

# NMR measurement and Brownian movement in the short-time limit

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Received 14 July 1993; revised 26 November 1993

## Abstract

This study is carried out to find relations between the time-dependent molecular self-diffusion and the attenuation of NMR spin-echo. Two cases of diffusion are considered: the Brownian motion in Ornstein's short-time limit and the random walk with memory [13]. The friction and the correlation time describe the mechanism of entrapping interactions between molecules or their bonding to macromolecule chains. The obtained formula for the self-diffusion attenuation is valid at short times and it develops into the well-known Torrey's result in the long-time limit. It fits very efficiently into the NMR data from Refs. [19–20].

## 1. Introduction

The determination of molecular migration with nuclear magnetic resonance (NMR) has a long history [1,2,3,5]. Being nondestructive and noninvasive, the method is attractive for the study of molecular random migration in various systems. It uses labelling of molecules by changing the phase of spin precession. A nonuniform magnetic field creates a nonuniform frequency of the spin precession and therefore the particle migration across the field inhomogeneity causes an attenuation of the spin-echo signal.

The expression [3] for the spin-echo attenuation due to the random migration along a time dependent magnetic field gradient ( $G_x = \delta B / \delta x$ ),

$$\ln \frac{S(t)}{S_0} = \beta(t) = \gamma^2 D \int_0^t \left| \int_0^u G_x(t') dt' \right|^2 du, \quad (1)$$

with  $\gamma$  being the giromagnetic ratio of the nuclei and  $D$  the self-diffusion coefficient, assumes Einstein's result from the Brownian movement theory. It states that a mean square of displacement [6] is a linear function of time:

$$\langle [x(t) - x(0)]^2 \rangle = 2Dt. \quad (2)$$

It was first pointed out by Einstein that this formula holds only in the limit of large  $t$ . Accordingly, as noted by Uhlenbeck and Ornstein [7], several later researchers obtained an equation that holds for all time:

$$\langle [x(t) - x(0)]^2 \rangle = 2D \left[ t - \frac{1}{\zeta} (1 - e^{-\zeta t}) \right] \quad (3)$$

where  $\zeta = f/m$ , with  $f$  the coefficient of friction and  $m$  the mass of the Brownian particle. We call it Uhlenbeck's short-time limit. It shows that Torrey's Eq. (1) is an approximation when the duration of measurement is long compared to the correlation time of migrations.

The interaction between particles or the particle interactions with their surroundings influences their migration and, particularly in a short time interval, there is a strong correlation between particle positions. We have shown [8] that the spin-echo attenuation includes the correlation of particle location  $\langle x(t)x(0) \rangle$  or the velocity single particle autocorrelation  $\langle v(t)v(0) \rangle$ . That invoke implies that the NMR spin-echo method may be used to study the correlation of the particle motion.

Recently much interest has been devoted toward the study of phenomena of anomalous self-diffusion. In several cases formula (2) is replaced by a nonlinear diffusion law or some dependence being a smooth function of time. This kind of behaviour follows the Brownian movement in a periodic potential [9] or in a random environment [10,12] where slowing down of the diffusion is a consequence of molecular trapping. NMR measurements in polymers [18,21,20], in a biological tissue [19], in microemulsions [16] and others show an anomalous time dependence of the self-diffusion constant in the long time interval. Some ambiguity is associated with the results of NMR measurement of the self-diffusion in polymers [14]. The authors claim that it is difficult to separate the contributions which are due to translation of a macromolecule as a whole from those due to intermolecular segmental movement. We believe that this ambiguity might appear as a consequence of ignoring the correlation effects hidden in the spin-echo attenuation (8).

In the following we consider the Brownian motion in Uhlenbeck's short-time limit, Eq. [3] and show its relation with the mean square of the particle displacement and with the attenuation of spin-echo. Thereafter, we evaluate the molecular displacement with the use of a generalised Langevin equation with memory formalism [11,13]. This approach may describe the effect of molecular entrapping. The result explains the short time behaviour of molecular migration and shows the relation between NMR spin-echo parameters and microscopic quantities like friction and correlation time of molecular entrapping.

## 2. Spin-echo attenuation in the short-time limit

In the magnetic field gradient  $G$  the phase of a particular spin depends upon its location and the migration of particles modulates the spin phase. In Ref. [8] we have shown that spin-echo damping includes the correlation between the particle velocities at different times. Namely, the central limit theorem allows a Gaussian approximation of the spin-phase modulation function, whenever the particle velocity changes in small independent steps due to the stochastic nature of the interaction. By assuming a uniform diffusion rate of particles, the resulting attenuation of the spin-echo signal is

$$S(\tau) = S_0 e^{-\beta(\tau)} \quad (4)$$

with

$$\beta(\tau) = \frac{1}{2} \int_0^\tau dt_1 \int_0^\tau dt_2 F(t_1) \langle v(t_1)v(t_2) \rangle F(t_2). \quad (5)$$

Here

$$F(t) = \gamma \int_0^t G_{\text{eff}}(t') dt'. \quad (6)$$

The effective magnetic field gradient  $G_{\text{eff}}(t')$  includes the effect of spin inverting by a  $\pi$  pulse [8]. The spin-echo attenuation depends on the autocorrelation of particle velocity. When the time interval of the spin-echo,  $\tau$ , is of same order as the characteristic time of velocity autocorrelations,  $\tau_c$ , the attenuation might contain information about intermolecular interactions. The relation between spin-echo attenuation and the spectrum of the velocity autocorrelation is shown in the Ref. [8]. We derived it by inserting the Fourier transform of the velocity autocorrelation function

$$\langle v(t_1)v(t_2) \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} \tilde{D}(\omega) e^{i\omega(t_1-t_2)} d\omega \quad (7)$$

into Eq. (5). The result is

$$\beta(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathbf{F}(\omega, \tau) \tilde{D}(\omega) \mathbf{F}(-\omega, \tau) d\omega. \quad (8)$$

It includes the definition of the Fourier transform of the spin phase

$$\mathbf{F}(\omega, \tau) = \int_0^{\tau} \mathbf{F}(t) e^{i\omega t} dt. \quad (9)$$

In Eq. (8) the tensor  $\tilde{D}(\omega)$  is the spectrum of the autocorrelation between the velocity components. Its product with the phase factor  $\mathbf{F}(t)$  acts only on diagonal components. At zero frequency these are the components of the self-diffusion tensor,  $\tilde{D}(0)$ .

We need a relation between the mean square of the particle displacement and  $\tilde{D}(\omega)$ :

$$\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle \mathbf{v}(t_1) \mathbf{v}(t_2) \rangle. \quad (10)$$

In the frequency domain [8] it is

$$\langle [x(t) - x(0)]^2 \rangle = \frac{1}{\pi} \int_{-\infty}^{\infty} D_{xx}(\omega) \frac{\sin^2(\omega t/2)}{(\omega/2)^2} d\omega. \quad (11)$$

Uhlenbeck and Ornstein [7] have shown that the frequency spectrum of the velocity autocorrelation follows from Eq. (3) as

$$D(\omega) = \frac{D\zeta^2}{\omega^2 + \zeta^2}. \quad (12)$$

The usual spin-echo pulse sequence, which has two identical gradient pulses of width  $\delta$  and being separated for  $\tau$ , has the spectrum of the spin phase, Eq. (9), in the form

$$\mathbf{F}(\omega, \tau) = \gamma G \frac{(1 - e^{i\omega\tau})(1 - e^{i\omega\delta})}{\omega^2}. \quad (13)$$

By inserting Eq. (12) and Eq. (13) into Eq. (8) it develops into

$$\beta(\tau) = \gamma^2 G^2 \frac{8}{\pi} \int_{-\infty}^{\infty} \frac{\sin^2(\omega\delta/2) \sin^2(\omega\tau/2)}{\omega^4} \times \frac{D\zeta^2}{\omega^2 + \zeta^2} d\omega. \quad (14)$$

Its integration gives the spin-echo attenuation as a function of  $\tau$ ,  $\delta$ ,  $D$  and the constant of friction  $\zeta$ :

$$\beta(\tau) = \gamma^2 G^2 D \left\{ \delta^2 \left( \tau - \frac{\delta}{3} \right) - \frac{2}{\zeta^2} \delta + \frac{1}{\zeta^3} [2 + e^{-(\tau-\delta)\zeta} + e^{-(\tau+\delta)\zeta} - 2e^{-\tau\zeta} - 2e^{-\delta\zeta}] \right\}. \quad (15)$$

We can apply this very general relation in a broad time interval. When  $\tau_c \approx 1/\zeta \ll \tau$  all terms but the first one can be neglected. This term is a well-known classical result [3]. In the limit of short intervals between the gradient pulses, when  $1/\zeta \approx \tau$ , the spin-echo damping (15) (Fig. 1) follows the law

$$\beta(\tau) = \frac{1}{2} \gamma^2 G^2 \zeta D \tau^2 \delta^2 \quad (16)$$

and when  $\delta \ll \tau$ , Eq. (15) develops into

$$\beta(\tau) = \gamma^2 G^2 \delta^2 D \left[ \tau - \frac{1}{\zeta} (1 - e^{-\tau\zeta}) \right]. \quad (17)$$

It is obvious from Eq. (3), that the last formula is the well-known relation between the self-diffusion attenuation and the mean square of the particle displacement

$$\beta(\tau) = \frac{1}{2} \gamma^2 G^2 \delta^2 \langle [x(t) - x(0)]^2 \rangle. \quad (18)$$

On Fig. 1 we can compare the short-time displacement following expression (3) with the classical Brownian movement.

The correlation time of small molecules ( $10^{-9}$  s– $10^{-10}$  s) is much shorter than the interval between the gradient pulses at NMR spin-echo,  $\tau \gg \tau_c$ . Thus we can assume that the velocity

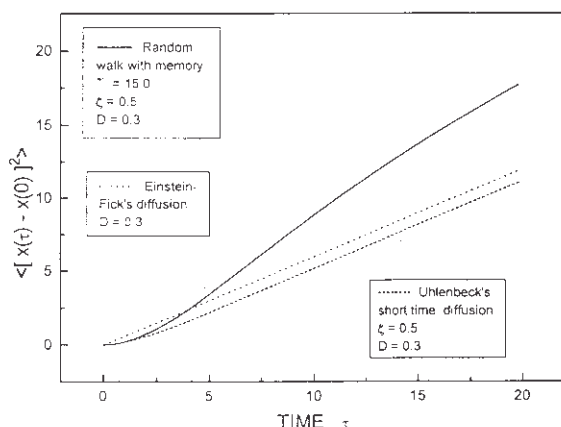


Fig. 1. Mean square of the particle displacement in the short-time limit for three kinds of random motion: Einstein-Fick law, Uhlenbeck and Ornstein's extension of Einstein's diffusion and random motion with memory describing the entrapped diffusion.

autocorrelation function in Eq. (5) is a delta function. It results into Torrey's formula Eq. (1).

### 3. Brownian movement with memory

The measurements show that the deviation from the Einstein-Fick law at NMR self-diffusion measurements appears mostly in fluids containing macromolecules [21,20] or large particles as in a microemulsion [16]. Uhlenbeck and Ornstein [7] show that friction is the main parameter that determines the ordinary Brownian movement in a short-time limit. In dealing with a random migration of molecules in a complex environment there are also other kinds of interaction that may cause the nonclassical behaviour of the self-diffusion. The experimental data and the model calculation show an anomalous time-dependent self-diffusion in the environment that, in addition to friction, acts on molecules with some sort of trapping mechanism. This kind of deviation has been found in the model of Brownian movement in a periodic potential [9] and in some specific cases of macromolecules in the random environment [10–12].

In the following we will use the approach with

the Langevin equation that includes the memory function [13] in order to consider a Brownian movement of partially entrapped molecules. The projection operator technique leads to a decomposition of the rates of change of variables into several parts resulting into the general Langevin equation of movement for stochastic movement

$$\frac{dA(t)}{dt} - i\omega A(t) + \int_0^t \phi(t-s)A(s) ds = F(t). \quad (19)$$

$\phi(t)$  is the memory function obtained for damping of collective movement determined by  $\omega$ . This extension of the Langevin equation is proposed to incorporate the case when the Brownian particle is not necessarily of large mass compared with the molecules constituting the fluid. The implication of this generalisation is that the relaxation time of the random force, being very small compared with the velocity relaxation time, has to be abandoned.

This model describes a random walk of molecules or parts of macromolecules with two basic constraints of motion:

- a friction that slows down their motion;
- a localised movement provided by direct pair interaction with nearby molecules or by interaction of segments of macromolecule with remaining parts.

It is a random molecular movement that is neither distinct Brownian movement nor only a movement of bonded particles but something in between both models.

The Langevin equation with memory can take the form

$$m \frac{dv(t)}{dt} + m \int_0^t K(t-\tau)v(\tau) d\tau = F(t) \quad (20)$$

where the particle velocity  $v(t)$  is the dynamic variable and  $F(t)$  is a stochastic driving force defined by the coupling of the particle to the surroundings. With included collective oscillation  $\omega$ , the memory function  $K(t)$  describes the viscoelastic damping properties of the surrounding. With short memory,  $K(t) = \zeta\delta(t)$ , it is the classi-



cal Langevin equation describing a damped diffusion of free particles. In the case of infinite memory,  $K = \text{const.}$ , it describes a Brownian movement of bounded particles [7] i.e. the random movement of harmonic oscillators.

Equation (20) can be written as

$$\frac{dv(t)}{dt} + \int_{-\infty}^t \zeta(\tau)v(t+\tau) d\tau = f(t) \quad (21)$$

with the assumption that  $f(t) = D\delta(t)$ . Since  $f(t)$  is Gaussian,  $v(t)$  is also a Gaussian random process [7] with a single-particle velocity autocorrelation spectrum

$$D(\omega) = \frac{f_\omega}{|i\omega + \zeta_\omega|^2}. \quad (22)$$

$\zeta_\omega$  is the spectrum of the memory function. The simplest form of the memory function is the exponential function

$$\zeta(t) = \frac{\zeta}{T} e^{-t/T} \quad (23)$$

with  $T$  being the relaxation time, which determines the degree of particle bonding. Equation (23) gives the spectrum of the velocity autocorrelations

$$D(\omega) = \frac{D\zeta^2}{|i\omega + \zeta/(-i\omega T + 1)|^2} \quad (24)$$

$$= \frac{D\zeta^2 T^2 [(\omega T)^2 + 1]}{[(\omega T)^2 + \zeta T]^2 + (\omega T)^2}. \quad (25)$$

Knowing the spectrum of the velocity autocorrelation function we can obtain the mean square of the displacement as a function of time by substituting Eq. (25) into Eq. (11). Its integration gives

$$\langle [x(t) - x(0)]^2 \rangle = 2D[t + A(1 - e^{-t\kappa_1/T}) - B(1 - e^{-t\kappa_2/T})] \quad (26)$$

with

$$A = \frac{x_1^2 x_2^2 (1 - x_1^2)}{(x_2^2 - x_1^2) x_1^3} T \quad (27)$$

and

$$B = \frac{x_1^2 x_2^2 (1 - x_2^2)}{(x_2^2 - x_1^2) x_2^3} T \quad (28)$$

where

$$x_{1,2}^2 = \frac{1}{2} + \zeta T \mp \sqrt{\frac{1}{4} + \zeta T}. \quad (29)$$

This equation has the following properties.

- In the limit of short correlation times  $1/\zeta \gg T$ , Eq. (26) is converted into Eq. (3) and behaves like Uhlenbeck and Ornstein's extension of Einstein's diffusion in the short-time limit [7].

- When  $T\zeta \gg 1$  it exhibits the long-time asymptotic behaviour

$$\langle [x(t) - x(0)]^2 \rangle = 2D \left[ t + \frac{T\sqrt{T\zeta}}{2} (1 - e^{-t\sqrt{\zeta/T}}) \right] \quad (30)$$

which diverges into a line with slope of the normal Einstein–Fick law, see Fig. 1.

Figure 1 shows a strong deviation from these behaviours at intermediate times when  $\zeta T \approx 1$  and  $t \approx T$ . The mean square of displacement for the Brownian diffusion and Uhlenbeck's limits of Einstein's diffusion is shown on Fig. 1. For the same value of  $D$  they exhibit very different behaviour for certain values of friction  $\zeta$  and correlation time  $T$ .

Schweizer formulated [17] a polymeric mode–mode coupling theory, with the relevant bilinear variables being the product of the collective density field and the single chain segmental densities. He derives the segmental mean square displacement in the Markov regime, which has an identical time dependence as Eq. (30):

$$\langle [r(t) - r(0)]^2 \rangle \approx Dt + \frac{N\sigma^2}{36} (1 - e^{-tK_s/M_t(0)}). \quad (31)$$

Here the  $M_t(0)$  term is associated with the intramolecular elastic restoring forces induced by intermolecular excluded volume interactions, and the  $K_s$  term is the entropic spring constant. It predicts that the center of mass and the internal modes make a comparable contribution to diffusion.

For the spin-echo pulse sequence when  $\delta \ll \tau$ , we can use the relation between the spin-echo

attenuation and the square of particle displacement Eq. (18). Together with Eq. (26) and Eq. (30) it can be used to evaluate the experimental data. But whenever at spin-echo the gradient pulse width is comparable with the pulse interspace,  $\delta \approx \tau$ , we have to carry out a little bit more elaborate integration in order to get the spin-echo attenuation. The substitution of Eq. (25) and Eq. (13) in Eq. (8) gives

$$\beta(\tau) = \gamma^2 G^2 D \frac{\zeta^2 T^2}{x_2^2 - x_1^2} \left[ \frac{1 - x_1^2}{x_1^2} f\left(\tau, \delta, \frac{x_1}{T}\right) - \frac{1 - x_2^2}{x_2^2} f\left(\tau, \delta, \frac{x_2}{T}\right) \right] \quad (32)$$

with

$$f(\tau, \delta, a) = \delta^2 \left( \tau - \frac{\delta}{3} \right) - \frac{2}{a^2} \delta + \frac{1}{a^3} [2 + e^{-(\tau-\delta)a} + e^{-(\tau+\delta)a} - 2e^{-\tau a} - 2e^{-\delta a}]. \quad (33)$$

In the limit of  $\delta \ll \tau$ , it is equal to Eq. (18) and in the limit of  $\zeta T \ll 1$ , it becomes equal to Eq. (15). Figure 2 shows the spin-echo attenuation (divided by the square of the gradient pulse width and its magnitude) as a function of the interval between gradient pulses  $\tau$  and the pulse width  $\delta$ .

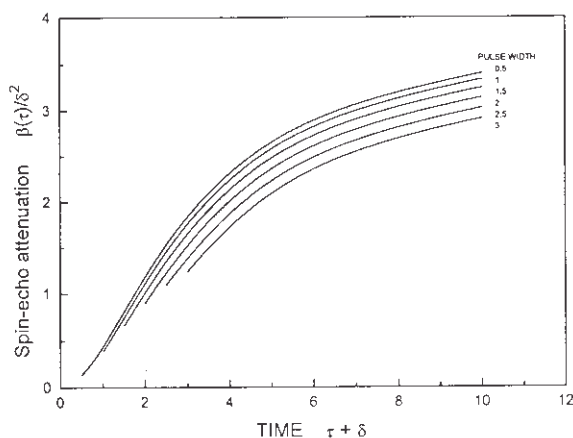


Fig. 2. Spin-echo attenuation of the random walk with memory for different widths of gradient pulses  $\delta$  and gradient pulse interspace  $\tau$ .

We can see that a broader gradient pulse causes only a shift of curve and does not alter its shape.

#### 4. Experimental evidence

We fit expression (26) into the experimental NMR data of different authors reporting about the time dependent of self-diffusion. These are measurements of self-diffusion of polymers [21], of polydispersed media [20] and water in the lung tissue [19].

In the first two cases the diffusing particles are large molecule-polymers, and we assume that the time of particle correlation may be on the time scale of the NMR measurement, since the correlation time of migration increases with molecular mass [3]. The anomalous diffusion described by Eq. (31) or Eq. (26) may take part in these systems.

In Ref. [21] the authors found a spin-echo attenuation in the solution of a polymer that does not match an exponential law. The digression increases with concentration of the solvent. They attribute it to the distribution of the self-diffusion coefficient due to different diffusion rates of macromolecules having different size (polydispersity). Zupančič et al. [18] have found a similar deviation from an exponential law in spite of very small polydispersity of their polymers. Thus there might be an alternative explanation of these results. We have found a very good fit of these data into a curve drawn according to Eq. (26). The experimental values of  $\tau$ ,  $G$  and  $\delta$  are not available to us and we obtain the parameters  $T$ ,  $D$  and  $\zeta$  in arbitrary units, see Fig. 3. The fit shows that an increasing octane concentration reduces the self-diffusion constant  $D$  while the correlation time  $T$  and the friction  $\zeta$  remain almost unchanged. It can be explained with the fact that at higher concentration octane decreases only the diffusion rate of the macromolecules as a whole, but it does not effect the trapping mechanism of macromolecules segments. The short-time behaviour of diffusion depends on the segmental motion and reflects the interactions between adjacent molecules inside the macromolecular chain.

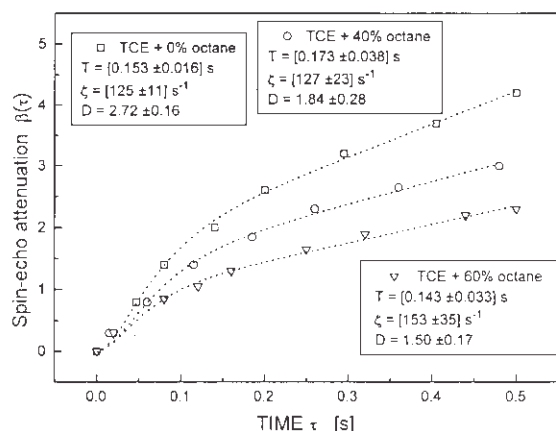


Fig. 3. Fit of the squared random displacement of entrapped diffusion to NMR measurements from Grinberg et al. [21].

The measurement of water self-diffusion in a lung tissue [19] is another example of our consideration. Kveder et al. found that the self-diffusion coefficient is nearly an order of magnitude smaller than that of free water and varies with time. They found the mean-square displacement that varies as an inverse square root. It agrees with the fractal kind of diffusion. Good matching of their data [19] into Eq. (26), see Fig. 4, raises the question about a possible alternative explanation. The shape of the fitting curve is in favour of the interpretation with the model of entrapped molecules. It may be due to a clustering of

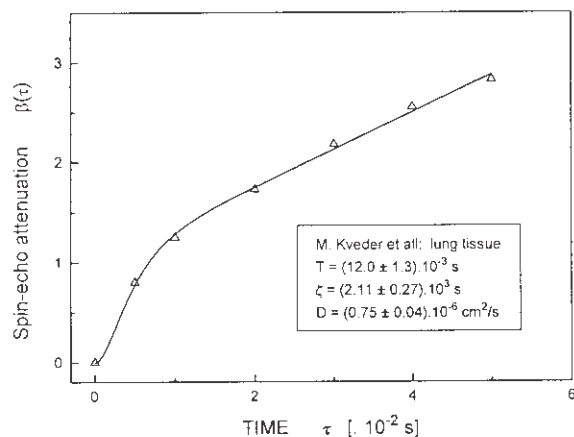


Fig. 4. Fit of the squared random displacement of entrapped diffusion to NMR data from Kveder et al. [19].

water molecules or to their bonding to other macromolecules in a lung tissue.

Von Meerwall [20] has systematically studied the effects of polydispersity on spin-echo attenuation and he attributes to it a small deviation of his data from a linear law. Our expression, Eq. (26), fits into his data very well too and we believe that it can not be explained only by polydispersity. We only mention it in order to additionally stress our arguments but it is not shown here.

## 5. Conclusion

We believe that microscopic cooperative phenomena are responsible for the anomalous results of the self-diffusion coefficient measured by NMR in short time intervals. The description of the entrapping mechanism by the memory function in the Langevin equation is a rough model but it gives a shape of the correlation function that is very similar to that obtained by the calculation of more specific models [9,10,12]. We believe that in a macromolecular fluid or in a system with a kind of molecular clustering the correlation time can be long enough to be seen on the time scale of an NMR experiment. The development of fast spin-echo sequences may enable the NMR investigation of still faster particle migrations.

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