Nuclear Magnetic Resonance Measurements of Diffusion in Granular Media

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This research develops a method for the study of diffusion in granular materials such as sand, seeds, and gravel. The proposed method is based on modulation of the longitudinal magnetization by using spin-tagging. It is shown that changes due to flow and diffusion manifest themselves as distortions of initial magnetization profiles and can be used to calculate the density probability function. [S0031-9007(96)00627-8]

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Granular materials are aggregates of large solid particles. Gravity is usually the dominant force holding these particles together. Granular materials often demonstrate unusual behavior and have features that distinguish them from solids and liquids [1,2]. In the last several decades a number of new theories and experimental techniques [3–7] have been developed for the purpose of studying the properties of granular materials. Nevertheless, there are few experimental data concerning diffusion in granular media. The goal of this work is to develop a new method for the study of diffusion in granular materials using nuclear magnetic resonance (NMR).

While NMR has long been demonstrated to be an efficient tool for diffusion and flow measurements in liquids [8], it has only more recently been used for flow measurements in granular media [3–4]. Conventional NMR methods for diffusion studies are based on measuring the signal attenuation due to diffusion in the presence of applied pulsed magnetic field gradients [8]. In general, any displacement of spins in a nonuniform magnetic field results in changes in the phase of the transverse magnetization. Therefore, the use of external magnetic field gradients for diffusion measurements makes conventional methods sensitive to any motion. Separation between diffusion and flow, characterized by nonzero mean displacements, can be achieved by using a copensating pulse train which can eliminate additional phase shifts due to constant laminar flow [9]. However, flow compensation may not be possible in the case of nonstationary motion where the rate of the phase accumulation becomes a function of time. Another major difficulty arises when conventional NMR techniques are used for diffusion measurements in granular materials due to short transverse relaxation times T_2 and T_2^* [10].

Use of a new method for diffusion and flow measurements in granular media implemented in [10] avoids the difficulties discussed above. The main idea behind this method is to create an initial periodic, spatial modulation of the longitudinal magnetization (M_z), often referred to as spine tagging, and then study changes in this modulation due to motion [10–13]. We have demonstrated experimentally that grranular flow causes shifts in the positions of maxima and minima of the modulated magnetization while diffusion results in changes of their amplitudes [10]. Because this spin-tagging method uses only the longitudinal component of magnetization of encode changes due to diffusion and flow, it is less sensitive to T_2 and T_2^* relaxations than conventional NMR techniques for diffusion measurement.

The purpose of this study is to further develop this method for simultaneous measurement of diffusion and flow in granular materials. We obtain an equation for fluctuations of the longitudinal magnetization caused by a finite number of acquisitions and particles in the imaging voxel. Finally, we demonstrate that the proposed method can be used to calculate the density probability function. This may be particularly important for the studies of diffusion in granular media when the conventional Gaussian approximation for the probability function may not apply because of the significantly smaller number of collisions in a given time period relative to liquids.

Diffusion and flow measurements in the case of a Gaussian probability distribution function.—To describe diffusion in granular media, it is convenient to introduce the density probability function $P(r', t \mid r, t + dt)$ [14] that a particle being at r' at time t has moved to position r during a time interval dt. The average displacement and the mean square deviation from the average displacement during interval dt for a particle being at r' at time t are defined as follows:

$$\langle dr_i \rangle = \int (r_i - r_i')P(r', t \mid r, t + dt)\, dr ,$$
$$\sigma_i^2 = \int (r_i - r_i' - \langle dr_i \rangle)^2 P(r', t \mid r, t + dt)\, dr , \quad (1)$$

where $r_1 = x$, $r_2 = y$, $r_3 = z$. If the interval between consecutive particle collisions is much shorter than dt, we expect the density probability function to be Gaussian [15]:

$$P(r', t \mid r, t + dt) = (8\pi^3 \sigma_1^2 \sigma_2^2 \sigma_3^2)^{-1/2} \times \exp\left(- \sum_{i=1}^{3} (r_i - r_i' - \langle dr_i \rangle)^2 / 2\sigma_i^2 \right). \quad (2)$$

The new technique presented here employs spatial encoding of the longitudinal magnetization M_z shown schematically in Figure 1. In general, a spin-tagging sequence results in modulation of the longitudinal magnetization in the sample by some tagging function $T_{\mathrm{ag}}(r)$ varying between -1 and 1: $M_z(r, t = 0) = M_0 T_{\mathrm{ag}}(r)$, where the z axis is chosen to be parallel to the applied field B_0, and M_0 is the steady-state magnetization. We assume that the tagging sequence can be made short enough to neglect T_2 and T_2^* relaxations and displacements during spin tagging.

To simplify further derivations we assume that the concentration of grains and T_1 are constant and do not depend on coordinates. In the presence of flow and diffusion, the dynamics of the longitudinal magnetization is described by the following equation [10]:

$$
\begin{aligned}
M_z(r, t) &= M_0 \int \{1 + \exp(-t/T_1)[T_{\mathrm{ag}}(r') - 1]\} P(r', 0 \,|\, r, t)\, dr' \\
&= M_0[1 - \exp(-t/T_1)] + M_0 \exp(-t/T_1) \int T_{\mathrm{ag}}(r') P(r', 0 \,|\, r, t)\, dr'.
\end{aligned} \tag{3}
$$

We consider a simple case when one-dimensional periodic tagging function $T_{\mathrm{ag}}(x)$ has only one harmonic. In this case the tagging function can be written as follows [10,13]:

$$T_{\mathrm{ag}} = 1 + (\cos kx - 1)\sin^2\alpha\,, \tag{4}$$

where α is the flip angle.

Using Eqs. (2), (3), and (4), and assuming that spatial variations in $\langle dx \rangle$ and σ_x are small (see [10] for more details), one can obtain the following equation for the longitudinal magnetization:

$$
\begin{aligned}
M_z(x, t) = {} & M_0(1 - E_1 \sin^2\alpha) \\
& + M_0 E_1 E_2 \sin^2\alpha \cos k(x - \langle dx \rangle)\,,
\end{aligned} \tag{5}
$$

where $E_1 = \exp(-t/T_1)$, $E_2 = \exp(-k^2\sigma_x^2/2)$. According to Eq. (5) diffusion decreases the amplitudes of harmonics by a factor of $\exp(-k^2\sigma_x^2/2)$.

The spatial modulation of the longitudinal magnetization can be observed if an imaging sequence is used after spin tagging [3,4,10,12,13]. A radio-frequency pulse used for imaging rotates M_z magnetization and places it in the transverse plane [10]. Therefore, the local image intensity is proportional to the magnitude of the longitudinal magnetization immediately before the first imaging rf pulse. The resulting image consists of stripes or bands with periodic variation of intensity. Figures 2(a), and 2(b) show NMR images of granular media obtained on a 2 T GE/Bruker Imaging and Spectroscopy system at the University of Illinois at Chicago. Figure 2(a) shows a control 256×256 spin-echo image of a slice of a glass container (diameter 32 mm, height 50 mm) with small white poppy seeds ($\leq$1 mm) after spin tagging. The height of the pile of seeds and the slice thickness are approximately 40 and 3 mm, respectively. The in-plane spatial resolution is 0.35 mm $\times$ 0.35 mm. The tagging period ($L = 2\pi/k$) is 2.7 mm. Figure 2(b) demonstrates changes in the magnetization profiles due to vibration of the container with seeds at a maximum acceleration of $4g$. The vibration is produced by a VG100 vibration exciter (Vibration Test Systems), located approximately 3 m from the magnet. By using rotary motion of a nonmagnetic rigid shaft, vibrations are transmitted from the exciter to the container with seeds. Each vibration consists of two up-and-down shakes. Spin tagging is implemented right before the shaking. The imaging takes place after a time delay including the time needed for shaking and for reaching a new stable configuration of the seeds (for more experimental details, see [4,10]). Two major effects are noticeable in Fig. 2(b): (1) distortions in the shape of the

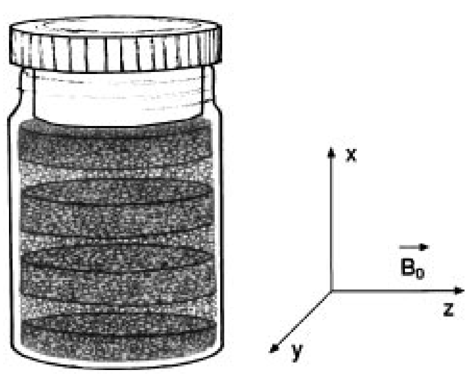

FIG. 1. Schematic representation of the modulation of M_z in a cylindrical sample placed in a homogeneous external field B_0. Darker and lighter regions correspond to $M_z < 0$ and $M_z > 0$, respectively.

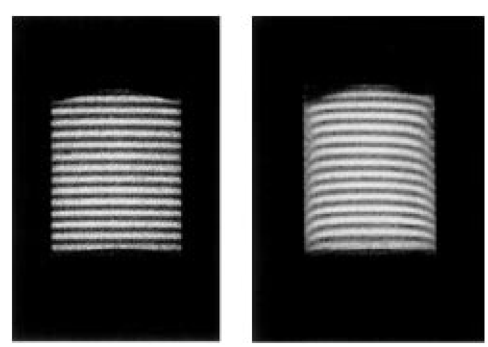

FIG. 2. (a) Control 256×256 spin-echo image of a single slice (2 mm thickness) of a glass container with seeds; (b) image showing changes in the magnetization profile due to vibration of the container with seeds at a maximum acceleration of $4g$.

magnetization profiles due to displacements (flow) of the seeds; (2) blurring of the image due to random deviations from the average trajectories. The blurring effect is most noticeable in regions with large diffusion.

If the maxima and minima of the signal intensity with and without vibration are known, the standard deviation from the average trajectory can be determined. Without vibration the maximum ($S_{\max}$) and minimum ($S_{\min}$) signal intensity can be obtained using Eq. (5) and assuming that $2E_1 \sin^2\alpha < 1$:

$$S_{\max} \sim M_0, \; S_{\min} \sim M_0(1 - 2E_1 \sin^2\alpha) . \qquad (6)$$

Because of diffusion during vibration the maximum signal intensity ($S'_{\max}$) decreases and the minimum signal intensity ($S'_{\min}$) increases:

$$S'_{\min,\max} \sim M_0[1 - E_1 \sin^2\alpha(1 \pm E_2)] , \qquad (7)$$

where "+" and "−" in the last expression correspond to $S'_{\min}$ and $S'_{\max}$, respectively. Using Eqs. (6) and (7) one can obtain the following equation for σ_x:

$$\sigma_x = \{-(2/k^2)\ln[(2S'_{\max} - S_{\max} - S_{\min}) / (S_{\max} - S_{\min})]\}^{1/2}. \qquad (8)$$

According to Eqs. (7)–(8) in the case of small σ_x ($\sigma_x^2 k^2 \ll 1$), the maximum and minimum signal intensities remain constant: $S'_{\min,\max} \approx S_{\min,\max}$. In the case of large σ_x ($\sigma_x^2 k^2 > 1$), the initial spatial modulation is destroyed by diffusion during shaking: $S'_{\max} \approx S'_{\min} \approx (S_{\max} + S_{\min})/2$. Figure 3 shows typical radial distributions of $\langle dx \rangle$ and σ_x at a $4g$ acceleration. It is interesting to notice that while the average displacement decreases from its largest positive value near the axis to its largest negative value near the walls, σ_x remains relatively small near the axis and approaches its maximum values in the region with downward flow (negative displacements) indicating a large contribution from collisions in this region.

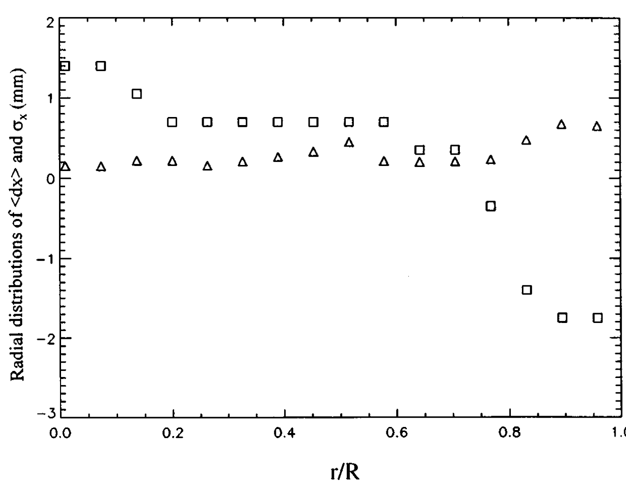

FIG. 3. The vertical displacement (per shake) and σ_x as functions of the distance from the axis of the container (radius $R = 16$ mm) at a constant height of 30 mm from the bottom of the container: □ − $\langle dx \rangle$, △ − σ_x.

Fluctuations of the longitudinal magnetization.—In the present study we restrict the discussion of this method to two-dimensional imaging in one plane. In high-resolution NMR imaging [4,10] the number of particles in the imaging voxel is relatively small ($\lesssim$10). This and a finite number of acquisitions of the NMR signal may cause fluctuations of the longitudinal magnetization with corresponding changes in the signal intensity. To estimate the magnitude of these fluctuations we assume that grains are identical. The longitudinal magnetization of each individual grain right before the first imaging rf pulse can be written as follows:

$$m = m_0\{1 - E_1 \sin^2\alpha[1 - \cos k(x - \langle dx \rangle - \delta x)]\}, \qquad (9)$$

where m_0 is the steady-state magnetization of a grain and δx is a random deviation from the average trajectory. Using Eq. (9), the average longitudinal magnetization (M_z) of a voxel can be written as a sum:

$$M_z = \sum_{n=1}^{N_{\mathrm{aq}}} \sum_{s=1}^{N_g} m_0\big(1 - E_1 \sin^2\alpha \times \{1 - \cos k[x - \langle dx \rangle - \delta x(n,s)]\}\big), \qquad (10)$$

where N_g is the number of grains in the voxel, N_{aq} is the number of acquisitions, n is the acquisition counter, $n = 1, \ldots, N_{\mathrm{aq}}$; s is the seed counter in the voxel, $s = 1, \ldots, N_g$. Using Eq. (10), assuming that the probabilities of $\delta x(n,s)$ are defined by the Gaussian probability function and neglecting correlations between particle displacements we obtain the following expressions for the average maximum $M_{z\,\max}$ and minimum $M_{z\,\min}$ longitudinal magnetizations, and their standard deviations $M_{s\,\max}$ and $M_{s\,\min}$, respectively:

$$M_{z\,\max,z\,\min} = N_{\mathrm{aq}} N_g m_0[1 - E_1 \sin^2\alpha \times (1 \pm E_2)], \qquad (11)$$

$$M_{s\,\max,s\,\min} = (N_{\mathrm{aq}} N_g/2)^{1/2} m_0 \sin^2\alpha \times E_1(1 - E_2^2)], \qquad (12)$$

where as in Eq. (7) "+" and "−" in (11) correspond $M_{z\,\min}$ and $M_{z\,\max}$, respectively. From the last equation it follows that the ratio $M_{s\,\max,s\,\min}/M_{z\,\max,z\,\min}$ is proportional to $(N_{\mathrm{aq}} N_g)^{-1/2}$.

Calculation of the density probability function.—The proposed method can also be used to determine the density probability function in one particular case when granular diffusion occurs in the presence of constant laminar flow and $\langle dr \rangle$ does not depend on coordinates. To simplify further derivations we assume that the following conditions are satisfied: (a) The probability function can be expressed as a product of three functions describing diffusion along x, y, and z axis, respectively,

$$P(r', t \,|\, r, t + dt) = \prod_{i=1}^{3} P_i(r'_i, t \,|\, r_i, t + dt) ; \qquad (13)$$

(b) $P_i(r_i', t \,|\, r_i, t + dt)$ depends only on the absolute value of $|r_i - r_i' - \langle dr_i \rangle|$; and (c) the density probability function is significantly different from zero within an interval $|r_i - r_i' - \langle dr_i \rangle| \approx \sigma_i$ and approaches zero outside of this interval,

$$P_i(r_i', t \,|\, r_i, t + dt) \approx 0, \quad \text{if } |r_i - r_i' - \langle dr_i \rangle| \gg \sigma_i\,. \tag{14}$$

The first two conditions are valid, for example, when diffusion occurs in a homogeneous system far from its boundaries. The last condition implies that in the system being considered large deviations from the average trajectories (i.e., $|r_i - r_i' - \langle dr_i \rangle| \gg \sigma_i$) are unlikely.

If, as explained above, an imaging sequence follows spin tagging, the amplitude of the signal S is proportional to the local $M_z(x, t)$. Using Eqs. (3) and (4) one can easily obtain the following expression for the signal:

$$\delta S(x, k) = S(x, k) - \langle S \rangle \sim M_0 E_1 \sin^2 \alpha \times \left[\int \{\cos(kx')\} \times P_1(x', 0 \,|\, x, t) dx' \right], \tag{15}$$

where $\langle S \rangle$ denotes the average magnitude of the signal; $\langle S \rangle \sim M_0(1 - E_1 \sin^2 \alpha)$. Consider a discrete set of values for k in the expression for the tagging function: $k(n) = 2\pi n/L$, $n = 0, \ldots, N/2$, where L is the tagging period. Because of the fact that $\delta S(x, k(n))$ is an even function of k, we define $\delta S(x, k(-n))$ as follows: $\delta S(x, k(-n)) = \delta S(x, k(n))$. A discrete Fourier transform of $\delta S(x, k(n))$ will result in the following equation:

$$(1/N) \times \sum_{n'=-N/2}^{N/2-1} \delta S(x, k(n')) \times \exp(-j2\pi n' n/N = \text{const} \times \left[\int \{H(x'/L - n/N) + H(-x'/L - n/N)\} \times P_1(x', 0 \,|\, x, t)\, dx' \right], \tag{16}$$

where const is a constant dependent on M_0, the flip angle α and T_1 relaxation time; $H(\pm x' - n/N)$ is a point spread-function defined as follows:

$$H(\pm x' - n/N) = 0.5 \exp[j\pi(\mp x'/L + n/N)] \times \sin[\pi N(\pm x'/L - n/N)] / \sin[\pi(\pm x'/L - n/N)]\,. \tag{17}$$

From Eq. (17) it follows that contributions to the integral in Eq. (16) come from all points x' such as $x' = L(\pm n/N + m)$, where $-N/2 \le n \le N/2 - 1$ and m is an arbitrary integer. However, if the period of the tagging function is large enough so that $L \gg \sigma_x$, almost all of these contributions are negligibly small due to condition (14). Let us consider a result of Eq. (16) at a point $x - \langle dx \rangle = sL$, where s is an integer. From Eqs. (14) and (17) it is easy to see that only contributions from $x' = sL \pm L(n/N)$ have to be taken into account. At the same time, due to our second assumption that $P_1(x', 0 \,|\, x, t)$ is an even function of $x - x' - \langle dx \rangle$, these contributions are equal to each other. Therefore, the integral in (16) is proportional to $P_1(x - \langle dx \rangle - Ln/N, 0 \,|\, x, t)$ [or $P_1(x - \langle dx \rangle + Ln/N, 0 \,|\, x, t)$]. From Eqs. (16) and (17) it follows that the probability function can be defined with spatial resolution of L/N. To avoid aliasing, the period of the tagging function should be greater than σ_x; therefore, the best spatial resolution is σ_x/N.

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