

Investigations of Random Molecular Motions by NMR

R. Lenk

Departement de Physique de la Matière Condensée
et Laboratoire de Physiologie Végétale
Université de Genève
Genève, Switzerland

I. INTRODUCTION

The aim of this contribution is to demonstrate that NMR spin relaxation is an efficient method for the investigation of random molecular motions. Information on random motion is important for the characterization of liquids, polymers, and biological samples. Random motions are time-dependent phenomena and have to be treated with time-dependent statistical mechanics. On the other hand, spin relaxation is also time-dependent and its irreversible character has some analogy in the mechanism of random motions.

II. DUALITY OF SPIN RELAXATION AND RANDOM MOTIONS

The irreversible character of spin relaxation can be described as follows: (a) The spin system is excited by a very short pulse of the radiofrequency (RF) field to a nonequilibrium state. (b) After the end of the RF pulse, the system returns to equilibrium by a relaxation process which reflects the microscopic situation in the sample. The free induction decay (FID) is given by a correlation function for nuclear magnetization: $f_A(t) = C_M(t) = \langle MM(t) \rangle$, as shown in Figure 1.

On the other hand, a time-dependent random phenomenon is given by a sequence of microirreversible processes, as schematically presented in Figure 1. This has the following significance: A Brownian particle, which exhibits a random motion, increases and decreases its kinetic energy during collisions with other particles. One can demonstrate that the decrease of kinetic energy for all molecules is represented by the same correlation function: $C_A(t) = \langle EE(t) \rangle$.

An experimental demonstration of the identity of correlation functions for individual particles can be given by an electronic device, called the *correlator*. In this case, the random phenomenon is represented by noise.

The operation of a correlator is illustrated in Figure 2. The randomly varying electric potential $V(t)$ (noise) is presented at the input and split into two channels: $V_A(t) = V_1(t) + V_2(t)$. The second channel has a time-delay device (td). Afterwards, the voltages in the two channels are multiplied in the multiplier (m) and integrated in the integrator (I).

It is clear that the correlator replaces, by electronic means, the calculus of a correlation function of noise, $C_n(\tau)$. At the output, the voltage is

$$V_{out}(\tau) \propto C_n(\tau) = \overline{V_1(t) V_2(t-\tau)} \quad (1)$$

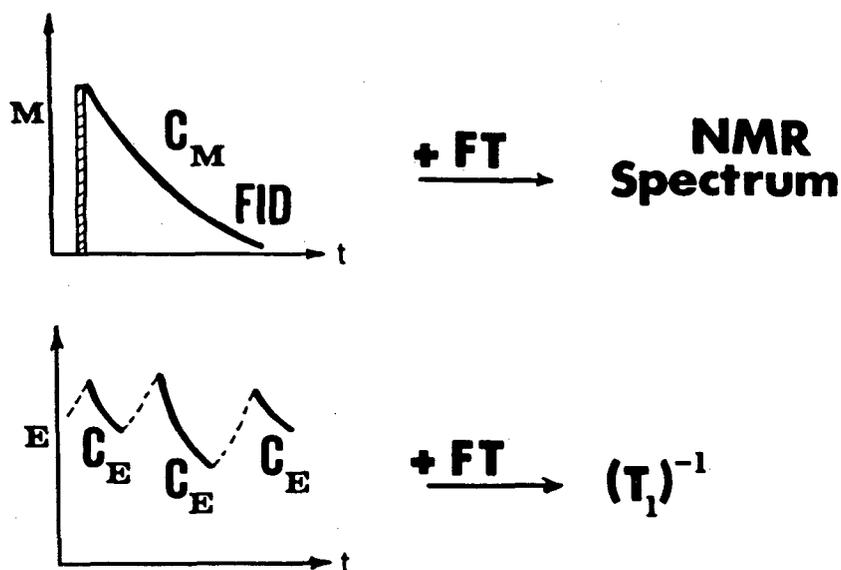


Figure 1. Physical duality between spin relaxation and random phenomena: The Fourier transform (FT) of the NMR correlation function $C_M(t)$, (= FID), yields the NMR spec-

trum; the FT of correlation functions of the random modulation of a local field, represented by the correlation functions $C_E(t)$, yields the spin-lattice relaxation rate $(T_1)^{-1}$.

The output voltage of a correlator, fed by noise, is proportional to its correlation function.

Thus, correlation functions represent a central problem in the theories of time-dependent random phenomena and of spin relaxation. Molecular motions in samples with a high degree of freedom are random and can be described in terms of correlation functions. (In the theory of probability, correlation determines the degree of statistical dependence and/or measures the similarity of two processes. Physically, the cross-correlation measures the interaction of two systems, and the correlation function determines the shape of the irreversible decay.)

On the other hand, all existing theories of spin relaxation have established that the Fourier transform (FT) of a correlation function of random motions is proportional to the spin-lattice relaxation rate $(T_1)^{-1}$. This relationship makes it possible to use the spin-relaxation phenomenon as a powerful tool for the investigation of molecular motions.

III. INTRODUCTORY REMARKS ON THE THEORY OF BROWNIAN MOTION

Randomly moving (Brownian) particles can be theoretically described by several methods (1).

A. Langevin Equation

In this approach, the random mode of the reception and dissipation of energy by a Brownian particle is given by

$$m dv/dt = -\xi v + F_r(t) \quad (2)$$

where v is the velocity of the particle, m is the mass, ξ is the friction constant, and $F_r(t)$ is the random driving force. The influence of the surrounding medium is then split into a systematic part, $-\xi v$, which causes the friction, and a fluctuating part, $F_r(t)$. The following assumptions are usually made: The mean value of $F_r(t)$ is zero and its correlation function, $C_r(t_1 - t_2) = \langle F_r(t_1)F_r(t_2) \rangle$, is very narrow.

This case is called a random process without after-effect (Markovian random process).

B. Random Walk

The simplest one-dimensional representation of general problems characterized by properties resulting from a superposition of a large number of variables is given by the random walk (1,2). In this approach, the particle exhibits displacements along a

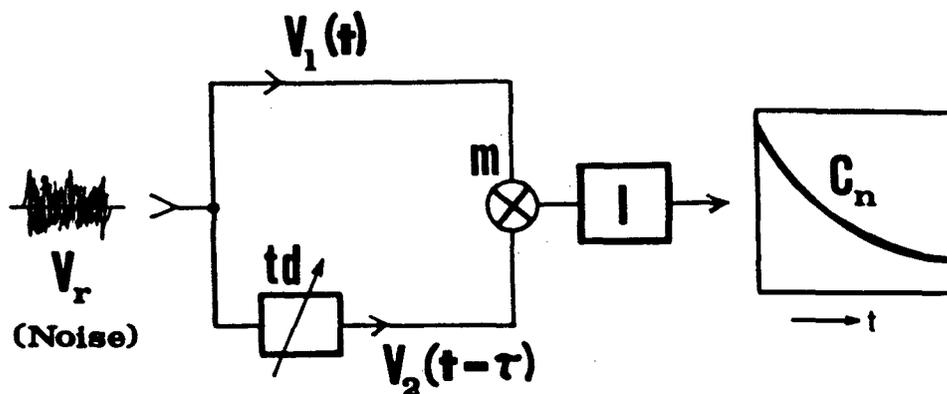


Figure 2. Functional design of the electronic correlator: td = time-delay device; m = multiplier; I = integrator.

straight line in the form of a series of steps of equal length, each taken in either the forward or backward direction with equal probability $p = 1/2$. We are interested in the probability $W(m, N)$ that the particle will arrive at the point m after N displacements. It can be shown (1,2) that this probability is

$$W(m, N) = N!(1/2)^N / [(N + m)/2]! [(N - m)/2]! \quad (3)$$

When N is large, it is convenient to introduce instead of m the variable $x = m l$ (l is the length of each step). If the particle exhibits n displacements per unit time, the probability $W(x, N)$, after some mathematical simplifications (1,2), becomes

$$W(x, t) = (4\pi Dt)^{-1/2} \exp(-x^2/4Dt) \quad (4)$$

where the time variable $t = N\tau$, and the diffusion coefficient $D = 1/2 n l^2$.

C. Fokker-Planck (FP) Equation

This is a diffusion-like equation for the probability distribution. It can be used to solve many problems in Brownian motion, irreversibility, and spin relaxation. The development of the FP equation starts from the random-walk method. The conditional probability $P(n > m; N)$, that the particle will be at $x = m l$ at time $t = N\tau$ if it starts at $x_0 = n l$, satisfies the difference equation

$$P(n|m; N+1) = 1/2 P(n|m-1; N) + 1/2 P(n|m+1; N) \quad (5)$$

Further development of Eq. 5 points out a striking connection between the discrete (random walk) and continuous approaches. Eq. 5 can be written in the form of the differential equation

$$\partial P / \partial t = D \partial^2 P / \partial x^2 \quad (6)$$

which is the simplest one-dimensional FP equation. In the case of anisotropic diffusion, for example, one obtains the more complicated

$$\partial P / \partial t = \nabla D \nabla P \quad (7)$$

The FP equation is mathematically equivalent to the partial differential equation for heat conduction (3,4). There are many solutions of this category of partial differential equations, depending on the particular initial and boundary conditions.

More details concerning the development and solution of the FP and related equations are given in the six selected papers on noise and stochastic processes edited by Wax (1) and in books by Carslaw and Jaeger (3) and Crank (4).

IV. LINEAR IRREVERSIBLE PROCESSES

The simplest approach to the theory of irreversibility is the linear relationship between a "driving force" \vec{X} and the "flux" \vec{J} of a physical property as follows

$$\vec{J} = L \vec{X} \quad (8)$$

where \vec{L} is the matrix of the "phenomenological coefficients" L_{ij} . The latter obey Onsager's reciprocity relation (5)

$$L_{ij} = L_{ji} \quad (9)$$

Generally, the vector of the driving force \vec{X} is given in terms of a potential function f_p

$$\vec{X} = -\vec{\nabla} f_p(x, y, z) \quad (10)$$

A. Phenomenological Laws

The linear relationship between fluxes and forces, Eq. 8, gives rise to the following phenomenological laws:

a) *Fourier's Law*

$$\vec{J}_Q = -\kappa_Q \vec{\nabla} T \quad (11)$$

where J_Q is the heat flux vector, κ_Q the thermal conductivity tensor, and $T = T(x, y, z, t)$ the temperature.

b) *Fick's law*

$$\vec{J}_D = -\vec{D} \vec{\nabla} C \quad (12)$$

where \vec{J}_D is the mass flux vector, \vec{D} the diffusion tensor, and $C \equiv C(x, y, z, t)$ the mass concentration.

c) *Ohm's Law*

$$\vec{J}_e = -\kappa_e \vec{\nabla} V_e \quad (13)$$

In this case, the flux is the electric current density \vec{J}_e , and κ_e is the electric conductivity tensor. $V_e \equiv V(x, y, z, t)$ is the electric potential.

B. Diffusion-like equations

The linear phenomenological relations lead to the diffusion-like equations. This will be demonstrated in the following way. We begin with the conservation law

$$\vec{\nabla} \vec{J}_D + \partial C / \partial t = 0 \quad (14)$$

The application of the operator $\vec{\nabla}$ to Eq. 12 and insertion of the result into Eq. 14 yield

$$-\vec{\nabla} \vec{D} \vec{\nabla} C + \partial C / \partial t = 0 \quad (15)$$

This relation has the same mathematical form as the FP equation, Eq. 7, which has been developed using the random-walk method. It may be taken for a proof of the microirreversible character of fluctuations represented by the random walk.

This procedure has been used by Torrey (6) for the development of the Bloch equations, including diffusion and flow.

C. Bilinear Relation in Fluxes and Forces

A significant relation in the theory of the linear irreversible processes is given by

$$T\sigma = \vec{J} \vec{X} = \vec{L} \quad (16)$$

where σ is the entropy production per unit time ($\sigma = ds/dt$), and T the temperature. Frequently, in place of $T\sigma$, a new thermodynamic function called the "dissipation function" or the "entropy source strength" is used.

Eq. 16 can be developed as follows. Consider the dissipation of the electric power in a linear and homogeneous solid bar (Ohm's phenomenological law)

$$dW = i_x dV_e(x) = J_x^e A \vec{\nabla}_x V_e(x) dx \quad (17)$$

where A is the area of the cross section of the bar and J_x^e is the x component of the electric current density.

In a homogeneous system, in which the flux and the force do not depend on x , one obtains, after integration

$$W = J_x^e X_x^e A l \quad (18)$$

where $X_x^e = \nabla_x V_e(x)$, and l is the total length of the bar.

Because the dissipation function Tj is defined as the power dissipated per unit volume ($T\sigma = W/A$),

one obtains the simplest alternative to the bilinear relation in fluxes and forces, Eq. 16, by dividing Eq. 18 by A :

$$T\sigma = J_i X_i$$

D. Thermal Relaxation

It is established (7) that spin-lattice relaxation has the character of a thermal irreversible process. Generally, a relaxation process is a time-dependent transition of a physical system from a non-equilibrium state toward equilibrium. In this context, the following thermodynamic phenomena must be taken into consideration:

- A) The transfer of heat and energy between the investigated systems
- B) The irreversible entropy production

The development of the equation for thermal relaxation starts with the entropy production in a non-equilibrium, two-mode thermodynamic system (I + B), shown in Figure 3. Because this system is isolated from the environment, the entropy production $d_i S$, due to the irreversible processes inside the system, is given by

$$d_i S = dS_i + dS_{ii} = k(\beta_i dE_i + \beta_{ii} dE_{ii}) \quad (19)$$

where E_i and E_{ii} are the energies of the corresponding subsystems, $\beta = 1/kT$, and k is the Boltzmann constant.

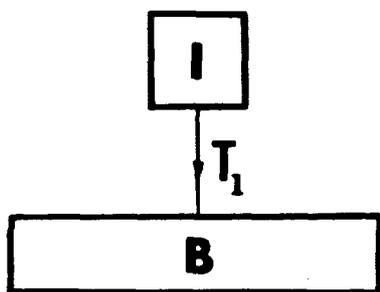


Figure 3. Thermodynamic situation of the thermal relaxation between the subsystem I (the nuclear-spin system) and the heat-bath B. T_1 is the thermal (spin-lattice) relaxation time.

The thermal isolation of the whole system during the relaxation process requires that $-dE_i = dE_{ii}$, which modifies Eq. 19 as follows

$$d_i S/k = dE_i(\beta_i - \beta_{ii}) \quad (20)$$

This relation yields the following dissipation function of the system (I + B)

$$T_0 \sigma = \dot{E}_i(\beta_i - \beta_{ii})/\beta_0 \quad (21)$$

in which $T_0 = 1/k\beta_0$ is the mean temperature of the (I + B) system.

Suppose that the "B" subsystem represents the heat bath for the "I" subsystem and that the latter is not far from equilibrium after the initial excitation. One can then approximately put $T_0 \approx T_B$. Now, comparing Eq. 21 with Eq. 16, it is apparent that the following fluxes and forces are present

$$J_i = \dot{E}_i \quad (22a)$$

$$X_i = (\beta_i - \beta_{ii})/\beta_B \quad (22b)$$

Eq. 22 leads to the simplest form of the linear irreversible relation (8)

$$\dot{E}_i = L_{ii}(\beta_i - \beta_{ii})/\beta_B = L_{ii} X_i \quad (23)$$

E. Bloch Equations for Paramagnetic Relaxation

Eqs. 23 and 24 lead to the Bloch phenomenological equation (7) for the nuclear magnetization in the z-direction. In this development, we consider that the specific heat is the same in the spin system and in the heat reservoir, so $c_v = k\beta$, $E_i = k\beta_B E_{ii}$, which modifies Eq. 23 as follows

$$\dot{E}_i = L_{ii}(E_{ii} - E_i)/E_B \quad (24)$$

Furthermore, replacing E_i by $-B_0 M_z(t)$, and E_{ii} by $-B_0 M_0$, yields

$$\dot{M}_z(t) = (T_1)^{-1} [M_0 - M_z(t)] \quad (25)$$

where $(T_1)^{-1} = L_{ii}/E_B$ is the spin-lattice relaxation rate.

The molecular expression for the T_1 relaxation time can be developed using quantum-statistical methods, as will be presented in the next section.

On the other hand, the development of the Bloch equations in the x and y directions is less straightforward because this relaxation is caused by a mechanism other than the spin-lattice relaxation process. An adequate thermodynamic approach for this case has been discussed by von Borries (8).

Linear thermodynamics of irreversible processes can also be applied to develop the additional terms of Bloch equations concerning diffusion and flow in continuous systems (6).

V. NEW TRENDS IN SPIN RELAXATION THEORY

A. Present State

Spin relaxation is an irreversible process and can be handled in terms of procedures introduced in the preceding section. The microscopic information on the investigated samples, depending on the molecular expressions for the relaxation times, can be obtained by time-dependent quantum mechanics and statistical thermodynamics.

Up to now, spin relaxation theory has been developed using two principal approaches:

- a) *Wangness-Bloch-Redfield* (9-11). This consists of an iterative solution of the Liouville-Neumann equation with a particular convention for the irreversibility (12). This approach is based on the perturbation method. Consequently, its validity is restricted within a certain time scale and within the limit of weak coupling.
- b) *Linear-response*. This method, proposed by Kubo and Tomita (13), is a generalization of the "fluctuation-dissipation" theorem (14). It yields directly an irreversible equation without a particular convention and can be used as a tool for interpreting and predicting experimental results on transport and relaxation phenomena.

The Wangness-Bloch-Redfield approach, which focuses on the approximate equation of motion of density operator, appears to be more basic than the linear-response theory and more adequate for the treatment of systems in which more than two relaxation times are required. This occurs particularly in samples with several species of spins, where cross-relaxation occurs.

B. Advanced Methods

1. Local-equilibrium Distribution

This method, developed by Mori (15), introduces a particular initial condition for the Liouville-von Neumann equation. It is assumed that in a physical state not far from equilibrium, a "local equilibrium" is established in small volumes of the system, and that this distribution is close in form to the equilibrium canonical distribution, with variables and parameters depending on initial conditions. In the language of spin relaxation, the local-equilibrium state exists immediately after the pulse excitation of the spin system, and the corresponding local-distribution density operator is given by

$$\rho_{loc} = Z^{-1} \exp \left[\sum_{i=1}^N \beta_i \mathcal{K}_i + \beta_B \mathcal{K}_B + \beta_B \mathcal{K}' \right] = Z^{-1} \exp(-A) \quad (26)$$

$$\rho_0 = Z^{-1} \exp \left[-\beta_B \left(\sum_{i=1}^N \mathcal{K}_i + \mathcal{K}_B + \mathcal{K}' \right) \right] \quad (27)$$

We can rewrite the exponent on the right-hand side of Eq. 26 as follows

$$A = \beta_B \left(\sum_{i=1}^N \mathcal{K}_i + \mathcal{K}_B + \mathcal{K}' + R \right) = \beta_B (\mathcal{K} + R) \quad (28)$$

The new operator R , which expresses the deviation of the local-equilibrium distribution from equilibrium, is given by

$$R = \sum_{i=1}^N \mathcal{K}_i (\beta_i - \beta_B) / \beta_B = \sum_{i=1}^N \mathcal{K}_i X_i \quad (29)$$

2. Non-equilibrium Density Operator

This method is based on the construction of local integrals of motion (16). For a physical property \mathbf{a} , the latter is given by

$$\mathbf{a} = \mathbf{a} - \int_{-\infty}^0 \exp(\alpha t) \dot{\mathbf{a}}(t) dt \quad (30)$$

where α is a small parameter. In the following, we will put $\alpha \rightarrow 0$.

With this method (16), the non-equilibrium statistical operator, ρ_{ne} is

$$\rho_{ne} = Z^{-1} \exp[-\beta_B (A - B)] \quad (31)$$

where $A = \sum_i X_i \mathcal{K}_i + \mathcal{K} = R + \mathcal{K}$

$$B = \sum_i X_i \int_{-\infty}^0 \dot{\mathcal{K}}_i(t) dt$$

and X_i are the driving forces introduced above.

Using the well-known identity for the development of exponential operators, one obtains, in the classical limit ($\hbar \rightarrow 0$)

$$\rho_{ne} = \rho_{loc} [1 + \beta_B \sum_i X_i \int_{-\infty}^0 \dot{\mathcal{K}}_i(t) dt] \quad (32)$$

3. Generalized Transport Equation (Zwanzig - Mori Theory)

Mori's (17) local-equilibrium assumption has been combined with the elegant projection-operator technique developed by Zwanzig (18). This leads to a generalized transport (master) equation for the density or physical-property operator \underline{a} .

$$\partial \underline{a}(t) / \partial t = - \int_0^t \underline{K}(s) \underline{a}(t-s) ds \quad (33)$$

where $\underline{K}(t)$ is the memory super-operator.

In the language of the Brownian-motion theory (19), the memory super-operator is given in terms of the correlation function of the random force $F_r(t)$ in the Langevin equation (2)

$$\underline{K}(t) = \langle \underline{F}_r, \underline{F}_r(t) \rangle \quad (34)$$

Note that Eq. 33 is exact and valid for all time (19). It describes a non-Markovian process, or a process with after-effect, because it involves the history of the investigated system at earlier times (the memory effect). Another feature of Eq. 34 is its irreversibility, because the total ensemble density, which is initially in a certain subspace, "leaks out" of this subspace.

On the other hand, the generalized transport equation can also be used for the description of strong-collision phenomena, which are limited in NMR by the condition $\tau_c \sim T_1$. This condition means that a

jump of the molecular reorganization is followed by a flip of spins.

The Zwanzig-Mori theory leads to the development of the generalized Bloch equations without the restriction in the time scale, in which the spin-relaxation rates are time-dependent and the relaxation decays are no longer exponential (19).

C. Quantal Non-equilibrium Thermodynamics of Spin-lattice Relaxation (20)

As the starting point, we use Eq. 23 in which the energy E_i is replaced by the average Hamiltonian $\langle \mathcal{K}_i \rangle = -Z^{-1} \beta_i \text{Tr} \mathcal{K}_i^2$. This leads to the following irreversible relation

$$\dot{\beta}_i = (T_i)^{-1} (\beta_i - \beta_B) \quad (35)$$

in which

$$(T_i)^{-1} = Z(\beta_B \text{Tr} \mathcal{K}_i^2)^{-1} L_{ii} \quad (36)$$

In the next step we shall find the molecular relation for the phenomenological coefficient L_{ii} . First, a linear-irreversible relation is introduced

$$\langle \dot{\mathcal{L}}_i \rangle_{ne} = \text{Tr} \rho_{ne} (t) \dot{\mathcal{K}}_i = L_{ii} X_i \quad (37)$$

Inserting the non-equilibrium operator Eq. 32 into Eq. 37 yields the following energy flux from the subsystem "I" toward equilibrium

$$\langle \dot{\mathcal{L}}_i \rangle_{ne} - \langle \dot{\mathcal{L}}_i \rangle_{loc} = X_i \beta_B \int_{-\infty}^0 \langle \dot{\mathcal{K}}_i(t) \mathcal{K}_i \rangle_{loc} dt \quad (38)$$

which immediately yields

$$L_{ii} = \beta_B \sum_{-\infty}^0 \langle \dot{\mathcal{K}}_i(t) \dot{\mathcal{K}}_i \rangle_{loc} dt \quad (39)$$

The application of Eq. 39 to Eq. 36 gives the following spin-lattice relaxation rate

$$(T_i)^{-1} = Z(\text{Tr} \mathcal{K}_i^2)^{-1} \int_{-\infty}^0 \langle \dot{\mathcal{K}}_i(t) \dot{\mathcal{K}}_i \rangle_{loc} dt \quad (40)$$

This is a similar result to that obtained by Kubo and Tomita (13). The spin-lattice relaxation rate is also

proportional to the time integral over a correlation function of the energy fluxes.

The further development of Eq. 40 for the spin-lattice relaxation by the dipolar interaction in the two-particle approximation (2) gives

$$(T_1)^{-1} = (3/2)\gamma^4\hbar^2 I(I+1)[J_1(\omega) + J_2(2\omega)] \quad (41)$$

The spectral density functions $J_1(\omega)$ and $J_2(2\omega)$ in Eq. 41 have their origin in the time integral over the corresponding correlation functions.

VI. NMR RANDOM MOTIONS AND DIFFUSION

As shown above, molecular diffusion is a physical phenomenon which reflects small-step random displacements in space and time. If the particles in the investigated molecular system have non-zero spins, the local magnetic fields created by magnetic interactions within the spin system depend on random motions and diffusion. As shown by Eq. 41, the spin-lattice relaxation rate is proportional to the Fourier transform of the correlation function over the randomly modulated local field.

A. Isotropic Rotational Diffusion

The simplest example of the random modulation of the dipolar interaction can be presented as follows: We have two protons. One is fixed in the z-axis and the second exhibits a small-step, rotational random walk about it. The distance between the protons, r_0 , is constant and the radius vector r_0 is perpendicular to the z-axis ($\theta = 0$). The random displacement of the second "walking" proton modulates the local field, H_{loc} . The dipole-dipole interaction Hamiltonian is given by a scalar product of spherical tensor operators. For our particular orientation of the proton pair, the time-dependent tensorial function $F_1(2)$ is zero. Consequently, the relation for the spin-lattice relaxation rate is simplified in this case

$$(T_1)^{-1} = (3/2)\gamma^4\hbar^2 I(I+1)J_2(2\omega) \quad (42)$$

Our principal task is to calculate the correlation function $C_{2,2}(t) = \langle F_2^{(2)}(0) F_2^{(2)}(t) \rangle$

which is

$$C_{2,2}(t) = \int F_2^{(2)}(0) p(\phi_1) d\phi_1 \int p_\phi(\phi_1, \phi_2, t) F_2^{(2)}(t) d\phi_2 \quad (43)$$

This correlation function is given by an integral over the double space of two random variables, ϕ_1 and ϕ_2 . The initial probability $p(\phi_1) = 1/2\pi$, and the conditional probability p_ϕ can be calculated by the solution of the Fokker-Planck Eq. 7 which has, in the case of isotropic rotation, a simple form

$$\partial P_\phi / \partial t = D_\phi \partial^2 P_\phi / \partial \phi^2 \quad (45)$$

The solution of Eq. 45 is the Gaussian distribution

$$P_\phi = (4D_\phi t)^{-1/2} \exp(-\phi^2/4D_\phi t) \quad (46)$$

Using Eq. 46, one obtains finally the exponential correlation function

$$C_{2,2}(t) = r_0^{-6} \exp(-4D_\phi t) \quad (47)$$

in which the rotational diffusion coefficient can be replaced by the rotational correlation time $D_\phi = 1/4\tau_\phi$.

Furthermore, the Fourier transform over the exponential correlation function Eq. 47 leads to the Debye-Bloembergen spectral density function. Consequently, Eq. 42 can be rewritten as follows

$$(T_1)^{-1} = (3/2)\gamma^4\hbar^2 I(I+1)r_0^{-6}\tau_\phi/(1+4\omega^2\tau_\phi^2) \quad (48)$$

The properties of the spin-lattice relaxation by the dipolar interaction, modulated by the random isotropic rotation, can be summarized by:

a) In the high-temperature region, for $\omega^2\tau_\phi^2 \ll 1$, the spin-lattice relaxation time is independent of the Larmor frequency ω .

b) In the low-temperature region, for $\omega^2\tau_\phi^2 \gg 1$, the spin-lattice relaxation time is proportional to ω^2 .

c) In both the high- and low-temperature regions, the logarithm of the spin lattice relaxation time, $\ln(T_1)$, is linearly dependent on the inverse temperature. The slope equals E_a/k , where E_a is the activation energy of the rotational motion.

d) In the high-temperature region, the spin-lattice and the spin-spin relaxation times have the same values, $T_1 = T_2$. (This equality is valid only for the case of isotropic rotational relaxation. For all other mechanisms of relaxation, $T_1 > T_2$.)

B. Anisotropic Rotational Diffusion - Asymmetric Top

Anisotropic diffusion is defined by the diffusion tensor \vec{D} . In this presentation, we assume that the axis of the molecular system of coordinates is chosen in such a way that the diffusion tensor is

diagonal with the components $D_{xx} = D_1$, $D_{yy} = D_2$, and $D_{zz} = D_3$. The asymmetric top is characterized by $D_1 \neq D_2 \neq D_3$. In this case, one has five correlation times which can be defined in terms of the above diagonal matrix elements as follows (21):

$$\begin{aligned} 1/\tau_2 &= 6D_1 + 2\Delta \\ 1/\tau_1 &= 3D_1 + 3D_2 \\ 1/\tau_0 &= 6D_1 + 2\Delta \\ 1/\tau_{-2} &= 3D_1 + 3D_3 \\ 1/\tau_{-1} &= 3D_2 + 3D_3 \end{aligned}$$

Here $D_1 = (D_1 + D_2 + D_3)/3$ and Δ is the anisotropy factor of the diffusion tensor, given by

$$\Delta = (D_1^2 + D_2^2 + D_3^2 - D_1D_2 - D_1D_3 - D_2D_3)^{1/2}$$

In the case of a spherical top, in which $D_{xx} = D_1 = D_2 = D_3$, the anisotropy factor Δ is zero. Consequently, one obtains one correlation time only, $\tau_{xx} = 1/6D_{xx}$.

C. Translational Diffusion

A simple model for one-dimensional translational diffusion has been elaborated by Hunt and Powles (22). In this "defect-diffusion" model, the spectral density function, $J_d(\omega)$ is given by

$$J_d(\omega) = [2\omega^{-1/2} \tau_d^{-1/2}] / [1 + \omega\tau_d + (2\omega\tau_d)^{-1/2}] \quad (49)$$

which, at the high-temperature limit, becomes

$$J_d(\omega) \approx 2\omega^{-1/2} \tau_d^{-1/2} \quad (50)$$

and at low temperatures

$$J_d(\omega) \approx 2\omega^{-(3/2)} \tau_d^{-1/2} \quad (51)$$

Translational diffusion has been discussed in a more general way by several authors (23). It can be demonstrated that the theories of translational diffusion in three dimensions also lead to the above relations at the high- and low-temperature limits.

D. Generalized Spectral Density Functions

The analysis of results presented here shows that in the "small-step" diffusion models the spectral density function and the spin-lattice relaxation rate in the high- or low-temperature region behave in the following manner

$$J(\omega) \propto (T_1)^{-1} \propto \omega^{-a} \tau_c(1-a) \quad (52)$$

In this relation, for $a = 0$ and $a = 2$, one obtains the spectral densities and spin-lattice relaxation rates for isotropic rotational diffusion; and for $a = 1/2$ and $a = (3/2)$, one has the translational spectral densities, given by Eqs. 50 and 51.

Furthermore, we introduce temperature, T , into Eq. 52 as $\tau_c(T) = \tau_\infty \exp(E_a/kT)$ and rewrite the result as follows

$$-\ln T_1 = -a \ln \omega + (1-a)\tau_\infty + (1-a) \quad (E_a/kT) + \text{const.} \quad (53)$$

This relation may be used to determine the exponent a , which characterizes the random motion.

The usefulness of Eq. 52 has been experimentally verified by measurements of spin-lattice relaxation times in the elastomers polyisoprene (PIP) and polybutadiene (PB) (24). These polymers are especially useful to demonstrate the properties of random molecular motions because of their high configurational entropy, significant random motions, and elasticity. All these properties seem to have the same molecular origin. At high temperature, the coefficient a was found to be 0.5 and at low temperature, 1.36.

E. Entropy of Fluctuations and Biophysical Aspects

In unoriented or partially oriented samples with significant molecular motions, only the statistical parameters are meaningful for characterizing the system. One of these, for example, is the correlation frequency, $f_c = 1/\tau_c$. Note that the correlation time is given by the time-integral of the corresponding correlation function

$$\tau_c = \int_0^\infty \langle AA(t) \rangle dt \quad (54)$$

In this context, the system can be studied in a particular representation, with the correlation frequency f_c as a variable. In this representation, one can determine some thermodynamic functions, e.g. entropy. The latter is significant in the investigations of liquid-like samples and biological systems in which the spectral distribution of the micro-Brownian fluctuations is determined by the molecular configuration of the matter.

Consequently, the configurational entropy can be replaced by so-called entropy of fluctuations (25) which is an explicit function of the correlation frequency, f_c .

As the starting point for this development, we shall use the statistical (Boltzmann's) formula for entropy, as is usual in information theory (26). In this case, one has

$$S = -kI \quad (55)$$

where I is the information function given by

$$I = \sum_i p_i \ln p_i \quad (56)$$

and k is the Boltzmann constant. The probability p_i that the system is in the quantum state " i " will be taken as proportional to the Boltzmann factor

$$p_i = Z^{-1} \exp(-\beta E_i) \quad (57)$$

E_i is the energy of the i th quantum state, $\beta = 1/kT$, and the partition function Z is

$$Z = \sum \exp(-\beta E_i) \quad (58)$$

The statistical entropy for a two-level system is given by

$$S_{21} = -k_{p2} \ln p_2 \quad (59)$$

If the random motion is thermally activated, the temperature-dependent correlation frequency $f_c(T)$ is also given by the Boltzmann factor

$$f_c(T) = f_\infty \exp(-\beta E_{21}) \quad (60)$$

where f_∞ is the correlation frequency for $T = \infty$.

Combining Eqs. 58 and 60 and introducing the result into Eq. 59 yield

$$S_{21} = -k(f_c/f_\infty) \ln(f_c/f_\infty) \quad (61)$$

Consider a physico-chemical or physiological transition between two different states A and B. This transition leads to a change of entropy $S_A \rightarrow S_B$. The ratio of these entropies is given by

$$S_A/S_B = (f_{cA}/f_{cB}) [\ln(f_{cA}/f_\infty)] [\ln(f_{cB}/f_\infty)]^{-1} \quad (62)$$

The analysis of Eqs. 61 and 62 shows that entropy of fluctuations increases monotonically with increasing correlation frequency and, roughly, the ratio of entropies in different states equals the ratio of the corresponding correlation frequencies.

These results allow us to relate entropy with nuclear relaxation times. As shown above, in the high-temperature region the isotropic small-step rotation leads to a linear relationship between the spin-lattice relaxation time and the rotational correlation frequency. This, together with Eq. 62, leads to the following ratio of entropies in the different states

$$T_{1A}/T_{1B} = f_{cA}/f_{cB} \sim S_A/S_B \quad (63)$$

For example, in random translational diffusion, Eq. 50 relates the spin-lattice relaxation time to the correlation frequency by the "one-half law". Combining Eqs. 50 and 62, we obtain

$$T_{1A}/T_{1B} = (f_{cA}/f_{cB})^{-1/2} \sim (S_A/S_B)^{1/2} \quad (64)$$

The above considerations and results are applicable to "motional biothermodynamics" which attempts to establish how a molecular motion in a biological sample reflects the state of the system.

The time-evolution of entropy in biological systems was investigated using Eqs. 62, 63, and 64. According to Prigogine's derivation (27) based on the thermodynamics of open systems, the entropy should decrease during the life of a system. This is opposite to the situation in physics where a system's entropy increases during evolution from a non-equilibrium state toward equilibrium. (A nice example of increasing entropy in a physical system is NMR free induction decay after a $\pi/2$ pulse. Just after the pulse, the spin system is aligned and therefore has lower entropy. During the subsequent evolution, local fields destroy the alignment and increase the entropy.)

Our recent work (25) on identification of physiological states in spinach leaves by NMR is an experimental contribution to this field. It seems that the evolution of entropy in living systems and physiological transitions originate in molecular reorganizations in matter. These include the increase of intracellular compartmentation, modifications in cross-linking in the intracellular protein system, modification of diffusivity of substances across membranes, helix-random coil transitions, and others. Some of these considerations have been experimentally confirmed by NMR in animal systems and tissues (28, 29).

References

- * N. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1945).
- † G.E. Uhlenbeck and L.S. Ornstein, *Phys. Rev.* **36**, 823 (1930).

- ^c M.C. Wang and G.E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945).
- ^d S.O. Rice, *Bell Syst. Techn. J.* **23**, 1 (1955).
- ^e M. Kac, *Amer. Math. Month.* **54**, 369 (1947).
- ^f J.L. Doob, *Ann. Math.* **43**, 351 (1942).
- ¹ Collected in *Noise and Stochastic Processes*, N. Wax, Ed., Dover, New York, 1954.
- ² R. Lenk, *Brownian Motion and Spin Relaxation*, Elsevier, Amsterdam, 1977.
- ³ H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, Oxford, 1959, 2nd ed.
- ⁴ J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1956.
- ⁵ S.R. Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, McGraw-Hill, New York, 1962.
- ⁶ H.C. Torrey, *Phys. Rev.* **104**, 563 (1956).
- ⁷ F. Bloch, *Phys. Rev.* **70**, 460 (1946).
- ⁸ D.F.W. von Borries, *Advan. Mol. Relax. Proc.* **3**, 133 (1972).
- ⁹ R.K. Wangness and F. Bloch, *Phys. Rev.* **89**, 728 (1953).
- ¹⁰ F. Bloch, *Phys. Rev.* **105**, 1206 (1957).
- ¹¹ A.G. Redfield, *IBM J. Res. Dev.* **1**, 19 (1957).
- ¹² U. Fano, *Rev. Mod. Phys.* **19**, 74 (1957).
- ¹³ R. Kubo and K. Tomita, *J. Phys. Soc. Jap.* **9**, 888 (1954).
- ¹⁴ H. Callen and T.A. Welton, *Phys. Rev.* **83**, 34 (1951).
- ^{15a} H. Mori, *J. Phys. Soc. Jap.* **11**, 1029 (1956).
- ^b H. Mori, *Phys. Rev.* **11**, 1829 (1958).
- ^{16a} D.N. Zubarev, *Sov. Phys.-Doklady* **6**, 766 (1962).
- ^b D.N. Zubarev, *Fortschr. der Phys.* **18**, 125 (1970).
- ¹⁷ H. Mori, *Progr. Theor. Phys.* **33**, 423 (1965).
- ^{18a} R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960).
- ^b R. Zwanzig, *Phys. Rev.* **124**, 983 (1961).
- ^c R. Zwanzig, *Physica* **30**, 1109 (1964).
- ¹⁹ Reference 2, Chap. 7.
- ^{20a} R. Lenk, *Advan. Mol. Relax. Proc.* **9**, 47 (1976).
- ^b R. Lenk, *Chem. Phys. Lett.* **63**, 416 (1979).
- ^{21a} L.D. Favro, *Phys. Rev.* **119**, 53 (1960).
- ^b K.A. Valiev and E.N. Ivanov, *Sov. Phys.-Uspekhi* **16**, 1 (1974).
- ²² B.J. Hunt and J.G. Powles, *Proc. Phys. Soc.* **88**, 513 (1966).
- ^{23a} H.C. Torrey, *Phys. Rev.* **92**, 962 (1953).
- ^b P.S. Hubbard, *Proc. R. Soc.* **A291**, 537 (1966).
- ^c J.F. Harmon and B.H. Muller, *Phys. Rev.* **182**, 400 (1969).
- ^d L. Passemann and H. Schneider, *J. Magn. Reson.* **9**, 255 (1973).
- ²⁴ R. Lenk, *Advan. Mol. Relax. Proc.* **3**, 3 (1972).
- ^{25a} M. Bonzon, P. Descouts, H. Greppin, and R. Lenk, *Abstracts F2*, British Radio Spectroscopy Group Meeting, Dundee, Sept. 1977.
- ^b R. Lenk, *Chem. Phys. Lett.* **62**, 399 (1979).
- ²⁶ H. Haken, *Synergetics*, Springer, Berlin-Heidelberg, 1977.
- ²⁷ I. Prigogine, G. Nickolis, and A. Baloyanz, *Physics Today*, Nov. 1974, p. 23.
- ²⁸ D.C. Chang, C.F. Hazlewood, and D.E. Woessner, *Biochim. Biophys. Acta* **437**, 253, (1976).
- ^{29a} R. Damadian, *Science* **171**, 1151 (1971).
- ^b R. Damadian, K. Zaner, D. Hor, and T. DiMaio, *Proc. Natl. Acad. Sci. USA* **71**, 1471 (1974).
- ^c P.T. Beall, D. Medina, D.C. Chang, P.K. Seitz, and C.F. Hazlewood, *Physiol. Chem. Phys.* **8**, 281 (1976).