Calculation of the NMR Second Moment for Solid Benzene with Rotation and Diffusion of Molecules – Numerical Approach

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Numerical calculations of the NMR second moment in case of rotation and diffusion of molecules were performed. As an example computer simulations of molecular reorientation and self-diffusion in solid benzene have been performed. For each model and rate of motion the Van Vleck's second moment of the proton NMR absorption spectrum was calculated, and these values were compared with experimental data. It is concluded that restricted self-diffusion must be implied in order to obtain better agreement between calculated and experimental NMR second moments. The temperature at which self-diffusion was detected through NMR line-width narrowing was found to be about 120 K, nearly 80 K less than the temperature at which the self-diffusion was detected by $T_{1\rho}$ relaxation measurements.

Key words: NMR, molecular rotation, self-diffusion, numerical approach.

1. Introduction

Solid benzene C_6H_6, being a typical molecular crystal, is of great interest in physical chemistry of solids. It was the first substance in which rotation of molecules was detected by the NMR method [1], and later numerous papers have been published on this subject [2 - 7].

Narrowing of the proton NMR lines of benzene with increasing temperature, discovered by Andrew [1], was first interpreted in terms of rotation of C_6H_6 molecules about its sixfold symmetry axis. Later NMR measurements of the dipolar relaxation time T_1, performed by Van Steenwinkel [5], showed the existence of an additional type of motion near the melting point. Van Steenwinkel suggested an out-of-plane reorientation of benzene molecules, that is reorientation about an axis passing trough the pair of opposite carbon atoms in the benzene ring. There are three such axes in the molecule. This interpretation however was not consistent with the crystal structure of benzene [8]. The packing of molecules in the crystal prohibits such a type of motion, as was pointed out by O'Reily and Petersen [9]. They suggested translational diffusion by vacancy migration as the additional type of motion. The possibility of translational diffusion in solid benzene and the details of rotational motion have been a subject of interest since that time and promoted many experimental and theoretical studies.

Noack et al. [7] have measured the NMR relaxation times in the rotating frame $-T_{1\rho}$. They obtained good agreement between experimental and calculated values of relaxation times assuming rotation of molecules about a 6-fold axis of symmetry in the low temperature region (100 to 175 K), and rotation plus translational self-diffusion in the high temperature region (250 to 275 K). The activation energy for diffusion obtained from their analysis of $T_{1\rho}$ measurements (94.0 kJ/mol) agreed well with the average value of 96.8 kJ/mol deduced from tracer diffusion studies [10]. However, the diffusion coefficients obtained by the NMR method are about three thousand times smaller then the coefficient obtained with the tracer method. Such a discrepancy seems to be beyond any reasonable explanation and, as McGuigan at al. [11] pointed out, "the interpretation of the NMR relaxation in terms of self-diffusion or some other mechanism is therefore an open question".

One of the most comprehensive studies of the problems connected with molecular motion in solid benzene was undertaken by Craven et al. [12 - 14].

In the present paper the problem of rotation and diffusion of molecules in solid benzene is confronted by comparing Van Vleck's proton second moments

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calculated for different types of motion with the experimental values taken from [2]. Each type of motion is simulated by a numerical method, and the Van Vleck's second moment is calculated for every model of motion.

2. Theoretical Basis

2.1 General consideration

The second moment of the NMR absorption spectrum can be measured with the proper equipment and calculated if the crystal structure of the material is known.

This is a basis for studying the molecular and crystal structure of solids by means of the NMR method (Abragam [15], page 451). In this type of studies we can talk about:

– rigid structure, when any type of motion of molecules, ions, or its "building" units (e. g. CH_3, CH_2, OH) occurs with a frequency lower then the NMR line width (in frequency units) for the "absolutely" rigid substance,

– structure with rotation (or any type of motion), when this type of internal motion occurs with a frequency comparable or higher than the NMR line width for the rigid structure.

At a given temperature, at which a fast enough motion of molecules already occurs, there is one experimental second moment value and there might be a few theoretical values calculated for different models of motion. The best agreement between the experimental and one of the calculated values suggests the most probable model of motion. Measurements of the NMR second moment can be done with any CW or pulse NMR spectrometer. Calculation of the NMR second moment on the basis of crystal structure is a standard procedure, widely used for the rigid structure. The meaning of rigid is in accordance with the definition given above.

2.2 Van Vleck's second moment for the rigid structure

Calculation of the second moment can be done on the basis of the famous Van Vleck formula [16]. For the rigid structure, the second moment M_2^{rig} is given by the equation

$$M_2^{\text{rig}} = KN^{-1} \sum_{i \neq j}^{N} B_{ij}^2, \tag{1}$$

where

$$K = \frac{3}{4}\gamma^2 \hbar^2 I(I+1),$$

$$B_{ij} = (3\cos^2\theta_{ij} - 1) r_{ij}^{-3};$$

γ is the magnetogyric ratio of the nuclei studied, I the nuclear spin, N the number of nuclei considered in the summation, r_{ij} the internuclear distance, θ_{ij} the angle between the direction of the external magnetic field (B_0) and the r_{ij} vector, and $\hbar$ the Planck constant divided by 2π. From (1) results that the contribution to the second moment decreases with the 6-th power of the internuclear distance; therefore a practical cut-off radius for calculation is about 15 Å. In the case of solid benzene, with crystal lattice parameters at 138 K: a = 7.390 Å, b = 9.420 Å, and c = 6.810 Å, it is sufficient to consider for calculation a block of 3 × 3 × 3 unit cells. In such a block, the central unit cell is surrounded by one "layer" of unit cells and the distances between the nuclei in the centre of the block and the nuclei in the most distant molecules are about 20 Å.

For practical reasons, the summation in (1) is usually divided into two terms. In the first the nuclei i and j belong to the central molecule, and in the second only the nuclei i. The first term is called intramolecular part of the second moment, and the second intermolecular. In single crystals, the intramolecular part of the second moment might differ for different molecules. This is because the angles θ_{ij} depend on the orientation of the molecule with respect to the direction of magnetic field. In such situations, the second moment must be calculated for two or more molecules taken as one symmetrical unit. In the lowest symmetry case, the whole unit cell must be considered for calculation as a "molecule". To translate the above explanations into the formula for the second moment, (1) must then be rewritten as

$$M_2^{\text{rig}} = \frac{K}{N_1} \sum_{i=1}^{N_1} \left(\sum_{j=1}^{N_1} B_{ij}^2 + 2 \sum_{j=N_1+1}^{N_2} B_{ij}^2 \right), \tag{1a}$$

where N_1 is the number of nuclei in one molecule (or larger symmetrical unit considered for calculation as a "molecule"), and N_2, the total number of nuclei taken for summation. As in (1), i must be different form j. The second sum in the brackets is multiplied by 2 because the intermolecular part is calculated only for

$j > i$, while the coefficient K corresponds to double summation (for $i < j$ and $i > j$).

To use (1a) for any particular material it is necessary to know the coordinates x, y, and z of all nuclei considered in the summation, and the direction of the external magnetic field B_0. This information allows us to calculate all internuclear distances r_{ij} and angles θ_{ij}. With a fixed direction of magnetic field we will get the second moment for the single crystal sample at a particular orientation of the crystallographic axis with respect to the B_0 direction. To obtain M_2^{rig} for a powder made of crystallites of random orientations it is sufficient to average the B_{ij}^2 term of (1) over all angles θ. This can be done analytically, but for our purpose - calculation of the second moment with rotating molecules - it must be done numerically, as we explain later in this paper. Equation (1a) for polycrystaline material may be written as

$$M_2^{\text{rig}} = \frac{K}{N_1} \sum_{i=1}^{N_1} \left(\sum_{j=1}^{N_1} \overline{B_{ij}^2} + 2 \sum_{j=N_1+1}^{N_2} \overline{B_{ij}^2} \right), \qquad (2)$$

where the bars over B_{ij}^2 denote an average over all orientations of crystallites with respect to the external field direction. This averaging is equivalent to averaging over all θ_{ij} angles. As mentioned above, this averaging may be done analytically or numerically.

In the powdered material all molecules are equivalent, if we consider their orientations with respect to the external magnetic field, and therefore N_1 in (2) is always equal to the number of nuclei in one molecule, N_2 being the total number of nuclei considered for calculation. This is true for molecular crystals. For ionic crystals we have to take the pair ion-cation as the periodically repeated "molecule". All these explanations should help to realize that in spite of the simplicity of (1a) amd (2), their practical application requires some structural consideration.

2.3 *Van Vleck's second moment for structure with internal motions*

The influence of motion on the NMR line width and the second moment has been discussed in basic NMR monographs [17, 15] and in many papers, e. g. [18] and references cited there in. The problem is, that in these papers the second moment is calculated for an idealized structure. For example, Latanowicz et al. [18] consider a two nuclei system and calculate the intramolecular part of the second moment for a given model of motion. In any practical case, when a molecule has at least a few nuclei and there are a few molecules in the crystal unit cell, the contribution to the second moment arising from two nuclei will be completely masked by the contribution from all other nuclei in the studied material. A little more general case is analyzed in [19], but the "single crystal", consisting of 27 methyl groups, is still quite far from any real material. But the method of calculation of the second moment for the material with rotating molecules, described in [19], is completely general, and only computational possibilities available at that time to the author restricted his analysis to such a simple structure.

It is important to mention, that the second moment of a dipolar broadened NMR spectrum is invariant with respect to motion of nuclei in the considered sample. How it happens that measured and calculated second moments depend on the rate of motion is explained by Abragam [15] and in other papers cited above, therefore we will not repeat this reasoning here. The formula for the second moment of a powdered material with any type of internal motion can be written as

$$M_2^{\text{rig}} = \frac{K}{N_1} \sum_{i=1}^{N_1} \left(\sum_{j=1}^{N_1} \overline{\langle B_{ij} \rangle^2} + 2 \sum_{j=N_1+1}^{N_2} \overline{\langle B_{ij} \rangle^2} \right), \qquad (3)$$

where brackets $\langle\ \rangle$ denote averaging of B_{ij} terms over all positions taken by nuclei in the course of the motion of molecules. Therefore, to obtain the second moment for the polycrystal material with internal motion of nuclei we must first take the average over orientations arising from the motion of the molecule, and then take the average over orientations of crystallites in powdered material. The first averaging we call dynamic, the second one static. This dynamic averaging is the essential point in all second moment calculations in the case of motion of nuclei, therefore we will treat it in more details.

Let us remind the expression

$$B_{ij} = (3 \cos^2 \theta_{ij} - 1) r_{ij}^{-3},$$

with i denoting nuclei of the molecule situated in the centre of the considered block of unit cells, and j, all the nuclei in this block. Of course, we are talking about nuclei on which the NMR signal is recorded.

In the case of benzene these are protons of hydrogen. We do not have to take into account carbon atoms, as the natural abundance of ^{13}C, the carbon isotope possessing magnetic moments, is negligible. To calculate the average $\langle B_{ij} \rangle$ we must assume a model of reorientation of the benzene molecule. The generally accepted model of such reorientation are 60° jumps about the sixfold axis of the molecule. The second type of motion of benzene molecules, which we will consider, is self-diffusion. Regardless of the type of motion, the average of B_{ij} can be written as

$$\langle B_i j \rangle = \sum_{k=1}^{L} B_{ij}^k P^k / \sum_{k=1}^{L} P^k, \tag{4}$$

where B_{ij}^k is the B_{ij} term for a given orientation labelled k, and P^k the probability of the occurrence of this orientation. The reorientation between energetically nonequivalent sites, as in [18], can easily be treated with properly chosen values of these probabilities. Substituting (4) into (3) yields the formula for the second moment of arbitrary material with internal motion of nuclei. We will not describe here the details of the spatial averaging denoted by the horizontal bar in (3), as this is a standard textbook procedure. But we do emphasize the order of performing averaging, first with respect to the motion, next, over all orientations of the crystallites.

The practical application of (3) for any type of motion depends on our possibility to calculate $\langle B_{ij} \rangle$, and this, in turn, depends on the possibility of expressing any position of a nucleus, taken in course of reorientation, by x, y, z coordinates of this nucleus. Such calculations required knowledge of the crystal structure. For some types of motions it might be a quite complicated task, from the analytical geometry point of view, but always possible. Complicated, because we have to remember that reorientation of molecules means reorientation of all molecules within the block considered for calculation. The details of calculation depend on the crystal structure and on the assumed model of rotation. These details for benzene will be given later in this paper.

The dynamical averaging of B_{ij} can be done analytically only for very limited and simple cases, e. g. [18], usually for nuclei belonging to one molecule. This is the reason why there is no general analytical formula for the second moment of the motionally narrowed NMR line. Equation (4) for numerical averaging of B_{ij} is completely general and may be applied to any material, if only we know its crystal structure and have enough experience with analytical geometry in space to simulate coordinates of the nuclei taken during reorientation.

2.4 Temperature dependence of the second moment

Van Vleck's second moment depends on the temperature as the result of the temperature dependence of the rate of the motion averaging dipolar interactions. This rate of motion is represented in (4) by the number of positions L taken for dynamical averaging. Usually the reorientation frequency is described by the Arrhenius equation

$$\nu_c = \nu_0 \exp(-U_R / k_B T), \tag{5}$$

where U_R is the potential energy barrier height, hindering the reorientation. The physical meaning of ν_0 is not well defined. The analogous equation describing self-diffusion can be written as

$$\nu_D = \nu_{0D} \exp(-U_D / k_B T), \tag{6}$$

where ν_D is the number of diffusional jumps per second. This equation can be obtained from the Arrhenius equation for the self-diffusion coefficient, taking into account that the frequency of diffusional jumps is proportional to the diffusion coefficient.

To calculate the second moment as function of temperature, that is of ν_c and ν_D, one has to take into account conditions which must be satisfied by rate of motion to influence the NMR linewidth. It results from these conditions that the number of positions L taken for averaging is completely different from the absolute number of positions taken during one second.

3. Details of Calculations

3.1 Structural considerations

A program was written to generate x, y, z coordinates within the symmetrical block of units cells $n \times n \times n$ with n being an odd number. The crystal structure of benzene at 123 K determined by Jeffrey et al. [20] was taken for our calculations. For all calculations we use the block of units cells $3 \times 3 \times 3$, which

contains 108 molecules of benzene. The proton second moment calculated from (2) for this structure is 9.41 [10^{-8} T^2], with 3.19 for the intramolecular part and 6.22 for the intermolecular, respectively. These were the values obtained with numerical averaging over all orientations in the powdered material. The averaging was done with 5 degree steps for both angles describing orientation of r_{ij} in the spherical coordinate system. Using the form of (2) after analytical averaging of the B_{ij}^2 term (Abragam [15], page 112) gives values different by less then 0.5%. Averaging with 9 degree steps gives a second moment value different from the "true" value by less then 1%, which is good enough for comparison with the experimental value 9.65 [10^{-8} T^2] given with about 5% accuracy. The CPU time required for this averaging increases with the square of number of steps, therefore it is important to avoid unnecessarily small steps.

In the next step of preparation for the main calculations, the height of the barrier hindering rotation was calculated. This was done on the basis of formula

$$U_{\alpha\beta} = B_{\alpha\beta} \exp(-C_{\alpha\beta} R) - A_{\alpha\beta}/R^6,$$

where α, β label the atoms (H or C), $A_{\alpha\beta}$, $B_{\alpha\beta}$, and $C_{\alpha\beta}$ are the coefficients, and R is distance between atoms α and β. These coefficients were taken from [21], and correction for electrostatic interaction was introduced into calculation. The value obtained for U_{0R} was 22.0 kJ/mol and was outside the range for this height (15.5 kJ/mol to 18.4 kJ/mol) cited by Craven et al. [14]. Repeating these calculations for the benzene structure determined by Bacon et al. [22] at 138 K gave U_{0R} = 16 kJ/mol, a value close to 15.5 kJ/mol given by Andrew et al. [2], but the second moment obtained for this structure was about 8.0 [10^{-8} T^2], a value too small compared with the experimental one, 9.65 [10^{-8} T^2]. We consider the agreement between calculated and experimental second moments as more important then agreement between the barrier height calculated in this paper and estimated from different NMR experiments, and therefore we take for further calculations the benzene structure determined by Jeffrey et al. [20].

3.2 Simulation of rotation of molecules

In the case of benzene the generally accepted model of rotation of molecules are 60 degree jumps about the sixfold axis of molecule. Such rotation can be very easily simulated by proper permutation of the x, y, z coordinates of nuclei in the molecule. The second moment is calculated for the protons, therefore we do not need coordinates of carbon nuclei for this simulation. For the central molecule with proton labelled 1 to 6, the permutation

1→2, 2→3, 3→4, 4→5, 5→6, and 6→1

simulates a jump in one direction (e. g. clockwise), and the permutation

1→6, 6→5, 5→4, 4→3, 3→2, and 2→1

simulates a jump in the opposite (to previous one) direction. Simulating a jump for any molecule in the considered block of unit cells comes down to the proper numbering of protons in all molecules, and remembering these numbers for each molecule.

The important step in modelling these jumps is the determination of the number of jumps L, taken for averaging in (4). L is not an absolute number of jumps per second, but the number of jumps during the time of recording the NMR signal. When using the pulsed technique, this time is approximately equal to the spin-spin relaxation time T_2, and therefore L can be calculated from the equation

$$L = T_2 \nu_c = T_2 \nu_0 \exp(-U_R/k_B T). \tag{7}$$

It is quite obvious that at a given temperature not all molecules have the same rotation frequency ν_c, and some kind of distribution for these frequencies must be simulated. The distribution of the frequencies was replaced in our calculations by the distribution of the number of rotating molecules. With increasing temperature the number of molecules allowed to rotate was increasing, and rotating molecules were chosen randomly. The probabilities of taking any position P^k were set to be 1.

3.3 Simulation of the diffusion of molecules

Numerical simulation of self-diffusion can be performed by different methods, one of which is described by Faux et al. [23]. One of the purposes of our simulations was to determine the existence or absence of diffusion in solid benzene. Solving this problem does not require a very sophisticated model of diffusion. The diffusional jump is introduced into our calculation as an exchange of the nearest molecules. As will be seen from the results, this model is sufficient

to confirm the existence of self-diffusion in solid benzene, far below the melting point. At the same time such a "diffusion" can be very easily simulated by the exchange of coordinates of atoms between two molecules.

Self-diffusion is, from the NMR point of view, the change of position of the molecule, therefore the (4) is used to evaluate diffusionally averaged B_{ij} terms. The number of positions taken for averaging must be in this case obtained from the equation

$$L = T_2\nu_D = T_2\nu_{0D}\exp(-U_D/k_BT), \qquad (8)$$

which is completely analogous to (7). The probabilities of taking any position P^k were here set to be 1, as in case of rotational motion. To approve this simple model, it must be emphasised that we do not attempt to establish a precise model of self-diffusion but only its eventual existence, as this is still not a definitely solved problem.

4. Computational Techniques

The calculations were performed on the CRAY Y-MP EL (4 processors system) in the Poznan Supercomputing Centre. All computer programs used to obtain results analyzed in this work were written in C language by the author. To spare the CPU time on CRAY, programs were debugged and tested on an IBM PC 486 for small numbers of molecules - 17 and then, after making some minor changes, they were moved to CRAY where calculations were performed for the block of 27 unit cells - 108 molecules. Calculations for the block of 125 unit cell (500 molecules) were also performed, but the final results in this case differ by less then 1% from the results obtained for 108 molecules. As the experimental values of the NMR second moment for benzene are known with about 5% accuracy, it is obvious that taking 108 molecules for the calculation is completely sufficient from the accuracy point of view.

The average CPU time needed to calculate the second moment for temperatures form 80 K to 220 K, every 5 K, was 250 minutes. A few runs up to 250 K used 2000 minutes each.

5. Results of Calculations

Calculations were performed for the models of rotation and diffusion described above, with different sets of values U_R, ν_0, and U_D, ν_{0D}. Intra- and intermolecular contributions to the second moment were calculated for each temperature. Knowledge of these partial values allows better analysis of results and especially permits judgment as to the correctness of calculation. For example, it is known that rotation about an axis perpendicular to r_{ij} vectors must reduce the intramolecular part of the second moment in powdered material to 1/4 of its rigid value (Abragam [15], page 454). This reduced value cannot be further diminished, no matter how fast a rotation will occur. This was true in our calculations, when diffusion was excluded by taking a very high value for U_D. In the high temperature region, the total second moment calculated for this case (rotation only) was by about 15% larger then the experimental value, therefore we conclude that some other type of motion must be present in this temperature region.

In the case with rapid rotation and unrestricted self-diffusion of molecules, the total second moment should decrease to zero. In our calculations the total second moment with internal rotation and self-diffusion restricted to jumps between adjacent molecules, decreased to 0.25 [10^{-8} T^2]. Comparing this value with the experimental high temperature second moment of 1.65 [10^{-8} T^2] we had to assume that self-diffusion must be somehow restricted. We introduced into our calculations the percentage of molecules allowed to perform diffusional jumps. This is a very realistic restriction, as the proposed mechanism of self-diffusion in solid benzene [7] required vacancies to be present, and only a few percent of the molecules might find a vacancy instead of its nearest neighbour molecule.

Finally we found that thermally activated rotation and self-diffusion (restricted to about 0.1% of molecules) gave the second moment, calculated for high temperature, in reasonably good agreement with the experimental value in the same temperature region. The second moment calculated for the rigid structure was 9.4 [10^{-8} T^2], which is 3% less then the experimental value 9.7 [10^{-8} T^2]. The results of calculations are presented in the Table I.

Table I. NMR proton second moment for benzene in [10^{-8} T^2].

	Measured	Model of structure	Calculated
$T < 90$ K	9.7	Rigid	9.4
$T > 140$ K	1.6	Rotation only	1.9
		Rotation & unrestricted diff.	0.25
		Rotation & limited diffusion	1.45

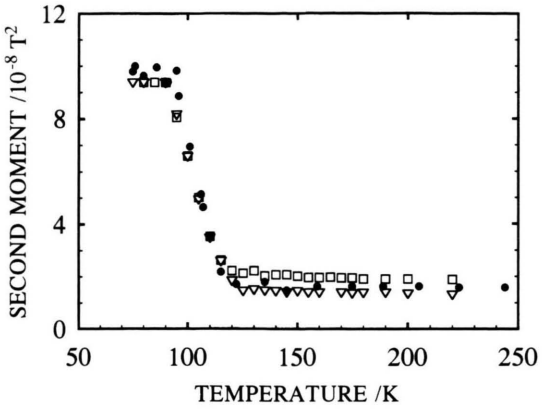

Fig. 1. Proton NMR second moment versus temperature for solid benzene. Full circles: experimental values, squares: values calculated for structure with rotation of molecules only, triangles: values calculated with rotation and self-diffusion of molecules.

The calculated values given in Table I can be obtained for different sets of activation energies (U_R, U_D) and preexponential factors (ν_0, ν_{0D}). The values of these parameters determine the temperature region in which the decrease of the second moment occurs, but do not influence the rigid and high temperature values. The best agreement between experimental and calculated temperature dependence of the second moment was obtained for the following values of energies and preexponential factors:

$$U_R = 16.0 \text{ kJ/mol}, \quad \nu_0 = 8.0\times10^{13} \text{ s}^{-1},$$
$$U_D = 24.0 \text{ kJ/mol}, \quad \nu_{0D} = 5.8\times10^{14} \text{ s}^{-1}.$$

Results of calculations with these parameters are depicted in Figure 1. The U_D value is 4 times smaller than determined by other methods, and this discrepancy is mainly due to the fact that the observed diffusion of molecules in solid benzene has a very small influence on the measured second moment. We must state, therefore, that the results concerning diffusion are rather qualitative, proving the existence of this phenomenon, but not giving accurate and reliable numerical values of the parameters describing it.

6. Conclusions

The main results of this work can be summarized as follows:

- a general prescription has been presented for calculation of the second moment for solids with any type of molecular motion, including jumps between nonequivalent sites,
- the existence of self-diffusion in solid benzene, a process still doubted by some researches, has been confirmed.

The evidence that in solid benzene some kind of diffusion is present far below the melting point results from our calculations, because without introducing self-diffusion into the model of motion of molecules, the calculated second moment in the high temperature region is by about 18% larger than the experimental value. We do not mention the existence of rotation of molecules about the sixfold axis as the conclusion of our work, as this was known since 1950 [1] and never objected. Nevertheless, rotational jumps are confirmed by the calculations presented in this paper.

Our conclusion as to the occurrence of self-diffusion supports a previous suggestion [7], but differs in one important way. The temperature of the onset of diffusional motion is much lower then suggested before. The diffusion starts influencing the NMR line width is at about 120 K, whereas $T_{1\rho}$ relaxation measurements [7] suggest this temperature as being above 200 K. Such a large difference in the temperatures obtained from relaxation and second moment measurements might be partially due to the very simple model of diffusion used in our calculations. Some explanation of this temperature difference may be found in the comparison of diffusion coefficients determined by the relaxation method [7] and the tracer diffusion studies [11]. This coefficient determined from NMR relaxation is about four orders of magnitude smaller then the one obtained from tracer studies. This means, that relaxation studies "see" diffusion as occurring much slower then observed by the tracer method.

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