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Diffusion-Broadened Velocity Spectra of Convection in Variable-Temperature BP-LED Experiments

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When NMR diffusion experiments are performed at temperatures different from ambient temperature, temperature gradients due to probe design can cause thermal convection and therefore significantly affect the signal amplitude. Fourier transformation of the signal amplitude gives rise to a diffusion-broadened velocity spectrum, which contains information about the convection velocity. It is shown that when the diffusion broadening factor is smaller than the maximum velocity, the broadening has little effect on the determination of the maximum velocity. Thus, convection velocity can be determined in the presence of diffusion.

INTRODUCTION

As the PFG-NMR diffusion experiment (*1*) has become a routine technique for studies in physical chemistry, many investigations are aimed at detecting molecular diffusion at varying temperatures. However, due to the design of the heating device in an NMR probehead, moderate differences between the target temperature and ambient temperature can result in a temperature gradient inside the cylindrical NMR sample. As a result, convection occurs (*2*), which greatly distorts the NMR signal intensities in diffusion measurements. The Rayleigh–Benard state, a state of convection in which the motion of molecules reaches a steady state, has attracted much attention in recent years (*3–13*). Methods have been proposed to compensate for the convection effects (*3–7*). In order to better understand convection in NMR tubes, convection rates have been measured (*8, 9*) and convection flow patterns have been imaged (*10–12*). Convection effects have also been utilized in magnetic resonance imaging studies (*13*).

The imaging experiments performed by Jerschow (*12*) have demonstrated that the Rayleigh–Benard convection in an NMR tube can, in the active region of the RF coil, be viewed as mass transport in the z dimension, comparable to the directed flow in electrophoretic NMR (ENMR) experiments (*15*). Thus, ENMR theory can be directly applied to convection studies. Loening and Keeler (*9*) have used a diffusion-free velocity spectrum method to determine the maximum velocities in convection. In this paper, we use the BP-LED pulse sequence (*1, 14*) to image the convection velocity distribution without removing the diffusion effect. The Fourier transformation of the convection-affected BP-LED amplitude gives rise to a diffusion-broadened velocity spectrum, which contains information about the velocity distribution and the maximum convection velocity. The method has been demonstrated to be useful for gravity-driven flow and electroosmosis flow (*16*) and is now applied to the study of convection. The diffusion broadening effect on the velocity spectrum is discussed.

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THEORY

In NMR diffusion experiments with the BP-LED pulse sequence, the echo amplitude is given by

$$I_1(q) = I_0 \exp[-Dq^2(\Delta - \delta/3)], \qquad [1]$$

where $q = \gamma\delta g$; γ is the gyromagnetic ratio, $\delta/2$ is the gradient pulse length, g is the gradient pulse amplitude, and Δ is the diffusion time. In the following, we assume that in experiments g is varied while Δ and δ are kept constant. If there is an inherent velocity in the direction of, or opposite to, the field gradient, Eq. [1] should be modified by an oscillation factor

$$I_2(q) = I_1(q) \exp(-iqv\Delta). \qquad [2]$$

Equation [2] implies that the velocity v is constant for all spins in a given cross section. However, in a cross section of the cylindrical NMR tube, the velocity of the convection flow is a function of the distance from the section center, and the NMR signal intensity in the diffusion experiment should be an integral over all velocities (*9*)

$$I_2(q) = I_1(q) \int_{-\infty}^{\infty} P(v) \exp(-iqv\Delta)\, dv, \qquad [3]$$

where $P(v)$ is the distribution of velocities. On the other hand, $P(v)$ is the inverse Fourier transform of $I_2(q)/I_1(q)$ with respect to q (*9*); that is, the Fourier transformation of $I_2(q)$ with respect

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to q gives rise to the *diffusion-broadened velocity spectrum* with a Gaussian broadening factor $B_{1/2}$

$$B_{1/2} = 4[(\ln 2)(D/\Delta)]^{1/2} = 3.33(D/\Delta)^{1/2}, \qquad [4]$$

where δ in $\exp[-Dq^2(\Delta - \delta/3)]$ has been neglected. When the Gaussian broadening is not significant, the Fourier transformation of the experimental data $I_2(q)$ can also give a clear picture of the velocity distribution.

A few words should be devoted to the derivation of Eq. [4]. In fact, the velocity spectrum is obtained by Fourier transformation of $I_2(q)$ with respect to $q\Delta$ rather than to q. The Gaussian function $\exp(-q^2\Delta D)$ can be rewritten as $\exp[-(q\Delta)^2(D/\Delta)]$. The Fourier transformation of this expression with respect to $q\Delta$ yields $(\pi\Delta/D)^{1/2}\exp[-v^2(\Delta/4D)]$, which is also a Gaussian function. The half-height of the Gaussian function in the velocity domain corresponds to $v = \pm 2[(\ln 2)(D/\Delta)]^{1/2}$. Hence we have the line broadening factor $B_{1/2}$ given in Eq. [4].

How significant is the diffusion broadening for the determination of velocity? The answer can be obtained by considering laminar flow. The velocity as a function of r can be written as (*15, 16*)

$$v(r) = v_1 - v_2\left(\frac{2r^2}{a^2} - 1\right), \qquad [5]$$

where v_1 and v_2 are constants, and a is the radius of the sample tube. In this case, $P(v)$ is a rectangular function; i.e., in the range from $r = 0$ ($v = v_1 + v_2$) to $r = a$($v = v_1 - v_2$) it is a constant and outside the range it is zero. By inserting Eq. [5] into Eq. [3] and integrating from $r = 0$ to $r = a$, we obtain the NMR intensity

$$I = I_0\exp[-Dq^2\Delta]\cos(qv_1\Delta)\frac{\sin(qv_2\Delta)}{qv_2\Delta}, \qquad [6]$$

where the complex function $\exp(-iqv_1\Delta)$ has been replaced by a real function $\cos(qv_1\Delta)$. For the steady-state laminar flow, where $v_1 = v_2$ (*9, 16*), Eq. [6] can be simplified to

$$I = I_0\exp[-Dq^2\Delta]\frac{\sin(qv_{\max}\Delta)}{qv_{\max}\Delta}, \qquad [7]$$

where $v_{\max} = v_1 + v_2$. In Fig. 1 we show a set of Fourier transforms of Eq. [7] with respect to $q\Delta$ with a constant Gaussian broadening factor ($B_{1/2} = 0.2$ mm/s) and a range of $v_{\max}$. For a, b, c, d, and e, $v_{\max}$ is 0, 0.1, 0.2, 0.3, and 0.4 mm/s, respectively. The half-height velocities for these five curves are 0.11, 0.14, 0.204, 0.302, and 0.401 mm/s, respectively. It is clear that, when $v_{\max} \geq B_{1/2}$, the velocity at the half-height of each curve can be taken as the maximum velocity, and the effect of diffusion broadening on the determination of $v_{\max}$ can be neglected.

It should be pointed out that, when convection occurs, temperature in the sample is not uniform and the diffusion coefficient will not be constant over the whole sample. Thus, when Eq. [7] is used to describe convection, the diffusion coefficient D can be interpreted only as an average value.

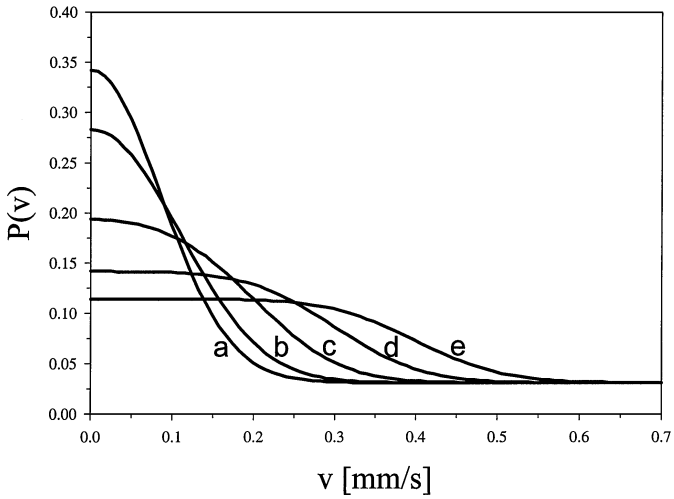

FIG. 1. Fourier transform of $I(q, v)$ in Eq. [7] with respect to $q\Delta$ by assuming $\Delta = 0.554$ s and $D = 2 \times 10^{-9}$ m^2/s ($B_{1/2} = 0.2$ mm/s). From (a) to (e), $v_{\max}$ is 0, 0.1, 0.2, 0.3, and 0.4 mm/s.

EXPERIMENTAL AND CALCULATIONS

The sample used in this study was 10% H_2O/90% D_2O in a 5-mm NMR tube with a sample height of 5.9 cm. NMR experiments were conducted on a Bruker Avance 500 spectrometer using a Nalorac probehead tuned to 500.13 MHz for proton acquisition and equipped with a z gradient. The BP-LED pulse sequence (*1, 16*) was used with a diffusion time $\Delta = 200$ ms, a longitudinal eddy-current delay $T_e = 20$ ms, and a duration for each gradient pulse $\delta/2 = 1$ ms. The gradient strength was calibrated with 50% H_2O/50% D_2O at 298 K and the maximum gradient strength was 103.6 G/cm. The temperature was varied from 298 to 328 K in steps of 5 K, and was controlled with a Bruker VT-3000 unit with an air flow of 400 L/hr. Each time the temperature was changed, the system was allowed to equilibrate for a period of 20 min. Fluctuations in the ambient temperature, 294 K, were small (the difference between daytime and nighttime temperature was less than ± 0.2 K), which was essential for maintaining a stable temperature gradient in the sample.

In the experiments, 32 increments of gradient strength g were used according to the logarithmic spacing rule (*1, 17*). Before Fourier transformation, interpolation by the B-spline method was performed to make g equally spaced and zero filling to 256 points was applied to enhance the digital resolution. Interpolation and Fourier transformation were performed using the PC computer program MATHCAD (Version 8, MathSoft, Inc).

RESULTS AND DISCUSSION

In BP-LED experiments below 313 K, no appreciable convection effects were observed in the NMR signal intensity. However,

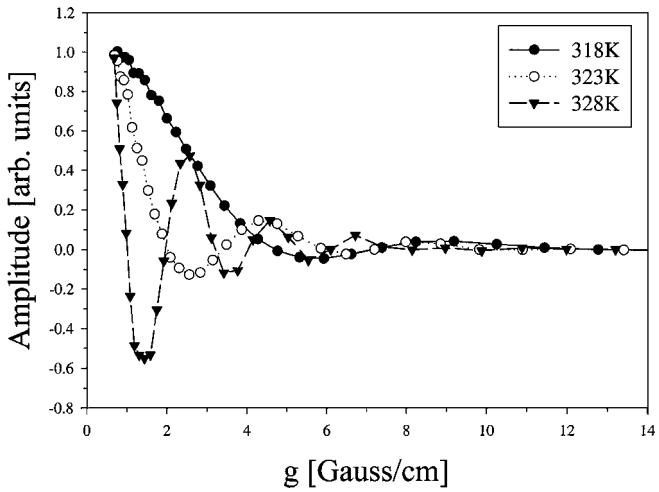

FIG. 2. The BP-LED amplitude of the proton signal in 10% H_2O/90% D_2O versus the gradient strength g (in G/cm) at three temperatures, 318, 323, and 328 K.

when the temperature reached 318 K, an oscillation in the detected amplitude appeared. This effect became more pronounced as the temperature was further increased. In Fig. 2 the BP-LED amplitudes at three temperatures (318, 323, 328 K) are plotted versus the gradient amplitude g (in G/cm). The oscillation is obviously induced by the convection due to the temperature gradient and is predicted by the oscillation factor in Eq. [3]. The data at 328 K indicate that when the target sample temperature (328 K) is 30 K above room temperature, the loss of NMR intensity in PFG experiments can be significant.

The Fourier transforms of the BP-LED data, i.e., the velocity spectra, are shown in Fig. 3. A velocity spectrum similar to that at 323 K has been obtained by Loening and Keeler (*9*) and has been predicted by the theory of Rayleigh–Benard convection (*12*). The last inflection point of each velocity spectrum (indicated by a hollow circle) would yield the maximum velocity. So tentatively, we obtained $v_{max} = 0.7$, 1.6, and 2.9 mm/s at $T = 318$, 323, and 328 K, respectively. The diffusion coefficients of the proton in 10% H_2O/90% D_2O at the three temperatures can be estimated by the known diffusion coefficient of H_2O (*18*) and the known isotope effect (*19*) which does not change much over the experimental temperature range (*20*). Thus, $D_{sample} = (0.1 + 0.9/\eta)D_w$, where 0.9 is the percentage of D_2O in the sample, η (=1.23) (*19*) is the H/D isotope effect factor of the self-diffusion coefficient of water, and D_w is the diffusion coefficient of H_2O. D_{sample} was estimated to be 3.58, 3.96, and 4.34 (10^{-9} m^2/s). Thus, the Gaussian broadening factor for the three velocity spectra would be 0.134, 0.140, and 0.147 mm/s, respectively. Compared to the would-be v_{max} data, the broadening factors are too small to show appreciable effects on the v_{max} measurements. Loening and Keeler (*9*) reported maximum convection velocities between 0.05 and 0.2 mm/s for H_2O in D_2O and DMSO at 315 K, using a diffusion-free velocity spectrum method. Jerschow (*12*) showed that DMSO had the maximum convection velocity 0.6 mm/s at 311 K, using an MRI method. We have obtained $v_{max} = 0.7$ mm/s for 10% H_2O/90% D_2O at 318 K. There is a considerable difference between our results and the literature values. However, since the convection rate depends on the temperature gradient rather than temperature itself, and the temperature gradients vary with the probehead used, the maximum convection velocities measured at different laboratories may vary, even when the same sample is used.

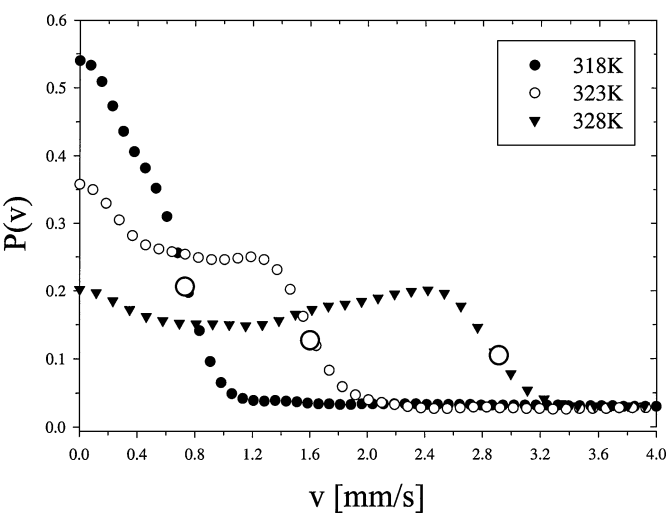

FIG. 3. Fourier transform of the BP-LED amplitudes in Fig. 2 with respect to $q\Delta$. The large hollow circles indicate the last inflection point at high velocity for each curve.

The velocity spectra at 318 and 323 K indicate that lower velocities are more probable than higher ones, but the velocity spectrum at 328 K indicates that the probabilities of both high and low velocities are larger than that of medium velocities. All velocity spectra in Fig.3 differ from those shown in Fig.1, suggesting that the observed convection is different from laminar flow. Compared to the velocity spectrum predicted by the Rayleigh–Benard convection theory (*12*), the velocity spectrum at 328 K is an indication that the sample was neither under a linear temperature gradient nor at steady state. Hence, the velocity spectra can serve as a simple way of monitoring whether the sample inside the magnet has reached steady state or not. Thus, it is obvious that for the experiment at 328 K, 20 min is not enough for the sample to reach a thermal steady state. It should be pointed out that not all probes have the same temperature-controlling ability. Some probes require a longer time than others to reach a thermal steady state.

The diffusion-broadened velocity spectrum method presented in this article could find possible applications in the study of water (or blood) velocities in blood vessels in animal or human bodies. The method could also be utilized for plant physiology studies if the velocity of water absorption is of interest. Since the broadening factor, $B_{1/2}$, is dependent on the experimental parameter Δ, $B_{1/2}$ is adjustable in experiments. Smaller $B_{1/2}$ can be obtained by choosing a longer Δ. In BP-LED

experiments, the magnetization is kept mainly in the longitudinal direction during the Δ period (*1*, *14*). Hence, Δ can be comparable to the longitudinal relaxation time. Other advantages of the BP-LED pulse sequence include eddy-current reduction and J-modulation minimization (*1*, *14*).

It should be emphasized that it is not possible to obtain more than an estimate for diffusion coefficients from the velocity spectra. In other words, diffusion coefficients cannot be measured accurately in the presence of any convection, regardless of whether the convection is stable or not. Diffusion coefficients should be measured only when the temperature in the sample is uniform. Accordingly, for diffusion measurements it is important to minimize convection.

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