pyDIFRATE: A generalized approach to timescale analysis of dynamics

Albert A. Smith

1 A brief introduction

The detector analysis provides a straightforward methodology for analyzing data sensitive to correlation times. We rely on a basic assumption, that some correlation function describes the motion, and that correlation function can be assumed to be a sum of an arbitrary number of decaying exponential terms,[1] such that it may be written

$$\begin{aligned} C(t) &= \sum_i A_i \exp\left(-t/(10^{z_i} \cdot 1\text{ s})\right) \\ &= \int_{-\infty}^{\infty} \theta(z) \exp\left(-t/(10^{z_i} \cdot 1\text{ s})\right) \\ & z = \log_{10}(\tau_c/\text{ s}) \end{aligned} \tag{1}$$

The correlation function then may have an arbitrary number of terms, each depending on an amplitude, A_i, and correlation time, $z_i = \log_{10}(\tau_i/\text{s})$, which is given on a logarithmic scale. We generalize this to a distribution, where $\theta(z)$ describes the amplitude at all possible correlation times, although we note that this can be reduced to a simple sum of δ-functions, leading to the discrete sum ($\theta(z) = \Sigma_i A_i \delta(z - z_i)$). Note that depending on the type of correlation function, we may denote the distribution slightly differently, and put requirements on the integral of the distribution. For example, for NMR, we replace $\theta(z)$ with $(1-S^2)\theta(z)$, where S^2 is the generalized order parameter for the total motion, and $\theta(z)$ must integrate to 1.

Then, if a given experiment, which we will denote ζ, depends linearly on the distribution of motion, we can state the following about the observable parameters, denoted R_ζ^θ (R is used due to detector's origin in NMR, where relaxation rate constants are used).

(2)

2 References

[1] A. A. Smith, M. Ernst, B. H. Meier, *J. Chem. Phys.* **2018**, *148*, 045104.