

*I think there's something
strangely musical about noise*

Trent Reznor

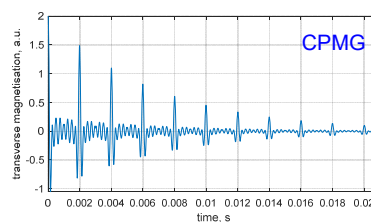
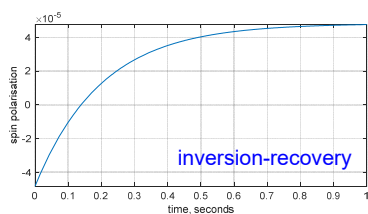
Spin relaxation theory: a very gentle introduction

*the general idea and a complete
treatment for a simple system*

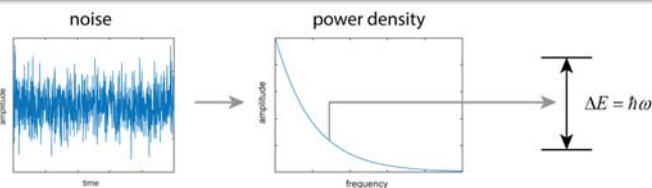
Ilya Kuprov, University of Southampton

What is relaxation?

Relaxation is the process whereby an *ensemble* of systems returns to *equilibrium*.



NMR relaxation is caused by external noise hitting transition frequencies.



► Sources of noise: Brownian motion, vibrations, conformational mobility, external particles.

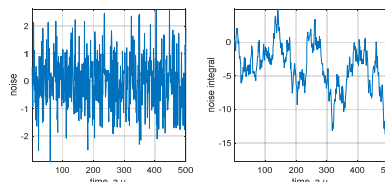
The mathematics of noise

Noise does not play well with QM and its differential equations:

$$\frac{\partial}{\partial t} \psi(t) = -i [\hat{H}_0 + \hat{H}_1(t)] \psi(t)$$

↓

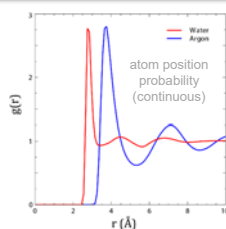
a different noise $\rightarrow \psi(t)$



Solutions must be sought in terms of *statistical properties* of noise:

Statistical descriptors:

- mean value
- standard deviation
- distribution law
- stat. parameters
- stat. functions



noises vary significantly in their SPD functions

► Most relevant noises are stationary: the statistics does not depend on time.

The simplest system with all the features

The simplest possible system that captures all the essentials:

$$\frac{\partial}{\partial t} \psi(t) = -i [\hat{H}_0 + \hat{H}_1(t)] \psi(t) \quad \Rightarrow \quad \frac{\partial}{\partial t} f(t) = -i [\omega_0 + \omega_1(t)] f(t)$$

An oscillator with a noisy frequency. In the absence of noise, the solutions are:

$$x(t) = \cos(\omega_0 t), \quad p(t) = -\sin(\omega_0 t), \quad f(t) = x(t) + ip(t) = e^{-i\omega_0 t}$$

↙ coordinate
↙ momentum
↙ shorthand



Assume the noise is *weak* and *stationary*, with a zero mean:

$$\omega(t) = \omega_0 + \omega_1(t), \quad |\omega_1(t)| \ll |\omega_0|, \quad \langle \omega_1(t) \rangle = 0$$

In a real NMR experiment, the frequency will be the NMR line frequency.

► When the molecule tumbles, shifts and dipolar interactions change, and therefore frequencies do.

Dealing with the noise

First, let us try to isolate the noise into its own equation:

$$\frac{df(t)}{dt} = -i[\omega_0 + \omega_1(t)]f(t) \quad f(t) = e^{-i\omega_0 t} \varphi(t) \quad \text{(we expect oscillation times decay)}$$

Substitution and simplification (aka *rotating frame transformation*) yields:

$$\frac{d\varphi(t)}{dt} = -i\omega_1(t)\varphi(t) \quad \text{we took out the known oscillation to focus on the interesting part}$$

No way to solve this directly, and no way to average. Let us try making this:

$$g(t, t') = \langle \omega_1(t) \omega_1(t') \rangle \quad \text{correlation function; it is continuous and well-behaved}$$

$$g_{a,b} = \langle (a - \mu_a)(b - \mu_b) \rangle \quad \text{correlation coefficient}$$

If we can find a solution in terms of these, all problems with the noise disappear.

► The objective is to find the answer in terms of the statistical properties of the noise.

Walking the narrow path

Let us take the equation and simply integrate it (because we can):

$$\frac{d\varphi(t)}{dt} = -i\omega_1(t)\varphi(t) \quad \Rightarrow \quad \varphi(t) = \varphi(0) - i \int_0^t \omega_1(t') \varphi(t') dt'$$

...and then put the result back into the original equation (because we can):

$$\frac{d\varphi(t)}{dt} = -i\omega_1(t)\varphi(0) - \int_0^t \omega_1(t)\omega_1(t')\varphi(t') dt' \quad \text{something resembling a correlation function is now there}$$

Let us take the ensemble average of both sides:

$$\frac{d\langle \varphi(t) \rangle}{dt} = - \int_0^t \langle \omega_1(t)\omega_1(t')\varphi(t') \rangle dt' \quad \text{- remember that } \langle \omega_1(t) \rangle = 0$$

This is as far as we can get without approximations...

► This is actually time-dependent perturbation theory, but with multiple weird twists...

Walking the narrow path

First approximation - assume that the noise is too weak to *drive* the system:

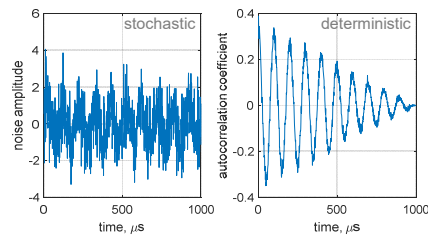
$$\langle \omega_1(t) \omega_1(t') \varphi(t') \rangle = \langle \omega_1(t) \omega_1(t') \rangle \langle \varphi(t') \rangle \quad \text{i.e. system dynamics is not correlated with the noise}$$

Remember that our noise is *stationary*, meaning that:

$$\langle \omega_1(t) \omega_1(t') \rangle = a^2 g(|t-t'|) \quad g(0) = 1 \quad \text{amplitude squared, times some function that is a property of the noise itself}$$

After a simple variable substitution that swaps t and t' :

$$\begin{aligned} \frac{d\langle \varphi(t) \rangle}{dt} &= -a^2 \int_0^t g(t-t') \langle \varphi(t') \rangle dt' \\ &\Downarrow \\ \frac{d\langle \varphi(t) \rangle}{dt} &= -a^2 \int_0^t g(t') \langle \varphi(t-t') \rangle dt' \end{aligned}$$



► And so we managed to replace a stochastic differential equation with an ordinary one...

Walking the narrow path

Let us now drop the brackets and return to the original oscillator function:

$$\frac{d\varphi(t)}{dt} = -a^2 \int_0^t g(t') \varphi(t-t') dt' \quad \varphi(t) = e^{i\omega_0 t} f(t)$$

$$\begin{aligned} &\Downarrow \\ \frac{df(t)}{dt} &= \underbrace{-i\omega_0 f(t)}_{\text{noiseless dynamics}} - \underbrace{a^2 \int_0^t g(t') e^{-i\omega_0 t'} f(t-t') dt'}_{\text{something to do with the noise}} \end{aligned}$$

the memory time of the molecular scale noise is very short (nanoseconds)

Our next approximation uses the fact that the time scale of the noise is very short:

$$t' \ll t \Rightarrow f(t-t') \approx f(t) \quad \text{and} \quad \int_0^t g(t') e^{-i\omega_0 t'} dt' \approx \int_0^\infty g(t') e^{-i\omega_0 t'} dt'$$

These are the least obvious assumptions, called "coarse-graining of time".

► This relaxation theory only works when the noise is very fast (usually true in liquids).

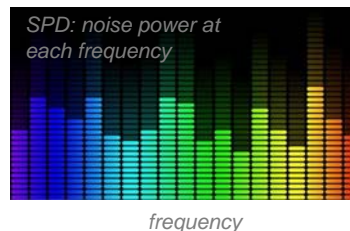
Walking the narrow path

Our final equation of motion is:

$$\frac{df(t)}{dt} = -i\omega_0 f(t) - a^2 f(t) \int_0^\infty g(t') e^{-i\omega_0 t'} dt'$$

The Fourier transform of the autocorrelation function is called spectral power density:

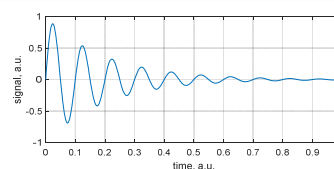
$$J(\omega_0) = \int_0^\infty g(t') e^{-i\omega_0 t'} dt'$$



The result is an equation describing a *decaying* oscillation:

$$\frac{df(t)}{dt} = -i\omega_0 f(t) - \underbrace{a^2 J(\omega_0)}_{\text{decay rate}} f(t)$$

quadratic
frequency



► We did it: the noise makes our ensemble of oscillators irreversibly go out of phase.

Where is noise in the spin Hamiltonian?

$$\hat{H} = \hat{H}_Z + \hat{H}_{NN} + \hat{H}_{EN} + \hat{H}_{EE} + \hat{H}_{MW}$$

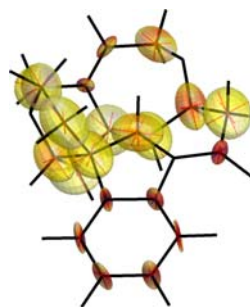
Zeeman interactions
electron-nuclear interactions
microwave and radiofrequency terms
inter-nuclear and quadrupolar interactions
inter-electron interactions and zero-field splitting

Zeeman interactions: chemical shielding tensors for nuclei and g -tensors for electrons.

$$\hat{H}_Z = \sum_k \vec{B}_0 \cdot \mathbf{A}_E^{(k)} \cdot \hat{E}^{(k)} + \sum_k \vec{B}_0 \cdot \mathbf{A}_N^{(k)} \cdot \hat{N}^{(k)}$$

trigonometric functions of molecular orientation

CSA relaxation is *quadratic* in the magnetic field – this is why bigger magnet is not always better.



► Various tricks exist for playing CSA against the dipolar interaction: see TROSY.

Where is noise in the spin Hamiltonian?

$$\hat{H} = \hat{H}_Z + \hat{H}_{\text{NN}} + \hat{H}_{\text{EN}} + \hat{H}_{\text{EE}} + \hat{H}_{\text{MW}}$$

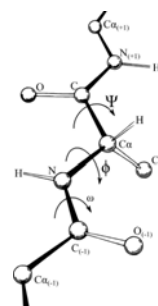
Zeeman interactions → \hat{H}_Z electron-nuclear interactions → \hat{H}_{EN} microwave and radiofrequency terms → \hat{H}_{MW}

inter-nuclear and quadrupolar interactions → \hat{H}_{NN} inter-electron interactions and zero-field splitting → \hat{H}_{EE}

functions of conformation functions of orientation

$$\hat{H}_{\text{NN}} = 2\pi \sum_{j < k} J_{\text{NN}}^{(j,k)} (\hat{N}_j \cdot \hat{N}_k) + \sum_k \hat{N}_k \cdot \mathbf{A}_Q^{(k)} \cdot \hat{N}_k - \frac{\mu_0}{4\pi} \sum_{j < k} \frac{\gamma_N^{(j)} \gamma_N^{(k)} \hbar}{r_{jk}^5} \left(3(\hat{N}_j \cdot \vec{r}_{jk})(\vec{r}_{jk} \cdot \hat{N}_k) - r_{jk}^2 (\hat{N}_j \cdot \hat{N}_k) \right)$$

functions of orientation



► Dipolar coupling goes as $1/r^3$ with distance, and so dipolar relaxation goes as $1/r^6$

Where is noise in the spin Hamiltonian?

$$\hat{H} = \hat{H}_Z + \hat{H}_{\text{NN}} + \hat{H}_{\text{EN}} + \hat{H}_{\text{EE}} + \hat{H}_{\text{MW}}$$

Zeeman interactions → \hat{H}_Z electron-nuclear interactions → \hat{H}_{EN} microwave and radiofrequency terms → \hat{H}_{MW}

inter-nuclear and quadrupolar interactions → \hat{H}_{NN} inter-electron interactions and zero-field splitting → \hat{H}_{EE}

Electron-nuclear interactions: isotropic (aka Fermi contact) and anisotropic hyperfine couplings.

$$\hat{H}_{\text{EN}} = \sum_{j,k} \hat{E}_j \cdot \mathbf{A}_{\text{EN}}^{(j,k)} \cdot \hat{N}_k$$

trigonometric functions of molecular orientation

x660 and then a square!

Note the strong directionality of some HFC tensors.



► Hyperfine coupling dominates nuclear relaxation in paramagnetic molecules.

Spectral power densities

$$\frac{df(t)}{dt} = -i\omega_0 f(t) - a^2 J(\omega_0) f(t)$$

frequency

decay rate

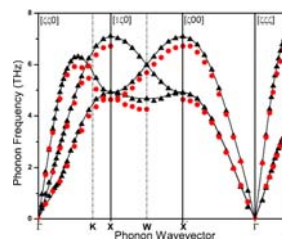
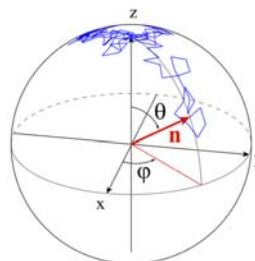
In liquids, the autocorrelation function decays exponentially, and SPD is Lorentzian:

$$g(t) = e^{-t/\tau_c}$$

↓

$$J(\omega_0) = \int_0^{\infty} e^{-t/\tau_c} e^{-i\omega_0 t} dt = \frac{1}{1 + \omega_0^2 \tau_c^2} + \dots$$

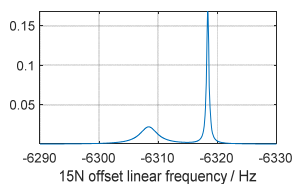
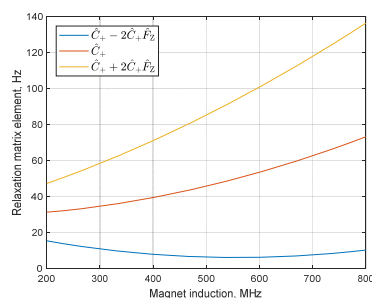
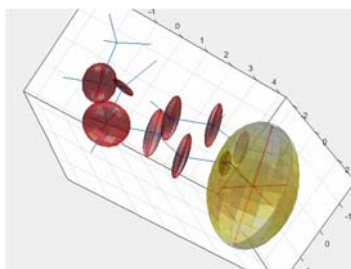
In solids, the power density of the noise may be very different at different frequencies.



► In most cases, the phonon spectrum and the spin-phonon coupling tensors are unpredictable.

Cross-correlations and TROSY

A molecule may tumble randomly, but *relative* atom positions stay the same...



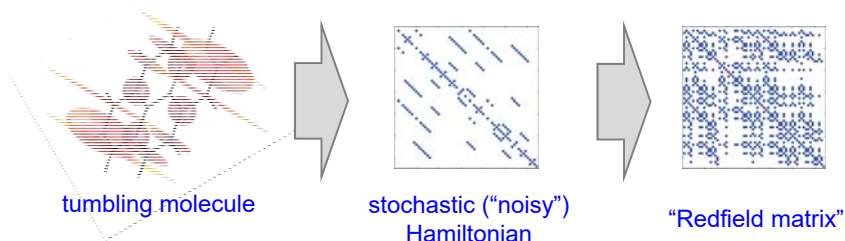
TROSY effect:

In geometrically rigid J -coupled DD-CSA pairs, one component of the doublet can be *much* narrower than the other.

► TROSY is used with great effect in protein NMR spectroscopy.

Bloch-Redfield-Wangsness relaxation theory

BRW is essentially a second-order time-dependent perturbation theory for a spin system affected by external noise. The properties of the noise matter a great deal.



$$\hat{R} = - \sum_{kmpq} \int_0^{\infty} G_{kmpq}(\tau) \hat{Q}_{km} e^{-i\hat{H}_0\tau} \hat{Q}_{pq}^\dagger e^{i\hat{H}_0\tau} d\tau$$

"Redfield integral" – a very tough thing to compute.

BRW theory is handled automatically within *Spinach* – specify your interactions, anisotropies and correlation times, press *enter*.

► BRW theory is very accurate – 10% error or less if the anisotropies / correlation times are good.

How to run relaxation theory analysis



DO NOT, UNDER ANY CIRCUMSTANCES

1. Perform relaxation theory analysis by hand, or
2. Use equations from papers without numerical tests.

Spinach relaxation module syntax:

```
% System specification
sys.magnet=14.1;
sys.isotopes={'13C'};
inter.zeeman.matrix={[100 20 15
                     20 0 30
                     25 10 -30]};

% Relaxation theory parameters
inter.relaxation={'redfield'};
inter.equilibrium='zero';
inter.rlx_keep='labframe';
inter.tau_c={2e-12};
```

The program supports every interaction there is, and all cross-correlations.

Symbolic engine in *Mathematica*:

```
R1 = Rate[Lz, Lz] // FullSimplify;
R2 = Rate[L, L] // FullSimplify;
R1 // SpectralDen // Simplify // CleanItUp
R2 // SpectralDen // Simplify // CleanItUp
```

$$-\frac{2 \Delta_A^2 \tau_c \omega_1^2}{15 + 15 \tau_c^2 \omega_1^2}$$

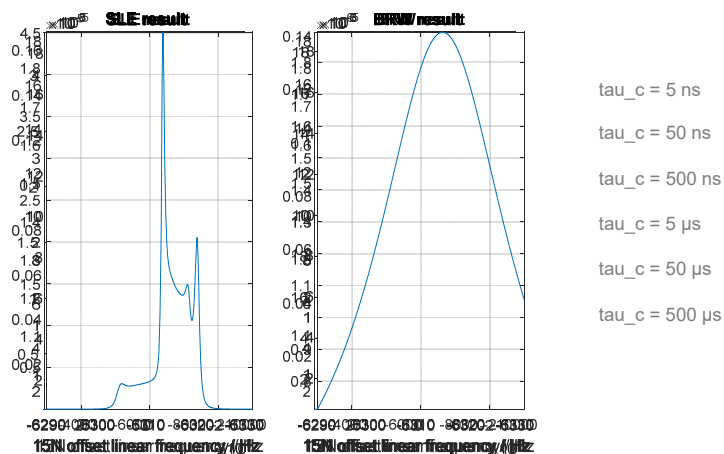
$$-\frac{1}{45} \Delta_A^2 \tau_c \omega_1^2 \left(4 + \frac{3}{1 + \tau_c^2 \omega_1^2} \right)$$

Systems with more than two spins can only realistically be done numerically; only *Spinach* can do 10+ spins.

► Decades of work have gone into relaxation theory software – use it.

Some health warnings

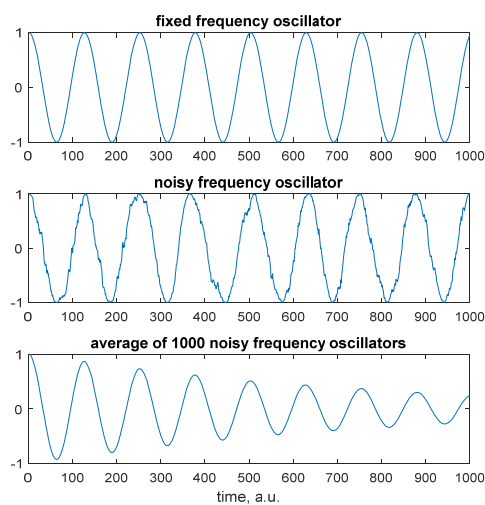
As the motion gets slower, Redfield theory fails:



► In NMR, Redfield theory is strictly valid only for correlation times below 100 ns.

Summary

1. Spin relaxation is caused by noise in the Hamiltonian.
2. Relaxation rate is quadratic in the noise amplitude.
3. Relaxation rate depends on the frequencies in the noise.
4. Full quantum mechanical treatment is stupidly hard.
5. Good software exists that will do most things for you.



► Liquids are fine; solid state relaxation theory does not really exist (too many unknowns).