# Theory of diffusive damping of spin-echo signal in a medium with random obstacles

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The information embodied in the amplitude of the stimulated nuclear spin echo with pulsed gradients of the magnetic field of a particle moving in a random force field is discussed. The motion of the particle is described by the Smoluchowski equation. An equation is derived for the instantaneous diffusion coefficient $\tilde{D}(t)$ of a particle; this diffusion coefficient depends on the time. The most informative characteristic of the interaction of the particle with the random medium is shown to be the initial value of the time derivative of this diffusion coefficient: $[d\tilde{D}(t)/dt]_{t=0}$. This initial value is proportional to the dispersion of the random force between the particle and the medium.

## 1. INTRODUCTION

The problem of a random walk in a medium with random obstacles or, more generally, in the field of a random potential arises in a natural way in many fields of physics. Examples are the diffusion of molecules through porous media, the passage of molecules through the membranes of biological cells, and the diffusion of molecules in disperse solutions (Refs. 1–6, for example).

One of the most important methods for experimentally studying spatial movements of molecules is the stimulated spin echo with a pulsed magnetic field gradient.[7–9] That method is also used fairly widely in research on spatially varying heterogeneous media.[6] The quantity which is measured in this method is the so-called amplitude of the diffusive damping of the spin echo, which contains information about spatial displacements of the molecules of interest. The displacements depend on the particular way in which the particle interacts with the random heterogeneous medium. The spin-echo method could thus in principle be used to study the characteristics of the random field.

To the best of our knowledge, there is no comprehensive theory for this method in random media. The primary difficulties are in constructing a detailed description of the self-diffusion of a particle in a random force field. In papers closely related to the spin-echo method, the heterogeneous medium is usually treated as a system of "geometric" obstacles. When that approach is taken, diffusion equations arise in a natural way, and the heterogeneity of the medium is reflected in the particular boundary conditions at the obstacles. Not surprisingly, the only more or less meaningful results which have been found in this case are on highly symmetric (i.e., nonrandom) systems (see, for example, Refs. 6 and 10–13).

Another drawback of that approach is the complexity of using boundary conditions to reflect the details of the interaction of the particle with the random medium, e.g., solvation effects and the depth of the surface layer in which the particle interacts effectively with the obstacles.

In this paper we attempt to derive on a more general basis a theory for the diffusion attenuation of the spin-echo signal of a particle moving through a random force field and to determine what type of information is embodied in the amplitude of the diffusion attenuation.

## 2. THE SMOLUCHOWSKI EQUATION; INSTANTANEOUS DIFFUSION COEFFICIENT

We describe the obstacles by means of an effective random potential $U(\mathbf{r})$, which is induced by the heterogeneous medium. Inside an obstacle we have $U(\mathbf{r}) \to \infty$, and outside it $U(\mathbf{r}) \to 0$. At the boundaries of the obstacles, the potential grows; in all cases of physical interest, this growth can be assumed to be smooth. We assume that the random field $U(\mathbf{r})$ does not depend on the time, i.e., that the obstacles are fairly massive in comparison with the molecules of interest, so their motion can be ignored.

The probability density $W(\mathbf{r}, t)$ for displacements of a molecule—the Green's function—satisfies the Smoluchowski equation (Refs. 14 and 15, for example)

$$\frac{\partial}{\partial t} W(\mathbf{r}, t) = D_0 \frac{\partial}{\partial \mathbf{r}} \left[ \frac{\partial}{\partial \mathbf{r}} - \frac{1}{kT} \mathbf{f}(\mathbf{r}) \right] W(\mathbf{r}, t), \qquad (1)$$

where $D_0$ is the self-diffusion coefficient of molecules in the absence of obstacles, i.e., in the pure liquid, $f(\mathbf{r}) = -\partial U(\mathbf{r})/\partial \mathbf{r}$ is the force induced by the random potential, $t$ is the time, and $\mathbf{r}$ is the radius vector of the molecule.

Knowing the Green's function, we can calculate in the standard way the mean square displacement of a molecule which starts from the point $\mathbf{r} = 0$:

$$\langle r^2(t) \rangle_t = \int r^2 W(\mathbf{r}, t)\, d^3 r. \qquad (2)$$

We define the instantaneous diffusion coefficient:

$$\tilde{D}(t) \equiv \frac{1}{6} \frac{d}{dt} \langle r^2(t) \rangle_t. \qquad (3)$$

Using (1) and (2), changing the order of integration and differentiation, we can put (3) in the form

$$\tilde{D}(t) = \frac{D_0}{6} \int r^2 \frac{\partial}{\partial \mathbf{r}} \left( \frac{\partial}{\partial \mathbf{r}} - \frac{\mathbf{f}(\mathbf{r})}{kT} \right) W(\mathbf{r}, t)\, d^3 r. \qquad (4)$$

Replacing the differential operator in (4) by its adjoint, i.e., integrating by parts twice, we find the following expression for the instantaneous self-diffusion coefficient:

$$\tilde{D}(t) = D_0 \left( 1 + \frac{1}{3kT} \langle \mathbf{r} \mathbf{f}(\mathbf{r}) \rangle_t \right), \qquad (5)$$

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where

$$\langle \mathbf{r}\mathbf{f}(\mathbf{r})\rangle_t \equiv \int \mathbf{r}\mathbf{f}(\mathbf{r})\, W(\mathbf{r},t)\, d^3r$$

mean an average over the Green's function.

Taking the limit of (5) as $t\to\infty$, we find the self-diffusion coefficient of the molecule in the random field:

$$\tilde{D}=D_0\left(1+\frac{1}{3kT}\langle \mathbf{r}\mathbf{f}(\mathbf{r})\rangle_\infty\right), \qquad (6)$$

where $\langle\ldots\rangle_\infty = \lim_{t\to\infty}\langle\ldots\rangle_t$. The second term in (6) describes the correction to the self-diffusion coefficient due to the interaction with the random field. For random fields which are spatially uniform at the macroscopic level, i.e., for fields with a finite correlation radius $\xi$, expression (6) is independent of the choice of origin of coordinates. For fields of more complex structure, solutions of the Smoluchowski equation generally do no have a diffusive asymptotic behavior, and expression (6) is a random function of the choice of starting point of the particle.

We also note that, although the expression for the coefficient $\tilde{D}$ actually is exceedingly simple in structure, an actual calculation of this coefficient from (6) has serious mathematical problems. The basic difficulty is that the operations of taking the limits $t\to\infty$ and $V\to\infty$ ($V$ is the spatial volume of the system) do not commute. These limits appear in expression (6). The limit $V\to\infty$ should be taken first, and then $t\to\infty$. Unfortunately, we are then unable to make use of the well-known fact that the Green's function tends in the limit $t\to\infty$ toward the equilibrium Boltzmann distribution. The details of the process by which the equilibrium is established turn out to be of fundamental importance, as can be seen from the presence of a quantity in (6) which is singular in the limit $V\to\infty$, the radius vector of the particle. For fields which are spatially uniform at the macroscopic level, the equilibrium average, on the other hand, is identically zero: $\langle \mathbf{r}\mathbf{f}(\mathbf{r})\rangle_{eq}\equiv 0$. It is thus natural to turn to an analysis of properties the motion which can at least in principle be calculated exactly. A search for such properties is aided by the following considerations.

The initial ($t=0$) value of the Green's function is known exactly: $W(\mathbf{r},0)=\delta(\mathbf{r})$. By virtue of this one can hope that any average over it can be taken all the way to a numerical result. It is thus clear that the properties we need must be average values of physical quantities which are nonsingular in the limit $t\to 0$.

The simplest nontrivial quantity of this sort is the rate of change of the instantaneous diffusion coefficient, $d\tilde{D}(t)/dt$. It is useful, however, to slightly alter the definition of $\tilde{D}(t)$ in (5) because $\tilde{D}(t)$, unlike its limiting value $\tilde{D}$, depends on the choice of origin or coordinates. At finite times $t$ the Green's function will always evolve in different ways, depending on whether the starting point for the particle is a minimum or maximum of the potential $U(\mathbf{r})$. We will thus understand $\tilde{D}(t)$ below as the quantity in (5) averaged over all possible initial positions of the particle with an equilibrium Boltzmann distribution. The angle brackets $\langle\ldots\rangle_t$ will now contain two integrations:

$$\langle \mathbf{r}\mathbf{f}(\mathbf{r})\rangle_t = \int d^3r_0\, W_{eq}(\mathbf{r}_0) \int \mathbf{r}'\mathbf{f}(\mathbf{r})\, W(\mathbf{r}',t)\, d^3r, \qquad (7)$$

where $\mathbf{r}'=\mathbf{r}-\mathbf{r}_0$, and $W_{eg}(\mathbf{r}_0)$ is an equilibrium Boltzmann distribution with a potential $U(\mathbf{r}_0)$. Using Eq. (1), we then find the following equation for the rate of change of the instantaneous diffusion coefficient:

$$\frac{d}{dt}\tilde{D}(t)=\frac{D_0^2}{3kT}\int d^3r_0\, W_{eq}(\mathbf{r}_0)\int d^3r\, \mathbf{r}'\mathbf{f}(\mathbf{r})\hat{\mathscr{L}}W(\mathbf{r}-\mathbf{r}_0,t), \qquad (8)$$

where $\hat{\mathscr{L}}$ is the differential Smoluchowski operator,

$$\hat{\mathscr{L}}\equiv\frac{\partial}{\partial\mathbf{r}}\left[\frac{\partial}{\partial\mathbf{r}}-\frac{\mathbf{f}(\mathbf{r})}{kT}\right].$$

For convenience in the discussion below, we rewrite the Green's function $W(\mathbf{r}-\mathbf{r}_0,\ t)$ in the form

$$W(\mathbf{r}-\mathbf{r}_0,\ t)=\hat{S}(t)\,\delta(\mathbf{r}-\mathbf{r}_0), \qquad (9)$$

where the evolution operator is $\hat{s}(t)\equiv\exp(D_0 t\hat{\mathscr{L}})$.

Replacing the operators $\hat{\mathscr{L}}$ and $\hat{s}(t)$ in (8) by their adjoints, we find

$$\frac{d}{dt}\tilde{D}(t)=\frac{D_0^2}{3kT}\int d^3r_0\, W_{eq}(\mathbf{r}_0)\int \delta(\mathbf{r}-\mathbf{r}_0)\,\hat{S}^*(t)\,\hat{\mathscr{L}}^*\mathbf{r}'\mathbf{f}(\mathbf{r}). \qquad (10)$$

The validity of the following commutation relations for $\hat{\mathscr{L}}^*$ and the "coordinate operator" $x'_\alpha$ is easily verified:

$$[\hat{\mathscr{L}}^*, x_\alpha{}']=2\frac{\partial}{\partial x_\alpha{}'}+\frac{1}{kT}f_\alpha(r)\equiv\hat{\psi}_\alpha. \qquad (11)$$

We expand the adjoint of the evolution operator, $\hat{S}^*(t)$, in (10) in a Taylor series. Then using the commutation relations (11) we "pull" the "coordinate operators" $x'_\alpha$ of the particle through the operator product $\hat{s}^*(t)\hat{\mathscr{L}}^*$. After integration over $\mathbf{r}$, we find the following equation for the rate of change of the instantaneous diffusion coefficient:

$$\frac{d}{dt}\tilde{D}(t)=\frac{D_0^2}{3kT}\int d^3r_0\, W_{eq}(\mathbf{r}_0)\sum_{n=0}^{\infty}\frac{(D_0t)^n}{n!}\sum_{k=0}^{n}\hat{\mathscr{L}}^{*k}\hat{\psi}_\alpha\mathscr{L}^{*n-k}f_\alpha(\mathbf{r}_0). \qquad (12)$$

A repeated coordinate index implies summation.

Equation (10) contains a $\delta$-function, so the differential operators in (12) depend on $\mathbf{r}_0$ alone. We can thus replace these operators by their adjoints again. Doing this, and assuming that the equilibrium distribution $W_{eg}(\mathbf{r}_0)$ belongs to the kernel of the operator $\hat{\mathscr{L}}$ i.e., $\hat{\mathscr{L}}W_{eq}(\mathbf{r}_0)=0$, we put (12) in the form

$$\frac{d}{dt}\tilde{D}(t)=\frac{D_0^2}{3kT}\int d^3r\, f_\alpha(\mathbf{r})\,\hat{S}(t)\left[-2\frac{\partial}{\partial x_\alpha}+\frac{1}{kT}f_\alpha(r)\right]W_{eq}(\mathbf{r}). \qquad (13)$$

We now make use of

$$W_{eq}(\mathbf{r})=\frac{1}{Z}\exp\left[\frac{-U(\mathbf{r})}{kT}\right], \qquad (14)$$

where

$$Z=\int d^3\mathbf{r}\,\exp\left[\frac{-U(\mathbf{r})}{kT}\right]$$

is the partition function of the particle in the random field. Substituting (14) into (13), we find

$$\frac{d}{dt}\tilde{D}(t)=-\frac{D_0^2}{3(kT)^2}\int\frac{d^3r}{Z}\mathbf{f}(\mathbf{r})\,\hat{S}(t)\mathbf{f}(\mathbf{r})\exp\left[\frac{-U(\mathbf{r})}{kT}\right]. \qquad (15)$$

The quantity

$$\mathbf{f}(t)\equiv\frac{1}{Z}\hat{S}(t)\mathbf{f}(\mathbf{r})\exp\left[-\frac{U(r)}{kT}\right]$$

may be interpreted as the force acting on the particle at the time $t$ if a force $\mathbf{f}(\mathbf{r})\equiv\mathbf{f}(0)$ was acting at the time $t=0$. Equation (15) then has the very simple structure

$$\frac{d}{dt}\tilde{D}(t)=-\frac{D_0^2}{3(kT)^2}\langle\mathbf{f}(t)\mathbf{f}(0)\rangle_t. \qquad (16)$$

The limiting value of the diffusion coefficient $\tilde{D}$ can be written as an integral of the autocorrelation function $\langle\mathbf{f}(t)\mathbf{f}(0)\rangle_t$:

$$\tilde{D}=D_0\left(1-\frac{D_0}{3(kT)^2}\int_0^\infty\langle\mathbf{f}(\mathbf{t})\mathbf{f}(0)\rangle_t dt\right). \qquad (17)$$

For the initial time $t=0$ we have $\hat{S}(0)=1$, so the initial rate of change of the diffusion coefficient is proportional to the variance of the random force. A calculation of this variance requires knowledge only of the equilibrium Boltzmann distribution:

$$\frac{d}{dt}\tilde{D}(t)\,|_{t=0}=-\frac{D_0^2}{3(kT)^2}\langle f^2(\mathbf{r})\rangle_{eq}. \qquad (18)$$

## 3. DIFFUSIVE DAMPING OF A STIMULATED SPIN ECHO

In the method of the stimulated spin echo (SSE), the measured quantity, called the "amplitude of the diffusive damping," is the following dynamic correlation function of the molecules of interest:

$$A(g^2)=\left\langle\exp\left\{-i\gamma g\int_0^\delta[z_i(t+\tau)-z_i(\tau)]d\tau\right\}\right\rangle. \qquad (19)$$

Here $g$, $\delta$, and $t$ are parameters which can be controlled experimentally; $g$ is the magnitude of the pulsed magnetic-field gradients along the $z$ axis; $\delta$ is the length of the gradient pulses; $t$ is the duration of the "diffusion," i.e., the time interval between the first and second gradient pulses; $\gamma$ is the gyromagnetic ratio of the nuclei of the molecules; $z_i(\tau)$ is the coordinate of molecule $i$ at time $\tau$; and the angle brackets mean an average over all random trajectories of all molecules.

In general, SSE experiments are carried out in such a way that the inequality $t\gg\delta$ always holds. One can thus ignore the displacements of the nuclei of the molecules over times of order $\delta$ in comparison with displacements over the "diffusion" time $t$. In such cases, expression (19), for the amplitude of the diffusive damping, can be simplified:

$$A(g^2,t)=\langle\exp\{-i\gamma g\delta[z(t)-z(0)]\}\rangle. \qquad (20)$$

The amplitude in (20) is the same as the dynamic incoherent Van Hove structure factor (Ref. 14, for example):

$$A(k^2,t)=\langle e^{-ikr}\rangle. \qquad (21)$$

This structure factor can be measured by neutron scattering. In the SSE method, $\gamma\delta g$ is the analog of the wave vector $\mathbf{k}$ of the neutron scattering.

Taking the time derivative of Eq. (21), and using Eq. (1), we find

$$\frac{d}{dt}A(k^2)=D_0\int e^{-i\mathbf{kr}}\frac{\partial}{\partial\mathbf{r}}\left[\frac{\partial}{\partial\mathbf{r}}-\frac{1}{kT}\mathbf{f}(\mathbf{r})\right]W(\mathbf{r},t)d^3r. \qquad (22)$$

Replacing the differential Smoluchowski operator in (22) by its adjoint, we can put the equation for the dynamic structure factor in the form

$$\frac{d}{dt}A(k^2)=k^2D_0A(k^2)+i\frac{D_0}{kT}k_\alpha\int W(\mathbf{r},t)e^{-i\mathbf{kr}}f_\alpha(\mathbf{r})d^3r. \quad (23)$$

The first term in (23) describes the free diffusion of the molecules of a liquid, and the second describes the perturbation of this motion caused by the random field. The presence of this perturbation makes Eq. (23) an integral equation and seriously complicates efforts to solve it. However, certain general properties of the solution which are important to the SSE method are amenable to analysis.

We seek solutions of Eq. (23) in the form

$$A(k^2)=\exp[-\alpha_1(t)k^2+\alpha_2(t)k^4+\ldots], \qquad (24)$$

where the series coefficients $\alpha_1(t)$ and $\alpha_2(t)$ are unknown functions of the time. The medium is assumed to be neutral and, for simplicity, macroscopically isotropic. We can thus restrict the series (24) to even powers of the wave vector, in the simplest algebraic combinations.

We expand $\exp(-i\mathbf{k}\cdot\mathbf{r})$ in (24) in a Taylor series and substitute (24) into Eq. (22). Comparing the coefficients of the terms proportional to $k^2$ and $k^4$, we find the equations

$$\frac{d}{dt}\alpha_1(t)=\tilde{D}(t)=D_0\left(1+\frac{1}{3kT}\langle\mathbf{rf}(\mathbf{r})\rangle_t\right), \qquad (25)$$

$$\frac{d}{dt}\alpha_2(t)=\frac{D_0}{3kT}\left\{\frac{1}{2}\langle(\mathbf{ef})(\mathbf{er})^3\rangle_t-\langle\mathbf{rf}(\mathbf{r})\rangle\alpha_1(t)\right\}, \qquad (26)$$

where $\mathbf{e}$ is a unit vector which is collinear with the wave vector $\mathbf{k}$.

The quantity $\alpha_1(t)$ determines the initial slope of the spin-echo amplitude which is measured experimentally, $\ln A(k^2)$. As can be seen from Eq. (25), this initial slope is closely related to the mean square displacement of a particle during the experiment:

$$\langle r^2(t)\rangle_t=6\int_0^t\tilde{D}(t)dt=6\alpha_1(t). \qquad (27)$$

Experiments generally use not the quantity $\alpha_1(t)$ itself but a quantity which is closely related to it, by

$$\alpha_1(t)\equiv D^*(t)t. \qquad (28)$$

The "effective self-diffusion coefficient" $D^*(t)$ is related in the obvious way to the instantaneous self-diffusion coefficient $\tilde{D}(t)$:

$$D^*(t)=\int_0^t\frac{d\tau}{t}\tilde{D}(\tau). \qquad (29)$$

The quantity $\alpha_2(t)$ determines the initial deviation of the quantity $\ln A(k^2)$, measured experimentally, from a straight line. It can be seen from Eq. (26) that early in the process, at times $6D_0t\ll\xi^2$, where $\xi$ is the correlation radius of the random field, we have

$$\lim_{t\to 0}\frac{d}{dt}\alpha_2(t)=0.$$

After a sufficiently long time, $6\tilde{D}(\infty)t \gg \xi^2$, on the other hand, the solutions of Eq. (1) reach the diffusive asymptotic behavior. The distribution of spatial positions of a particle thus tends toward a normal distribution. By virtue of the Wick theorem for quantities with a normal distribution, however, we then have

$$\langle(\mathbf{ef})(\mathbf{er})^3\rangle_t \to 3\langle(\mathbf{ef})(\mathbf{er})\rangle_t\langle(\mathbf{er})^2\rangle_t = \langle\mathbf{rf}(\mathbf{r})\rangle_t\langle(\mathbf{er})^2\rangle_t,$$

and thus

$$\lim_{t\to\infty}\frac{d}{dt}\alpha_2(t) = 0$$

in comparison with quantities on the order of $t$. We thus find

$$\begin{aligned} &\alpha_2(t) \approx 0, \quad t \ll \xi^2/D_0,\\ &\alpha_2(t)t^{-2} \approx 0, \quad t \gg \xi^2/\tilde{D}. \end{aligned} \tag{30}$$

Experiments by the SSE method are carried out in such a way that the condition $\delta^2 t = \text{const}$ holds. Since $k = \gamma\delta g$, it follows from (30) that the diffusive damping tends toward an exponential behavior with an effective diffusion coefficient $D^*(t)$ at early times and at late times.

The initial rate of change of the effective coefficient $D^*(t)$ is related in a simple way to the initial rate of change of the instantaneous diffusion coefficient $D^*(t)$, as can be seen from the definition (29):

$$\frac{d}{dt}D^*|_{t=0} = \frac{1}{2}\frac{d}{dt}\tilde{D}|_{t=0} = -\frac{D_0^2}{6(kT)^2}\langle f^2(\mathbf{r})\rangle_{eq}. \tag{31}$$

## 4. DISCUSSION OF RESULTS

Experimental studies of the interaction of molecules with heterogeneous media by the method of the diffusive damping of the spin echo (see the review of this work in Ref. 6) have focused primarily on measuring the effective diffusion coefficient $D^*(t)$ and then interpreting it in some way or other. The expressions derived in the present paper for $D^*(t)$ and for the related quantity $\tilde{D}(t)$ [see (5), (6), (16), and (18)] are distinguished by their exceptionally simple physical meaning. However, some formidable mathematical difficulties lurk in the operation $\langle\ldots\rangle_t$, i.e., the operation of taking an average with the exact Green's function of Smoluchowski equation (1). These difficulties are serious impediments to calculations of $D^*(t)$ and $\tilde{D}(t)$ and thus to a reliable interpretation.

We first see from (17) and (31) that the initial rates of change of the instantaneous and effective diffusion coefficients $[d\tilde{D}(t)/dt)_{t=0}$ and $[dD^*(t)/dt\,]_{t=0}$ are directly related to the nature of the interaction of the molecules with the random medium. A point of even greater importance for a theoretical interpretation is that these rates of change contain only the operation of taking an average with the equilibrium distribution function. Second, fairly general considerations show that the initial rate of change $[dD(t)/dt\,]_{t=0}$ is in principle more informative than the limiting value $\tilde{D}(\infty)$.

The limiting value of the self-diffusion coefficient $\tilde{D}(\infty)$ contains information about a huge number of collisions of the molecule of interest with various centers of the random field $U(\mathbf{r})$. The information about it is thus averaged out to a great extent. The initial value of the derivative, $[dD(t)/dt\,]_{t=0}$, contains mostly information about the first encounter of the molecule with a force center; this information is "fresher" and "has suffered less erosion."

For greater clarity we consider the situation in which the random field is induced by a system of randomly positioned geometric obstacles. Approximate calculations show (see, for example, Refs. 2, 3, 5, and 6) that the limiting value of the diffusion coefficient, $\tilde{D}(\infty)$, is a function exclusively of the volume fraction of obstacles; it does not depend on even the dimensions of these obstacles. The quantity $\langle f^2(\mathbf{r})\rangle_{eq}$, on the other hand, which appears in (18) and (31), is considerably more informative. For example, omitting the elementary but fairly lengthy calculations involved, we write the result for a system of geometric spheres scattered randomly in space [these spheres have a radius $r_0$ and a volume concentration $\varphi$; they repel the liquid molecules with a potential $U(r) = \varepsilon/|r - r_0|^n$ at $r > r_0$, where $\varepsilon$ is an energy parameter of the interaction]:

$$\langle f^2(\mathbf{r})\rangle_{eq} = 3n\Gamma\left(2+\frac{1}{n}\right)\frac{(kT)^2}{a_0 r_0}\frac{\varphi}{1-\varphi}. \tag{32}$$

The quantity $\alpha_0 = (\varepsilon/kT)^{1/n} \ll r_0$ may be thought of as the depth of a surface layer; $\Gamma(x)$ is the gamma function.

Expression (32) shows that the quantity $\langle f^2(\mathbf{r})\rangle_{eq}$ reflects the details of the interaction of the molecule with the random field, at least for random fields induced by certain geometric obstacles, e.g., a porous medium or a system of protein molecules. It thus seems to us that the initial rate of change of the diffusion coefficient, $[d\tilde{D}(t)/dt\,]_{t=0}$, is a matter of primary concern in spin-echo experiments on heterogeneous media.

We would like to point out another aspect of (32): In the limit $n \to \infty$ we have $\langle f^2(\mathbf{r})\rangle_{eq} \to \infty$ and thus $d\tilde{D}(t)/dt \to \infty$ at $t = 0$. The reason is that Smoluchowski equation (1) is itself inapplicable to fields which vary rapidly in space, since (for example) it ignores the relaxation in terms of the momentum distribution. A corresponding modification of the analysis is required for such situations.

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