Monte Carlo Calculation of the Correlation Functions for Molecular Rotation – Application to NMR

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The Monte Carlo method for calculating correlation functions for the rotational motion of atoms is presented. This method applies to crystalline solids and allows the determination of the correlation functions for any model of rotating atoms, molecules or ions constituting the material of interest, if only its crystal structure is known. The presented method permits the calculation of the correlation functions for a whole block of unit cells, not only for a single group of particles. The described method can be employed to calculate correlation functions used in the theoretical description of NMR, dielectric or neutron diffraction experiments. As an example the correlation functions and NMR relaxation time T_1 of solid benzene are calculated by the Monte Carlo method for the.

Key words: Correlation Function; Monte Carlo; NMR; Relaxation.

I. Introduction

Correlation functions play an important role in the theoretical description of all physical phenomena which are influenced by molecular motion. On the one hand it would be difficult to overestimate the role of correlation functions in the theory of such physical processes, but on the other hand in most cases these functions are approximated by one or few exponential functions. This is because the analytical expression for correlation functions can be derived only for a very restricted configuration of particles, like a single methyl group or any other similar arrangement of particles in which distances between them do not change in the course of its reorientation. The Monte Carlo method, when properly modified to include the time scale, permits the evaluation of correlation functions for any reasonable number of particles undergoing any type of reorientation. The number of particles, model of reorientation and the accuracy of results are limited only by the available computing power and ability of the researcher to build a mathematical model of the studied motion. The correlation function can also be determined by a molecular dynamics simulation, but this method is far more complicated and requires much more powerful computers.

To make the presentation of the Monte Carlo method for the calculation of correlation functions more specific, this paper is restricted to nuclear magnetic resonance (NMR) phenomena, particularly to calculation of the spin-lattice relaxation time T_1 in solid benzene, but the described procedures can be employed to any other material and any other type of correlation functions.

NMR is a very effective method for studying atomic motion in solids. Measurements of the spin-lattice relaxation times T_1 and $T_{1\rho}$ as a function of temperature permit the determination of the correlation times and activation energies characterizing molecular motions which influence these relaxation times [1, 2]. In order to extract detailed information concerning the geometry of molecular reorientation from experimental NMR results, the temperature dependence of the spectral densities $J(\omega)$ for each model of motion must be calculated. These spectral densities are the Fourier transforms of the proper correlation functions. As the Fourier transform is a standard procedure and can be performed analytically or numerically for any type of function, the emphasis is put on calculating the correlation functions, as this is a very difficult task tractable analytically only for a few very simple cases.

The classical example of an analytical derivation of correlation functions used in NMR may be found in the paper by Hilt and Hubbard [3]. It was done for a single methyl group in the case of rotational jumps and

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rotational diffusion about its C_3 axis. An other model of molecular motion most often treated in connection with correlation functions is diffusion in monoatomic crystals [4]. One of the latest papers dealing with the analytical form of correlation functions in NMR considers two-dimensional lattice diffusion [5].

There is a general agreement that the first application of the Monte Carlo method to the calculation of correlation functions used in NMR was described by Bustard [6]. Since that time, due to the increasing power of available computers, the Monte Carlo method has been applied more and more often, but still to rather simple models of motion [7].

In the present paper the method for the calculation of correlation functions for solids with internal rotation of groups of atoms is presented. This method is based on applying the Monte Carlo procedure to simulate rotating atoms and on calculating values of the properly defined functions at the right steps of simulation. The most important thing in this method is the possibility of calculating correlation functions not only for a single group of atoms but for a whole block of unit cells. This means that the obtained correlation functions are much more realistic than previous results.

To perform such a calculation the crystal structure of the material of interest must be known. One of the difficulties with the Monte Carlo simulation of rotation is the algebraic complexity of the required formulas. The other one lies in constructing the proper algorithm which will simulate the rotation using the derived equations.

II. Basic Theory

The correlation function for any type of stochastic motion of N particles is defined by equation

$$G^{(q)}(\tau) = N^{-1} \sum_{i=1}^{N} \sum_{m=1}^{N} \langle F_{im}^{(q)}(t) F_{im}^{(q)*}(t+\tau) \rangle_t, \quad (1)$$

where $F_{im}^{(q)}(t)$ are functions of the vectors connecting *two different* particles i and m evaluated at the time t, $F_{im}^{(q)*}(t+\tau)$ are the complex conjugates of these functions at time $t+\tau$. These functions depend on the physical phenomenon for which one wants to calculate correlation functions and will later be described in detail. The brackets $\langle\ \rangle_t$ denote the time average. In general the correlation functions $G^{(q)}(\tau)$ are complex, but in most cases it is sufficient to consider their real part. Since for a sample fit to measure the NMR relaxation time the number of particles N is about 10^{21}, a numerical calculation based directly on (1) is impossible, but in practice we are dealing with ergodic systems and the time average in (1) may be replaced by an ensemble average, resulting in

$$G^{(q)}(\tau) = N^{-1} \sum_{i=1}^{N} \sum_{m=1}^{N} F_{im}^{(q)}(\boldsymbol{r}_{im}) \cdot \sum_{k=1}^{L} P(\boldsymbol{r}_{im} \mid \boldsymbol{r}_k, \tau) F_{im}^{(q)*}(\boldsymbol{r}_{im} + \boldsymbol{r}_k). \quad (2)$$

$\boldsymbol{r}_{im}$ are the vectors connecting particles included in the calculation, and $\boldsymbol{r}_k$ are changes of these vectors in time τ. The summation must be taken only over different particles, so the vectors $\boldsymbol{r}_{im}$ have lengths different from zero. $P(\boldsymbol{r}_{im} \mid \boldsymbol{r}_k, \tau)$ is the relative probability that two particles initially separated by a vector $\boldsymbol{r}_{im}$, change their separation by $\boldsymbol{r}_k$ in the time τ. The definitions in (2) leave the meaning of functions $F_{im}^{(q)}$ the same as in (1). L is the number of steps into which we divide the changes of vectors $\boldsymbol{r}_{im}$ in the course of the rotation of atoms. The values of these steps are then used to calculate the probabilities of finding particles which change their position by $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, ... $\boldsymbol{r}_k$.

The further discussion will be restricted to NMR phenomena. In this case the functions $F_{im}^{(q)}$ are defined [1] as

$$F_{im}^{(0)} = (1 - 3\cos^2\theta_{im})/r_{im}^3, \quad (2a)$$

$$F_{im}^{(1)} = \sin\theta_{im}\cos\theta_{im}\exp(-i\varphi_{im})/r_{im}^3, \quad (2b)$$

$$F_{im}^{(2)} = \sin^2\theta_{im}\exp(-2i\varphi_{im})/r_{im}^3, \quad (2c)$$

θ and φ are the spherical co-ordinates of the vectors $\boldsymbol{r}$ connecting particles which in this case are nuclear spins. The direction of the z axis from which θ is determined is taken to be parallel to external magnetic field H_0.

III. General Formulation of the Numerical Approach

As already mentioned, an analytical expression for correlation functions can be derived only for very limited configurations of small groups of atoms and for

simple models of atomic motion. On the other hand, numerical evaluations based on (2) require a modification of this equation which reduces the number of particles N to a value that is reasonable from the computational point of view. This can be done on the basis of the crystal symmetry. The reasoning is as follows.

In the worst case, that is for the lowest possible symmetry of the considered material, the atoms in the unit cell constitute the smallest structure. Therefore each unit cell has exactly the same symmetry of surrounding atoms, and we can assume that the interaction of any spin in one unit cell with its surrounding equals that of the analogical spin in any other unit cell with its surrounding. Therefore it is sufficient to include in the calculation interactions between atoms in one unit cell with all atoms in the properly chosen surrounding. Such an assumption is true for crystalline material, and the considered interactions, whatever their nature, decrease with increasing separation between the interacting atoms.

We denote the number of atoms in a unit cell by N_U and choose one cell as an origin with atoms numbered from 1 to N_U. In the calculation of the correlation functions we include all possible combinations of pairs of atoms, one always belonging to the central unit cell. The calculation will be limited to those pairs of spins for which the separation $\boldsymbol{r}_{im}$ is less than properly chosen cut-off radius $\boldsymbol{r}_{cut}$. This is justified by the fact that the components of the sums in (2), calculated with functions $F_{im}^{(q)}$ given by (2a), (2b), and (2c), are proportional to $\boldsymbol{r}_{im}^{-6}$, and their value for atoms separated by more that some cut-off radius are negligibly small.

Such a procedure of summation in (2) leaves us with atoms within a block of unit cells defined by a properly chosen cut-off radius. Usually it is sufficient to have a block of $5\times5\times5$ unit cells, which can be seen as the central unit cell surrounded by 124 unit cells. The calculation for materials having a small unit cell, like ammonium chloride, will require a block of $11\times11\times11$ unit cells, resulting in a central unit cell surrounded by 1330 unit cells. For many materials of interest the total number of atoms within the required block of unit cells will be of the order of few thousands, and this is a reasonable value for numerical calculation.

Very often two halves or four quarters of the crystallographic unit cell are equivalent from the point of view of the definition of the correlation function. In such a case, the number of atoms creating this basic unit, denoted by N_U, is smaller than the number of atoms in a crystallographic unit cell, and this simplifies the calculation. In the case of the NMR phenomena only nuclei possessing a spin $I > 0$ must be considered Therefore the term spin will also be used in this paper. Talking about NMR, we can once again justify the introduction of the cut-off radius. Correlation functions are calculated for spin pairs whose separation is small enough to give rise to not negligible dipol-dipol interactions.

Taking into account the above arguments, we may write the correlation function as

$$G^{(q)}(\tau) = N_U^{-1} \sum_{i=1}^{N_U} \sum_{m=1}^{N_T} F_{im}^{(q)}(\boldsymbol{r}_{im}) \cdot \sum_{k=1}^{L} P(\boldsymbol{r}_{im} \mid \boldsymbol{r}_k, \tau) F_{im}^{(q)*}(\boldsymbol{r}_{im} + \boldsymbol{r}_k), \tag{3}$$

where N_T denotes all spins included in the summation. The most important difference compared to (2) is the drastically reduced number of particles over which the summation must be performed. Equation (3) may be interpreted as the average correlation function resulting from interactions of N_U spins from one unit cell with all N_T spins taken for the calculation. The total number of spins also includes N_U spins from the central unit cell, but the summation must, of course, exclude terms with $i = m$. With this general scheme of the numerical approach we can proceed to a more detailed description of that procedure.

IV. Details of Computer Simulation

Equation (3) cannot be used for direct numerical calculation, therefore we rewrite it in the form

$$G^{(q)}(\tau) = N_U^{-1} \sum_{i=1}^{N_U} \sum_{m=1}^{N_T} \sum_{k=1}^{L} P(\theta_{im}, \varphi_{im}, r_{im} \mid \theta_k, \varphi_k, r_k, \tau) F_{im}^{(q)}(\theta_{im}, \varphi_{im}, r_{im}) \cdot F_{im}^{(q)*}(\theta_{im} + k\Delta\theta, \varphi_{im} + k\Delta\varphi, r_{im} + k\Delta r), \tag{4}$$

where θ_{im}, φ_{im}, and r_{im} are the spherical co-ordinates of the vectors $\boldsymbol{r}_{im}$. $\Delta\theta_{im}$, $\Delta\varphi_{im}$, and Δr_{im} are the values of steps in which changes, in course of motion, of relevant co-ordinates are determined. These steps are equal to the maximum allowed

changes divided by the number of assumed steps L. For practical calculation it is more convenient to have all values in (4) expressed in Cartesian co-ordinates x, y, z of the spins involved in the summation. This can be done through the relations

$$\begin{aligned} \theta_{im} &= f_1(x_{im}, y_{im}, z_{im}), \\ \varphi_{im} &= f_2(x_{im}, y_{im}, z_{im}), \\ r_{im} &= f_3(x_{im}, y_{im}, z_{im}), \end{aligned} \tag{4a}$$

which have to be taken from elementary analytical geometry. Thus the correlation functions will be finally expressed by x, y, z co-ordinates of all particles involved in calculations. It is necessary to mention that (4) defines the correlation functions for single crystal material, and spatial averaging must be performed to get correlation functions for polycrystalline samples. In the Monte Carlo calculationsdescribed above only numerical spatial averaging is possible. This procedure is very tedious and time consuming, but being elementary will not be described here.

To perform the calculation we have to generate Cartesian co-ordinates of spins within a volume large enough to embrace the cut-off radius of the order of 2 nm. The value of this radius required for a particular material may be estimated as follows. We must find the smallest spin-spin distances $r_{\min}$ existing in the crystal. Usually these will be the spin-spin distances within the molecule, and for hydrogen nuclei this distance is in the range 0.16 nm to 0.25 nm. Taking the $r_{\min} = 0.2$ nm we obtain the ratio $(r_{\text{cut}}/r_{\min})^{-6} = 1\times10^{-6}$, which means that contributions to the correlation functions from the spins located outside the sphere with given cut-off radius are so small, as compared to contributions from the spins within this sphere, that they can be neglected.

With the knowledge of the crystallographic data of our sample one generates relative x/a, y/b, and z/c co-ordinates of all spins of interest within the block of unit cells $3\times3\times3$, or with larger dimension if necessary. Spins of interest means spins which contribute to the NMR processes we want to analyze. For example, there is no need to consider ^{13}C nuclei if we are dealing with ^{1}H NMR and the sample has a natural abundance of carbon ^{13}C.

Depending on the assumed model of motion it may be necessary to add co-ordinates of points determining the axis of rotation. For the methyl group these will be the co-ordinates of a C atom from a CH_3 group and the co-ordinates of the atom to which this carbon is attached in the molecule or in the ion. In a general situation, like rotation of a benzene ring about its C_6 axis, the co-ordinates of the rotation axis have to be determined. They must be calculated for the whole crystallographic unit cell and expressed in the same form as the co-ordinates of spins present in the crystallographic data. This is because the points determining the axis of rotation must be generated for other unit cells by the same procedure as spin co-ordinates.

Once the block of unit cells of proper dimensions is generated, all co-ordinates, for spins and for rotation axis, must be ortogonalized and multiplied by lattice dimensions to change the relative co-ordinates into absolute ones. The co-ordinates of all spins and those determining the rotation axis must be labeled, because during the calculation the program must know which co-ordinates have to be rotated and around which axis. The program must also distinguish between points representing the spins, therefore contributing to functions $F_{im}^{(q)}$, and points representing the axis of rotation or any other spins excluded intentionally from the calculations.

The rotation of a spin around a given axis is performed with the help of the formula

$$\begin{aligned} C_{\boldsymbol{k}}(\alpha)\boldsymbol{r} = \boldsymbol{r}_0 + \boldsymbol{k}(\boldsymbol{k}\cdot\boldsymbol{r})(1-\cos\alpha) - \boldsymbol{r}\cos\alpha \\ + (\boldsymbol{k}\times\boldsymbol{r})\sin\alpha, \end{aligned} \tag{5}$$

which is a formula given by Lybarskii [8] modified by the term $\boldsymbol{r}_0$. $\boldsymbol{k}$ is the unit vector along the rotation axis, $\boldsymbol{r}$ the vector determining the position of the rotating spin, with its origin on the rotation axis, at the point nearest to the considered spin, $\boldsymbol{r}_0$ is the vector connecting the point (0,0,0) of the Cartesian co-ordinate system with the origin of the $\boldsymbol{r}$ vector, α is the angle of clockwise rotation, looking along the vector $\boldsymbol{k}$. Dot $(\cdot)$ and cross $(\times)$ have their usual meanings, generally accepted in vector algebra.

For practical calculation, (5) must be expressed in terms of x, y, z co-ordinates of all points of interest, that is positions of spins, and points determining the rotation axis. This is an elementary but quite cumbersome task which requires special attention. Once the procedure of rotation based on (5) is worked out and coded as a proper subroutine in the computer program, any group of atoms can be rotated by any angle about any axis introduced by us.

The model of rotational jumps applied in our calculation can be summarized by the following steps. The

angle of jumps is set to be 60 degrees, as it is generally accepted for benzene. The molecule to be rotated and the direction of rotation are chosen randomly, the rotational jump results in a new set of co-ordinates of spins belonging to the rotated molecule. The procedure is repeated until the desired number of jumps is performed.

According to the number of jumps, the time scale is introduced into the computer simulation. Following Bustard [6], the unit of time τ_d is defined as the time during which on average each molecule of the block considered in the calculation performs one rotational jump. The sampling rate in evaluating the correlation functions determines the details of the spectral densities functions used in the T_1 calculation. To have a high frequency information a high sampling rate is required, but low frequency information may be obtained only from values of correlation functions for long values of time τ. The compromise is necessary because a calculation with high sampling rate and for long times would be unreasonably long and costly. One solution may be calculation with a high sampling rate at times τ close to zero, and decreasing this rate for longer times.

V. Results of Calculation for Polycrystalline Benzene

The crystal structure data needed for the calculation were taken from the paper published by Bacon et al. [9]. The simulation of the rotation of molecules was performed for a block of unit cells $5\times5\times5$ and $3\times3\times3$, that is for 500 and 108 molecules. In order to get a reliable ensemble average, the simulation for each number of jumps was repeated 300 times. An other solution leading to correct statistics might be increasing the dimension of the block used in the simulation, but this would be less favorable as far as computational time is concerned. The spatial averaging was performed with 10 degree steps along the horizontal and azimuthal angle. The trial averaging with 2 degree steps gave results different only by less then 1%, but the CPU time needed in this case was 25 times longer; therefore all calculations were performed with 10 degree steps in spatial averaging.

The sampling rate S_r was chosen to be $100/\tau_d$ for $\tau < 2\tau_d$ and $50/\tau_d$ for the largest values of τ. For the time unit τ_d defined [6] as the time required for performing one jump by each molecule within the block of unit cells considered in the calculation, the sampling rate S_r is represented in the calculation by the number of jumps performed between calculating the subsequent values of $F_{im}^{(q)}$.

An important stage of the calculation is determining the probabilities P from (4). For analyzing the change of vectors $\boldsymbol{r}_{im}$, the following logic was applied. The assumed maximum change of their spherical co-ordinates are π for θ_{im}, and for φ_{im}. The maximum possible change Δr_{max} of the length of the vector $\boldsymbol{r}_{im}$ depends on the crystal and molecular structure of the studied material and must be determined individually. For benzene in our calculation this change was chosen to be $\Delta r_{max} = 1.0$ nm, which is approximately equal to two diameters of the benzene ring. These maximum possible changes are divided by L, which in our calculation was usually 100. Such a procedure results in $100\times100\times100 = 10^6$ distinguishable changes of each vector $\boldsymbol{r}_{im}$, but the program records only the largest change. For example, if the given vector changes its spherical angle by $12\pi/L$, its azimuthal angle by $30\pi/L$ and its length by $7\Delta r_{max}/L$, it will be tagged as a vector which changes its value by 30 units.

In the course of the calculation the spherical co-ordinates of all vectors $\boldsymbol{r}_{im}$ at the time $t = 0$ are stored in one array, and a new set of co-ordinates, obtained after performing a given number of jumps equivalent to a particular time τ, is stored in another array. Then the program determines the change of each vector and calculates probabilities of finding the vectors with a given change in value. These are simply the numbers of vectors which change the value by the given number of steps (1 or 2 ... or L) divided by the total number of vectors.

It is worth to notice that in (4) the functions $F_{im}^{(q)}$ and $F_{im}^{(q)*}$ are located at the end of the formula and are not separated by a term defining probabilities. It is a purely technical manipulation, but important from the point of view of numerical calculation, because we first calculate the product of two complex functions, which may result in only one real value, and this is easier to handle than the previous order of multiplication present in (3).

The correlation functions $G^{(q)}$ for $q = 0$, 1, and 2 were calculated according to the procedure described above. The results are presented in Fig. 1 with the graph limited to $\tau = 2\tau_d$, because this emphasizes the differences between the functions for different q. At longer times all correlation functions decrease to zero and the differences between them vanish. The

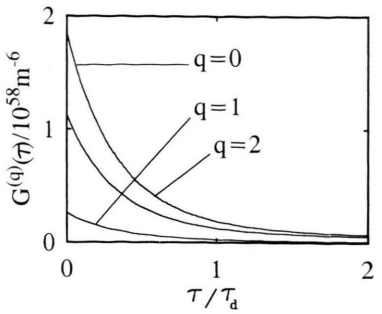

Fig. 1. Correlation functions calculated for 108 molecules of polycrystalline benzene.

calculations themselves were carried out up to times $\tau = 20\tau_d$. For any calculation at a specific temperature, τ_d must be replaced by a correlation time τ_c corresponding to the desired temperature.

To compare the results of the calculation with experimental data taken from [10] the τ_d was set to be 6.29×10^{-9} s, which corresponds to the correlation time τ_c at 150 K. The spin-lattice relaxation time T_1 was calculated according to the formula [1]

$$\frac{1}{T_1} = \frac{3}{2}\gamma^4\hbar^2 I(I+1)\left\{J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)\right\}, \quad (6)$$

where γ is the giromagnetic ratio of the resonant nuclei, I their spin, $\hbar$ Planck's constant divided by 2π, ω_I the Larmor frequency of the resonant nucleus, and

$$J^{(q)}(\omega) = \int_0^\infty G^{(q)}(\tau)e^{-i\omega\tau}\mathrm{d}\tau \quad (7)$$

are the spectral densities of the correlation functions. For further calculation only the real part of these spectral densities was used. $\omega_I/2\pi$ was set to 22 MHz to be equal to the frequency at which the relaxation measurements were performed [10].

The spectral densities defined by (7) were calculated by two methods, first numerically from the correlation functions obtained by the Monte Carlo method, then the correlation functions were approximated by a linear sum of three decaying exponentials and the analytical Fourier transform was calculated. This second method allowed the determination of the spectral density without restrictions due to the limited number of discrete values of the correlation function. The obtained spectral densities were then normalized according to rules described in Abragam [1], and the relaxation time T1 was calculated from (6). The calculated value $T_{1\,\mathrm{calc}} = .035$ s. is in reasonably good agreement with the experimental value $T_{1\,\mathrm{exp}} = 0.030$ s.

Part of the discrepancy may be due to the inaccuracies in the crystallographic data of benzene. Some confirmation of such a suggestion was found in the value of Van Vleck's [11] second moment M_2 calculated for the rigid structure from crystallographic data used in our T_1 calculation. This value was by about 4% smaller then the experimental one, and a difference in this direction means that T_1 calculated from these crystallographic data is by about 4% longer then it would be when calculated from data resulting in a larger value of the second moment. The accuracy of the experimental values of T_1 was estimated [10] to be ±2%. The relaxation times $T_{1\,\mathrm{calc}}$ obtained from different runs of the computer program differ by about 2%, therefore the difference between $T_{1\,\mathrm{calc}}$ and $T_{1\,\mathrm{exp}}$, which cannot be accounted for, is about 4%, which can be considered as a satisfactory result.

VI. Summary

Applying the Monte Carlo techniques to calculations of the correlation functions for molecular motions gives results much more realistic than is possible when the determination of the correlation functions is based on the approximations extended to thousand particles from two or three particle models. The Monte Carlo calculations may be performed for numbers of particles of the order of a few thousand, therefore may be considered as "nearly exact" calculations. The main advantage of the described method is its application to any model of motion of the molecules, and much simpler numerical technics required than in the case of molecular dynamics simulation. The method allows calculation of the correlation function for nearly any model of motion of atoms, ions or molecules. The actual accuracy of the Monte Carlo calculation of the correlation functions depends on the accuracy of input data and on the available computational power, and both these factors are growing continuously.

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