = (3^{1/2}/8)(\cos 2\phi + \cos 2\phi').$</td>
</tr>
<tr>
<td>$\lambda_2 = 2D_{xx}(1 + 2\Delta_+ - \Omega)$</td>
<td>$\Delta_+ = (D_{xx} + D_{yy})/2D_{zz}$</td>
</tr>
<tr>
<td>$\lambda_3 = 2D_{xx}(1 + 2\Delta_+ + \Omega)$</td>
<td>$\Delta_- = (D_{xx} - D_{yy})/D_{zz}$</td>
</tr>
<tr>
<td>$\Omega = (1 + 3/4\Delta^2 + \Delta^2 / 2 - 2\Delta_+) 1/2$</td>
<td>$\phi = \phi_{a\theta}$, $\phi' = \phi_{cd}$</td>
</tr>
</tbody>
</table>
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Assuming equal bond distances $\langle r_{CH}^{-3}\rangle^{-1/3}$ for all CH vectors the ratio of relaxation rates is equal to a ratio of correlation times,

$$\rho = \frac{1/2 \left[ \tau_{\text{eff}}(\text{ortho}) - \tau_{\text{eff}}(\text{meta}) \right]}{\tau_{\text{eff}}(\text{para})}$$  \hspace{1cm} (84)

Woessner's equations, (79) and (80), can be used when the principal axis system is chosen as shown in figure 15a. The orientation of the principal axis system must be as shown from symmetry considerations. If we adopt per definitionem an equal in-plane $(D_{yy})$ and out-of-plane $(D_{zz})$ rotational diffusion constant (both $D_\perp$), two effective correlation times

$$\tau_{\text{eff}}(\text{ortho}) = \tau_{\text{eff}}(\text{meta}) \quad \text{since} \quad \tau_{\text{eff}}(\theta = 60^\circ) = \tau_{\text{eff}}(\theta = 120^\circ)$$

and

$$\tau_{\text{eff}}(\text{para}) = \tau_{\text{eff}}(\theta = 0^\circ)$$

are sufficient to determine $D_\parallel$ and $D_\perp$. The equality

$$D_{xx} = D_{yy} = D_\perp$$

is a stringent demand, absolute values of $D_\parallel$, $D_\perp$ for asymmetric top molecules calculated with the symmetric rotor approximation may be quantitatively unsatisfactory.

On the other hand the ratio $\rho$ is meaningful as a qualitative motional probe (we discuss this again for monosubstituted benzenes). In figure 15b we show the indexing of the axis system for the application of the equations valid for an asymmetric tumbler, see table 3. Here $D_{zz}$ is the out-of-plane diffusion constant. Results of model calculations are shown in figure 16. As for the symmetric model we have $\tau_{\text{eff}}(o) = \tau_{\text{eff}}(m)$ and therefore only the ratio $\rho = \tau(o)/\tau(p)$ is shown. $\rho$ is contained in a relatively narrow band for a large variation of the value of the third (out-of-plane) diffusion constant $D_{zz}$. $D_{zz}/D_{yy} = 1$ corresponds to the symmetric rotor model. For isotropy with respect to the ring plane, $D_{xx} = D_{yy}$, one calculates $\rho = 1$, independent of $D_{zz}$. $\rho \neq 1$ contains information on all three diffusion constants, but one given value is consistent with a family of triples $(D_{xx}, D_{yy}, D_{zz})$—defined by a horizontal cut through the band of curves in figure 16. (More generally, we will learn below when discussing specific examples that in planar systems, (auto-correlation) relaxation rates alone cannot give a value of $D_{zz}$.

![Figure 15](image)

**Figure 15.** Conventional choice of indexing of axes for the model of (a) asymmetric rotor (b) an asymmetric rotor for planar molecules, in particular monosubstituted benzenes. The orientation of the principal diffusional axis system in monosubstituted benzenes is determined by symmetry; O indicates substitution.
Figure 16. Motional parameter $\rho$ as a function of the anisotropy ratio of the rotational diffusion constant $D_{xx}/D_{yy}$ for various values of the out-of-plane rotational diffusion constant $D_{zz}$.

but only a precise figure for $D_{yy}/D_{xx}$. (Kratochwill and Vold 1980,)) If we are interested only in a qualitative evaluation the sign of $(\rho - 1)$ immediately indicates the anisotropy with respect to the ring plane, $\rho < 1$ means $D_{xx} > D_{yy}$, i.e. faster reorientation around the 1,4-axis for any arbitrary $D_{zz}$. Such values $\rho < 1$ have experimentally been found for 1-substituted benzenes where steric effects result in anisotropic motion or systems where strong intermolecular hydrogen-bonds can be formed.

To summarize the theoretical framework we have two important quantitative models to interpret relaxation rates in terms of anisotropic motion: the models of a symmetric and of an asymmetric (diffusive) rotor. For planar rings ratios of correlation times, or relaxation times respectively, can be used to obtain information about the motional anisotropy with respect to the ring plane, in favourable situations even quantitatively.

7.2 Experimental examples

To study the anisotropy of molecular reorientation one has to measure more than one effective correlation time associated with different vectors in the molecule under consideration. The most general situation, the asymmetric tumbler, can be evaluated if $n \geq 3$ independent effective correlation times $\tau_{\text{eff}}$ are known. It is favourable to refer to only one experimental method, i.e. in our case to base the analysis upon NMR relaxation rates alone. In principle correlation times being the result of other types of spectroscopy e.g. light scattering can be used in a combined analysis.

We shall first discuss symmetric tumblers; mono- or trisubstituted methanes are a convenient series of chemical compounds to shed light on the principles of the procedure. From molecular geometry the orientation of the rotational diffusion tensor is known and the symmetric model provides an exact description as long as rotational diffusion is accepted. Methylene compounds $\text{CH}_2\text{X}_2$ have been treated with the (approximate) symmetric and the (correct) asymmetric model. Planar aromatic rings
Nuclear spin relaxation and intermolecular interactions were studied in the pure phase as well as in binary mixtures. Since internal rotation is not present these systems are convenient for studies of overall motional anisotropy. Such investigations provide information about the symmetry of the intermolecular potential. With conventional relaxation rates (auto-correlation) and with an approximate procedure (observation of the ratio of correlation times) meaningful qualitative results can be obtained. More refined methods allow a quantitative analysis as will be demonstrated below.

For symmetric top molecules $ZX_3Y$ with $C_{3v}$ symmetry Woessner's theory (Woessner 1962b) can be applied in a straightforward manner. Figure 17 shows the orientation of the principal axis system of the rotational diffusion tensor. The $||$-motion is around the figure axis ($C_3$) and $D_\perp$ describes the orientation of the figure axis. According to (79) and (80) the effective correlation time associated with a $Z-X$ vector depends only on $D_\perp$, the corresponding $\tau_{\text{eff}}$ may be determined by a $Z-X$ dipolar relaxation rate or a quadrupolar relaxation rate of the $X$ nucleus. (Generally $\tau_{\text{eff}}$ associated with a vector parallel to one principal axis is determined by the two diffusion constants perpendicular to this direction.) $\tau_{\text{eff}}$ associated with a $Z-Y$ vector depends on $D_\parallel$ and $D_\perp$. Henceforth we have two equations to solve for the unknowns $D_\parallel$ and $D_\perp$. Experiments have been evaluated according to these lines. The analysis revealed that this model may be oversimplified. The calculated rotational diffusion constant $D_\parallel$ for the motion around the figure axis shows that the $||$ motion is barely in the limit of small step angular diffusion but inertial effects are also important. The discussion of more refined models ('extended diffusion'), elaborated for spherical and symmetric rotors, is beyond the scope of this review. Essentially such models describe collision interrupted free inertial motion where either only the orientation ($M$-diffusion) or the orientation and the magnitude ($J$-diffusion) of the angular momentum vector are randomized in each 'collision' McClung 1977.

The anisotropic reorientation of acetonitrile has been investigated by Bopp (1967) and Woessner et al (1968) and $^{14}\text{N}$ and $^2\text{H}$ or $^1\text{H}$ relaxation rates used to determine $D_\parallel$ and $D_\perp$. Consistent results were obtained: the reorientation of the methyl group about its symmetry axis is approximately ten times faster than the reorientation of the nitrile group, see table 4. Different activation energies for $||$- and the $\perp$-motion corroborate the statement that motional anisotropy exists. For the $||$-motion inertial effects are important as has been pointed out by Bull and Jonas (1970). The activation volume for $||$-motion, $\Delta V^+(D_\parallel)$, is $\approx 0$, and $\Delta V^+(D_\perp) = 8.5 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$. The relative import-

![Figure 17. Principal diffusional axis system in symmetric top molecules ZXY₃.](image-url)
Table 4. Symmetric tumblers: anisotropy of motion and Arrhenius' activation energies (kJ mol\(^{-1}\)).

<table>
<thead>
<tr>
<th>System</th>
<th>(D_{\parallel}/D_{\perp})</th>
<th>(E_a(D_{\parallel}))</th>
<th>(E_a(D_{\perp}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)Br</td>
<td>(\approx 8) (25°C)</td>
<td>3.8</td>
<td>7.1*</td>
<td>Lassigne and Wells (1977b)</td>
</tr>
<tr>
<td>CH(_3)I</td>
<td>10 (25°C)</td>
<td>3.3</td>
<td>7.9*</td>
<td>Gillen et al (1971)</td>
</tr>
<tr>
<td>CH(_3)CN</td>
<td>10-35 (25°C)</td>
<td>3.1</td>
<td>8.4</td>
<td>Woessner et al (1968)</td>
</tr>
<tr>
<td>CH(_2)CN</td>
<td>8.9 (25°C)</td>
<td>3.3</td>
<td>7.1</td>
<td>Bopp (1967)</td>
</tr>
<tr>
<td>CH(_2)C=CH</td>
<td>14.1 (--30°C)</td>
<td>2.1</td>
<td>7.1</td>
<td>Jonas and DiGennaro (1969)</td>
</tr>
<tr>
<td>CH(_3)NO(_2)</td>
<td>(\approx 9) (25°C)</td>
<td>3.8</td>
<td>7.9</td>
<td>Suchanski and Canepa (1979)</td>
</tr>
<tr>
<td>CH(_3)H(_2)CH(_3)</td>
<td>(\approx 40) (25°C)</td>
<td>5.4</td>
<td>3.6</td>
<td>Lassigne and Wells (1977a)</td>
</tr>
<tr>
<td>CH(_2)Cl(_3)</td>
<td>1.9 (20°C)</td>
<td>2.9</td>
<td>6.7</td>
<td>Huntress (1969)</td>
</tr>
<tr>
<td>CH(_2)Br(_3)</td>
<td>1.5 (20°C)</td>
<td>7.5</td>
<td>10.5</td>
<td>Yamamoto and Yanagisawa (1977)</td>
</tr>
<tr>
<td>VO(_3)(_2)</td>
<td>1.4 (30°C)</td>
<td>9.6</td>
<td>8.2*</td>
<td>Gillen and Noggle (1970)</td>
</tr>
<tr>
<td>CCl(_3)CN</td>
<td>2.1 (25°C)</td>
<td>8.0</td>
<td>11.2*</td>
<td>Gillen and Noggle (1970)</td>
</tr>
<tr>
<td>BCl(_3)</td>
<td>0.75 (0°C)</td>
<td>6.9</td>
<td>5.3*</td>
<td>Gillen and Noggle (1970)</td>
</tr>
</tbody>
</table>

*Calculated from a hydrodynamic approach.

Motional anisotropy was found for nitromethane, \(D_{\parallel}/D_{\perp} \approx 9\) (Suchanski and Canepa 1979). The present authors denote \(D_{\parallel}\) as 'internal rotational diffusion constant \(D_{\parallel}'\). In dimethylmercury(II) Lassigne and Wells (1977a) found the large anisotropy \(D_{\parallel}/D_{\perp} \approx 40\). This ratio can increase even more if the methyl group is an internally rotating group in a larger molecule. To quote an example, Brown et al (1977) report \(D_{\parallel}/D_{\perp} \approx 120\) for methylacetatomercury(II).

CH\(_3\)Br was investigated by Lassigne and Wells (1977b). \(D_{\perp}\) was estimated from dielectric relaxation data,

\[
D_{\perp} = \frac{1}{2D_{\parallel}},
\]
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and consequently from $^2\text{H}$ relaxation rates $D_\parallel$ could be calculated. At 25°C the reorientation about the figure axis is about eight times faster than the reorientation of the axis. The temperature dependence of $D_\perp$ was approximated by the temperature dependence of $D_\mu$ calculated from a hydrodynamic approach (Gillen and Noggle 1970),

$$D_\perp \approx D_\mu = 115 \cdot 10^8 \frac{Td}{\eta M}$$

where $M$ is the molecular mass, $\eta$ the viscosity and $d$ the density. With these results from the $^2\text{H}$ relaxation rates, $E_a(D_\parallel)$ could be calculated. This approximate evaluation procedure has been applied to many studies of symmetric molecules. Wallach and Huntress (1969), Huntress (1970) and Gillen and Noggle (1970) have proposed a quantitative test for whether the small angular step diffusion model may be valid: the ratio

$$\chi = \frac{\tau_{\text{eff}}}{\tau_{\text{FR}}}$$

should be larger than 5; $\tau_{\text{FR}}$ is the correlation time for free inertial behaviour. The result $\chi \approx 1-2$, found for CH$_3$Br and in other studies of symmetric molecules mentioned here, reveals that the absolute figures of $D_\parallel$ should be regarded with caution.

CH$_3$I has been treated earlier with the identical evaluation procedure (Gillen et al 1971). Anisotropic reorientation and likewise different activation energies for parallel and perpendicular motion were found. The authors pointed out that the similarity of motional anisotropy in CH$_3$I and CH$_3$CN is not surprising because of similar shapes and moments of inertia of the two compounds.

Trihalomethanes CHX$_3$, X = F, Cl, Br have been investigated. In fluoroform the comparison of correlation times from $^2\text{H}$ quadrupolar and $^1\text{H}$-$^19\text{F}$ intramolecular dipolar relaxation rates revealed approximately isotropic reorientation (Chaffin III and Hubbard 1967; Harre 1976). The anisotropic motion of chloroform has been studied in the neat liquid by Huntress (1969). Although inertial effects were important, $^2\text{H}$ and $^{35}\text{Cl}$ relaxation rates were evaluated with the diffusion model, $D_\parallel = 18 \cdot 10^{10}$ sec$^{-1}$ and $D_\perp = 9 \cdot 10^{10}$ sec$^{-1}$ at 20°C. The conclusion that anisotropy exists is supported by different activation energies for the two motional modes. Briguet et al (1977) investigated 0.05 m solutions of $^{12}\text{CHCl}_3$ and $^{13}\text{CHCl}_3$ in CS$_2$. At 30°C they found $D_\parallel = 20.9 \cdot 10^{10}$ sec$^{-1}$ and $D_\perp = 15 \cdot 10^{10}$ sec$^{-1}$. With decreasing concentration of electric dipole moments the motion becomes more isotropic but $\chi < 2$ for $\parallel$ and $\perp$ motion emphasizes the importance of inertial effects. Free rotor correlation times for chloroform in the gas phase lead to the result that the perpendicular motion is faster than the $C_3$ motion. The reverse situation in the liquid is probably caused by ‘closer packing and by self-association through hydrogen bonding along the $C_3$ axis’ (Huntress 1970). In binary systems with benzene (Huntress 1969), with ethers (Eckert et al 1974; Helm and Kratochwill 1978) and with hexamethylphosphoramide (Briguet et al 1978) an increase of the ratio $D_\parallel/D_\perp$, as compared with the pure liquid, was observed. The reorientation of the $C_3$ axis (tumbling motion) is hindered relative to the situation in pure chloroform; hetero-association via hydrogen bonds may neatly explain this slowing down of motion. Support comes from the observed increase of the activation energies in the mixture with benzene—a larger increase for the tumbling motion than for the $C_3$ motion. Consequently the experimental results of an investigation of the rotational motion in bromoform were interpreted analogously: the smaller ratio
$D_{||}/D_{\perp}$ ≈ 1.5 was attributed to 'less dense packing and less self-assocation than in chloroform' (Yamamoto and Yanagisawa 1977).

Gillen and Noggle (1970) studied BCl₃ (no dipole moment), VOCl₃ ($\mu \approx$ 0.3 D) and CCl₃CN ($\mu \approx$ 2.0 D). Their evaluation procedure has been described above (see CH₃Br). BCl₃ and VOCl₃ are two borderline cases concerning the application of diffusional models: in BCl₃ $D_{||}$ and $D_{\perp}$ are in the inertial limit, and the anisotropy $D_{||}/D_{\perp} = \tau_{||}/\tau_{\perp} = 0.75$ agrees well with the ratio of the moments of inertia ($I_{||}/I_{\perp})^{1/2} = 0.71$. In VOCl₃ both motions are in the diffusional limit. Since in most other studies $D_{||}$ is in the inertial and $D_{\perp}$ in the diffusional limit VOCl₃ can be considered as a singular case for the correct quantitative application of the diffusion model. The authors presented a general discussion of rotational motion of spherical top molecules and they arrived at the conclusion that dipole forces were more important than steric or inertial factors in determining motional anisotropy. Recently Chandler (1973, 1978) has argued that the repulsive part of the intermolecular potential is dominant. Indeed all results for symmetric top molecules can be explained on the basis of molecular shape alone. An indication of the importance of attractive forces for molecules with a large dipole moment has been given by Pedersen et al (1978), see below. Beyond any doubt hydrogen bonding on the other hand provides a source of motional anisotropy.

Sandhu studied CD₂Cl₂ (1978), CD₂Br₂ (1977) and CD₂I₂ (Sandhu and Peemöller 1976). In these molecules the dipole axis coincides with the symmetry axis (C₂). Assuming fastest reorientation about this axis a symmetric model may be justified. Sandhu measured $^2$H relaxation rates and calculated $D_{\perp}$ from hydrodynamic equations (this procedure has been described above, see (86)). As a result, the (assumed) fast reorientation about the C₂ axis was always verified, $D_{||}/D_{\perp} \approx 4$ (CD₂Cl₂), $\approx 6$ (CD₂Br₂), and $\approx 7$ (CD₂I₂). The activation energies for $||$ and $\perp$ motion are nearly equal, $E_a(D_{\perp})/E_a(D_{||}) = 1.01$ (CD₂Cl₂), $= 1.07$ (CD₂Br₂), and $= 1.00$ (CD₂I₂). The absolute values increase with increasing size of the substituent X, $E_a(D_{||}) = 8.07$ (CD₂Cl₂), $= 8.73$ (CD₂Br₂), and $= 12.96$ (CD₂I₂) kJ mol⁻¹. The $||$ motion is inertial, $\chi \sim 0.5 - 2$. Because of the multitude of approximations (hydrodynamic model and symmetric model for an asymmetric tumbler) we have only the qualitative result that the motion is more isotropic when the size of the substituent increases; molecular shape is sufficient to rationalize these findings. Mayne et al (1976) studied coupled spin relaxation of $^{13}$CH₂I₂ dissolved in benzene-d₆ (34 Wt %). The reorientation which involves the least displacement of the bulky iodines was found to be fastest; the ratios $D_{zz}/D_{xx} = 4.9$ and $D_{zz}/D_{yy} = 12.7$ when compared with Sandhu's result, $D_{||}/D_{\perp} \approx 7$, reveal that the symmetric model is indeed an oversimplification.

We discuss now relaxation studies of planar aromatic molecules. The exact evaluation has to be done using the model of an asymmetric tumbler; expressions for the effective correlation times as a function of the rotational diffusion constants have been given in table 3. An approximate analysis can be based on the symmetric model and we have demonstrated in figure 16 that the qualitative conclusions remain valid even if the assumed equality of one in-plane and the out-of-plane rotational diffusion constant is not fulfilled. The influence of shape as well as of intermolecular interactions upon motional anisotropy have been investigated.

Levy et al (1973) studied $^{13}$C relaxation rates of monosubstituted benzenes. The ratio $\rho$ of (o, m) and (p)-carbon relaxation rates, see (83), provides a qualitative measure of motional anisotropy. We prefer this viewpoint instead of giving a quantitative evaluation in terms of the symmetric model (with $D_{||}$ and $D_{\perp}$). Monosubstituted
benzenes $C_6H_5X$ show a ratio $\rho < 1$ which is consistent with a hindered rotational motion of the $C_2$ symmetry axis compared with a motion about this axis. Inertial effects (lower momentum of inertia around the C–X bond axis) and steric repulsions (by a motion around the C–X axis fewer surrounding molecules have to be 'pushed away') can explain the experimental result. The anisotropy of motion increases with increasing size of the substituent X; we quote some examples: X = CH$_3$, $\rho = 0.73$; X = NO$_2$, $\rho = 0.70$; X = CCH, $\rho = 0.60$; X = C(CH$_3$)$_3$, $\rho = 0.55$; X = C$_6$H$_5$, $\rho = 0.54$.

The influence of intermolecular hydrogen bonding has been studied by analogous procedures (Levy 1972; Levy et al 1973). $^{13}$C relaxation rates of phenol evidence anisotropic motion in concentrated solutions in CCl$_4$, $\rho = 0.58$, the reorientation of phenol becomes more isotropic on dilution, $\rho = 0.77$ in an 4 mol\% solution in CCl$_4$. Linear aggregates are assumed for self-associated phenol which break up at higher dilution. Possibly specific solvent effects are present in an 1:1 mixture of phenol and acetone, $\rho = 0.90$ may indicate 'folded complexes'. Slightly anisotropic tumbling is observed for aniline in carbontetrachloride and dimethylsulphoxide, $\rho = 0.77$ and 0.90. In acidic solution $\rho$ decreases markedly, $\rho = 0.35$ in CH$_3$CO$_2$H and $\rho = 0.23$ in CF$_3$CO$_2$H (20 vol\% solutions). A motion where the anilinium ion is 'locked' in the solvent lattice by ion pairing or electrostatic interactions has been proposed. The self-association via carboxyl groups has its counterpart in the motional anisotropy of benzoic acid where long-lived linear dimers may be formed, $\rho = 0.5$ and the non-associated methylbenzoate, $\rho = 0.8$; both 1 M solutions in (CDCl)$_2$ at 30°C (Levy and Terpstra 1976).

Pyridine has been shown to be a convenient motional probe for studying heteroassociation with hydrogen donor molecules. Campbell et al (1975) investigated 1/1 mixtures with monohydric alcohols. The authors observed a monotonous decrease of $\rho$ with increasing size of the alcohol, for example $\rho = 0.76$ (methanol), $\rho = 0.60$ (n-pentanol), and $\rho = 0.53$ (n-decanol). Kratochwill (1978) has studied the system pyridine-methanol in the concentration range pure pyridine to 10 mol\% solutions. The ratio $\rho$ decreases with increasing methanol concentration. Assuming a simple one-step equilibrium, $A + B \rightarrow AB$, an anisotropy ratio $D_\parallel/D_\perp \approx 4$ for the complexed state $AB$ was found. The $AB$ hetero association leads to a motional anisotropy of the same magnitude as observed for monosubstituted benzenes with a large substituent, e.g. C$_6$H$_5$. This may be explained by a methanol-pyridine complex which is stable within the time range of rotational correlation times (psec). Similar specific interactions were detected in binary systems of pyridine and water; the slowest motion is the reorientation of the C$_{para}$-N axis (Goldammer et al 1974; Kintzinger 1975).

We proceed now to a discussion of experiments in which the (full) motional anisotropy of planar rings was determined, mainly by combining $^{13}$C relaxation rates with the relaxation rate of one quadrupolar nucleus with a large asymmetry parameter of the quadrupole coupling tensor (Huntress 1970). Some of the results were obtained by using $^{13}$C relaxation rates and light-scattering data (Bauer et al 1974).

In benzene we have isotropy of motion with respect to the molecular plane (by symmetry) but the rotation about the sixfold axis is about 3.5 times faster than about the axes in the plane (Gillen and Griffiths 1972; Bauer et al 1974). Steric effects dominate (Bauer et al 1974). By investigating aza-substituted benzenes of approximately equal shape but with different electric dipole moments one may learn about the importance of dipole forces. Kintzinger and Lehn have studied the molecular dynamics of liquid pyridine (Kintzinger and Lehn 1971) and s-triazine (Kintzinger and
Lehn (1974) by combining $^2$H and $^{14}$N relaxation data. With analogous procedures—
combination of $^{13}$C and $^{14}$N relaxation rates—Pedersen et al. (1978) studied pyrimidine
and pyridazine. See figure 18 for structural formulas and orientation of tensor axes!
The motional behaviour of pyridine ($\mu = 2.22$ D), pyridine ($\mu = 2.33$ D) and s-triazine
($\mu = 0$) is similar; an anisotropy $D_{\parallel}/D_{\perp} > 1$ (or $D_{zz}/D_{yy,xx}$) was found at low
temperatures and the motion becomes more isotropic with increasing temperature.
Repulsive forces dominate and dipolar forces can only be verified by comparing
motions which are stericly unhindered. For example the $\parallel$ motion is slightly more
hindered in pyrimidine and pyridine ($\mu \neq 0$) than in triazine and benzene ($\mu = 0$).
Pyridazine ($\mu = 4.22$ D) shows evidence of the importance of dipolar forces.

The evaluation of motional anisotropy is strongly dependent on a proper choice of
the $^{14}$N quadrupole coupling constant and the asymmetry parameter. To illustrate the
experimental problems we mention the results for pyridine: the figure $D_{\parallel}/D_{\perp} \approx 3$ at
$-20^\circ$C (Kintzinger and Lehn 1971) has been reevaluated to $D_{\parallel}/D_{\perp} \approx 1.4$ (Schweitzer
and Spieß 1974; Spieß 1978a)—based on a new value of the quadrupole coupling
constant and on CSA (chemical shift anisotropy) relaxation rates $^{15}$N. Isotropic motion
with respect to the ring plane is revealed by equal relaxation rates for all carbons
(Goldammer et al. 1974); Spieß's result—approximately overall isotropic
reorientation—may indicate specific interactions in pyridine (dipolar ?) not present in
benzene.

Further information come from the temperature dependence of the rotational
diffusion coefficients evaluated with the absolute rate equation

$$D_{ii} = \frac{kT}{h} \exp \left( \frac{\Delta S_i^* - \Delta H_i^*}{R} \right) \quad \text{or} \quad i = x, y, z$$

$$D_{ii} = \frac{kT}{h} \exp \left( \frac{\Delta S_i^* - \Delta H_i^*}{RT} \right) \quad \text{or} \quad i = \parallel, \perp$$

The activation enthalpies for $D_{\parallel}$ (or $D_{xx}$ and $D_{yy}$) are similar for pyridine, pyrimidine
and s-triazine, $\approx 10$ kJ mol$^{-1}$, and are $\approx 6$ times larger than $\Delta H^*(D_{\parallel})$; activation
entropies $\Delta S^*(D_{\parallel})$, or $\Delta S^*(D_{xx}, D_{yy})$ respectively, are zero within experimental error,
supporting the concept that steric interactions dominate. $\Delta S^*(D_{\parallel})$ has a large negative
value, $-30$ J mol$^{-1}$ K$^{-1}$; for free inertial behaviour one calculates $\Delta S^* =
-0.1$ J mol$^{-1}$ K$^{-1}$ (Pedersen et al. 1978). Activation enthalpies $\Delta H^*(D_{xx}, D_{yy})$
for pyridazine are smaller, 6.3 and 9.2 kJ mol$^{-1}$, and the $\parallel$ motion is thermally activated,
$\Delta H^*(D_{zz}) = 9.2$ kJ mol$^{-1}$. Activation entropies are large for $\perp$ motions, $\Delta S^*(D_{xx})
= 25$, $\Delta S^*(D_{yy}) = 15$ J mol$^{-1}$ K$^{-1}$ and vanish for the $\parallel$ motion, $\Delta S^*(D_{zz}) \approx 0$.
Attractive forces between electric dipoles lead to a strong self-association, for example a
stacking of molecules with antiparallel dipoles and thereby a hindered in-plane
spinning motion ($D_{zz}$).

Stark et al. (1977) investigated $^{13}$C and $^{14}$N relaxation of neat nitrobenzene and
50 vol % solutions of nitrobenzene in eight solvents. In their evaluation procedure the

![Figure 18. Structural formulas of azabenzenes and orientation of diffusion tensor axes.](image-url)
vibrationally averaged bond distance $<r_{CH}^{-3}>^{-1/3} = 1.107 \text{Å}$ was used and the orientation of the principal axis system of the quadrupole coupling tensor, (asymmetry parameter $= 0.404$) with respect to the molecule fixed rotational diffusion tensor, was determined by seeking a physically acceptable viscosity dependence of the calculated diffusion constants. The results were in quantitative disagreement with figures given by Bauer et al (1974) and Alms et al (1973), where $^{13}\text{C}$ relaxation rates have been combined with results from depolarized Rayleigh scattering. Nevertheless the qualitative conclusions remain identical: $D_{yy}$ is smaller than $D_{xx}$ or $D_{zz}$ since the corresponding motion involves the greatest displacement of surrounding solvent molecules. (The axis system of the diffusion tensor is defined as in figure 15b.) This qualitative feature is also retained in a recent analysis of Stark’s measurements using a different $^{14}\text{N}$ quadrupole coupling constant $(e^2\kappa Q/\hbar)$ and asymmetry parameter (Lohmann et al 1978). In this work the orientation of the principal axis system of the quadrupole coupling tensor disagrees with that used by Stark and that found for solid nitrobenzene. As we have also seen for pyridine the quantitative application of the method of quadrupolar nuclei in planar systems suffers from the lack of knowledge of precise values of the quadrupole coupling tensor in the liquid.

The analysis of coupled spin relaxation in planar aromatic rings offers a possibility for determination of the full diffusion tensor from dipolar relaxation rates alone. This method proved to be a promising new way avoiding the difficulties concerned with quadrupolar relaxation. For $AB_2$ proton spin systems the principles of the method have been elaborated in full detail and a possible extension to more difficult spin systems has been demonstrated. The non-exponential recovery of individual lines in a high-resolution $^1\text{H}$ spectrum to their equilibrium values in a non-selective $180^\circ - \tau - 90^\circ$ experiment can be analyzed to obtain individual spectral densities $J_{ijkl} (i,j,k,l \text{ refer to spin numbering})$, see (75). This evaluation step is independent of any assumption of a motional model. Matrix elements of tensor operators provide selection rules which spectral densities may be determined with sufficient accuracy. In $AB_2$ spin systems (even in the $AX_2$ limit) one autocorrelation spectral density $J_{ABAB}$ and one cross-correlation term $J_{ABAB}$ are such ‘good’ spectral densities. The two other spectral densities $J_{ABBB}$ and $J_{BBBA}$ are too strongly dependent on the magnitude of external (not intramolecular dipolar) relaxation contributions, e.g. a contribution from the solvent. Two more autocorrelation spectral densities come from the $^{13}\text{C}$ relaxation rates of the $C_4$ and $C_6$ carbons. Only the rotational diffusion model allows formulation of consistent expressions for all individual effective correlation times $\tau_{ijkl}$, and all evaluations performed therefore rely on this model. Quotients $\tau_{ijkl}/\tau_{ijkl}$ define an allowed range of pairs $\Delta_+ , \Delta_-$ (see (81) and (82)), and with the absolute value of one autocorrelation term $\tau_{ijkl}$ the three diffusion constants $D_{ii}$, $i = x, y, z$ (in the principal axis system) can be calculated.

Vold et al (1977) studied tri-substituted benzenes with $C_{2v}$ symmetry. $-\text{OH}$ and $-\text{OCH}_3$ groups are treated as effectively symmetric substituents located on the $x$-axis, see figure 19. The results are listed in table 5. The data could be explained in terms of molecular shape. For example $D_{yy}$ increases—relative to $D_{xx}$ and $D_{zz}$—when the substituent $\beta$, see figure 19, becomes smaller; in 2,6-dichloroanisole we have $D_{zz} > D_{xx} > D_{yy}$, in 1,2,3-trichlorobenzene $D_{zz} > D_{yy} > D_{xx}$, and in 2,6-dichlorophenol $D_{yx} > D_{zz} > D_{xx}$. With decreasing size of the substituent $\beta$ a rotation about the $y$ axis is facilitated because the surrounding solvent structure has to be less perturbed. The ratios of diffusion constants are virtually independent of the solvent, the absolute values follow
A B C

Figure 19. Orientation of the principal diffusional axis system and indexing of nuclei in planar aromatic molecules which provide $AB_2$ proton spin systems.

Table 5. Rotational diffusion constants of small molecules, in $10^{10} \text{sec}^{-1}$, obtained by analysis of coupled spin relaxation.

<table>
<thead>
<tr>
<th>System</th>
<th>$D_{xx}$</th>
<th>$D_{yy}$</th>
<th>$D_{zz}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichlorobenzene$^a$</td>
<td>2.17 ± 0.06</td>
<td>2.7 ± 0.2</td>
<td>3.8 ± 0.2</td>
<td>Vold et al (1977)</td>
</tr>
<tr>
<td>Trichlorobenzene$^b$</td>
<td>3.38 ± 0.06</td>
<td>4.5 ± 0.4</td>
<td>5.4 ± 0.1</td>
<td>Vold et al (1977)</td>
</tr>
<tr>
<td>Dichloroanisol$^b$</td>
<td>3.61 ± 0.06</td>
<td>3.1 ± 0.2</td>
<td>4.4 ± 0.1</td>
<td>Vold et al (1977)</td>
</tr>
<tr>
<td>Dichlorophenol$^b$</td>
<td>5.4 ± 0.7</td>
<td>2.3 ± 0.7</td>
<td>4.5 ± 0.9</td>
<td>Vold et al (1977)</td>
</tr>
<tr>
<td>Dichlorophenol$^c$</td>
<td>1.32 ± 0.02</td>
<td>2.84 ± 0.08</td>
<td>2.43 ± 0.19</td>
<td>Kratochwill et al (1979)</td>
</tr>
<tr>
<td>Dichlorophenol$^d$</td>
<td>1.01 ± 0.05</td>
<td>1.02 ± 0.30</td>
<td>1.52 ± 0.07</td>
<td>Kratochwill et al (1979)</td>
</tr>
<tr>
<td>Dichlorophenol$^e$</td>
<td>1.12 ± 0.03</td>
<td>0.76 ± 0.30</td>
<td>0.94 ± 0.09</td>
<td>Kratochwill et al (1979)</td>
</tr>
<tr>
<td>2-chloropyrimidine$^b$</td>
<td>8.8 ± 0.3</td>
<td>1.8 ± 0.8</td>
<td>19.2 ± 1.9</td>
<td>Nery and Canet (1978)</td>
</tr>
<tr>
<td>o-Dichlorobenzene$^f$</td>
<td>4.9 ± 1.3</td>
<td>3.1 ± 0.9</td>
<td>8.8 ± 0.1</td>
<td>Stark et al (1978)</td>
</tr>
</tbody>
</table>

The orientation of the principal axis system is shown in figures 19 and 20; $^a$0.1 M in CDCl$_3$, 24°C; $^b$0.1 M in CS$_2$, 24°C; $^c$0.1 M in CCl$_4$, 22°C; $^d$0.1 M in CCl$_4$, +0.1 M added pyridine, 22°C; $^e$0.1 M in CCl$_4$, +0.5 M added pyridine, 22°C; $^f$0.07 M in CS$_2$, 25°C.

closely the ratio of the viscosities (trichlorobenzene in CDCl$_3$ and in CS$_2$). The assumption of Gillen and Noggle (1970) that motions which reorient an electric dipole should be slower than those which cannot be confirmed by these data. In contrast to this 'guideline', in trichlorobenzene ($\mu \approx 3.4$ D) $D_{yy} > D_{xx}$, but only the motion about $y$ reorients the electric dipole.

Nery and Canet (1978) investigated 0.1 M solutions of 2-chloropyrimidine in CS$_2$. They found strongly anisotropic reorientation, $D_{zz} > D_{xx} > D_{yy}$, $\chi_{zz} = 1$ shows that the motion around the $z$ axis is determined by inertial effects, as for triazine (Kintzinger and Lehn 1974) and benzene (Gillen and Griffiths 1972). The authors attribute the large anisotropy of motion to 'specific effects of the two nitrogens'. Previous work of Bovee (1975) showed nearly isotropic reorientation of 2-aminopyridine in an acetone-d$_6$-$D_2$O mixture. This may be ascribed to friction forces between D$_2$O and 2-aminopyridine (Nery and Canet 1978) but can also artificially result from an approximate data treatment, e.g. neglecting intermolecular contributions from the deuterons of the solvent (Vold and Vold 1978). We have hinted above at the importance of a careful analysis of the 'external contributions'.
Stark et al (Stark et al 1979) extended the technical procedure of coupled spin relaxation to an AA'BB' spin system in their study of o-dichlorobenzene. A comparison of the results for o-dichlorobenzene (ODCB) with the results for 1,2,3-trichlorobenzene (TCB) reveals the importance of steric effects for $D_{xx}$ and $D_{yy}$. $D_{xx}$ (ODCB) > $D_{xx}$ (TCB) because the bulky chlorines are closer to the axis of rotation in ODCB, compare figures 19 and 20, $D_{xx}$(ODCB) ≈ $D_{yy}$ (TCB) since both motions have to reorient the chlorines. The differences in $D_{zz}$, or $\tau_z = 1/6 D_{zz}$ respectively, were rationalized in part by inertial effects $I_{zz}$(ODCB) = 1.062 \times 10^{-37}$ g cm$^2$, $I_{zz}$(TCB) = 1.588 \times 10^{-37}$ g cm$^2$, and $\tau_z \approx I_{zz}^{1/2}$ for free inertial behaviour.

The influence of intermolecular hydrogen bonding upon molecular reorientation was studied in the system 2,6-dichlorophenol/pyridine (Kratochwill et al 1979). 0.1 M solutions of 2,6-dichlorophenol (DCP) in CCl$_4$ were studied in ternary systems where the acceptor pyridine was added in the ratio 1:1 and 1:5, DCP : pyridine. Due to nearly equal viscosities of pyridine and CCl$_4$ the acceptor concentration can be varied without changing the macroscopic viscosity. An observed variation of the rotational diffusion constants of DCP with increasing pyridine concentration can therefore safely be ascribed to a direct structural effect and not to a 'background effect' (Grüner and Hertz 1972; Hertz et al 1976). $^{13}$C relaxation rates of pyridine can in addition be used to study the anisotropy of the motion of pyridine with respect to the ring plane. This provides a qualitative consistency check: intermolecular hydrogen bonding should influence the motional behaviour of both components. Compared with a 0.1 M solution of DCP in CS$_2$ the rotational diffusion constants in the CCl$_4$ solution are smaller as can be expected from the ratio of the viscosities. On addition of pyridine $D_{yy}$ and $D_{zz}$ decrease monotonously with increasing acceptor concentration but $D_{xx}$ exhibits only a small variation. Intermolecular association slows down all the above reorientational motions of DCP around axes perpendicular to the axis of the hydrogen bond. Likewise for pyridine the expected anisotropy was found: compared with $\rho = 1$ in pure pyridine (Py) it is $\rho = 0.54$ (DCP : Py 1 : 5) and $\rho = 0.41$ (DCP : Py = 1 : 1). The decreasing ratio $\rho$ indicates motional anisotropy $D_{xx}/D_{yy} \gg 1$, i.e. faster reorientation about the axis of the intermolecular hydrogen bond. In model systems where DCP was substituted by 1,2,3-trichlorobenzene and where intermolecular hydrogen bonding is excluded $\rho$ for pyridine remains essentially 1. Intermolecular hydrogen bonding constitutes a strongly anisotropic intermolecular potential and leads to a characteristic variation of motional anisotropy. In the complex a relatively free reorientation about the hydrogen bond axis is preserved and a completely rigid DCP-pyridine complex with a lifetime $\tau_{eff}$ can be ruled out.

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Figure 20. Principal axis system of o-dichlorobenzene.
Anisotropic motion with respect to the ring plane, $D_{yy}/D_{xx} = 2.0 \pm 0.2$ and the orientation of the diffusional tensor, $20^\circ$ shifted relative to the principal inertial system, could be determined for 2-bromothiophene (Kratochwill and Vold 1980). The $ABC$ spin system proved to be unfavourable in a technical sense because only autocorrelation terms are ‘good’ spectral densities. Approximate figures for cross-correlation terms give an upper limit, $D_{zz} < 1 \cdot 10^{11}$ sec$^{-1}$. The authors showed that vibrationally averaged internuclear distances must be used in the analysis of $^{13}$C relaxation rates. As figure 21 demonstrates the principal axis system is shifted into a direction where the rotation about the $y$ axis has minimum steric hindrance in the condensed phase (the $z$ axis is determined by symmetry). This shift is also towards the easy axis for electric dipole reorientation comparable to the axis shift found in N,N-dimethylformamide (Wallach and Huntress 1969). The anisotropy $D_{yy}/D_{xx} = 2$ is not surprising in view of steric hindrance. The determination of such an axis shift can provide information about the symmetry of the intermolecular potential. $D_{i}$ is a symmetric tensor in an isotropic liquid and can always be diagonalized (confusing statements are found in the literature), but the principal axis system has not to coincide with the principal axis system that diagonalizes the momentum of inertial tensor!

Summarizing we see that in systems without hydrogen bonding the repulsive part of the intermolecular potential dominates. The influence of electric dipole or dispersive forces can only be detected in sterically unhindered motions. Hydrogen-bonding on the other hand constitutes a source of motional anisotropy: motions which retain the favourable geometry for hydrogen bonds are slightly influenced by this attractive force. The corresponding rotational diffusion constants change only slightly on association. Rotational diffusion constants about axes perpendicular to the direction of the hydrogen bond normally show a decrease on association, the corresponding motions are slowed down.

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