Long-time behaviour of spin coherences in solids

LETTER TO THE EDITOR

Long-time behaviour of spin coherences in solids

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Abstract. The long-time behaviour ($t \geqslant 1$ ms) of dipolar coupled nuclear spin systems, highlighted by the high resolution nuclear magnetic resonance (NMR) spectra of abundant nuclei in rigid solids, is explained satisfactorily as a manifestation in NMR of the famous 'long-time tail effect'. The time dependence of the transverse magnetization at the long-time limit, which is fundamentally different from the initial exponential decay, is closely related to the dimension of the spin network embedded in real space, opening a new approach to measuring the fractal dimension of coupled spins in solids.

Recently, we have observed an extraordinary phenomenon in the nuclear magnetic resonance (NMR) spectra of abundant high gyromagnetic ratio nuclear spins (hydrogen or fluorine nuclei) in rigid solids [1]. In summary, after the nuclear magnetization, which was originally at the z-direction, is irradiated by a radio-frequency (RF) pulse, so that the magnetization vector is flipped to the x–y plane, the transverse magnetization of the nuclear spins decays much slower at long times (typically several hundred or thousand microseconds) than at the initial stage (tens of microseconds). This observation not only shows, in a very direct manner, that the long-held opinion that transverse relaxation is exponential is incorrect, but also offers a simple, though less sensitive, technique to obtain high resolution NMR spectra of protons or fluorine nuclei in rigid solids, which would otherwise be very demanding technically. This technique is called SPEDA (single pulse excitation with delayed acquisition) NMR spectroscopy, with which the resolution can easily be increased by three orders of magnitude. Applications of this method have been described by several authors [1–10].

The most intriguing aspect of this phenomenon is its physical explanation. Numerically, extensive lineshape simulations [2] were made to model this phenomenon using Mori's memory function approach [11–14]. With this formalism, the lineshape can be computed by solving the following integro-differential equation:

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = \int_0^t M(t')K(t - t')\mathrm{d}t' \tag{1}$$

where $M(t)$ is the transverse magnetization of the nuclear ensemble and the kernel, $K(t - t')$, is the memory function, which is a complicated functional of the spin interaction Hamiltonians [12–14]. The memory function cannot be exactly calculated for a realistic spin system and approximations must be made to accomplish a calculation. Satisfactory results were obtained for static and spinning samples, as well as for compounds with large chemical shift anisotropies [2]. However, one central question, hitherto unanswered, concerns the fundamental physical origin of this memory effect. Consequently, the choice of memory function form and the

approximations to use in its evaluation lack sufficient physical reasoning. This question is important not only for the understanding of this phenomenon itself but also for the further exploration of its potential applications. Therefore, in this letter, a reasonable physical picture is presented and a more interesting example of the application of this method is proposed.

The pulse Fourier transform NMR signal of a nuclear spin system is proportional to the time correlation function $C_{Ix}(0, t)$ of its transverse components $I_\alpha(\alpha = x, y) \equiv \sum_{i=1}^{N} I_{\alpha i}$ where N is the total number of spins [15].

$$M(t) \propto C_{Ix}(0, t) \equiv \text{Tr}\,[I_x(0)I_x(t)]$$

$$= \text{Tr}\left[I_x e^{-i\int_0^t H(t')dt'} I_x e^{i\int_0^t H(t')dt'}\right]$$

$$= \text{Tr}\left[\sum_{i<j} I_{xi} e^{-i\int_0^t H(t')dt'} I_{xj} e^{i\int_0^t H(t')dt'}\right] \tag{2}$$

$$\equiv \sum_{i<j} M_{ij}$$

where M_{ij} is the correlation between spin i and spin j. The major part of the Hamiltonian is the homonuclear dipolar interaction given by

$$H_D = \sum_{i>j} \omega_{ij}^D (3I_{zi}I_{zj} - \mathbf{I}_i \cdot \mathbf{I}_j) \tag{3}$$

where ω_{ij}^D is the dipolar coupling constant between spin i and spin j.

Equation (1) is sufficient to describe the time evolution of the total magnetization but it is difficult to extract a physical picture from it. An equation governing the individual spin correlations, M_{ij}, is needed. Indeed, such an equation can be derived from the work described in [16, 17] as follows

$$\frac{dM_{ij}(t)}{dt} = \sum_l \int_0^t M_{il}(t')K_{lj}(t - t')dt'. \tag{4}$$

Since we are interested in the behaviour of the spin system at long times, when the long-range spin correlations become dominant in the dynamical spin evolution, we may expand the memory function and the corresponding correlations into their respective Fourier components and concentrate on the short-time limit:

$$M_k(t) = \sum_{i\neq j} M_{ij} e^{ik\cdot r_{ij}} \tag{5}$$

$$K_k = \sum_{i\neq j} K_{ij} e^{ik\cdot r_{ij}}. \tag{6}$$

With $k \to 0$, equation (4) can be reduced as

$$\frac{dM_k(t)}{dt} = -\sum_{\alpha,\beta} k_\alpha k_\beta D_{\alpha,\beta} M_k(t) \tag{7}$$

with

$$D_{\alpha,\beta} = -\frac{1}{2}\left[\frac{\partial^2}{\partial k_\alpha \partial k_\beta} \int_0^\infty dt' K_k(t - t')|_{k\to 0}\right]. \tag{8}$$

Equation (7) is obviously a diffusion equation with $D_{\alpha,\beta}$ as the diffusion coefficient.

Because of the homogeneous characteristics of the spin system under study and the fact that we use the rotating frame of reference so that the effect of the applied magnetic field

is removed, it is reasonable to use the spherical symmetry assumption to solve equation (7). Therefore, the solution can be found to be

$$M_k(t) = M_k(t_0)e^{-Dk^2(t-t_0)}. \tag{9}$$

Transforming back to the real space, the free induction decay (FID) signal can be written as

$$M(t) = M(t_0)(t - t_0)^{-d/2} \tag{10}$$

where d is the dimension of the real space in which the spin system is embedded and t_0 can be understood as a characteristic time after which the non-exponential decay becomes significant.

Equation (10) points to the similarity between this phenomenon and the well-known long-time tail effect first discovered in dilute gases [18], which shows the failure of the Boltzmann equation to describe the long-time behaviour of velocity correlations. It is interesting to establish the correspondence between the present phenomenon and the gas velocity correlation, a seemingly rather different phenomenon. According to mode–mode coupling theory [19], the long-time tail is interpreted as the coupling between the shear mode and the diffusion (translation) mode in gas molecules. Figuratively, it is the 'velocity diffusion' among gas molecules that causes the slow long-time decay. An analogous explanation can be given for our experimental NMR observations. In dipolar coupled spin systems, after the excitation pulse, the local magnetization dephases rapidly because, at the early stage, the short-range dipolar couplings dominate the spin evolution. Thus, a broad spectrum is observed, as verified by experiments. At long time scales (typically hundreds of microseconds to milliseconds for nuclear spins), long-range dipolar couplings start to take effect (corresponding, in wave vector space, to the region with $k \rightarrow 0$) which removes the inhomogeneity of magnetization at different (mesoscopic) ranges. This is a diffusion process as confirmed by the equations (7) and (8). In terms of real space, the local magnetization is given by $\langle I_x I_x(t) \rangle_i$ where i represents 'local' volume elements. As time increases, this magnetization is 'shared' by a larger space. Suppose the space dimension is d, then the diffusion process causes the local magnetization to be distributed in a space of $Dt^{d/2}$. This is exactly the same as the phenomenological explanation of long-time tail effect in gases [19]. Therefore, we conclude that the SPEDA NMR experimental results can be satisfactorily interpreted as a manifestation of the long-time tail effect among dipolar-coupled nuclear spins in solids.

While the physical foundation of the long-time tail effect has been firmly established [19] over the past decades, only a very limited number of experimental results [20–22] have been presented from studies of viscosity coefficients, abnormal diffusion effects etc. Our SPEDA NMR experiments give a very simple and reliable demonstration of the long-time tail effect in many-body systems.

We can evaluate the mesoscopic network size by two different approaches. One approach is to take $Dk^2(t - t_0) \rightarrow 5$ from equation (9) and then calculate the change of k (thus of r). For example, for proton systems, the typical diffusion coefficient is in the order of 10^{-16} m^2 s^{-1} which leads to a space size of 50 Å if we reasonably assume that the long-time tail is around 10 ms. Another approach is to evaluate the dipolar coupling. According to the above picture, at long-time regime, the coupling takes place among distant spins and, therefore, the largest distance between coupled spins can be deduced from the narrowest NMR linewidth. Usually it is in the order of 1 Hz (with the long-time tail being around 10 ms) which gives a distance of 50 Å, in agreement with the first evaluation. This agreement further supports our view that the long-time tail explanation of SPEDA NMR spectra is correct.

Furthermore, a series of experimental verifications of the above explanation has been carried out with different systems. Figure 1 shows the relationship between the ^{19}F NMR signal intensity and time delay for polycrystalline calcium fluoride. It is noted that the magnetization decays slower than exponentially. This is more clearly expressed by plotting the same data with
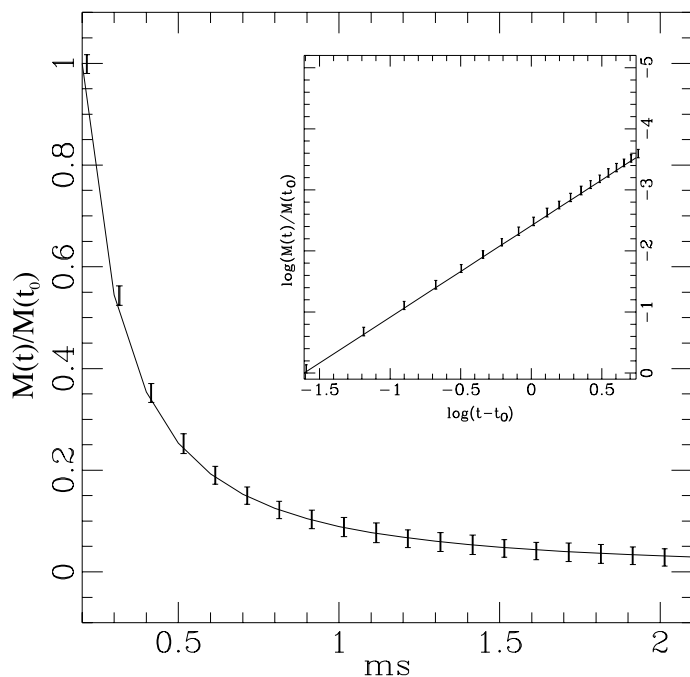
Figure 1. The normalized ^{19}F MAS NMR spectral intensities of polycrystalline calcium fluoride at long times. The intensity decays according to $(t - t_0)^{-1.5}$ are shown in the inset of this diagram. The error range for each experimental datum is indicated with a vertical line segment.

a different time graduation, as shown in the inset. The dimension of the ^{19}F spin network can be read from the diagram as $d = 3$. This means the spin network can reflect the space filling of the compound. This is understandable considering that the ^{19}F nucleus has an abundance of 100% and the crystal structure of calcium fluoride is cubic. Figure 2 is similar to figure 1 but for the case of proton NMR spectra. The sample was powdered polyethylene. Although the normal magic angle spinning (MAS) NMR spectrum is broad and structureless, two resolved peaks can be observed at long delay times in figure 2, presumably from the crystalline and amorphous sites in the polymer. It is interesting to note that the decay times for these two sites are slightly, but notably, different. As shown in the dimension evaluation given in the inset of figure 2, two values of the dimensions are obtained as $d = 1.8$ and 1.4 for the crystalline and amorphous parts, respectively. This means that in both the crystalline and amorphous parts, the spins are arrayed in a more chain-like way than in a three-dimensional network. Moreover, the amorphous part has a lower dimension, meaning it is less densely stacked. From these figures and from the above analysis, therefore, a correlation between the SPEDA NMR spectra and the fractal dimension of the spin network can be established. The size of the fractals, as estimated above, is at the nanometre scale. It is thus clear that the SPEDA NMR method, with the physical interpretation given in the present work, may have many important applications in structural and dynamic investigations of chemical and biological materials, particularly at the mesoscopic level. It may be regarded as an adjunct to the multi-quantum method of investigating spin clusters in solids [23–30]. The multi-quantum method is mainly based on the coherent dynamics whereas the SPEDA method exploits the incoherent characteristics during incoherent evolution processes.
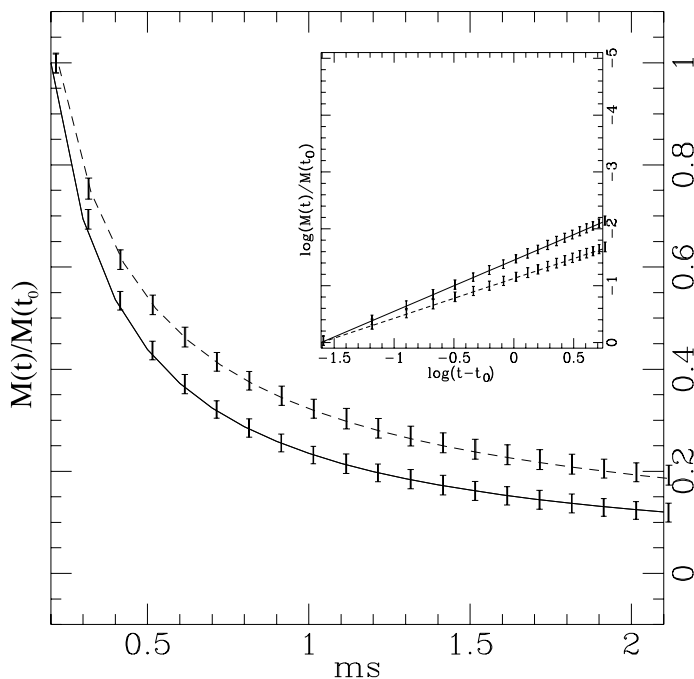
Figure 2. The normalized proton MAS NMR spectral intensities of powdered polyethylene at long times. The solid curves are for crystalline sites and the dashed curves for amorphous sites. The intensities decay according to $(t - t_0)^{-0.9}$ and $(t - t_0)^{-0.7}$ for crystalline and amorphous sites, respectively, as shown in the inset of this diagram.

Because of the unique relationship between the NMR signal intensity and the space dimension, as shown above both theoretically and experimentally, the long-time behaviour of spin systems can be used to study the structure at the mesoscopic scale, and the SPEDA technique may be significant for many applications in practice, such as the fractal characteristics of porous materials and polymers, including biologically important macromolecules such as DNA, nucleopeptides and proteins. A very interesting phenomenon is the folding process of proteins, and the different conformations at different stages of folding may exhibit different fractal dimensions. This may be verified by the SPEDA technique based on the above explanation. Above, we assumed the presence of solid state samples. However, the long-time tail effect can also exist in partially ordered spin systems (e.g., liquid crystals) and solutions. There have been some reports [3, 9] using liquid crystal samples which verify our observations, but for solutions there is no such report to date. One may contend that such a phenomenon cannot be found in solutions because the dipolar coupling is completely averaged out by rapid molecular motions. However, as reported recently [31], the long-range dipolar couplings cannot be averaged out and, therefore, we believe this SPEDA-type experiment may soon be shown: that is, the long delay before acquisition can increase resolution and the mechanism can be attributed to the long-time tail effect. It is also clear this phenomenon may be observed in spin systems other than nuclear spins, such as electron spin resonance (ESR) or electron-nuclear double resonance (ENDOR).

In summary, a satisfactory physical origin of the slow decay of transverse spin magnetization in solids at long times is given and the potential application of this phenomenon for the determination of mesoscopic structure is discussed. Finally, it should be noted that

nuclei other than protons and fluorine nuclei should also exhibit the phenomenon discussed in this work if the dipolar coupling among them is pronounced enough (e.g. in ^{31}P systems and isotopically enriched samples).

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