RESPONSE TO "SPIN RELAXATION: UNDER THE SUN, ANYTHING NEW?" BY B.A. RODIN AND D. ABERGEL.

The work by Rodin and Abergel revisits some of the early developments of spin relaxation theory in NMR and discusses their relation to the Lindblad equation, which is commonly employed in quantum optics and the mathematical physics literature. A detailed discussion on classical and quantum mechanical correlation functions/spectral densities with respect to detailed balance is also included.

The paper seems to be in response to a recent publication "A master equation for spin systems far from equilibrium" (doi.org/10.1016/j.jmr.2019.106645) authored by Malcolm Levitt and myself. However, several references and conclusions regarding our work are incorrect or misstated.

In their abstract Rodin and Abergel claim that our work has "recently questioned" the "underlying theory" worked out by the founding fathers of spin relaxation theory. This is incorrect, we clearly state at the beginning of the article that our work explores the disadvantage and advantages of several thermalization techniques (IME, Jeener, Levitt-di-Bari) in the context of highly polarised spin systems (see section 4). In particular we show that the inhomogeneous master equation (IME) may lead to non-physical results for such systems. At no point do we cast doubt upon the underlying theory developed by Bloch, Wangness, Redfield, etc. On the contrary, we give full credit to the "founding fathers" already being "fully aware that semiclassical relaxation theory [...] is of limited validity" for highly polarised systems. If anything we cast doubt upon the current use of the IME for highly polarised spin systems within the NMR community.

Within this context section 2.2 by Rodin and Abergel seems to stipulate that we imply that it is impossible to derive the Lindblad equation from the quantized theory of Bloch and Redfield. However, we simply presented the Lindblad method as a convenient approach to extend the semiclassical relaxation theory to systems outside the weak-order limit. We rather hoped that it would be clear that the Lindblad equation follows from the quantized BWR theory given that the starting point of our derivation in section 5 coincides with the starting point of BWR. However, it is true that we could have stated this fact in more detail as has recently been done by Tom Barbara (https://doi.org/10.5194/mr-2-689-2021). The authors conclude section 2.2 with "the Lindblad equation [...] is thus derived from the usual

quantized theory of relaxation." I am not sure if the authors are trying to claim novelty for this result (it also appears to be core statement of their abstract), if so they should consult the books by Breuer (DOI:10.1093/acprof:oso/9780199213900.001.0001), Schaller (10.1007/978-3-319-03877-3), and the recent article by Tom Barbara.

Unfortunately some mischaracterisation of our analysis of singlet-triplet relaxation in highly polarised spin systems may be found within the conclusion. The authors state: "The author's interpretation was that "thermalization" was not properly taken into account by the inhomogeneous semiclassical version of the Redfield equation, which was ascribed to the fact that the classical approach does not comply with the detailed balance condition." No such statements are made. The deviation between these results was not ascribed to detailed balance, but to the fact that the IME generates the unphysical situation in which singlet order may directly flow into Zeeman magnetisation (clearly illustrated in figure 1). The provided discussion by the authors on this subject is also somewhat confusing. If I understand correctly the authors strongly emphasise the validity of detailed balance for the bath (in example the equilibrium distribution of the liquid follows Boltzmann). But this does not matter very much if the *spin transitions* do not obey detailed balance, which is clearly what our work refers to when talking about detailed balance. Consider for example equation (77) with a spectral density $J^\theta(\omega) = \theta(\omega)J(\omega)$, where $\theta(\omega)$ enforces detailed balance of the *spectral densities*. Consider now an ensemble of spin-1/2 particles experiencing random field relaxation in solution. According to equation (77) the relaxation superoperator is given by

$$\hat{\Gamma} = -\frac{1}{2}\xi_{\text{erf}} \sum_{m=-1}^{+1} J(|m|\omega)\theta(m\omega)\hat{T}_{1m}^\dagger \hat{T}_{1m}.$$ (1)

It is straightforward to verify the following matrix elements

$$
\begin{aligned}
W_{\alpha \leftarrow \beta} = (P_\alpha|\hat{\Gamma}|P_\beta) = \frac{\xi_{\text{erf}}}{4} J(\omega)(\theta(+\omega) + \theta(-\omega)) \\
W_{\beta \leftarrow \alpha} = (P_\beta|\hat{\Gamma}|P_\alpha) = \frac{\xi_{\text{erf}}}{4} J(\omega)(\theta(+\omega) + \theta(-\omega)),
\end{aligned}
$$ (2)

where P_α and P_β are the α and β population operators, respectively. The two transition rates per unit time $W_{\alpha \leftarrow \beta}$ and $W_{\beta \leftarrow \alpha}$ are *equal*. So even if the detailed balance condition holds for the bath it *does not* hold for the spin-state transitions when equation (77) is used. In other words it is correct to say that the equilibrium density operator for the spin system is not in the nullspace of $\hat{\Gamma}$ because it does not obey detailed balance for spin transitions. This has been discussed extensively in appendix A.2 of our work.

Besides the very unfortunate misinterpretation of our work, the provided discussion regarding classical and quantum mechanical correlation functions is interesting and is used to introduce a "thermalized double-commutator" in section 4. The thermalized double-commutator renders the relaxation superoperator Redfield like and it is shown that this approach is fully equivalent to the Lindblad method. However advantages and disadvantages, if there are any, are not discussed. For example, the thermalized double-commutator does not represent a double-commutator in a strict mathematical sense and might be awkward to incorporate into existing simulation software. Additionally, representing the relaxation superoperator in Lindblad form does not only provide a simple check on positivity and Markov compatibility, but is also in agreement with the majority of the literature outside NMR.

Apart from that there also some technical issues.

- The trace operator Tr should not be italicized.

- The interaction frame transformation above equation (4) should read as $\exp\left(-\mathcal{L}_0 t\right)$.

- The authors switch to a time difference variable $\tau = t - t'$ in equation (6), but this is not consistent with equations (7)-(19).

- Something appears to be wrong with equation (19), take for example $\mathcal{L}_1 = A \otimes B$. Then starting from equation (16) one has

$$
\begin{aligned}
e^{+\mathcal{L}_S t} \mathrm{Tr}_B \{ (e^{-\mathcal{L}_S t} A e^{+\mathcal{L}_S t} \otimes e^{-\mathcal{L}_B t} B e^{+\mathcal{L}_B t}) (e^{-\mathcal{L}_S t'} A e^{+\mathcal{L}_S t'} \otimes e^{-\mathcal{L}_B t'} B e^{+\mathcal{L}_B t'}) \rho_B^e \} e^{-\mathcal{L}_S t} \sigma(t) = \\
\mathrm{Tr}_B \{ (A \otimes e^{-\mathcal{L}_B t} B e^{+\mathcal{L}_B t}) (e^{\mathcal{L}_S (t-t')} A e^{-\mathcal{L}_S (t-t')} \otimes e^{-\mathcal{L}_B t'} B e^{+\mathcal{L}_B t'}) \rho_B^e \} \sigma(t) = \\
\mathrm{Tr}_B \{ (\tilde{A}(0) \otimes \tilde{B}(0)) (\tilde{A}(t - t') \otimes \tilde{B}(t - t')) \rho_B^e \} \sigma(t) = \\
\mathrm{Tr}_B \{ \tilde{\mathcal{L}}(0) \tilde{\mathcal{L}}(t - t') \rho_B^e \} \sigma(t),
\end{aligned}
\tag{3}
$$

  which appears to be different from equation (19). Equation (20) on the other hands appears to be correct again.

To conclude, although this work approaches spin relaxation from an interesting angle, the paper overall appears as somewhat sloppy and rushed. I suggest to the authors to correct their misinterpretation regarding Malcom Levitts and my work, as well as some of the technical issues, before publication can be considered.