

# Spin-Noise Gradient Echoes – Supporting Information

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## 1 Simulations of spin-noise gradient echo

To assess the effect of SNGE, we perform simulations using Mathematica (Wolfram Research Inc., 2012) based on the Bloch  
10 equations (Bloch, 1946), and neglecting any effect of radiation damping. This last assumption corresponds to the used  
experimental conditions where the inhomogeneous broadening by the gradients exceeds the radiation-damping rate. In these  
simulations, spin noise originates from a series of random excitation events of random timing, random phase and a random  
small flip angle supposed to be below 0.01°. For a single noise event, the evolution of magnetization in the rotating reference  
frame is simulated by assuming a weak randomized initial transverse magnetization  $m_0$  starting at a random time  $\tau$  within the  
15 first gradient  $G_1$ . Using  $z$  as the position coordinate along the gradient axis, we get for a single isochromat with offset 0 at the  
end of  $G_1$ :

$$I(G_1) = m_0 e^{-i\gamma z G_1 \delta_1} \quad (\text{S1})$$

In the case of a distribution of components along  $z$ , it is necessary to integrate:

$$I_l(G_1) = \int_{-l/2}^{l/2} I(G_1) dz \quad (\text{S2})$$

20 For the sample with length  $l$ , it results in:

$$I_l(G_1) = m_0 \frac{\sin(0.5\gamma G_1 \delta_1 l)}{0.5\gamma G_1 \delta_1} \quad (\text{S3})$$

Then, the evolution during the second gradient leads further to:

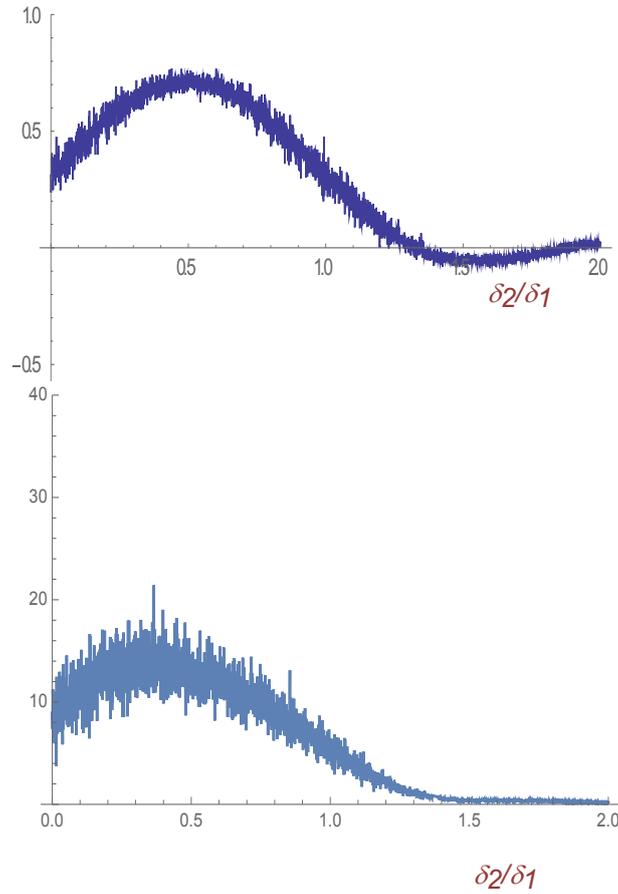
$$I(G_2) = m_0 e^{-i\gamma z (G_1 \delta_1 + G_2 \delta_2)} \quad (\text{S4})$$

Here we assume the delays  $\Delta$  and  $\varepsilon$  (Fig. 1) to be negligibly short. After integration over the sample, we get the expression:

$$25 \quad I_l(G_2) = \int_{-l/2}^{l/2} I(G_2) dz = m_0 \frac{\sin[0.5\gamma(G_1 \delta_1 + G_2 \delta_2)l]}{0.5\gamma(G_1 \delta_1 + G_2 \delta_2)} \quad (\text{S5})$$

By numeric summation over 100 uniformly random distributed (with respect to starting times, phases, and amplitudes) initial  
magnetizations  $m_0$ , we obtain the curves shown in Fig. S1. The case including  $T_2$  relaxation is described by Eq. (S6):

$$I_l(G_2, T_2) = \int_{-l/2}^{l/2} I(G_2) dz = m_0 \frac{\sin[0.5\gamma(G_1 \delta_1 + G_2 \delta_2)l]}{0.5\gamma(G_1 \delta_1 + G_2 \delta_2)} e^{-\frac{\delta_1 + \delta_2}{T_2}} \quad (\text{S6})$$



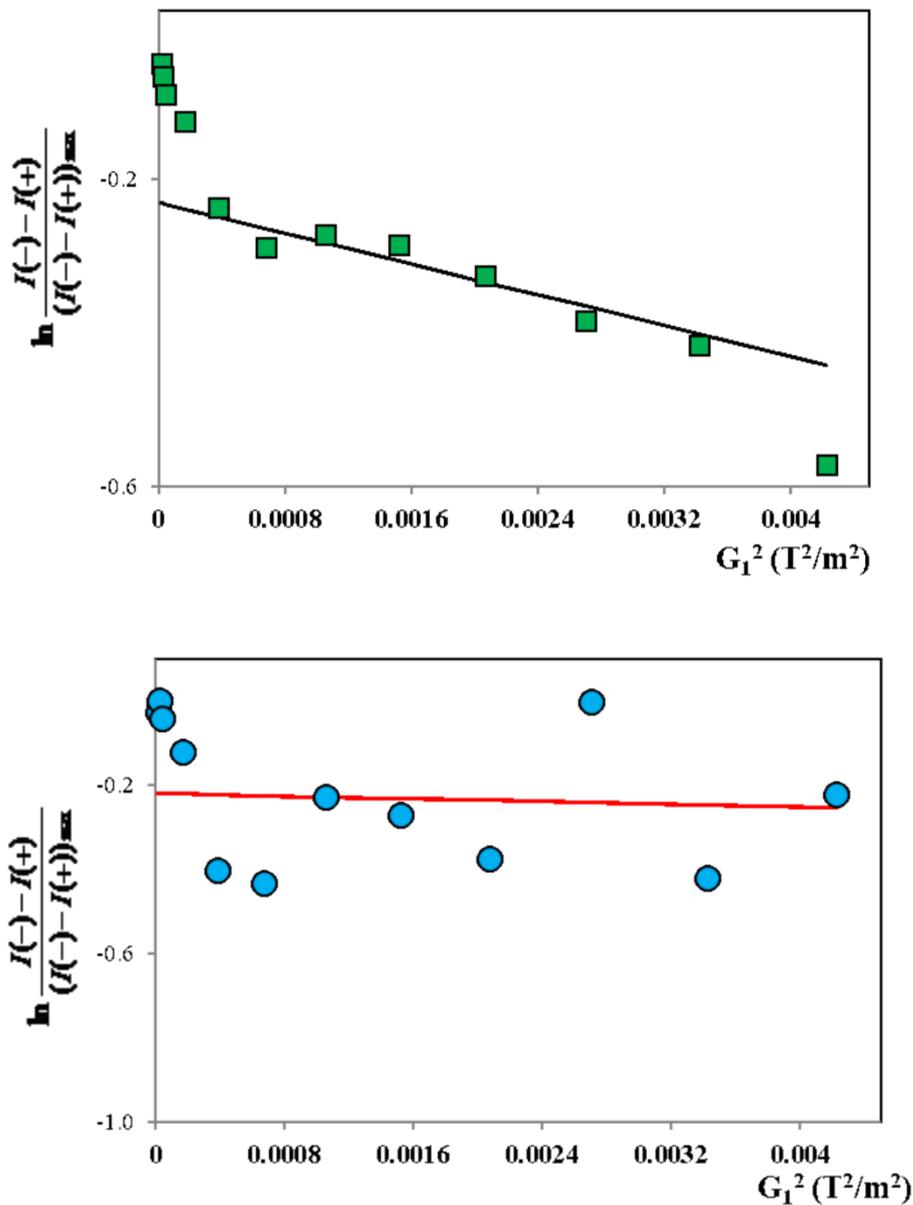
30 **Figure S1. Numerical simulation of the time course of refocused spin noise during the second gradient of Fig. 1a, as a function of the relative gradient duration neglecting transverse relaxation and diffusion (a).  $G_1 = -10$ ;  $G_2 = 10$ ;  $\gamma = 1$ ;  $m_0=1$ ;  $l = 1$ . In (b) transverse relaxation time of 10 was assumed. No additional non-spin random noise was added. It would exceed the echo amplitude without extensive averaging.  $G_1 = -10$ ;  $G_2 = 10$ ;  $\gamma = 1$ ;  $m_0 = 1$ ;  $l = 1$ ;  $T_2 = 10$ .**

These simulations assume that for small radiation damping contribution (gradient broadening of the linewidth larger than the  
 35 initial linewidth due to transverse relaxation and radiation damping), spin noise can be envisaged as a series of spontaneous excitation events of random phase. Because of creating a series of random coherences, they cannot be applied to the cases with weaker gradients or for strong polarization situations, as it was the case in (Desvaux, 2013; Pöschko et al., 2017). After these excitations, the individual coherences can be defocused and refocused by field-gradient pulses, as usual. Fig. S1 only shows the contribution from the refocused noise initiated during  $\delta_1$ . The signal envelope indicates an echo maximum before the  
 40 midpoint of  $\delta_2$  in the presence of transverse relaxation (Fig. S1(b)). The location of the maximum gradient echo is typically that observed with coherent excitation ( $\frac{\delta_2}{\delta_1} \approx 0.5$ ).

As a consequence of these simulations, the noise power amplitude of the  $I(+)$  experiments (Fig. 1) is due to transverse coherences excited during the second gradient only. However, the additional contributions observed in the  $I(-)$  experiments originate from events during first gradient with length of  $\delta_1$  refocused by the second gradient during  $\delta_2$ .

#### 45 **2 Molecular diffusion characterization**

Figure S2 presents the results of SNGE attenuation vs gradient values for a mixture composed of acetone and benzene in 1:1 concentration. The associated spectra are reported in Fig. 4.



50 **Figure S2.** SNGE attenuations vs gradient increase for separate signals of acetone (top) and benzene (bottom) in a 1:1 mixture of acetone and benzene (with 10% of acetone-d6 for locking) recorded according to the scheme of Fig. 3. Experimental spectra are reported in Fig. 4.

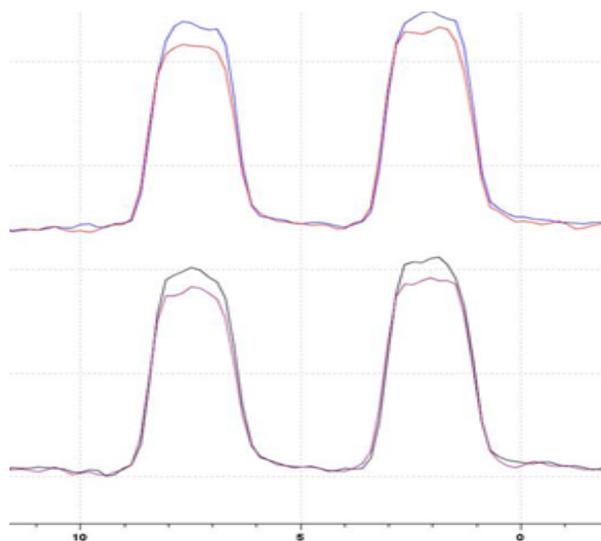
As in Fig. 5, Fig. S2 reveals a correct linear behaviour for not too small  $G_1^2$  values. This is particularly true for acetone, while for benzene which molecular diffusion coefficient is smaller, more scattered measurements are observed. From this SNGE attenuation vs  $G_1^2$  experiment (Fig. S2), an estimation of ratio of slope for acetone component in this mixture to that for benzene component results can be determined. This ratio is comparable to the independent determination of diffusion coefficients in

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pure solvents (acetone and benzene) measured with a SNGE NMR-diffusion experiment (Fig. 3) with a small RF pulse of  $0.2\mu\text{s}$  added ( $2.4 \cdot 10^{-9} \frac{\text{m}^2}{\text{s}}$  for benzene and  $4.58 \cdot 10^{-9} \frac{\text{m}^2}{\text{s}}$  for acetone). These self-diffusion coefficients agree well with literature values of benzene and acetone as obtained by canonical RF NMR spin-echo experiments. (Ertl, and Dullien, 1973) This experiment (Fig. S2) illustrates that in two-component mixture with different chemical shifts it is possible to acquire SNGE attenuation data (Fig. 4) and to extract SNGE attenuation curves separately for each diffusion component. So, qualitative comparison of how SNGE signal is attenuated in diffusion experiment in mixtures with differently diffusing (and chemically shifted) molecules. The issue resides in obtaining enough measurements in the range of gradient values (i.e., in such linear range of  $G_1^2$ ) where mostly diffusion effect should result in measurable decrease in echo intensity (Fig. 4 and S2). However, experimental points (at the largest gradient values) have been measured at  $70 \frac{\text{mT}}{\text{m}}$  to  $75 \frac{\text{mT}}{\text{m}}$  (Fig. 5 and Fig. S2). This is still not enough to get data set for calculation of diffusion coefficient according to Eq. (3). We could not increase measurable gradient values to carry out reliable SNGE experiment at gradients higher than  $75 \frac{\text{mT}}{\text{m}}$ . So, implementation of diffusion experiment limited by the fast gradient duty cycle – this is too fast for our high-resolution probe. Therefore, a search of additional experimental facilities can result in new advantages for realization of spin-noise gradient echo measurements.

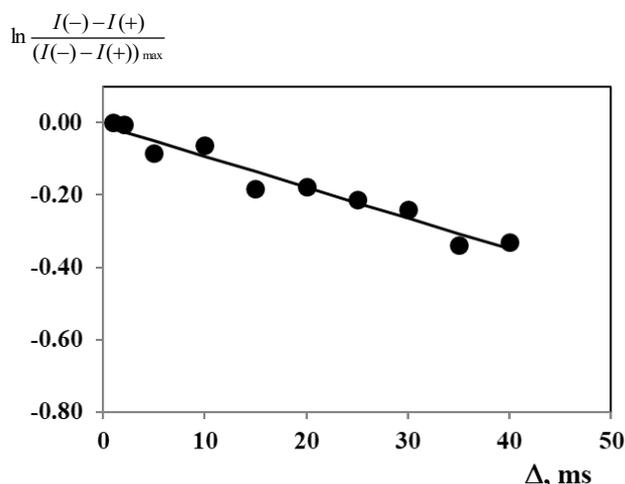
### 3 Molecular diffusion and relaxation measurements

70 Figure S3 illustrates how 3 gradient pulses scheme (Fig. 3) produces SNGE data sets in 1:1 acetone-benzene mixture vs  $\Delta$ .



75 **Figure S3. SNGE experiments as a function of  $\Delta$  between  $G_1$  and  $G_2$  with a triple gradient sequence (Fig. 3) on a 1:1 mixture of acetone and benzene (with 10% of acetone- $d_6$  for locking). The respective lower traces correspond to the  $I(+)$  sub-experiment, the higher ones are to the  $I(-)$  measurements. SNGE spectra are presented for 2 values of delay increasing from top to bottom: 8 ms, 20 ms. Chemical shifts: 2.1 ppm (acetone); 7.2 ppm (benzene).**

Data presented show that in the mixture of two pure solvents with different chemical shifts of their molecules (for instance, benzene and acetone) SNGE attenuation (i.e., normalised difference between z-profile signals in  $I(-)$  and  $I(+)$  spin-noise experiments vs gradient history) can be presented separately with measurable relaxation constants. An estimation of relaxation constant for separate component (benzene) in mixture appears similar to that measured in SNGE experiment on pure solvent  
80 (benzene) (Fig. 6 and Fig. S4).



85 **Figure S4.** The  $I(+)$  and  $I(-)$   $^1\text{H}$  SNGE experiments on pure benzene for different delays  $\Delta$  between  $G_1$  and  $G_2$  with triple gradient sequence. Relaxation constant for benzene  $T_2^* = 87\text{ms}$  to  $93\text{ms}$ .

## References

- Bloch, F.: Nuclear induction, Phys. Rev., 70(7–8), 460–474, doi:10.1103/PhysRev.70.460, 1946.
- Desvaux, H.: Non-linear liquid-state NMR, Prog. Nucl. Magn. Reson. Spectrosc., 70, 50–71, doi:10.1016/j.pnmrs.2012.11.001, 2013.
- 90 Ertl, H. and Dullien, F.A.L.: Self-diffusion and viscosity of some liquids as a function of temperature. AIChE J., 19, 1215–1223. doi:10.1002/aic.690190619, 1973.
- Pöschko, M. T., Rodin, V. V., Schlagnitweit, J., Müller, N. and Desvaux, H.: Nonlinear detection of secondary isotopic chemical shifts in NMR through spin noise, Nat. Commun., 8(1), 1–9, doi:10.1038/ncomms13914, 2017.
- Wolfram Research Inc.: Mathematica, Version 9, Champaign, Illinois. [online] Available from:  
95 <https://www.wolfram.com/mathematica>, 2012.