MANIFESTATION OF THE FREQUENCY MIGRATION MECHANISM IN DECAY OF ECHO SIGNALS

A. B. DOKTOROV and A. I. BURSHTEĬN

Institute of Chemical Kinetics and Combustion, Siberian Division, USSR Academy of Sciences

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The kinetics of echo signal decay is determined under conditions when the resonance frequency randomly migrates within the limits of the observable spectrum. It is found that, even in a highly correlated case, frequency migration cannot always be regarded as spectral diffusion and in all cases attraction to the center of gravity of the spectrum should be taken into account. Variation of free induction (either directly or on the basis of the three-pulse echo technique by a prescribed procedure) and a measurement of the echo signal permit one to easily distinguish correlated variation of the frequency from noncorrelated variation. Concurrently the width of the spectrum involving migration and the migration rate can be determined.

THE migration of the resonance frequency in an inhomogeneously broadened spectrum is often called "spectral diffusion." This term is taken not in its literal sense, but refers instead to a phenomenon caused by random modulation of the frequency of an atom or molecule. The physical cause of frequency migration in glasses or in crystals is the reorientation of the molecule or of an individual group of molecules[1]. It is a sudden, random process, which shifts the frequency jumpwise to the right or left on the spectrum by some interval $\delta\omega$, by an amount that depends on the anisotropy existing in the medium and on the angle of rotation. In exactly the same fashion, the phase and Doppler shift of the atomic frequency vary as a result of collisions in the gas phase[2], as does the number of the hyperfine components in magnetic-resonance spectra when quantum transitions change the angle between spins.[3] In all the given examples, frequency migration is brought about by a succession of jumps of different magnitude separated by time intervals of varying lengths.

Strictly speaking, a diffusion description of such processes in frequency space is not always possible, and is inadmissible in principle for some spectrum shapes. It is more correct to distinguish between correlated and non-correlated migration on the basis of whether the magnitude of the jump is small compared to the full breadth of the spectrum, or commensurate with it. This, in turn, depends on the mechanism of the molecular process that is causing the frequency modulation. The rotation angle of a molecule in the elementary act of rotational diffusion may be either large or small; the velocity after collision may retain some value close to its previous value or assume other values, with equal probability. The selection rules for dipole transitions of nuclear spins only permit successive variation of the hyperfine-structure components, whereas spin diffusion as a result of transport or an exchange process removes that prohibition. If we had the ability to differentiate between correlated and non-correlated frequency migration, it would then be possible to reach important conclusions about the mechanism of the elementary processes that cause it.

Unfortunately, in most physical manifestations of migration only its rate is important, regardless of whether it is composed of small but frequent steps or of a few large ones. It is known that so long as that rate is small compared with the width of the statistical spectrum, frequency modulation merely broadens its components, without changing either the shape of the envelope or the gist of the matter—that the spectrum continues to remain inhomogeneous. On the other hand, very rapid modulation levels out the differences between components, while the spectrum as a whole, becoming homogeneous, is transformed and turns Lorentzian; it begins to broaden or to narrow down, depending on its original form[4]. Although in both cases the migration rate can be determined experimentally, it is quite difficult to ascertain from the form of the stationary observed spectrum (or from the fading of the free induction) whether a strong or weak shift of frequency is taking place in a separate act of migration; the degree of correlation in the process is only revealed in the fine details of the transition from the slow to fast migration. Such an opportunity presents itself rather rarely. As a rule one has to deal with the inhomogeneously broadened spectrum alone, and then only the echo method permits one to distinguish in principle between the two types of spectra. Static frequency dispersion has no effect on the decay of this signal, while the modulation manifests itself in diverse and detailed fashion. In this paper we have calculated the kinetics of echo fading by the two- and three-pulse methods; in the quasistatic limit this kinetics is qualitatively different for correlated and non-correlated migration, being exponential in the latter case and intrinsically connected with the shape of the static spectrum in the former, as many observers have found[3,5,6].

1. GENERAL FORMALISM

Echo signal fading, caused by frequency modulation, is determined by the expression[5]

$$V(t)=\left\langle \exp\left(-i\int_0^t s(t')\omega(t')dt'\right)\right\rangle, \qquad (1.1)$$

in which the function s(t) is given by the method of measurement and equals

$$s(t)=\begin{cases}1 \text{ for } 0<t<\tau,\\ -1 \text{ for } \tau<t,\end{cases}\qquad s(t)=\begin{cases}1 \text{ for } 0<t<\tau,\\ 0 \text{ for } \tau<t<T,\\ -1 \text{ for } T<t,\end{cases}\tag{1.2}$$

for the two-pulse and three-pulse schemes, respectively. Here τ is the instant of action of the second pulse and T that of the third pulse. The brackets indicate averaging over the different realizations of the random process in the time interval (0, 5), from the onset of the pulse to the time when the echo is observed. Without loss of generality, we assume in what follows that the random process is centered, i.e., $\overline{\omega}(t) = 0$, for otherwise the corresponding average can be included in the Larmor frequency, which is the carrier frequency of the signal.

It is absolutely necessary to have most detailed information about the random process in order to carry out the averaging that is required in (1.1). Jumpwise variation of the frequency greatly facilitates this task, since it allows us to regard $\omega(t)$ as a purely discontinuous Markov process whose characteristics are determined by the mean time τ_0 between jumps and by two probability density distributions $\varphi(\omega)$ and $f(\omega', \omega)$. The first of these defines the probability of any frequency value at an arbitrary time of the process, and is nothing more than the normalized-to-unity frequency distribution in the observed static spectrum of the system. The second distribution gives the conditional probability that, as the result of a jump the value ω' will be replaced by a new value ω (Fig. 1). Its width determines in fact the degree of frequency-migration correlation.

The two distributions are related[7] by the requirement that the process be stationary:

$$\varphi(\omega)=\int f(\omega',\omega)\varphi(\omega')d\omega',\tag{1.3}$$

which becomes unique if we assume that

$$f(\omega',\omega)=f(\omega-\gamma\omega').\tag{1.4}$$

Some assumption about the form of $f(\omega', \omega)$ is indispensable in order to make the process concrete, and (1.4) is one of the most general assumptions. It is compatible with symmetric spectra $\varphi(\omega)$ of any form, although it had been used only for a Gaussian contour[7,8]. By taking the Fourier transforms of both parts of (1.3), with allowance for (1.4), we easily establish that

$$F(t)=X(t)\,/\,X(\gamma t),\tag{1.5}$$

where

$$F=\int f(z)e^{izt}dz,\qquad X=\int\varphi(\omega)e^{i\omega t}d\omega$$

are the Fourier transforms of f and φ.

The differential form of the argument in f(z), as postulated in (1.4), simplifies not only the definition of this function in terms of φ but also the solution of the integral equations for V(t), of which it is the kernel. In doing this we retain the possibility of comparing solutions that pertain to static spectra of various forms. If we distinguish among them in what follows on the basis of their Fourier transform

$$X(t)=e^{-Q(t)},\tag{1.6}$$

it is essential to bear in mind that in the polynomial representation

$$Q(t)=\Delta^n|t|^n\tag{1.6a}$$

n = 2 corresponds to the Gaussian contour, n = 1 to the Lorentzian contour, and n = 1/2 represents a spectrum even narrower than Lorentzian, similar in form to the static line wings in gases and solid solutions. The parameter Δ determines the width of the corresponding spectrum. If we use (1.5), we can easily verify that F(t) has the same form as (1.6), but the fall-off rate of this function is given by the width $\delta = \Delta(1-\gamma^n)^{1/n}$ of the conditional probability distribution, which differs from Δ according to the parameter γ, which ranges from 0 to 1. When $\gamma \ll 1$, the two widths roughly coincide and the process is weakly correlated, because in practice all memory of the previous frequency value is lost after the very first jump. In the limiting case $\gamma = 0$, which is particularly favorable for study, both widths and distributions coincide fully:

$$f(\omega',\omega)=\varphi(\omega),\tag{1.7}$$

as follows directly from (1.3) and (1.4). If, however, $\gamma \approx 1$, the conditional distribution is much narrower than $\varphi(\omega)$ and a large number of jumps are required before the frequency is significantly moved away from its initial value. This case, too, is more convenient to study in the limit as $1-\gamma \to 0$ and $\tau_0 \to 0$, but the migration rate, the order of which is $(1-\gamma)/\tau_0$, is fixed. Taking this circumstance into account, we consider first a method of calculating the response in general, and proceed to the study of the two limiting situations each by itself.

In the three-pulse method of observing the echo, the averaging that one must carry out in (1.1) breaks up naturally into three stages:

$$V(t)=\int d\alpha\int d\beta\left\langle\exp\left(i\int_0^\tau\omega(t')dt'\right)\right\rangle_\alpha\varphi(\alpha,\beta;T-\tau)\times\left\langle\exp\left(-i\int_T^t\omega(t')dt'\right)\right\rangle_\beta,\tag{1.8}$$

where the end of one stage serves as the beginning of the other, and both occur at the same frequency: α at the instant τ and β at the instant T. In the first stage, the response of the system is averaged over all possible random-perturbation values that terminate in the same value of α, in the last stage over all possible values having the common initial value β, and between them the averaging leads to a simple summation of probabilities of all processes that begin at a value α at the instant τ and end with the value β at the instant T. The latter gives the ordinary conditional probability $\varphi(\alpha, \tau; \beta, T) = \varphi(\alpha, \beta; T-\tau)$, which by virtue of the stationarity of the process depends only on the differ-

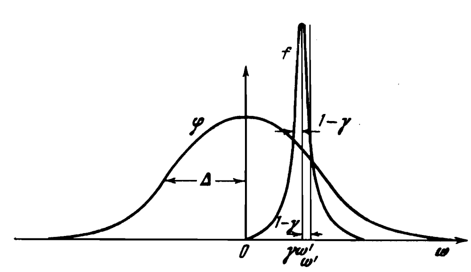

FIG. 1

ence of its time arguments. The echo-signal decay in the two-pulse method is described by a formula obtained easily from (1.8), if it is noted that at $T = \tau$ we have $\varphi(\alpha, \beta; 0) = \delta(\alpha - \beta)$.

Noting that the echo-signal maximum is reached when $t = T + \tau$, we easily obtain the shape of the envelope for the three-pulse method from (1.8):

$$V(T+\tau) = \int d\alpha \int d\beta\, K^{\cdot}(\alpha,\tau)\varphi(\alpha,\beta; T-\tau)K^{+}(\beta,\tau), \quad (1.9)$$

and likewise for the two-pulse method

$$V(2\tau) = \int K^{\cdot}(\alpha,\tau)K^{+}(\alpha,\tau)\,d\alpha. \quad (1.10)$$

Here

$$K(\alpha,\tau) = \left\langle \exp\left(-i\int_0^\tau \omega(t')\,dt'\right)\right\rangle_\alpha, \quad K^{+}(\alpha,\tau) = {}_\alpha\!\left\langle \exp\left(-i\int_0^\tau \omega(t')\,dt'\right)\right\rangle$$

are partial averages that differ only as to whether the averaging, which was specially formulated for the subsequent procedure in (1.9) or (1.10), is carried out over the initial or the final frequency. In view of the stationary character of the process K and K^+, as well as $\varphi(\alpha, \beta; t)$, depend only on the time differences.

The conditional probability of a purely discontinuous Markov process satisfies Feller's equation[7,9].

$$\frac{\partial}{\partial t}\varphi(\alpha,\omega;t) = -\frac{1}{\tau_0}\left[\varphi(\alpha,\omega;t) - \int f(\omega',\omega)\varphi(\alpha,\omega';t)\,d\omega'\right]. \quad (1.11)$$

An equation similar in form has been derived for the partial response[7]:

$$\frac{\partial}{\partial\tau}K(\omega,\tau) = i\omega K(\omega,\tau) - \frac{1}{\tau_0}\left[K(\omega,\tau) - \int f(\omega',\omega)K(\omega',\tau)\,d\omega'\right]. \quad (1.12a)$$

The equation for K^+ is obtained in completely analogous fashion[10]:

$$\frac{\partial}{\partial\tau}K^{+}(\omega,\tau) = i\omega K^{+}(\omega,\tau) - \frac{1}{\tau_0}\left[K^{+}(\omega,\tau) - \int f(\omega,\omega')K^{+}(\omega',\tau)\,d\omega'\right] \quad (1.12b)$$

and forms the natural complement of (1.12a). Taken together, these equations form a system similar to the Kolmogorov-Feller equations for the conditional probability. Although from the formal point of view both equations are of equal weight, until recently it has not been necessary to employ the second of them, since all the information could be extracted from $K(\omega, \tau)$. It is only in our problem that the sought quantity is expressed in terms of $K(\omega, \tau)$ and $K^+(\omega, \tau)$ perfectly on par. Thus, to obtain results pertaining to the two-pulse method it is necessary to solve the entire system of equations (1.12) with initial conditions

$$K(\omega,0) = \varphi(\omega), \quad K^{+}(\omega,0) = 1, \quad (1.13)$$

while for the three-pulse method one must add the solution of (1.11) satisfying the condition $\varphi(\alpha, \omega; 0) = \delta(\alpha - \omega)$. The final result is obtained after averaging these solutions in (1.10) and (1.9), respectively.

2. THE NON-CORRELATED PROCESS

In the limiting situation defined by condition (1.7) the problem is greatly simplified. In that case Feller's equation becomes differential, and its solution is easily found[7]:

$$\varphi(\alpha,\omega;t) = \delta(\alpha-\omega)\exp(-t/\tau_0) + \varphi(\omega)[1-\exp(-t/\tau_0)]. \quad (2.1)$$

In the same way the integral part of both equations (1.12) is appreciably simplified. As a consequence it turns out that

$$K(\omega,\tau) = \varphi(\omega)K^{+}(\omega,\tau) \quad (2.2)$$

and it then becomes a matter of solving the single equation

$$\frac{\partial}{\partial\tau}K^{+}(\omega,\tau) = i\omega K^{+}(\omega,\tau) - \frac{1}{\tau_0}[K^{+}(\omega,\tau) - K(\tau)], \quad (2.3a)$$

in which

$$K(\tau) = \int K(\omega,\tau)\,d\omega = \int K^{+}(\omega,\tau)\varphi(\omega)\,d\omega = \left\langle \exp\left(i\int_0^\tau \omega(t')\,dt'\right)\right\rangle \quad (2.3b)$$

is none other than the free induction signal (the Fourier transform of the stationarily-observed stationary spectrum).

An identity transformation reduces the system (2.3) to a single integral equation[4,7]:

$$K(\tau) = X(\tau)\exp\left(-\frac{\tau}{\tau_0}\right) + \frac{1}{\tau_0}\int_0^\tau X(\tau-t)\exp\left(-\frac{\tau-t}{\tau_0}\right)K(t)\,dt. \quad (2.4)$$

Its solution determines uniquely $K(\tau)$, and through it K^+ as well, according to a formula obtained from (2.3a) by direct integration:

$$K^{+} = \left[1 + \frac{1}{\tau_0}\int_0^\tau K(t)\exp(-i\omega t + t/\tau_0)\,dt\right]\exp(i\omega\tau - \tau/\tau_0). \quad (2.5)$$

Relation (2.2) considerably simplifies the general formulas (1.9) and (1.10). From the latter we obtain, in particular,

$$V(2\tau) = \int |K^{+}(\omega,\tau)|^2\varphi(\omega)\,d\omega, \quad (2.6)$$

while (1.9) with the help of (2.1) takes on the form[3]

$$V(T+\tau) = V(2\tau)\exp\left(-\frac{T-\tau}{\tau_0}\right) + |K(\tau)|^2\left[1 - \exp\left(-\frac{T-\tau}{\tau_0}\right)\right]. \quad (2.7)$$

K^+ can be eliminated completely from the last formulas by using (2.5) in (2.6). The resulting cumbersome expression can be further simplified by recourse to (2.4). The final result is of the following form:

$$V(2\tau) = \left[1 + \frac{2}{\tau_0}\int_0^\tau |K(t)|^2\exp\left(\frac{2t}{\tau_0}\right)dt\right]\exp\left(-\frac{2\tau}{\tau_0}\right). \quad (2.8)$$

From this it obviously follows that in the noncorrelated process the echo damping is expressed by both procedures directly in terms of the decay of free-induction signal $K(\tau)$.

The rest of the calculations reduce, therefore, to the solution of a Volterra of the second kind with a difference kernel, which Eq. (2.4) is. This equation was recently considered in connection with another problem[7], and we can therefore proceed directly to the results:

$$K(\tau) = \begin{cases} X(\tau)\exp(-\tau/\tau_0)^{2(1-n)}, & \Delta\tau_0 \gg 1, \quad n = 1, {}^1/_2, \quad (2.9a) \\ \exp(-W\tau), & \Delta\tau_0 \ll 1, \quad (2.9b) \end{cases}$$

where

$$W = \frac{1}{\tau_0}\int_0^\infty Q(t)\exp\left(-\frac{t}{\tau_0}\right)\frac{dt}{\tau_0} = \begin{cases} 2\Delta\tau_0, & n = 2, \\ \Delta, & n = 1, \\ \sqrt{\pi\Delta/4\tau_0}, & n = {}^1/_2. \end{cases} \quad (2.10)$$

Here we observe the natural parameter $\Delta\tau_0$ that determines whether we are dealing with the quasi-static situation (2.9a) or with fast migration (2.9b). In both cases the behavior of $K(\tau)$ correlates with the form of the stationarily observed spectrum, which coincides in practice with $\varphi(\omega)$ at $\Delta\tau_0 \gg 1$, and has at $\Delta\tau_0 \ll 1$ the form of a Lorentz contour of width W.

The long-term asymptotic result (2.9a) can be observed only in the wings, in the case of the gently-sloping static spectrum ($n \geq 1$), or on the tail of the free-induction decay. In both cases it is masked by the noise, and so important information about the migration frequency in the quasi-static limit eludes our direct observation. Only the echo method permits the study of migration on an inhomogeneous contour as the main effect. Indeed, using (2.9a) in (2.8) we obtain an expression of first order in $(\Delta\tau_0)^{-1}$

$$V(2\tau)=\left[1+\frac{2}{\tau_0}\int_0^\tau X^2(t)\,dt\right]\exp\left(-\frac{2\tau}{\tau_0}\right), \qquad (2.11)$$

in which the exponential decay and the static decay exchange roles. In the zeroth approximation in $(\Delta\tau_0)$, the echo-signal decay in the two-pulse method is exponential at a rate equal to double the migration frequency. This conclusion is firmly supported by experiment[3] and is of a quite general character. It is valid for all contours of $\varphi(\omega)$, since the shapes of the latter determine only the form of the correction term in (2.11), of first order in $(\Delta\tau_0)^{-1}$. To explain its role, one must substitute (1.6) in (2.11) and expand the exponential in a series in τ/τ_0, retaining all terms of first order. It turns out then that in

$$V(2\tau)=1-2\left\{\frac{\tau}{\tau_0}-\frac{1}{\Delta\tau_0}\int_0^{\Delta\tau}\exp\left[-2Q\left(\frac{t}{\Delta}\right)\right]dt\right\} \qquad (2.12)$$

the integral term is small compared to the linear term when $\tau > 1/\Delta$, and therefore the two-pulse echo decay can be considered as purely exponential from this time on. On the other hand, when

$$V(2\tau)\approx e^{-\Theta(\tau)},$$

$$\Theta(\tau)=\frac{4}{\tau_0}\int_0^\tau Q(t)\,dt=\frac{4}{n+1}\frac{\Delta^n}{\tau_0}\tau^{n+1}, \qquad (2.13)$$

and a marked qualitative difference in the time dependence of $V(2\tau)$ is observed for contours of different shapes, the decay being slower the narrower the contour. This effect is not observable in practice, however, since the non-exponential start of the decay is so short-lived that after its completion the signal amplitude decreases at most by an amount on the order of $(\Delta\tau_0)$ (Fig. 2a).

In the three-pulse method of echo measurement, as seen from (2.7), the exponentially varying $V(2\tau)$ and the rapidly vanishing $K(\tau)$ compete with each other as additive components of the decay, wherein the statistical weight of each is set by the pause $T - \tau$ between the second and third pulse. When that pause is lengthened the role of $V(2\tau)$ is diminished while that of $K(\tau)$ increases. This uncovers a possibility of measuring $K(\tau)$ directly by varying τ at a fixed value of T. One must bear in mind that this is the only reliable means of determining the spectrum of the frequencies actually involved in the migration, which in general may not coincide with the stationarily observed spectrum. If, however, T is varied with τ fixed, this way of observing the echo may serve as a direct means of measuring the migration frequency $1/\tau_0$.

In the case of fast migration the result is relatively trivial. Substitution of (2.9b) in (2.8) gives the exponential decay

$$V(2\tau)=V(T+\tau)=|K(\tau)|^2=e^{-2W\tau}, \qquad (2.14)$$

which takes place at the same rate as the fading of the free-induction signal W. That is what we must expect, when we recall that fast migration changes an inhomogeneous contour into an homogeneous one. For this reason neither the two-pulse nor the three-pulse echo can extract τ_0 from the measurable magnitude (2.10).

In the case of a Lorentz contour (n = 1) it is possible to trace by echo decay the manner in which the broadening gradually becomes homogeneous as the migration is speeded up. The point is that in this special case Eq. (2.4) has the exact solution:

$$K(\tau)=e^{-\Delta\tau} \quad \text{at} \quad \Delta\tau_0 \gtrless 1, \qquad (2.15)$$

which, substituted in (2.8), gives

$$V(2\tau)=\frac{e^{-2\Delta\tau}-\Delta\tau_0 e^{-2\tau/\tau_0}}{1-\Delta\tau_0}\approx\begin{cases} e^{-2\tau/\tau_0}, & \Delta\tau_0 \gg 1 \\ e^{-2\Delta\tau} & \Delta\tau_0 \ll 1\end{cases}, \qquad (2.16)$$

in full agreement with the limiting equations obtained above. It is a fact worthy of attention that the decay of the free induction $K(\tau)$, as well as its Fourier transform (the stationarily observed spectrum), is invariant with respect to the migration, i.e., the Lorentz contour, as distinct from all the others, changes neither in width nor in shape when the migration is speeded up, so that it is impossible to tell from its shape whether we are dealing with an homogeneous spectrum or an inhomogeneously broadened one. This can be decided only by comparison of $K(\tau)$ and $V(2\tau)$. In homogeneous spectra the free-induction signal and the echo disappear in the same manner, whereas in inhomogeneous ones the induction signal remains unchanged, while the echo is damped at the migration rate $1/\tau_0$, which differs radically from Δ both in nature and in its magnitude.

3. CORRELATED PROCESS

It is clear from (1.5) that $F(t) \to 1$ as $\gamma \to 1$ from which it might seem that $f(\omega', \omega) \to \delta(\omega - \gamma\omega')$. In reality, however, narrowing f(z) does not always change it into a δ-function, since the remote asymptote of F(t) coincides with X(t) for any $\gamma \neq 1$. If the F(t) and X(t) fail to decrease quickly enough, as for example when $n \leq 1$, of the sought functions in the integral parts of (1.11) and (1.12) cannot be expanded in power series, since all the moments except the zeroth diverge. This excludes the possibility of a diffusion description of migration, as well as the solution approach that can be used in the case of a normal frequency distribution[11]. To prevent the appearance of divergences in the general

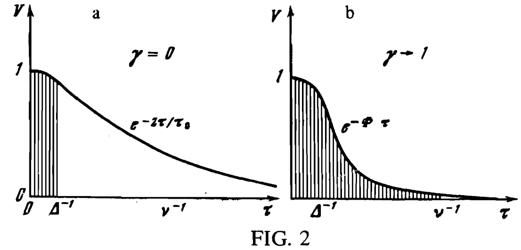

FIG. 2

case, one must resort to the Fourier transformation, making use of the fact that a kernel of the form (1.4) permits convolution of the integral parts of the equations. As a result, we obtain in place of (1.11) and (1.12) respectively

$$\frac{\partial}{\partial\tau}\varkappa(t',t;\tau)=-\frac{1}{\tau_0}[\varkappa(t',t;\tau)-F(-t)\varkappa(t',\gamma t;\tau)], \tag{3.1}$$

$$\frac{\partial}{\partial\tau}R(t,\tau)=\frac{\partial}{\partial t}R(t,\tau)-\frac{1}{\tau_0}[R(t,\tau)-F(t)R(\gamma t,\tau)], \tag{3.2a}$$

$$\frac{\partial}{\partial\tau}R^+(\gamma t,\tau)=\frac{1}{\gamma}\frac{\partial}{\partial t}R^+(\gamma t,\tau)-\frac{1}{\tau_0}\left[R^+(\gamma t,\tau)-\frac{F(-t)}{\gamma}R^+(t,\tau)\right], \tag{3.2b}$$

where

$$\varkappa=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\varphi(\alpha,\beta;\tau)e^{i\alpha t'-i\beta t}\,d\alpha\,d\beta,\qquad R=\int_{-\infty}^{\infty}K(\omega,\tau)e^{i\omega t}\,d\omega, \tag{3.3}$$

$$R^+=\int_{-\infty}^{\infty}K^+(\omega,\tau)e^{i\omega t}\,d\omega,$$

with

$$\varkappa(t',t;0)=2\pi\delta(t'-t),\quad R(t,0)=X(t),\quad R^+(t,0)=2\pi\delta(t).$$

The general procedures for determining the free induction and echo decay are redefined by newly introduced quantities in the following manner:

$$K(\tau)=R(0,\tau), \tag{3.4}$$

$$V(2\tau)=\frac{1}{2\pi}\int_{-\infty}^{\infty}R^*(t,\tau)R^+(t,\tau)\,d\tau, \tag{3.5}$$

$$V(T+\tau)=\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}R^*(t',\tau)\varkappa(t',t;T-\tau)R^+(t,\tau)\,dt'\,dt. \tag{3.6}$$

These formulas can only be profitably employed if (3.2) and (3.1) have been solved. Unfortunately, even with a specified $f(\omega',\omega)$, the problem for arbitrary γ still remains too complicated for analytic solution. Success is achieved only by going to the limit as $1-\gamma\to 0$ at a fixed migration frequency $\nu=(1-\gamma)/\tau_0=\mathrm{inv}$. This situation is the complete opposite of that treated in the preceding section, and by comparing them one is able to clarify the role of memory in frequency-modulation processes.

The limit is taken after expanding all the γ-dependent functions in a series in $1-\gamma$ and retaining only terms of first order in that parameter. As a result, Eqs. (3.1) and (3.2) are transformed, with allowance for (1.5), into the following

$$\frac{\partial\varkappa}{\partial\tau}+\nu t\frac{\partial\varkappa}{\partial t}+\Phi^*(t)\varkappa=0, \tag{3.7}$$

$$\frac{\partial R}{\partial\tau}-(1-\nu t)\frac{\partial R}{\partial t}+\Phi(t)R=0, \tag{3.8a}$$

$$\frac{\partial R^+}{\partial\tau}-(1+\nu t)\frac{\partial R^+}{\partial t}+[\Phi^*(t)-\nu]R^+=0, \tag{3.8b}$$

where

$$\Phi(t)=\lim_{\gamma\to1,\,\tau_0\to0}\frac{1-F(t)}{\tau_0}=-\nu t\frac{d\ln X^*(t)}{dt}. \tag{3.9}$$

This reduces then to the solution of first-order partial differential equations with boundary conditions (3.3). We find, by the standard method,

$$\varkappa=2\pi\delta(t'-te^{-\nu\tau})\frac{X^*(t)}{X^*(te^{-\nu\tau})}, \tag{3.10}$$

$$R=X(t)\exp\left(\int_t^{\xi_-}\frac{d\ln X(z)}{dz}\frac{dz}{1-\nu z}\right), \tag{3.11a}$$

$$R^+=2\pi\delta(\xi_+)\frac{X(\xi_+)}{X^*(t)}\exp\left(\nu\tau-\int_{-t}^{\xi_+}\frac{d\ln X(z)}{dz}\frac{dz}{1-\nu z}\right), \tag{3.11b}$$

where

$$\xi_\pm=\frac{1}{\nu}[1-(1\pm\nu t)e^{\pm\nu\tau}]. \tag{3.12}$$

If we now take the inverse transform of (3.10) to reconstruct the form

$$\varphi(\omega',\omega;\tau)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dy\exp\left[iy(\omega-\omega'e^{-\nu\tau})-\int_0^{\tau}\Phi(ye^{-\nu t})dt\right], \tag{3.13}$$

we can see that this distribution determines the random process considered by Klauder and Anderson[5], who characterized it by the function $\Phi(z)$. Formula (3.9) permits one to determine the form of this function for any given static contour, and to establish by the same token a unique correspondence of both approaches to the problem. In this way it becomes evident that the random process implicitly defined in[5] is due to purely discontinuous frequency migration in the case when the frequency is distributed after each jump in a narrow interval near the preceding value, and furthermore exactly as was assumed in (1.4). For the model contours (1.6), the function $\Phi(z)$ may be determined from (3.9) explicitly:

$$\Phi(z)=n\nu\Delta^n|z|^n=\begin{cases}kz^2 & n=2\\ m|z|, & n=1\end{cases}, \tag{3.14}$$

and turns out to be a polynomial of the same degree as the argument of the exponential term in (1.6). Relation (3.14) establishes a one-to-one correspondence between the natural parameters of the problem Δ and ν, and the symbols k and m introduced in[5], thus explaining their physical meaning. The correspondence established is such that the final result can be extracted directly from the formulas obtained in[5] by transforming them as required. However, it is obtained more easily from (3.4) and (3.5) by substituting in them (3.10) and (3.11). If we express it in terms of the function $\Phi(z)$ defined in (3.9) we have:

$$K(\tau)=\exp\left(-\int_0^{\tau}\frac{\Phi(\eta)}{\nu\eta}dx\right),$$

$$V(2\tau)=\exp\left(-2\int_0^{\tau}\frac{\Phi(-\nu\eta^2)+\nu\eta\Phi(-\eta)}{\nu\eta(1+\nu\eta)}dx\right), \tag{3.16}$$

where $\eta=(1-e^{-\nu x})/\nu$. For the three-pulse echo we find in exactly the same fashion:

$$V(T+\tau)=\exp\left\{-\int_0^{\tau}\frac{\Phi(\eta)(1+\nu\mu\eta)-\Phi(\mu\eta)+\Phi(\mu\eta-\eta(1+\nu\mu\eta))}{\nu\eta(1+\nu\mu\eta)}dx\right\}, \tag{3.17}$$

where $\mu=e^{-\nu(T-\tau)}$. At $T=\tau$ this formula can be reduced by a change of variables to the previous one.

Before distinguishing among the possible situations according to the spectral inhomogeneity parameter Δ/ν, it is useful to analyze the time variation of the sought functions at an arbitrary ratio of ν to Δ, but at different stages of the decay. Expanding up to first-order terms in $\nu\tau$, we can simplify the general formulas

(3.15) and (3.16) to the perfectly lucid forms:

$$K(\tau) = X(-\tau)\exp\left(-\int_0^\tau \Phi(x)\,dx + {}^1/_2\Phi(\tau)\tau\right), \tag{3.18}$$

$$V(2\tau) = \exp\left(-2\int_0^\tau \Phi(x)\,dx - 2\int_0^\tau \frac{\Phi(-\nu x^2)}{\nu x}\,dx\right). \tag{3.19}$$

These expressions differ from those in formulas (2.12) and (2.15) of the paper of Klauder and Anderson[5] in that the latter lack the second terms in the arguments of the exponentials. The absence of these terms is a result of an incorrect transition to the limit in[5]. Klauder and Anderson maintain that by assuming $\nu = 0$ in (3.13) they effect the required transition with an accuracy up to zeroth-order terms in $\nu\tau$. Since they had not established a relationship similar to (3.9) between Φ and the static contour, they overlooked the fact that Φ is not of zeroth but of first order in ν, and it is therefore necessary to retain in the expansion of the exponential at ω' in (3.13) a term of that order of magnitude. This mathematical misunderstanding appears to be the result of having introduced the inappropriate symbols k and m, whose actual dependence on the parameter ν, observed in (3.14), was obscured.

The resultant descrepancies cannot, however, be reduced to purely mathematical ones. Random frequency migration in accordance with (2.14) shifts the frequency distribution towards the center of gravity of the spectrum after each jump, whereas for $f(\omega', \omega) = f(\omega - \omega')$ the center always stays at the same spot as in the beginning. The first process is called inhomogeneous and transforms any initial frequency distribution into a stationary one, while the second (homogeneous) process causes an unlimited broadening of the distribution, inconsistent with any contour of finite width. The limiting transition recommended in[5] has reduced the inhomogeneous process during its initial stage to a simpler homogeneous one which, in the opinion of the authors, was supposed to approximate it correctly.

It was thought that as long as the width of the diffusing distribution was small compared to Δ, the limited nature of the spectrum $\varphi(\omega)$ should not have a telling effect on the course of the process. In reality, however, it does not work that way, and the inhomogeneous process is in principle not reducible to the homogeneous one. The limiting situation in which $\gamma \to 1$ at the same time as $\tau_0 \to 0$ is qualitatively different from the one that can arise when $\gamma \equiv 1$. The difference between them is the same as between diffusion in a parabolic potential well and in free space. The first process is stationary regardless of the degree of curvature of the well, and a particle flow towards the center occurs for any nonequilibrium distribution, however narrow it might be. To top it all, in a one-parameter distribution of type (1.4), to which Klauder and Anderson had recourse in practice, the shift of the function f and its width are given by the same quantity $1 - \gamma$. The diffusion and flux terms are therefore of the same order in $1 - \gamma$: they enter in the diffusion equation that describes frequency migration at n = 2 with linearly-related coefficients[7], similar to the mobility and diffusion coefficients in Einstein's equation. The limiting transition, which is equivalent in effect to dropping the flux term, is therefore not valid, and is the exact reason for the vanishing of equivalent terms in the arguments of the exponentials.

One may estimate the degree to which this affects the results of the calculations by substituting $\Phi(t)$ from (3.9) and (1.6) in (3.18) and (3.19):

$$K(\tau) = X(-\tau)\exp\left\{-\nu\int_0^\tau [Q(\tau) - Q(t)]\,dt + \frac{1}{2}\nu\tau^2\frac{dQ}{d\tau}\right\}, \tag{3.20}$$

$$V(2\tau) = \exp\left\{-2\nu\int_0^\tau [Q(\tau) - Q(t)]\,dt - Q(\nu\tau^2)\right\}. \tag{3.21}$$

The integral terms in the arguments of these exponentials correspond to the "diffusion" components in $K(\tau)$ and $V(2\tau)$, while the others correspond to the "flux" components. Making these formulas specific with the aid of (1.6a) we get:

$$K(\tau) = X(\tau)\exp\frac{\nu\Delta^n n(n-1)}{2(n+1)}\tau^{n+1}, \tag{3.20a}$$

$$V(2\tau) = \exp\left\{-\Delta^n\tau^n\left[\frac{2n}{n+1}\nu\tau + (\nu\tau)^n\right]\right\}. \tag{3.21a}$$

As one can see from (3.18), the competing terms in the exponential arguments have different signs. The numerical coefficients calculated from (3.20a) differ therefore from those given in[5] not only in magnitude, but in sign as well: 1/3 instead of −2/3 for n = 2 and 0 instead of −1/2 for n = 1. In spite of the radical character of these corrections, their effect on free-induction decay is insignificant, since the kinetics is determined principally by the function $X(\tau)$. On the other hand, the fading of the echo signal is given only by the exponential factor, and changes in its argument are even more significant.

The Klauder and Anderson result is obtained from (3.21a) by retaining only the first term in the curly brackets. It is easily seen that for n = 2 this is quite sufficient since the flux term is of the next higher order in $\nu\tau$. For n = 1 these terms are of equivalent magnitude, and consequently the decay rate is increased twofold, while for n = 1/2 the very kinetics of the process is transformed, changing from $\exp(-2/3\nu\sqrt{\Delta}\tau^{3/2})$ into $\exp(-\tau\sqrt{\Delta\nu})$. The latter contour occupies the same intermediate position among the others in the series with respect to the two-pulse echo as the Lorentz contour does in regard to free induction: for $n > 1/2$ decay is faster than exponential, and for $n < 1/2$ it is slower. This case (n = 1/2) is degenerate also in the sense that the decay remains exponential to the very end, whereas all the others retain their form only till $\tau \sim 1/\nu$, taking on an exponential asymptotic form beyond this time limit. Indeed, for $\nu\tau \ll 1$ we get from (3.15) and (3.16)

$$K(\tau) = A\exp\ -\Phi\left(\frac{1}{\nu}\right)\tau\Big] = A\exp\left(-\frac{n\Delta^n}{\nu^{n-1}}\tau\right), \tag{3.22}$$

where

$$A = \exp\left[\left(\frac{\Delta}{\nu}\right)^n n\int_0^1 \frac{1 - x^{n-1}}{1 - x}\,dx\right] \to 1 \quad \text{for} \quad \Delta \ll \nu.$$

Such is the asymptotic decay of all the echo signals: it is exponential and proceeds with the same rate, and at $\Delta \ll \nu$ we have the relation:

$$V(2\tau) = V(T + \tau) = |K(\tau)|^2. \tag{3.23}$$

At n = 1/2 the rate is the same as in the beginning, whereas at $n < 1/2$ it is greater than in the beginning of the process, and at $n > 1/2$ it is less. This rate, as direct comparison with (2.10) shows, differs only by a numerical factor from the one which takes place in the

	$n=2$		$n=1$		$n={}^1/_2$		$n={}^1/_4$	
$-\ln K$	$\Delta^2\tau^2$		$\Delta\tau$		$(\Delta\tau)^{1/2}$		$(\Delta\tau)^{1/4}$	
$-\ln V$	$2\nu\tau$ $(\gamma=0)$	${}^4/_3\,\nu\Delta^2\tau^3$ $(\gamma\to 1)$	$2\nu\tau$ $(\gamma=0)$	$2\Delta\nu\tau^2$ $(\gamma\to 1)$	$2\nu\tau$ $(\gamma=0)$	$(\Delta\nu)^{1/2}\tau$ $(\gamma\to 1)$	$2\nu\tau$ $(\gamma=0)$	$(\Delta\nu)^{1/4}(\tau)^{1/2}$ $(\gamma\to 1)$

noncorrelated process. From the obtained asymptotic estimates, it is easy to form an idea of the kinetics of the process as a whole. In the quasi-static situation ($\Delta \gg \nu$) all signals, disappear almost completely in the interval $0 < \tau < 1/\nu$, while at the end of this interval their amplitude is of the order of $\exp[-(\Delta/\nu)^n] \ll 1$. In this way the observed kinetics of echo decay is described by formulas (3.20) and (3.21), and, in general, has a non-exponential character. The decay rate does not coincide here with the migration frequency and reveals a clear dependence on the width and shape of the static contour. This sharp qualitative difference from what takes place in the noncorrelated process permits us to distinguish them easily (Fig. 2b).

If, however, $\Delta \ll \nu$, i.e., the contour becomes homogeneous, then in full agreement with the foregoing, the decay of all the signals is identical and proceeds at a rate equal to the width of the observed spectrum, starting with the time $\tau > 1/\nu$ where its value is still imperceptibly close to unity: $\exp[-(\Delta/\nu)^n] \approx 1$. This situation replaces the preceding one by a simple shift of the boundary between the non-exponential and exponential decay.

If a situation is encountered intermediate between the two discussed, the form of the solution can still be determined exactly for any n by simple substitution of (3.9) in the general formulas (3.15) and (3.16):

$$K(\tau) = \exp\left(-n\Delta^n \int_0^\tau \eta^{n-1}\,dx\right), \tag{3.24}$$

$$V(2\tau) = \exp\left[-2n\nu\Delta^n \int_0 \frac{\eta^n(1+\nu^{n-1}\eta^{n-1})}{1+\nu\eta}\,dx\right], \tag{3.25}$$

whose limiting behavior agrees with that described above.

As to the three-pulse echo decay, the same thing holds as in the noncorrelated case; it duplicates the shape of free-induction decay at $T-\tau \gg 1/\nu$, as seen directly from (3.12) by putting $\mu = 0$.

CONCLUSION

The aggregate of the information obtained leads to the unambiguous conclusion that it is possible to distinguish between processes with correlated and noncorrelated frequency variation. To this end it is necessary to focus attention on the regions of significant variation of the echo signals and to compare the results that are primarily accessible to observation.

In the quasi-static situation, in view of the variety of the results, the essential data were extracted from the general formulas and reduced to tabular form, allowing one to consider separately and compare the kinetics of echo damping for specific contours, among them the Gaussian (n = 2) and the Lorentzian (n = 1). For the sake of uniformity, the migration frequency is everywhere designated by the letter ν, although in the noncorrelated process it is none other than $1/\tau_0$. It follows obviously from the table that, by comparing the kinetics of free-induction decay and two-pulse decay, it is easy to choose between noncorrelated ($\gamma = 0$) and correlated ($\gamma \to 1$) frequency variation, determining at the same time the parameters of Δ and ν the problem. For all contours, the choice between these mutually exclusive possibilities is unambiguous. And only if n = 1/2, when the kinetics of two-pulse echo decay is exponential in both cases, it is essential to compare the rates at which $K(\tau)$ and $V(2\tau)$ vanish, and their temperature or concentration dependance for a conclusive answer to the question.

Thus, two measurements of the free induction and of two-pulse echo, permit one to distinguish easily between correlated and noncorrelated frequency variation for any contour shape. This conclusion does not, however, extend to homogeneous spectra observed during fast migration ($\Delta \ll \nu$), since in that situation the decay of all signals is identical. It is likewise very important to be able to compare the echo signal with the free induction, the direct observation of which is no simple task. If this is impossible and the Fourier transformation of the spectrum is unreliable, we can obtain the essential information from the three-pulse echo by varying τ at fixed T.

It is interesting to note that for all n > 1, when the "flux" term in the exponent of (3.21) is not significant, the remainder of the expression coincides, apart from a numerical factor, with its analog obtained from formula (2.13). It would seem that the original, non-exponential stage of decay, which exists but is not observed in the noncorrelated process, shifts with increasing correlation ($\gamma \to 1$) towards the region of large times, displacing the exponential asymptote (see Fig. 2).

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