

## COMMUNICATIONS

# Sizing of Emulsion Droplets under Flow Using Flow-Compensating NMR-PFG Techniques

M. L. Johns<sup>1</sup> and L. F. Gladden

*Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, United Kingdom*

Received May 29, 2001; revised October 16, 2001

Using the nuclear magnetic resonance (NMR) pulsed field gradient (PFG) technique, it is possible to determine the size distribution of emulsion droplets. This method is extended so that the same measurements can be performed in the presence of flow. The resultant flow-compensating NMR-PFG technique is used to determine the oil droplet-size distribution of an oil-in-water emulsion flowing in a narrow tube at various flow rates. Comparison with the nonflowing oil droplet-size distribution enables the effect of velocity shear on the oil droplet-size distribution to be quantified. © 2002 Elsevier Science

**Key Words:** emulsions; PFG; flow compensation; shear.

on the use of the NMR-PFG technique in processing equipment or as a research tool for the study of emulsion evolution under shearing conditions. In addition, the technique can also be compromised by the presence of convection currents in stationary samples (4). In this paper we report the use of a flow-compensated NMR-PFG technique to examine the droplet-size distribution of a xylene-in-water emulsion, in response to an increasing flow rate. This is performed in a narrow tube under well-developed laminar flow conditions.

### INTRODUCTION

Emulsions, where one liquid is dispersed in another liquid in the form of droplets with radii of the order of micrometers, are extensively used in a range of industries including cosmetics, detergents, foodstuffs, and pharmaceuticals. The characteristics of an emulsion relevant to their functionality (e.g., viscosity, stability, and turbidity) all depend on the size distribution of the droplets. Hence an ability to experimentally determine this size distribution is essential. The nuclear magnetic resonance (NMR) pulsed field gradient (PFG) technique has been proven as a quantitative tool for characterizing emulsion droplet-size distributions under nonflowing conditions. This technique measures the self-diffusion behavior of liquid molecules in a completely non-invasive manner (1). When such molecules are restricted to the interior of droplets, the resultant restricted self-diffusion behavior can be interpreted so as to provide the emulsion droplet-size distribution. NMR-PFG was used first by Packer and Rees in 1972 (2) to measure the size distribution of emulsion droplets. Use of the technique has since been frequently reported in the literature, including studies of multiple emulsions (3).

The conventional NMR-PFG technique is unable to distinguish between molecular self-diffusion and a velocity distribution in the sample of interest. Hence this is a severe limitation

### EMULSION DROPLET-SIZING THEORY

When using NMR-PFG, the signal intensity,  $S$ , for free unrestricted self-diffusion can be related to experimental acquisition parameters using the formula

$$\frac{S}{S_0} = \exp\left(-D_0(\gamma g d)^2\left(\Delta - \frac{\delta}{3}\right)\right), \quad [1]$$

where  $g$  is the strength of the applied magnetic field gradient,  $S_0$  is the signal intensity when the magnetic field gradient  $g = 0$ ,  $\gamma$  is the gyromagnetic ratio ( $= 2.68 \times 10^8$  for  $^1\text{H}$ ),  $D_0$  is the free molecular self-diffusion coefficient,  $\delta$  is the time period over which  $g$  is applied, and  $\Delta$  is the time period over which diffusion is observed. Hence, by measuring  $S$  as a function of  $g$ , it is possible to determine the value of  $D_0$ .

The restricted self-diffusion of molecules in a spherical cavity has been modeled theoretically and the following equation developed to describe the resulting NMR signal,  $S$  (5),

$$H(R) = \frac{S}{S_0} = -\frac{2\gamma^2 g^2}{D_0} \sum_{m=1}^{\infty} \frac{\alpha_m^{-4}}{\alpha_m^2 R^2 - 1} \times \left[2\delta - \frac{G}{\alpha_m^2 D_0}\right], \quad [2a]$$

where

$$G = 2 + \exp(-\alpha_m^2 D_0(\Delta - \delta)) - 2 \exp(\alpha_m^2 D_0 \delta) - 2 \exp(\alpha_m^2 D_0 \Delta) + \exp(-\alpha_m^2 D_0(\Delta + \delta)), \quad [2b]$$

<sup>1</sup>To whom correspondence should be addressed. E-mail: mlj21@cheng.cam.ac.uk.

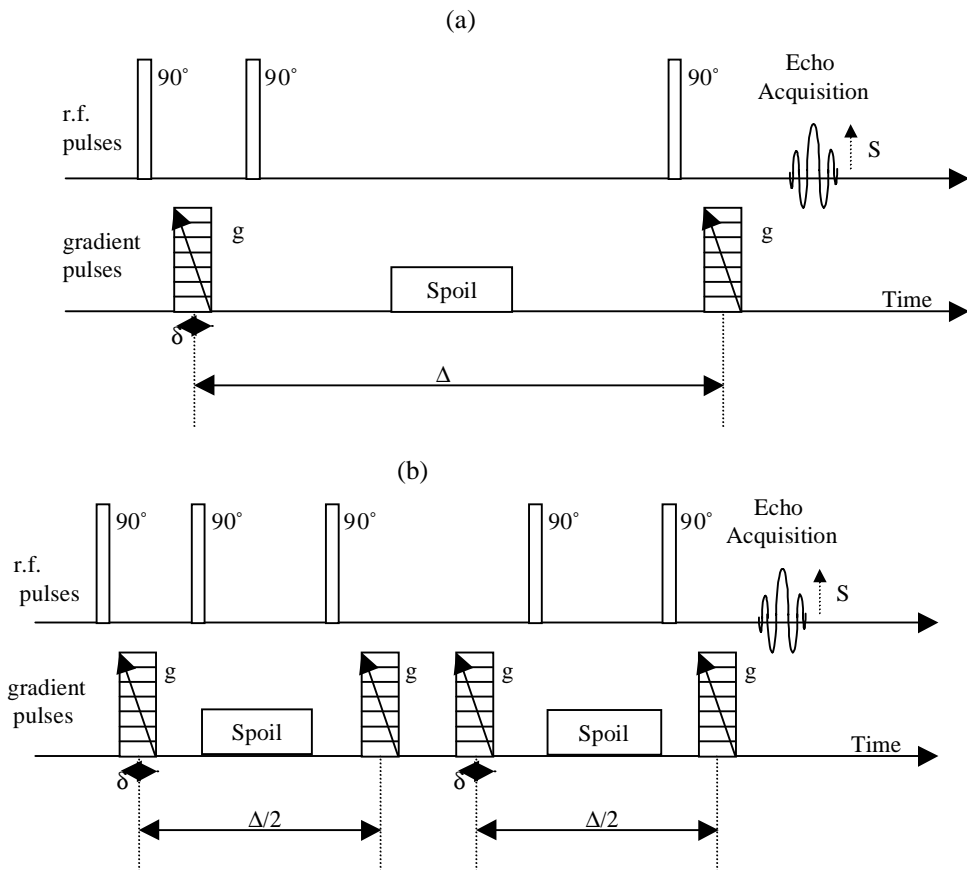


FIG. 1. (a) The conventional stimulated-echo NMR-PFG pulse sequence, used to measure self-diffusion. (b) The flow-compensated stimulated-echo NMR-PFG pulse sequence, which allows self-diffusion to be measured in the presence of a velocity distribution.

and  $\alpha_m$  is the  $m$ th root of

$$\frac{1}{\alpha R} J_{3/2}(\alpha R) = J_{5/2}(\alpha R). \quad [2c]$$

The radius of the spherical cavity,  $R$ , is the only free parameter in Eq. [2]. Hence by measuring  $S$  as a function of  $g$ , and subsequently fitting Eq. [2] to the resultant experimental data, it is possible to determine  $R$ . Most emulsions however contain a distribution of droplet sizes; hence Eq. [3] has to be used,

$$\frac{S}{S_0} = \int H(R) \cdot F(R) dR, \quad [3]$$

where  $H(R)$  is the function shown in Eq. [2], while  $F(R)$  is the volumetric probability distribution of droplets with a radius  $R$ .  $F(R)$  can thus be determined by fitting Eq. [3] to the experimental data ( $S$  as a function of an increasing  $g$ ). To simplify this process, a log-normal functional form is usually assumed for  $F(R)$  (e.g., 6). This requires that only two parameters be determined, namely the mean and the variance of this log-normal

distribution. These are determined by minimizing the sum of the errors squared between the predictions of Eq. [3] and the corresponding experimental data.

In conventional stimulated-echo NMR-PFG,  $S$  is measured as a function of  $g$  using the pulse sequence shown in Fig. 1a. However, when a distribution of velocities is present in the sample being investigated, as is the case for flow in a cylindrical tube, both velocity and self-diffusion contribute to the attenuation of  $S$  as  $g$  is increased. Hence emulsion droplets in flowing streams cannot be sized using the conventional NMR-PFG pulse sequence. An alternative pulse sequence is shown in Fig. 1b, which compensates for the effects of a velocity distribution on the acquired signal,  $S$ . This is a stimulated-echo variant of the flow-compensating spin-echo sequence described in Callaghan and Xia (7). Provided that the displacement due to flow of each individual molecule during the initial time period,  $\Delta/2$ , is equal to the displacement due to flow of the molecule during the second  $\Delta/2$  time period, the effect of flow on the NMR signal,  $S$ , is eliminated. This requirement is met for laminar flow in a tube, provided that transverse diffusion between streamlines is negligible during the observation time,  $\Delta$ . For the case of self-diffusion of the liquid molecules, the magnitude of the

displacement during the second  $\Delta/2$  time period is independent of the magnitude of displacement during the first  $\Delta/2$  time period. Thus self-diffusion attenuates the acquired signal,  $S$ , as  $g$  is increased, while the effects of flow on  $S$  are eliminated. Hence the pulse sequence in Fig. 1b can be used to measure the droplet-size distribution of an emulsion under flowing conditions.

## MATERIALS AND METHODS

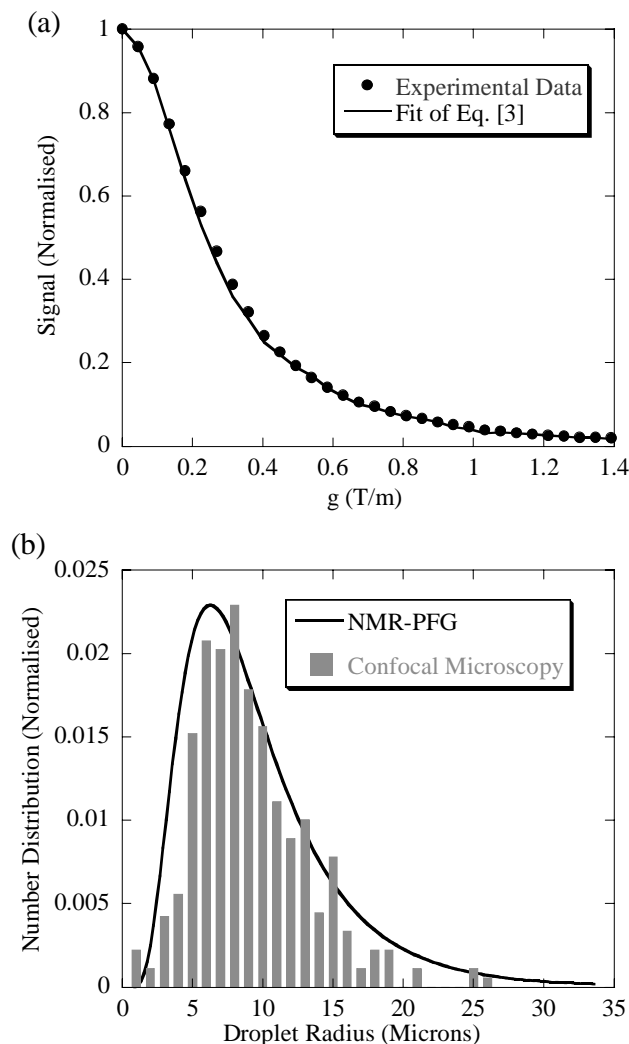
The oil-in-water emulsion investigated consisted of 37 wt% xylene, 6 wt% Tween 40, and 57 wt% water. Tween 40 is a non-ionic surfactant in which the poly oxyethylene chains contain an average of 40 units. All chemicals were purchased from Sigma Aldrich (Dorset, UK) at purities in excess of 99%. The emulsion was prepared by first dissolving the surfactant in the water. The xylene was then emulsified in the resultant solution using a magnetic stirrer. Four liters of emulsion was prepared. The emulsion was transferred to a gently stirred storage vessel from where it was pumped in a continuous flow loop using a positive displacement pump, through a 2-m-long glass tube with an internal diameter of 10 mm. The pump was fitted with a dampener to ensure a constant flow rate. The NMR signal was detected from a 15-mm-long section of the glass tube, located 1 m from the entrance point of the liquid.

The NMR equipment used consisted of a 7-T vertical-bore magnet equipped with a 15-mm-diameter bird-cage rf coil, tuned to 300.13 MHz in order to detect  $^1\text{H}$  NMR signal. Chemical shift differences were used to differentiate the xylene signal from the water and surfactant signals. Magnetic field gradients were available in three mutually orthogonal directions with a maximum gradient strength of 97 G/cm. Standard and velocity-compensated self-diffusion data were acquired when the emulsion was nonflowing in a glass vial with an inner diameter of 9 mm and a depth of 10 mm. Velocity-compensated self-diffusion measurements were then acquired for the emulsion in the flow loop at superficial velocities of 0, 0.01, and 0.05  $\text{ms}^{-1}$ . The values of  $\delta$  and  $\Delta$  used for each measurement were 4 and 150 ms, respectively. Varying the value of  $\Delta$  between 50 and 500 ms for each superficial velocity considered produced no variation in the droplet-size distributions produced. The total experimental time for each droplet-size distribution measurement was 3 min. Repetition of each measurement revealed that the system was stable over periods in excess of 3 h.

In addition, for verification purposes, optical micrographs of the stationary emulsion were acquired using a Zeiss LSM510 confocal microscope. A size distribution based on 730 emulsion droplets was extracted from the resultant micrographs for comparison with the droplet-size distribution produced by NMR-PFG under nonflowing conditions.

## RESULTS AND DISCUSSION

The raw experimental NMR-PFG data ( $S$  versus  $g$ ) for the nonflowing xylene-in-water emulsion is shown in Fig. 2a. The



**FIG. 2.** (a) The xylene NMR signal,  $S$ , is shown as a function of  $g$ , the magnetic field gradient strength for the xylene-in-water emulsion. The fit of Eq. [3], describing self-diffusion in spherical cavities with a distribution of sizes, to these data is also shown. Agreement between the model and the experimental data is excellent. (b) The resultant size distribution produced by the NMR-PFG technique is shown along with the size distribution obtained from a confocal microscope. The agreement between the two is good, and serves as verification of the NMR-PFG technique of sizing emulsion droplets.

fit of Eq. [3] to these data is also shown. The quality of the fit is excellent and the droplet-size distribution produced is shown in Fig. 2b, along with the size distributions produced by the optical micrograph. Agreement between the two independent methods of determining the droplet-size distributions in the xylene emulsion, confocal microscopy and NMR-PFG self-diffusion measurement, is very good and serves as verification of the NMR-PFG droplet-sizing technique. In Fig. 3, the droplet-size distributions produced by conventional NMR-PFG (Fig. 1a) and by flow-compensated NMR-PFG (Fig. 1b) for the nonflowing xylene-in-water emulsion are shown. The two droplet-size distributions are virtually identical; this serves as proof that the

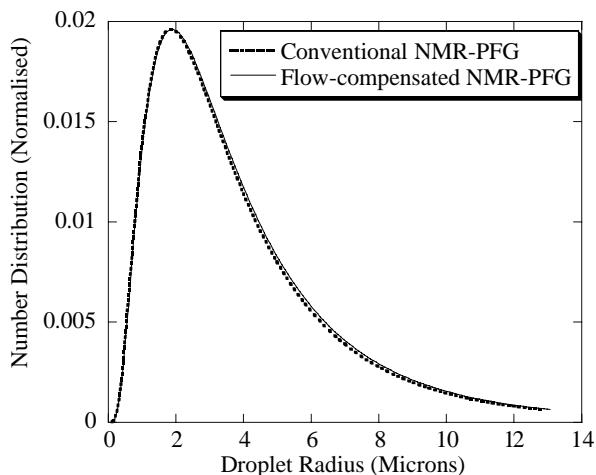


FIG. 3. The droplet-size distributions for the stationary xylene-in-water emulsion are shown, as predicted by the conventional NMR-PFG technique and by the flow-compensated NMR-PFG technique. Agreement between the two is excellent and verifies that the flow-compensated NMR-PFG technique is not introducing any additional error relative to the conventional NMR-PFG technique.

flow-compensated NMR-PFG technique is not introducing additional sources of error relative to the conventional NMR-PFG technique.

In Fig. 4, the emulsion droplet-size distributions are shown for the xylene-in-water emulsion flowing at superficial velocities of 0.01 and 0.05  $\text{ms}^{-1}$ . The droplet-size distribution for the

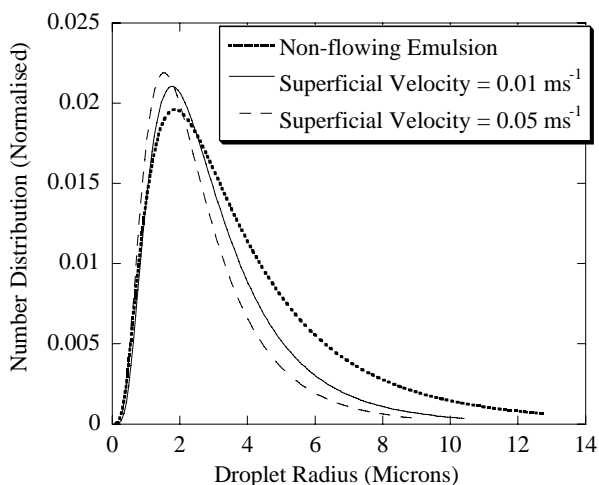


FIG. 4. The droplet-size distributions for the xylene-in-water emulsion for nonflowing conditions, as well as flowing at superficial velocities of 0.01 and 0.05  $\text{ms}^{-1}$ . The effect of increasing velocity shear in breaking up the larger emulsion droplets is clearly evident.

nonflowing emulsion is also shown. Comparing the droplet-size distributions for the nonflowing emulsion to those for the emulsion flowing at superficial velocities of 0.01 and 0.05  $\text{ms}^{-1}$ , it is clear that some of the larger droplets have been broken up as superficial velocity is increased. In addition, as the superficial velocity is increased from 0.01 to 0.05  $\text{ms}^{-1}$ , a further reduction in the size of the larger droplets occurs. This result is encouraging since, if the velocity distribution were distorting the diffusion measurements by contributing to signal attenuation, via Taylor dispersion, for example, it would be expected that the droplet-size distribution would be distorted significantly toward larger radii. This is clearly not the case. The droplet-size distributions were also determined in different directions, both parallel and perpendicular to the principal flow direction. Identical droplet-size distributions were produced, suggesting that for the system studied, shear is not significantly distorting the spherical shapes of the droplets. Future work will focus on the stability of the technique at higher superficial velocities and its inclusion in magnetic resonance imaging protocols.

## CONCLUSIONS

A flow-compensated NMR-PFG technique was successfully used to investigate the droplet-size distribution of a xylene-in-water emulsion flowing in a narrow tube. As the flow rate was increased, the resultant increase in velocity shear was seen to decrease the size of the larger droplets present, thereby narrowing the droplet-size distribution. For the case of the non-flowing emulsion, the droplet-size distributions produced by optical microscopy, the conventional NMR-PFG technique and the implemented flow-compensated NMR-PFG technique, were found to be identical to within experimental error.

## REFERENCES

1. P. T. Callaghan, "Principles of Magnetic Nuclear Resonance Microscopy," Clarendon Press, Oxford (1991).
2. K. J. Packer and C. Rees, Pulsed NMR studies of restricted diffusion. 1. Droplet size distributions in emulsions, *J. Colloid Interface Sci.* **40**, 206 (1972).
3. I. Lonnqvist, B. Hakansson, B. Balinov, and O. Soderman, NMR self-diffusion studies of the water and the oil components in a W/O/W emulsion, *J. Colloid Interface Sci.* **192**, 66 (1997).
4. B. Manz, J. D. Seymour, and P. T. Callaghan, PGSE NMR measurements of convection in a capillary, *J. Magn. Reson.* **125**, 153 (1997).
5. J. S. Murday and R. M. Cotts, Self-diffusion coefficient of liquid lithium, *J. Chem. Phys.* **48**, 4938 (1968).
6. J. C. Van den Eden, D. Waddington, H. Van Aalst, C. G. Van Kralingen, and K. J. Packer, Rapid determination of water droplet size distributions by PFG-NMR, *J. Colloid Interface Sci.* **140**, 105 (1990).
7. P. T. Callaghan and Y. Xia, Velocity and diffusion imaging in dynamic NMR microscopy, *J. Magn. Reson. A* **91**, 326 (1991).