Granular Matter (2007) 9:331–335
DOI 10.1007/s10035-007-0045-3

NMR measurements of grain and gas motion in a gas-fluidized granular bed

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Received: 26 August 2005 / Published online: 7 July 2007

Abstract Nuclear magnetic resonance (NMR) experiments are described for gas-fluidized granular beds, which are important systems for many materials-processing operations. Using pulsed field gradient, magnetic resonance imaging, and hyperpolarized gas NMR, detailed information is obtained for the density and motions of both grains and interstitial gas. In particular, dynamic correlations in the grain density are used to measure the bubble velocity and hyperpolarized xenon gas NMR is used to measure the bubble-emulsion exchange rate. A goal of these measurements is to verify in earth gravity first-principles theories of granular flows.

Keywords Granular · Fluidized bed · NMR · Hyperpolarized gas

1 Introduction

Nuclear magnetic resonance (NMR) enables noninvasive measurements to be made on dense, opaque systems such as granular media. We are engaged in a program of experiments to build up detailed pictures of dense, three-dimensional granular systems in Earth gravity using NMR methods combining MRI, PFG-NMR, and hyperpolarized-gas NMR. Using these methods we are able to measure density profiles, and grain as well as gas motions over millisecond to second time scales. Recently, we applied these methods to study grain motions in vibrofluidized granular beds [7]. Here we report preliminary results for a different granular flow system, the bubbling gas-fluidized bed. Although it is more complex than the vibrofluidized bed, the gas-fluidized bed is technologically important and is especially well matched to the capabilities of combined grain and gas NMR.

This work was supported by US National Science Foundation Grant No. CTS-0310006.

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2 The gas-fluidized bed: grain and gas NMR

Gas-fluidized granular beds are widely used in industry for catalytic cracking, efficient combustion, and many other large-scale processes [6,10,11] It is reasonable to imagine that gas fluidization (or pneumatic transport of granular material, which is closely related) would play a prominent role in in-situ resource utilization on the moon or Mars, yet the behavior of a gas-fluidized bed in reduced gravity is almost completely unknown at present.

To promote mixing, gas-fluidized beds are typically used in the bubbling regime, in which large bubble-like voids devoid of grains rise through the bed at a velocity much larger than the mean gas velocity. From a theoretical standpoint the bubbling gas-fluidized bed is extremely complex, with significant motion over a wide range of length scales (from grain to bubble) and fluid dynamics with self-consistently moving boundary conditions. Microscopically-motivated theories of fluidized-bed behavior have been formulated (see, for example Ref. [8]) yet to achieve closure these theories must make various unverified assumptions. For example, in a "two fluid" model it might be assumed that the grains and gas behave like two interpenetrating Newtonian fluids [8]. Yet, at present it is not established theoretically or experimentally

that a *dense* granular medium is ever well described as a Newtonian fluid.

In common with other granular media, the gas-fluidized bed is difficult to probe experimentally in a non-invasive manner. To better understand the dynamics of the bubbles and their interaction with the dense ("emulsion") phase of the bed, many techniques have been tried including x-ray photography and tracer-gas injection [6]. Here we show preliminary data for three projects we are carrying out using NMR to probe the bubbles: (a) height-resolved measurements of grain-displacement distributions, which reveal information about the bubble structure; (b) noninvasive measurements of the bubble velocity, using a new NMR technique; and (c) measurement of gas exchange between the bubbles and the dense granular emulsion, using hyperpolarized ^{129}Xe NMR. Other workers have also recently reported studies of the gas-fluidized bed using NMR [5,13–15], although not to our knowledge using hyperpolarized ^{129}Xe gas as we reported earlier [12,18] and in the present work.

3 NMR techniques for granular flows

Broadly, two requirements must be met to carry out NMR experiments on a flowing granular medium. First, a system must be set up in the desired granular flow state (e.g., bubbling gas-fluidized bed) which also gives a substantial NMR signal for the subsystem to be measured (grains or gas). Second, suitable NMR protocols must be devised to extract the desired information such as density, velocity, diffusion, exchange between phases, etc. The ways in which these two requirements are met are quite different for grain and gas NMR, yet sometimes it is possible to carry out grain and gas measurements on nearly identical systems.

3.1 Grain NMR techniques

For grain-phase studies, we typically use NMR pulse sequences that can encode both the motion of the grains and their positions (Fig. 1). Using strong gradient pulses (up to 1,000 G/cm), it is possible to resolve grain motion over times of one millisecond or less. In this type of study, the individual grains are not imaged. Rather, the joint probability distribution over all grains is measured as a function of grain position and grain displacement in a specified time interval [2]. Note that for our studies of systems with continuous, rapid grain movement both the NMR techniques used and the type of data obtained are quite different from earlier studies of quasistatic flows [9].

Due to the rapid molecular tumbling, fluids give NMR signals much more suitable for imaging-type studies than do solids [1]. Botanical seeds, which typically contain liquid oil that gives a strong NMR signal, have been one popular type

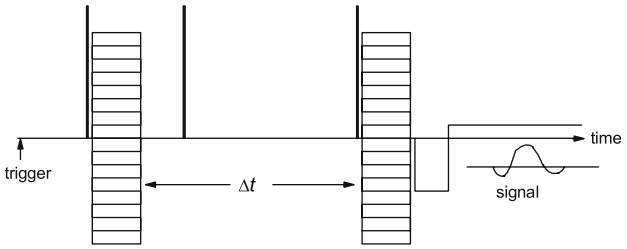

Fig. 1 NMR pulse sequence used for grain measurements in granular flows. The *vertical lines* indicate radio-frequency pulses, and the rectangles indicate gradient pulses of variable strength. Using this type of sequence, it is possible to measure the joint distribution of grain motions during the interval Δt with μm resolution, and grain positions with sub-mm resolution. The entire sequence can be completed in as little as 2 ms, although it must be repeated many times to build up the distribution information

of sample for granular-media studies [3,9]. To allow NMR studies over a wider range of grain sizes, small amounts of organic liquids can be adsorbed onto substrates such as porous catalyst particles [15]. Earlier experiments in our laboratory on *vibrofluidized* granular beds employed mustard seeds as the grains [7]. For the experiments described here on gas-fluidized beds, porous alumina grains with a small amount of adsorbed dodecane were employed.

Figure 2 shows data obtained using this technique for a bubbling gas-fluidized bed of alumina particles (EMD Chemicals, Gibbstown, NJ, USA) which were sieved to limit

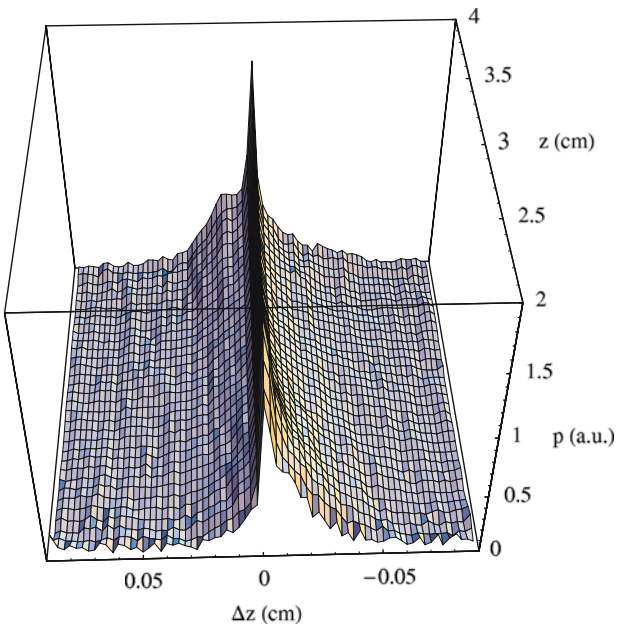

Fig. 2 Joint distribution $p(\Delta z, z)$ of vertical displacements Δz in $\Delta t = 20$ ms and heights z, for the grains in a bubbling gas-fluidized bed of alumina particles. The z component is measured from the height of the gas diffuser at the bottom of the bed. An evolution of the displacement distribution with height is visible in this plot, corresponding to an increase of the typical bubble size and approach to slugging near the top of the bed

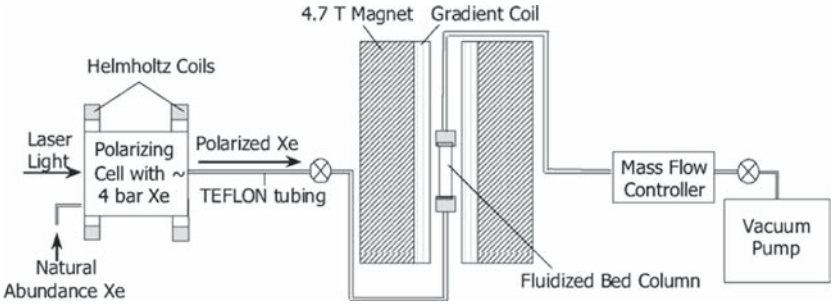

Fig. 3 Simplified diagram of apparatus for using hyperpolarized xenon to study gas motion in a fluidized granular bed

the size range to 75–105 μm. The bed was contained in a 1 cm ID glass tube in the bore of an NMR magnet operating at 1.0 T. It was fluidized by dry nitrogen which entered the bed via a sintered-glass diffuser at the bottom. For the data shown in Fig. 2 the gas flow rate was set to 66.1 cm^3/min which placed the bed in a bubbling state. In a tall granular bed the bubble size increases with height via coalescence, until a "slugging" regime is reached where the bubbles are the full bed diameter [6,10]. Experimentally, the transition to slugging coincides with the appearance of a second, broad peak in the displacement distribution.

3.2 Gas NMR techniques

Under equilibrium conditions, the NMR signal from gasses is very weak (due to their low density), often making gas-phase NMR studies difficult. By using hyperpolarized gas, which has been shown to be practical for ^{3}He and ^{129}Xe, the NMR signal can be increased by a factor of order 10^4 [16]. Figure 3 shows a simplified diagram of the apparatus we use to study the gas motion in a gas-fluidized granular bed. In this apparatus, xenon gas is polarized by spin exchange with rubidium vapor in a laser optical pumping cell. The hyperpolarized xenon is then used as the fluidizing gas for a small granular bed located within the NMR magnet.

3.3 Measurement of bubble velocity using grain NMR

Simple and basic questions for the bubbling gas-fluidized bed are: what is the velocity v_b of the rising bubbles, and how is the velocity related to the bubble diameter d, gas flow rate, and other bed parameters? In analogy with gas bubbles in a liquid (or by dimensional analysis), it can be argued $v_b \sim (dg)^{1/2}$, where g is the acceleration of gravity, and such a relation has been proposed for the gas-fluidized granular bed with a phenomenological prefactor [4]. Yet it is not easy to measure the mean velocity of bubbles rising in the interior of a chaotically bubbling gas-fluidized bed.

We have devised a new method to measure the mean velocity and other characteristics of the bubbles, using NMR on the grains. A pulse sequence (different from that shown in Fig. 1) is used to measure the bed density profile twice, separated by a time interval Δt, and the experiment is repeated many times. Bubbles in the bed appear as localized, downward fluctuations in the bed density. We reduce the data statistically by computing the cross correlations between the fluctuations in the two time-separated density measurements.

Figure 4 shows a plot of the density cross correlations measured in this way on the same bubbling gas-fluidized bed described above. In this plot a ridge appears corresponding to fluctuations that propagate at a definite velocity. The mean velocity of the bubbles can be accurately measured from the slope of the ridge (12.4 cm/s for the data shown in Fig. 4), while the width and shape of the ridge indirectly reflect the size and shape of the bubbles. The bubble velocity and size deduced from this plot (from the slope and width of the ridge) are approximately consistent with estimates from the excess gas flow over minimum fluidization flow. Similarly, the bubble size and velocity from the graph are approximately consistent with the d versus v_b correlation proposed in Ref. [4].

3.4 Measurement of bubble-emulsion exchange using hyperpolarized gas NMR

Using the setup shown in Fig. 3, we are able to perform NMR experiments directly on the gas within the fluidized bed. Significantly, we have used the same porous alumina particles and the same bed diameter as for the grain-NMR experiments summarized above. Therefore, we can correlate grain and gas NMR information in essentially identical fluidization conditions (as verified by visual measurements of the bed-height hysteresis curve, which is extremely sensitive to the fluidization state). For the gas-phase data shown here, the alumina-particle bed was positioned in at 4.7 T NMR magnet and fluidized by hyperpolarized xenon at a pressure of 2.5 bar.

The ^{129}Xe NMR frequency is sensitive to the physical environment of the gas molecule, which makes it possible to distinguish spectroscopically between gas in the bubbles, gas between the grains, and gas adsorbed onto the grains (Fig. 5). In particular, the gas in the quasi-spherical bubbles experiences a much more homogeneous magnetic field than

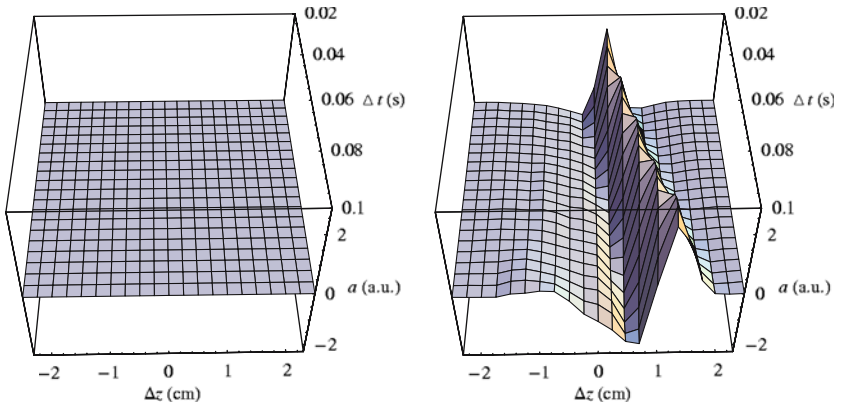

Fig. 4 Measurement of correlations between fluctuations in the density of a gas-fluidized bed of 75–106 μm diameter alumina particles, measured using NMR. A small quantity of dodecane is adsorbed onto the porous particles, to give NMR sensitivity. The correlations are plotted as a function of the time shift Δt and the height shift Δz. For the *left plot*, there is no gas flow through the bed and hence no fluctuations. For the *right plot*, there is a gas flow sufficient to put the bed into the bubbling regime (superficial gas velocity $v_g = 1.4$ cm/s). In this case there are large density fluctuations, due to the bubbles, and the bubble velocity $v_b = 12.4$ cm/s can be measured directly from the slope of the ridge in the correlation plot

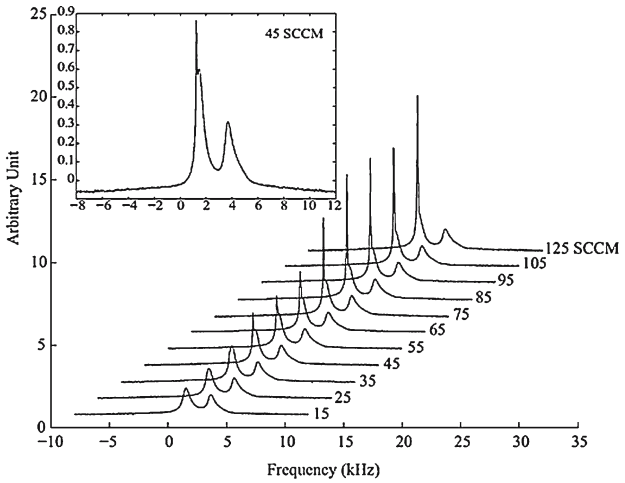

Fig. 5 ^{129}Xe spectra for an alumina-particle bed fluidized by hyperpolarized xenon gas, measured at 11 different gas flow rates ranging from 15 to 125 sccm. Three peaks may be distinguished: a narrow peak due to gas within the bubbles, a broader peak at nearly the same frequency due to gas within the interstitial volume of the emulsion (dense granular) phase, and a second broad peak shifted to higher frequency due to gas adsorbed on the porous alumina particles. As the flow rate is increased, the fraction of gas in the bubbles also clearly increases

the adsorbed and interstitial gas, and hence has a longer transverse dephasing time T_2^*.

We have used the T_2^* contrast to devise an NMR pulse sequence that selectively eliminates the signal from gas outside the bubbles [17], and then measures the re-growth of this signal due to gas motion in the bed. In this way an important engineering parameter for gas-fluidized beds, the bubble-emulsion exchange rate, can be directly and noninvasively measured. The exchange rate K is defined by the following equation [10]:

$$\frac{1}{V_b}\frac{dN_b}{dt} = -K(C_b - C_e)$$

where N_b is the quantity of a tracer gas within a bubble of volume V_b, and C_b, C_e are the concentrations of the tracer in the bubble and emulsion phase, respectively.

For our experiments the hyperpolarized xenon gas serves as a completely neutral tracer, and its concentration in the various phases can be measured accurately and noninvasively using NMR. In particular, the re-growth rate of NMR signal from gas outside the bubbles is directly related (after suitable normalization) to the exchange of gas between the bubbles and the rest of the bed. Figure 6 shows a preliminary measurement using this method of the bubble-emulsion exchange rate in an alumina-particle bed, for a range of gas flow rates in the bubbling regime. A full analysis of this experiment requires consideration of the coupled rate equations for the nuclear magnetization in the three phases (bubble, emulsion, adsorbed) including relaxation, exchange, and inflow/outflow contributions. This analysis will be the subject of a future publication.

4 Conclusions

Using NMR methods, it is possible to measure the densities and motion of both grains and gas in continuously excited granular systems such as the vibrofluidized and gas-fluidized beds. Quantitative results can be obtained for many parameters including the grain density profile, granular temperature (mean random grain kinetic energy), grain bubble velocity and size, and gas bubble-emulsion exchange rate.

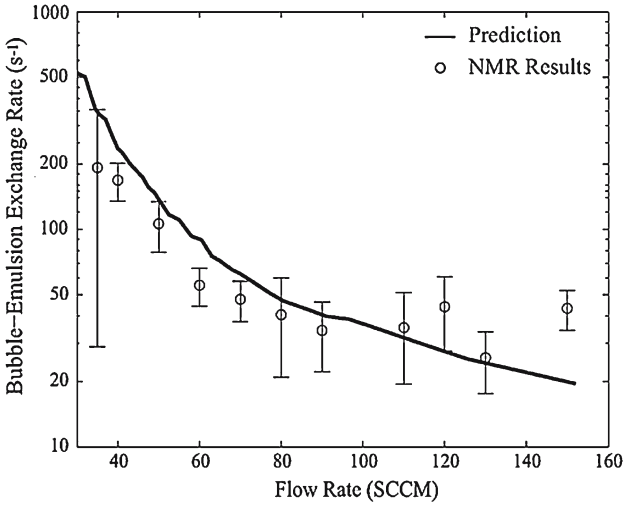

Fig. 6 Preliminary measurement of bubble-emulsion exchange rate as a function of gas flow rate for a bed of alumina particles fluidized by hyperpolarized xenon gas. The exchange rate gives the rate at which gas within the bubbles interchanges with gas within the dense granular phase, and is a key parameter for engineering applications of fluidized beds. The *solid curve* shows the exchange rate calculated from the measured bed expansion along with the phenomenological theory from Ref. [4], while the points with error bars show a direct measurement of the exchange rate using ^{129}Xe NMR

Where first-principles physical theories exist for the granular flow state, e.g., the highly excited vibrofluidized bed, these theories can be directly tested [7]. Conversely, for more complex systems like the gas-fluidized bed theoretical models must make more ad-hoc assumptions (for example that the bubbles behave approximately as bubbles in a fluid). In this case non-invasive NMR measurements offer possibilities to directly test the results of such assumptions (e.g., predictions of the bubble velocity-size relationship and bubble-emulsion exchange rate).

In both cases, a key goal is to understand the granular system sufficiently well to enable extrapolations to as yet unexplored regions of parameter space, such as reduced-gravity operations.

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