

Seven Conjectures of NMR Relaxometry

by Stan Sykora (www.ebyte.it)

Given a stochastic [spin] Hamiltonian

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{S}(t), \quad \langle \mathbf{S}(t) \rangle = 0,$$

under certain conditions (secular vs stochastic time scales)
one obtains a secular equation for the density matrix

$$\frac{d}{dt} \boldsymbol{\sigma}(t) = -\frac{1}{2} \mathbf{J}(\mathbf{H}_0) \{ \boldsymbol{\sigma}(t) - \boldsymbol{\sigma}_0 \}$$

where

$$\mathbf{J}(\mathbf{H}_0) = \int_{-\infty}^{\infty} d\tau \mathbf{C}(\tau) = \int_{-\infty}^{\infty} \langle \mathbf{S}^*(0) \mathbf{S}^*(\tau) \rangle d\tau$$

and

$$\mathbf{S}^*(0) = \mathbf{S}(0) \quad \mathbf{S}^*(\tau) = e^{i\mathbf{H}_0\tau} \mathbf{S}(\tau) e^{-i\mathbf{H}_0\tau}$$

with the italics denoting commutation super-operators

This is where [relaxation] **correlation functions** $\mathbf{C}(\tau)$, **spectral densities** $\mathbf{J}(\omega)$ and **relaxation rates** $\mathbf{R}_{\parallel}(\omega)$ and $\mathbf{R}_{\perp}(\omega)$ for $\langle \boldsymbol{\sigma} \cdot \mathbf{m}_{\parallel} \rangle$ and $\langle \boldsymbol{\sigma} \cdot \mathbf{m}_{\perp} \rangle$ come from. ($\omega = H_0/\hbar$)

Spin Hamiltonian: has moderate complexity, is well studied and known

$$\mathbf{H} = \mathbf{H}_Z + \mathbf{H}_{SR} + \mathbf{H}_C + \mathbf{H}_{DD} + \mathbf{H}_{DE} + \mathbf{H}_F + \mathbf{H}_J + \mathbf{H}_Q +$$

Energy =

Interaction with external field(s)	Z (Zeeman)
+ spin-rotation interactions	SR
+ chemical shifts	C
+ dipolar interactions with other nuclei	DD
+ dipolar interactions with electrons	DE
+ contact interactions with electrons	F (Fermi)
+ indirect couplings	J
+ quadrupolar interactions	Q
+ etc.	

Molecular dynamics models: have considerable complexity; are mostly guesses

- Ever-growing, amazing number of [equally amazing] models
- Sub-molecular, molecular, oligo-molecular, and collective motions
- Huge range of correlation times (1 Hz to tens of GHz)
- Observable by many methods which should be always compared

Molecular motions are harder to manage than spin interactions:

They are the “weak spot” of MR Relaxometry *Theory* but ...
... they are the *principal goal* of MR Relaxometry *Practice*

Summing it up (kind of)

Interactions:

- DD Dipole-dipole interaction between nuclei
- DE Nucleus-electron dipole-dipole interaction
- CE Nucleus-electron contact interaction (the Fermi term)
- NQ Nuclear quadrupole interaction with local electric field gradients
- SR Spin rotation interaction
- CSA Chemical shift anisotropy (part of CS)
- CS Chemical shift (isotropic part) when not constant (exchange)
- JA J coupling anisotropy (part of J)
- J Scalar part of J coupling when not constant (exchange)
- etc. including interactions with SPIO's and other "exotica"

Motions:

- Rot Rotational diffusion (global, unconstrained)
- IRot Internal rotations (partial, tunnelling, kinks, you name it ...)
- Rept Reptations
- Libr Librations
- Vibr Vibrations with angular components (bending motions)
- Trans Translations (free or constrained)
- Crawl on surfaces, like Kimmich's caterpillars
- Hits Collisions (like against pore walls)
- Jump across barriers, between hydration shells, and the like
- Coll Collective motions (like in liquid crystals)
- etc. like Halle's flickering aqueducts in proteins, ...

Combinatorics weighs in: *the Grid of Formulas*

Principal interactions versus principal types of motions

	Rot	IRot	Rept	Libr	Vibr	Trans	...
DD	BPP	F _{1b}	F _{1c}	F _{1d}	F _{1e}	F _{1f}	...
DE	F _{2a}	F _{2b}	F _{2c}	F _{2d}	F _{2e}	F _{2f}	...
CE	F _{3a}	F _{3b}	F _{3c}	F _{3d}	F _{3e}	F _{3f}	...
NQ	F _{4a}	F _{4b}	F _{4c}	F _{4d}	F _{4e}	F _{4f}	...
SR	F _{5a}	F _{5b}	F _{5c}	F _{5d}	F _{5e}	F _{5f}	...
CSA	F _{6a}	F _{6b}	F _{6c}	F _{6d}	F _{6e}	F _{6f}	...
...

Leading terms formulas: 100+

Combinatorics weighs in: the *SuperGrid of Formulas*

Relaxation is a second-order phenomenon!

Cross terms may be sometimes small ($\approx 1-15\%$) and sometimes forbidden, but they are many and enough of them are not really negligible:

formulas $F_{m\alpha, n\beta}$

If we have N leading-term relaxation formulas,
the total number of potentially useful ones is

$$\approx 0.5 * 0.5 * N(N+1)$$

All formulas of potential interest: ≈ 1000

BPP formula ... just one case among hundreds

Combines dipole-dipole interaction with molecular reorientations

$$R_1 \equiv \frac{1}{T_1} = \frac{\hbar^2 \gamma^4}{d^6} I(I+1) P_1(\tau, \omega),$$

$$R_2 \equiv \frac{1}{T_2} = \frac{\hbar^2 \gamma^4}{d^6} I(I+1) P_2(\tau, \omega)$$

$$P_1(\tau, \omega) = \frac{2}{5} J(\tau, \omega) + \frac{8}{5} J(\tau, 2\omega),$$

$$P_2(\tau, \omega) = \frac{12}{11} J(\tau, 0) + \frac{2}{11} J(\tau, \omega) + \frac{8}{11} J(\tau, 2\omega)$$

$$J(\tau, \omega) = \frac{\tau}{1 + (\omega\tau)^2}$$

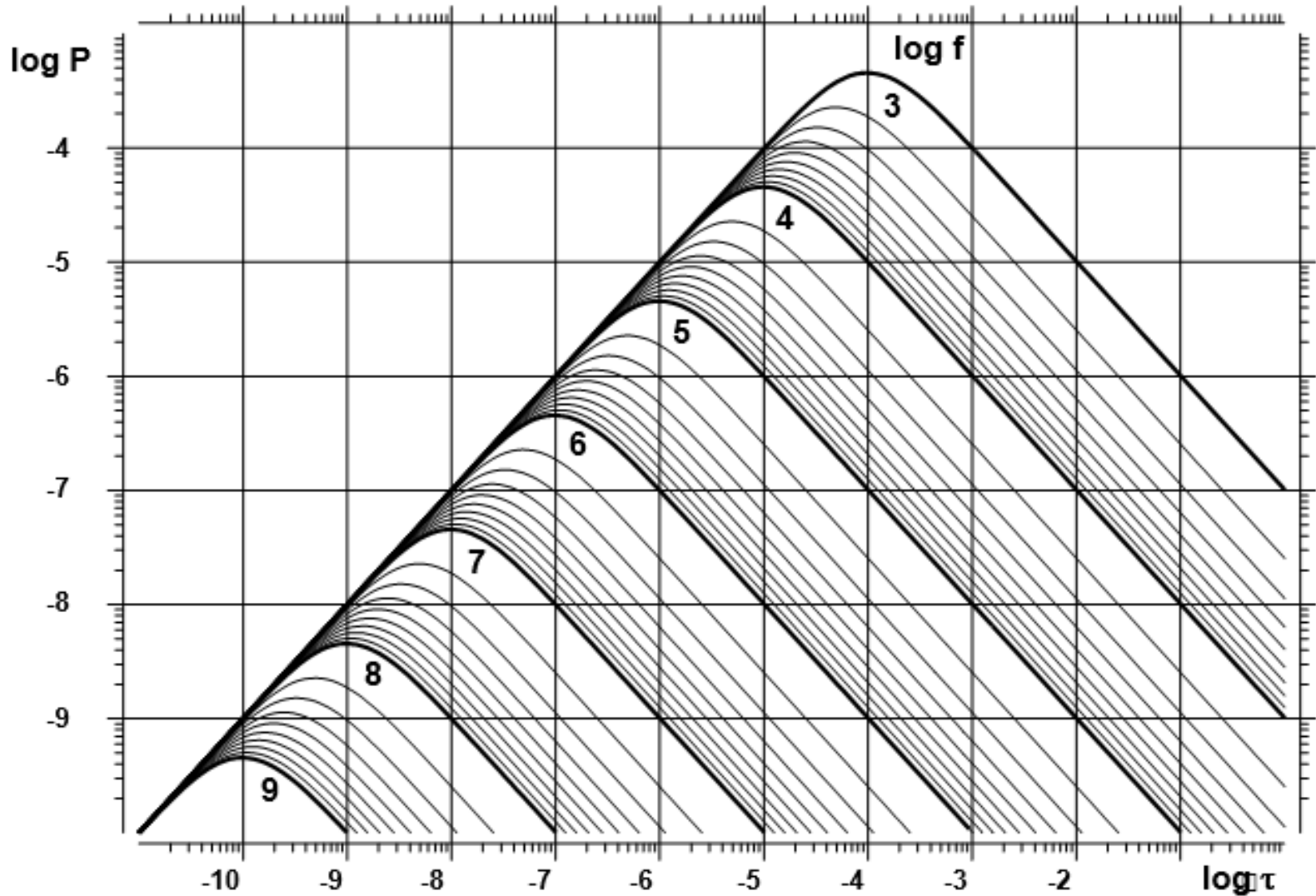
This is only one of the leading terms!

! But this one does have a pivotal position !

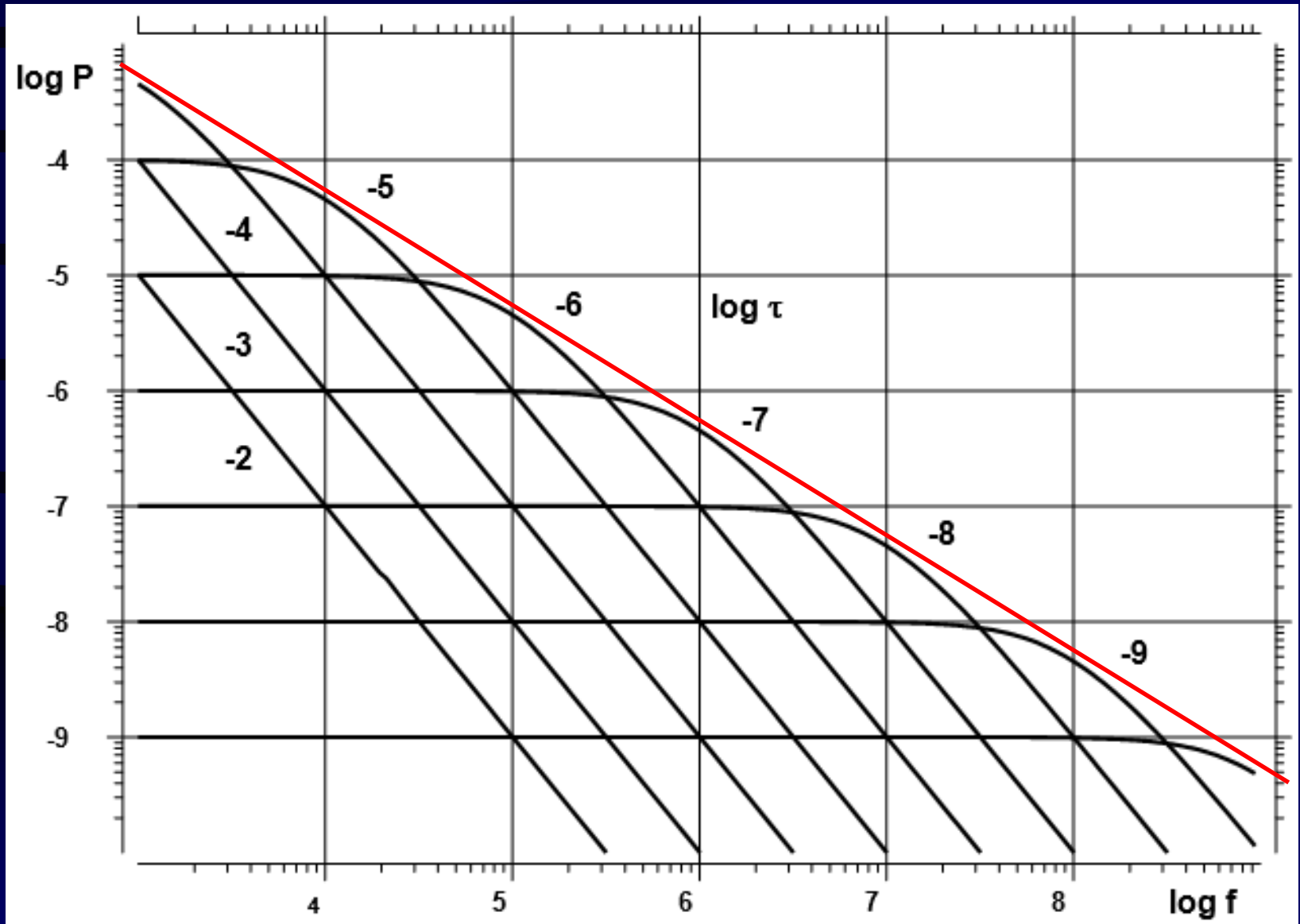
(Mother of all Relaxation Formulas)

BPP: one graphical rendering

$P(\tau, f) = J_\tau(\omega) + 4 J_\tau(2\omega)$, where $J_\tau(\omega) = 2\tau/[1+(\omega\tau)^2]$ and $\omega = 2\pi f$
for a pair of spin $\frac{1}{2}$ nuclides of the same kind under isotropic rotational diffusion (dipolar interaction)



BPP: another graphical rendering



Example of a model: log-normal distribution of τ values

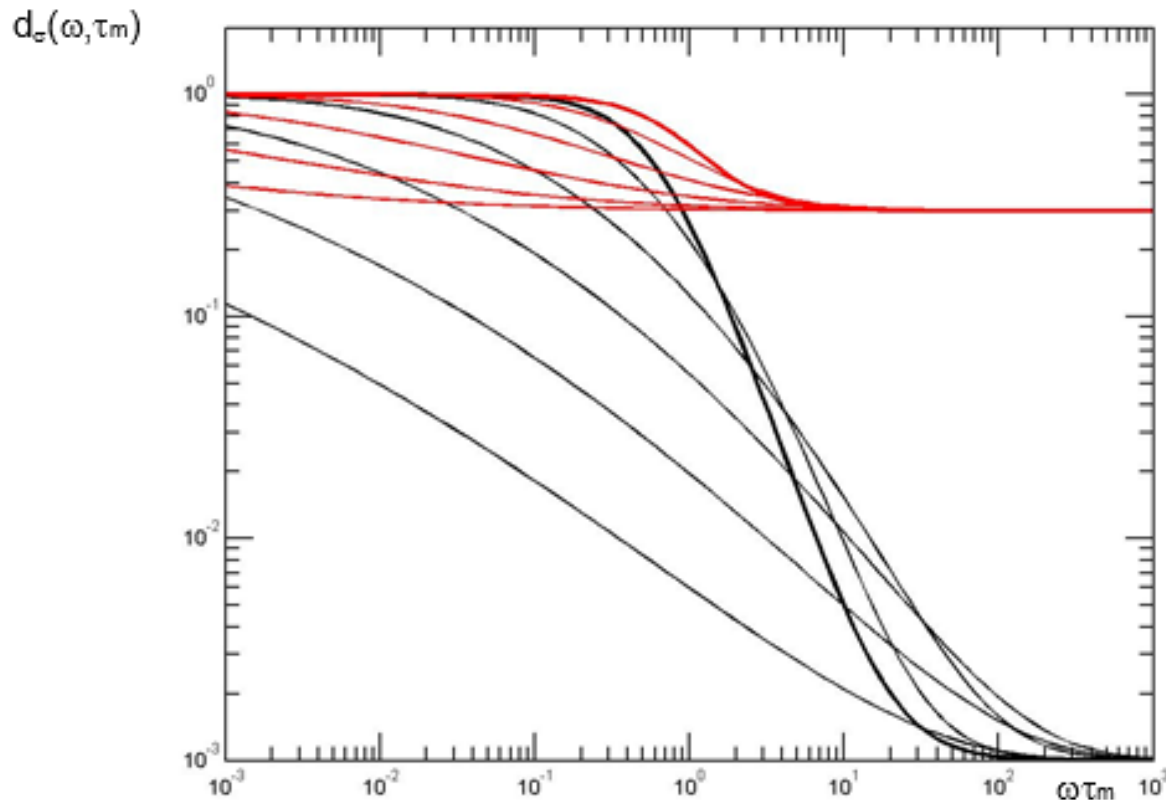
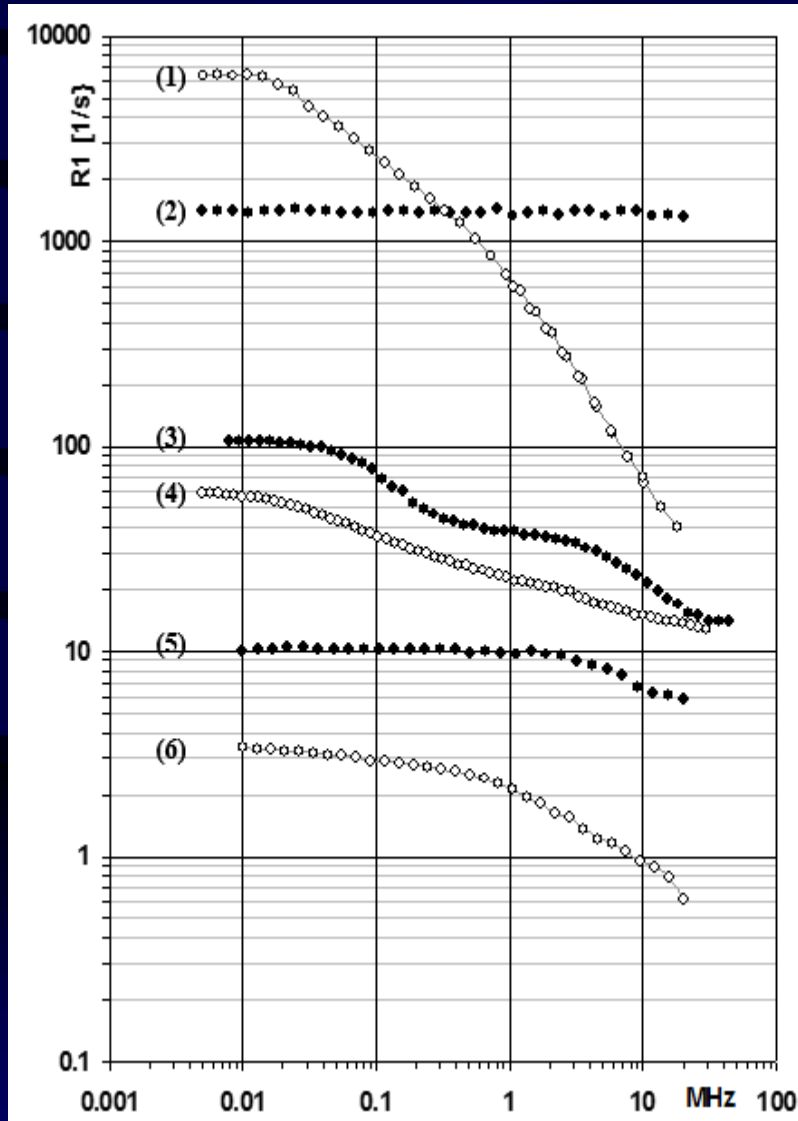


Fig.1. Log-normal stretched dispersion functions $d_{1\sigma}(\omega, \tau)$ and $d_{2\sigma}(\omega, \tau)$ plotted against $\omega \tau_m$ for various values of σ . The bold lines correspond to $\sigma = 0$ (classical BPP shape). The other lines correspond to $\sigma = 1, 2, 3, 4,$ and 5 . A small offset (0.001) has been added in order to simulate the effect of background high-frequency motions.

A wide range of profiles ...



- .. (1) Parafilm M
- .. (2) 2.1M $\text{Dy}(\text{ClO}_4)_3$ in H_2O
- .. (3) 2mM MnCl_2 in H_2O
- .. (4) Egg yolk
- .. (5) 10 mM Gd^{3+} in D_2O
- .. (6) Egg albumen

Ferrante G., Sykora S., [Stelar srl](#),
Technical Aspects of Fast Field Cycling in Advances in
Inorganic Chemistry, Editors van Eldik R., Bertini I.,
Elsevier 2005 (ISBN 0-120-23657-5), Vol.57.
([link to draft](#))

The Seven Conjectures

- 1) $R_1 = R_2$ at $\omega = 0$ in all isotropic systems
- 2) $R_1 \leq R_2$ at any ω
- 3) $dR_1/d\omega = dR_2/d\omega = 0$ at $\omega = 0$
- 4) $R_1 = R_2$ at an $\omega_0 > 0$, then $R_1 = R_2 = \text{constant}$ for any $0 \leq \omega \leq \omega_0$

In the absence of hetero-relaxation (quad glitches, paramagnetics, SPIO), at any ω :

- 5) $dR_1/d\omega \leq 0$ and $dR_2/d\omega \leq 0$
- 6) $-d \ln R_1 / d \ln \omega \leq 2$, $-d \ln R_2 / d \ln \omega \leq 1$
- 7) $R_2(0) / R_2(\omega) \leq 11/6 \Rightarrow \ln R_2(0) - \ln R_2(\omega) \leq \ln(11/6) \cong 0.26$

Conjecture [1]

$$\mathbf{R}_1(\mathbf{0}) = \mathbf{R}_2(\mathbf{0}) \text{ (R}_1 \text{ and R}_2 \text{ meet at origin)}$$

This is not really a conjecture, because of the imperatives of symmetry
($\omega = 0 \Rightarrow$ no field \Rightarrow no externally imposed axial anisotropy)

Where we expect this to break down:

Wherever $\omega = 0$ does not imply $B_0 = 0$:

- Presence of local magnetic fields (ferromagnetic resonance)
- NQR (in solids, a local axis is defined by the electric field gradient)
- Zero-field splittings (EPR in solids)

In all such cases, the very definition of \mathbf{R}_2 becomes problematic

Conjecture [1], a consideration using BPP formulas

$$\mathbf{R}_1(\mathbf{0}) = \mathbf{R}_2(\mathbf{0})$$

??? Is it trivial when it comes to formulas ???

$$R_1 \equiv \frac{1}{T_1} = \frac{\hbar^2 \gamma^4}{d^6} I(I+1) P_1(\tau, \omega),$$

$$R_2 \equiv \frac{1}{T_2} = \frac{\hbar^2 \gamma^4}{d^6} I(I+1) P_2(\tau, \omega)$$

$$P_1(\tau, \omega) = \frac{2}{5} J(\tau, \omega) + \frac{8}{5} J(\tau, 2\omega),$$

$$P_2(\tau, \omega) = \frac{12}{11} J(\tau, 0) + \frac{2}{11} J(\tau, \omega) + \frac{8}{11} J(\tau, 2\omega)$$

$$J(\tau, \omega) = \frac{\tau}{1 + (\omega\tau)^2},$$

Not quite:

$$2/5 + 8/5 = 12/11 + 2/11 + 8/11$$

In this case, it comes out from Clebsch-Gordon coefficients of the rotation group, but it turns out also for translations, and any other types of motions.

Conjecture [2]

$$\mathbf{R}_1(\omega) \leq \mathbf{R}_2(\omega) \text{ at any } \omega$$

This comes out of every theoretical model,
and it is so well confirmed by experiments,
that one suspects the existence of
a very conceptual reason, something like:

“if it were not true, we could use spins to build a perpetuum mobile” or
maybe “if it were not true, we could overcome Boltzmann distribution”

But so far neither I, nor anybody else, could figure it out !
That is why I feel compelled to classify it as a **conjecture**

Conjecture [2], a theoretical model example

$$\mathbf{R}_1(\omega) \leq \mathbf{R}_2(\omega)$$

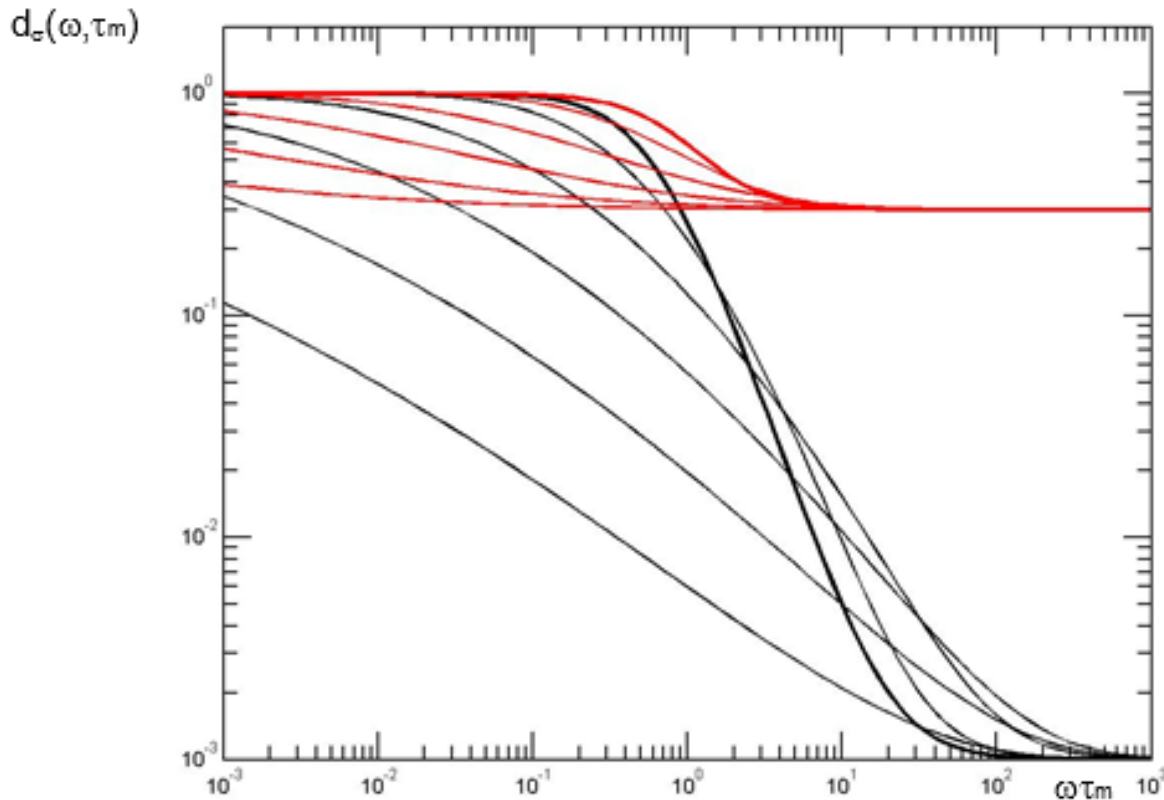


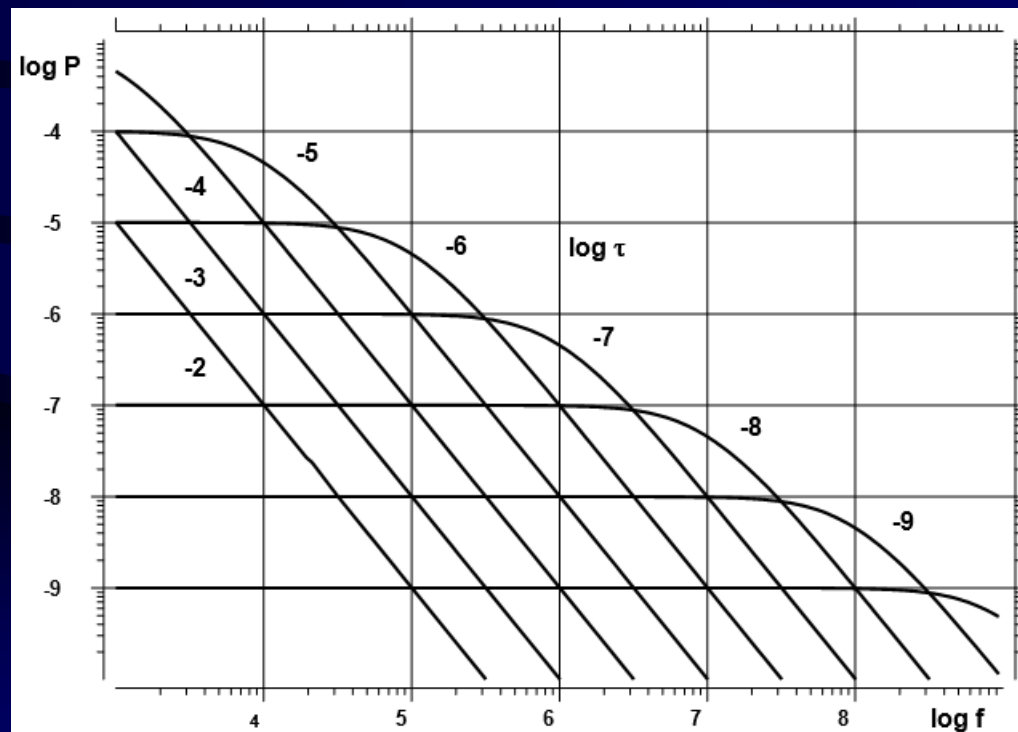
Fig.1. Log-normal stretched dispersion functions $d_{1\sigma}(\omega, \tau)$ and $d_{2\sigma}(\omega, \tau)$ plotted against $\omega\tau_m$ for various values of σ . The bold lines correspond to $\sigma = 0$ (classical BPP shape). The other lines correspond to $\sigma = 1, 2, 3, 4,$ and 5 . A small offset (0.001) has been added in order to simulate the effect of background high-frequency motions.

Conjecture [3]

At $\omega = 0$, $dR_1/d\omega = dR_2/d\omega = 0$ (curves are flat at origin)

This requires the correlation functions $C(\tau)$ to decay fast enough with respect to $\cos(\omega\tau)$ for small ω . But for $\omega \rightarrow 0$, $\cos(\omega\tau) \rightarrow 1 - \omega^2\tau^2$ which means that this condition is mathematically quite weak.

Practically, it is sufficient that $C(\tau)$ be integrable over the interval $(0, \infty)$



Conjecture [4]

**If $R_1(\omega_0) = R_2(\omega_0)$ at some $\omega_0 > 0$, then
 $R_1(\omega) = R_2(\omega) = \text{constant}$ for every $\omega \leq \omega_0$**

In other words:

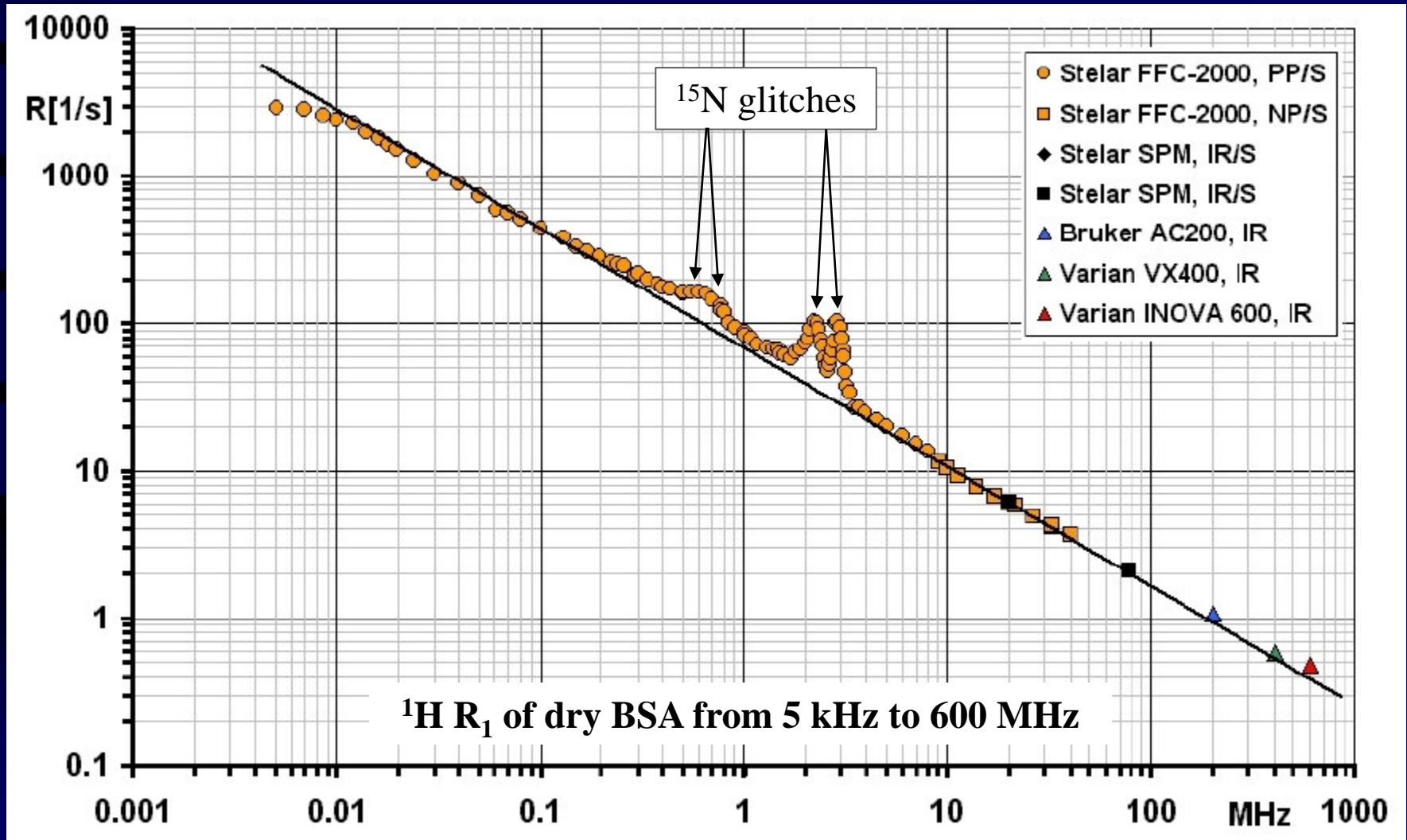
The equality of R_1 and R_2 at some frequency ω_0 is possible if, and only if, the curves $R_1(\omega)$ and $R_2(\omega)$ are identical and completely flat (**dispersionless**) in the whole interval $(0, \omega_0)$.

This is a very strong statement which holds in all theoretical models. Experimental verification is good, but limited to low-viscosity diamagnetic liquids – the only systems where R_1 and R_2 can be equal even at quite high Larmor frequencies.

Conjecture [5]

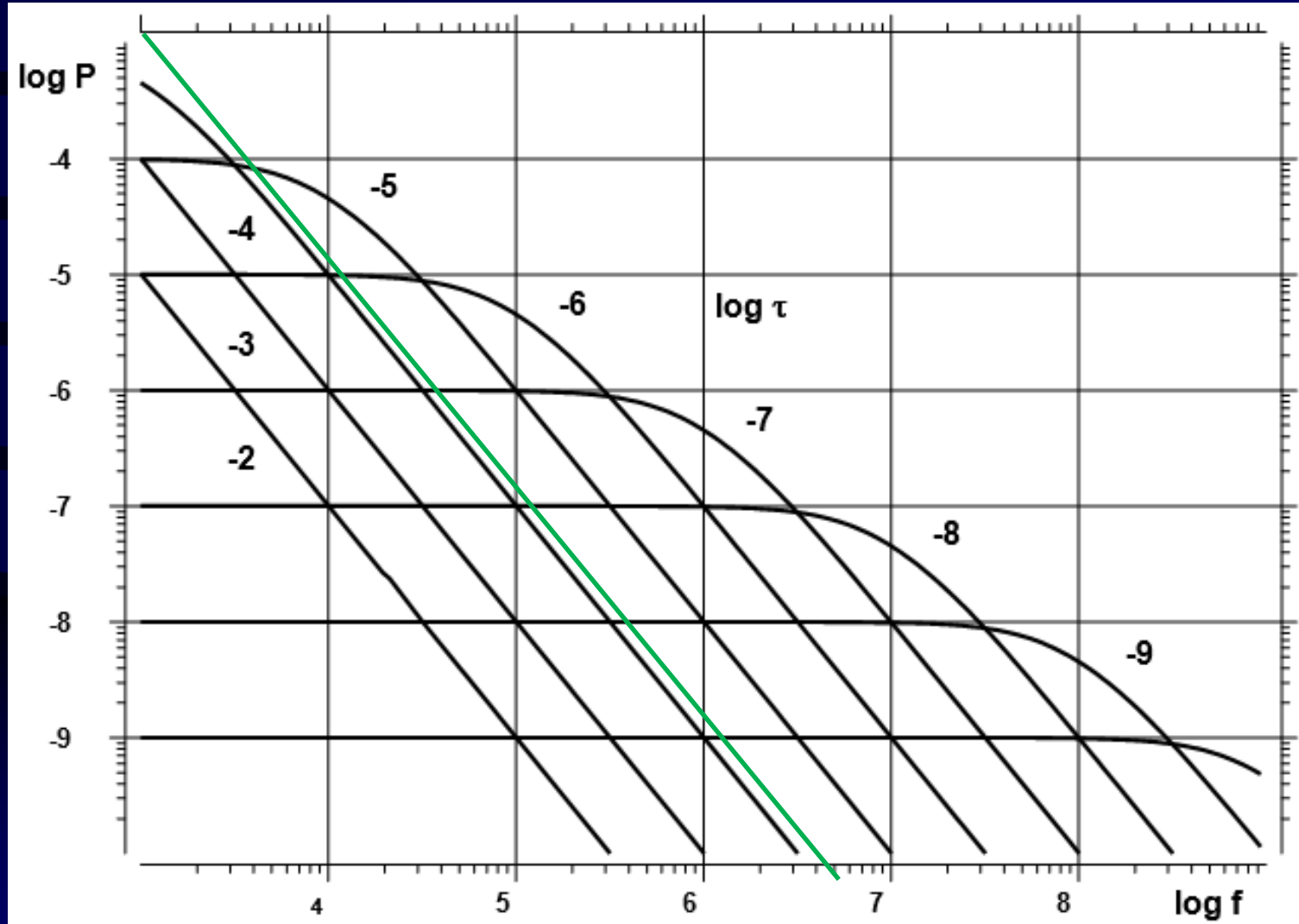
$$dR_1/d\omega \leq 0, dR_2/d\omega \leq 0 \text{ (curves are non-increasing)}$$

Valid only in absence of heteronuclear cross-relaxation (no quad glitches, paramagnetics, SPIO)



Conjecture [6]

$-\frac{d \ln R_1}{d \ln \omega} \leq 2$ (curves are never steeper than that)



Conjecture [6], a theoretical model example

$-\frac{d \ln R_1}{d \ln \omega} \leq 2$

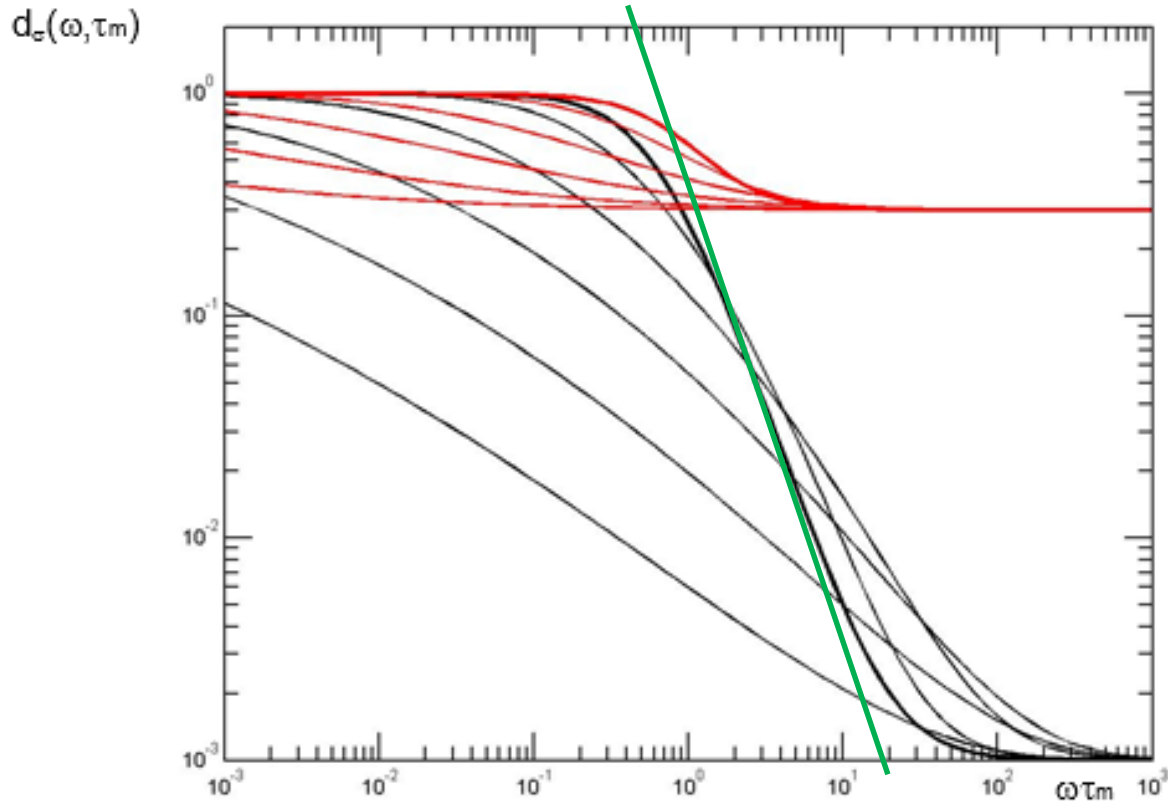
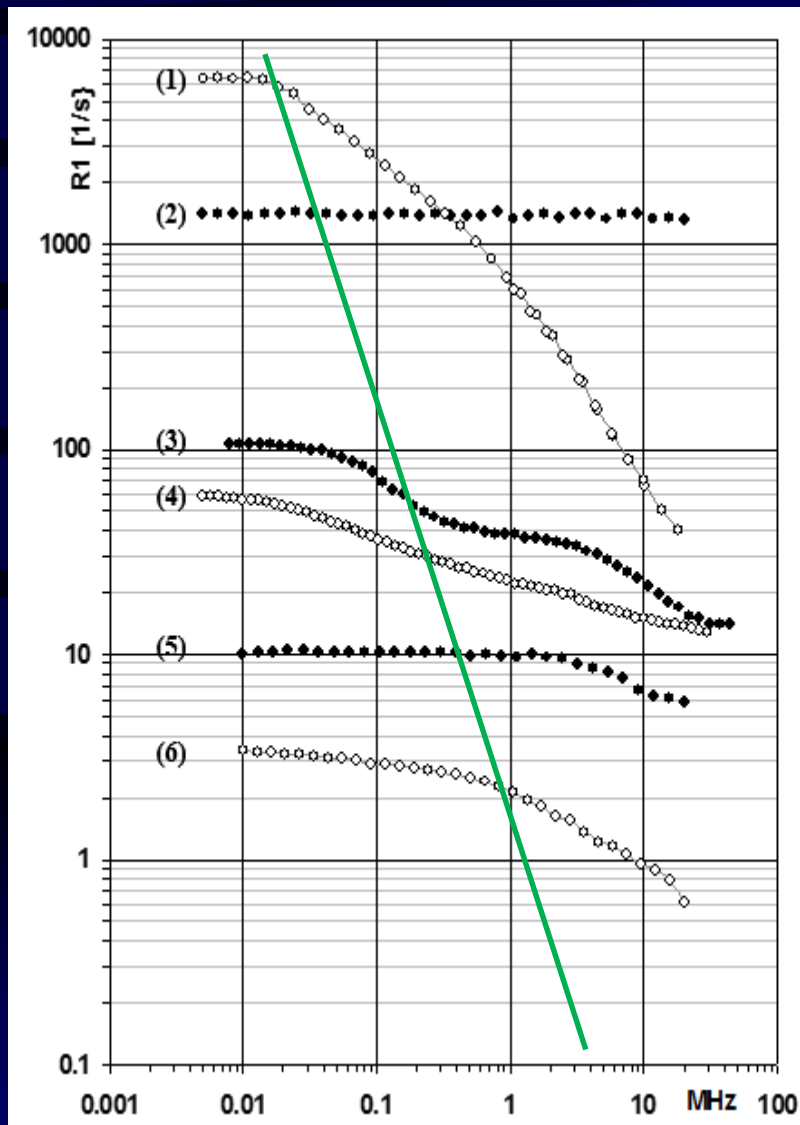


Fig.1. Log-normal stretched dispersion functions $d_{1\sigma}(\omega, \tau)$ and $d_{2\sigma}(\omega, \tau)$ plotted against $\omega\tau_m$ for various values of σ . The bold lines correspond to $\sigma = 0$ (classical BPP shape). The other lines correspond to $\sigma = 1, 2, 3, 4,$ and 5 . A small offset (0.001) has been added in order to simulate the effect of background high-frequency motions.

Conjecture [6], practical examples

$-\frac{d \ln R_1}{d \ln \omega} \leq 2$

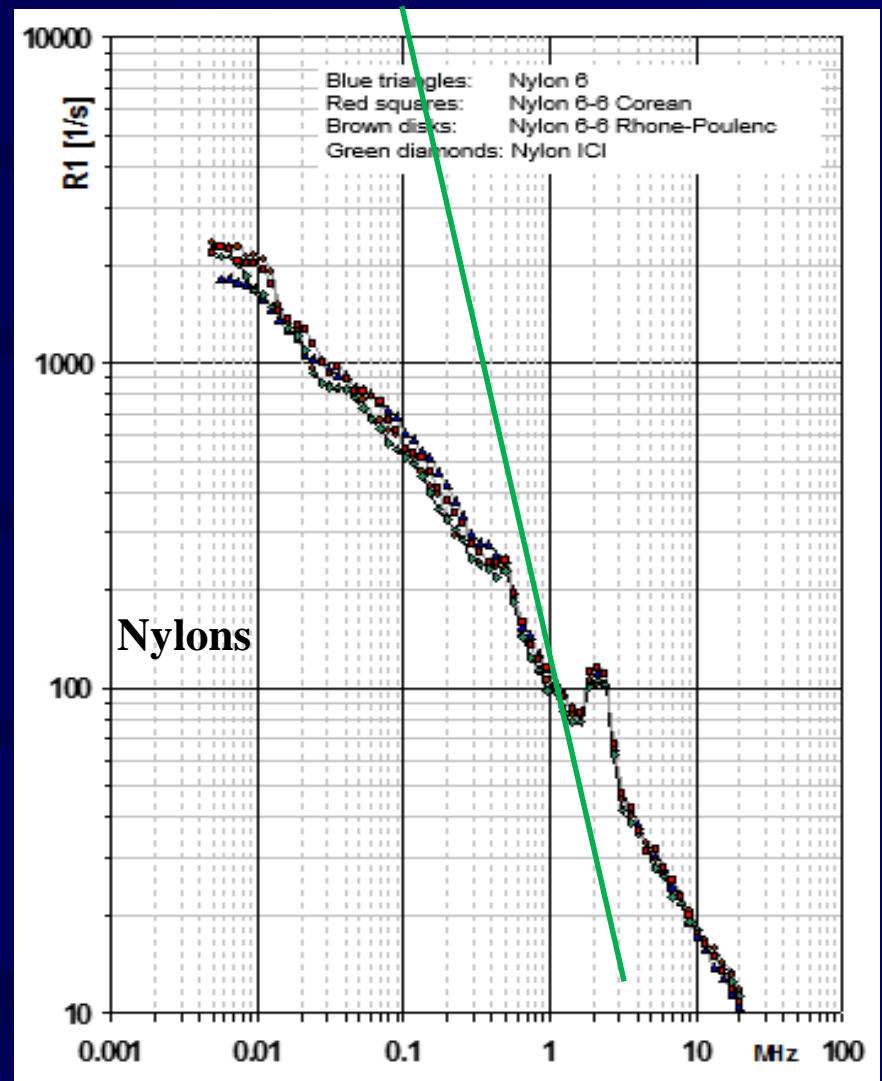
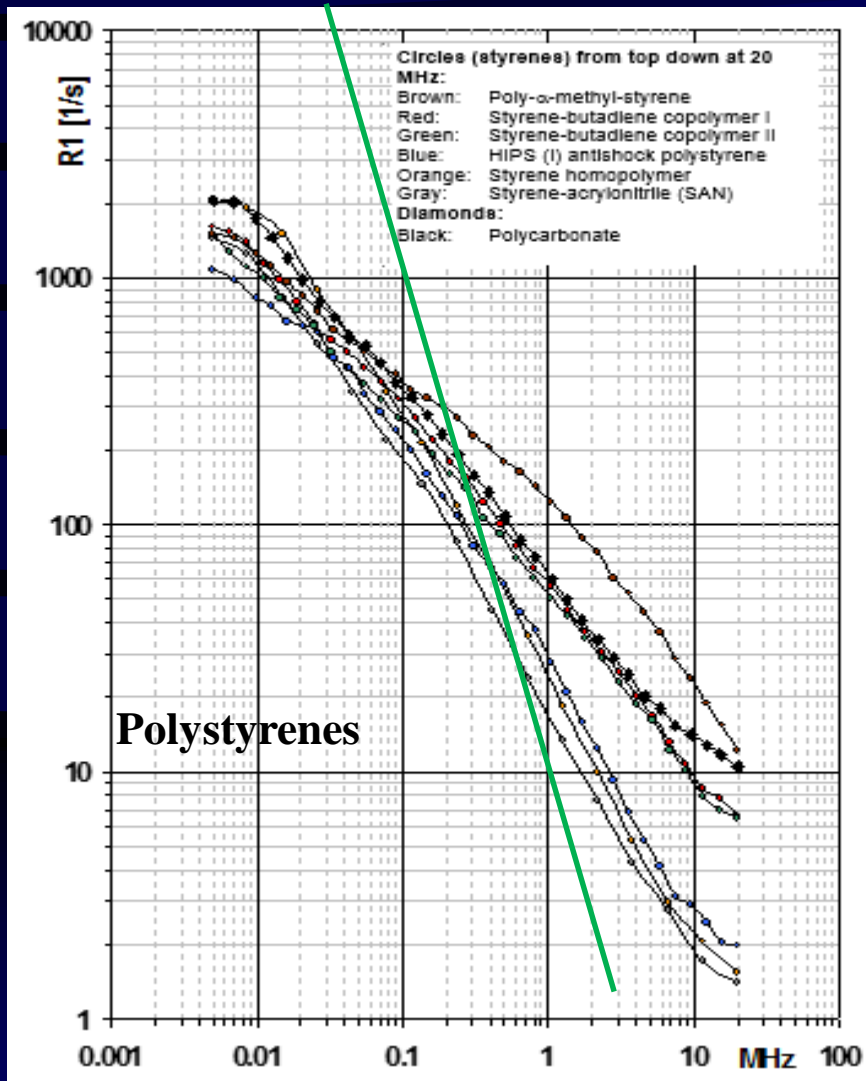


- .. (1) Parafilm M
- .. (2) 2.1M $\text{Dy}(\text{ClO}_4)_3$ in H_2O
- .. (3) 2mM MnCl_2 in H_2O
- .. (4) Egg yolk
- .. (5) 10 mM Gd^{3+} in D_2O
- .. (6) Egg albumen

Ferrante G., Sykora S., [Stelar srl](#),
Technical Aspects of Fast Field Cycling in Advances in
Inorganic Chemistry, Editors van Eldik R., Bertini I.,
Elsevier 2005 (ISBN 0-120-23657-5), Vol.57.
([link to draft](#))

Conjecture [6], more practical examples

$-d \ln R_1 / d \ln \omega \leq 2$



Reference DOI: [10.3247/SL1Nmr03.001](https://doi.org/10.3247/SL1Nmr03.001)

Conjecture [7]

$$\ln R_2(0) - \ln R_2(\omega) \leq \ln(11/6) \cong 0.26$$

In other words: R_2 can't drop too much!

One might even say that R_2 is not very 'interesting'

A cool, pragmatic usage:

- Measure R_1, R_2 at some fixed frequency ω_0 ,
- Guess the likely value of $R_1 = R_2$ at $\omega = 0$...
- ... and you get a fair idea of the R_1 dispersion profile between 0 and ω_0 .

Thank you all
and
see you again at
FFC NMR Relaxometry Meeting
in 2015

This document was uploaded with
DOI [10.3247/SL4Nmr13.004](https://doi.org/10.3247/SL4Nmr13.004)