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Thermal diffusivity and nuclear spin relaxation: A continuous wave free precession NMR study

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Abstract

Continuous wave free precession (CWFP) nuclear magnetic resonance is capable of yielding quantitative and easily obtainable information concerning the kinetics of processes that change the relaxation rates of the nuclear spins through the action of some external agent. In the present application, heat flow from a natural rubber sample to a liquid nitrogen thermal bath caused a large temperature gradient leading to a non-equilibrium temperature distribution. The ensuing local changes in the relaxation rates could be monitored by the decay of the CWFP signals and, from the decays, it was possible to ascertain the prevalence of a diffusive process and to obtain an average value for the thermal diffusivity.

Keywords: Thermal diffusivity; Natural polymer; CWFP; SSFP; Freezing

1. Introduction

Steady-state free precession (SSFP) [1–4] has been very effective in fast magnetic resonance imaging and in the study of flow and diffusion [5–7]. Recently, we have demonstrated that continuous wave free precession (CWFP), a special case of SSFP, can be used in several applications. For example: for signal to noise ratio improvement in quantitative determinations using low-resolution NMR equipment [8,9], to monitor flow [10], and for fast simultaneous measurements of T_1 and T_2 [11].

The CWFP regime is attained when a train of short $\pi/2$ pulses, with period T_p small compared to $T_2^* = 1/\Delta\varpi_0$, is applied to a liquid or motionally narrowed solid obeying Bloch's equations. Here $\Delta\varpi_0$ denotes the dispersion of precession frequencies about a central frequency ϖ_0 caused by an inhomogeneous magnetic field. Furthermore, the applied radiofrequency is shifted from the central frequency ϖ_0 by a frequency offset chosen such that $\omega_0 T_p = (2n + 1)\pi$, where n is an integer. This causes the signal amplitude just preceding a $\pi/2$ pulse to be equal to the amplitude following the pulse. Since the condition $T_p < T_2^*$ implies that dephasing of isochromats in each interval T_p is relatively small a continuous wave periodic signal with practically constant amplitude, displaying n nodes within each T_p interval, is obtained [8]. If the condition $T_p \ll T_2$, T_1 is satisfied the amplitude of the transverse CWFP magnetization, under steady-state conditions, can be shown to be given by [8] $|M_{s+}| = M_0/(1 + T_1/T_2)$. Here T_2 is the spin–spin relaxation time and M_0 denotes the thermal equilibrium magnetization.

When a CWFP steady state is established under equilibrium conditions its amplitude is determined by the time-independent ratio $\Gamma = T_1/T_2$. Moreover, in a non-equilibrium situation, the steady-state signal can evolve in time as changes in the relaxation times, which could be caused by a variety of processes, take place. Such processes might include: temperature changes due to heat transfer,

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fast polymerization reactions, phase changes, etc. Provided the response of the CWFP signal is fast enough, valuable information about the kinetics of these processes could be obtained.

CWFP can be used effectively to monitor such processes provided some specific conditions are met. Denoting by τ the correlation time of the relevant molecular motion CWFP can be sensitive to the kinetics of the process provided the motion is in the slow correlation time regime [12] characterized by $\varpi_0\tau > 1$. In this regime, the spin–lattice relaxation time can become appreciably longer than the spin–spin relaxation time. Conversely, in extreme narrowing regime characterized by $\varpi_0\tau \ll 1$, the condition $T_1 \approx T_2$ prevails and the CWFP signal becomes independent of the relaxation times.

The response time of the CWFP signal to changes in the relaxation times is an important factor for the proposed application. The establishment of a steady-state CWFP signal starting from thermal equilibrium has been studied in considerable detail. It has been shown to consist of an initial oscillatory transient [11], with a short time constant determined by T_2^* superimposed on an exponential approach to the steady state with time constant [13] $T_s = 2T_1T_2/(T_1 + T_2)$. One could expect that, if the rate of change of the relaxation ratio $\Gamma = T_1/T_2$ for the ongoing process is smaller than $1/T_s$ the CWFP signal should be able to follow the kinetics of the process. In a regime characterized by $\varpi_0\tau > 1$ the spin–lattice relaxation time T_1 may become quite longer than T_2 and the response time approaches the value $T_s \approx 2T_2$.

Although several applications can be conceived we here consider, as an example, the heat transport process in spheres of a polyisoprene elastomer (natural unvulcanized latex rubber without any filler). In spite of being able, in principle, to monitor faster processes, there exists some interest in measuring thermal transport properties by NMR [14–16].

Starting from a spatially non-uniform temperature distribution the system under study, with a well-defined geometrical shape, is allowed to evolve towards equilibrium via thermal diffusion. As the local temperature varies the changes in ^{1}H relaxation times that take place can be monitored through the decay of the CWFP signal. By varying the size of the system it is possible to make sure that the scaling of the decays obeys a diffusion equation and to ascertain that the response time comfortably permits to monitor the kinetics of the process.

Using low-resolution bench-top NMR equipment, and combining CWFP measurements under non-equilibrium conditions with equilibrium CWFP measurements at various temperatures, we are able to obtain thermal diffusivity data.

2. Theory

In several elastomers, such as natural rubber, at Larmor frequencies in the range $\varpi_0/2\pi \sim 5$ MHz, the condition $\varpi_0\tau > 1$ is satisfied for T_1 somewhat below room temperature. Here τ represents the correlation time of the motion, which in the present case, corresponds to the reorientation of elementary polymer segments.

If a uniform polymer sample of spherical shape, initially in equilibrium at a temperature θ_0, is placed in contact with a thermal bath at a lower temperature θ_b, the time evolution of the local temperature $\Theta(r,t)$ resulting from heat flow to the bath can be described by a diffusion equation. For spherical symmetry the local temperature $\Theta(r,t)$ obeys the equation

$$\frac{\partial\Theta}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\lambda(\Theta)r^2\frac{\partial\Theta}{\partial r}\right), \tag{1}$$

where the thermal diffusivity $\lambda(\Theta)$ is, in general, a function of temperature and is related to the heat conductivity κ, the specific heat at constant pressure c_p, and the mass density ρ through [17]

$$\lambda = \frac{\kappa}{c_p\rho}. \tag{2}$$

In particular, if the thermal diffusivity can be assumed to be temperature independent in the interval of interest, the diffusion equation takes the simpler form

$$\frac{\partial\Theta}{\partial t} = \frac{\lambda}{r}\frac{\partial^2}{\partial r^2}(r\Theta). \tag{3}$$

Denoting by a the radius of the sphere, Eq. (3) permits an analytical solution [17], satisfying the boundary conditions of our problem, which is given in closed form by

$$\frac{\Theta(r,t) - \theta_0}{\theta_b - \theta_0} = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\lambda\pi^2 t/a^2)\frac{\sin(\pi nr/a)}{\pi nr/a}, \tag{4}$$

in the range $t > 0$ and $r < a$.

On the other hand, when the thermal diffusivity changes appreciably in the temperature interval of interest, Eq. (2) can be solved numerically using, for example, the finite differences method of Crank–Nicholson [17,18] with a temperature dependent $\lambda(\Theta)$.

As the local temperature within the sphere decreases from its initial uniform value θ_0 towards its final equilibrium value θ_b the relaxation ratio $\Gamma = T_1/T_2$ rapidly increases and the CWFP signal amplitude decays to zero. Strictly speaking not only the relaxation ratio increases but also the thermal equilibrium magnetization increases at a rate limited by $1/T_1$. However, given that the changes in M_0 are small in the present problem, the effect is practically negligible.

If the rate of change of the ratio T_1/T_2 is small compared with $1/T_s$ the CWFP signal amplitude as a function of time can be assumed to be determined by the time evolution of a succession of steady-state regimes. Denoting by $\Gamma(\Theta) = T_1(\Theta)/T_2(\Theta)$ the temperature-dependent relaxation ratio, the normalized CWFP signal amplitude $S(t)$ would be given simply by an integral over all spherical shells of form