SPIN-ECHO EXPERIMENT WITH NMR SPECTRA ONLY PARTIALLY NARROWED BY AN INSUFFICIENTLY FAST MOTION

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The spin-echo experiment on a spin system with only partial motional narrowing and an exponential field autocorrelation function is considered. The pattern of the intensity decrease in the echo spectra depends on the ratio τ/τ_c of the time delay τ in the echo experiment to the correlation time τ_c of the narrowing motion. With the large ratios (fast motion), the decrease is the same as in the case of extreme narrowing; to obtain undistorted T_2 values, the ratio should be at least several units in the single-echo experiment and at least few decades in the multiple-echo experiment. With the small ratios (slow motion), the logarithmic decrease depends non-linearly on τ, and the T_2 value found by the linear least-squares adjustment is much longer than that obtained from the extreme narrowing approximation. At very small ratios, the multiple echo yields about $3\tau_c/(\omega_p\tau)^2$ for T_2 as compared with $1/(\omega_p^2\tau_c)$ obtained from the extreme narrowing approximation; ω_p^2 is the second moment of the Gaussian line being narrowed. The expression for T_2 in the multiple spin echo is similar to that previously found for T_{2e} in the solid multiple spin echo. The echo experiment changes the line shape, which at large τ/τ_c approaches the Lorentzian one. The case of a multiexponential field autocorrelation function is also briefly considered.
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A multiexponential relaxation of transverse magnetization with a peculiar behaviour of T_2 relaxation times obtained in the spin-echo experiment was observed with poly(2-ethylhexyl acrylate)-*block*-poly(acrylic acid) micelles dispersed in water, where the narrowing of spectral lines in magic angle spinning was found as well[1]. As a first step to analysis of such spectra, a method of calculation of the shapes of partially narrowed spectral lines was developed[2]. The next step, an analysis of the spin-echo experiment with partially narrowed NMR spectra, is considered in the present paper.

In the spin-echo experiment, an excitation $\pi/2$ pulse is followed by a π pulse after a time delay τ. The effect of the latter is as if all the spins change the sense of precession. As a consequence, the incoherence (the phase dis-

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tribution) caused by permanent frequency deviations of individual spins (due to, *e.g.*, the magnetic field inhomogeneity) is compensated after another time interval τ and a spin echo is created. On the other hand, the incoherence caused by random frequency deviations (due to, *e.g.*, thermal motion) continues its development within the other τ interval. This allows to find the transversal relaxation time T_2 without a contribution of the field inhomogeneity by following the exponential decrease in magnetization at time delay 2τ with increasing τ. There are reasons for preferring a sequence of n π pulses at time delays τ, 3τ, 5τ, ..., $(2n - 1)\tau$ after the excitation $\pi/2$ pulse, instead of increasing τ, and following the exponential decrease in magnetization at time delay $2n\tau$ with increasing n (multiple spin echo).

The situation is more complicated when the thermal motion is too slow to allow for the extreme narrowing approximation with an exponential decrease in magnetization. With no echo and assuming a Gaussian distribution of the fluctuating frequency, the free induction decay (FID) $\varphi(\tau)$ equals $\exp(-\overline{X^2}/2)$ (see ref.[3], Eq. (*30*)), where $\overline{X^2}$ is the central second moment at time delay τ of the phase distribution caused by the frequency fluctuation. Setting $-\overline{X^2}/2 = f(\tau)$ yields

$$\varphi(\tau) = \exp\,(f(\tau)) \qquad (1)$$

and using the subsequent expression[3] for $\overline{X^2}$

$$2f(\tau) = -\int_0^\tau\int_0^\tau \overline{(\omega(t') - \omega_0)(\omega(t'') - \omega_0)}\,\mathrm{d}t''\,\mathrm{d}t'. \qquad (2)$$

Defining reduced field autocorrelation function $g(\tau) = \overline{(\omega(t+\tau) - \omega_0)(\omega(t) - \omega_0)}\,/\,\omega_p^2$, where $\omega_p^2 = \overline{(\omega(t) - \omega_0)^2}$ is the central second moment of the fluctuating frequency, $f(\tau) = -\omega_p^2\int_0^\tau g(x)(\tau - x)\,\mathrm{d}x$. For the exponential $g(\tau) = \exp\,(-\tau/\tau_c)$,

$$f(\tau) = \omega_p^2\tau_c^2\,(1 - \tau/\tau_c - \exp\,(-\tau/\tau_c))\,, \qquad (3)$$

τ_c being the correlation time. For the single spin echo in the case of a Gaussian distributed fluctuating frequency with fluctuations caused by spin-flipping, it was found (ref.[4], p. 578) that FID $\varphi(t)$ equals $\exp\,(2f(\tau)$ +

$2f(\tau + t) - f(2\tau + t)$) with $f(\tau)$ given by Eq. (*3*). (The time t is counted from the echo moment in the absence of flipping at time delay 2τ, so that the time delay from the excitation $\pi/2$ pulse equals $2\tau + t$. Note that R in the reference quoted equals $1/\tau_c$.)

In dealing with the partially narrowed spectra (with residual dipolar interactions), it is more usual to use some sequences compensating for incomplete narrowing, like, *e.g.*, the WH or WHH sequence. Such experiments are called solid spin echo. These were considered by Gründer *et al.*[5,6] and by Ursu *et al.*[7] Motional consequences of the solid spin-echo experiments were discussed in ref.[8], pp. 73–76 and 98–103. Quite recently, the effect of the non-zero width of the $\pi/2$ pulses in the solid spin echo on the time position and the amplitude of the echo signal was considered[9]; other references concerning the solid echo can be found therein. Although, in studying spectra with residual dipolar interactions, the solid spin-echo experiments are undoubtedly more effective than ordinary spin echoes, the ordinary echoes may be useful as well, especially when the difference from complete narrowing is small. A detailed consideration of the ordinary spin-echo experiment in the case of partial narrowing does not seem to have been given yet.

The object of the present paper is to extend the above expression for single spin-echo FID in an only partially narrowed spectrum to multiple spin-echo FID and to discuss the intensity decrease and the shape changes in the echoed spectra for both cases.

MATHEMATICAL METHODS

To find out FID $\varphi(t)$ in the multiple spin-echo experiment with n π pulses, we have to return to Eq. (*2*), where both integrals run from zero to $2n\tau + t$ now. Since the effect of each π pulse is as if all spins change the sense of the precession, the integrand in Eq. (*2*) should bear the minus sign in the regions where the time delays t' and t'' are separated by an odd number of intervening π pulses, whereas it keeps its plus sign elsewhere. In the single echo ($n = 1$), the minus sign applies when $t' < \tau$, $t'' > \tau$ and when $t' > \tau$, $t'' < \tau$, with the plus sign applying elsewhere. It is easily seen that such a double integral can be expressed as the sum of three terms of form (*2*), where in the first term integrals run from zero to τ, in the next from τ to $2\tau + t$, and in the last from zero to $2\tau + t$, the first two terms bearing the factor of two and the last one being taken with the minus sign. In the second term, we are alternatively allowed to let the integrals run from zero to $\tau + t$, since the integrand in Eq. (*2*) depends only on the difference $t' - t''$. Writing $\varphi(t) =$

$\exp(f_1(t, \tau))$, one gets $f_1(t, \tau) = 2f(\tau) + 2f(\tau + t) - f(2\tau + t)$, as above. A similar decomposition holds for the multiple echo with n π pulses as well. There are $(n + 2)(n + 1)/2$ terms of form (*2*), each of which runs from zero or from a π pulse time delay (*i.e.*, from either of $(2k - 1)\tau$ values, $k = 1, 2, ..., n$) to another (longer) π pulse delay or to $2n\tau + t$. At this, the terms running from zero to a π pulse delay and those running from a π pulse delay to $2n\tau + t$ acquire a factor of two, the terms running from a π pulse delay to another (longer) one bear a factor of four, and the term running from zero to $2n\tau + t$ is factor-free. The sign of each term is minus when the integration interval spans an odd number of π pulse delays (not counting those at integral limits) and is plus elsewhere. Remembering that any term depends on the integration interval length only and realizing that the term with the length of $2k\tau$ appears $(n - k)$ times (it can start at either of $\tau, 3\tau, 5\tau, ..., (2n - 2k - 1)\tau$ delays), we obtain eventually for FID $\varphi(t)$ in the multiple spin echo with n π pulses

$$\varphi(t) = \exp(f_n(t, \tau)) \tag{4}$$

$$f_n(t, \tau) = (-1)^n f(2\tau + t) + \sum_{k=1}^{n} (-1)^{k-1} (2f((2k-1)\tau) + 2f((2k-1)\tau + t) + 4(n-k)f(2k\tau)) . \tag{5}$$

Explicit expressions for small n's are

$$f_1(t, \tau) = 2f(\tau) + 2f(\tau + t) - f(2\tau + t)$$

$$f_2(t, \tau) = 2f(\tau) + 4f(2\tau) - 2f(3\tau) + 2f(\tau + t) - 2f(3\tau + t) + f(4\tau + t)$$

$$f_3(t, \tau) = 2f(\tau) + 8f(2\tau) - 2f(3\tau) - 4f(4\tau) + 2f(5\tau) + 2f(\tau + t) - 2f(3\tau + t) + 2f(5\tau + t) - f(6\tau + t)$$

$$f_4(t, \tau) = 2f(\tau) + 12f(2\tau) - 2f(3\tau) - 8f(4\tau) + 2f(5\tau) + 4f(6\tau) - 2f(7\tau) + 2f(\tau + t) - 2f(3\tau + t) + 2f(5\tau + t) - 2f(7\tau + t) + f(8\tau + t) .$$

For the exponential $g(\tau) = \exp(-\tau/\tau_c)$,

$$f_n(t, \tau) = \omega_p^2 \tau_c^2 (u_n - v_n t/\tau_c + (1 - v_n)(1 - t/\tau_c - \exp(-t/\tau_c))), \qquad (6)$$

where

$$u_n = 2n + 1 - 2n\tau/\tau_c - (-1)^n \exp(-2n\tau/\tau_c) +$$

$$+ 4\sum_{k=1}^{n} (-1)^k [\exp(-(2k-1)\tau/\tau_c) + (n-k)\exp(-2k\tau/\tau_c)] =$$

$$= n[2(1 - \exp(-2\tau/\tau_c))/(1 + \exp(-2\tau/\tau_c)) - 2\tau/\tau_c] +$$

$$+ (1 - (-\exp(-2\tau/\tau_c))^n)(1 - \exp(-\tau/\tau_c))^4/(1 + \exp(-2\tau/\tau_c))^2$$

$$v_n = (1 - \exp(-\tau/\tau_c))^2 \sum_{k=0}^{n-1} (-\exp(-2\tau/\tau_c))^k =$$

$$= (1 - \exp(-\tau/\tau_c))^2 (1 - (-\exp(-2\tau/\tau_c))^n)/(1 + \exp(-2\tau/\tau_c)),$$

ω_p^2 is the second moment of the Gaussian line being narrowed. For small n's,

$$u_1 = 3 - 4\exp(-\tau/\tau_c) + \exp(-2\tau/\tau_c) - 2\tau/\tau_c$$

$$u_2 = 5 - 4\exp(-\tau/\tau_c) - 4\exp(-2\tau/\tau_c) + 4\exp(-3\tau/\tau_c) - \exp(-4\tau/\tau_c) - 4\tau/\tau_c$$

$$u_3 = 7 - 4\exp(-\tau/\tau_c) - 8\exp(-2\tau/\tau_c) + 4\exp(-3\tau/\tau_c) + 4\exp(-4\tau/\tau_c) -$$

$$- 4\exp(-5\tau/\tau_c) + \exp(-6\tau/\tau_c) - 6\tau/\tau_c$$

$$u_4 = 9 - 4\exp(-\tau/\tau_c) - 12\exp(-2\tau/\tau_c) + 4\exp(-3\tau/\tau_c) + 8\exp(-4\tau/\tau_c) -$$

$$- 4\exp(-5\tau/\tau_c) - 4\exp(-6\tau/\tau_c) + 4\exp(-7\tau/\tau_c) - \exp(-8\tau/\tau_c) - 8\tau/\tau_c$$

$$v_1 = 1 - 2\exp(-\tau/\tau_c) + \exp(-2\tau/\tau_c)$$

$$v_2 = 1 - 2\exp(-\tau/\tau_c) + 2\exp(-3\tau/\tau_c) - \exp(-4\tau/\tau_c)$$

$$v_3 = 1 - 2\exp(-\tau/\tau_c) + 2\exp(-3\tau/\tau_c) - 2\exp(-5\tau/\tau_c) + \exp(-6\tau/\tau_c)$$

$$v_4 = 1 - 2\exp(-\tau/\tau_c) + 2\exp(-3\tau/\tau_c) - 2\exp(-5\tau/\tau_c) + $$
$$+ 2\exp(-7\tau/\tau_c) - \exp(-8\tau/\tau_c)\ .$$

The echoed line shape with FID given by Eqs (*4*) and (*6*) is the convolution of the Anderson shape[2,3] originating from the second moment ω_p^2 reduced by the factor $(1 - v_n)$ with the Lorentz shape originating, in the extreme narrowing approximation, from the second moment ω_p^2 reduced by the factor v_n, with the integral intensity of the convolution reduced by the factor $\exp(u_n \omega_p^2 \tau_c^2)$ (u_n is always negative). The shape can be calculated using Eq. (*49*) or Eq. (*50*) of ref.[2] with $x = \omega_p^2 \tau_c^2$, $y = (\omega - \omega_0)\tau_c$, $v = v_n$ and multiplying the result by $\exp(u_n \omega_p^2 \tau_c^2)$.

Multiexponential Field Autocorrelation Function

The multiexponential reduced field autocorrelation function reads (ref.[2], Eq. (*45*))

$$g(\tau) = \sum_{i=1}^{r} \alpha_i \exp(-\tau/\tau_i)\,, \qquad \sum_{i=1}^{r} \alpha_i = 1\,.$$

Then, from Eq. (*46*) of ref.[2], we get for FID of the parent partially narrowed line

$$\varphi(\tau) = \exp\left(\sum_{i=1}^{r} \alpha_i f(\tau,\ \tau_i)\right),$$

where $f(\tau, \tau_c)$ is given by Eq. (*3*), with the τ_c dependence explicitly shown now. With Eqs (*4*) and (*6*) and considering the linearity of Eq. (*5*), we obtain for FID $\varphi(t)$ of the *n*-th echo in our case

$$\exp\left(\sum_{i=1}^{r}\alpha_i\omega_p^2\tau_i^2[u_n(\tau_i) - v_n(\tau_i)t/\tau_i + (1 - v_n(\tau_i))(1 - t/\tau_i - \exp(-t/\tau_i))]\right) \quad (7)$$

with $u_n(\tau_c)$ and $v_n(\tau_c)$ given by the expressions following Eq. (*6*), the τ_c dependence again being explicitly shown now. Whereas the parent line is the convolution of r partially narrowed lines with ω_p^2 reduced to $\alpha_i\omega_p^2$ and correlation times τ_i, the echoed line is given by convolution of lines produced by n-fold echo from the lines forming the parent line by the convolution. At this, all Lorentz components form a single Lorentz line of half-width of $2\omega_p^2\sum_{i=1}^{r}\alpha_i\tau_i v_n(\tau_i)$ and this is convoluted with a convolution of r Anderson lines. The integral intensity is reduced by a factor of $\exp(\omega_p^2\sum_{i=1}^{r}\alpha_i\tau_i^2 u_n(\tau_i))$.

Particularly, when all τ_i's but a single one allow for the extreme narrowing approximation, we obtain for n-th echo FID $\varphi(t)$

$$\exp(\alpha\omega_p^2\tau_c^2[u_n(\tau_c) - v_n(\tau_c)t/\tau_c + (1 - v_n(\tau_c))(1 - t/\tau_c - \exp(-t/\tau_c))]) \times$$
$$\times \exp(-(1 - \alpha)\omega_p^2\tau_f(2n\tau + t)) ,$$

similarly to Eq. (*47*) of ref.[2] Here τ_f is the average fast correlation time, and the correlation time τ_c appears with the factor of α in the field autocorrelation function. So, the echoed line is the convolution of an Anderson line with the Lorentz line of half-width of $2\omega_p^2(\alpha\tau_c v_n(\tau_c) + (1 - \alpha)\tau_f)$, the integral intensity being reduced by a factor of $\exp(\omega_p^2[\alpha\tau_c^2 u_n(\tau_c) - 2n\tau(1 - \alpha)\tau_f])$. Such a line shape again can be calculated using Eq. (*49*) or Eq. (*50*) of ref.[2]

RESULTS AND DISCUSSION

Single Spin Echo

For the integral intensity decrease after the spin echo, we obtain $\ln(I_0/I_e) = d = -u_1\omega_p^2\tau_c^2$, where I_0 is the integral intensity of the parent line and I_e that of the echoed line. At small τ/τ_c, d is proportional to τ^3, $d \doteq 2\omega_p^2\tau^3/(3\tau_c)$, reaching the asymptote $2\omega_p^2\tau_c\tau - 3\omega_p^2\tau_c^2$ at sufficiently great τ/τ_c. This means that the d–τ dependence is non-linear unless the asymptote is reached. The slope is $\mathrm{d}d/\mathrm{d}\tau = 2(1 - \exp(-\tau/\tau_c))^2\omega_p^2\tau_c = 2v_1\omega_p^2\tau_c$. It reaches the slope of the asymptote within 1% when τ/τ_c > 5.2958, and within 0.1% when $\tau/\tau_c \geq$ 7.6007; simultaneously, the Lorentz shape of the echoed line is reached within 1 and 0.1%, respectively. To reach the asymptote before the integral intensity decreases to 50% of that of the parent line, $\omega_p\tau_c$ should be less than 0.3018 in the former case and 0.2383 in the latter, before the decrease to 25% – less than 0.4268 and 0.3370, before the decrease to 10% – less than 0.5500 and 0.4344, respectively. The τ/τ_c plots of $\ln (I_0/I_e)/(\omega_p\tau_c)^2 = -u_1$ with its asymptote and of v_1 are shown in Fig. 1. Note that the spin-diffusion contribution to the logarithmic decrease in the intensity in the single spin echo also increases with τ^3 at increasing τ (ref.[4], p. 61), like d at small τ. In an exponential analysis of the I_e/I_0 decrease, no other decreasing exponential term (besides that first) is allowed, the biexponential analysis fails.

Hence, trying to pick up the T_2 relaxation time from the d–τ dependence does not yield a good fit unless the asymptote is reached; so, the d values before reaching the asymptote should be discarded and a linear fit, not mere proportionality should be used. If not, we obtain the T_2 value distorted by the factor $1/v_1$, where v_1 is some average from the v_1 values corresponding to the individual τ's used in fitting. So, a dependence of the T_2 value on the set of τ values used in the echo sequence indicates an occurrence of partial narrowing, including that as small as non-detectable. This is justified by the fact that when $\omega_p\tau_c$ is of the order of 10^0 (partial narrow-

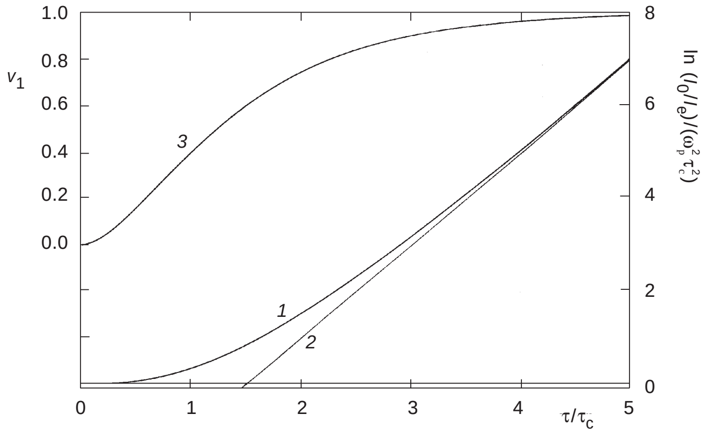

FIG. 1

The τ/τ_c plots of the logarithmic decrease $\ln (I_0/I_e)$ in the echo intensity divided by $\omega_p^2\tau_c^2$ and of the fraction v_1 of the Lorentzian shape in the convolution forming the echoed line shape. *1* $\ln (I_0/I_e)/(\omega_p^2\tau_c^2)$, *2* the asymptote of *1* approached at great τ/τ_c, *3* v_1

ing), the requirement for a measurable intensity decrease dictates τ/τ_c to be of the order of 10^0 (see the next paragraph), in which τ/τ_c region the T_2–τ dependence occurs. Particularly, starting the echo sequence with a 5% integral intensity decrease requires $\omega_p^2\tau_c\tau$ *ca* 0.025, and to reveal a d–τ dependence, τ/τ_c less than *ca* 5, hence $\omega_p^2\tau_c^2$ should be greater than 0.005, which means a *ca* 0.5% intensity increase in the line center as compared with the extreme narrowing approximation, which is roughly the detectable limit. The distorted T_2 value corresponds just to the width of the Lorentz component in the convolution forming the echoed line, neglecting the Anderson component completely. Better results could be obtained adjusting d's to the values of $-u_1\omega_p^2\tau_c^2$ with two adjustable parameters ω_p and τ_c, then $1/T_2 = \omega_p^2\tau_c$ corresponds to the Lorentz line obtained from the extreme narrowing approximation.

In experiments, the intensity decrease in echoes should not be too low (at least few per cent) for the decrease not to be hidden in experimental errors, and also some intensity (at least few per cent) should be left to be measurable. For this, τ should be of the order of $1/(\omega_p^2\tau_c)$ when $\omega_p\tau_c < 1$ and of the order of $(\tau_c/\omega_p^2)^{1/3}$ when $\omega_p\tau_c > 1$.

Since the Anderson shape is narrower than that of Lorentz from the extreme narrowing approximation, the echoed lines broaden with increasing τ as the amount of the Lorentz shape increases with v_1. So, the central intensity decrease is greater than exp $(u_1\omega_p^2\tau_c^2)$, whereas the far wings with the $(\omega - \omega_0)^{-2}$ decrease first grow and later decrease with increasing τ. The τ_m of the maximum wing intensity can be found solving $x/(1 - x)^3 = \omega_p^2\tau_c^2$ for x and setting $\tau_m = -\tau_c \ln x$. For small $\omega_p\tau_c$, $\tau_m \doteq -2\tau_c \ln(\omega_p\tau_c)$; for great ones, $\tau_m \doteq \tau_c/(\omega_p\tau_c)^{2/3}$. When, in wings, the intensity maximum is found late in the echo sequence or is not reached at all, an average increase in the intensity follows. Trying, with the non-negativity constraint, a least-squares exponential analysis of the echo sequence at that wing frequency then yields infinite T_2 and the intensity over the sequence constant at its average value.

Multiple Spin Echo

In the multiple spin-echo experiment, the integral intensity decrease is $\ln(I_0/I_n) = d_n = -u_n\omega_p^2\tau_c^2$, where I_0 is the integral intensity of the parent line and I_n that of n-th echo. At this, d_n's oscillate around the asymptote $2\omega_p^2\tau_c^2[n(\tau/\tau_c - \tanh(\tau/\tau_c)) - 2\sinh^4(\tau/(2\tau_c))/\cosh^2(\tau/\tau_c)]$, the odd being lower and the even greater, the deviations tending to zero with increasing n. So, the first decrease in the integral intensity is lower than the next.

A linear least-squares adjustment yields the d_n–n dependence close to the asymptote with the result $1/T_2 \doteq \omega_p^2 \tau_c (1 - \tanh(\tau/\tau_c)\tau_c/\tau)$; this is similar to the expression for the effective T_{2e} in the solid spin-echo experiment with the OW4 sequence (ref.[10], Eq. (*11*)), save for a factor of four in the denominator. At small values of τ/τ_c, this is about $\omega_p^2 \tau^2/(3\tau_c)$ with a strong underestimation compared with the value valid for the Lorentz line in the extreme narrowing approximation. The slope s of the asymptote (divided by $\omega_p^2 \tau_c^2$) together with that for extreme narrowing approximation is plotted *versus* τ/τ_c in Fig. 2. When $\exp(-2\tau/\tau_c)$ dies off, the d_n values lie on the asymptote (perhaps except d_1 when $\exp(-\tau/\tau_c)$ is not yet negligible), which still misses the origin ($n = 0$, $d_0 = 0$). At this, $1/T_2 = \omega_p^2 \tau_c (1 - \tau_c/\tau)$ is obtained. Hence, the time delay τ in the multiple spin-echo experiment should be at least two or three decades longer than the correlation time τ_c to obtain undistorted T_2 values of the Lorentz line in the extreme narrowing approximation within the 1 or 0.1% accuracy, respectively. The deviation of the asymptote from the origin increases with increasing τ approaching the value $\omega_p^2 \tau_c^2$ at great τ/τ_c. The deviation of d_n from the asymptote passes through a maximum at $\tau = x\tau_c$, where x is obtained by solving for x the equation $\cosh x \tanh(x/2) = 1/n$. The maximum deviation of d_1 of $0.018194\omega_p^2 \tau_c^2$ appears at $\tau = 1.2188\tau_c$ and that of d_2 of $0.0025955\omega_p^2 \tau_c^2$ at $\tau = 0.7910\tau_c$. The maximum deviation of the asymptote from the origin,

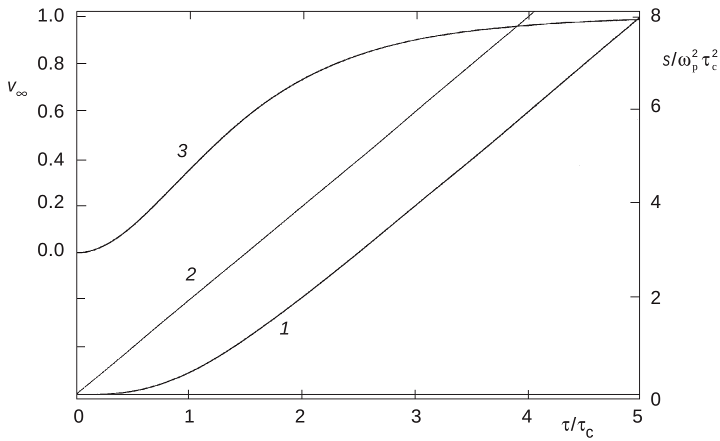

FIG. 2

The τ/τ_c plots of the slope s of the asymptote of $\ln(I_0/I_n)$ approached at great n in the multiple spin echo, divided by $\omega_p^2\tau_c^2$, and of the limiting fraction v_∞ at great n of the Lorentzian shape in the convolution forming the echoed line shape. *1* $s/(\omega_p^2\tau_c^2)$, *2* $s/(\omega_p^2\tau_c^2)$ in the extreme narrowing approximation, *3* v_∞

relative to the asymptote slope, is 27.8216% and appears at $\tau = 1.4267\tau_c$, the maximum of such relative deviation of d_1 of 6.3155% appears at $\tau = 0.4264\tau_c$ and that of d_2 of 3.3621% at $\tau = 0.2380\tau_c$.

Like in the single spin echo, a dependence of T_2 on the time delay τ in the multiple spin-echo experiment is indicative of possible presence of partial narrowing. Here, however, due to the corrective factor of $1 - \tau_c/\tau$ and the possibility of choosing shorter τ when n is increased, the T_2–τ dependence may be traced also when the line is essentially Lorentzian (when the line center intensity increase is, say, *ca* 0.01% and the shape is unresolvable from the Lorentzian). No other decreasing exponential term is allowed in the exponential analysis of the I_n/I_0 decrease with n.

In experiments, τ again should be chosen of the order of $1/\omega_p^2\tau_c$ when $\omega_p\tau_c < 1$ and of $(\tau_c/\omega_p^2)^{1/3}$ when $\omega_p\tau_c > 1$. It is also possible to choose shorter τ and to increase n accordingly. Halving τ requires an eight-fold increase in n to obtain a comparable intensity decrease and yields four times longer T_2 when $\omega_p\tau_c >> 1$; when $\omega_p\tau_c << 1$, n requires to be doubled and T_2 is left unchanged.

The v_n values oscillate around the limiting value $v_\infty = 2\sinh^2(\tau/(2\tau_c))/\cosh(\tau/\tau_c)$, the odd being greater and the even lower, the deviations tending to zero with increasing n. The v_∞ limiting value is plotted *versus* τ/τ_c in Fig. 2. Since the lines are the broader the greater is v_n, the first decrease in the central intensity is greater than the next. Another exponential term with zero T_2 (infinite line width) is therefore allowed in the exponential analysis of the central intensity decrease with n. In going to wings, the other term decreases and is lost at some moment. No average local intensity growth is expected (neglecting odd-even oscillations).

Multiexponential Field Autocorrelation Function

First, we consider the case where the τ values region in the single spin echo or the τ value in the multiple spin echo is far from all correlation times τ_i. We define $\sum_i \alpha_i = \alpha$, where the summation runs over such i's for which $\tau_i >> \tau$, and $\sum_i \alpha_i\tau_i/(1-\alpha) = \tau_f$, with the summation now running over such i's for which $\tau_i << \tau$; τ_f is the average fast correlation time. In this case, $d = \ln(I_0/I_n) = 2n\tau(1-\alpha)\omega_p^2\tau_f$, giving a linear dependence of d on τ and n, and $1/T_2 = (1-\alpha)\omega_p^2\tau_f$ independent of τ. When, simultaneously with $\tau_i >> \tau$, also $\tau_i >> 1/\omega_p$ and with $\tau_i << \tau$ also $\tau_i << 1/\omega_p$, then for FID of the parent (non-echoed) line we get $\varphi(t) = \exp(-\alpha\omega_p^2 t^2 - (1-\alpha)\omega_p^2 \tau_f t)$ and for that of the echoed line $\varphi(t) = \exp(-\alpha\omega_p^2 t^2 - (1-\alpha)\omega_p^2 \tau_f (2n\tau + t))$. We have the Voigt shape (a convolution of a Gaussian with a Lorentzian shape) unless α is zero (yielding a Lorentzian shape) or unity (yielding a Gaussian shape); the found T_2 corresponds to the Lorentz component leaving the Gaussian component neglected. When $1/\omega_p$ does not fulfil the above conditions, the Voigt shape is somewhat distorted.

With the biexponential field autocorrelation function ($\tau_s >> \tau$, $\tau_f < \tau$), one gets, similarly to the single-exponential one, that the T_2–τ independence occurs if and only if the fast component is in the extreme narrowing (is Lorentzian) in the case of the single spin echo. Now, the τ dependence found in the single-exponential case even with a very slow motion is hidden in the contribution of the fast component, which prevents using sufficiently long τ to reveal the τ dependence caused by the slow τ_s. With the multiple spin echo, a slight T_2–τ dependence may occur even when the fast component is Lorentzian but close to partial narrowing, similarly to the single-exponential autocorrelation function. When the slow component is dominant ($\alpha \geq 1/2$), it is essentially unnarrowed (Gaussian), whereas with small α, it might be partially narrowed. A similar behaviour can be expected in the case of a multiexponential autocorrelation function; however, its rigorous consideration is too complicated.

On the other hand, when there are some τ_i('s) not sufficiently far from τ, T_2 is τ-dependent according to Eq. (*7*) considering the τ dependence of $u_n(\tau_i)/\tau$ for such τ_i's. T_2 decreases with increasing τ.

CONCLUSIONS

Generally, the spin-echo experiment with a Gaussian line only partially narrowed by an insufficiently fast motion yields a non-linear dependence of the logarithmic decrease in the echo intensity on the time delay(s) τ used in the echo experiment. In a single-echo experiment, a good fit cannot be obtained and the resulting T_2 value is dependent on the τ set used in the experiment. In a multiple echo, the logarithmic intensity decrease in the echo sequence slightly oscillates around a linear asymptote, enabling a fit to a linear function (save for the oscillations). With a single-exponential field autocorrelation function of the narrowing motion, the degree of the distortion of T_2 depends on the ratio τ/τ_c of the time delay τ in the echo experiment to the correlation time τ_c of the motion. To obtain undistorted T_2 values (corresponding to the Lorentzian line in the extreme narrowing approximation), the ratio should be at least several units for all the τ's used in the single echo, giving, at the same time, the linearity of the dependence of the logarithmic decrease in the echo intensity on τ, and the ratio should be at least few decades in the multiple echo. In the single echo, an apparent distortion and a non-linearity of the logarithmic intensity decrease occur if and only if the line is only partially narrowed (*i.e.*, it has an apparent deviation from the Lorentzian shape), including the case when it is essentially unnarrowed (with the shape remaining Gaussian within experimental errors), when the τ values are within what causes a measurable intensity decrease. In the multiple echo, some distortion may be found even with a Lorentzian line when it is close to only partial narrowing.

With a multiexponential field autocorrelation function, T_2 is dependent on τ if some correlation time is not sufficiently far from τ or there are no correlation times shorter than τ. In the opposite case, T_2 is independent of τ and corresponds to the convolution of fast components in extreme narrowing, neglecting slow components. In the single-echo experiment, with the biexponential field autocorrelation function having one correlation time much longer than τ and the other shorter than τ, T_2 depends on τ if and only if the fast component is only partially narrowed. In the multiple echo, some dependence may be traced even when the fast component is Lorentzian, but close to partial narrowing.

The echoed line shape changes, approaching that of Lorentzian at long τ.

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