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NMR of diffusing atoms in a periodic porous medium in the presence of a nonuniform magnetic field

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A detailed theory is developed for calculating the average time-dependent precessing nuclear spin of an atom diffusing through a porous medium in the presence of a nonuniform aligning field. An expansion in cumulant averages of the phase shift of the precessing spin is set up in terms of the diffusion propagator. For a periodic porous medium, a practical scheme of computation is exhibited which is based upon the diffusion eigenstates. This scheme is used to calculate the second and fourth order cumulants, both numerically and by asymptotic expansions for short and long precession times, when the field inhomogeneity is caused either by susceptibility differences between pore fluid and solid matrix or by an externally imposed field gradient. The results are used to calculate the diffusion effect on the transverse relaxation rate of spin polarization, and to discuss the validity of the Gaussian approximation for the distribution of phase shifts of the precessing spins.

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I. INTRODUCTION

Even when the static magnetic field which is used to align the nuclear magnetic moments in a homogeneous macroscopic sample is somewhat nonuniform, the concomitant dephasing of the precessing moments is effectively cancelled when one performs a spin-echo experiment. However, if the nuclear spins can displace away from their initial position by diffusive motion of the atoms, this introduces an additional decay of the spin-echo signal. The decay is then characterized by the function [1]

$$\exp\left(-\frac{2\tau}{T_2}-(\gamma\nabla H)^2\frac{2}{3}D_p\tau^3\right). \tag{1.1}$$

Here, $1/T_2$ is the decay rate of transverse (i.e., precessing) magnetization in a uniform field, τ is the time interval used in the dephasing and rephasing periods of the spin echo experiment, D_p is the appropriate self-diffusion coefficient, γ is the nuclear gyromagnetic ratio, and ∇H is the field gradient, assumed to be uniform. In many situations one wishes to avoid the extra decay caused by diffusion in a slightly nonuniform field—ingenious tricks, such as the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [1], have been devised for that purpose. Alternatively, measurements of enhanced spin-echo decay in an externally applied field gradient can be used to measure the self-diffusion coefficient D_p in a homogeneous medium [2].

In a fluid filled porous medium, the self-diffusion of atoms or molecules in the fluid is strongly affected by the microgeometry of the pore space. In addition, inhomogeneities of the magnetic field are induced locally by a combined effect of the microstructure and the magnetic susceptibility difference between the pore fluid and the matrix component, even when the externally applied field is very uniform. Experiments have been carried out to measure spin echos in such systems [3–7], but the theoretical interpretation of those experiments is usually difficult. In the case where there is only a uniform applied field gradient, exact results have been obtained for isolated pores of simple shape [8,9], and an approximate treatment has been given for more complicated microstructures [10]. A more recent discussion exploits the known form of the diffusion propagator in the presence of a perfectly reflecting planar boundary in order to develop an asymptotic calculation of the effects of such a gradient which is valid at short enough times [11]. Some qualitative estimates of the long time effects were also attempted in that reference. The more complicated field inhomogeneities which are due to the susceptibility difference were discussed by making assumptions about the distribution of either the phase shifts of individual nuclear spins [12,13], or the relaxation times of different spins [14], or by assuming a particular spatial variation of the magnetic field [15]. The main source of difficulty in all of these discussions is the inherently disordered character of the pore microstructure and the associated dearth of information about its details.

In contrast with those discussions, our approach is first to try and develop a detailed theoretical understanding of diffusion effects on T_2 relaxation in a porous medium

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with a *periodic microstructure* that is known precisely. We expect that the most important effects will not depend in a crucial way on the exact long range periodicity but rather on certain important details of the local microstructure, like the existence of narrow constrictions in the pore space or long tubes which connect between large pores. Thus functional relationships between important physical parameters, such as the relaxation rate, echo spacing, bulk effective diffusion coefficient, magnetic field gradient, pore size scale, etc., can be studied. Also, experience in other areas of condensed matter physics has shown that a good understanding of periodic systems is a prerequisite to the successful tackling of disordered systems. Finally, although natural porous media are usually disordered, it is possible to make synthetic porous media which are periodic. Experiments on such artificial systems should teach us a great deal about what to expect from disordered systems, especially when they can be compared with good calculations on the same systems. We already applied this philosophy to a discussion of pulsed-field-gradient spin-echo (PFGSE) experiments and to the calculation of the time dependent bulk effective diffusion coefficient $D(t)$ of a periodic porous medium [16–18]. Here we apply it to a discussion of spin-echo experiments in the presence of a time independent but nonuniform spin aligning magnetic field.

The remainder of this paper is organized as follows. In Sec. II we develop a basic theory for calculating the average precessing spin carried by a single diffusing atom as an expansion in cumulant averages of the time dependent phase shift associated with the diffusive motion. Assuming a spatially periodic structure for the pore space, the diffusion eigenstates are used to construct a practical scheme for computing the second and fourth order cumulants for cases where the field inhomogeneity is due either to differences in magnetic susceptibility between pore fluid and solid matrix, or to an externally imposed field gradient ∇H. In Sec. III this scheme is used to calculate those cumulants for a range of spin-echo times τ that spans the gap between very short and very long times, where the behavior can be analyzed using asymptotic expansions. We calculate the diffusion related enhancement of the transverse relaxation rate of spin polarization. We also discuss the question of whether a Gaussian approximation for the distribution of phase shifts is valid in the porous medium, as has often been assumed without proof in the literature on this topic. In Sec. IV we present some conclusions. In the Appendix we discuss some important technical properties of the diffusion propagator and the probabilities of time reversed paths of a diffusing particle in a porous medium.

II. THEORY

A. Averaging of phase shifts over diffusion paths

We focus upon a single nuclear spin which is aligned by a strong magnetic field H_0 along the z axis. When that spin is flipped into the x, y plane, it begins to precess around H_0 at the Larmor angular frequency $\omega_0 = \gamma H_0$, where γ is the gyromagnetic ratio. It is convenient and conventional to transform to a reference frame which rotates around the z axis at that frequency. In that frame, the precessing spin is at rest as long as H_0 is the only field present. When other time independent fields are also present, the flipped spin, described by the complex quantity

$$s_+(t) \equiv s_x(t) + is_y(t), \tag{2.1}$$

satisfies a Langevin-type equation of motion

$$\frac{\partial s_+}{\partial t} = -\frac{s_+}{T_2} - i\gamma\delta H[\mathbf{r}(t)]s_+ + F(t). \tag{2.2}$$

Here, $1/T_2$ is the average transverse relaxation rate due to interactions with other degrees of freedom of the system. Those interactions also give rise to the random force $F(t)$, which fluctuates rapidly both in time and in space. The middle term describes the effect of small local deviations $\delta H(\mathbf{r})$ in the z component of the static field away from H_0. These can arise either from an externally applied field gradient, which we will always take to have a uniform value, or from local field heterogeneities caused by the magnetic susceptibility difference between pore fluid and solid matrix. A time dependence is introduced into this term by the fact that the position of the nuclear spin $\mathbf{r}(t)$ changes with time as the molecule in which it resides moves through the pore fluid by diffusion.

If we ignore the rapidly fluctuating force $F(t)$, then (2.2) can be solved to yield

$$\frac{s_+(t)}{s_+(0)} = \exp\left(-\frac{t}{T_2} - i\gamma\int_0^t dt'\delta H[\mathbf{r}(t')]\right). \tag{2.3}$$

In a simple spin-echo experiment, with a $\pi/2$ rf pulse applied at $t = 0$ and a π pulse applied at $t = \tau$, the measured quantity would be

$$\left\langle\frac{s_+(2\tau)}{s_+(0)}\right\rangle = e^{-\frac{2\tau}{T_2}}\left\langle\exp\left[-i\gamma\left(\int_0^\tau dt\delta H[\mathbf{r}(t)] - \int_\tau^{2\tau} dt\delta H[\mathbf{r}(t)]\right)\right]\right\rangle, \tag{2.4}$$

where the average must be taken over *all the actual paths* $\mathbf{r}_i(t)$ of all the spins i during the time interval $(0, 2\tau)$. The field dependent exponent in (2.4) is the phase shift $i\Phi$ accumulated by a precessing spin at time $t = 2\tau$

$$\Phi = -\gamma\left(\int_0^\tau dt\delta H[\mathbf{r}(t)] - \int_\tau^{2\tau} dt\delta H[\mathbf{r}(t)]\right) \tag{2.5}$$

and it is clearly a functional of the path $\mathbf{r}(t)$. An important property of this expression is that any time independent additive term in δH makes a vanishing contribution to Φ. That is why Φ would vanish in the absence of diffusion, or if δH were uniform in space.

The required average can be expressed as an expansion in cumulant averages of powers of Φ ($\langle\rangle_c$ denotes a cumulant average):

$$\langle e^{-i\Phi}\rangle = \exp\langle e^{-i\Phi} - 1\rangle_c = \exp\left[-i\langle\Phi\rangle_c - \frac{1}{2}\langle\Phi^2\rangle_c + \frac{i}{6}\langle\Phi^3\rangle_c + \frac{1}{24}\langle\Phi^4\rangle_c + \cdots\right]. \quad (2.6)$$

These cumulant averages can be expressed in terms of simple averages $\langle\,\rangle$ (see, e.g., Ref. [19]):

$$\begin{aligned}
&\langle\Phi\rangle_c = \langle\Phi\rangle,\\
&\langle\Phi^2\rangle_c = \langle\Phi^2\rangle - \langle\Phi\rangle^2 \equiv \langle(\Delta\Phi)^2\rangle, \quad \Delta\Phi \equiv \Phi - \langle\Phi\rangle,\\
&\langle\Phi^3\rangle_c = \langle(\Delta\Phi)^3\rangle,\\
&\langle\Phi^4\rangle_c = \langle(\Delta\Phi)^4\rangle - 3\langle(\Delta\Phi)^2\rangle^2,
\end{aligned}$$

etc. When the distribution of values of Φ is Gaussian, then all cumulants beyond the second one vanish. For non-Gaussian distributions, the magnitudes of $\langle\Phi^3\rangle_c$, $\langle\Phi^4\rangle_c$, etc., are a measure of the deviation from Gaussian shape. The cumulant expansion is useful mainly if those deviations are small.

Averages over possible paths $\mathbf{r}(t)$ of a diffusing particle will be calculated by using the diffusion propagator $G(\mathbf{r}\mathbf{r}'|t)$: $G(\mathbf{r}\mathbf{r}'|t)dV$ is the probability that a particle is found in the volume element dV around $\mathbf{r}$ at time t if it was at $\mathbf{r}'$ at time 0. Mathematically this propagator is the solution of the following boundary value and initial value problem, involving the time dependent diffusion equation:

$$\frac{\partial G}{\partial t} = D_p \nabla^2 G \quad (2.7)$$

in the pore space,

$$\frac{\partial G}{\partial n} = 0, \quad (2.8)$$

at the pore-matrix interface, and

$$G|_{t=0} = \delta^3(\mathbf{r} - \mathbf{r}'). \quad (2.9)$$

The boundary condition at the pore-matrix interface expresses the fact that there is no net particle flux into the interface, which means that there is no absorption of particles or extra spin relaxation there. As a result of this, the probability density $G(\mathbf{r}\mathbf{r}'|t)$ preserves its normalization for all times (V_p is the total volume of the pore space)

$$\int_{V_p} dV\, G(\mathbf{r}\mathbf{r}'|t) = 1. \quad (2.10)$$

It is easy to show, using Green's theorem, that G is symmetric, i.e., $G(\mathbf{r}\mathbf{r}'|t) = G(\mathbf{r}'\mathbf{r}|t)$ (see the Appendix). Therefore if the particles are uniformly distributed at $t = 0$ (with density $1/V_p$) then that property is also preserved for all times

$$\frac{1}{V_p}\int_{V_p} dV'\, G(\mathbf{r}\mathbf{r}'|t) = \frac{1}{V_p}\int_{V_p} dV'\, G(\mathbf{r}'\mathbf{r}|t) = \frac{1}{V_p}. \quad (2.11)$$

In practice, there often is some extra nuclear spin relaxation at the interface—that would require replacing the boundary condition (2.8) by the more general one

$$D_p \frac{\partial G}{\partial n} + \rho G = 0, \quad (2.12)$$

where ρ is the interface absorption coefficient. Here we will always assume $\rho = 0$.

We also note that any possible path $\mathbf{r}(t)$ is as probable as the time reversed path $\mathbf{r}'(t) \equiv \mathbf{r}(2\tau - t)$ when $\rho = 0$ (this is proved in the Appendix). Moreover, the phase shift Φ' associated with the time reversed path is equal to $-\Phi$, as can easily be shown by transforming the integration variable from t to $t' \equiv 2\tau - t$ in the expression for Φ'

$$\begin{aligned}
\Phi' &= -\gamma\left(\int_0^\tau dt - \int_\tau^{2\tau} dt\right)\delta H[\mathbf{r}'(t)]\\
&= -\gamma\left(\int_\tau^{2\tau} dt' - \int_0^\tau dt'\right)\delta H[\mathbf{r}(t')] = -\Phi. \quad (2.13)
\end{aligned}$$

As a result of this symmetry, it follows that any odd power of Φ averages out to 0. It follows that we have $\langle\Phi^2\rangle_c = \langle\Phi^2\rangle$, and that the next nontrivial cumulant average is $\langle\Phi^4\rangle_c$.

Averages of even powers of Φ can be simplified by noting that the diffusion process described by (2.7) has no memory. Therefore the joint probability distribution for paths which include the points $\mathbf{r}(t_1), \mathbf{r}(t_2)\cdots\mathbf{r}(t_n)$, $t_1 \le t_2 \le \cdots \le t_n$ has a density which is just a simple product of diffusion propagators (see the Appendix)

$$G(\mathbf{r}_n\mathbf{r}_{n-1}|t_n - t_{n-1})G(\mathbf{r}_{n-1}\mathbf{r}_{n-2}|t_{n-1} - t_{n-2})\cdots \times G(\mathbf{r}_2\mathbf{r}_1|t_2 - t_1). \quad (2.14)$$

This probability density is properly normalized, as can be seen by integrating it over $\mathbf{r}_n \cdots \mathbf{r}_2$ and using (2.10).

The expression for $\langle\Phi^{2n}\rangle$

$$\frac{1}{\gamma^{2n}}\langle\Phi^{2n}\rangle = \left(\int_0^\tau dt_{2n} - \int_\tau^{2\tau} dt_{2n}\right)\cdots \left(\int_0^\tau dt_1 - \int_\tau^{2\tau} dt_1\right)\langle\delta H[\mathbf{r}(t_{2n})]\cdots\delta H[\mathbf{r}(t_1)]\rangle \quad (2.15)$$

is best rewritten by expanding all the large circular brackets, and rearranging the time integrations in chronological order, to give

$$\frac{1}{\gamma^{2n}}\langle\Phi^{2n}\rangle=(2n)!\sum_{k=0}^{2n}(-1)^k\left(\int_{\tau}^{2\tau}dt_{2n}\int_{\tau}^{t_{2n}}dt_{2n-1}\cdots\int_{\tau}^{t_{k+2}}dt_{k+1}\right)\left(\int_0^{\tau}dt_k\cdots\int_0^{t_2}dt_1\right)$$
$$\times\langle\delta H[\mathbf{r}(t_{2n})]\delta H[\mathbf{r}(t_{2n-1})]\cdots\delta H[\mathbf{r}(t_{k+1})]\delta H[\mathbf{r}(t_k)]\cdots\delta H[\mathbf{r}(t_1)]\rangle. \quad (2.16)$$

A further simplification is achieved by using the following theorem about integration over hypertriangular domains in an n-dimensional space

$$\int_0^{\tau}dt_n\int_0^{t_n}dt_{n-1}\int_0^{t_{n-1}}dt_{n-2}\cdots\int_0^{t_2}dt_1=\int_{\tau}^{2\tau}dt_1'\int_{\tau}^{t_1'}dt_2'\int_{\tau}^{t_2'}dt_3'\cdots\int_{\tau}^{t_{n-1}'}dt_n', \quad (2.17)$$

where $t_i'\equiv 2\tau-t_i$. This shows that the terms in (2.16) which correspond to k and $2n-k$ are equal, leading finally to

$$\langle\Phi^{2n}\rangle=\gamma^{2n}(2n)!\sum_{k=0}^{n}\epsilon_k(-1)^k\left(\int_{\tau}^{2\tau}dt_{2n}\cdots\int_{\tau}^{t_{k+2}}dt_{k+1}\right)\left(\int_0^{\tau}dt_k\cdots\int_0^{t_2}dt_1\right)$$
$$\times\langle\delta H[\mathbf{r}(t_{2n})]\cdots\delta H[\mathbf{r}(t_{k+1})]\delta H[\mathbf{r}(t_k)]\cdots\delta H[\mathbf{r}(t_1)]\rangle, \quad (2.18)$$

where $\epsilon_k=2$ for $k<n$ and $\epsilon_n=1$. Similar to what was noted in connection with (2.5), it is easy to see from (2.15) that any additive contribution to the averaged product of $\delta H[\mathbf{r}(t)]$ factors in the integrand, which is independent of even one of the integration times t_i, makes a vanishing contribution to the final result for $\langle\Phi^{2n}\rangle$.

The averages in the integrand are evaluated as follows:

$$\langle\delta H[\mathbf{r}(t_n)]\cdots\delta H[\mathbf{r}(t_1)]\rangle$$
$$=\frac{1}{V_p}\int_{V_p}dV_1\int_{V_p}dV_2\cdots\int_{V_p}dV_n\delta H(\mathbf{r}_n)\cdots\delta H(\mathbf{r}_1)$$
$$\times G(\mathbf{r}_n\mathbf{r}_{n-1}|t_n-t_{n-1})\cdots G(\mathbf{r}_2\mathbf{r}_1|t_2-t_1)$$
$$\text{for } t_1\le t_2\le\cdots\le t_n. \quad (2.19)$$

We take the field fluctuation δH to be a sum of two contributions

$$\delta H(\mathbf{r})=\mathbf{r}\cdot\nabla H+\delta H_{\rm susc}(\mathbf{r}), \quad (2.20)$$

where the first term represents a uniform, time independent gradient of the spin aligning magnetic field, while the second term is the result of the fluid-matrix magnetic susceptibility difference $\Delta\chi\equiv\chi_p-\chi_m$ (χ_p, χ_m are the magnetic susceptibilities of pore fluid and matrix, respectively).

The problem of local magnetic field fluctuations of a two-component (in this case, fluid and matrix) composite, where the components have different values of magnetic susceptibility, is mathematically identical to the dielectric problem of a two-component composite, where the components have different values of dielectric constant. The latter problem has been treated previously for a composite whose microstructure is periodic [20]. From that discussion we conclude that the static field distortion $\delta H_{\rm susc}(\mathbf{r})$ can be written as the gradient of a periodic scalar potential $\psi(\mathbf{r})$, which can be expanded in an appropriate Fourier series

$$\psi(\mathbf{r})=\sum_{\mathbf{g}}\psi_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{r}}. \quad (2.21)$$

The sum here is over all the vectors $\mathbf{g}$ of the reciprocal lattice that is dual to the Bravais lattice which characterizes the periodicity of the microstructure. The expansion coefficients satisfy the following infinite set of linear algebraic equations:

$$i|\mathbf{g}|\psi_{\mathbf{g}}=\frac{4\pi\Delta\chi}{1+4\pi\chi_m}\left(H_0\cos(\mathbf{g},\mathbf{e}_z)\theta_{\mathbf{g}}+\sum_{\mathbf{g}'\neq 0}\Gamma_{\mathbf{g}\mathbf{g}'}i|\mathbf{g}'|\psi_{\mathbf{g}'}\right)\text{ for }\mathbf{g}\neq\mathbf{0}, \quad (2.22)$$

$$\Gamma_{\mathbf{g}\mathbf{g}'}\equiv\cos(\mathbf{g},\mathbf{g}')\theta_{\mathbf{g}-\mathbf{g}'}, \quad (2.23)$$

where $(\mathbf{g},\mathbf{e}_z)$ and $(\mathbf{g},\mathbf{g}')$ indicate the angles between $\mathbf{g}$ and $\mathbf{e}_z$, and $\mathbf{g}$ and $\mathbf{g}'$, respectively, $\mathbf{e}_z$ is a unit vector along the z direction, and $\theta_{\mathbf{g}}$ is the Fourier expansion coefficient of the characteristic function of the pore space $\theta_p(\mathbf{r})$ (V_a is the volume of a single unit cell of the microstructure):

$$\theta_p(\mathbf{r})\equiv\begin{cases}1 & \text{for } \mathbf{r} \text{ inside the pore space,}\\ 0 & \text{otherwise,}\end{cases} \quad (2.24)$$

$$\theta_{\mathbf{g}}\equiv\frac{1}{V_a}\int_{V_a}dV\,\theta_p(\mathbf{r})e^{-i\mathbf{g}\cdot\mathbf{r}}. \quad (2.25)$$

Because χ_p, χ_m, and $\Delta\chi$ are all much less than one, an excellent approximation to the solution of (2.22) is

$$i|\mathbf{g}|\psi_{\mathbf{g}}\cong 4\pi\Delta\chi H_0\cos(\mathbf{g},\mathbf{e}_z)\theta_{\mathbf{g}}, \quad (2.26)$$

and this leads to

$$\delta H_{\rm susc}(\mathbf{r})=\frac{\partial\psi(\mathbf{r})}{\partial z}\cong 4\pi\Delta\chi H_0\sum_{\mathbf{g}\neq 0}\cos^2(\mathbf{g},\mathbf{e}_z)\theta_{\mathbf{g}}e^{i\mathbf{g}\cdot\mathbf{r}}. \quad (2.27)$$

In contrast with $\delta H_{\rm susc}(\mathbf{r})$, which is periodic in space and therefore bounded, the constant gradient term of (2.20) is nonperiodic and unbounded. This can lead to nonconverging spatial integrals in calculations of averages such as (2.19). In order to avoid this, we recall that any additive contribution to the average of the product $\delta H[\mathbf{r}(t_{2n})]\cdots\delta H[\mathbf{r}(t_1)]$ which is independent of one of the times t_i makes a vanishing contribution when integrated over t_i in (2.15). Therefore we can replace the average of $[\mathbf{r}(t_{2n})\cdot\nabla H]\cdots[\mathbf{r}(t_1)\cdot\nabla H]$ by the average of

$$\frac{(-1)^n}{2^n}\left([\mathbf{r}(t_{2n})-\mathbf{r}(t_{2n-1})]\cdot\nabla H\right)^2\cdots \times\left([\mathbf{r}(t_2)-\mathbf{r}(t_1)]\cdot\nabla H\right)^2 \qquad (2.28)$$

in (2.15). In order to see this note, for example, that the last factor expands to a sum of three terms $[\mathbf{r}(t_1)\cdot\nabla H]^2 - 2[\mathbf{r}(t_1)\cdot\nabla H][\mathbf{r}(t_2)\cdot\nabla H]+[\mathbf{r}(t_2)\cdot\nabla H]^2$. The first of these is independent of t_2 while the third is independent of t_1, therefore they make a vanishing contribution to the time integral. However, before transforming to (2.18) we have to symmetrize this product, i.e., replace it by

$$\frac{2^n n!}{(2n)!}\sum_{\mathcal{P}}\mathcal{P}\left\{\frac{(-1)^n}{2^n}([\mathbf{r}(t_{2n})-\mathbf{r}(t_{2n-1})]\cdot\nabla H)^2\cdots \times([\mathbf{r}(t_2)-\mathbf{r}(t_1)]\cdot\nabla H)^2\right\}, \qquad (2.29)$$

where $\mathcal{P}$ is a permutation of $t_1\cdots t_{2n}$ which transforms the set of time pairs $(t_{2n},t_{2n-1})\cdots(t_2,t_1)$ into a different set of time pairs. The sum over all such permutations $\mathcal{P}$ comprises $(2n)!/(2^n n!)$ different terms, and is symmetric under *any* further permutation of $t_1\cdots t_{2n}$.

B. Calculation of $\langle\Phi^2\rangle$

From (2.18) we get that

$$\frac{1}{2\gamma^2}\langle\Phi^2\rangle = \left(2\int_\tau^{2\tau}dt_2\int_\tau^{t_2}dt_1 - \int_\tau^{2\tau}dt_2\int_0^\tau dt_1\right) \times\langle\delta H[\mathbf{r}(t_2)]\delta H[\mathbf{r}(t_1)]\rangle. \qquad (2.30)$$

The average over diffusion paths is

$$\langle\delta H[\mathbf{r}(t_2)]\delta H[\mathbf{r}(t_1)]\rangle = \frac{1}{V_p}\int_{V_p}dV_1\int_{V_p}dV_2\,G(\mathbf{r}_2\mathbf{r}_1|t_2-t_1)\delta H(\mathbf{r}_2)\delta H(\mathbf{r}_1). \qquad (2.31)$$

We note that for a microstructure that has inversion symmetry, $\theta_{\mathbf{g}}$ is real and satisfies $\theta_{-\mathbf{g}}=\theta_{\mathbf{g}}$. Therefore $\delta H_{\text{susc}}(\mathbf{r})$ is even under space inversion. Finally, for an inversion symmetric microstructure the diffusion propagator satisfies

$$G(-\mathbf{r}-\mathbf{r}'|t) = G(\mathbf{r}\mathbf{r}'|t). \qquad (2.32)$$

Consequently, since the product $(\mathbf{r}_1\cdot\nabla H)\delta H_{\text{susc}}(\mathbf{r}_2)$ is odd under space inversion, its contribution to the integrand of (2.31) vanishes upon integration. As a result of this, the external field gradient and the susceptibility difference make separate, additive contributions to the averages in (2.30), without any cross terms:

$$\begin{aligned}\langle\delta H[\mathbf{r}(t_2)]\delta H[\mathbf{r}(t_1)]\rangle &= \frac{1}{V_p}\int_{V_p}dV_1\int_{V_p}dV_2\,G(\mathbf{r}_2\mathbf{r}_1|t_2-t_1)\\ &\quad\times\left[(\mathbf{r}_1\cdot\nabla H)(\mathbf{r}_2\cdot\nabla H)+(4\pi\Delta\chi H_0)^2\sum_{\mathbf{g}_1\neq0}\sum_{\mathbf{g}_2\neq0}\cos^2(\mathbf{g}_1,\mathbf{e}_z)\cos^2(\mathbf{g}_2,\mathbf{e}_z)\theta_{\mathbf{g}_1}\theta^*_{\mathbf{g}_2}e^{i\mathbf{g}_1\cdot\mathbf{r}_1-i\mathbf{g}_2\cdot\mathbf{r}_2}\right]\\ &= (\text{external field gradient contribution}) + (\text{susceptibility difference contribution}).\end{aligned} \qquad (2.33)$$

We can therefore evaluate these two contributions separately.

1. *Susceptibility difference terms*

In order to compute the integrals in (2.33), we use the expansion of G in the Bloch-type eigenfunctions $\phi_{n\mathbf{q}}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}$ of the diffusion equation [$\phi_{n\mathbf{q}}(\mathbf{r})$ is periodic, $\mathbf{q}$ is a wave vector in the first Brillouin zone, and n is a band index] [17]

$$G(\mathbf{r}\mathbf{r}'|t) = \frac{1}{V}\sum_{n\mathbf{q}}e^{-\lambda_{n\mathbf{q}}|t|}\phi_{n\mathbf{q}}(\mathbf{r})\phi^*_{n\mathbf{q}}(\mathbf{r}')e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}, \qquad (2.34)$$

where $\lambda_{n\mathbf{q}}$ are the eigenvalues and V is the total volume of the pore space and matrix. For a microstructure with cubic symmetry and for small $\mathbf{q}$, the eigenvalues $\lambda_{n\mathbf{q}}$ can be expanded in the form

$$\lambda_{n\mathbf{q}} = \tilde{\lambda}_{n\mathbf{q}}\frac{D_p}{a^2} = \frac{D_p}{a^2}[\tilde{\lambda}_{n0}+B_n q^2a^2+C_n q^4a^4+O(q^6a^6)], \qquad (2.35)$$

where a is the edge of the cubic unit cell and $\tilde{\lambda}_{n\mathbf{q}}$ is the dimensionless reduced eigenvalue, which is usually of order 1 or greater [17]. The coefficients $\tilde{\lambda}_{n\mathbf{0}}$, B_n, C_n, etc., depend upon the *shape* of the microstructure, but are independent of the absolute size scale a. [Actually, the fourth order term here and in (2.36) below, as well as the higher order terms, can depend on $\mathbf{q}$ in a more complicated way, even for cubic symmetry. We avoid this complication by always taking $\mathbf{q} \parallel x$, since we only need to know the order of magnitude of these terms.] The lowest band of eigenvalues $\lambda_{0\mathbf{q}}$ is an exception to this rule, since $\tilde{\lambda}_{00} = 0$. The next coefficient in the expansion of $\tilde{\lambda}_{0\mathbf{q}}$ in powers of qa (i.e., $B_0 = D_e/D_p$) is related to the bulk effective stationary diffusion coefficient $D_e \equiv D(t \to \infty)$, where $D(t)$ is defined in (2.61) below [17]. Therefore we can rewrite (2.35) for the case $n = 0$ as

$$\lambda_{0\mathbf{q}} = D_e q^2 + D_p C_0 q^4 a^2 + O(q^6), \tag{2.36}$$

The eigenfunctions are assumed to be normalized as follows,

$$\frac{1}{V_a}\int_{V_a} dV\, \theta_p(\mathbf{r})\phi^*_{n\mathbf{q}}(\mathbf{r})\phi_{m\mathbf{q}}(\mathbf{r}) = \delta_{nm}, \tag{2.37}$$

and their values restricted to the inside of the pore space can be expanded in a Fourier series as follows:

$$\theta_p(\mathbf{r})\phi_{n\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{g}} \tilde{\phi}_{n\mathbf{q}}(\mathbf{g})e^{i\mathbf{g}\cdot\mathbf{r}} \tag{2.38}$$

$$\tilde{\phi}_{n\mathbf{q}}(\mathbf{g}) = \frac{1}{V_a}\int_{V_a} dV\, \theta_p(\mathbf{r})\phi_{n\mathbf{q}}(\mathbf{r})e^{-i\mathbf{g}\cdot\mathbf{r}}. \tag{2.39}$$

The eigenfunction $\phi_{n\mathbf{q}}(\mathbf{r})$ depends on the detailed shape of the microstructure, however, if expressed as a function of $\mathbf{q}a$ and $\mathbf{r}/a$, it has no further dependence on a. Similarly, if $\tilde{\phi}_{n\mathbf{q}}(\mathbf{g})$ is expressed as a function of $\mathbf{q}a$ and $\mathbf{g}a$, then it too has no further dependence on a. We note here, and use later, the fact that $\phi_{00}(\mathbf{r}) = 1/\sqrt{\phi}$, a constant ($\phi \equiv V_p/V$, i.e., the volume fraction of the pore space). Using this we get

$$\tilde{\phi}_{00}(\mathbf{g}) = \frac{1}{\sqrt{\phi}}\theta_{\mathbf{g}}, \tag{2.40}$$

$$\tilde{\phi}_{n0}(\mathbf{0}) = \sqrt{\phi}\,\delta_{n0}. \tag{2.41}$$

From the orthogonality property (2.37) the following useful results can be shown to follow:

$$\sum_{\mathbf{g}} \tilde{\phi}^*_{n\mathbf{q}}(\mathbf{g})\tilde{\phi}_{m\mathbf{q}}(\mathbf{g}) = \delta_{nm}, \tag{2.42}$$

$$\theta_p(\mathbf{r})\theta_p(\mathbf{r}')\sum_n \phi_{n\mathbf{q}}(\mathbf{r})\phi^*_{n\mathbf{q}}(\mathbf{r}') = V_a\theta_p(\mathbf{r})\delta^3(\mathbf{r}-\mathbf{r}'), \tag{2.43}$$

$$\sum_n \tilde{\phi}_{n\mathbf{q}}(\mathbf{g})\tilde{\phi}^*_{n\mathbf{q}}(\mathbf{g}') = \theta_{\mathbf{g}-\mathbf{g}'}. \tag{2.44}$$

Another useful result which follows from (2.38) is

$$\sum_{\mathbf{g}'} \theta_{\mathbf{g}-\mathbf{g}'}\tilde{\phi}_{n\mathbf{q}}(\mathbf{g}') = \tilde{\phi}_{n\mathbf{q}}(\mathbf{g}). \tag{2.45}$$

This means that $\tilde{\phi}_{n\mathbf{q}}(\mathbf{g})$ is an eigenvector of the matrix $\theta_{\mathbf{g}-\mathbf{g}'}$ with the eigenvalue 1.

When (2.34) is used in (2.33), the double integral of the susceptibility difference contribution (the second term in the square brackets) separates into a product of single integrals,

$$\frac{1}{VV_p}\left(\int_{V_p} dV_2 e^{-i\mathbf{g}_2\cdot\mathbf{r}_2}\phi_{n\mathbf{q}}(\mathbf{r}_2)e^{i\mathbf{q}\cdot\mathbf{r}_2}\right) \times \left(\int_{V_p} dV_1 e^{i\mathbf{g}_1\cdot\mathbf{r}_1}\phi^*_{n\mathbf{q}}(\mathbf{r}_1)e^{-i\mathbf{q}\cdot\mathbf{r}_1}\right). \tag{2.46}$$

Because of the periodicity of $\phi_{n\mathbf{q}}(\mathbf{r})$ and $e^{i\mathbf{g}\cdot\mathbf{r}}$, these integrals vanish unless $\mathbf{q} = 0$. In that case they can be calculated by restricting the integration volume to a single unit cell of volume V_a. When this is done, (2.46) becomes

$$\frac{1}{\phi}\left(\frac{1}{V_a}\int_{V_a} dV\theta_p(\mathbf{r})e^{-i\mathbf{g}_2\cdot\mathbf{r}}\phi_{n0}(\mathbf{r})\right) \times \left(\frac{1}{V_a}\int_{V_a} dV\theta_p(\mathbf{r})e^{-i\mathbf{g}_1\cdot\mathbf{r}}\phi_{n0}(\mathbf{r})\right)^* = \frac{1}{\phi}\tilde{\phi}_{n0}(\mathbf{g}_2)\tilde{\phi}^*_{n0}(\mathbf{g}_1). \tag{2.47}$$

We thus get for the susceptibility difference contribution to (2.33)

$$\langle\delta H[\mathbf{r}(t_2)]\delta H[\mathbf{r}(t_1)]\rangle_{\rm susc} = \frac{1}{\phi}(4\pi\Delta\chi H_0)^2\sum_n e^{-\lambda_{n0}|t_2-t_1|}|a_n|^2, \tag{2.48}$$

$$a_n \equiv \sum_{\mathbf{g}\neq 0}\cos^2(\mathbf{g},\mathbf{e}_z)\theta^*_{\mathbf{g}}\tilde{\phi}_{n0}(\mathbf{g}). \tag{2.49}$$

We note that a_0 can be calculated explicitly for the case of microgeometry with cubic point symmetry: From (2.40) we get

$$a_0 = \frac{1}{\sqrt{\phi}}\sum_{\mathbf{g}\neq 0}\cos^2(\mathbf{g},\mathbf{e_z})|\theta_{\mathbf{g}}|^2. \tag{2.50}$$

Invoking the cubic symmetry of $\theta_{\mathbf{g}}$ we can replace $\cos^2(\mathbf{g},\mathbf{e_z})$ in the sum by $\frac{1}{3}[\cos^2(\mathbf{g},\mathbf{e_x}) + \cos^2(\mathbf{g},\mathbf{e_y}) + \cos^2(\mathbf{g},\mathbf{e_z})] = \frac{1}{3}$. This leads to

$$a_0 = \frac{1}{3\sqrt{\phi}}\left(\sum_{\mathbf{g}}|\theta_{\mathbf{g}}|^2 - \theta_0^2\right) = \frac{1}{3}\sqrt{\phi}(1-\phi). \tag{2.51}$$

Using (2.44) we can also show that the sum over all the terms $|a_n|^2$ satisfies the following inequality:

$$\sum_n |a_n|^2 = \sum_{\mathbf{g}\neq 0}\sum_{\mathbf{g}'\neq 0}\cos^2(\mathbf{g},\mathbf{e_z})\theta^*_{\mathbf{g}}\theta_{\mathbf{g}-\mathbf{g}'}\theta_{\mathbf{g}'}\cos^2(\mathbf{g}',\mathbf{e_z}) \le \sum_{\mathbf{g}\neq 0}\cos^4(\mathbf{g},\mathbf{e_z})|\theta_{\mathbf{g}}|^2 \le \sum_{\mathbf{g}\neq 0}\cos^2(\mathbf{g},\mathbf{e_z})|\theta_{\mathbf{g}}|^2 = \frac{1}{3}\phi(1-\phi). \tag{2.52}$$

Here we used the fact that the eigenvalues of the matrix $\theta_{\mathbf{g}-\mathbf{g}'}$ are 0 and 1 in order to get the first inequality sign, and the cubic point symmetry to get the last equality sign. From (2.52) and (2.51) we also get

$$\sum_{n>0} |a_n|^2 = \sum_n |a_n|^2 - a_0^2 \leq \frac{1}{3}\phi(1-\phi)\frac{2+\phi}{3}. \quad (2.53)$$

In order to get the corresponding contribution to $\langle\Phi^2\rangle$, we still need to calculate the following integrals over times:

$$2\int_0^\tau dt_2 \int_0^{t_2} dt_1 e^{-\lambda_{n0}(t_2-t_1)} - \int_0^\tau dt_2 \int_0^\tau dt_1 e^{-\lambda_{n0}(t_2-t_1+\tau)}$$
$$= \frac{2\tau}{\lambda_{n0}} - \frac{1}{\lambda_{n0}^2}(1-e^{-\lambda_{n0}\tau})(3-e^{-\lambda_{n0}\tau})$$
$$\equiv b_n(\tau) \text{ for } \lambda_{n0} \neq 0. \quad (2.54)$$

This quantity has a simple form in two limiting cases

$$b_n(\tau) \cong \begin{cases} \frac{2}{3}\lambda_{n0}\tau^3 & \text{when } \lambda_{n0}\tau \ll 1, \\ \frac{2\tau}{\lambda_{n0}} & \text{when } \lambda_{n0}\tau \gg 1. \end{cases} \quad (2.55)$$

These results are not valid for $n = 0$, since $\lambda_{00} = 0$—in that case the integrands of (2.54) are time independent and the result is 0.

We finally get for the susceptibility difference contribution to $\langle\Phi^2\rangle$

$$\langle\Phi^2\rangle_{\text{susc}} = \frac{2}{\phi}(4\pi\gamma\Delta\chi H_0)^2 \sum_{n>0} b_n(\tau)|a_n|^2 \quad (2.56)$$

$$\cong \frac{4}{\phi}(4\pi\gamma\Delta\chi H_0)^2$$
$$\times \frac{\tau^3 D_p}{3a^2}\sum_{n>0}\tilde{\lambda}_{n0}|a_n|^2 \text{ when } \frac{D_p\tau}{a^2} \ll 1$$
$$\times \frac{\tau a^2}{D_p}\sum_{n>0}\frac{1}{\tilde{\lambda}_{n0}}|a_n|^2 \text{ when } \frac{D_p\tau}{a^2} \gg 1. \quad (2.57)$$

The simple asymptotic results are valid only if all the eigenvalues λ_{n0} which contribute substantially lie in the same asymptotic limit (i.e., either $\lambda_{n0}\tau \ll 1$ or $\lambda_{n0}\tau \gg 1$ for all the relevant eigenstates).

2. Fixed gradient terms

We now calculate the uniform gradient contribution to $\langle\Phi^2\rangle$, denoted by $\langle\Phi^2\rangle_{\text{grad}}$. Using (2.18) and (2.29) we get

$$\frac{1}{\gamma^2}\langle\Phi^2\rangle_{\text{grad}} = \left(2\int_\tau^{2\tau} dt_2 \int_\tau^{t_2} dt_1 - \int_\tau^{2\tau} dt_2 \int_0^\tau dt_1\right)$$
$$\times\left(-\frac{1}{V_p}\right)\int_{V_p} dV_1 \int_{V_p} dV_2[(\mathbf{r}_2-\mathbf{r}_1)\cdot\nabla H]^2$$
$$\times G(\mathbf{r}_2\mathbf{r}_1|t_2-t_1). \quad (2.58)$$

The spatial integrals are evaluated by taking derivatives of the Fourier transform of G

$$-\frac{1}{V_p}\int_{V_p} dV_1 \int_{V_p} dV_2[(\mathbf{r}_2-\mathbf{r}_1)\cdot\nabla H]^2 G(\mathbf{r}_2\mathbf{r}_1|t_2-t_1)$$
$$= \left(\nabla H\cdot\frac{\partial}{\partial\mathbf{k}}\right)^2 M(\mathbf{k},t_2-t_1)\bigg|_{\mathbf{k}=0}, \quad (2.59)$$

where

$$M(\mathbf{k},t) \equiv \frac{1}{V_p}\int_{V_p} dV \int_{V_p} dV' G(\mathbf{r}\mathbf{r}'|t)e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}. \quad (2.60)$$

The function $M(\mathbf{k},t)$ is the so-called pulsed-field-gradient spin-echo (PFGSE) amplitude which can be measured in a PFGSE experiment [21]. Recently it has been discussed in great detail in connection with both experimental and theoretical studies of diffusion in a porous medium [22–28,16–18,29]. For small $\mathbf{k}$, this function has a simple Gaussian shape

$$M(\mathbf{k},t) \cong e^{-D(t)|t|k^2}, \quad (2.61)$$

where $D(t)$ is the time dependent bulk effective diffusion coefficient. This coefficient is useful for characterizing the small $\mathbf{k}$ behavior of $M(\mathbf{k},t)$, but can also be used to construct an approximate representation for $M(\mathbf{k},t)$ at arbitrary $\mathbf{k}$ [25]. The asymptotic behavior of $D(t)$ at short times has been worked out explicitly [27]. Here we only note that when t is either very small or very large, $D(t)$ tends the following simple limits

$$D(t) = \begin{cases} D_p & \text{for small } t \\ D_e & \text{for large } t. \end{cases} \quad (2.62)$$

For a periodic porous medium $M(\mathbf{k},t)$ has a convenient expansion in terms of the eigenstates of the diffusion equation (see, e.g., Refs. [26,17])

$$M(\mathbf{k},t) = \frac{1}{\phi}\sum_n e^{-\lambda_{n\mathbf{q}}|t|}|\tilde{\phi}_{n\mathbf{q}}(\mathbf{g}_\mathbf{k})|^2, \quad (2.63)$$

where $\mathbf{g}_\mathbf{k}$ is the reciprocal lattice vector which is closest to $\mathbf{k}$, and $\mathbf{q} = \mathbf{k} - \mathbf{g}_\mathbf{k}$. Using this expansion in (2.59) and noting that $\mathbf{g}_\mathbf{k} = 0$ for small $\mathbf{k}$, the result of the spatial integration becomes

$$\frac{1}{\phi}\left[\left(\nabla H\cdot\frac{\partial}{\partial\mathbf{q}}\right)^2 \sum_n e^{-\lambda_{n\mathbf{q}}|t_2-t_1|}|\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})|^2\right]_{\mathbf{q}=0}. \quad (2.64)$$

We now use (2.35), (2.36), and (2.41) to rewrite this as

$$-2(\nabla H)^2 D_e|t_2-t_1|$$
$$+\frac{1}{\phi}\sum_n e^{-\lambda_{n0}|t_2-t_1|}\left[\left(\nabla H\cdot\frac{\partial}{\partial\mathbf{q}}\right)^2|\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})|^2\right]_{\mathbf{q}=0}. \quad (2.65)$$

The time integration then yields

$$\langle\Phi^2\rangle_{\rm grad} = (\gamma\nabla H)^2\frac{4}{3}D_e\tau^3 + \frac{1}{\phi}\sum_{n>0} b_n(\tau)\left[\left(\gamma\nabla H\cdot\frac{\partial}{\partial\mathbf{q}}\right)^2|\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})|^2\right]_{\mathbf{q}=\mathbf{0}}, \tag{2.66}$$

where $b_n(\tau)$ was defined in (2.54). Note that the $n=0$ term in the sum of (2.65) is time independent and therefore makes a vanishing contribution to the time integrations and does not appear in (2.66). In the same limits that were considered before, we find that the second term of this expression becomes

$$\frac{2}{3}\frac{D_p\tau^3}{\phi}\sum_{n>0}\tilde{\lambda}_{n0}\left[\left(\frac{\gamma\nabla H}{a}\cdot\frac{\partial}{\partial\mathbf{q}}\right)^2|\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})|^2\right]_{\mathbf{q}=\mathbf{0}} \tag{2.67}$$

for $\frac{D_p\tau}{a^2}\ll 1$,

$$\frac{2a^4\tau}{\phi D_p}\sum_{n>0}\frac{1}{\tilde{\lambda}_{n0}}\left[\left(\frac{\gamma\nabla H}{a}\cdot\frac{\partial}{\partial\mathbf{q}}\right)^2|\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})|^2\right]_{\mathbf{q}=\mathbf{0}} \tag{2.68}$$

for $\frac{D_p\tau}{a^2}\gg 1$.

Using (2.61) we can also write the result of (2.59) as $-2(\nabla H)^2D(t_2-t_1)|t_2-t_1|$. Comparing this with (2.65), we get the following representation for $D(t)$

$$D(t) = D_e - \frac{1}{2|t|\phi}\sum_n e^{-\lambda_{n0}|t|}\left[\frac{\partial^2}{\partial q_H^2}|\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})|^2\right]_{\mathbf{q}=\mathbf{0}}, \tag{2.69}$$

where $q_H \equiv (\mathbf{q}\cdot\nabla H)/|\nabla H|$ is the component of $\mathbf{q}$ along ∇H. We can also write

$$\frac{1}{2}\langle\Phi^2\rangle_{\rm grad} = -(\gamma\nabla H)^2\left(2\int_\tau^{2\tau}dt_2\int_\tau^{t_2}dt_1 - \int_\tau^{2\tau}dt_2\int_0^\tau dt_1\right)\times D(t_2-t_1)(t_2-t_1). \tag{2.70}$$

In the limiting case of a uniform fluid, $D(t)\equiv D_p$ and the time integral can be evaluated to yield the following well known result [1]

$$\frac{1}{2}\langle\Phi^2\rangle_{\rm grad} = (\gamma\nabla H)^2\frac{2}{3}D_p\tau^3, \tag{2.71}$$

which is exactly the same as the second term in the exponent of (1.1).

Clearly, for sufficiently long times τ, the first term in (2.66) dominates the behavior of $\langle\Phi^2\rangle_{\rm grad}$. Since that term is similar in form to the uniform fluid result, one might be tempted to conclude that measurement of a CPMG spin-echo train in a porous medium would simply measure the bulk effective stationary diffusion coefficient D_e, in the same way that it measures D_p when performed in a uniform fluid. This conclusion is, however, premature as will become clear in the following subsection: it is only correct if the higher order cumulants can be neglected. Note also that, although the asymptotic forms of $D(t)$ are independent of the size scale a [see (2.62)], at intermediate times $D(t)$ does depend on a (see, e.g., Ref. [27]). Therefore, $\langle\Phi^2\rangle_{\rm grad}$ should also depend on a, and not just on the shape of the microstructure.

C. Calculation of $\langle\Phi^4\rangle$

In the case under discussion, of a pore structure with simple cubic periodicity and inversion symmetry, $\langle\Phi^4\rangle$ is a sum of three contributions: pure susceptibility difference terms, pure fixed gradient terms, and cross terms. Each of these will now be discussed separately.

1. *Susceptibility difference terms*

For the pure susceptibility difference term we need to calculate the following integral

$$\frac{1}{V_p}\int_{V_p}dV_1\cdots\int_{V_p}dV_4\,G(\mathbf{r_4r_3}|t_{43})G(\mathbf{r_3r_2}|t_{32})G(\mathbf{r_2r_1}|t_{21})\times e^{i\mathbf{g}_1\cdot\mathbf{r}_1+\cdots+i\mathbf{g}_4\cdot\mathbf{r}_4}, \tag{2.72}$$

where $t_{21}\equiv t_2-t_1$, etc. If we substitute the expansion (2.34) for G, then the volume integrals can be performed independently, resulting in some Fourier expansion coefficients of the diffusion eigenfunctions or of products of those eigenfunctions. The integral of (2.72) now becomes

$$\frac{1}{\phi}\sum_n\sum_m\sum_l e^{-\lambda_{n0}|t_{43}|-\lambda_{m0}|t_{32}|-\lambda_{l0}|t_{21}|}\times\tilde{\phi}_{n\mathbf{0}}(-\mathbf{g}_4)\omega_{nm}(-\mathbf{g}_3)\omega_{ml}(-\mathbf{g}_2)\tilde{\phi}^*_{l\mathbf{0}}(\mathbf{g}_1), \tag{2.73}$$

where the matrix elements of $\hat{\omega}(\mathbf{g})$ are given by

$$\omega_{nm}(\mathbf{g}) \equiv \frac{1}{V_a}\int_{V_a\cap V_p}dV\,\phi^*_{n\mathbf{0}}(\mathbf{r})\phi_{m\mathbf{0}}(\mathbf{r})e^{-i\mathbf{g}\cdot\mathbf{r}} = \sum_{\mathbf{g}'}\tilde{\phi}^*_{n\mathbf{0}}(\mathbf{g}')\tilde{\phi}_{m\mathbf{0}}(\mathbf{g}+\mathbf{g}'), \tag{2.74}$$

$$\omega^*_{nm}(\mathbf{g}) = \omega_{mn}(-\mathbf{g}), \tag{2.75}$$

$$\omega_{nm}(\mathbf{0}) = \delta_{nm}. \tag{2.76}$$

It is useful to note that, because of (2.40), the expression for $\omega_{nm}(\mathbf{g})$ simplifies whenever either $n=0$ or $m=0$:

$$\omega_{0m}(\mathbf{g}) = \frac{1}{\sqrt{\phi}}\tilde{\phi}_{m\mathbf{0}}(\mathbf{g}), \tag{2.77}$$

$$\omega_{n0}(\mathbf{g}) = \frac{1}{\sqrt{\phi}}\tilde{\phi}^*_{n\mathbf{0}}(-\mathbf{g}). \tag{2.78}$$

Using (2.44) and (2.45) we can also calculate the product of two $\hat{\omega}$ matrices:

$$\sum_m \omega_{nm}(\mathbf{g}_1)\omega_{ml}(\mathbf{g}_2) = \sum_{\mathbf{g}'_1}\sum_{\mathbf{g}'_2} \tilde{\phi}^*_{n0}(\mathbf{g}'_1)\theta_{\mathbf{g}_1+\mathbf{g}'_1-\mathbf{g}'_2}\tilde{\phi}_{l0}(\mathbf{g}_2+\mathbf{g}'_2)$$
$$= \sum_{\mathbf{g}} \tilde{\phi}^*_{n0}(\mathbf{g}_1)\tilde{\phi}_{l0}(\mathbf{g}_1+\mathbf{g}_2+\mathbf{g})$$
$$= \omega_{nl}(\mathbf{g}_1+\mathbf{g}_2). \tag{2.79}$$

The matrix $\omega_{nn}(\mathbf{g}-\mathbf{g}')$ is easily shown to be non-negative and bounded: for any vector $A_{\mathbf{g}}$ we find [$A(\mathbf{r})$ is the function whose Fourier coefficients are $A_{\mathbf{g}}$]

$$\sum_{\mathbf{g}}\sum_{\mathbf{g}'} A^*_{\mathbf{g}}\omega_{nn}(\mathbf{g}-\mathbf{g}')A_{\mathbf{g}'} = \sum_{\mathbf{g}}\left|\sum_{\mathbf{g}'}\tilde{\phi}_{n0}(\mathbf{g}-\mathbf{g}')A_{\mathbf{g}'}\right|^2 = \frac{1}{V_a}\int_{V_a} dV\,\theta_p(\mathbf{r})|\phi_{n0}(\mathbf{r})A(\mathbf{r})|^2$$
$$\leq \max_{\mathbf{r}\in V_a\cap V_p} |\phi_{n0}(\mathbf{r})|^2 \sum_{\mathbf{g}}|A_{\mathbf{g}}|^2,$$
$$> 0. \tag{2.80}$$

Thus the eigenvalues of $\omega_{nn}(\mathbf{g}-\mathbf{g}')$ lie between 0 and $\max|\phi_{n0}(\mathbf{r})|^2$, which is usually of order 1.

The necessary time integrals are

$$\left(2\int_\tau^{2\tau} dt_4\int_\tau^{t_4} dt_3\int_\tau^{t_3} dt_2\int_\tau^{t_2} dt_1 - 2\int_\tau^{2\tau} dt_4\int_\tau^{t_4} dt_3\int_\tau^{t_3} dt_2\int_0^{\tau} dt_1 + \int_\tau^{2\tau} dt_4\int_\tau^{t_4} dt_3\int_0^{\tau} dt_2\int_0^{t_2} dt_1\right)$$
$$\times e^{-\lambda_n t_{43}-\lambda_m t_{32}-\lambda_l t_{21}} \equiv b_{nml}(\tau), \tag{2.81}$$

where we have omitted the 0 subscript from λ_{n0}, etc., and where the last equality serves to define $b_{nml}(\tau)$. The precise form of this function, which can be obtained by straightforward though tedious integration, is

$$b_{nml}(\tau) = \frac{2}{\lambda_l\lambda_m\lambda_n}\left(\tau - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right) - \frac{2}{\lambda_l\lambda_m(\lambda_n-\lambda_m)}\left(\frac{1-e^{-\lambda_m\tau}}{\lambda_m} - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right)$$
$$-\frac{2(2-e^{-\lambda_l\tau})}{\lambda_l(\lambda_m-\lambda_l)}\left[\frac{1}{\lambda_n-\lambda_l}\left(\frac{1-e^{-\lambda_l\tau}}{\lambda_l} - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right) - \frac{1}{\lambda_n-\lambda_m}\left(\frac{1-e^{-\lambda_m\tau}}{\lambda_m} - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right)\right]$$
$$+\frac{1}{\lambda_l(\lambda_n-\lambda_m)}\left(\frac{1-e^{-\lambda_m\tau}}{\lambda_m} - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right)\left(\frac{1-e^{-\lambda_m\tau}}{\lambda_m} - \frac{e^{-\lambda_l\tau}-e^{-\lambda_m\tau}}{\lambda_m-\lambda_l}\right). \tag{2.82}$$

This form is strictly valid only when λ_n, λ_m, and λ_l are all different and nonzero. The special cases when two or more of these eigenvalues are equal, or when one or two of them vanish, can be obtained as limiting cases of this form. Thus, for example, $b_{n0l}(\tau)$ is obtained from (2.82) by taking the limit $\lambda_m \to 0$, leading to

$$b_{n0l}(\tau) = \frac{\tau^2}{\lambda_l\lambda_n} - \frac{2}{\lambda_l\lambda_n}\left(\frac{1}{\lambda_n} + \frac{2-e^{-\lambda_l\tau}}{\lambda_l}\right)\left(\tau - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right) + \frac{2}{\lambda_l^2}\frac{2-e^{-\lambda_l\tau}}{\lambda_n-\lambda_l}\left(\frac{1-e^{-\lambda_l\tau}}{\lambda_l} - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right)$$
$$+\frac{1}{\lambda_l\lambda_n}\left(\tau - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right)\left(\tau - \frac{1-e^{-\lambda_l\tau}}{\lambda_l}\right). \tag{2.83}$$

The further limits $\lambda_n \to 0$ and $\lambda_l \to 0$ lead to

$$b_{n00}(\tau) = -\frac{2}{3}\frac{\tau^3}{\lambda_n} - \frac{\tau^2}{\lambda_n^2} + \left(\frac{\tau^2}{2\lambda_n} + \frac{2\tau}{\lambda_n^2} + \frac{2}{\lambda_n^3}\right)\left(\tau - \frac{1-e^{-\lambda_n\tau}}{\lambda_n}\right), \tag{2.84}$$

$$b_{00l}(\tau) = \frac{5}{6}\frac{\tau^3}{\lambda_l} - \frac{2(2-e^{-\lambda_l\tau})}{\lambda_l^2}\left(\frac{1-e^{-\lambda_l\tau}}{\lambda_l^2} - \frac{\tau}{\lambda_l} + \frac{\tau^2}{2}\right) - \frac{\tau^2}{2\lambda_l}\frac{1-e^{-\lambda_l\tau}}{\lambda_l}. \tag{2.85}$$

An important property of $b_{nml}(\tau)$ is its asymptotic behavior when τ is either very large or very small. This is summarized by

$$b_{nml}(\tau) \cong \frac{9\lambda_l - 6\lambda_m - \lambda_n}{60}\tau^5 \quad \text{for small } \tau, \tag{2.86}$$

and by the following expressions, which are valid for large τ:

$$b_{nml}(\tau) \cong \frac{2\tau}{\lambda_l\lambda_m\lambda_n} + O(1) \quad \text{for } n,m,l > 0, \tag{2.87}$$

$$b_{nm0}(\tau) \cong -\frac{\tau^2}{\lambda_m\lambda_n} + \frac{\tau}{\lambda_m^2\lambda_n} + O(1) \quad \text{for } n,m > 0, \tag{2.88}$$

$$b_{n0l}(\tau) \cong \frac{2\tau^2}{\lambda_l\lambda_n} - \frac{5\tau}{\lambda_l^2\lambda_n} - \frac{3\tau}{\lambda_l\lambda_n^2} + O(1) \quad \text{for } n,l > 0, \tag{2.89}$$

$$b_{0ml}(\tau) \cong \frac{\tau^2}{\lambda_l\lambda_m} - \frac{4\tau}{\lambda_l^2\lambda_m} - \frac{\tau}{\lambda_l\lambda_m^2} + O(1) \quad \text{for } m,l > 0, \tag{2.90}$$

$$b_{n00}(\tau) \cong -\frac{\tau^3}{6\lambda_n} + \frac{\tau^2}{2\lambda_n^2} + O(1) \quad \text{for } n > 0, \tag{2.91}$$

$$b_{0m0}(\tau) \cong -\frac{2\tau^3}{3\lambda_m} + \frac{2\tau^2}{\lambda_m^2} - \frac{2\tau}{\lambda_m^3} + O(1) \quad \text{for } m > 0, \tag{2.92}$$

$$b_{00l}(\tau) \cong \frac{5\tau^3}{6\lambda_l} - \frac{5\tau^2}{2\lambda_l^2} + \frac{4\tau}{\lambda_l^3} + O(1) \quad \text{for } l > 0. \tag{2.93}$$

The pure susceptibility difference part of $\langle\Phi^4\rangle$ is given by

$$\frac{1}{24}\langle\Phi^4\rangle_{\text{susc}} = \frac{1}{\phi}(4\pi\Delta\chi\gamma H_0)^4 \sum_{n,m,l} b_{nml}(\tau)a_n a_{nm} a_{ml} a_l^*, \tag{2.94}$$

where a_n is given by (2.49), and

$$a_{nm} \equiv \sum_{\mathbf{g}\neq 0} \cos^2(\mathbf{g},\mathbf{e}_z)\theta_{\mathbf{g}}^* \omega_{nm}(\mathbf{g}). \tag{2.95}$$

From (2.75)–(2.78) we get that

$$a_{nm}^* = a_{mn}, \tag{2.96}$$

$$a_{0m} = \frac{1}{\sqrt{\phi}} a_m, \tag{2.97}$$

$$a_{n0} = \frac{1}{\sqrt{\phi}} a_n^*. \tag{2.98}$$

The a_{nm} coefficients can be bounded by considering the following sum:

$$\begin{aligned}\sum_m |a_{nm}|^2 &= \sum_{\mathbf{g}\neq 0}\sum_{\mathbf{g}'\neq 0} \cos^2(\mathbf{g},\mathbf{e}_z)\theta_{\mathbf{g}}^*\omega_{nn}(\mathbf{g}-\mathbf{g}')\theta_{\mathbf{g}'}\cos^2(\mathbf{g}',\mathbf{e}_z) \\ &\leq \max|\phi_{n\mathbf{0}}(\mathbf{r})|^2 \sum_{\mathbf{g}\neq 0}\cos^4(\mathbf{g},\mathbf{e}_z)|\theta_{\mathbf{g}}|^2 \\ &\leq \max|\phi_{n\mathbf{0}}(\mathbf{r})|^2 \sum_{\mathbf{g}\neq 0}\cos^2(\mathbf{g},\mathbf{e}_z)|\theta_{\mathbf{g}}|^2 \\ &= \frac{1}{3}\phi(1-\phi)\max|\phi_{n\mathbf{0}}(\mathbf{r})|^2. \end{aligned} \tag{2.99}$$

From the asymptotic behaviors of $b_n(\tau)$ ($\propto \tau^3$) and $b_{nml}(\tau)$ ($\propto \tau^5$), at short times it is clear that $\langle\Phi^4\rangle_{\text{susc}}$ is asymptotically much greater than $3\langle\Phi^2\rangle_{\text{susc}}^2$, but much less than $\langle\Phi^2\rangle_{\text{susc}}$. Thus for times τ that are short enough, the Gaussian approximation will be valid for the probability distribution of Φ. By contrast, when τ is large, it appears at first sight as though $\langle\Phi^4\rangle_{\text{susc}}$ includes terms that are asymptotically much greater than both $3\langle\Phi^2\rangle_{\text{susc}}^2$ and $\langle\Phi^2\rangle_{\text{susc}}$. However, a remarkable set of cancellations occur which can lead to a situation where the Gaussian approximation is valid even then. From the asymptotic behaviors of $b_n(\tau)$ and $b_{nml}(\tau)$ at long times we get for the fourth order cumulant average, after some algebra,

$$\frac{1}{24}\langle\Phi^4\rangle_{c,\text{susc}} \cong (4\pi\gamma\Delta\chi H_0)^4\tau\left(\frac{a^2}{D_p}\right)^3 \mathcal{F}_4 \quad \text{for large } \tau, \tag{2.100}$$

where

$$\frac{\mathcal{F}_4}{2} \equiv \sum_{n,m,l>0} \frac{a_n a_{nm} a_{ml} a_l^*}{\phi\tilde{\lambda}_l\tilde{\lambda}_m\tilde{\lambda}_n} - \sum_{n,m>0}\left(\frac{(1-\phi)a_n a_{nm} a_m^*(\tilde{\lambda}_m+\tilde{\lambda}_n)}{3\phi\tilde{\lambda}_m^2\tilde{\lambda}_n^2} + \frac{|a_n|^2|a_m|^2}{\phi^2\tilde{\lambda}_m\tilde{\lambda}_n^2}\right) + \sum_{n>0}\frac{(1-\phi)^2|a_n|^2}{9\phi\tilde{\lambda}_n^3} \tag{2.101}$$

is a dimensionless numerical factor of order 1, which tends to 0 when $\phi \to 0$ or $\phi \to 1$. From (2.57) we can also write

$$\frac{1}{2}\langle\Phi^2\rangle_{\text{susc}} \cong (4\pi\gamma\Delta\chi H_0)^2\tau\frac{a^2}{D_p}\mathcal{F}_2 \quad \text{for large } \tau, \tag{2.102}$$

where

$$\mathcal{F}_2 \equiv \frac{2}{\phi}\sum_{n>0}\frac{|a_n|^2}{\tilde{\lambda}_n} \tag{2.103}$$

is another dimensionless factor of order 1. The distribution of Φ will be approximately Gaussian for large τ if the ratio $\frac{1}{24}\langle\Phi^4\rangle_{c,\text{susc}}/\frac{1}{2}\langle\Phi^2\rangle_{\text{susc}} \ll 1$, i.e., if

$$(4\pi\gamma\Delta\chi H_0)^2\left(\frac{a^2}{D_p}\right)^2\frac{\mathcal{F}_4}{\mathcal{F}_2} \ll 1. \tag{2.104}$$

Since $\mathcal{F}_2$, $\mathcal{F}_4$ are both independent of a, therefore the left-hand side of this inequality is proportional to a^4. In Sec. III we present results of a numerical study of $\langle\Phi^2\rangle_{\text{susc}}$ and $\langle\Phi^4\rangle_{c,\text{susc}}$ over a range of times τ, including large τ, in order to study the validity of the Gaussian approximation.

2. Fixed gradient terms

For the pure uniform gradient contribution to $\langle\Phi^4\rangle$ we need to calculate the following spatial integral [see (2.20), (2.18), and (2.29)]:

$$\frac{2}{V_p}\int_{V_p} dV_4\cdots\int_{V_p} dV_1[(\mathbf{r}_{43}\cdot\nabla H)^2(\mathbf{r}_{21}\cdot\nabla H)^2+(\mathbf{r}_{42}\cdot\nabla H)^2(\mathbf{r}_{31}\cdot\nabla H)^2+(\mathbf{r}_{41}\cdot\nabla H)^2(\mathbf{r}_{32}\cdot\nabla H)^2] \times G(\mathbf{r}_4\mathbf{r}_3|t_{43})G(\mathbf{r}_3\mathbf{r}_2|t_{32})G(\mathbf{r}_2\mathbf{r}_1|t_{21}). \quad (2.105)$$

This is again done by taking derivatives of an appropriate Fourier transform

$$M_3(\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3|t_{21}t_{32}t_{43})\equiv\frac{1}{V_p}\int_{V_p} dV_1\cdots\int_{V_p} dV_4 G(\mathbf{r}_4\mathbf{r}_3|t_{43})G(\mathbf{r}_3\mathbf{r}_2|t_{32})G(\mathbf{r}_2\mathbf{r}_1|t_{21})e^{-i\mathbf{k}_3\cdot\mathbf{r}_{43}-i\mathbf{k}_2\cdot\mathbf{r}_{32}-i\mathbf{k}_1\cdot\mathbf{r}_{21}}, \quad (2.106)$$

where $\mathbf{r}_{21}\equiv\mathbf{r}_2-\mathbf{r}_1$, etc. The result of (2.105) is obtained as

$$2\left[\frac{\partial^2}{\partial k_1^2}\frac{\partial^2}{\partial k_3^2}+\left(\frac{\partial}{\partial k_1}+\frac{\partial}{\partial k_2}\right)^2\left(\frac{\partial}{\partial k_3}+\frac{\partial}{\partial k_2}\right)^2+\left(\frac{\partial}{\partial k_1}+\frac{\partial}{\partial k_2}+\frac{\partial}{\partial k_3}\right)^2\frac{\partial^2}{\partial k_2^2}\right]M_3(\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3|t_{21}t_{32}t_{43})\Big|_{k_i=0}, \quad (2.107)$$

where each partial derivative actually stands for the scalar product of the gradient operator in k space with ∇H, i.e.,

$$\frac{\partial}{\partial k_i}\equiv\nabla H\cdot\frac{\partial}{\partial\mathbf{k}_i}. \quad (2.108)$$

Using (2.34) to expand the diffusion propagators, we get the following representation for M_3 in the case where all the $\mathbf{k}_i$ are inside the first Brillouin zone, and are therefore replaced by $\mathbf{q}_i$:

$$M_3(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3|t_{21}t_{32}t_{43})=\frac{1}{\phi}\sum_{\mathbf{g}_1}\sum_{\mathbf{g}_2}\sum_{n,m,l}e^{-\lambda_{l\mathbf{q}_1}|t_{21}|-\lambda_{m\mathbf{q}_2}|t_{32}|-\lambda_{n\mathbf{q}_3}|t_{43}|} \times\tilde{\phi}_{l\mathbf{q}_1}(\mathbf{g}_1)\tilde{\phi}^*_{l\mathbf{q}_1}(\mathbf{0})\tilde{\phi}_{m\mathbf{q}_2}(\mathbf{g}_2)\tilde{\phi}^*_{m\mathbf{q}_2}(\mathbf{g}_1)\tilde{\phi}_{n\mathbf{q}_3}(\mathbf{0})\tilde{\phi}^*_{n\mathbf{q}_3}(\mathbf{g}_2). \quad (2.109)$$

When the time integrations of (2.81) are applied to this result, the time dependent exponential factor is replaced by $b_{nml}(\tau)$ as given in (2.82), but with λ_l, λ_m, λ_n replaced by $\lambda_{l\mathbf{q}_1}$, $\lambda_{m\mathbf{q}_2}$, $\lambda_{n\mathbf{q}_3}$. We denote this quantity by $b_{n\mathbf{q}_3m\mathbf{q}_2l\mathbf{q}_1}(\tau)$. We thus get for the uniform field gradient contribution to $\langle\Phi^4\rangle$

$$\langle\Phi^4\rangle_{\text{grad}}=\left[\frac{\partial^2}{\partial q_1^2}\frac{\partial^2}{\partial q_3^2}+\left(\frac{\partial}{\partial q_1}+\frac{\partial}{\partial q_2}\right)^2\left(\frac{\partial}{\partial q_3}+\frac{\partial}{\partial q_2}\right)^2+\left(\frac{\partial}{\partial q_1}+\frac{\partial}{\partial q_2}+\frac{\partial}{\partial q_3}\right)^2\frac{\partial^2}{\partial q_2^2}\right] \times\frac{2}{\phi}(\gamma\nabla H)^4\sum_{n,m,l}b_{n\mathbf{q}_3m\mathbf{q}_2l\mathbf{q}_1}(\tau)\tilde{\phi}_{n\mathbf{q}_3}(\mathbf{0})\varpi_{n\mathbf{q}_3m\mathbf{q}_2}\varpi_{m\mathbf{q}_2l\mathbf{q}_1}\tilde{\phi}^*_{l\mathbf{q}_1}(\mathbf{0})\Big|_{\mathbf{q}_i=0}, \quad (2.110)$$

where

$$\varpi_{m\mathbf{q}n\mathbf{q}'}\equiv\sum_{\mathbf{g}}\tilde{\phi}^*_{m\mathbf{q}}(\mathbf{g})\tilde{\phi}_{n\mathbf{q}'}(\mathbf{g}) \quad (2.111)$$

is a Hermitian matrix which satisfies

$$\varpi^*_{m\mathbf{q}n\mathbf{q}'}=\varpi_{n\mathbf{q}'m\mathbf{q}}, \quad (2.112)$$

$$\varpi_{m\mathbf{q}n\mathbf{q}}=\delta_{mn}, \quad (2.113)$$

$$\varpi_{m\mathbf{0}n\mathbf{0}}=\omega_{mn}(\mathbf{0})=\delta_{mn}. \quad (2.114)$$

If the partial derivatives are applied to the time dependent exponential factor before the time integration, (2.110) has the following form:

$$\langle\Phi^4\rangle_{\text{grad}}=(\gamma\nabla H)^4\left\{\frac{16}{3}D_e^2\tau^6-9.6D_pa^2C_0\tau^5+\frac{2}{\phi}\sum_{n,m,l}\Big[b_{nml}(\tau)(\mathcal{AB}+\mathcal{CD}+\mathcal{EF})\mathcal{G} -2D_ec_{nml}(\tau)(\mathcal{A}+\mathcal{C}+\mathcal{F})\mathcal{G}-2D_ed_{nml}(\tau)(\mathcal{C}+\mathcal{D}+\mathcal{E}+\mathcal{F})\mathcal{G}-2D_ee_{nml}(\tau)(\mathcal{B}+\mathcal{D}+\mathcal{F})\mathcal{G}\Big]\right\}, \quad (2.115)$$

where C_0 is given by (2.36), $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, $\mathcal{D}$, $\mathcal{E}$, and $\mathcal{F}$ are partial differential operators defined by

$$\mathcal{A} \equiv \frac{\partial^2}{\partial q_1^2}, \quad \mathcal{B} \equiv \frac{\partial^2}{\partial q_3^2},$$
$$\mathcal{C} \equiv \left(\frac{\partial}{\partial q_1} + \frac{\partial}{\partial q_2}\right)^2, \quad \mathcal{D} \equiv \left(\frac{\partial}{\partial q_3} + \frac{\partial}{\partial q_2}\right)^2,$$
$$\mathcal{E} \equiv \left(\frac{\partial}{\partial q_1} + \frac{\partial}{\partial q_2} + \frac{\partial}{\partial q_3}\right)^2, \quad \mathcal{F} \equiv \frac{\partial^2}{\partial q_2^2} \qquad (2.116)$$

operating on the function $\mathcal{G}$

$$\mathcal{G}(q_1, q_2, q_3) \equiv \tilde{\phi}_{n\mathbf{q_3}}(\mathbf{0}) \varpi_{n\mathbf{q_3}m\mathbf{q_2}} \varpi_{m\mathbf{q_2}l\mathbf{q_1}} \tilde{\phi}^*_{l\mathbf{q_1}}(\mathbf{0}), \quad (2.117)$$

and $c_{nml}(\tau)$, $d_{nml}(\tau)$, and $e_{nml}(\tau)$ are obtained by time integrations like those in (2.81) for $b_{nml}(\tau)$, but with different integrands defined as follows

$$c_{nml}(\tau) \equiv \int \cdots \; t_{43} e^{-\lambda_n t_{43} - \lambda_m t_{32} - \lambda_l t_{21}}, \qquad (2.118)$$

$$d_{nml}(\tau) \equiv \int \cdots \; t_{32} e^{-\lambda_n t_{43} - \lambda_m t_{32} - \lambda_l t_{21}}, \qquad (2.119)$$

$$e_{nml}(\tau) \equiv \int \cdots \; t_{21} e^{-\lambda_n t_{43} - \lambda_m t_{32} - \lambda_l t_{21}}. \qquad (2.120)$$

Note that besides the explicit dependence on a, which is exhibited in (2.115), $b_{nml}(\tau)$, $c_{nml}(\tau)$, $d_{nml}(\tau)$, $e_{nml}(\tau)$ also all depend on a through the eigenvalues λ_{n0}, $n \neq 0$, etc.

In Sec. III below we present results of numerical evaluations of $\langle\Phi^4\rangle_{\rm grad}$. Here we confine our discussion to the limits of small or large τ. Because $\langle\Phi^2\rangle_{\rm grad} \propto \tau^3$ in both of these limits [see (2.66)–(2.68)], therefore we also investigate the asymptotic behavior of $\langle\Phi^4\rangle_{\rm grad}$ in those two limits.

At short times τ, the leading behavior is $\langle\Phi^4\rangle_{\rm grad} \propto \tau^5 a^2$ [see (2.86)]. This is much greater than $3\langle\Phi^2\rangle^2_{\rm grad} \propto \tau^6 a^0$, but much smaller than $\langle\Phi^2\rangle_{\rm grad}$, therefore the Gaussian approximation for the distribution of Φ will again be valid for sufficiently short times. This result differs from what is quoted in Ref. [11], where it was found that $\langle\Phi^4\rangle_{c,\rm grad} \propto \tau^{13/2}$ at short times. We believe our result is correct, although the conclusion regarding the validity of the Gaussian approximation at short times remains unchanged.

At long times, the situation is more complicated. The leading behavior of $\langle\Phi^4\rangle_{\rm grad}$ is obtained from the $n = m = l = 0$ terms in the sum of (2.110), and when the q derivatives all act upon $b_{n\mathbf{q_3}m\mathbf{q_2}l\mathbf{q_1}}(\tau)$. It shows up as the first term in (2.115). Hence, we have

$$\langle\Phi^4\rangle_{\rm grad} = \frac{16}{3}(\gamma\nabla H)^4 D_e^2 \tau^6 + O(\tau^5) \quad \text{for large } \tau. \qquad (2.121)$$

Comparing this with (2.66) shows that it is exactly equal to the leading term of $3\langle\Phi^2\rangle^2_{\rm grad}$, therefore the $O(\tau^6)$ term of the fourth order cumulant average $\langle\Phi^4\rangle_{c,\rm grad}$ vanishes.

The next terms in the large τ expansion of $\langle\Phi^4\rangle_{\rm grad}$ are $O(\tau^5 a^2)$, and they arise from the $n = m = l = 0$ terms in (2.110) when exactly two q derivatives are applied to the $b_{n\mathbf{q_3}m\mathbf{q_2}l\mathbf{q_1}}(\tau)$ factor, which shows up as the second term in (2.115). The terms of order $O(\tau^5)$ do not appear to cancel out, therefore

$$\langle\Phi^4\rangle_{c,\rm grad} = O(\tau^5 a^2) \gg \langle\Phi^2\rangle_{\rm grad} = O(\tau^3) \quad \text{for large } \tau. \qquad (2.122)$$

This leads to the conclusion that the Gaussian approximation for the distribution function of Φ in the presence of a uniform field gradient must always break down if τ is large enough, and that this will occur sooner when a is larger.

In the limiting case of a uniform medium, the result (2.121) is exact with $D_e \to D_p$. This is due to the fact that $\tilde{\phi}_{n\mathbf{q}}(\mathbf{g}) = \delta_{\mathbf{g}\mathbf{g}_n}$ is then independent of $\mathbf{q}$ and that (2.36) is then also exact with $D_e \to D_p$ and $C_0 \to 0$. It is therefore clear that, for a uniform fluid medium with a low density of solid obstacles, the deviations from Gaussian behavior must remain small for all values of Φ which have a non-negligible probability, i.e., the coefficients of the τ^5, τ^4, and τ^3 terms in $\langle\Phi^4\rangle_{c,\rm grad}$ are sufficiently small that those terms can be neglected for all times at which $\langle\Phi^2\rangle_{\rm grad}$ is not too large. It remains to be seen whether this can occur also in a non-dilute system of obstacles—this will be investigated numerically in the following section, using (2.115).

3. Cross terms

In contrast with $\langle\Phi^2\rangle$, the fourth moment $\langle\Phi^4\rangle$ contains cross terms where both the susceptibility difference and the uniform field gradient parts of $\delta H(\mathbf{r})$ contribute. In the integrand of the symmetric time integration of (2.15) these terms are

$$\langle(\mathbf{r}_1 \cdot \boldsymbol{\nabla} H)(\mathbf{r}_2 \cdot \boldsymbol{\nabla} H)\delta H_{\rm susc}(\mathbf{r}_3)\delta H_{\rm susc}(\mathbf{r}_4) + 5 \text{ similar terms}\rangle. \qquad (2.123)$$

A discussion similar to the one at the end of Sec. II A leads to the replacement of this average by

$$-12\langle[(\mathbf{r}_1 - \mathbf{r}_2) \cdot \boldsymbol{\nabla} H]^2 \delta H_{\rm susc}(\mathbf{r}_3)\delta H_{\rm susc}(\mathbf{r}_4) + 5 \text{ similar terms}\rangle, \qquad (2.124)$$

and replacement of the symmetric integration over the four times $t_1 \cdots t_4$ by the combination of integrations which appears in (2.81). A somewhat tedious calculation, in which G is represented as in (2.34), and the eigenfunctions are expanded as in (2.38), results in the following expression for the cross term in $\langle\Phi^4\rangle$:

$$\langle\Phi^4\rangle_{\rm cross} = \frac{12}{\phi}(4\pi\Delta\chi H_0\gamma^2)^2\left(\nabla H\cdot\frac{\partial}{\partial\mathbf{q}}\right)^2 \times\sum_{n,m,l}[b_{n\mathbf{0}m\mathbf{0}l\mathbf{q}}(\tau)a_n a_{nm}\varpi_{m\mathbf{0}l\mathbf{q}}\tilde{\phi}^*_{l\mathbf{q}}(\mathbf{0}) +b_{n\mathbf{0}m\mathbf{q}l\mathbf{q}}(\tau)a_n\varpi_{n\mathbf{0}m\mathbf{q}}a_{m\mathbf{q}l\mathbf{q}}\tilde{\phi}^*_{l\mathbf{q}}(\mathbf{0}) +b_{n\mathbf{q}m\mathbf{q}l\mathbf{q}}(\tau)\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})a_{n\mathbf{q}m\mathbf{q}}a_{m\mathbf{q}l\mathbf{q}}\tilde{\phi}^*_{l\mathbf{q}}(\mathbf{0}) +b_{n\mathbf{0}m\mathbf{q}l\mathbf{0}}(\tau)a_n\varpi_{n\mathbf{0}m\mathbf{q}}\varpi_{m\mathbf{q}l\mathbf{0}}a_l^* +b_{n\mathbf{q}m\mathbf{q}l\mathbf{0}}(\tau)\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})a_{n\mathbf{q}m\mathbf{q}}\varpi_{m\mathbf{q}l\mathbf{0}}a_l^* +b_{n\mathbf{q}m\mathbf{0}l\mathbf{0}}(\tau)\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})\varpi_{n\mathbf{q}m\mathbf{0}}a_{ml}a_l^*], \quad (2.125)$$

where

$$a_{n\mathbf{q}m\mathbf{q}} \equiv \sum_{\mathbf{g}\neq 0}\cos^2(\mathbf{g},\mathbf{e}_z)\theta^*_{\mathbf{g}}\sum_{\mathbf{g}_1}\tilde{\phi}^*_{n\mathbf{q}}(\mathbf{g}_1)\tilde{\phi}_{m\mathbf{q}}(\mathbf{g}_1+\mathbf{g}). \quad (2.126)$$

Again, if the partial derivatives are applied to the time dependent exponential factor before the time integration, (2.125) has the following form:

$$\langle\Phi^4\rangle_{\rm cross} = \frac{12}{\phi}(4\pi\Delta\chi H_0\gamma^2)^2\,(\nabla H)^2\left\{\sum_{n,m,l}b_{nml}(\tau)\frac{\partial^2}{\partial q^2}[a_n a_{nm}\varpi_{m\mathbf{0}l\mathbf{q}}\tilde{\phi}^*_{l\mathbf{q}}(\mathbf{0}) + a_n\varpi_{n\mathbf{0}m\mathbf{q}}a_{m\mathbf{q}l\mathbf{q}}\tilde{\phi}^*_{l\mathbf{q}}(\mathbf{0}) +\tilde{\phi}_{n\mathbf{q}}(\mathbf{0})a_{n\mathbf{q}m\mathbf{q}}a_{m\mathbf{q}l\mathbf{q}}\tilde{\phi}^*_{l\mathbf{q}}(\mathbf{0}) + a_n\varpi_{n\mathbf{0}m\mathbf{q}}\varpi_{m\mathbf{q}l\mathbf{0}}a_l^* + \tilde{\phi}_{n\mathbf{q}}(\mathbf{0})a_{n\mathbf{q}m\mathbf{q}}\varpi_{m\mathbf{q}l\mathbf{0}}a_l^* + \tilde{\phi}_{n\mathbf{q}}(\mathbf{0})\varpi_{n\mathbf{q}m\mathbf{0}}a_{ml}a_l^*] - \sum_{n>0}2D_e|a_n|^2[c_{00n}(\tau)+d_{nnn}(\tau)+e_{n00}(\tau)+c_{0nn}(\tau)+d_{0nn}(\tau)+c_{0n0}(\tau)+d_{0n0}(\tau) +e_{0n0}(\tau)+d_{nn0}(\tau)+e_{nn0}(\tau)]\right\}. \quad (2.127)$$

These expressions are used in Sec. III in order to calculate $\langle\Phi^4\rangle_{\rm cross}$ numerically for some specific examples of a periodic porous medium. In order to examine its large τ behavior, we notice that the leading terms come from the second summation in (2.127), hence,

$$\langle\Phi^4\rangle_{\rm cross} \cong \frac{32}{\phi}(4\pi\Delta\chi H_0\gamma^2\nabla H)^2 D_e \times\sum_{n>0}|a_n|^2\left(\frac{\tau^4}{\lambda_n}-\frac{3\tau^3}{2\lambda_n^2}+\cdots\right) \quad \text{for large } \tau. \quad (2.128)$$

The leading $\tau^4 a^2$ behavior is exactly cancelled by the leading large τ behavior of $6\langle\Phi^2\rangle_{\rm susc}\langle\Phi^2\rangle_{\rm grad}$. In the next order, τ^3a^4, there are also contributions from other parts of (2.127). The τ^3 terms in $\langle\Phi^4\rangle_{\rm cross}$ are not cancelled by similar terms in $6\langle\Phi^2\rangle_{\rm susc}\langle\Phi^2\rangle_{\rm grad}$, therefore $\langle\Phi^4\rangle_{c,\rm cross}\propto\tau^3a^4$ for large τ.

III. RESULTS AND DISCUSSION

One of our goals in the foregoing theoretical development is to try to address several issues facing the interpretation of T_2 CPMG measurements for porous media, such as rocks. For instance, an increase in τ causes an increase in relaxation rate due to diffusion effects. How does this increase in rate relate to the time dependent effective diffusion coefficient or other physical parameters such as pore size, formation factor, and susceptibility difference? If the assumption of a Gaussian distribution for the phase angle eventually breaks down, as discussed in the previous section, over what range of τ values is the assumption valid? How does the length of this time frame depend on some of the parameters mentioned above?

The magnetic field inhomogeneities affecting the T_2 measurements for porous media come from two sources. One is the field gradient externally applied to the system. It occurs over a much larger scale compared to pore dimensions, and in the above treatment, we have assumed that it is uniform throughout the system. Another source of field inhomogeneities is the magnetic susceptibility difference between the pore fluid and solid matrix, which makes the *local field* nonuniform even when the *applied field* is accurately uniform. The resultant spatial variations are at the pore size scale and can be strongly affected by the local pore geometry. Assuming the phase angles of spins have a Gaussian distribution (which is a good approximation if $\langle\Phi^4\rangle_c \ll \langle\Phi^2\rangle$), the magnetization of the system at time 2τ is given by

$$\frac{M(2\tau)}{M(0)} = \exp\left(-\frac{2\tau}{T_2}-\frac{1}{2}\langle\Phi^2\rangle_{\rm susc}-\frac{1}{2}\langle\Phi^2\rangle_{\rm grad}\right), \quad (3.1)$$

where $\langle\Phi^2\rangle_{\rm susc}$ and $\langle\Phi^2\rangle_{\rm grad}$ are given by (2.56) and (2.66), respectively.

Frequently, in T_2 CPMG measurements, increased relaxation rates are measured. Using Brown and Fantazzini's method [14], it can be shown that from (2.56) and (2.66) we get

$$-\ln\frac{M(2n\tau)}{M(0)}-\frac{2n\tau}{T_2} = (\gamma\nabla H)^2\left[\frac{2n\tau^3}{3}D_e+\frac{1}{2\phi}\sum_{m>0}c_m(\tau)\frac{\partial^2}{\partial q^2}\left|\tilde{\phi}_{m\mathbf{q}}(\mathbf{0})\right|^2_{\mathbf{q}=0}\right] +\frac{1}{\phi}(4\pi\gamma\Delta\chi H_0)^2\sum_{m>0}c_m(\tau)|a_m|^2, \quad (3.2)$$

where $c_m(\tau)$ is given by

$$c_m(\tau) = \frac{2n\tau}{\lambda_{m0}}\left[1 - \frac{\tanh(\lambda_{m0}\tau)}{\lambda_{m0}\tau}\right] + \frac{(1-e^{-\lambda_{m0}\tau})}{\lambda_{m0}^2(1+e^{-2\lambda_{m0}\tau})^2}[1+(-)^n e^{-2n\lambda_{m0}\tau}]. \quad (3.3)$$

The increase of relaxation rate is obtained by differentiating (3.2) with respect to elapsed time t, where $t = 2n\tau$. We note that for the magnetic susceptibility difference effect the increase of the relaxation rate is proportional to the square of the field strength and the magnetic susceptibility difference. From (3.3), it can be shown that at short times, the increase of relaxation rate is also proportional to $\lambda_{m0}\tau^2 = \tilde{\lambda}_{m0}D_p\tau^2/a^2$. At long times, it is inversely proportional to $\lambda_{m0} = \tilde{\lambda}_{m0}D_p/a^2$, where λ_{m0} can be considered as the dominant term in the summation. Hence, the total shift of relaxation rate due to magnetic susceptibility difference effect at sufficiently long time is proportional to a^2/D_p, where a is the edge length of a unit cell. For the external field gradient effect, the increase of the relaxation rate is proportional to the square of the field gradient. Its short time behavior is also proportional to $\tau^2 a^0$, but at long times it is dominated by the τ^2 behavior from the term containing D_e, and is again independent of a. The above statements are valid only when the phase distribution is Gaussian, or nearly Gaussian.

In the following, we present results of numerical calculations which we carried out for a periodic porous medium consisting of simple cubic arrays of identical spheres which just touch each other. Similar calculations can be extended to overlapping spheres or any periodic system. We believe that many of the properties studied here do not have to do with the long range order and can be extended to disordered systems such as porous rocks.

In Fig. 1, we show results of the computations for $\langle\Phi^2\rangle_{\rm susc}$ and $\langle\Phi^2\rangle_{\rm grad}$ as functions of τ using (2.56) and (2.66) for three different values of a (10, 20, and 30 μm), where a is the edge length of the unit cell. The phase angle Φ is in radians. The spin aligning magnetic field was chosen to yield a resonance frequency of 1 MHz for protons, which is quite close to the commercially available NMR logging tools used in the petroleum industry. The external magnetic field gradient was arbitrarily chosen to be 1 G/cm. The behavior for other values of magnetic field or field gradient can be easily scaled according to (2.56) and (2.66). The magnetic susceptibilities used here are: solid matrix (quartz) $\chi_m = -1.3 \times 10^{-6}$ emu/cm^3 and pore fluid (water) $\chi_p = -0.7 \times 10^{-6}$ emu/cm^3. (The magnetic susceptibility of sandstones varies, ranging from slightly diamagnetic to paramagnetic with typical values of $\chi_m = 2 \times 10^{-6}$ emu/cm^3.) The effect of these values can also be scaled as $(\Delta\chi)^2$, according to (2.56). Unless otherwise specified, we have assumed the same values quoted here for H_0, ∇H, χ_m, and χ_p for all the numerical results presented in the following.

In laboratory measurements, the applied magnetic field gradient is typically quite small. Thus the susceptibility difference effect can dominate the T_2 relaxation behavior.

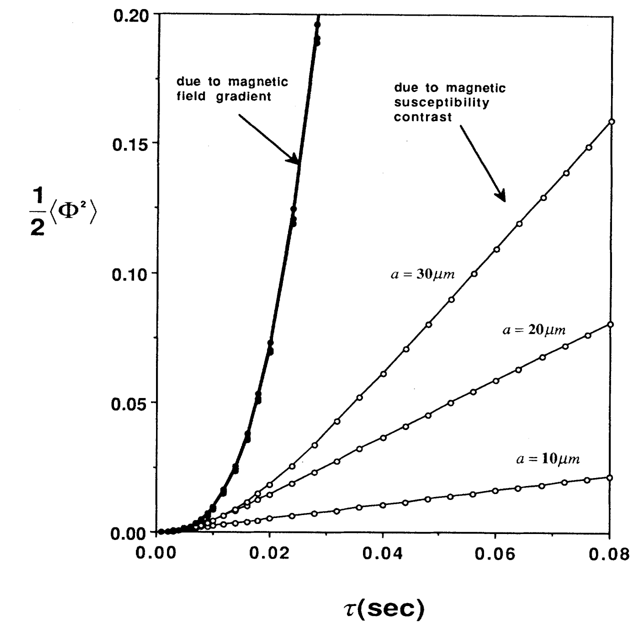

FIG. 1. Results for $\frac{1}{2}\langle\Phi^2\rangle$ vs τ for a periodic porous medium consisting of a simple cubic array of identical touching spheres with unit cell edge lengths of a = 10, 20, and 30 μm. The external magnetic field gradient is assumed to be 1 G/cm and the magnetic susceptibilities are those for pure quartz and pure water.

This may also be true for NMR logging tools designed to probe a region of uniform field. On the other hand, if the external magnetic field gradient is significantly larger than 1 G/cm, the susceptibility difference effect will be negligible. Figure 1 also shows the effect of unit cell size variation (hence, grain size) from 10 to 30 μm. From this graph it is clear that the fixed gradient contribution to $\langle\Phi^2\rangle$ is dominated by the D_e term [i.e., the first term in (2.66)] for *all times* τ—that is why there is almost no dependence on a.

Figure 2(a) shows the results for the increase of relaxation rates due to susceptibility and gradient effects, using (3.2), for three different values of a (10, 20, and 30 μm). Note that the pure susceptibility effect is proportional to $\tilde{\lambda}_{m0}D_p\tau^2/a^2$ at short times, and to $a^2/(\tilde{\lambda}_{m0}D_p)$ at long times. Hence, initially, as τ increases from 0, the relaxation rate increases faster for small a than that for large a, but eventually approaches a constant value which is proportional to a^2. For the gradient effect it has two contributions [see (3.2)], one from the term containing D_e, the other from the summation term, which involves the higher diffusion eigenstates. For clarity, they are replotted in Fig. 2(b). The term containing D_e has a τ^2 behavior at all times. The summation term has a similar behavior as that of the pure susceptibility effect. It varies as τ^2 at short times and approaches a constant value at long times, except that the asymptotic value is proportional to a^4 instead of a^2 because of the second derivative factor $\partial^2|\tilde{\phi}_{m\mathbf{q}}(0)|^2/\partial q^2$. For a equal to 10, 20, and 30 μm, apparently the D_e term is dominant for both short and long times. As a increases, the contribution from the summation term will become important. However, for sufficiently long times, the D_e term will eventually dominate.

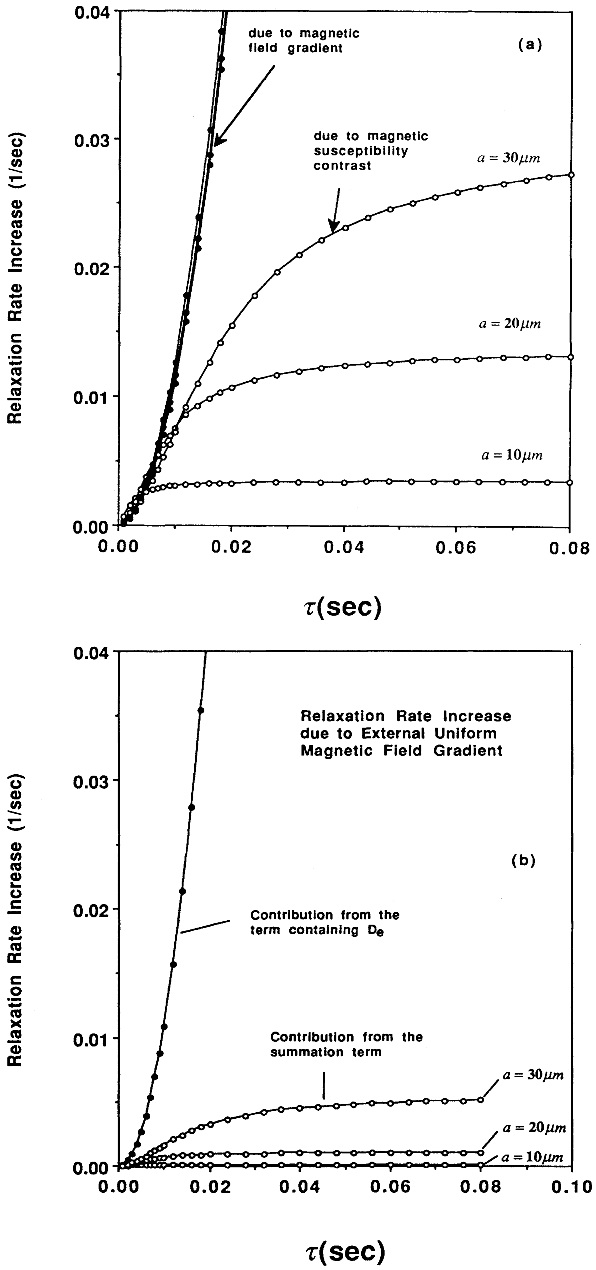

FIG. 2. Relaxation rate increases due to (a) both effects of external field gradient and magnetic susceptibility difference, and (b) only the effect of external field gradient with contributions from the D_e term and the summation term, as functions of τ for $a = 10$, 20, and 30 μm.

Figure 3(a) shows $\langle\Phi^4\rangle_{\rm susc}$, $\langle\Phi^4\rangle_{\rm grad}$, and $\langle\Phi^4\rangle_{\rm cross}$ as functions of τ using (2.94), (2.115), and (2.127) for the case of $N = 2$, 3, and 4. N denotes the size of the reciprocal lattice used in the Fourier expansion of the eigenfunctions: The reciprocal lattice vectors have the form $\mathbf{g} = (2\pi/a)(n_x, n_y, n_z)$, where n_x, n_y, and n_z are arbitrary integers between $-N$ and $+N$.

For the periodic system we are considering, i.e., a simple cubic array of identical touching spheres, the porosity is $\phi = 0.476$. The constants D_e and C_0 in (2.115) were evaluated from the lowest eigenvalue band computed at $\mathbf{q}a = (0,0,0)$, (0.05,0,0), and (0.1,0,0) for the case of $N = 5$, i.e., $D_e = 0.722D_p$, where $D_p(\text{water}) = 2.5 \times 10^{-5}$ cm^2/sec and $C_0 = -0.0157$. The corresponding values for the case of $N = 4$ are $D_e = 0.722D_p$ and $C_0 = -0.0092$. These values indicate that the convergence of the numerical computations is quite good for D_e, where only the second derivatives of the eigenfunctions are involved, but not so good for C_0, which involves fourth order differentiations.

The computations of $\langle\Phi^4\rangle$ take much longer than those for $\langle\Phi^2\rangle$. To compute $\langle\Phi^4\rangle$ for the case of $N = 5$ would take a prohibitively long time on the workstation we used. Hence, we use the $N = 5$ values for D_e and C_0, which are likely to be more accurate than those for $N = 4$, but compute the summation term in (2.115) only up to $N = 4$. This procedure was followed in obtaining all the numerical results for $\langle\Phi^4\rangle$. On the other hand, the results presented in Figs. 1 and 2 for $\langle\Phi^2\rangle$ come from calculations using $N = 5$.

Figure 3(a) shows that the convergences of $\langle\Phi^4\rangle_{\rm grad}$, $\langle\Phi^4\rangle_{\rm cross}$, and $\langle\Phi^4\rangle_{\rm susc}$ with increasing N are all very good for the unit cell size $a = 10$ μm. The numerical computations yield dimensionless eigenvalues $\tilde{\lambda}_{n\mathbf{q}}$ and eigenvectors $\tilde{\phi}_{n\mathbf{q}}(\mathbf{g})$. In the computations for $\langle\Phi^4\rangle_{\rm susc}$, scale dependent eigenvalues $\lambda_{n\mathbf{q}} = \tilde{\lambda}_{n\mathbf{q}}D_p/a^2$ were used but differentiations of eigenvectors were not needed. Hence, it has the best numerical results of the three. On the other hand, for $\langle\Phi^4\rangle_{\rm grad}$ and $\langle\Phi^4\rangle_{\rm cross}$, fourth and second order derivatives of the eigenvectors with respect to q had to be calculated. We computed eigenvectors for five different $\mathbf{q}$ values, i.e., $\mathbf{q}a = (0.03, 0, 0)$, (0.05,0,0), (0.07,0,0), (0.09,0,0), and (0.11,0,0), in order to carry out fourth order differentiation numerically. For the second order differentiations, eigenvectors for the first three q values were used. These derivatives are scale dependent. As the unit cell size a increases, the errors in the eigenvectors magnify through differentiations. This is illustrated in Figs. 3(b) and 3(c) which show, respectively, the results for $\langle\Phi^4\rangle$ for the unit cell sizes $a = 20$ and 30 μm with increasing N. Among the three quantities calculated, only $\langle\Phi^4\rangle_{\rm susc}$ is reasonable over the whole time regime. This is not true for $\langle\Phi^4\rangle_{\rm grad}$ and $\langle\Phi^4\rangle_{\rm cross}$. For the case of $\langle\Phi^4\rangle_{\rm grad}$, an increase of a by a factor of 2 (or 3) causes a magnification of error by a factor of 2^4 (or 3^4) through the differentiation, which coupled with the errors in scale dependent eigenvalues renders the result below 25 ms in Fig. 3(b) [or 50 ms in Fig. 3(c)] completely unreliable. The effect on $\langle\Phi^4\rangle_{\rm cross}$ is less severe, but the results below 12 ms in Fig. 3(b) [or 30 ms in Fig. 3(c)] are probably also unreliable. In fact, some of the early values for $\langle\Phi^4\rangle_{\mathrm{grad}}$ and $\langle\Phi^4\rangle_{\mathrm{cross}}$ were negative, and are not shown.

Figure 4(a) shows $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{susc}}$ and $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}$ as functions of τ for the unit cell size of a = 10 μm for two different values of $\Delta\chi$. The results for quartz ($\chi_m = -1.3 \times 10^{-6}$ emu/cm^3) and water are shown as data points connected by lines. The dashed lines are those for the solid matrix with $\chi_m = 2 \times 10^{-6}$ emu/cm^3 and water. In the second case χ_m is closer to what is found in ordinary sandstones. Both results indicate that the ratio $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}/\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{susc}}$ is so small that the phase angle distribution is essentially Gaussian. However, this ratio increases as $(\Delta\chi H_0)^2$. We have assumed a resonance frequency of 1 MHz for the numerical computations. Hence, for a resonance freuency of 100 MHz or so, the distribution may no longer be Gaussian. Notice that $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}$ is negative below 40 ms and positive above that.

Figure 4(b) shows $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{susc}}$ and $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}$ as func-

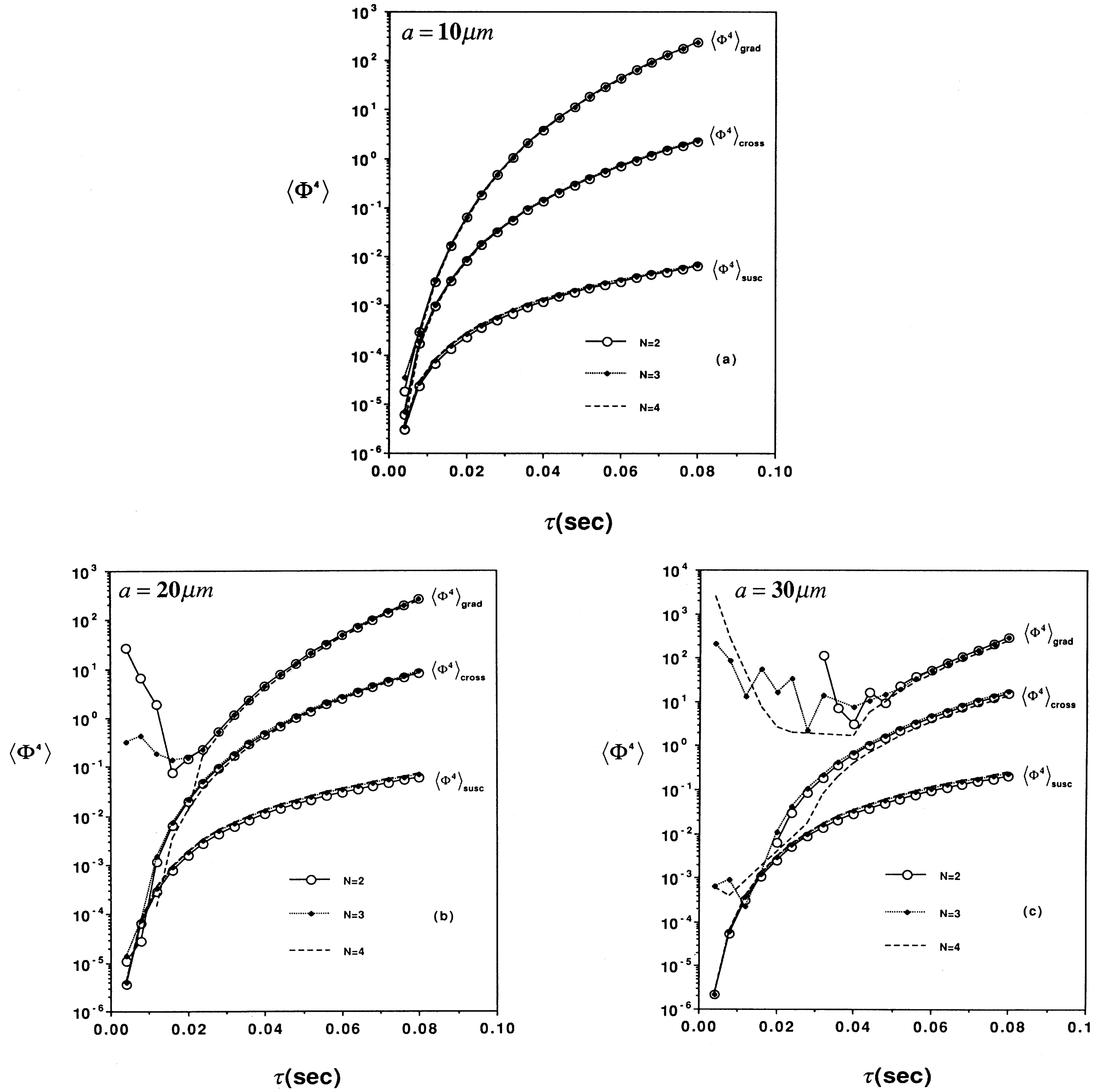

FIG. 3. Results of $\langle\Phi^4\rangle$ due to susceptibility difference, fixed gradient, and cross terms as functions of τ for N = 2, 3, and 4, for (a) a = 10 μm, (b) a = 20 μm, and (c) a = 30 μm, where N is the size of the reciprocal lattice used in the truncated Fourier expansions.

tions of τ for different values of a. Again, the results show that the ratio of $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}/\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{susc}}$ is so small that the phase angle distribution is essentially Gaussian. Often $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}$ is negative which means the phase angle distribution is narrower than Gaussian.

Figure 5(a) shows $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{grad}}$ and $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}$ as functions of τ for the unit cell size of $a = 10$ μm for two different values of field gradients. The result for 1 G/cm indicates that the ratio $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}/\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{grad}}$ is so small that the phase angle distribution is essentially Gaussian up to $\tau = 80$ ms. This ratio increases as $(\nabla H)^2$. For the results with a field gradient of 20 G/cm, this ratio reaches 0.37 by 20 ms. At later times, a Gaussian approximation is no longer adequate. However, when $\tau = 20$ ms, the spin-echo signal has already decayed to $\exp(-\langle\Phi^2\rangle_{\mathrm{grad}}/2) \cong \exp(-28)$. Thus the signal is un-

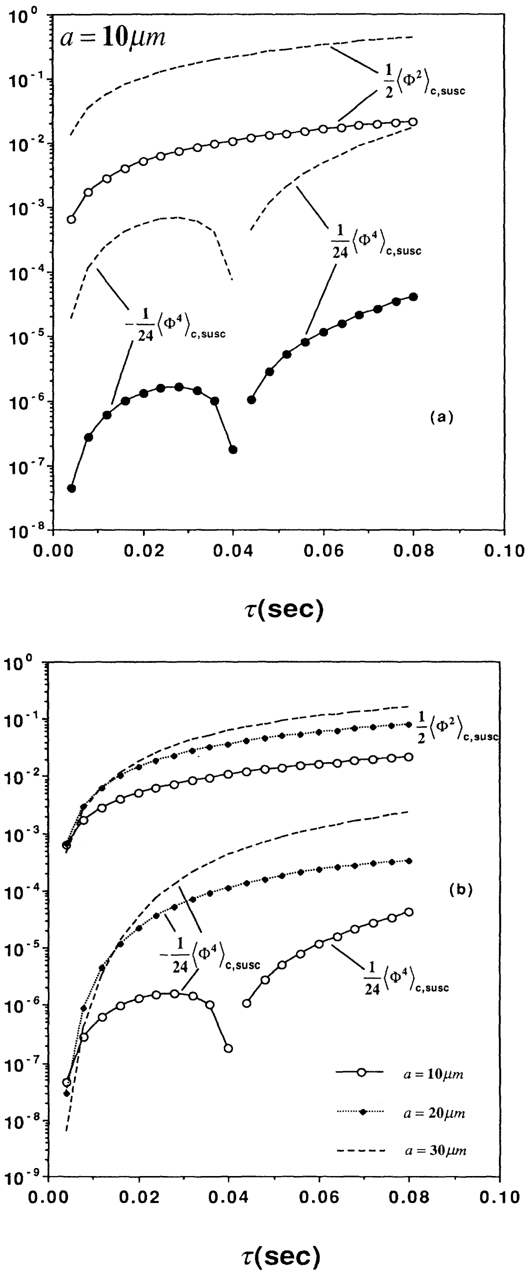

FIG. 4. Results of $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{susc}}$ and $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}$ vs τ for (a) $a = 10$ μm, $|\Delta\chi| = 0.6 \times 10^{-6}$emu/cm^3 (circles) and $|\Delta\chi| = 2.7 \times 10^{-6}$emu/cm^3 (dashed lines), and (b) one $|\Delta\chi|$ (0.6×10^{-6}emu/cm^3) but three different values of a. Note that $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{susc}}$ is positive for $a = 10$ μm when τ is greater than 40 ms, and negative for all other values of a and τ.

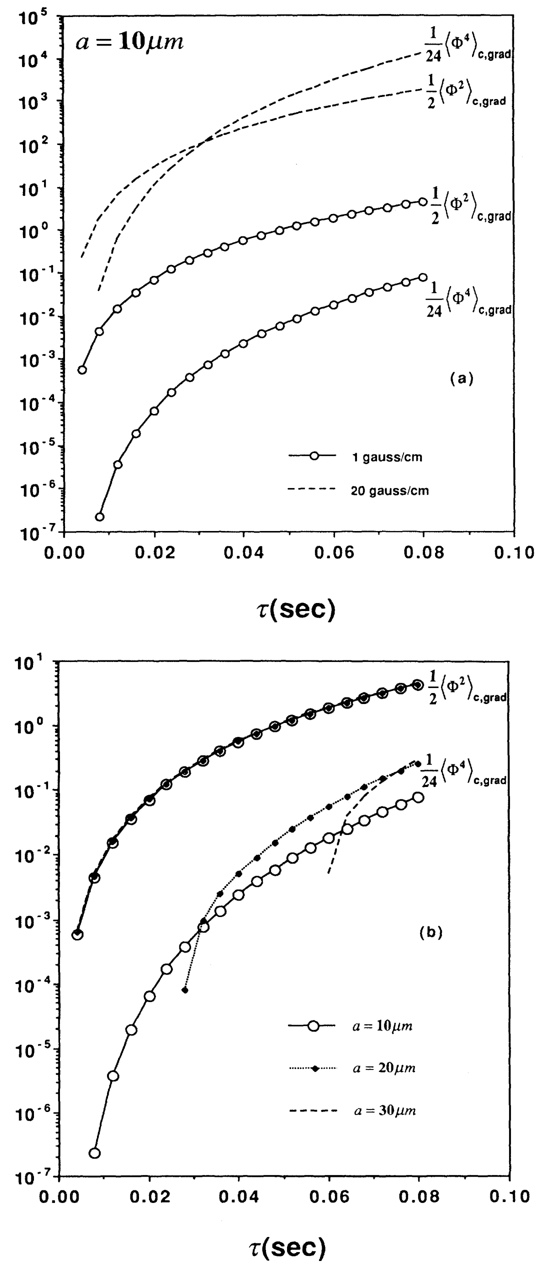

FIG. 5. Results of $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{grad}}$ and $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}$ vs τ for (a) $a = 10$ μm and two different values of magnetic field gradient, and (b) one magnetic field gradient (1 G/cm) for different values of a.

observable, and the question of validity of the Gaussian approximation is purely academic.

Figure 5(b) shows $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{grad}}$ and $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}$ as functions of τ for different values of a (i.e., 10, 20, and 30 μm). The results for $a = 10$ μm indicate that the ratio $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}/\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{grad}}$ is quite small as discussed previously in Figure 5(a). The results for $a = 20$ and 30 μm indicate that the values for $\frac{1}{2}\langle\Phi^2\rangle_{c,\mathrm{grad}}$ do not change much from those for $a = 10$ μm as already shown in Fig. 1. But the limited good results for $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}$ when $a = 20$ and 30 μm seem to suggest that as a increases, $\frac{1}{24}\langle\Phi^4\rangle_{c,\mathrm{grad}}$ also increases, as expected from (2.122).

Figures 4 and 5 show results for the magnetic susceptibility difference and the external field gradient effects separately. If both effects are present in the porous system, then we have to consider the cross terms too. Figure 6 shows results for different values of a (i.e., 10, 20, and 30 μm) where the cross terms are included in the computation of $\frac{1}{24}\langle\Phi^4\rangle_c$. Again, the ratio of $\frac{1}{24}\langle\Phi^4\rangle_c/\frac{1}{2}\langle\Phi^2\rangle_c$ is quite small up to $\tau = 80$ ms. In general, $\frac{1}{24}\langle\Phi^4\rangle_c$ is positive which means the phase angle distribution is broader than Gaussian. Here, as before, we compute the cumulants only up to $\tau = 80$ ms, becasue for porous rocks, the T_2 signal usually becomes very small when τ is greater than that.

Frequently, as pointed out earlier, one is tempted to take the increase of relaxation rate due to nonzero τ in a CPMG spin-echo experiment and calculate an apparent $D(t)$ using a formula identical to that for a uniform fluid. It is not clear whether the apparent $D(t)$ obtained in this manner is the same as the time dependent $D(t)$ for the porous medium obtained from the pulsed field spin-echo (PFGSE) experiment [i.e., (2.69)]. Figure 7 shows $D(t)$ obtained from PFGSE calculations [17], as compared to the apparent $D(t)$ [using (3.2)] for $a = 10$ μm and a field gradient of 1 G/cm. Note that the time t for $D(t)$ from PFGSE is the diffusion time, whereas the apparent $D(t)$ obtained from the increase of relaxation rate [which should really be denoted as $D(\tau)$] is plotted as a function of τ. We notice that the difference between them is quite small provided the assumption of Gaussian distribution for the phase angle is valid. We already pointed out that this assumption breaks down for τ greater than 20 ms for a field gradient of 20 G/cm in Fig. 5(a). It will probably also break down at larger grain size for a smaller field gradient.

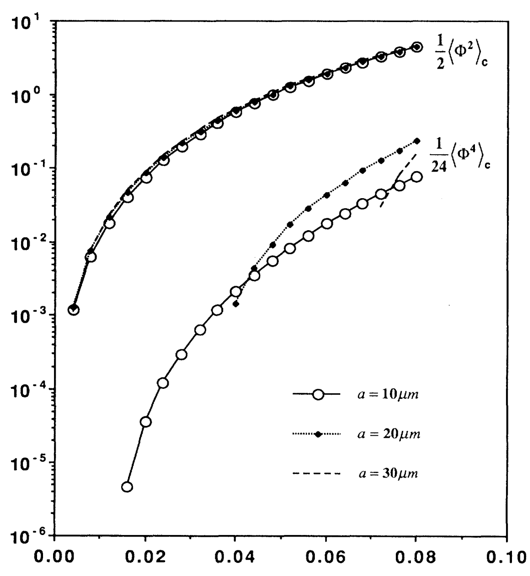

FIG. 6. Results of $\frac{1}{2}\langle\Phi^2\rangle_c$ and $\frac{1}{24}\langle\Phi^4\rangle_c$ vs τ for different values of a including all three contributions, i.e., susceptibility difference, fixed gradient, and cross terms.

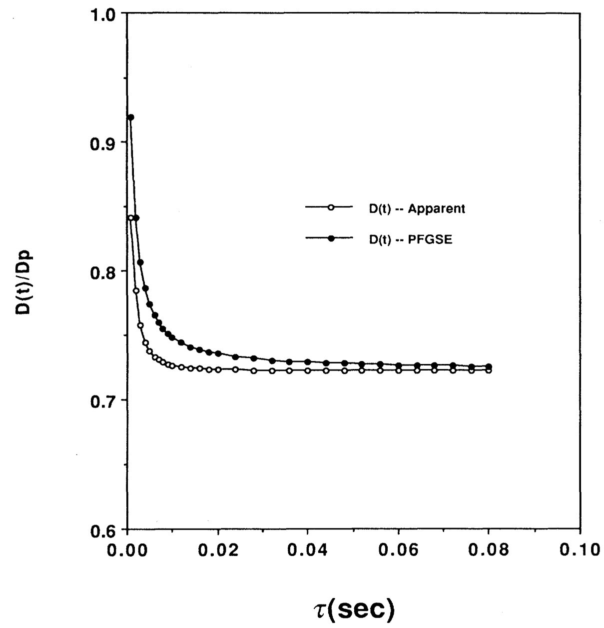

FIG. 7. Results for $D(t)/D_p$ obtained from theoretical expression for pulsed-field-gradient spin-echo (PFGSE) type experiments, and apparent $D(t)/D_p$ obtained from relaxation rate increase in T_2 CPMG experiments for a constant field gradient using a formula identical to that for a uniform fluid.

The numerical results presented above, though not necessarily representative of disordered systems, can nevertheless serve as good starting points for learning more about the T_2 relaxation behavior in complicated disordered systems. The system we considered has smooth curved surfaces, whereas porous media such as rocks can have solid grains with very sharp corners. These will increase the magnetic susceptibility difference effect. We believe our findings will also be useful for understanding NMR T_2 relaxation behavior for porous media in the presence of a nonuniform magnetic field.

A few remarks are probably worth mentioning regarding the numerical computations. As pointed out in Ref. [17], spurious eigenstates appear in the calculation due to the fact that we are dealing with finite size matrices. In order to reduce the computation time for $\langle\Phi^4\rangle$, we included only those eigenstates with the norm

$\sum_{\mathbf{g}} |\tilde{\phi}_{n\mathbf{q}}(\mathbf{g})|^2$ greater than 0.1 in our computations. In the computation of $\langle \Phi^2 \rangle$, where computing time is not a major concern, we found that including all eigenstates versus including only those with a norm greater than 0.1, 0.3, or 0.5 did not make a significant difference in the results. Because the functions $b_{nml}(\tau)$, $c_{nml}(\tau)$, $d_{nml}(\tau)$, and $e_{nml}(\tau)$ contain terms with differences of eigenvalues in some denominators, large numerical errors sometimes resulted when two different eigenstates were nearly degenerate, i.e., when the eigenvalues were nearly equal. This could be corrected either by making those eigenvalues exactly equal, and using appropriate limiting forms of the above mentioned functions, or by artificially increasing somewhat the separation between the eigenvalues, and using the generic forms of those functions. In practice, we found that it is more convenient to use the second method.

IV. CONCLUSIONS

In summary, we have developed a theory for T_2 relaxation in a periodic porous medium for the case where there is no enhanced relaxation at the pore-matrix interface. We identified relationships between the magnetization (or relaxation rate change) of the porous system and parameters such as magnetic field strength, field gradient, magnetic susceptibility difference between solid grains and pore fluid, pore size scale, echo spacing, etc. We also carried out numerical computations for a periodic porous medium consisting of a simple cubic array of identical touching spheres. These computations are used here in order to learn more about the phase angle distribution of spins and its relations with variations of grain size, susceptibility difference, and field gradient, in order to gain more insight as to the time frame for which the assumption of a Gaussian distribution is valid. They also serve as illustrative examples for understanding more complicated disordered systems.

To briefly summarize our results for the periodic porous medium, we find that: (1) For a uniform applied field, the magnetic susceptibility contrast effect can be significant. As τ increases, the T_2 relaxation rate also increases and eventually levels off. The total increase of relaxation rate is proportional to a^2, where a is the edge length of a unit cell. (2) For $a = 10$ to 30 μm, 1 MHz resonance frequency, and τ up to 80 ms, the phase angle distribution due to the magnetic susceptibility contrast effect is essentially Gaussian. (3) For the external field gradient effect, the assumption of Gaussian distribution for phase angle will eventually break down when τ is large enough. (4) For $a = 10$ μm and a field gradient of 1 G/cm, the Gaussian approximation is valid up to $\tau = 80$ ms, but not valid for a field gradient of 20 G/cm when τ is greater than 20 ms.

Clearly, the work we have described needs to be extended to more complicated microstructures, in order to study the effect of microgeometric features such as narrow constrictions and long tubes. In principle, such systems should be not more difficult to study than the simple microgeometry which we have focused upon: the only difference will be that $\theta_p(\mathbf{r})$, and hence $\theta_{\mathbf{g}}$, will have a different form. Our treatment also needs to be extended so as to allow for the possibility of enhanced spin relaxation at the pore-matrix interface. Finally, it is hoped that experiments will be done on synthetic porous media with a periodic pore structure, for comparison with these calculations. Such comparisons will hopefully enable us to identify those microgeometric features which have a dominant effect on the NMR relaxation rates.

ACKNOWLEDGMENTS

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APPENDIX

First we show that

$$G(\mathbf{r}_2\mathbf{r}_1|t_2 - t_1) = G(\mathbf{r}_1\mathbf{r}_2|t_2 - t_1) \qquad \text{(A1)}$$

for the general case of a porous medium (i.e., not necessarily periodic) with a boundary condition of partial absorption at the pore-matrix interface. We can assume $t_2 \geq t_1$, then, using Green's theorem and (2.12), we get

$$D_p \int_{t_1}^{t_2} dt \int_{V_p} dV [G(\mathbf{r}\mathbf{r}_2|t_2 - t)\nabla^2 G(\mathbf{r}\mathbf{r}_1|t - t_1) - G(\mathbf{r}\mathbf{r}_1|t - t_1)\nabla^2 G(\mathbf{r}\mathbf{r}_2|t_2 - t)]$$

$$= D_p \int_{t_1}^{t_2} dt \oint_{\partial V_p} dS \left[G(\mathbf{r}\mathbf{r}_2|t_2 - t)\frac{\partial G(\mathbf{r}\mathbf{r}_1|t - t_1)}{\partial n} - G(\mathbf{r}\mathbf{r}_1|t - t_1)\frac{\partial G(\mathbf{r}\mathbf{r}_2|t_2 - t)}{\partial n} \right] = 0. \qquad \text{(A2)}$$

Using the diffusion equation (2.7) and the initial condition (2.9), this can also be written as

$$\int_{V_p} dV \int_{t_1}^{t_2} dt \left[G(\mathbf{r}\mathbf{r}_2|t_2 - t)\frac{\partial G(\mathbf{r}\mathbf{r}_1|t - t_1)}{\partial t} - G(\mathbf{r}\mathbf{r}_1|t - t_1)\frac{\partial G(\mathbf{r}\mathbf{r}_2|t_2 - t)}{\partial t} \right]$$

$$= \int_{V_p} dV [G(\mathbf{r}\mathbf{r}_1|t - t_1)G(\mathbf{r}\mathbf{r}_2|t_2 - t)]_{t=t_1}^{t=t_2} = G(\mathbf{r}_2\mathbf{r}_1|t_2 - t_1) - G(\mathbf{r}_1\mathbf{r}_2|t_2 - t_1) = 0, \quad (A3)$$

which proves (A1).

Because diffusion is a process without memory, therefore the probability of a path that passes through a sequence of volume elements $dV_1 \cdots dV_n$ around $\mathbf{r}(t_1) \cdots \mathbf{r}(t_n)$ at the chronological sequence of times $t_1 \leq \cdots \leq t_n$, is

$$P(\mathbf{r}_1)dV_1 G(\mathbf{r}_2\mathbf{r}_1|t_2 - t_1)dV_2 G(\mathbf{r}_3\mathbf{r}_2|t_3 - t_2)dV_3 \cdots \times G(\mathbf{r}_n\mathbf{r}_{n-1}|t_n - t_{n-1})dV_n, \quad (A4)$$

where $P(\mathbf{r})$ is the probability density for finding a particle at $\mathbf{r}$. When $\rho = 0$, this density has the position independent value $1/V_p$. Otherwise, $P(\mathbf{r})$ varies with position, decreasing as $\mathbf{r}$ approaches any point on the interface. Similarly, the probability of the time reversed path $\mathbf{r}(-t_n) \cdots \mathbf{r}(-t_1)$, $-t_n \leq \cdots \leq -t_1$ is

$$P(\mathbf{r}_n)dV_n G(\mathbf{r}_{n-1}\mathbf{r}_n| - t_{n-1} + t_n)dV_{n-1} \cdots \times G(\mathbf{r}_1\mathbf{r}_2| - t_1 + t_2)dV_1. \quad (A5)$$

From (A1) it follows that this is equal to (A4) except for the factor $P(\mathbf{r}_n)$, which is equal to $P(\mathbf{r}_1)$ only when $\rho = 0$ but differs from it when $\rho \neq 0$.

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