The Effects of Paramagnetic Ions and Viscosity on the Spin-Lattice Relaxation Time (T_1)

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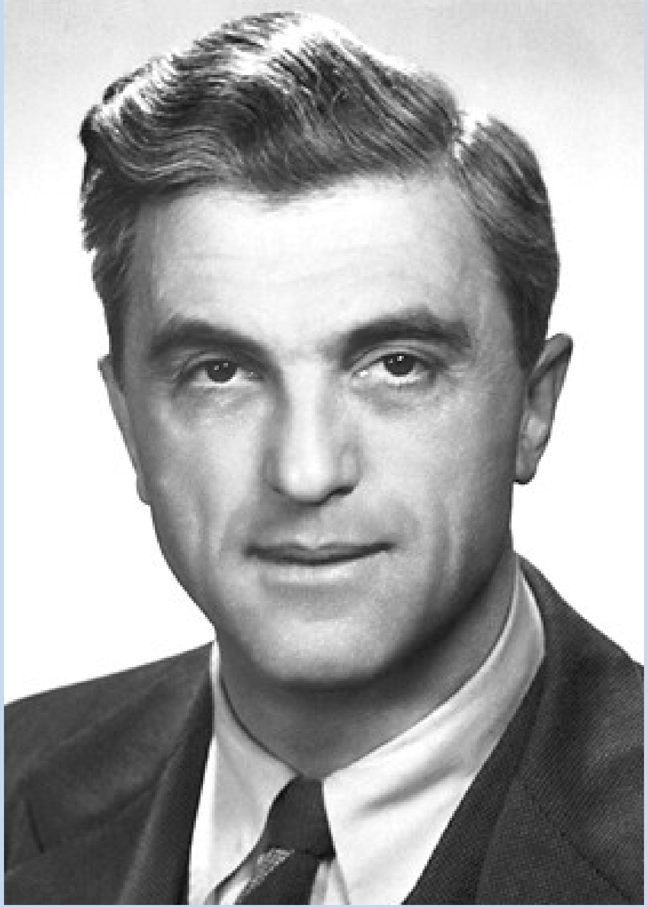
Introduction: Perturbed Systems

- Nuclear Magnetic Resonance:
  - Discovered by E.M. Purcell, Bloch using CW techniques
- A different method of measurement:
  - Perturb a system and observe the return to equilibrium
- Goal:
  - Measure the effects of viscosity and paramagnetic ions on the return to equilibrium



Felix Bloch
Taken from nobelprize.org

Theory: Nuclear Spins

- Nuclear spins: 2-dim Hilbert Space with $|\pm\rangle$ basis states corresponding to spins in the ±Z direction
- A spin pointing in the direction defined by the polar angles (θ, ϕ) is given by:

$$|\Psi, t\rangle = cos(\frac{\theta(t)}{2})|+\rangle + sin(\frac{\theta(t)}{2})e^{i\phi(t)}|-\rangle$$

Theory: Nuclear Spins in Magnetic Fields

- Choosing a basis: $|1\rangle = |+\rangle \quad |2\rangle = |-\rangle$
- In a constant magnetic field:

$$\vec{B} = B_0\hat{Z}$$

$$\hat{H} = \gamma S \begin{pmatrix} -B_0 & 0 \\ 0 & B_0 \end{pmatrix}$$

$$\theta(t) = \theta(0)$$
$$\phi(t) = \phi(0) - \gamma B_0 t$$

- With an RF pulse: $\vec{B} = B_0\hat{Z} + B_1(cos(\omega t)\hat{X} - sin(\omega t)\hat{Y})$
- Simple evolution when: $\omega = \gamma B_0$

$$\hat{H} = \gamma S \begin{pmatrix} -B_0 & B_1 e^{i\omega t} \\ B_1 e^{-i\omega t} & B_0 \end{pmatrix}$$

$$\theta(t) = \gamma B_1 t$$
$$\phi(t) = \frac{\pi}{2} - \gamma B_0 t$$

Theory: Pulses

- Spins are manipulated by pulsing the time-varying portion of the magnetic field
- Pulses can be classified by their effect on θ
- A 90° -pulse increases θ by 90° and is related to time by $t = \frac{\pi}{2\gamma B_0}$

Theory: Thermodynamics

- Imbalance in states produces a magnetization in the direction of the spin vector:

  $\vec{M}_{eq} = M_0 \hat{z}$

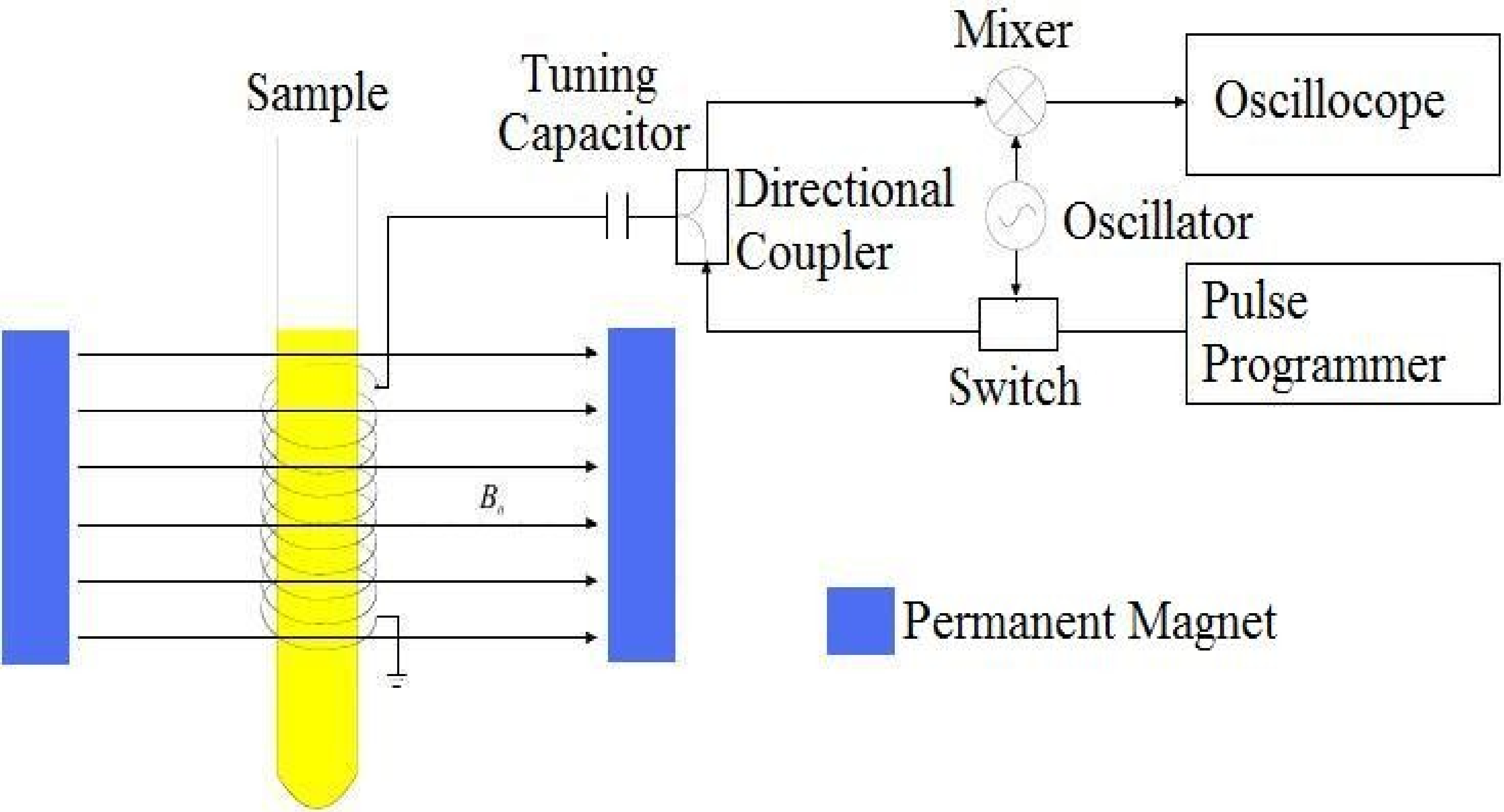
- Define a perturbed magnetization vector:

  $\vec{M}_p(t) = \vec{M}(t) - \vec{M}_{eq}$

- The z-component decays with time-constant T_1:

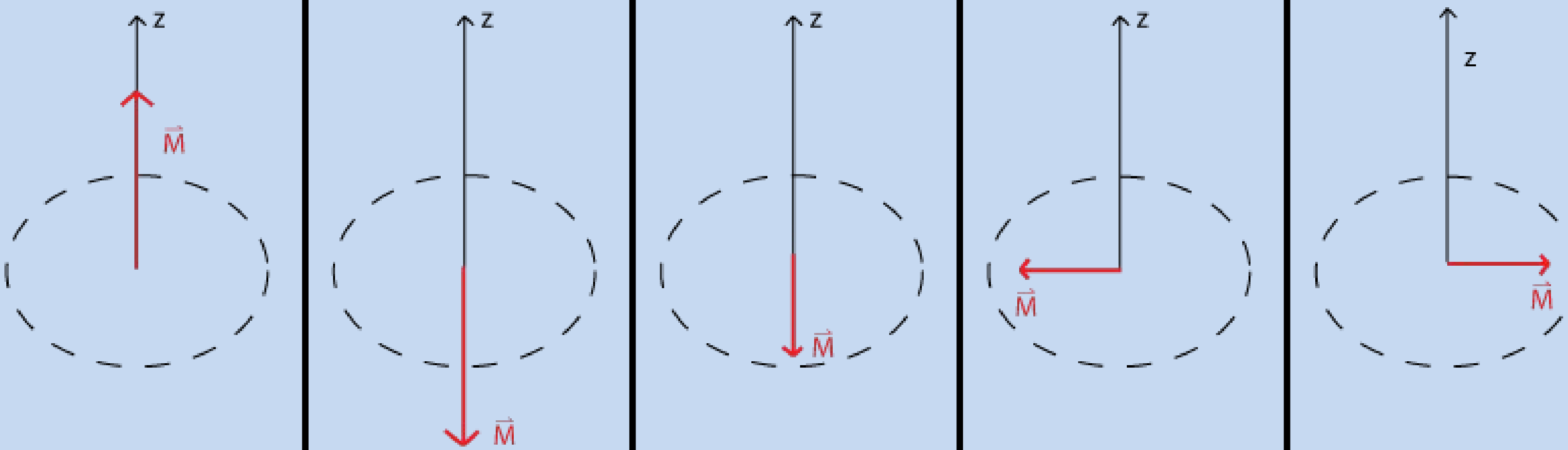
  $M_{p,z}(t) = M_{p,z}(0) exp(-\frac{t}{T_1})$

Experimental Setup



7.5MHz Signal

The 180° –T–90° –180° Pulse Sequence

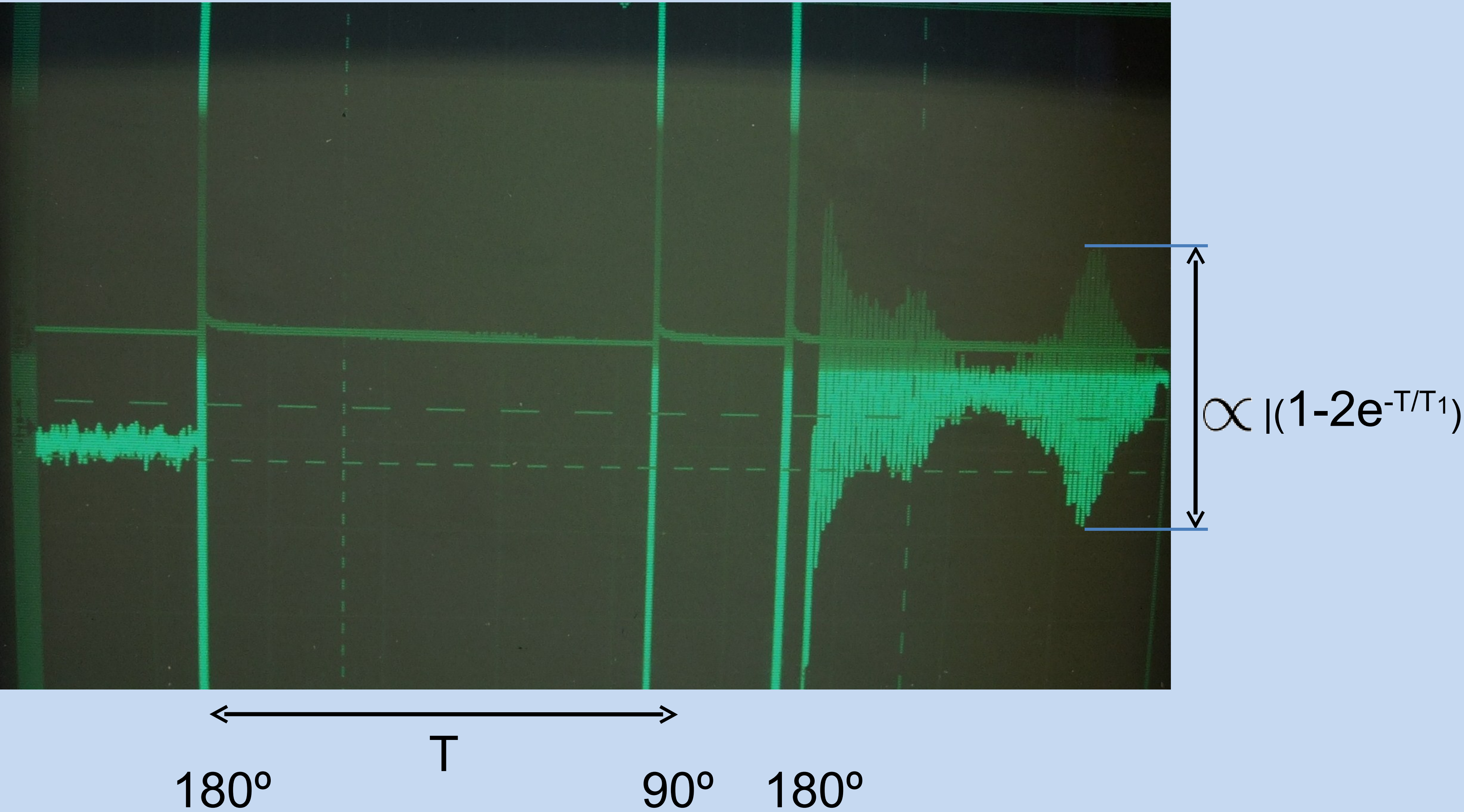


$\lvert\vec{M}\rvert=$	M_0	M_0	$M_0\lvert(1-2e^{-T/T_1})\rvert$	$M_0\lvert(1-2e^{-T/T_1})\rvert$	$M_0\lvert(1-2e^{-T/T_1})\rvert$

180º T 90º 180º

Increasing Time

The 180° –T– 90° –180° Pulse Sequence



Analysis: Error and Uncertainty

- Sources of amplitude error:
  - Statistical variance (≈0.2mV)
  - Cursor resolution (0.035mV)
- Error in T_1 determined through first-order error propagation
- Possible additional contributors to error:
  - Low repeat times (3s)
  - Sample contamination

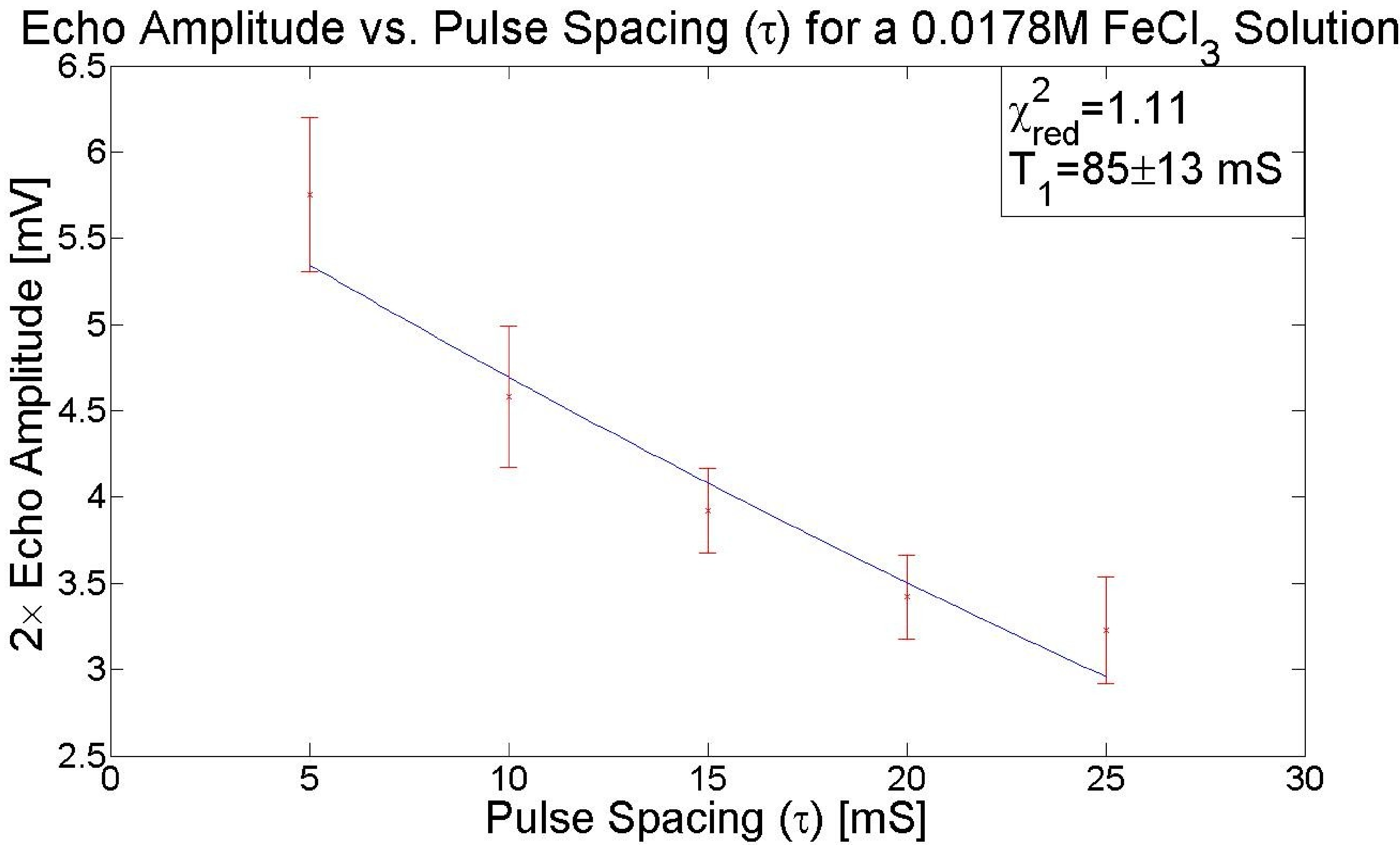
Analysis: Fitting

- For a variety of samples we collected 5 (amplitude, T) pairs.
- Using a gradient expansion method, these were fit to:

$$A(\tau) = A_0(1 - 2exp(-\frac{\tau}{T_1}))$$

- Chi Squared values were generally <1.5.

Analysis: Sample Data

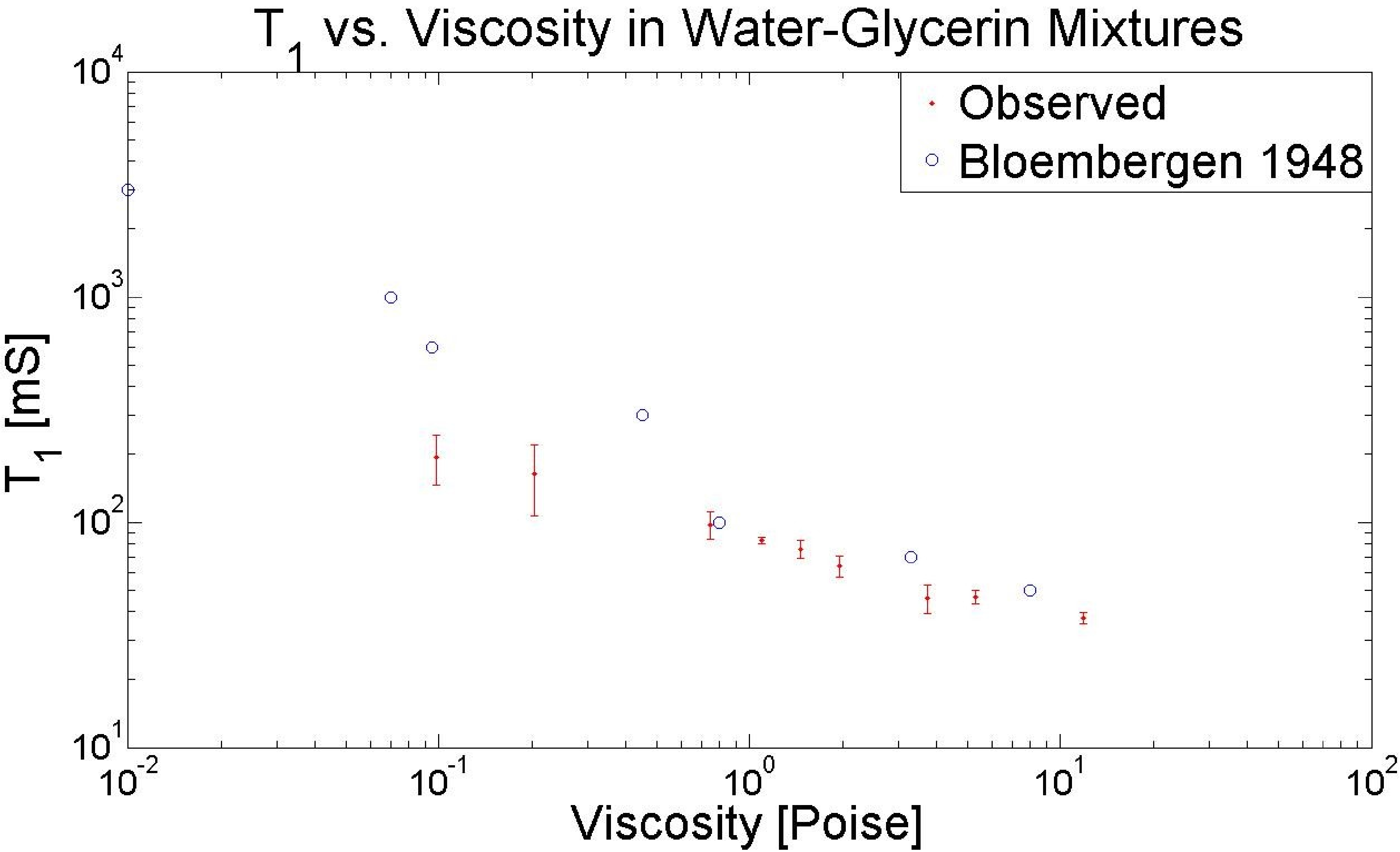


Conclusion: Effects of Viscosity

Representative T_1 vs. Viscosity Data Points Measured in Water-Glycerin Mixtures					
% Glycerin	100	94	82	70	60
Viscosity [Poise]	11.86	3.74	0.75	0.20	0.10
T_1 [mS]	38±2	46±7	97±14	163±57	195±49

- T_1 decreases with increasing viscosity
- Suggests that T_1 decreases with increasing molecular interactions
- Matches Bloembergen's data for high viscosity

Conclusion: Effects of Viscosity

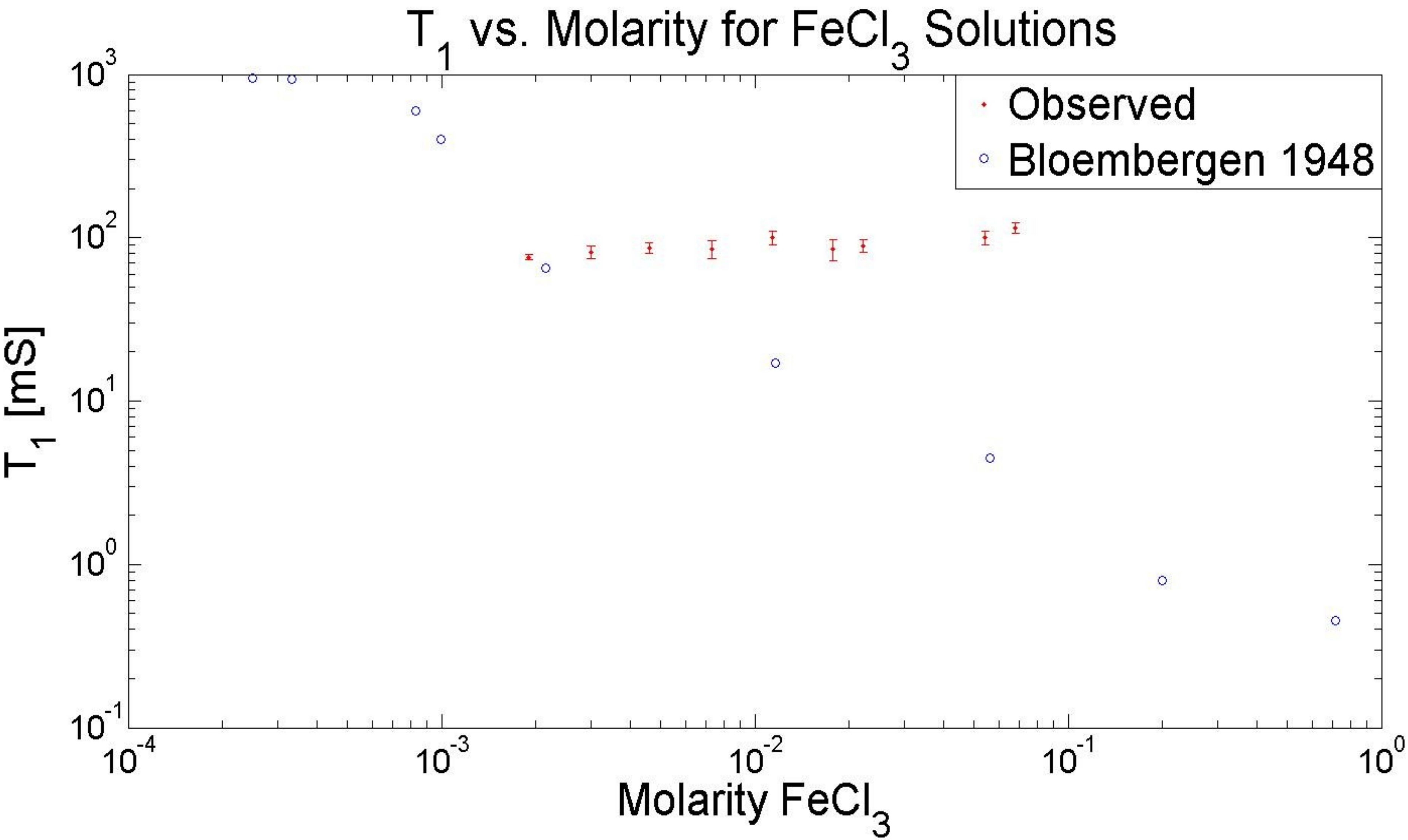


Conclusion: Effects of Paramagnetic Ions

Representative T_1 vs. Molarity Data Points Measured in FeCl3 Solutions					
Molarity	0.0019	0.0046	0.0114	0.0222	0.0680
Ions/cc	1.14e18	2.77e18	6.87e18	1.34e19	4.10e19
T_1 [mS]	76 ± 3	87 ± 7	100 ± 9	90 ± 80	115 ± 9

- T_1 roughly constant
- Significantly lower than a measured T_1 for water: 1.3 ± 0.1s and the accepted value 2.5 ± 0.5
- Suggests paramagnetic ions facilitate spin-lattice interactions

Conclusion: Effects of Paramagnetic Ions



Questions?