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Relaxation in quasiadiabatical limit. Saturation of Dipolar Order in slow rotating sample: Preprint ITEP 45-00/

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A NMR study of saturation of spin dipole order due to slow rotation of the sample was carried out on polycrystalline adamantane. Dependence of saturation rate on the angle ϑ_H between rotor axis and external static magnetic field was studied for the first time and simple $\sin^2\vartheta_H$ law was established. A new theory for quasiadiabatic evolution of thermodynamic systems is constructed basing on first principles and projection operator technique. The theory gives simple conceptually and correct description of obtained experimental results.

Релаксация в квазиадиабатическом пределе. Насыщение дипольного спинового резервуара в медленно вращающемся образце.

Т.Шарпентье, Ф.Джепаров, Ж.-Ф.Жакино, Дж.Вирле

Методом ЯМР на поликристаллическом адамантане изучено насыщение дипольного спинового резервуара вследствие медленного вращения образца. Впервые исследована зависимость скорости насыщения от угла ϑ_H между осью ротора и внешним магнитным полем и обоснован простой закон $\sin^2\vartheta_H$. Из первых принципов и на основе проекционной техники построена новая теория квазиадиабатической эволюции термодинамических систем. Теория дает простое с концептуальной точки зрения и корректное описание полученных экспериментальных результатов.

Fig – 3, Ref. – 19 names

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1 Introduction

The thermodynamical spin temperature concept is the framework of a general theory of nuclear magnetism in solids which has been extensively studied in the past [1, 2]. It has been mostly applied to spin systems in static samples. The introduction of the multipulse narrowing methods has shown that the spin temperature concept could also be applied to spin systems submitted to a strong periodic interaction [3, 4, 5]. Numerous theoretical and experimental studies of evolution of dipolar order under influence of various external or internal interactions have been carried out; of particular interest in connection with the present study are the works related to the influence of coherent [6, 7, 8, 9] or incoherent motion of the sample [10, 8].

The most widespread line narrowing method in solid state NMR is probably the magic-angle spinning (MAS) technique. The problem of dipolar order in rotating sample is then of physical and practical interest as being related to more general problems such as cross-polarization (CPMAS), multipulse line narrowing combined with MAS (CRAMPS) and so on. Investigation of the phenomenon seems also important for better understanding of general spin dynamics, including very deep problems of time dependent Hamiltonians and corresponding spin thermodynamics. In order to use such dipolar state, it must be understood how it will be influenced by the rotation of the sample. Compared to static sample, the (secular) part of the dipolar interaction, here denoted $H_{\mathrm{D}}(t)$, is time-dependent and does not commute with itself at different times. Therefore, the rotation of the sample produces a saturation of dipolar order that may be created.

We have investigated this saturation theoretically and experimentally in two limits. The slow spinning speed case, $\omega_r \ll \omega_l$ (ω_l is the typical dipolar linewidth) is presented in this paper. The fast spinning case, which is physically different, will be presented in a forthcoming paper. Here, we

have developed a general theory of dipolar order saturation due to the rotation of the sample in the quasiadiabatic limit. The present theory uses a time-dependent projection operator approach.

The problem of slow spinning speed was already studied in experiments [6, 7] and in theory [8], for orthogonal orientation of the rotation axis relative to the external magnetic field. We propose a new formal and general theory based on an extension of the Nakajima-Zwanzig projection technique. General part of the theory is detailed in the second Section together with simple and general approximations, used to obtain quantitative results. Third Section gives some experimental results. Here, the variation of the saturation with respect to the spinning speed has been studied in a polycrystalline sample of adamantane for rotation axis directed near magic orientation. Discussion of the results and approximate calculation of one of most important parameter $\langle A_S \rangle_{pc}$ is carried out in Section 4. More detailed calculations and additional information are placed in Appendixes.

2 Theory.

2.1 Spin temperature and adiabatic evolution.

We consider that the spinning speed of the sample is very slow so that the thermodynamical state of the system continuously adapts itself to the instantaneous Hamiltonian $H(t) = H_{\rm Z} + H_{\rm D}(t)$, where $H_{\rm Z} = -\omega_{\rm L} I_{\rm Z}$ and $H_{\rm D}(t)$ represent Zeeman and secular dipolar parts of spin interactions [2]. As usual $[H_{\rm Z}, H_{\rm D}] = 0$, therefore in this adiabatic limit the system, being initially prepared in Zeeman and dipolar order, reaches at each time τ a state of internal quasiequilibrium corresponding to a density matrix $\rho_{qs}(\tau)$ of the form

$$\rho_{qs}(\tau) = 1 - \beta_{\rm Z} H_{\rm Z} - \beta_{\rm D}(\tau) H_{\rm D}(\tau). \tag{1}$$

where $\beta_{\rm Z}$ and $\beta_{\rm D}(\tau)$ are Zeeman and dipolar (inverse) spin temperatures, and usual high temperature spin dynamics conventions [2] are used. The conservation of entropy $S = -{\rm Tr}\,\{\rho \ln \rho\}$ gives

$$\beta_{\rm D}^2(\tau) \cdot {\rm Tr}\left\{H_{\rm D}^2(\tau)\right\} = {\rm const.} \tag{2}$$

Then, during the adiabatic variation of the dipolar Hamiltonian, the spin temperature varies according to

$$\beta_{\rm D}(\tau) = \text{const}/\sqrt{\langle\, H_{\rm D}^2(\tau)\,\rangle}, \qquad \langle\cdots\rangle = \text{Tr}\,\{\cdots\}\,/\text{Tr}\,\{1\}\,, \tag{3}$$

or, in a differential form,

$$\frac{d\beta_{\rm D}}{dt} = -\frac{\beta_{\rm D}}{2}\frac{d}{dt}\left(\ln\langle\, H_{\rm D}^2(\tau)\,\rangle\right). \tag{4}$$

This last form of Eq.2 will be used later. At this stage, no saturation processes has been introduced. The expansion

$$H_{\rm D}(\tau+\Delta\tau) = H_{\rm D}(\tau) + \Delta\tau\dot{H}_{\rm D}(\tau) + \ldots \tag{5}$$

shows that the small term $\dot{H}_{\rm D}(\tau)$ ($\sim \omega_r/\omega_l \ll 1$) is the perturbation which produces the saturation. Thus, a correlation function like

$$\langle\, \dot{H}_{\rm D}(t+\tau)\, U_{\rm D}\, \dot{H}_{\rm D}(t)\, U_{\rm D}^{+}\,\rangle, \quad U_{\rm D} = \widehat{T}\exp\left(-i\int_t^{t+\tau} H_{\rm D}(u)\,du\right) \tag{6}$$

is expected in a saturation calculation. The Zeeman order is unaffected by the slow rotation because I_z commutes with $H_{\rm D}(\tau)$. This results must be obtained by any approach and it will be checked below. The set of observables of interest, in analogy with the static sample case, are I_z and $H_{\rm D}(t)$. Therefore, for the present theoretical treatment, we should introduce a time-dependent projection super-operator $\hat{\pi}(t)$ which acts on any vector $|\,A(t)\,\rangle$ in the Liouville space as

$$\hat{\pi}(t)|\,A(t)\,\rangle = \langle\, A(t)\,\rangle\,|\,\text{Id}\,\rangle + \frac{\langle\, I_z\,|A(t)\,\rangle}{\langle\, I_z^2\,\rangle}|\,I_z\,\rangle + \frac{\langle\, H_{\rm D}(t)\,|A(t)\,\rangle}{\langle\, H_{\rm D}^2(t)\,\rangle}|\,H_{\rm D}(t)\,\rangle \tag{7}$$

where

$$\langle\, X|Y\,\rangle = \frac{\text{Tr}\,\{X^{+}Y\}}{\text{Tr}\,\{\text{Id}\}}, \quad \text{and} \quad \langle\, X\,\rangle = \frac{\text{Tr}\,\{X\}}{\text{Tr}\,\{\text{Id}\}}. \tag{8}$$

Here X and Y are usual operators in standard Hilbert space of quantum mechanics [2].

In the remainder of this section, for notational convenience, the time dependence will be omitted when not necessary. Thus $\hat{\pi}(t)|\,A(t)\,\rangle$ will be simply denoted $\hat{\pi}|\,A\,\rangle$. The projection (super-)operator $\bar{\hat{\pi}}(t) = \hat{\text{Id}} - \hat{\pi}(t)$ is also introduced. Some useful properties, obtained after straightforward

calculations, are given in Appendix A. The Zeeman and dipolar time-dependent spin temperatures are then defined by

$$\beta_{\rm Z}(t) = -\frac{1}{\omega_{\rm L}}\frac{\langle I_{\rm Z}\,|\,\hat{\pi}(t)\,|\,\rho(t)\,\rangle}{\langle I_{\rm Z}^2\rangle}, \tag{9}$$

$$\beta_{\rm D}(t) = -\frac{\langle H_{\rm D}(t)\,|\,\hat{\pi}(t)\,|\,\rho(t)\,\rangle}{\langle H_{\rm D}^2(t)\,\rangle}. \tag{10}$$

and the quasiequilibrium density matrix is of the form

$$|\,\rho_{qs}(t)\,\rangle = \hat{\pi}(t)|\,\rho(t)\,\rangle = |\,1\,\rangle - \omega_{\rm L}\beta_{\rm Z}(t)|\,I_{\rm Z}\,\rangle - \beta_{\rm D}(t)|\,H_{\rm D}(t)\,\rangle. \tag{11}$$

The knowledge of the master equation for the reduced density operator $\hat{\pi}|\,\rho\,\rangle$ is then sufficient for obtaining the evolution of the spin temperatures. This calculation is detailed in the next section.

2.2 Master equation for $\hat{\pi}|\,\rho\,\rangle$.

We start from the Liouville equation for the spin density operator $|\,\rho(t)\,\rangle$ which is, in the conventional rotating frame,

$$\frac{d|\,\rho\,\rangle}{dt} = -i|\,[\,H_{\rm D}(t)\,,\,\rho(t)\,]\,\rangle = -i\hat{\mathcal{L}}_{\rm D}(t)\,|\,\rho(t)\,\rangle. \tag{12}$$

All following transformations of this equation are directed (as usual in deriving of master equations [2]) on separation of dynamics of slow and fast variables in the problem. From the present choice of slow variables, given by the projection operator $\hat{\pi}(t)$ (Eq.7), where $H_{\rm D}$ commutes which each of its component, one can obtain the relations

$$\hat{\pi}\hat{\mathcal{L}}_{\rm D} = \hat{\mathcal{L}}_{\rm D}\hat{\pi} = 0 \quad \text{and} \quad (1-\hat{\pi})\hat{\mathcal{L}}_{\rm D} = \overline{\hat{\pi}}\hat{\mathcal{L}}_{\rm D} = \hat{\mathcal{L}}_{\rm D}. \tag{13}$$

Multiplying Eq.12 on the left by $\hat{\pi}$ and $\overline{\hat{\pi}}$ leads to the two equations

$$\hat{\pi}\frac{d|\,\rho\,\rangle}{dt} = -i\hat{\pi}\hat{\mathcal{L}}_{\rm D}|\,\rho\,\rangle = 0, \tag{14}$$

$$\overline{\hat{\pi}}\frac{d|\,\rho\,\rangle}{dt} = -i\overline{\hat{\pi}}\hat{\mathcal{L}}_{\rm D}\left(\hat{\pi}+\overline{\hat{\pi}}\right)|\,\rho\,\rangle = -i\hat{\mathcal{L}}_{\rm D}\overline{\hat{\pi}}|\,\rho\,\rangle. \tag{15}$$

Therefore, introducing $\dot{\hat{\pi}} = d\hat{\pi}/dt$ and similarly $\dot{\overline{\hat{\pi}}} = -\dot{\hat{\pi}}$, one obtains

$$\frac{d}{dt}\hat{\pi}|\,\rho\,\rangle = \dot{\hat{\pi}}|\,\rho\,\rangle = \dot{\hat{\pi}}\hat{\pi}|\,\rho\,\rangle + \dot{\hat{\pi}}\overline{\hat{\pi}}|\,\rho\,\rangle, \tag{16}$$

and

$$\begin{aligned}\frac{d}{dt}\overline{\hat{\pi}}|\,\rho\,\rangle &= \dot{\overline{\hat{\pi}}}|\,\rho\,\rangle + \overline{\hat{\pi}}|\,\dot{\rho}\,\rangle = \dot{\overline{\hat{\pi}}}(\hat{\pi}+\overline{\hat{\pi}})|\,\rho\,\rangle - i\hat{\mathcal{L}}_{\mathrm{D}}\overline{\hat{\pi}}|\,\rho\,\rangle \\ &= -\dot{\hat{\pi}}\hat{\pi}|\,\rho\,\rangle - i\left(\hat{\mathcal{L}}_{\mathrm{D}} - i\dot{\hat{\pi}}\right)\overline{\hat{\pi}}|\,\rho\,\rangle \end{aligned} \tag{17}$$

Eq.17 can be formally solved by introducing the propagator

$$\hat{S}(t,\tau) = \widehat{T}\exp\left\{-i\int_{\tau}^{t}\left(\hat{\mathcal{L}}_{\mathrm{D}}(u) - i\dot{\hat{\pi}}(u)\right)du\right\}. \tag{18}$$

The result is

$$\overline{\hat{\pi}}|\,\rho(t)\,\rangle = -\int_0^t \hat{S}(t,\tau)\dot{\hat{\pi}}(\tau)|\,\rho(\tau)\,\rangle d\tau. \tag{19}$$

It can be checked directly by substitution of (19) into Eq.17 and taking into account the initial condition $\overline{\hat{\pi}}|\,\rho(t=0)\,\rangle = 0$. Therefore, combining Eqs.19 and 16 , we arrive at the master equation

$$\frac{d}{dt}\hat{\pi}|\,\rho\,\rangle = \dot{\hat{\pi}}\hat{\pi}|\,\rho\,\rangle - \hat{\pi}\dot{\hat{\pi}}\int_0^t \hat{S}(t,\tau)\dot{\hat{\pi}}(\tau)\hat{\pi}(\tau)|\,\rho(\tau)\,\rangle d\tau, \tag{20}$$

and to the other important equation

$$\hat{\pi}\frac{d}{dt}\hat{\pi}|\,\rho\,\rangle = -\hat{\pi}\dot{\hat{\pi}}\int_0^t \hat{S}(t,\tau)\dot{\hat{\pi}}(\tau)\hat{\pi}(\tau)|\,\rho(\tau)\,\rangle d\tau, \tag{21}$$

which follows immediately from (20) by multiplying on the left by $\hat{\pi}$ and taking into account that $\hat{\pi}\dot{\hat{\pi}}\hat{\pi} = 0$.

With the preceding equation, the evolution of the spin temperature may be, at least formally, calculated. Approximation for having more tractable expressions are detailed below.

2.3 Master equation for the spin temperatures.

It can be checked that the Zeeman order is unaffected by the rotation of the sample. Indeed, multiplying Eq.21 by $\langle\, I_{\mathrm{Z}}\,|$ and remembering that $\langle\, I_{\mathrm{Z}}H_{\mathrm{D}}\,\rangle = 0$ and $\langle\, I_{\mathrm{Z}}\dot{H}_{\mathrm{D}}\,\rangle = 0$ we immediately obtain that

$$\frac{d}{dt}\beta_{\mathrm{Z}} = 0. \tag{22}$$

The master equation for β_D can be derived directly from Eq.21 by multiplying it on the left by $\langle H_D(t)|$ and taking into account the relations (11) and

$$\langle H_D|\frac{d}{dt}(\beta_D|H_D\rangle) = \dot{\beta}_D\langle H_D^2\rangle + \frac{\beta_D}{2}\frac{d}{dt}\langle H_D^2\rangle = \langle H_D^2\rangle\left(\dot{\beta}_D + \frac{\beta_D}{2}\frac{d}{dt}\ln\langle H_D^2\rangle\right).$$

As a result

$$\frac{d\beta_D}{dt} = -\frac{\beta_D}{2}\frac{d}{dt}\left(\ln\langle H_D^2(t)\rangle\right) - \int_0^t M(t,\tau)\beta_D(\tau)d\tau. \tag{23}$$

where the memory function

$$M(t,\tau) = \frac{1}{\langle H_D^2(t)\rangle}\langle \dot{H}_D(t)\,|\,\bar{\hat{\pi}}(t)\hat{S}(t,\tau)\bar{\hat{\pi}}(\tau)\,|\,\dot{H}_D(\tau)\rangle, \tag{24}$$

is proportional to the (auto-)correlation function of the perturbation $\bar{\hat{\pi}}\dot{H}_D(t)$.

The first term of Eq.23, as discussed in 2.1, is the adiabatic contribution to the evolution of β_D. Its order of magnitude is $\sim \omega_r\beta_D$ while the second term of order $\sim \left(\omega_r^2/\omega_l\right)\beta_D$, is much smaller. The saturation occurs on a time scale which is much longer than the rotation time $1/\omega_r$. Therefore a new slow-varying spin temperature $\beta_S(t)$ can be defined by

$$\beta_D(t) = \left[\langle H_D^2(0)\rangle/\langle H_D^2(t)\rangle\right]^{1/2}\beta_S(t), \tag{25}$$

which evolves as

$$\frac{d\beta_S}{dt} = -\int_0^t M_S(t,t-\tau)\beta_S(t-\tau)d\tau. \tag{26}$$

The new memory function $M_S(t,\tau)$, in this new representation which may be seen as an *adiabatic frame*, is

$$M_S(t,\tau) = \frac{1}{\sqrt{\langle H_D^2(t)\rangle\langle H_D^2(\tau)\rangle}}\langle \dot{H}_D(t)\,|\,\bar{\hat{\pi}}(t)\hat{S}(t,\tau)\bar{\hat{\pi}}(\tau)\,|\,\dot{H}_D(\tau)\rangle. \tag{27}$$

This last equation is *exact* for any kind of motion of the sample and useful simplifications will be introduced in the next section.

2.4 Approximations and calculation of the saturation rate.

For slow rotation (or adiabatic evolution), the contribution $-i\dot{\hat{\pi}}$ in the propagator Eq.18 can be fully neglected with respect to $\hat{\mathcal{L}}_D$. On the time

scale $\tau \sim 1/\omega_l << 1/\omega_r$, the variation of $\hat{\mathcal{L}}_{\rm D}(t)$ can be also neglected (the free precession decay is much shorter than the period of rotation). Thus $\hat{S}(t, t-\tau)$ may be simplified as

$$\hat{S}(t, t-\tau) = \widehat{T} \exp\left\{-i \int_{t-\tau}^{t} \hat{\mathcal{L}}_{\rm D}(u) du\right\} \approx \exp\left\{-i\hat{\mathcal{L}}_{\rm D}(t)\tau\right\}. \tag{28}$$

Of course, this equation is strictly correct only if replaced in the memory function Eq.27. As a function of τ, $M_S(t, t-\tau)$ decreases in a time which is of the same order of magnitude as T_2 and the latter is smaller than the typical evolution time of $\beta_{\rm S}(t)$. Moreover, the difference between $\dot{H}_{\rm D}(t-\tau)$ and $\dot{H}_{\rm D}(t)$ and, $H_{\rm D}(t-\tau)$ and $H_{\rm D}(t)$ can be neglected leading to

$$M_S(t, t-\tau) \approx \frac{1}{\langle H_{\rm D}^2(t) \rangle} \langle \dot{H}_{\rm D}(t) \,|\, \overline{\hat{\pi}}(t) e^{-i\hat{\mathcal{L}}_{\rm D}(t)\tau} \overline{\hat{\pi}}(t) \,|\, \dot{H}_{\rm D}(t) \rangle, \tag{29}$$

and the upper limit of integration in Eq.26 can be extended to ∞ which gives

$$\frac{d\beta_{\rm S}}{dt} = -W_S(t)\beta_{\rm S}(t), \tag{30}$$

where the *instantaneous* saturation rate $W_S(t)$ is

$$W_S(t) = \frac{1}{\langle H_{\rm D}^2(t) \rangle} \int_0^{\infty} \langle \dot{H}_{\rm D}(t) \,|\, \overline{\hat{\pi}}(t) e^{-i\hat{\mathcal{L}}_{\rm D}(t)\tau} \overline{\hat{\pi}}(t) \,|\, \dot{H}_{\rm D}(t) \rangle d\tau. \tag{31}$$

With the same order of accuracy, an averaged $\overline{W}_S$ may be used

$$\beta_{\rm S}(t) = \beta_{\rm S}(0) \exp\left\{-\int_0^t W_S(\tau) d\tau\right\} \approx \beta_{\rm S}(0) e^{-\overline{W}_S t}, \tag{32}$$

$$\overline{W}_S = \frac{1}{T_{rot}} \int_0^{T_{rot}} W_S(t) dt, \tag{33}$$

here $T_{rot} = 2\pi/\omega_r$.

As usual, the correlation function

$$f(t, \tau) = \frac{1}{\langle \dot{H}_{\rm D}(t) \overline{\hat{\pi}}(t) \dot{H}_{\rm D}(t) \rangle} \langle \dot{H}_{\rm D}(t) \,|\, \overline{\hat{\pi}}(t) e^{-i\hat{\mathcal{L}}_{\rm D}(t)\tau} \overline{\hat{\pi}}(t) \,|\, \dot{H}_{\rm D}(t) \rangle \tag{34}$$

may be simplified into

$$f(t, \tau) = \frac{1}{\langle D^2(t) \rangle} \langle D(t) e^{-iH_{\rm D}(t)\tau} D(t) e^{+iH_{\rm D}(t)\tau} \rangle, \tag{35}$$

$$D(t) = \dot{H}_{\rm D}(t) - H_{\rm D}(t)\langle H_{\rm D}(t)\dot{H}_{\rm D}(t)\rangle / \langle\, H_{\rm D}^2(t)\,\rangle. \tag{36}$$

A natural scale for dependence of $f(t,\tau)$ on τ could be defined by an instantaneous second moment $m_{\rm S}(t)$ given by

$$m_{\rm S}(t) = \frac{\langle\, [\,\dot{H}_{\rm D}(t)\,,\, H_{\rm D}(t)\,]\,[\,H_{\rm D}(t)\,,\, \dot{H}_{\rm D}(t)\,]\,\rangle}{\langle\, D^2(t)\,\rangle}. \tag{37}$$

Then saturation rate W_S takes a form

$$W_S(t) = \frac{A_s(t)}{\sqrt{m_{\rm S}(t)}}\frac{\langle\, D^2(t)\,\rangle}{\langle\, H_{\rm D}^2(t)\,\rangle}, \tag{38}$$

where dimensionless value $A_s(t)$ is defined by the relation

$$A_s(t) = \int_0^\infty d\tau f\left(t, \frac{\tau}{\sqrt{m_s(t)}}\right) \tag{39}$$

It is natural, that (under slow rotation) in order of value $m_s \sim M_2^{st} = \omega_l^2$, where M_2^{st} is a second moment for static sample. Therefore $W_S \sim \omega_r^2/\omega_l$ which is in agreement with the previous theoretical approach [8].

For polycrystalline sample the law (32) must be averaged over crystallites orientations to obtain an observable value $\langle\, \beta_{\rm S}(t)\,\rangle_{pc}$. Rather good results are obtained from the usual simple approximation:

$$\langle\, \beta_{\rm S}(t)\,\rangle_{pc} = \langle\, \beta_s(0)\exp\left\{-\int_0^t W_S(\tau)d\tau\right\}\rangle_{pc} \approx$$

$$\approx \beta_{\rm S}(0)\exp\langle\left\{-\int_0^t W_S(\tau)d\tau\right\}\rangle_{pc} = \beta_{\rm S}(0)e^{-\langle W_S\rangle_{pc}t}. \tag{40}$$

Averaged saturation rate $\langle\, W_S\,\rangle_{pc}$ does not depend on time t, because general rotation of the sample around the $\mathbf{n}_r$ is one of elements, which define an orientation of the crystallite.

Similarly we make the following approximation

$$\langle\, W_S\,\rangle_{pc} = \left\langle \frac{A_s(t)}{\sqrt{m_{\rm S}(t)}}\cdot\frac{\langle\, D^2(t)\,\rangle}{\langle\, H_{\rm D}^2(t)\,\rangle}\right\rangle_{pc} \approx \frac{\langle\, A_s\,\rangle_{pc}}{\sqrt{\langle\, m_{\rm S}\,\rangle_{pc}}}\cdot\frac{\langle\,\langle\, D^2\,\rangle\,\rangle_{pc}}{\langle\,\langle\, H_{\rm D}^2\,\rangle\,\rangle_{pc}}. \tag{41}$$

Accuracy of approximations (40),(41) will be discussed below in Appendix B, as well as calculations giving

$$\frac{\langle\,\langle\, D^2\,\rangle\,\rangle_{pc}}{\langle\,\langle\, H_{\rm D}^2\,\rangle\,\rangle_{pc}} = 3(1+\epsilon_d)\omega_r^2\sin^2\vartheta_H, \quad \langle\, m_{\rm S}\,\rangle_{pc} = \frac{2}{3}\cdot\frac{1-\epsilon_m}{1+\epsilon_d}\langle\, M_2^{st}\,\rangle_{pc}. \tag{42}$$

Small numbers ϵ_m and ϵ_d are defened in (90) and (92). With this results

$$\langle W_S \rangle_{pc} = 3\sqrt{\frac{3}{2}}\kappa_w \langle A_s \rangle_{pc} \cdot \frac{\omega_r^2}{\sqrt{\langle M_2^{st} \rangle_{pc}}} \cdot \sin^2 \vartheta_H \ , \tag{43}$$

where $\kappa_w = (1+\epsilon_d)^{\frac{3}{2}}/(1-\epsilon_m)^{\frac{1}{2}}$, and for FCC lattice $\kappa_w = 1.025$.

Some models and problems related with calculation of correlation function $f(t,\tau)$ and $A_s(t)$, will be discussed in sections 4 and C.

3 Experimental results

Experiments have been performed on a DMX-300 spectrometer with a commercial Bruker MAS probe (4mm). Adamantane was purchased from ALDRICH and used without any further purification. To check the quality and purity of the sample the free induction decay was measured for a powder in static conditions, and the second moment was in agreement with theoretical expectation, given in Appendix B. Polycrystalline sample has been used in the studies because the variation of the saturation rate with spinning speed and orientation of the rotor has been investigated only. Thus the measured saturation rates could be considered only as effective ones for the powder.

Experiments were performed for three orientations of the rotor axis with the values of the angle ϑ_H between the magnetic field $\mathbf{H}_0$ and rotor axis $\mathbf{n}_r$ set to $\vartheta_H = \vartheta_{MAS} = 54.7(1)^o$, $\vartheta_1 = \vartheta_{MAS} + 2.7(3)^o$, and $\vartheta_2 = \vartheta_{MAS} + 7.4(8)^o$.

Dipolar order was produced by Jeener-Broeckaert sequence i.e. by $\left(\frac{\pi}{2}\right)_x$ pulse (whose phase defines the x direction in rotating frame) followed by a $\left(\frac{\pi}{4}\right)_y$ pulse [11].

Measurement of dipolar order at time t after the Jeener-Broeckaert pulses was achieved by applying a "reading" $\left(\frac{\pi}{4}\right)_x$ pulse and measuring the amplitude of the signal in the $x-$channel of the receiver.

The spin temperature hypothesis is experimentally confirmed by the observation of a dipolar spectrum and signal for slow spinning speed (figure 1). No differences are observed for various spinning axes angle in agreement with the fact that the rotation is only a perturbation of the static case. As shown in figure 2, the spin temperature decay is, after a thermalization delay of $\sim 200\mu s$, correctly described by Eq.32.

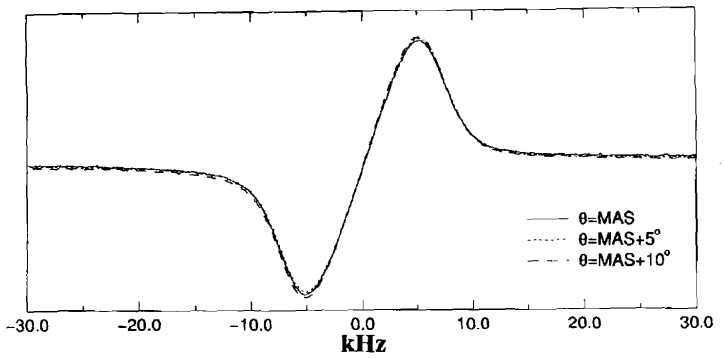

Figure 1: Comparison of dipolar spectra of a rotating adamantane powder sample at $\omega_r/2\pi = 200$ Hz for different orientation of the rotation axis ϑ and acquired with identical experimental conditions.

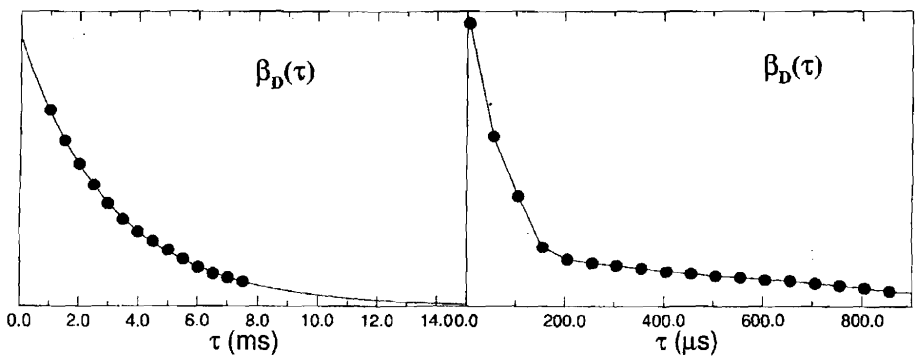

Figure 2: Variation of the dipolar spin temperature in a rotating adamantane powder sample $\omega_r/2\pi = 200$ Hz at the magic angle. Left figure shows the fit used for evaluating the saturation rate (here $T_s = 3$ ms). Right figure shows the short time behavior of the spin temperature. Thermalization of the system is obtained for $T_{\text{THERM.}} \approx 200\mu s$.

Figure 3 displays the variation of $\beta_D(\tau)$ for different spinning speeds at the magic angle, similar results being obtained for other angle. The variation of the averaged saturation rate with respect to the spinning speed plotted for different spinning axis orientation, is in agreement with Eq.43. For spinning speeds in the range $1\ kHz < \omega_r/2\pi < 3\ kHz$ no more dipolar order has been observed, although the zeeman spectrum at $\omega_r/2\pi = 1\ kHz$ is practically identical to the static spectrum.

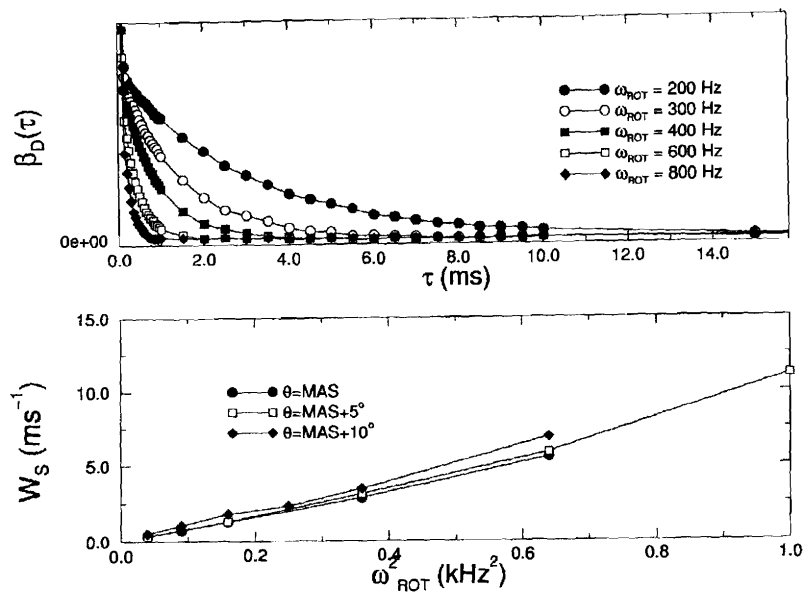

Figure 3: Top : Variation of the dipolar spin temperature $\beta_D(\tau)$ in a rotating adamantane powder sample at the magic angle. Bottom : variation of the saturation rate W_S with respect to ω_r^2.

4 Discussion of the results

The least mean square treatment of experimental dependence of $\langle W_S \rangle_{pc}$ on ω_r and ϑ_H by the law (43) in the form

$$\langle W_S \rangle_{pc} = q \cdot \left(\frac{\omega_r}{2\pi}\right)^2 \cdot \sin^2 \vartheta_H \tag{44}$$

produces the values $q_{exp} = 0.01271(18)s$, $\chi^2/n = 13/13$, assuming 5% error bars for W_S in fig.3. One exponential approximation produce rather good fitting for time dependence $\beta_D(t)$, nevertheless only time interval $250\mu s < t < 2000\mu s$ was used for checking the law (44) in order to overcome the influence of multiexponential decay, natural for polycrystalline sample. Measurements, carried out in the work [7] on polycrystalline adamantane for one angle $\vartheta_H = \frac{\pi}{2}$ give $q = 0.0123s$, that is in reasonable agreement with our result, and produce additional strong support for dependence (44) of $\langle W_S \rangle_{pc}$ on ϑ_H.

If correlation function $f(t,\tau)$ is chosen as Gaussian $f(t,\tau) = \exp(-\frac{1}{2}m_s(t)\tau^2)$, then relation (39) produces $\langle A_s \rangle_{pc} = A_G = \sqrt{\frac{\pi}{2}}$, and taking into account the relation (42) and theoretical value $\langle M_2^{st} \rangle_{pc} = (2\pi)^2 \cdot 16.86$ kHz^2 we obtain, according to Eq.43, that corresponding q is $q_G = 0.007222s$. The deviation of the relation $q_{exp}/q_G = 1.76(4)$ from 1 seems as large enough to require some better approximation. This problem is considered in Appendix C, where more satisfactory value $q_{theor}/q_G \approx 1.66$ is obtained, basing on simple general ideas of high temperature spin dynamics.

5 Conclusion

A new theoretical approach has been proposed for the description of quasiadiabatical relaxation phenomena in pp.2.1-2.3. The method is quite rigorous and general. In the limit of very slow motion, studied in p.2.4, the method reproduces results of the theory, constructed by Jeener at al. on a quite different mathematical formalism [8]. Our theory is based on very simple and reliable physical basis; it is a theory derived from first principles and it leads to physical results by the simplest and straightforward way. As usual, calculation of kinetic coefficients in our theory, outlined in pp.2.4,4 and in Appendixes B,C, requires estimations of some correlation functions;

we found a way to solve the problem by taking into account important general properties of the process. We hope that developed methods can be applied to many other problems.

In our experimental study, performed on a rotating powder sample, the angular dependence of saturation rate $\langle W_S \rangle_{pc}$ of dipole subsystem on orientation of the rotor axis was investigated for the first time, and very simple $\sin^2 \vartheta_H$ law (44) was established. Rather strict checking of theoretical results was carried out and reasonable agreement was found.

A Some properties of the time-dependent projection operators.

The general properties of the time-dependent projections operators are summarized in this appendix:

$$\hat{\pi}(t) + \overline{\hat{\pi}}(t) = \hat{\mathrm{Id}} \iff \dot{\hat{\pi}}(t) + \dot{\overline{\hat{\pi}}}(t) = 0 \tag{45}$$

$$\hat{\pi}(t)\overline{\hat{\pi}}(t)0 = 0 \iff \dot{\hat{\pi}}(t)\overline{\hat{\pi}}(t) + \hat{\pi}(t)\dot{\overline{\hat{\pi}}}(t) = 0 \tag{46}$$

$$\overline{\hat{\pi}}(t)\hat{\pi}(t) = 0 \iff \dot{\overline{\hat{\pi}}}(t)\hat{\pi}(t) + \overline{\hat{\pi}}(t)\dot{\hat{\pi}}(t) = 0 \tag{47}$$

From the previous relations, we obtain the two-terms products

$$\dot{\overline{\hat{\pi}}}(t)\overline{\hat{\pi}}(t) = \hat{\pi}(t)\dot{\overline{\hat{\pi}}}(t), \tag{48}$$

$$\dot{\overline{\hat{\pi}}}(t)\overline{\hat{\pi}}(t) = -\hat{\pi}(t)\dot{\hat{\pi}}(t), \tag{49}$$

$$\dot{\hat{\pi}}(t)\overline{\hat{\pi}}(t) = \hat{\pi}(t)\dot{\hat{\pi}}(t), \tag{50}$$

$$\dot{\hat{\pi}}(t)\hat{\pi}(t) = \overline{\hat{\pi}}(t)\dot{\hat{\pi}}(t), \tag{51}$$

$$\dot{\hat{\pi}}(t)\hat{\pi}(t) = -\overline{\hat{\pi}}(t)\dot{\overline{\hat{\pi}}}(t), \tag{52}$$

$$\dot{\overline{\hat{\pi}}}(t)\hat{\pi}(t) = -\overline{\hat{\pi}}(t)\dot{\overline{\hat{\pi}}}(t), \tag{53}$$

and the three-terms products

$$\overline{\hat{\pi}}(t)\dot{\overline{\hat{\pi}}}(t)\overline{\hat{\pi}}(t) = 0, \tag{54}$$

$$\overline{\hat{\pi}}(t)\dot{\hat{\pi}}(t)\overline{\hat{\pi}}(t) = 0, \tag{55}$$

$$\hat{\pi}(t)\dot{\hat{\pi}}(t)\hat{\pi}(t) = 0, \tag{56}$$

$$\hat{\pi}(t)\dot{\overline{\hat{\pi}}}(t)\hat{\pi}(t) = 0. \tag{57}$$

B Calculation of the moments.

Usual dipole-dipole Hamiltonian for homonuclear spin system of the crystal in strong static magnetic field $\mathbf{H}_0 = \mathbf{n_f} H_0$ contains secular part only and is of the form [2]

$$H_{\rm D} = \frac{1}{2}\sum_{i\neq j} b_{ij} T_{ij}, \quad T_{ij} = 3(\mathbf{n_f}\mathbf{I}_i)(\mathbf{n_f}\mathbf{I}_j) - \mathbf{I}_i\mathbf{I}_j, \tag{58}$$

$$b_{ij} = b_0 P_2(\mathbf{n}_{ij}\mathbf{n_f}) r_{ij}^{-3}, \quad \mathbf{n}_{ij} = \mathbf{r}_{ij}/r_{ij}, \quad \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j.$$

Here $b_0 = -\gamma^2\hbar, \gamma$ is gyromagnetic ratio, $\mathbf{I}_i$ is a spin operator for i-th nucleus, placed at $\mathbf{r}_i$, and $P_2(\xi) = (3\xi^2 - 1)/2$. Indices i and j in (58) run the values 1, 2, $\cdots$, N, where N is total number of (proton) spins in the sample.

Every adamantane molecule contains $z_0 = 16$ protons and at room temperature fast rotation around its geometrical center takes place. This rotation averages to zero intramolecular dipole interactions. Molecules are arranged in FCC crystal. Therefore Hamiltonian (58) can be written as

$$H_{\rm D} = \frac{1}{2}\sum_{i\neq j}^{0} b_{ij} T_{ij}^0 \ , \tag{59}$$

$$T_{ij}^0 = \bar{\delta}_{ij}[3(\mathbf{n_f}\mathbf{I}_i^0)(\mathbf{n_f}\mathbf{I}_j^0) - \mathbf{I}_i^0\mathbf{I}_j^0] \ , \quad \mathbf{I}_j^0 = \sum_{a=1}^{z_0} \mathbf{I}_{ja}, \quad \bar{\delta}_{ij} = 1 - \delta_{ij} \ .$$

Here and below a symbol Σ^0 represents the sum on $N_0 = N/z_0$ lattice sites in simple FCC lattice, Σ_a is a sum over spins inside one molecule, and $b_{jj} = 0$. $\mathbf{I}_j^0$ represent total nuclear spin of j-th adamantane molecule, these operators have the same commutation relations as usual one-particle spin operators, but $(\mathbf{I}_j^0)^2$ is an operator as well, in difference of one-spin case, where $(\mathbf{I}_{ja})^2 = I(I+1)$ is a constant.

Let us to suppose that a sample is rotated around an axis $\mathbf{n}_r$ with an angular velocity ω_r. We can choose a coordinate frame with z-axis directed along $\mathbf{n}_r$ and y−axis − along $[\mathbf{n}_r \times \mathbf{n_f}]$. Only $\mathbf{n}_{ij}$ depend on time in Eq.58. Therefore, using well known relation

$$P_2(\mathbf{n}_{ij}\mathbf{n_f}) = \frac{4\pi}{5}\sum_{m=-2}^{2} Y_m^2(\mathbf{n}_{ij}) Y_m^{2*}(\mathbf{n_f}), \tag{60}$$

where Y_m^2 is a spherical function, we have

$$b_{ij}(t) = \sum_{m=-2}^{2} e^{im\omega_r t} b_{ij}^m \ , \tag{61}$$

$$b_{ij}^m = \beta_0 Y_m^{2*}(\mathbf{n_f}) Y_m^2(\mathbf{n}_{ij}^0) r_{ij}^{-3}, \quad b_{jj}^m = 0, \quad \beta_0 = \frac{4\pi}{5} b_0 \ ,$$

and

$$H_{\mathrm{D}} = H_{\mathrm{D}}(t) = \sum_{m=-2}^{2} H_m e^{im\omega_r t}, \quad H_m = \frac{1}{2} \sum_{i \neq j} b_{ij}^m T_{ij}^0 \ . \tag{62}$$

Here $\mathbf{n}_{ij}^0 = \mathbf{n}_{ij}(t=0)$, and $Y_m^{2*}(\mathbf{n_f}) = Y_m^2(\mathbf{n_f})$ by definition of $\mathbf{n_f}$.

One group of values, required to calculate $\langle W_S \rangle_{pc}$ is connected with

$$\langle T_{ij}^0 T_{kl}^0 \rangle = 6J^2 \bar{\delta}_{ij} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \quad J = \frac{1}{3} \langle (\mathbf{I}_i^0)^2 \rangle = \frac{1}{3} I(I+1) z_0 \ . \tag{63}$$

With these definitions

$$\langle H_{\mathrm{D}}^2(t) \rangle = 3J^2 N_0 \sum_j{}^0 b_{0j}^2(t) = 3J^2 N_0 \sum_{mn} e^{i(n-m)\omega_r t} \sum_j{}^0 b_{0j}^{m*} b_{0j}^n, \tag{64}$$

$$\langle H_{\mathrm{D}}(t) \dot{H}_{\mathrm{D}}(t) \rangle = \frac{1}{2} \frac{d}{dt} \langle H_{\mathrm{D}}^2(t) \rangle, \tag{65}$$

$$\langle \dot{H}_{\mathrm{D}}^2(t) \rangle = 3J^2 N_0 \sum_j{}^0 \dot{b}_{0j}^2(t) = 3J^2 N_0 \omega_r^2 \sum_{mn} mn e^{i(n-m)\omega_r t} \sum_j{}^0 b_{0j}^{m*} b_{0j}^n. \tag{66}$$

Other important group of values is connected with a commutator

$$K(t) = [H_{\mathrm{D}}(t), \dot{H}_{\mathrm{D}}(t)] = i\omega_r \sum_{mn} m X_{mn} e^{i(m-n)\omega_r t}, \tag{67}$$

$$X_{mn} = [H_m, H_n^+] = \frac{i}{2} \sum_{ijk}{}^0 (b_{ij}^m b_{jk}^{n*} - b_{kj}^m b_{ji}^{n*}) \Theta_{ijk}, \tag{68}$$

$$\Theta_{ijk} = -i\bar{\delta}_{ijk} [T_{ij}^0, T_{jk}^0] = \bar{\delta}_{ijk} [3(F_{ijk} - F_{kji}) - H_{ijk}], \tag{69}$$

$$F_{ijk} = (\mathbf{I}_i \mathbf{n_f})(\mathbf{n_f}[\mathbf{I}_j \times \mathbf{I}_k]), \quad H_{ijk} = \mathbf{I}_i [\mathbf{I}_j \times \mathbf{I}_k], \quad \bar{\delta}_{ijk} = \bar{\delta}_{ij} \bar{\delta}_{ik} \bar{\delta}_{jk} \ .$$

It should be noticed that two-spin terms are absent in (67) and (68), because

$$[H_{\mathrm{D}}, T_{ij}^0] = \sum_{kl}{}^0 b_{kl} [T_{kl}^0, T_{ij}^0] = \sum_{kl}{}^0 b_{kl} [T_{kl}^0, T_{ij}^0] (1 - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \ ,$$

and last expression contains three-spin terms only.

Direct calculations produce

$$\langle \Theta_{ijk}\Theta_{i_1j_1k_1} \rangle = 18J^3\bar{\delta}_{ijk}\delta_{jj_1}(\delta_{ii_1}\delta_{kk_1} - \delta_{ik_1}\delta_{ki_1}), \tag{70}$$

and

$$Z(t) = \langle K(t)K^+(t) \rangle = 9J^3\omega_r^2 \sum_{mn\mu\nu} m\mu e^{i(m-n-\mu+\nu)\omega_r t} Z_{mn\mu\nu} \ , \tag{71}$$

$$Z_{mn\mu\nu} = \sum_{ijk}^{0} \bar{\delta}_{ijk}\bar{Z}_{ijk}^{mn\mu\nu} = \sum_{ijk}^{0} \bar{Z}_{ijk}^{mn\mu\nu}, \quad \bar{Z}_{ijk}^{mn\mu\nu} = (b_{ij}^{n*}b_{jk}^{m} - b_{kj}^{n*}b_{ji}^{m})(b_{ij}^{\nu}b_{jk}^{\mu*} - b_{kj}^{\nu}b_{ji}^{\mu*}) \ .$$

In order to take into account random orientations in polycrystalline sample we introduce a basic frame for every crystallite with axis $\tilde{x}, \tilde{y}, \tilde{z}$ directed along crystal directions [100],[010], and [001] correspondingly. Then

$$b_{ij}^{m} = b_{ij}^{m}(\phi, \vartheta, \gamma) = \tag{72}$$

$$= \beta_0 Y_m^2(\mathbf{n_f}) \sum_{n=-2}^{2} a_{ij}^{n} \mathcal{D}_{nm}^2(\phi, \vartheta, \gamma) = \beta_0 Y_m^2(\mathbf{n_f}) \sum_{n} a_{ij}^{n} e^{i(n\phi + m\gamma)} d_{nm}^2(\vartheta) \ ,$$

where $\mathcal{D}_{nm}^2(\phi, \vartheta, \gamma)$ and $d_{nm}^2(\vartheta)$ are standard Wigner rotation matrixes [12],

$$a_{ij}^{m} = \tilde{Y}_m^2(\mathbf{n}_{ij})/r_{ij}^3, \quad \tilde{Y}_m^2(\mathbf{n}_{ij}) = Y_m^2(\tilde{\vartheta}_{ij}, \tilde{\phi}_{ij}) \ , \tag{73}$$

and angles $\tilde{\vartheta}_{ij}, \tilde{\phi}_{ij}$ are defined relative to the basic frame of crystallite.

Dependence on γ in our problem is the same as on rotation angle $\omega_r t$, and therefore it will be omitted below.

It is useful to introduce a tensor

$$S_{mn} = \frac{1}{N_0} \sum_{ij}^{0} a_{ij}^{m*} a_{ij}^{n} = \sum_{j}^{0} a_{0j}^{m*} a_{0j}^{n} \ . \tag{74}$$

If the basic vectors of FFC lattice are chosen as

$$\mathbf{e}_1 = a_0(0,1,1), \quad \mathbf{e}_2 = a_0(1,0,1), \quad \mathbf{e}_3 = a_0(1,1,0), \tag{75}$$

then, according to cubic symmetry

$$S_{mn} = S_{nm} = S_{mn}^* = a_0^{-6}[\sigma_m \delta_{mn} + \mu \delta_{m,-n}(\delta_{m2} + \delta_{m,-2})] \ , \tag{76}$$

where

$$\sigma_0 = 0.1072, \quad \sigma_1 = \sigma_{-1} = 0.1682, \quad \sigma_2 = \sigma_{-2} = 0.1377, \quad \mu = -0.03051 \ . \tag{77}$$

Taking into account these definitions we obtain, that

$$\langle H_{\rm D}^2(t)\rangle = 3J^2\beta_0^2 N_0 a_0^{-6}\sum_{mn}\Lambda_{mn}, \tag{78}$$

$$\langle \dot{H}_{\rm D}^2(t)\rangle = 3J^2\beta_0^2 N_0 a_0^{-6}\sum_{mn} mn\Lambda_{mn}\ , \tag{79}$$

$$\Lambda_{mn} = Y_m^2(\mathbf{n_f})Y_n^2(\mathbf{n_f})[\cos((m-n)\omega_r t)f_{mn} + 2\cos((m-n)\omega_r t + 4\phi)g_{mn}]\ ,$$
$$Z(t) = 18N_0J^3\omega_r^2\beta_0^4 a_0^{-12}[h_1(t)h_2(t) - |h_3(t)|^2]\ , \tag{80}$$

where

$$f_{mn} = f_{mn}(\vartheta) = \sum_{\nu=-2}^{2}\sigma_\nu d_{\nu m}^2 d_{\nu n}^2, \quad g_{mn} = \mu d_{2,m}^2 d_{-2,m}^2\ , \tag{81}$$

$$h_1(t) = \sum_{m,n} mn\Phi_{mn}(t)\ ,\ \ h_2(t) = \sum_{m,n}\Phi_{mn}(t)\ ,\ \ h_3(t) = \frac{1}{2}\sum_{m,n}(m-n)\Phi_{mn}(t)\ , \tag{82}$$

$$\Phi_{mn}(t) = e^{i(m-n)\omega_r t}Y_m^2(\mathbf{n_f})Y_n^2(\mathbf{n_f})[f_{mn} + e^{4i\phi}g_{mn} + e^{-4i\phi}g_{nm}]\ . \tag{83}$$

Formulae (78),(79) can be averaged on crystallites orientations directly with a result

$$\langle\langle H_{\rm D}^2(t)\rangle\rangle_{pc} = \frac{3}{5}J^2N_0b_0^2a_0^{-6}\sigma_{00}\ ,\quad \sigma_{00} = \frac{4\pi}{5}\sum\sigma_m = \sum_j^0\left(\frac{a_0}{r_j}\right)^6 = 1.807\ , \tag{84}$$

$$\langle\langle \dot{H}_{\rm D}^2(t)\rangle\rangle_{pc} = 3\omega_r^2\sin^2\vartheta_H\langle\langle H_{\rm D}^2(t)\rangle\rangle_{pc},\quad \langle\langle H_{\rm D}(t)\dot{H}_{\rm D}(t)\rangle\rangle_{pc} = 0\ . \tag{85}$$

Well known relation [12]

$$\langle |d_{mn}^2(\vartheta)|^2\rangle_{pc} = \int_0^\pi d\vartheta\sin\vartheta|d_{mn}^2(\vartheta)|^2 = \frac{1}{5} \tag{86}$$

was used here.

It should be noticed, that connection between $\langle\langle \dot{H}_{\rm D}^2(t)\rangle\rangle_{pc}$ and $\langle\langle H_{\rm D}^2(t)\rangle\rangle_{pc}$ can be obtained as well from the relation

$$\langle \dot{b}_{ij}\dot{b}_{kl}\rangle_{pc} = 3\omega_r^2\sin^2\vartheta_H\langle b_{ij}b_{kl}\rangle_{pc}, \tag{87}$$

that follows immediately from (60),(72), and (86).

Averaging the Eq.80 we obtain

$$\langle Z\rangle_{pc} = 18N_0J^3\omega_r^2\beta_0^4\xi a_0^{-12}\ ,\quad \xi = 9.636\cdot 10^{-3}\sin^2\vartheta_H\ , \tag{88}$$

$$\xi = \sum_{mn\mu\nu} [mn - \frac{1}{4}(m-n)^2]\Delta(m-n-\mu+\nu) Y^{(4)}_{mn\mu\nu}(\mathbf{n_f})[\langle f_{mn} f_{\mu\nu} + 2 g_{mn} g_{\mu\nu} \rangle_{pc} \cdot$$

$$Y^{(4)}_{mn\mu\nu}(\mathbf{n_f}) = Y^2_m(\mathbf{n_f}) Y^2_n(\mathbf{n_f}) Y^2_\mu(\mathbf{n_f}) Y^2_\nu(\mathbf{n_f})$$

Here $\Delta(m) = \delta_{m0}$ is Kronecker's symbol, and numerical constant as well as dependence on angle ϑ_H were obtained by computer calculations.

If we apply to calculation of $\langle Z \rangle_{pc}$ the same decoupling method as in Eq.41, then

$$\langle Z \rangle_{pc} \approx 18 N_0 J^3 \omega_r^2 \beta_0^4 a_0^{-12} [\langle h_1 \rangle_{pc} \langle h_2 \rangle_{pc} - |\langle h_3 \rangle_{pc}|^2] = 18 N_0 J^3 \omega_r^2 \beta_0^4 \xi_0 a_0^{-12} , \tag{89}$$

$$\xi_0 = \frac{75}{(4\pi)^4} \sigma_{00}^2 \sin^2 \vartheta_H = 9.817 \cdot 10^{-3} \sin^2 \vartheta_H ,$$

It is evident from (82), that $\langle h_3 \rangle_{pc} = 0$. The value

$$\epsilon_m = (\xi - \xi_0)/\xi_0 = 0.0185 \tag{90}$$

gives one of estimations for decoupling in our problems.

By the same way

$$\langle \langle H_D \dot{H}_D \rangle^2 \rangle_{pc} = \frac{9}{4} (J^2 \beta_0^2 n \omega_r)^2 \xi_1 \tag{91}$$

$$\xi_1 = \sum_{mn\mu\nu} \Delta(m-n-\mu+\nu)(m-n)^2 Y^{(4)}_{mn\mu\nu}(\mathbf{n_f})[\langle f_{mn} f_{\mu\nu} + 2 g_{mn} g_{\mu\nu} \rangle_{pc} ,$$

and, with computer calculations according to (91), we come to

$$\epsilon_d = \frac{\langle \langle H_D \dot{H}_D \rangle^2 \rangle_{pc}}{\langle \langle H_D^2 \rangle \rangle_{pc} \langle \langle \dot{H}_D^2 \rangle \rangle_{pc}} = 0.0103 . \tag{92}$$

It should be noticed, that ϵ_m and ϵ_d do not depend on ϑ_H.

Combining relations (36) and (92) we get

$$\langle \langle D^2(t) \rangle \rangle_{pc} = (1+\epsilon_d) \langle \langle \dot{H}_D^2(t) \rangle \rangle_{pc} = 3(1+\epsilon_d) \omega_r^2 \sin^2 \vartheta_H \langle \langle H_D^2(t) \rangle \rangle_{pc} \tag{93}$$

Second moment for absorption signal in polycrystalline adamantane can be calculated by standard way with a result

$$\langle M_2^{st} \rangle_{pc} = \langle \langle [I_x, H_D][H_D, I_x] \rangle \rangle_{pc} / \langle I_x^2 \rangle = 9J \sum_j \langle (b_{0j})^2 \rangle_{pc} = \tag{94}$$

$$= \frac{9J}{5} b_0^2 a_0^{-6} \sigma_{00} = 4\pi^2 \cdot 16.86\ kHz^2$$

The values $2a_0 = 9.45 \cdot 10^{-8} cm$ [13], $\gamma/2\pi = 4.2576\ kHz/G$, and $\hbar = 1.0546 \cdot 10^{-27}$ CGS were used here.

One particle second moments m_x, m_y and m_z are introduced by the relations

$$m_x = m_y = m_{xy} = \tag{95}$$

$$= \langle [I_k^x, H_D][H_D, I_k^x] \rangle / \langle (I_k^x)^2 \rangle = \langle [I_k^+, H_D][H_D, I_k^-] \rangle / \langle I_k^+ I_k^- \rangle = \frac{5}{9} M_2^{st}$$

$$m_z = \langle [I_k^z, H_D][H_D, I_k^z] \rangle / \langle (I_k^z)^2 \rangle = \frac{2}{9} M_2^{st} \tag{96}$$

The second moment $\langle m_s \rangle_{pc}$, according to relations (39), (88-90) and (96), can be written as

$$\langle m_s \rangle_{pc} = \langle Z \rangle_{pc} / \langle \langle D^2 \rangle \rangle_{pc} = \frac{2}{3} \cdot \frac{(1-\epsilon_m)}{(1+\epsilon_d)} \langle M_2^{st} \rangle_{pc} \tag{97}$$

It should be noticed, that small values for parameters ϵ_d and ϵ_m are not very surprising, if we take into account, that relation

$$\langle (2\pi M_2^{st})^{-1/2} \exp(-\omega^2/(2M_2^{st})) \rangle_{pc} \approx (2\pi M_{2f})^{-1/2} \exp(-\omega^2/(2M_{2f}))$$

is valid for $\omega^2/M_{2f} < 16$ with meansquare deviation $\delta_G = 6 \cdot 10^{-4}$, if fitting parameter $M_{2f} = 0.9925 \cdot \langle M_2^{st} \rangle_{pc}$. Similarly, for the same ω,

$$\ln \langle (2\pi M_2^{st})^{-1/2} \exp(-\omega^2/(2M_2^{st})) \rangle_{pc} \approx -\omega^2/(2M_{2f}) - \frac{1}{2} \ln(2\pi M_{2f})$$

with meansquare deviation $\delta_{lG} = 0.03$, if $M_{2f} = 0.9828 \cdot \langle M_2^{st} \rangle_{pc}$.

C Calculation of $\langle A_S \rangle_{pc}$. Duration of the function $f(t, \tau)$.

The simplest way to improve the theoretical value of $q = q_G$ indicated in Section 4 is to take into account, that longitudinal and orthogonal (relative to external field $\mathbf{H}_0$) components of spin operators have rather different evolution. For example, behavior of orthogonal components can be described well if we know only second moments for corresponding correlation functions, whereas estimations for longitudinal components requires more

refined argumentation, which have to take into account, that a correlation function $f_z(t,\tau)$, introduced below by the relation (99) has at least three important part of evolution. It starts as $1 - M_z\tau^2/2$, then its decay is $\propto \exp(-2B\tau)$, and final part is $\propto \tau^{-3/2}$ [14]. The values M_z and B will be estimated below.

For the sake of simplicity we can rewrite D from (36) as $D = \dot{H}_{\rm D}$. This relation is correct up to small correction proportional to ϵ_d, that follows from relations (92) and (93). Then, using notations of Appendix B (see Eqs.58,59),

$$D = D_z + D_{xy} \ , \tag{98}$$

$$D_z = \sum_{ij}{}^0\dot{b}_{ij} I_i^{0z} I_j^{0z}, \quad D_{xy} = -\frac{1}{4}\sum_{ij}{}^0\dot{b}_{ij}(I_i^{0+}I_j^{0-} + I_i^{0-}I_j^{0+}) \ ,$$

The correlator (35) can be rewritten as

$$f(t,\tau) = p_z f_z(t,\tau) + p_{xy} f_{xy}(t,\tau) \ , \tag{99}$$

$$f_\alpha(t,\tau) = \langle\, D_\alpha(t) e^{-iH_{\rm D}(t)\tau} D_\alpha(t) e^{iH_{\rm D}(t)\tau} \,\rangle / \langle\, D_\alpha^2(t) \,\rangle, \quad \alpha = z, xy \ ,$$

$$p_z = \langle\, D_z^2 \,\rangle / \langle\, D^2 \,\rangle = \frac{2}{3}, \quad p_{xy} = \langle\, D_{xy}^2 \,\rangle / \langle\, D^2 \,\rangle = \frac{1}{3} \ .$$

A second moment for $f_\alpha(t,\tau)$ is

$$M_\alpha = \langle\, [D_\alpha, H_{\rm D}][H_{\rm D}, D_\alpha] \,\rangle / \langle\, D_\alpha^2 \,\rangle \ . \tag{100}$$

D_α is two spin operator, therefore we can expect, that

$$M_\alpha \approx 2m_\alpha \ . \tag{101}$$

Then, using definitions (95) and (96) of one spin second moments m_α, we obtain, that total second moment for $f(t,\tau)$ is

$$m_s = 2(p_z m_z + p_{xy} m_x) = \frac{2}{3} M_2^{st}, \tag{102}$$

in full agreement with relation (42), derived in Appendix B by more rigorous and long way.

Primary orthogonal one spin autocorrelation functions

$$g_x(t,\tau) = g_y(t,\tau) = g_{xy}(t,\tau) = \tag{103}$$

$$= \langle\, I_j^{0x} e^{-iH_{\rm D}(t)\tau} I_j^{0x} e^{iH_{\rm D}(t)\tau} \,\rangle / \langle\, (I_j^{0x})^2 \,\rangle = \langle\, I_j^{0+} e^{-iH_{\rm D}(t)\tau} I_j^{0-} e^{iH_{\rm D}(t)\tau} \,\rangle / \langle\, I_j^{0+} I_j^{0-} \,\rangle$$

can be approximated as

$$g_{xy}(t,\tau) = \exp(-\tau^2/(2m_x(t))) \ . \tag{104}$$

This representation does not reproduce exponential wings for

$$g_x(\omega) = \int_{-\infty}^{\infty} \frac{d\tau}{2\pi} \exp(i\omega\tau) g_x(\tau),$$

which are natural at large ω according to modern knowledge [15, 16], but Eq.102 is appropriate in the range $\omega^2 < m_x$ [15, 17] that is important for our study.

We can expect, that, in full analogy with (101),

$$f_{xy}(t,\tau) = (g_{xy}(t,\tau))^2. \tag{105}$$

At small and intermediate τ

$$f_z(\tau) \approx f_z^0(\tau) = \exp(-2m_z \int_0^\tau d\tau_1 (\tau - \tau_1) K(\tau_1)), \quad K(\tau) = e^{-3m_z\tau^2}. \tag{106}$$

Here simplest approximation for $K(\tau)$ is applied and its second moment was estimated by the same method as M_α and m_s in (101),(102). The duration of this initial part of the evolution is given by the time

$$\tau_0 = \int_0^\infty d\tau f_z^0(\tau) = 1.804/(2m_z)^{1/2} \tag{107}$$

In evolution of $f_z(t,\tau)$ at $t > \tau_0$ the conservation low $\sum_{ja} I_{ja}^z(\tau) = const$ should be taken into account. We can rewrite $f_z(t,\tau)$ as

$$f_z(t,\tau) = \left(\sum_{ij} \dot{b}_{ij}^2\right)^{-1} \sum_{ijkl} \dot{b}_{ij}\dot{b}_{kl} G_{ik}^z(\tau) G_{jl}^z(\tau). \tag{108}$$

Here $G_{ij}^z(\tau) = \langle I_i^{0z}(\tau) I_j^{0z} \rangle / \langle (I_j^{0z})^2 \rangle$. Starting with time $\tau \geq T_2 = 1/\omega_l$ the evolution of $G_{ij}^z(\tau)$ is mastered by the equation

$$\dot{G}_{ij}^z = -\sum_l \left(W_{li} G_{ij}^z - W_{il} G_{lj}^z\right). \tag{109}$$

Therefore, $\sum_k G_{ik}^z(\tau) G_{kj}^z(\tau) = G_{ij}^z(2\tau)$, and as consequence of translational invariance,

$$f_z(t,\tau) = \left(\sum_{ij} \dot{b}_{ij}^2\right)^{-1} \sum_{ijkl} \dot{b}_{ij} G_{jk}^z(\tau) G_{kl}^z(\tau) \dot{b}_{il} = \left(\sum_{ij} \dot{b}_{ij}^2\right)^{-1} \sum_{ijk} \dot{b}_{ij}\dot{b}_{ik} G_{jk}^z(2\tau). \tag{110}$$

Averaging on polycrystalline orientations with application of relations (87),(72) and (73) we obtain, that

$$f_z(\tau) = \left(\sum_m \sum_{\mathbf{r}} |a_{\mathbf{r}}^m|^2\right)^{-1} \sum_m \sum_{\mathbf{xr}} a_{\mathbf{x}}^{m*} G_{\mathbf{xr}}^z(2\tau) a_{\mathbf{r}}^m. \tag{111}$$

Here enumeration by radius-vectors $\mathbf{r}$ and $\mathbf{x}$ of molecules is used instead of numbers i and j, symbol a_j^m is introduced in (73), and symbol $\langle \cdots \rangle_{pc}$ is omitted. Comparing the Eqs. 110 and 106 we see, that if $\tau > T_2$ then $\ln f_z^0(\tau) \approx -2B\tau$, where $B = \Sigma_{\mathbf{x}} W_{\mathbf{xr}} = \sqrt{\frac{\pi}{3} m_z}$.

At larger τ propagator $G_{\mathbf{xr}}^z(2\tau)$ becomes a smooth function of $\mathbf{x} - \mathbf{r}$, and corresponding lattice sums in (111) can be substituted by integrals with a result

$$f_z(\tau) = \phi_d G_{00}(2\tau), \quad \phi_d = \frac{a^6}{\sigma_{00}} \cdot \left(\frac{4\pi}{3\Omega}\right)^2 = 2.428, \tag{112}$$

where $\Omega = 2a^3$ is a prime cell volume. It should be noticed, that $G_{00}(\tau \to \infty) \propto t^{-3/2}$.

It is known [18] that $\tau_{Dsd} = \int_0^\infty d\tau G_{00}(2\tau) = 1.265/(2B)$ for simple cubic lattice. The same method of calculation produce $\tau_D = 1.21/(2B)$ for FCC lattice of adamantane. Therefore the time

$$\tau_1 = \int_0^\infty d\tau (G_{00}(2\tau) - \exp(-2B\tau)) \tag{113}$$

represents effective duration of diffusion long time tail of $G_{00}(2\tau) \sim \tau^{-3/2}$. According to (112) the tail is multiplied on ϕ_d in the case of $f_z(\tau)$, therefore its effective duration must be estimated as $\phi_d \tau_1$. Connecting all these results together, we come to

$$A_z = \sqrt{m_s}(\tau_0 + \phi_d \tau_1) = 2.11 \cdot A_G. \tag{114}$$

Therefore, as a whole,

$$\frac{q}{q_G} = \frac{A_s}{A_G} = [p_z A_z + 2p_x (m_s/M_x)^{1/2} A_G]/A_G = 1.66\ . \tag{115}$$

Of course, rather precise agreement of this value with experimental $q_{exp}/q_G = 1.76(4)$ is nothing more than coincidence, but our discussion indicates direct way and necessary methods for more quantitative analysis.

It should be noticed, that good agreement between calculated and measured values of $\langle W_S \rangle_{pc}$ was obtained in Ref.[7] as well. But calculation of

this article was based on very special hypothesis, which in our notation is of the form

$$f(\tau) = 1/(1 + \frac{1}{2} m_s \tau^2). \tag{116}$$

This phenomenological relation, suggested for other, but related correlation functions in Ref.[19], was thought to be a very good approximation at that time, but is has no justification within the more microscopical treatment, outlined above. One of its weakness consists in contradiction to relation (112), which is rather general and it is based on existence of spin diffusion and dipole long range interactions only. On the other side, the hypothesis (116) was introduced in Ref.[19] to explain nearly exponential dependence on ω of the correlation functions in frequency representation. Similar nearly exponential dependence can be obtained within our approach as well. More extended discussion of related problems can be found in [15].

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