T_1: the Longitudinal Relaxation Time

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Spin Polarization: Curie's Law of Magnetization

The laws of physics are microscopically reversible, which implies that the RF field will flip any isolated proton ↑ to ↓ and ↓ to ↑ equally well. So to see any proton signal at all, you have to have a disproportionation between spins aligned with and against $\vec{B}_{DC}$. The better polarized your sample, the bigger your signal will be. Ideas from statistical mechanics allow you to predict the polarization from $\vec{B}_{DC}$ and the temperature of the sample.

Given the energy difference between neighboring angular momentum states, $\Delta E = \hbar\omega_L$, the relative populations of these states at thermal equilibrium will be

$$\frac{N_\downarrow}{N_\uparrow} = e^{\frac{-\hbar\omega_L}{k_B T}}.$$

(The ↑ state is the one pointed along $\vec{B}$.) Here we are applying **Boltzmann's Law**. This statistical mechanical result does *not* mean that individual spins remain in the same state. Rather, it means that because of the availability of thermal energy $\hbar\omega_L$ at this temperature, the rates of transition $\mathbf{R}_{\uparrow\downarrow}$ and $\mathbf{R}_{\downarrow\uparrow}$ are balanced for this population ratio. (For more about this, see the next section.)

The polarization P_{eq} is the equilibrium population difference per unit volume

$$P_{eq} = N_\uparrow - N_\downarrow = N \tanh\left(\frac{\hbar\omega_L}{2k_B T}\right)$$

For $\hbar\omega_L \ll k_B T$,

$$P_{eq} = N \tanh\left(\frac{\hbar\omega_L}{2k_B T}\right) \approx N\frac{\hbar\omega_L}{k_B T},$$

as you can see by expanding the exponentials to first order. This result is called **Curie's Law** (for S=$\frac{1}{2}$ paramagnets)[1]. The higher the DC field (so the higher ω_L) and the lower the temperature, the larger the NMR signal. Calculate the equilibrium magnetization for protons at room temperature (roughly 300 K) as a function of magnetic field, and

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[1] Named for Pierre Curie.

plot the results. For your water samples–roughly 0.1 milliliter–how many protons can you hope to observe? Calculate the magnetization and estimate the maximum signal you could hope to see at a B_{DC} of 5000 Gauss. To do this, you will have to estimate the dimensions of your RF solenoid.

The Longitudinal Relaxation Time T_1

A polarized sample of water tends to depolarize when the DC field is turned off. This is because ever-present thermal fluctuations will tend to redistribute the spins according to Boltzmann's Law for the new energy level structure where there is no energy difference between ↑ and ↓. On the other hand, if the thermal equilibrium belongs to a polarized state, then the fluctuations tend to restore that equilibrium. If you subject your sample to a pulse and turn the polarization in some out of equilibrium direction, the polarization takes a certain amount of time to recover. The amount that you recover between successive pulses will also determine your signal strength. One way to characterize the strength of the fluctuations is the **longitudinal relaxation time**, T_1. The stronger the fluctuations, the shorter T_1, the quicker the recovery.

How T_1 Depends on the Fluctuations

Begin with the two fluctuation-induced transition probabilities per spin per unit time $\Gamma_{\downarrow\uparrow}$ and $\Gamma_{\uparrow\downarrow}$, denoting the probability per unit time of a single spin in either state to flip to the other state. The total rate of transition from down to up will be

$$\mathbf{R}_{\downarrow\uparrow} = N_{\downarrow}\Gamma_{\downarrow\uparrow}$$

and the total rate at which spins flip the other way will be

$$\mathbf{R}_{\uparrow\downarrow} = N_{\uparrow}\Gamma_{\uparrow\downarrow}.$$

At equilibrium, the difference of the transition rates will be zero:

$$\mathbf{R}_{\uparrow\downarrow} - \mathbf{R}_{\downarrow\uparrow} = N_{\uparrow}\Gamma_{\uparrow\downarrow} - N_{\downarrow}\Gamma_{\downarrow\uparrow} = 0,$$

which means that in thermal equilibrium

$$\frac{\Gamma_{\downarrow\uparrow}}{\Gamma_{\uparrow\downarrow}} = \frac{N_{\uparrow}}{N_{\downarrow}} = e^{\frac{E_{\downarrow}-E_{\uparrow}}{k_B T}} = e^{\frac{\hbar\omega_L}{k_B T}}.$$

In thermal equilibrium, the ratio of the transition probabilities depends on the thermal population of the states, and the tendency for a single spin to go from the higher energy state to the lower energy state is greater. This might sound paradoxical–after all, aren't the laws of nature supposed to be irreversible? The answer has to do with the conservation of energy. The fluctuating spin must exchange energy with its "environment," *e.g.*

the electromagnetic field and the electronic magnetic moments in the sample. So while the quantum mechanical matrix elements for a single spin-flip either way are the same, each spin flip probability must also factor in the availability of the energy necessary to make the transition. Thus the probablity of a transition involving a change in energy $\Delta\epsilon$ should look like

$$\Gamma_{\Delta\epsilon} \propto \mathcal{W} e^{\frac{-\Delta\epsilon}{k_B T}},$$

where $\mathcal{W}$ represents the quantum mechanical probability for the transition to go either way regardless of whether the energy is available.

If the environment is always at a temperature T regardless of what the spins are doing (that is, if the environment has a comparatively huge heat capacity), then the ratio of the rates for the out-of-equilibrium case will be the same as for the equilibrium case, and the transition rates will work the same way. Consider an out-of-equilibrium situation, with $N_\uparrow = N_{\uparrow eq} + \Delta N_\uparrow$, $N_\downarrow = N_{\downarrow eq} + \Delta N_\downarrow$, and $\Delta M = M - M_{eq} = \Delta N_\uparrow - \Delta N_\downarrow$. Writing plain Γ for $\Gamma_{\uparrow\downarrow}$,

$$\frac{d(N_{\uparrow eq} + \Delta N_\uparrow)}{dt} = -\Gamma(N_{\uparrow eq} + \Delta N_\uparrow) + e^{\frac{\hbar\omega_L}{k_B T}}\Gamma(N_{\downarrow eq} + \Delta N_\downarrow),$$

and

$$\frac{d(N_{\downarrow eq} + \Delta N_\downarrow)}{dt} = -e^{\frac{\hbar\omega_L}{k_B T}}\Gamma(N_{\downarrow eq} + \Delta N_\downarrow) + \Gamma(N_{\uparrow eq} + \Delta N_\uparrow).$$

Since these transition rates are precisely those that preserve equilibrium, the equilibrium parts of both equations already balance, leaving the out of equilibrium portions,

$$\frac{d\Delta N_\uparrow}{dt} = -\Gamma\Delta N_\uparrow + e^{\frac{\hbar\omega_L}{k_B T}}\Gamma\Delta N_\downarrow,$$

and

$$\frac{d\Delta N_\downarrow}{dt} = -e^{\frac{\hbar\omega_L}{k_B T}}\Gamma\Delta N_\downarrow + \Gamma\Delta N_\uparrow.$$

The total number of spins is constant, so that $\Delta N_\downarrow = -\Delta N_\uparrow$. Putting in this information, and then subtracting the second rate equation from the first,

$$\frac{d\Delta P}{dt} = -\Gamma(1 + e^{\frac{\hbar\omega_L}{k_B T}})\Delta P,$$

that is,

$$\Delta P(t) = \Delta P(0) e^{-t/T_1},$$

with

$$\frac{1}{T_1} = \Gamma(1 + e^{\frac{\hbar\omega_L}{k_B T}}) \approx 2\Gamma$$

for protons at room temperature.

An Experiment to Measure T_1

The following data was taken on the TeachSpin apparatus.

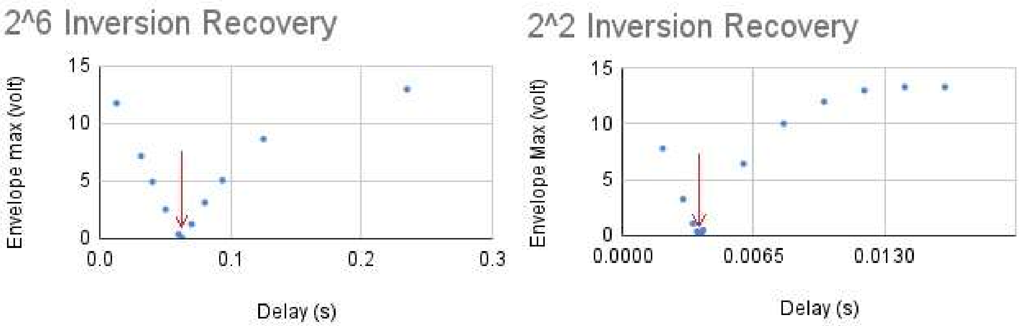

Figure 1: $\pi - \tau - \pi/2$ inversion recovery data for 2^n dilutions of saturated $CuSO_4$:H_2O, absolute signal amplitude as a function of τ between the pulses. Left: $n = 2$. Right: $n = 6$. The arrows indicate the zero crossing delay τ_0. In theory, $T_1 = \frac{\tau_0}{\ln 2}$, and the longitudinal relaxation rate $\frac{1}{T_1}$ is an increasing function of solute concentration.

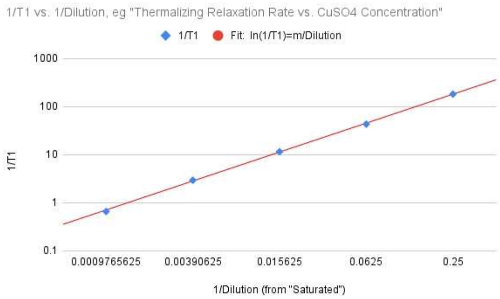

Figure 2: Relaxation rate $\frac{1}{T_1}$ vs. $CuSO_4$ concentration (relative to saturation conentration, blue points) along with a linear fit (red line) on a log / log plot.

Samples of $CuSO_4$:H_2O solution were subjected to the sequence $\pi - \tau - \pi/2$, with a variable delay τ. The first pulse inverted the equilibrium polarization, so that $P_0 = -P_{eq}$. During the delay, the initially inverted polarization partially recovered according to the rule

$$\Delta P(t) = \Delta P_0 e^{-t/T_1},$$

ie

$$P(t) - P_{eq} = -2P_{eq} e^{-t/T_1}$$

$$\to P(\tau) = P_{eq}(1 - 2e^{-\tau/T_1})$$

or equivalently

$$P(\tau) = \underbrace{P_{eq}(1 - e^{-\tau/T_1})}_{\text{Growing equilibrium population}} - \underbrace{P_{eq}e^{-\tau/T_1}}_{\text{Decaying anti-equilibrium population}} .$$

After the π pulse, the signal remained zero because the spin polarization was negative its equilibrium value: it was "anti-equilibrium". During the time delay τ, the spins began to rethermalize. Some downward spins flipped upward and some of the upward flipped downward, as the initial anti-equilibrium polarization decayed toward equilibrium and the equilibrated population recovered. The $\pi/2$ pulse turned whatever the net polarization was at time τ by 90° so that it precessed in the applied field, allowing a measurement of the polarization at that moment. The amplitude of the FID indicated the difference between the rethermalized polarization and the remnant of the initial polarization, because these started the FID exactly out of phase. *This* signal was zero at $\tau = \ln 2T_1$, when the rethermalized population and the antithermal remnant exactly canceled.

Changing the concentration of $CuSO_4$ changed $\frac{1}{T_1}$. The plots for different concentrations were quite similar, though. They displayed the same exponential recovery, just along different time scales depending on the concentration of solute. Starting with a saturated solution, successive solutions with solute concentration/saturated concentration $\frac{1}{2^n}$ showed a linearly increasing $\frac{1}{T_1}$ as a function of decreasing n.

One way to explain this data is to model the longitudinal relaxation as a consequence of the interaction between the proton spin and the magnetic moment of the Cu^{++} ion in solution. For a single proton, the probability of such a thermalizing interaction would be proportional to the likelihood of a close encounter with a Cu^{++}, which should be proportional to the solute concentration. You can confirm/disconfirm this behavior and take this idea further by:

1. Carefully measuring $\frac{1}{T_1}$ for distilled water, which would fix the intercept for this fit line
2. Carefully measuring $\frac{1}{T_1}$ of your own series of $CuSO_4$ solutions (the slope also depends on the sample temperture, which will vary from day to day
3. Carefully measuring $\frac{1}{T_1}$ for solutions of different paramagnetic or even nonmagnetc sulfates (the plot should remain linear, but the slope should change with the moment of the magnetic ion, and naively $\frac{1}{T_1}$ should not change for a nonmagnetic salt).

In order to avoid spurious relaxation effects due to field gradients (which might change the apparent zero crossing of your plots), your first task will be to carefully trim $\vec{B}_{DC}$, and you should be careful to place the same fairly small sample volume in the same part of the probe coil, independent of concentration. It is also important to start your measurements with your samples at P_{eq}. This means that your repeat period between pulse sequences should be at least several T_1 to relax away any remnant polarization–otherwise, you may never see a good zeroing. For $CuSO_4$ solutions, you can use the plotted line to pre-estimate your own repeat periods–though this will not apply to pure water, because my plot does not resolve that long relaxation time.

Since this study requires many measurements, it is a good idea to prepare saturated solutions beforehand. Also, once you have figured out what you are doing, it is not necessary to measure the recovered amplitude for every delay; rather, you just have to nail τ_0. So (at least for the more concentrated solutions for which short periods are appropriate) you can quickly dial through τ until you find what you are looking for.