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# Dynamic disorder and solid state NMR

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## Abstract

The temperature dependences of the second moment ( $M_2$ ) and spin–lattice relaxation times ( $T_1$  and  $T_{1\rho}$ ) in solids with dynamic disorder have been investigated assuming that the potential barrier  $E$  for the moving atom (or molecule) is a stochastic function of time. It has been shown that the temperature dependences of  $M_2$ ,  $T_1$  and  $T_{1\rho}$  exhibit a significant dependence on the kind of standard deviation of the distribution of  $E$  and on the form of the activation energy  $E_b$  at frequency  $\nu_0$  describing the temporal fluctuations of  $E$ . The obtained results have been applied to the interpretation of the temperature transformations of the second moment of <sup>1</sup>H NMR spectra of the diffusing water molecules in the mineral natrolite.

## 1. Introduction

The concept of a distribution of correlation times has been widely used in interpreting NMR data (line shape, second moment and relaxation times) [1–5]. A broad distribution of correlation times leads to the so called ‘apparent phase transition effects’, when the motional line narrowing and reduction of the second moment of the NMR line is observed in a broad temperature range and an asymmetric  $T_1(T)$  dependence of the spin–lattice relaxation time occurs [4].

In most works in which the concept of the correlation time distribution has been discussed, it was assumed that the randomness of correlation times appears due to a static set of random barriers and an atom (or molecule) moves without changing them. However, randomness of potential barriers must be dynamic rather than static, since, due to the collective character of the diffusion process, the fluctuations of the potential barriers would occur simultaneously with each jump of a moving particle [6–8]. In the present paper we consider the temperature dependences of the second moment ( $M_2$ ) and spin–lattice relaxation times ( $T_1$  and  $T_{1\rho}$ ) in solids with dynamic disorder. Here, in contrast to previous works [1–5], we will assume that the potential barrier for a moving particle is a stochastic function of time.

## 2. Theory

The temperature dependences of the second moment  $M_2$  of NMR line and spin–lattice relaxation rates in laboratory ( $T_1^{-1}$ )

and rotating ( $T_{1\rho}^{-1}$ ) frames in the polycrystalline sample are determined by the equations [9–14]

$$M_2(T) = \frac{1}{\pi} \int_{-\delta\omega}^{\delta\omega} J_0(\omega) d\omega, \quad (1)$$

$$T_1^{-1}(T) = \frac{1}{3} [J_0(\omega_0) + 4J_0(2\omega_0)], \quad (2)$$

$$T_{1\rho}^{-1}(T) = \frac{1}{6} [3J_0(2\omega_1) + 5J_0(\omega_0) + 2J_0(2\omega_0)]. \quad (3)$$

Here  $\omega_0$  is the Larmor frequency of nuclei ( $\omega_0 = \gamma B_0$ ) in the laboratory frame and  $\omega_1$  is the Larmor frequency of nuclei in the frame rotating with frequency  $\omega_0$  ( $\omega_1 = \gamma B_1$ ). The spectral density  $J_0(\omega)$  is determined by

$$J_0(\omega) = \text{Re} \int_{-\infty}^{\infty} h(t) \exp(i\omega t) dt, \quad (4)$$

where the dipolar correlation function  $h(t)$  ( $t > 0$ ) is

$$h(t) = K \sum_{i,j} \overline{b_{ij}(0)b_{ij}(t)}. \quad (5)$$

In equation (5) the upper bar denotes the average of value  $b_{ij}(0)b_{ij}(t)$  on the random motions of spin pair  $i - j$ ;

$$K = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \frac{1}{N} \quad (6)$$

and

$$b_{ij}(t) = R_{ij}^{-3}(t) [1 - 3 \cos^2 \theta_{ij}(t)]. \quad (7)$$

In equation (6)  $N$  is the number of nuclei in the sample;  $\gamma$  and  $I$  are the gyromagnetic ratio and nuclear spin, respectively.

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In equation (7)  $R_{ij}$  and  $\theta_{ij}$  are the spherical coordinates of spin pair  $i-j$  vector  $\vec{R}_{ij}$  in the laboratory frame where the vector of the external magnetic field  $\vec{B}_0$  is parallel to the  $z$  axis.

In order to calculate the correlation function  $h_{ij}(t) = \overline{b_{ij}(0)b_{ij}(t)}$  we assume that, as a result of the molecular motion (diffusion or molecular reorientation), the pair of  $i$  and  $j$  nuclei occupy the lattice sites  $\Omega_k$  ( $k = 1, 2, 3 \dots, n$ ), and write  $h_{ij}(0, t)$  in the form

$$h_{ij}(0, t) = \sum_{k,m} P(\Omega_k)P(\Omega_k, 0|\Omega_m, t)b_{ij}(\Omega_k)b_{ij}(\Omega_m), \quad (8)$$

where  $P(\Omega_k)$  is the probability that the random function  $b_{ij}(t)$  is equal to  $b_{ij}(\Omega_k)$  at time  $t = 0$ , while  $P(\Omega_k, 0|\Omega_m, t)$  is the conditional probability that, if at time  $t = 0$  the random function  $b_{ij}(t)$  is equal to  $b_{ij}(\Omega_k)$ , then at time  $t$  it will be equal to  $b_{ij}(\Omega_m)$  [15, 16].

For the random Markov process the conditional probability  $P(\Omega_k, 0|\Omega_m, t)$  satisfies the Smoluchowski equation [15, 16]

$$\frac{\partial}{\partial t} \hat{P}(t) = \hat{W} \cdot \hat{P}(t), \quad (9)$$

where  $\hat{P}(t)$  is the matrix with the elements  $P(\Omega_k, 0|\Omega_m, t)$ . The matrix element  $W_{km}$  ( $k \neq m$ ) of matrix  $\hat{W}$  is the rate constant which describes the probability of the random variable  $\Omega(t)$  varying from  $\Omega_k$  to  $\Omega_m$  by one jump [15, 16]. The matrix elements  $P(\Omega_k, 0|\Omega_m, t)$  and  $W_{km}$  fulfill the conditions [15, 16]

$$P(\Omega_k, 0|\Omega_m, 0) = \delta_{km}, \quad (10)$$

$$\sum_m P(\Omega_k, 0|\Omega_m, t) = 1, \quad (11)$$

$$\sum_m W_{km} = 0. \quad (12)$$

Now we will assume that the matrix  $\hat{W}$  in equation (9) is the stochastic matrix of the time and, for simplicity, we will assume that all  $W_{km}(t)$  ( $k \neq m$ ) are equal to

$$W_{km}(t) = W(t). \quad (13)$$

Introducing the matrix  $\hat{B}$  with elements

$$B_{kk} = n - 1, \quad B_{km} = -1 \quad (k \neq m), \quad (14)$$

where  $n$  is the number of the lattice sites  $\Omega_k$  occupied by the pair of  $i$  and  $j$  as a result of the molecular motion, we can write equation (9) in the form

$$\frac{\partial}{\partial t} \hat{P}(t) = -W(t) \cdot \hat{B} \cdot \hat{P}(t). \quad (15)$$

The average solution of equation (15) has the form

$$\langle \hat{P}(t) \rangle = \langle \hat{P}(0) \cdot \exp(-\hat{B} \cdot \varphi(t)) \rangle, \quad (16)$$

where

$$\varphi(t) = \int_0^t W(t') dt'. \quad (17)$$

Here, according to equation (10), the matrix  $\hat{P}(0)$  has the elements  $P_{km}(0) = \delta_{km}$ . The symbol  $\langle \dots \rangle$  means an operation of averaging over all possible values for the random variable  $\Omega(t)$ .

Since

$$\hat{B}^k = n^{k-1} \hat{B}, \quad (18)$$

we have from equation (16)

$$\begin{aligned} \langle \hat{P}(t) \rangle &= \left\langle \hat{P}(0) \cdot \left[ \hat{E} + \hat{B} \sum_{k=1}^{\infty} \frac{n^{k-1}}{k!} (-\varphi(t))^k \right] \right\rangle \\ &= \hat{P}(0) \cdot \left( \hat{E} - \frac{\hat{B}}{n} \right) + \left\langle \hat{P}(0) \cdot \frac{\hat{B}}{n} \exp \left[ -n \int_0^t W(t') dt' \right] \right\rangle. \end{aligned} \quad (19)$$

Here  $\hat{E}$  is a matrix with elements  $E_{km} = \delta_{km}$ .

Inserting equation (19) into equations (8) and (5) and assuming that  $P(\Omega_k) = 1/n$ , we have

$$h(t) = \overline{M_2} + \Delta M_2 \cdot f(t), \quad (20)$$

where

$$f(t) = \left\langle \exp \left[ - \int_0^t \nu(t') dt' \right] \right\rangle. \quad (21)$$

and  $\nu(t) = n \cdot W(t)$  is the correlation frequency of the stochastic process [15, 16].

In equation (20)

$$\overline{M_2} = K \sum_{i,j} \left[ \frac{1}{n} \sum_{k=1}^n b_{ij}(\Omega_k) \right]^2 \equiv K \sum_{i,j} (\overline{b_{ij}})^2, \quad (22)$$

is the second moment of the motionally narrowed NMR line [9, 17],

$$\Delta M_2 = M_2 - \overline{M_2} \quad (23)$$

and

$$M_2 = K \sum_{i,j} b_{ij}^2 \quad (24)$$

is the second moment of the NMR line in a rigid lattice [9, 17, 18].

Now we will assume that the distribution of all possible values of the correlation frequency  $\nu(t)$  is described by the function  $p(\nu)$  and the jumps from one value of the correlation frequency  $\nu(t)$  to the other are independent and distributed uniformly over time with density  $\nu_0$  (the value  $\nu_0 dt$  determines the average jump value happening in the time interval  $dt$ ) (figure 1). The calculations presented in the appendix lead to the following result for the Laplace transform of  $f(t)$ :

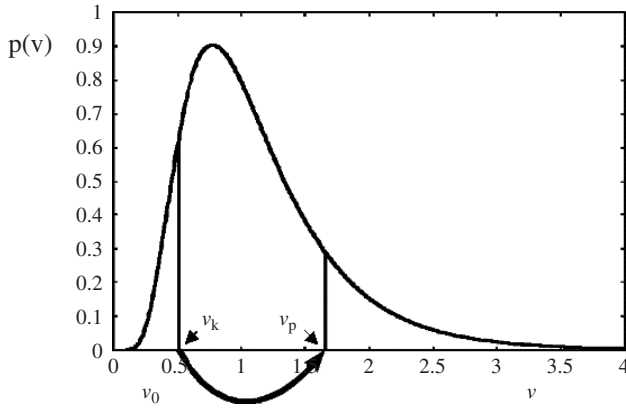
$$f(s) = \frac{p(s)}{1 - \nu_0 \cdot p(s)}, \quad (25)$$

where

$$p(s) \equiv \int_0^{\infty} \frac{p(\nu) d\nu}{s + \nu_0 + \nu}. \quad (26)$$

Using equations (25) and (20) we have from equation (4)

$$J_0(\omega) = \overline{M_2} \delta(0) + 2\Delta M_2 \cdot \text{Re}[f(i\omega)]. \quad (27)$$



**Figure 1.** Schematic presentation of the distribution function  $p(v)$ . The arrow designates the jump of the correlation frequency  $\nu(t)$  from the value  $\nu_k$  to the value  $\nu_p$ . The value  $\nu_0$  determines the density of these jumps.

Insertion of equation (27) into equations (1)–(3) gives

$$M_2(T) = \overline{M_2} + \Delta M_2 \frac{1}{\pi} \int_{-\delta\omega}^{\delta\omega} \text{Re}[f(i\omega)] d\omega, \quad (28)$$

$$T_1^{-1}(T) = \frac{2}{3} \Delta M_2 \cdot [\text{Re}[f(i\omega_0)] + 4\text{Re}[f(2i\omega_0)]], \quad (29)$$

$$T_{1\rho}^{-1}(\nu_C) = \frac{1}{3} \Delta M_2 \cdot [3\text{Re}[f(2i\omega_1)] + 5\text{Re}[f(i\omega_0)] + 2\text{Re}[f(2i\omega_0)]]. \quad (30)$$

The obtained equations (28)–(30) completely determine the temperature dependences of the second moment  $M_2$  of the NMR line and the spin–lattice relaxation rates in laboratory  $T_1^{-1}$  and rotating  $T_{1\rho}^{-1}$  frames in the polycrystalline sample with the dynamic disorder.

### 3. Discussion

First, we note that in the case when both dynamic and static randomness of the potential barriers are absent and the molecular motions in solids are described by one correlation frequency  $\nu_C = \tau_C^{-1}$  (for this case  $\nu_0 = 0$  and  $p(v) = \delta(v - \nu_C)$ ), from equations (25) and (26) it follows that

$$\text{Re}[f(i\omega)] = \frac{\tau_C}{1 + (\omega\tau_C)^2}. \quad (31)$$

Insertion of equation (31) into equations (28)–(30) gives the well known results [9–14]

$$M_2(\nu_C) = \overline{M_2} + \Delta M_2 \frac{2}{\pi} \tan^{-1} \left( \frac{\delta\omega}{\nu_C} \right), \quad (32)$$

$$T_1^{-1}(\nu_C) = \frac{2}{3} \Delta M_2 \cdot \left[ \frac{\tau_C}{1 + (\omega_0\tau_C)^2} + \frac{4\tau_C}{1 + (2\omega_0\tau_C)^2} \right], \quad (33)$$

$$T_{1\rho}^{-1}(\nu_C) = \frac{1}{3} \Delta M_2 \cdot \left[ \frac{3\tau_C}{1 + (2\omega_1\tau_C)^2} + \frac{5\tau_C}{1 + (\omega_0\tau_C)^2} + \frac{2\tau_C}{1 + (2\omega_0\tau_C)^2} \right]. \quad (34)$$

The concept of a static distribution of the correlation times in solids assumes the static (but not dynamic) scattering of the correlation frequencies  $\nu_C = \tau_C^{-1}$ , which is described by the

distribution function  $p(\nu_C)$ . In this case  $\nu_0 = 0$ , and from equations (25) and (26) it follows that

$$\text{Re}[f(i\omega)] = \int_0^\infty p(\nu_C) \frac{\tau_C}{1 + (\omega\tau_C)^2} d\nu_C. \quad (35)$$

and

$$M_2 = \int_0^\infty M_2(\nu_C) \cdot p(\nu_C) d\nu_C, \quad (36)$$

$$T_1^{-1} = \int_0^\infty T_1^{-1}(\nu_C) \cdot p(\nu_C) d\nu_C, \quad (37)$$

$$T_{1\rho}^{-1} = \int_0^\infty T_{1\rho}^{-1}(\nu_C) \cdot p(\nu_C) d\nu_C. \quad (38)$$

The values  $M_2(\nu_C)$ ,  $T_1^{-1}(\nu_C)$  and  $T_{1\rho}^{-1}(\nu_C)$  in equations (36)–(38) are determined by equations (32)–(34).

Now we consider the case of dynamic distribution of the potential barriers for which the distribution of the correlation frequencies  $\nu$  is described by the log-normal function

$$p(\nu) = \frac{kT}{\sigma_E \cdot \nu \sqrt{2\pi}} \exp \left[ -\frac{\left( kT \cdot \ln \left( \frac{\nu}{\nu_\infty} \right) + \bar{E} \right)^2}{2\sigma_E^2} \right]. \quad (39)$$

The log-normal distribution of  $\nu$  corresponds to the case when  $\nu$  fulfills the Arrhenius activation law

$$\nu = \nu_\infty \exp \left( -\frac{E}{kT} \right), \quad (40)$$

in which activation energy  $E$  has a normal (Gauss) distribution

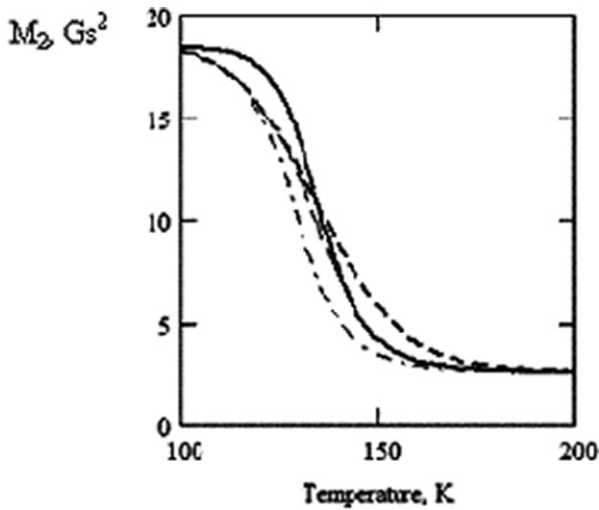
$$p(E) = \frac{1}{\sigma_E \sqrt{2\pi}} \exp \left[ -\frac{(E - \bar{E})^2}{2\sigma_E^2} \right]. \quad (41)$$

Assuming that

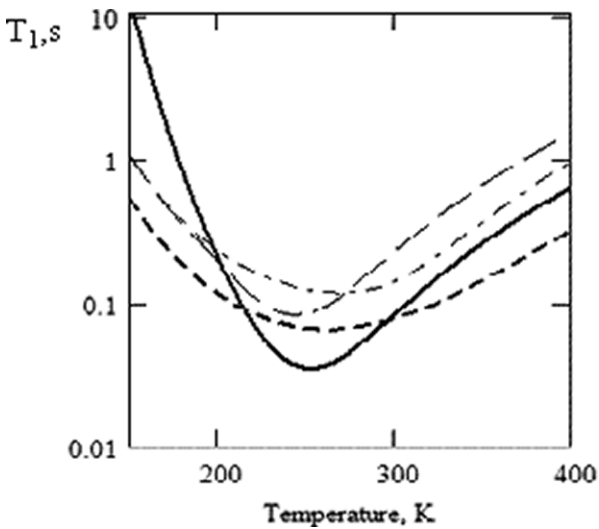
$$\nu_0 = \nu_\infty \exp \left( -\frac{E_b}{kT} \right), \quad (42)$$

where  $E_b$  is the activation energy which determines the temperature dependence of jump frequency  $\nu_0$  from one value of the correlation frequency  $\nu$  to the other, and using equations (28)–(30), we calculated the temperature transformations of the second moment  $M_2$  of the NMR line and the spin–lattice relaxation rates in laboratory  $T_1^{-1}$  and rotating  $T_{1\rho}^{-1}$  frames. The results of these calculations are shown in figures 2–4.

From figure 2, it follows that in the case of static distribution of the potential barriers the temperature dependence of  $M_2$  is a symmetrical function regarding the temperature at which  $M_2(T) = \Delta M_2/2$ . In the case of dynamic distribution of the potential barriers the temperature dependence of  $M_2(T)$  exhibits a significant dependence on the type of standard deviation  $\sigma_E$  of the distribution function  $p(E)$  (equation (41)) and on the form of the activation energy  $E_b$  at jump frequency  $\nu_0$  (equation (42)). It can also be seen that in the case of the dynamic disorder of the activation energy  $E$  the temperature interval in which the reduction of the second moment is observed

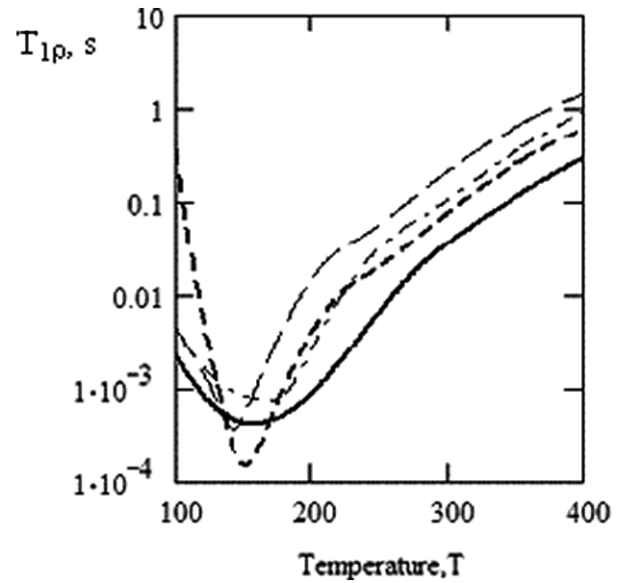


**Figure 2.** Temperature dependences of the second moment of NMR line  $M_2$ . The graphs were obtained for the following parameters:  $M_2 = 18.5 \times 10^{-8} T^2$ ,  $\overline{M}_2 = 2.67 \times 10^{-8} T^2$ ,  $\overline{E} = 20.8 \text{ kJ mol}^{-1}$ ,  $\sigma_E = 0.1 \overline{E}$  and  $\nu_\infty = 1.2 \times 10^{-13} \text{ Hz}$ . The bold continuous line represents equation (32). The bold broken line represents equation (36) (the case of static disorder) obtained with the normal distribution of  $E$  (equation (41)). Equation (28) (the case of dynamic disorder) is represented by the broken line ( $E_b = \overline{E}$ ) and by the dot-dash line ( $E_b = 0.88 \times \overline{E}$ ).



**Figure 3.** Temperature dependences of the spin-lattice relaxation time  $T_1$ . The graphs were obtained for the following parameters:  $M_2 = 18.5 \times 10^{-8} T^2$ ,  $\overline{M}_2 = 2.67 \times 10^{-8} T^2$ ,  $\overline{E} = 20.8 \text{ kJ mol}^{-1}$ ,  $\sigma_E = 0.2 \overline{E}$  and  $\nu_\infty = 1.2 \times 10^{-13} \text{ Hz}$ . The bold continuous line represents equation (33); The bold broken line represents equation (37) (the case of static disorder) obtained with the normal distribution of  $E$  (equation (41)). Equation (29) (the case of dynamic disorder) is represented by the broken line ( $E_b = 0.88 \times \overline{E}$ ) and by the dot-dash line ( $E_b = 1.2 \times \overline{E}$ ).

is smaller than that in the case of the static disorder of  $E$ . This effect reflects the motional average of the correlation frequency  $\nu$  induced by its temporal fluctuations with the jump frequency  $\nu_0$ . It should be also noted that the temperature at which the reduction of the second moment is observed shifts in the dynamic case to the side of the lower temperatures.



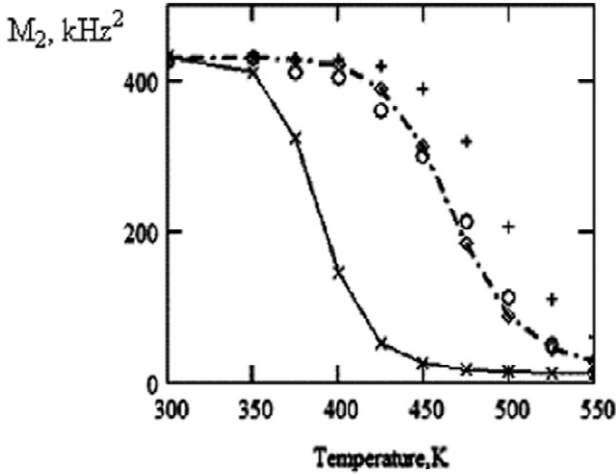
**Figure 4.** Temperature dependences of the spin-lattice relaxation time  $T_{1\rho}$ . The graphs were obtained for the same parameters as in figure 3.  $\omega_0 = 2\pi \times 60 = 376 \text{ MHz rad}$ ,  $\omega_1 = (\pi/2) \times (1/3.6) = 0.43 \text{ MHz rad}$ .

From figures 3 and 4, it follows that in the case of a dynamic distribution of the potential barriers the minima of the spin-lattice relaxation times in the laboratory frame  $T_1$  and in the rotating frame  $T_{1\rho}$  depend significantly on the choice of  $\sigma_E$  and  $E_b$ . In this case, the effect of the motional average of the correlation frequency  $\nu$ , induced by its fluctuations with the jump frequency  $\nu_0$ , is also observed.

#### 4. Comparison with the experimental data

Unusual temperature transformations of the  $^1\text{H}$  NMR line shapes have been observed in natrolite [3, 21, 22]. The mineral natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ) is a typical channel-type compound with porous structure. According to the NMR data [3, 23], at  $T > 250 \text{ K}$  the diffusion of the water molecules occurs along the vacancies whose positions coincide with regular positions of water molecules in the natrolite lattice. The anomalous temperature transformations of the NMR line shapes in natrolite are connected with the appearance of a wide temperature interval in which the reduction of the second moment was observed (figure 5). This behavior is not consistent with the assumption that the diffusion process of the water molecules can be described by one correlation time. In [3, 21] it was assumed that the observed temperature behavior of the NMR second moment is connected with the static distribution of the correlation times for the diffusing water molecules. However, this assumption does not agree with the NMR [21, 22] and neutron diffraction data [24] showing that all water molecules in the channels of natrolite are chemically and structurally equivalent.

From the results obtained in this paper it follows that the unusual temperature transformation of the NMR second moment in natrolite may be explained assuming that the potential barrier for the diffusion of the water molecules



**Figure 5.** The temperature dependence of the  $^1\text{H}$  NMR second moment in natrolite for the case where the external magnetic field  $\vec{B}_0$  lies in the [110] direction. The symbols  $\circ\circ\circ$  represent the experimental data [3, 21]; the symbols  $\diamond\diamond\diamond$  represent equation (28) (dynamic disorder) obtained with the parameters  $\bar{E} = E_b = 73 \text{ kJ mol}^{-1}$ ,  $\sigma_E = 0.02\bar{E}$ ; the symbols  $\times\times\times$  represent equation (32) obtained with  $\nu_c = 1.2 \times 10^{-13} \exp(-73 \text{ kJ mol}^{-1} \text{ kT}^{-1})$ ; the symbols  $+++$  represent equation (36) (static disorder) obtained with the normal distribution of  $E$  (equation (41)) and  $\bar{E} = 73 \text{ kJ mol}^{-1}$ ,  $\sigma_E = 0.02\bar{E}$ . For all the graphs  $M_2 = 432.3 \text{ (kHz)}^2$ ,  $\bar{M}_2 = 13 \text{ (kHz)}^2$ .

fluctuates chaotically as a function of time. The results of our calculations for this model are shown in figure 5. The data presented in this figure show that the model of the dynamic fluctuations of the potential barrier describes well the experimentally observed unusual temperature transformations of the second moment of NMR spectra in natrolite.

## 5. Conclusion

We investigated the temperature dependences of the second moment ( $M_2$ ) and the spin–lattice relaxation times ( $T_1$  and  $T_{1\rho}$ ) in solids with dynamic disorder. In our consideration it was assumed that the potential barrier  $E$  for the moving atom (or molecule) is a stochastic function of time. The model of the dynamic disorder of the potential barrier was applied to the interpretation of the temperature transformations of the second moment of  $^1\text{H}$  NMR spectra of the diffusing water molecules in the mineral natrolite.

## Appendix

For calculation of  $f(t)$  we will use the procedure described in [19, 20]. Dividing the time interval  $(0, t)$  into  $m$  subintervals  $\tau = t/m$  we can write equation (21) in the form

$$f(t) = \lim_{\tau \rightarrow 0} \int_0^\infty \cdots \int_0^\infty \exp\left(-\sum_{k=2}^{m+1} \tau \cdot \nu_k\right) \times p(\nu_{m+1}) p(\nu_{m+1} | \nu_m, \tau) p(\nu_m | \nu_{m-1}, \tau) \cdots p(\nu_2 | \nu_1, \tau) \times d\nu_1 d\nu_2 \cdots d\nu_{m+1}. \quad (43)$$

Here  $\nu_k (k = 1, 2, \dots, m+1)$  is the value of  $\nu$  on the time interval  $(k\tau, (k+1)\tau)$ .

The function  $p(\nu_k | \nu_{k-1}, \tau)$  fulfills the Feller equation [15, 16]

$$\frac{\partial p(\nu_k | \nu_{k-1}, \tau)}{\partial \tau} = -\nu_0 p(\nu_k | \nu_{k-1}, \tau) + \nu_0 \int d\nu \cdot f(\nu | \nu_{k-1}) p(\nu_k | \nu, \tau), \quad (44)$$

with the condition

$$p(\nu_k | \nu_{k-1}, 0) = \delta(\nu_k - \nu_{k-1}). \quad (45)$$

Here the function  $f(\nu_p | \nu_k)$  is the probability that the random variable  $\nu_p$  jumps to  $\nu_k$ ;  $\nu_0$  is the average frequency of jump from one  $\nu$  to the other.

If we assume that

$$f(\nu_k | \nu_p) = p(\nu_p), \quad (46)$$

where  $p(\nu)$  is the function that describes the distribution of all possible values  $\nu$ , then from equation (44) we have

$$p(\nu_k | \nu_{k-1}, \tau) = \delta(\nu_{k-1} - \nu_k) e^{-\tau/\tau_0} + p(\nu_{k-1}) \cdot (1 - e^{-\tau/\tau_0}). \quad (47)$$

Here  $\tau_0 = \nu_0^{-1}$ .

Inserting equation (47) into equation (43) we obtain

$$f(t) = \lim_{\tau \rightarrow 0} \int_0^\infty \cdots \int_0^\infty p(\nu_{m+1}) \exp\left(-\sum_{k=2}^{m+1} \tau \cdot (\nu_k + \nu_0)\right) \times g(\nu_{m+1} | \nu_m, \tau) g(\nu_m | \nu_{m-1}, \tau) \cdots g(\nu_2 | \nu_1, \tau) \times d\nu_1 d\nu_2 \cdots d\nu_{m+1}, \quad (48)$$

where

$$g(\nu_k | \nu_{k-1}, \tau) = \delta(\nu_{k-1} - \nu_k) + c \cdot p(\nu_{k-1}) \quad (49)$$

and  $c = \exp(\tau/\tau_0) - 1$ .

Integration in equation (48) over all variables  $\nu_p (p \leq m)$  gives

$$f(t) = p(t) + \frac{1}{\tau_0} \int_0^t dt_1 p(t_1) \cdot p(t - t_1) + \frac{1}{\tau_0^2} \int_0^t dt_1 p(t_1) \cdot \int_0^{t_1} dt_2 p(t_2) p(t - t_1 - t_2) + \frac{1}{\tau_0^3} \int_0^t dt_1 p(t_1) \int_0^{t_1} dt_2 p(t_2) \times \int_0^{t_2} dt_3 p(t_3) p(t - t_1 - t_2 - t_3) + \cdots, \quad (50)$$

where

$$p(t) = \int_0^\infty d\nu \cdot \exp[-(\nu + \nu_0)t] \cdot p(\nu). \quad (51)$$

After the Laplace transformation of equation (50) we have

$$f(s) \equiv \int_0^\infty e^{-st} f(t) dt = p(s) \cdot \left[ \sum_{k=0}^\infty (\nu_0 \cdot p(s))^k \right] = \frac{p(s)}{1 - \nu_0 \cdot p(s)}, \quad (52)$$

where

$$p(s) \equiv \int_0^\infty \frac{p(\nu) d\nu}{s + \nu + \nu_0}. \quad (53)$$

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