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Short-Time PFGSTE Diffusion Measurements

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The pulsed-field-gradient stimulated-echo method is a well-established technique for studying molecular motion without disturbing the system under investigation. In porous media, the short-time expansion of the mean-squared displacement can be used to measure the surface-to-volume ratio, S/V, of a system (*1*). Recently, Fordham *et al.* (*2*) showed that the effective diffusion time can be significantly altered by taking into account restricted diffusion during the gradient pulses in the evaluation of the diffusion coefficient at short diffusion times. Using their corrected effective diffusion times, measurements of the surface-to-volume ratio of compact mono-sized spheres will be presented, and it will be shown that their model yields a better fit to the experimental data set.

Mitra *et al.* (*1*) have shown that the diffusivity at short times, t, can be written as

$$\frac{D(t)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}}\frac{S}{V}\sqrt{D_0 t} - \left(\frac{S}{6V}\left\langle\frac{1}{R}\right\rangle + \frac{1}{6}\frac{\rho S}{D_0 V}\right)D_0 t + O((D_0 t)^{3/2}), \quad [1]$$

where $\langle 1/R\rangle$ is the mean curvature of the spheres, ρ is the surface relaxation strength, D_0 is the unrestricted diffusion coefficient, and S/V is the surface-to-volume ratio. The leading term in this perturbation expansion is dependent on the square root of time, the unrestricted diffusion coefficient, and the surface-to-volume ratio. A two-parameter fit to the data set therefore results in an experimental value for S/V and the unrestricted diffusivity. Regarding diffusion among compact spheres, the porosity ϕ of the sample must be known to extract a mean diameter for the spheres:

$$d = \frac{6(1/\phi - 1)}{S/V}. \quad [2]$$

The pulse sequence used is the 13-interval sequence with unequal bipolar gradients, where δ, δ_1, δ_2, and Δ are defined according to Fig. 1. This sequence has been shown to substantially remove or reduce signal following unwanted coherence-transfer pathways without the need for orthogonal spoiler gradients (*3*).

The echo attenuation for the sequence in Fig. 1 can be written as

$$\ln\frac{I}{I_0} = -\gamma^2(2\delta)^2 g^2 D(t)\left[\Delta + \frac{3}{2}\tau - \frac{\delta}{6}\right] \times\left[i - \frac{1}{2}\left(\frac{\Delta + \tau - \delta/6}{\Delta + \frac{3}{2}\tau - \delta/6}\right)x\right]^2, \quad [3]$$

where the diffusion time is given by

$$t = \Delta + \frac{3}{2}\tau - \frac{\delta}{6}. \quad [4]$$

Taking into consideration restricted diffusion during the gradient pulses, Fordham *et al.* (*2*) have shown that the corrected effective diffusion time employing squared pulses can be written as

$$t_{\mathrm{eff}} \simeq \left\{\frac{\frac{1}{4}[(\Delta + 3\tau)^{3/2} + 2(\Delta + 2\tau)^{3/2} + (\Delta + \tau)^{3/2}] - \frac{1}{2}\tau^{3/2} - \frac{4}{35}\delta^{3/2}}{\Delta + \frac{3}{2}\tau - \delta/6}\right\}^2. \quad [5]$$

Equation [5] differs from the result given by Fordham *et al.* (*2*) only because of a different notational definition of Δ. Using corrected diffusion times, the diffusion propagator (*1*) is no longer assumed to be Gaussian during the gradient pulses. Then the narrowing effect of the cavities will be taken into account, and will result in a larger and a more correct S/V ratio. This model yields a smaller diameter of the spheres.

To investigate the short-time diffusion among compact mono-sized spheres, soda-lime glass microspheres with a certified mean diameter of 98.7 ± 4.9 μm were immersed in distilled water. As the application of the short-time model by Mitra *et al.* (*1*) yields a mean diameter for the spheres, it may be compared to the certified mean diameter given by

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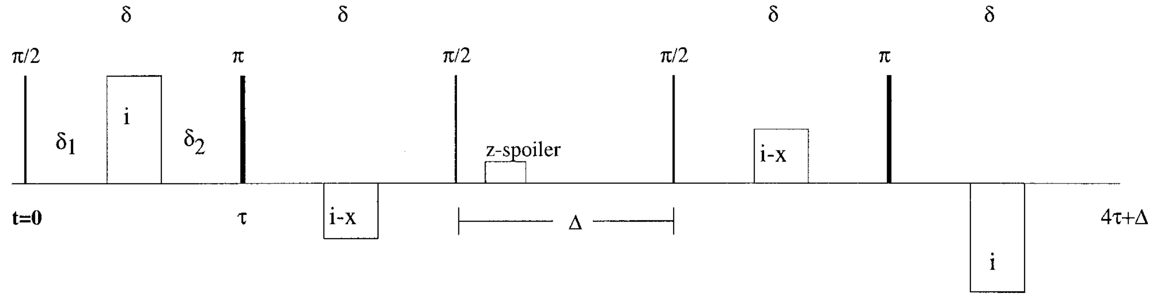

FIG. 1. The 13-interval PFGSTE sequence using bipolar gradients of different strengths.

the manufacturer, Duke Scientific (U.S.A.). The standard deviation for the mean diameter, ± 4.9 μm, must not be confused with the size distribution for the spheres, *given* a mean diameter. This deviation is 3.7%, given by the manufacturer.

The porosity ($\phi = 0.40 \pm 0.01$) was found by measuring the volume occupied by the spheres and the total volume of spheres and water. The experiments were performed on a Bruker DMX200 spectrometer using a homebuilt diffusion probe featuring actively shielded gradient coils constructed after the target field approach (*4*). Through linewidth measurements, the internal gradient strength was found to be of the same order of magnitude as the applied gradient strength. Thus δ_1 was chosen equal to δ_2. Assuming a constant internal gradient, the cross term between the applied gradient and the internal gradient should then cancel completely. Throughout the experiment, $\delta = 0.5$ ms and $\delta_1 = \delta_2 = 0.3$ ms.

The experiments were performed changing only the time between the second and third $\pi/2$ pulse, the ''z-storage'' time. The increment of the gradient strength was kept constant, leading to fewer data points within the linear $\ln(I/I_0)$ attenuation of the stimulated echo for longer diffusion times. It is of greater importance for the accuracy of the measurements to keep the conditions for the gradient strengths constant. For the longest diffusion times applied, there were still enough data points for accurate diffusion measurements within the second-cumulant approximation (*5*).

Figure 2 shows that the second-cumulant approximation is valid down to $\ln(I/I_0) \approx -0.9$. Taking the leading term of the short-time expansion in Eq. [1], a fit to the experimental data set using the least-squares method is found. As seen in Fig. 3, there seems to be a square-root dependency, regardless of whether restricted diffusion during the gradient pulses is taken into account or not. Regarding the uncertainty of the diameter of the spheres, the crucial factor is the porosity of the system. This is found by volumetric measurements to be 0.40 ± 0.01. Taking this uncertainty into account the values for the mean diameter of the spheres are 105.3 ± 4.0 μm using the standard effective diffusion time and 100.6 ± 4.0 μm using the corrected effective diffusion time.

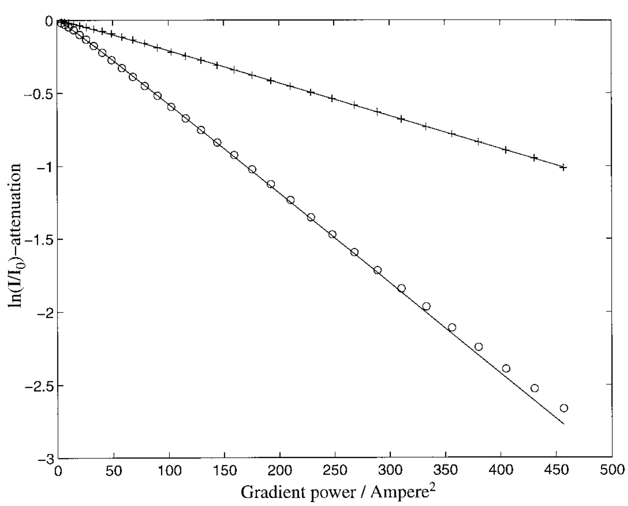

FIG. 2. The $\ln(I/I_0)$ attenuation for corrected diffusion times of 9.19 ms (+) and 24.27 ms (○). The solid lines represents weighted linear fits to the data sets.

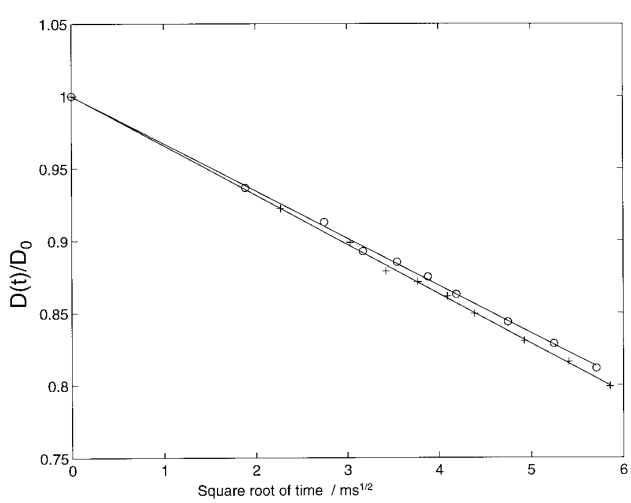

FIG. 3. Normalized diffusion coefficient as a function of diffusion times. (○) Data set using standard effective diffusion times; (+) data set using corrected diffusion times.

For both bulk diffusivities fitted to the data set, they are well within the uncertainty of the gradient strength ($\pm 2.5\%$). The error in the calibration of the gradient strength is constant throughout the experiment and will affect only the fitted bulk diffusivity at zero diffusion time. This uncertainty is therefore ruled out when estimating the uncertainty for the mean diameter of the spheres. The uncertainty for the fitted square root of time slope is negligible compared to the uncertainty of the porosity.

In Fig. 3 the difference from using the standard diffusion times is visualized, and one can see that a reduction of the diffusion coefficient is reached at a later stage using the standard diffusion times. This can be interpreted as the molecules are probing larger spheres, and therefore yields a smaller S/V.

Looking at the variance, σ^2, for the two fitted data sets, the model using corrected effective diffusion times is not sensitive to a weighting of the experimental data. For different weightings, $\sigma^2_{\text{corrected}}$ varied from 1.49×10^{-4} to 1.52×10^{-4}. With the same weightings on the data set using standard effective diffusion times, the variance $\sigma^2_{\text{standard}}$ varied significantly from 1.68×10^{-4} to 3.29×10^{-4}. One may therefore conclude that the best fit to the square root of time model indeed is the model which takes into account restricted diffusion during the gradient pulses.

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