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Nuclear spin thermodynamics in fast rotating samples.

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Nuclear spin thermodynamics in fast rotating samples.: Preprint ITEP 44-00/

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The thermodynamics of dipolar-coupled nuclear-spin system in a sample, fastly rotating at magic angle, is investigated. The rotation produces coherent averaging to zero of dipolar interactions. However, the spin dynamics in these conditions is governed by three spin interactions, and it is shown, by theory and experiment, that corresponding dipolar reservoir and dipolar spin order exist.

Ядерная спиновая термодинамика в быстро вращающихся образцах.
Т.Шарпентье, Ф.Джепаров, Ж.-Ф.Жакино, Дж.Вирле

Изучена термодинамика дипольно взаимодействующей ядерной спиновой системы в образце, быстро вращающемся под магическим углом. Вращение когерентно усредняет до нуля дипольное взаимодействие. Теоретически и экспериментально довазано, что в этих условиях спиноая динамика определяется трехспиновыми взаимодействиями и существуют соответствующий дипольный резервуар и дипольная температура.

Fig – 5, Ref. – 23 names

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In the general problem of understanding statistical properties of many-body systems, the model system of dipolar-coupled nuclear spins has been extensively studied. The spin temperature theory [1, 2] has provided a coherent understanding of nuclear spin systems in solids. Its most successful application is certainly the theoretical description of the phenomena of dipolar nuclear-spin order (including magnetic phase transitions) [3, 1] and cross-polarization [4, 5].

The spin temperature conception had originally been developed for static spins. Several kinds of modulation of the (secular) dipolar interaction H_d have been considered then: the modulation with frequency ω_R can originate from motion of nuclei in real space (atomic motion, sample rotation), or can be due to spin rotations imposed by applied RF fields. An important parameter is the relative magnitude of ω_R and ω_l - the width of the NMR line.

When $\omega_R \ll \omega_l$, the effect of motion has been treated in the quasi-adiabatic limit and shown to produce saturation of dipolar order with a speed $\propto \omega_R^2$ [6, 7, 8].

When $\omega_R \gg \omega_l$, the thermodynamics of the spins is governed by the time averaged dipolar Hamiltonian $\bar{H}_D$, if $\bar{H}_D \neq 0$. The case when $\bar{H}_D = 0$ is more complex. If multipulse irradiation is used to suppress dipolar broadening [13, 14, 15, 1], then the role of $\bar{H}_D$ is played by the lowest order non zero term in appropriate time dependent perturbation development [9, 10, 11, 12].

The important case of spin temperature in conditions of Magic Angle Spinning (MAS) has not been considered up to now. MAS is the most widespread solid state NMR method. It averages to zero H_D together with all space anisotropic interactions of second rank and allows observation of high-resolution spectra. Therefore the problem of understanding thermodynamic properties of spin systems under MAS conditions is of great importance both from fundamental and applied point of view.

The aim of this Letter is to prove, that when $\omega_R \gg \omega_l$, nuclear spins may be ordered by means of dipolar interactions in an equilibrium state (up to saturation rate, denoted W) that will be called *quasi-dipolar order* in the following. Our theoretical approach is briefly described below and we construct the master equation that enables the calculation of saturation rate W. The present approach does not assume any stroboscopic observation, as usually in so called average Hamiltonian theory (AHT) [14, 15]. It is based on non-linear averaging methods [16, 17, 18, 19], which are quite general and not limited to periodic problems [18, 19]. Phenomena like thermal mixing between Zeeman and quasi-dipolar order are considered also. All theoretical predictions are compared with experiments.

Measurements were carried out at room temperature on ^{1}H nuclei in an adamantane powder sample with Larmor frequency $\omega_L = 2\pi \cdot 300MHz$ using a commercial (Bruker) 4mm MAS probe. A typical MAS spectrum is shown in Fig.1.

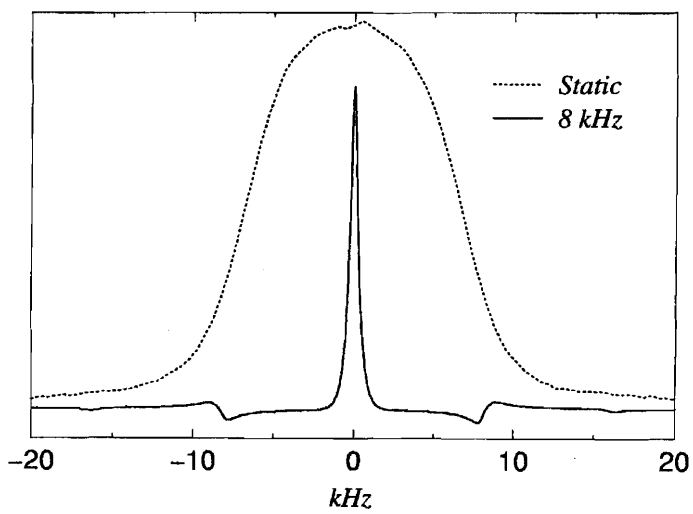

Figure 1: Solid line : ^{1}H MAS spectrum in powder adamantane observed at $\omega_R = 2\pi \cdot 8$ kHz. Dotted line : Static spectrum.

For a static sample placed in a strong static external field $\mathbf{H_0} = (0, 0, H_z)$, well established methods exist for creating dipolar order [1, 2]

corresponding to a quasiequilibrium density matrix of the form

$$\rho_{qe} = 1 - \beta_{\rm D} H_{\rm D}, \quad H_{\rm D} = \frac{1}{2}\sum_{i\neq j} b_{ij} T^{20}_{ij}, \tag{1}$$

in the high temperature approximation [1, 2]. Here $T^{20}_{ij} = \frac{1}{\sqrt{6}}(3I^z_i I^z_j - \mathbf{I}_i\mathbf{I}_j)$, $\beta_{\rm D}$ is the (inverse) dipolar temperature, $\mathbf{I}_j$ is spin operator for $j-$th nucleus and b_{ij} is usual dipolar coefficient [1].

For rotating samples, $H_{\rm D}$ becomes time-dependent through the spatial functions

$$b_{ij}(t) = \sum_{m=-2}^{2} b^m_{ij} \exp(im\omega_R t).$$

Under MAS conditions $b^0_{ij} = 0$ and the dipolar Hamiltonian $H_{\rm D}(t)$ may be expanded as

$$H_{\rm D}(t) = \sum_{m\neq 0} H_m e^{im\omega_R t}, \quad H_m = \frac{1}{2}\sum_{i\neq j} b^m_{ij} T^{20}_{ij}, \tag{2}$$

with $H_m = H^+_{-m}$. The density matrix evolves according to the Liouville von-Neuman equation [1] which is, in the conventional rotating frame,

$$i\frac{d}{dt}\rho(t) = [\, H_{\rm D}(t)\,,\, \rho(t)\,] \tag{3}$$

In order to obtain a representation, in which the spin temperature hypothesis holds, we perform a canonical transformation

$$\tilde{\rho}(t) = P^+(t)\rho(t)P(t), \quad P(t) = \exp(-iS(t)), \tag{4}$$

$$S(t) = \sum_{m\neq 0} \frac{H_m}{im\omega_R} e^{im\omega_R t}, \tag{5}$$

which leads to the new equation of motion

$$i\frac{d}{dt}\tilde{\rho}(t) = [\, \widetilde{H}_{\rm D}(t)\,,\, \tilde{\rho}(t)\,], \tag{6}$$

$$\widetilde{H}_{\rm D}(t) = H_{\rm S} + H_{\rm F}(t), \quad H_{\rm S} \sim H_{\rm F}(t) \sim \epsilon = \omega_l/\omega_R. \tag{7}$$

Here $H_{\rm S}$ and $H_{\rm F}(t)$ represent static and fast oscillating parts of the new effective Hamiltonian $\widetilde{H}_{\rm D}(t)$, and up to $o(\epsilon^2)$ they are of the form:

$$H_{\rm S} = \sum_{m\neq 0} \frac{1}{2m\omega_R} [\, H_m\,,\, H_{-m}\,], \tag{8}$$

$$H_{\rm F}(t) = \sum_{0\neq n\neq m\neq 0} \frac{1}{2m\omega_R} [\, H_m\,,\, H_{-n}\,]\, e^{i(m-n)\omega_R t}. \tag{9}$$

Similarly to the static case [3], we have two additive quasi-integrals of motion $I_z = \sum I_j^z$ and H_S (with $[I_z, H_S] = 0$). The perturbation $H_F(t)$ does not commute with Hs, and it produces, according to Eqs.22, 23, a saturation rate $W \ll \omega_{lf}$, where the local frequency $\omega_{lf} = (\langle {H_S}^2 \rangle_0 / \langle I_z^2 \rangle_0)^{1/2}$, and

$$\langle \cdots \rangle_0 = Tr(\cdots)/Tr(1).$$

Therefore for $t \gg T_2 = \omega_{lf}^{-1}$ and $t < 1/W$ the nuclei have time to reach a quasi-equilibrium of the form

$$\tilde{\rho}_{qe} = 1 - \gamma I_z - \beta_S H_S. \tag{10}$$

The existence of these two time-scales is the fundamental requirement for applying spin thermodynamics [1, 2]. It is fulfilled if $\omega_R \gg \omega_{lf}$.

One could argue that the transformation of Eq.4, which suppresses fast oscillating term of the Hamiltonian could be iterated to give, at the next step, a small correction ${H_S}^{(1)} \sim \epsilon H_S$ to H_S and a new smaller fast oscillating term ${H_F}^{(1)} \sim {H_S}^{(1)}$. As far as $\epsilon = \omega_{lf}/\omega_R \ll 1$, the correction ${H_S}^{(1)}$ is negligible. But the saturation rate $W^{(1)}$, produced by ${H_F}^{(1)}$, coincides with W up to $O(\epsilon)$ [19]. The argumentation is similar to the one of static case detailed in Chapter 6 of Ref.[2]. The fact that W does not decrease, when number of iterations increases, belongs to most important conceptual properties of the theory, and it should be included into physically acceptable definition of the norm, giving adequate estimation of the smallness of $H_F(t)$ [19].

The next problems are creation and observation of quasi-dipolar order. The properties of the new static effective Hamiltonian H_S, which is a three-spin operator, are rather different from those of the standard H_D. Nevertheless, an analysis of behavior of H_S with respect to 3d rotations in spin space reveals that it is a sum of zero and second rank tensor, as well as $[S(t), H_S]$:

$$H_S = T_{0,0} + T_{2,0}. \tag{11}$$

According to Floquet-Lyapunov theorem [20]

$$U(t,\tau) = Te^{-i\int_\tau^t dt_1 H_D(t_1)} = Q(t,\tau)e^{-iH_{FL}(\tau)(t-\tau)}, \tag{12}$$

with $Q(t + T_R, \tau) = Q(t, \tau)$.

Using the identity $U(t,\tau) = U(t,t_1)U(t_1,\tau)$ the Eq.12 can be written as

$$U(t,\tau) = Q(t,0)e^{-iH_{FL}(0)(t-\tau)}Q^+(\tau,0). \tag{13}$$

Representation (4),(8) corresponds to (12),(13) with $Q(t,0) = P(t)(1 + O(\epsilon^2))$ and $H_{FL} = H_s(1 + O(\epsilon))$.

Using Eqs.11,13 one can prove that the standard Jeener-Broekaert (JB) sequence [21] with $\pi/4$ reading pulse is efficient for creating and observing the quasi-dipolar order state. Starting from a typical thermal equilibrium state $\rho = 1 - \beta_0\omega_L I_z$ (here ω_L and β_0 are Larmor frequency and lattice temperature respectively), and after a $(\pi/2)_y$ pulse, rotating the spin system by an angle $\pi/2$ around the axis y at time 0, $(\pi/4)_x$ pulse at time τ, and thermalization delay of several T_2, quasi-dipolar spin temperature is

$$\beta_s = \frac{1}{2} \cdot \frac{\beta_0\omega_L}{\omega_{lf}^2} f(\tau) \tag{14}$$

$$f(\tau) = \sum_m e^{im\omega_R\tau} \left(\frac{d}{d\tau}\, g_m(\tau)\right) (1 + O(\epsilon)), \tag{15}$$

where $g_m(\tau)$ is the slow (according to H_s) decaying envelope of $m - th$ component of the free induction decay (FID)

$$g(\tau) = \frac{\langle\, I_x U(\tau,0) I_x U^+(\tau,0)\,\rangle_0}{\langle\, I_x^2\,\rangle_0} = \sum g_m(\tau) e^{im\omega_R\tau}. \tag{16}$$

Similarly it can be proved that reading pulse produces an in-phase signal $\propto \beta_s \cdot f(t)$ (quasi-dipolar FID).

Fig.2 shows measured shape of quasi-dipolar FID and the variation of $\beta_s(\tau)$ with respect to τ. Both have the same shape which can be related (according to Eq.14) to the FID signal $g(\tau)$.

The saturation of the quasi-dipolar order by $H_F(t)$ can be described by means of standard theoretical treatment used in relaxation calculation. Applying projector operator techniques in Liouville space [1] with the projectors

$$\hat{\pi} = \frac{|\,\mathrm{Id}\,\rangle\langle\,\mathrm{Id}\,|}{\langle\,\mathrm{Id}\,\rangle_0} + \frac{|\,I_z\,\rangle\langle\,I_z\,|}{\langle\,I_z^2\,\rangle_0} + \frac{|\,H_s\,\rangle\langle\,H_s\,|}{\langle\,H_s^2\,\rangle_0}, \tag{17}$$

$$\overline{\pi} = 1 - \hat{\pi}, \quad \langle\, A\,|B\rangle = \langle\, A^+ B\,\rangle_0, \tag{18}$$

an exact equation may be obtained:

$$\langle\, H_s^2\,\rangle_0 \frac{d}{dt}\beta_s = -\int_0^t \langle\, V^+(t)\hat{S}(t,\tau)V(\tau)\,\rangle_0 \beta_s(\tau) d\tau. \tag{19}$$

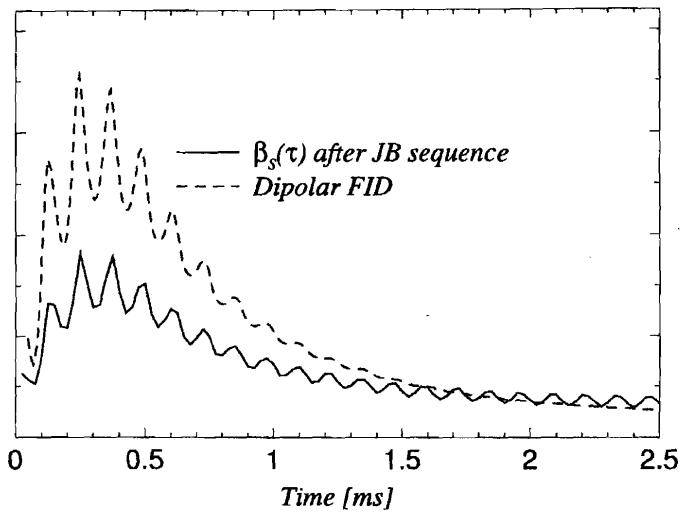

Figure 2: Creation and observation of quasi-dipolar order in powder adamantane at $\omega_R = 2\pi \cdot 8\text{kHz}$. Dashed line: in-phase FID signal observed after the JB sequence and reading pulse (thermalization delay = 10 ms). Solid line: amplitude of dipolar FID ($\propto \beta_s(\tau)$) as a function of τ, the delay between the two pulses in the JB sequence.

The propagator $\hat{S}(t,\tau)$ is

$$\hat{S}(t,\tau) = \widehat{T}\overline{\pi}\exp\left\{-i\int_\tau^t [\hat{\mathcal{L}}_{\rm S} + \overline{\pi}\hat{\mathcal{L}}_{\rm F}(u)]\overline{\pi}du\right\}\overline{\pi}, \tag{20}$$

and, for arbitrary operator ξ in Hilbert space,

$$\hat{\mathcal{L}}_{\rm S}\xi = [H_{\rm S},\xi], \quad \hat{\mathcal{L}}_{\rm F}(t)\xi = [H_{\rm F}(t),\xi], \tag{21}$$

$$V(t) = [\,H_{\rm F}(t)\,,\,H_{\rm S}\,] = \sum_m V_m e^{im\omega_R t}, \quad V_m = [\,H_{{\rm F},m}\,,\,H_{\rm S}\,].$$

For $\omega_R \gg \omega_{lf}$, $\hat{\mathcal{L}}_{\rm F}(t)$ can be neglected in Eq.20, and, for long time $t \gg T_R$ and $t \gg T_2 \sim 1/\omega_{lf}$, Eq.19 can be localized in time with the result:

$$\frac{d}{dt}\beta_{\rm S} = -W\beta_{\rm S}(t) \tag{22}$$

$$W = \sum_{m>0}\int_{-\infty}^{\infty} M_m(\tau)e^{im\omega_R\tau}d\tau \tag{23}$$

We have defined the memory functions $M_m(\tau)$, which decay in a time of order of T_2:

$$M_m(\tau) = \omega_R^2 G_m(\tau)/\langle\,(H_{\rm S})^2\,\rangle_0, \tag{24}$$

$$G_m(\tau) = \langle\,H_{{\rm F},m}\overline{\pi}e^{-iH_{\rm S}\tau}H^+_{{\rm F},m}e^{iH_{\rm S}\tau}\,\rangle_0. \tag{25}$$

Exact calculation of W would require exact knowledge of correlation functions $G_m(\tau)$, which is an impossible task. Nevertheless, it seems reasonable to think that the behavior of $G_m(\tau)$ is similar to that of the $g_m(\tau)$'s: $G_m(\tau)$ decays in times of order T_2 and is a smooth function of τ. Only the values $G(\omega_R) = \int dt\exp(i\omega_R t)G_m(t)$ are required; they correspond to asymptotics of $G_m(\omega)$ for large ω. According to modern point of view on high frequency asymptotics of spin correlation functions [22, 23], it can be expected that

$$W \propto \omega_R^2/\omega_{lf}\cdot\exp(-c\cdot\omega_R/\omega_{lf}) \tag{26}$$

with some $c \sim 1$. A comparision of predictions of Eq.26 with results of measurements of saturation rate W for several spinning speeds is shown on Fig.3.

In order to complete this study, and to check by other ways the existence of quasi-dipolar order, we have performed simple classical experiments of thermal mixing. We have studied the behavior of the system submitted to a RF irradiation close to the Larmor frequency ($\Delta = \omega_L - \omega \sim \omega_{lf}$) and

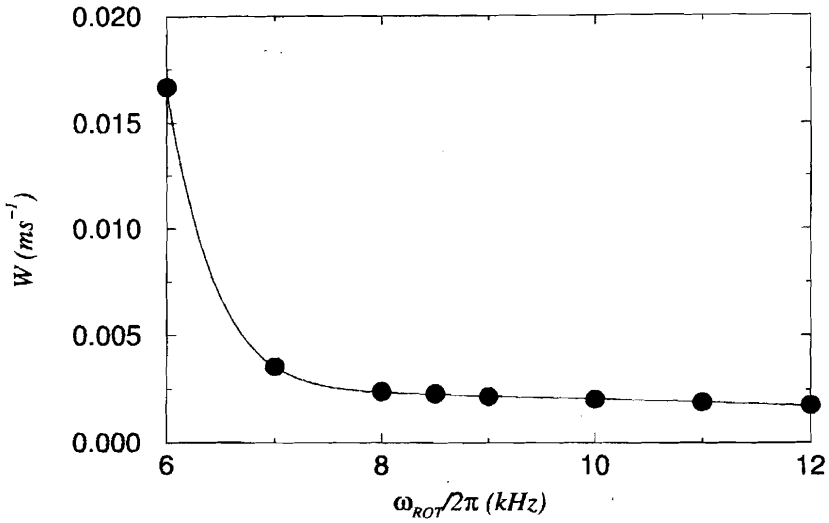

Figure 3: Saturation rate W of quasi-dipolar order measured as a function of ω_R. Theoretical line corresponds to Eq.26 (with $\omega_{lf} = a^2/\omega_R$, $a = 2.02kHz$ and $c = 0.93$) and with an additional constant relaxation rate $W_L = 0.00276ms^{-1}$.

with small magnitude $\omega_1 \ll \omega_{lf}$. In the canonical frame (Eq.4), effective Hamiltonian is, keeping only the static leading term,

$$H = \Delta I_z + H_s + \omega_1 I_x \tag{27}$$

Then, according the well-known Provotorov theory of saturation [3, 2], starting from the lattice equilibrium

$$\tilde{\rho}_L = 1 - \beta_L \omega_L I_z = 1 - \alpha_L \Delta I_z, \quad \alpha_L = \beta_L \omega_L / \Delta, \tag{28}$$

under the influence of the perturbation $\omega_1 I_x$, temperatures α and β vary exponentially with a mixing rate

$$W_{mix}(\Delta) = \pi \omega_1^2 \left(1 + (\Delta/\omega_{lf})^2\right) g_0(\Delta), \tag{29}$$

$$g_0(\Delta) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\Delta t} g_0(t) \ . \tag{30}$$

toward the state $\tilde{\rho}_c = 1 - \beta_c H$, characterized by a common spin temperature

$$\beta_c = \beta_0 \omega_L \Delta / (\Delta^2 + \omega_{lf}^2) \ , \tag{31}$$

for typical conditions where $W_{mix} \gg W$.

These formulae have been experimentally checked (Fig. 4 and 5). They allow determination of $\omega_{lf} = 315(15)\ Hz$ at $\omega_R = 8\ kHz$, in reasonable agreement with theoretical value $\omega_{lf} = 340\ Hz$. Additionally, it was found theoretically and checked by comparison with MAS spectrum, that $\omega_{lf}^2 = \frac{1}{2} M_{2,s}$, where $M_{2,s}$ is the second moment of $g_0(\Delta)$.

The thermal mixing on spinning sidebands matching $(\Delta - n\omega_R \sim \omega_{lf})$ gives similar results and will be detailed elsewhere.

We have demonstrated the existence of quasi-dipolar order under fast magic-angle spinning that results from three-spins interactions. From the theoretical point of view, the work gives the first framework for applying spin thermodynamic laws in fast rotating samples. Such an approach is quite general and may be applied to other systems as well.

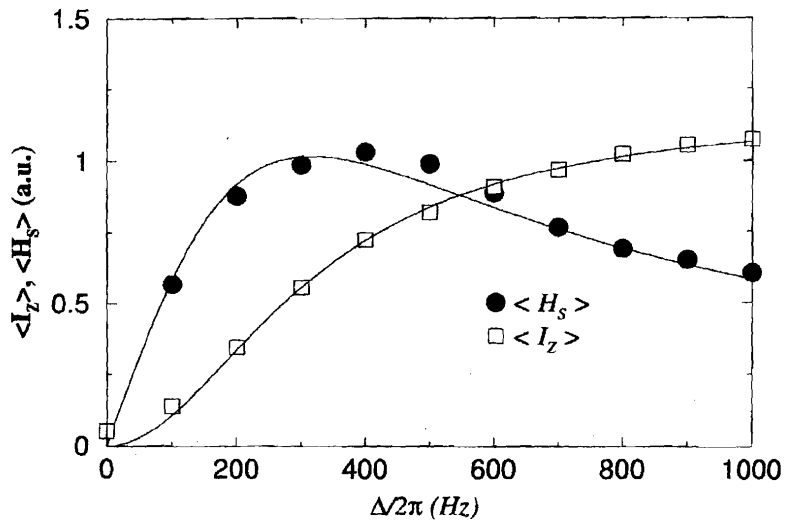

Figure 4: Values of $\langle H_s \rangle \propto \beta_s$ and of magnetization $\langle I_z \rangle \propto \alpha\Delta$ after the system has reached a common temperature β_s. theoretical lines are drown using Eq.31 with $\omega_{1f} = 2\pi \cdot 315$ Hz.

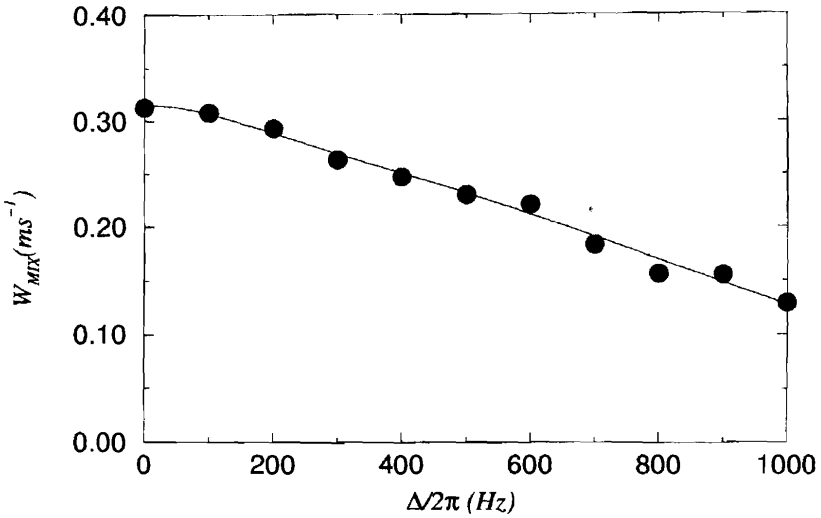

Figure 5: Rate of evolution of α and β_s toward a common temperature. The theoretical lines correspond to Eq.29 with $g_0(\Delta) = const \cdot \cosh(\Delta/s)/\cosh(\Delta/u)$ with $s = 435$ and $u = 180 \cdot 2\pi$ Hz.

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