A WORK IN PROGRESS: SIMULATION-INFORMED BAYESIAN INFERENCE FOR QUASI-ELASTIC NEUTRON SCATTERING

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INTRO: WHY IS THIS IMPORTANT?

QENS ANALYSIS IS HARD

The analysis of QENS data requires the application of an analytical model, i.e., Lorentzians to describe different motions.

These approaches may be over-parameterised and it is hard to discriminate which model is best...

Even where Q-dependent modelling is used, the models are based on user assumptions.

BAYESIAN EVIDENCE ESTIMATION CAN HELP

Bayes equation for models allows rational comparison between different models:

$$p(m \mid D) \propto p(D \mid m)\, p(m)$$

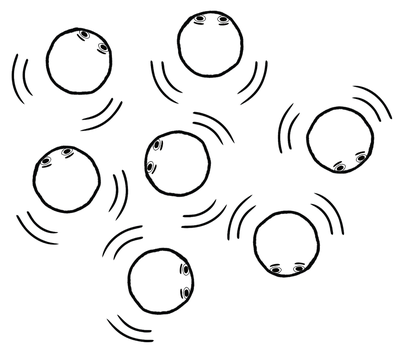
THIS DESCRIBES OUR PRIOR KNOWLEDGE FOR A GIVEN MODEL.

Evidence estimation has been narrowly applied to QENS analysis.[1] Focusing on how many Lorentzians are present at a single Q-vector.

MOLECULAR DYNAMICS CAN INFORM THE MODELS

MD simulations naturally complement QENS measurements, covering the same time- and length-scales.

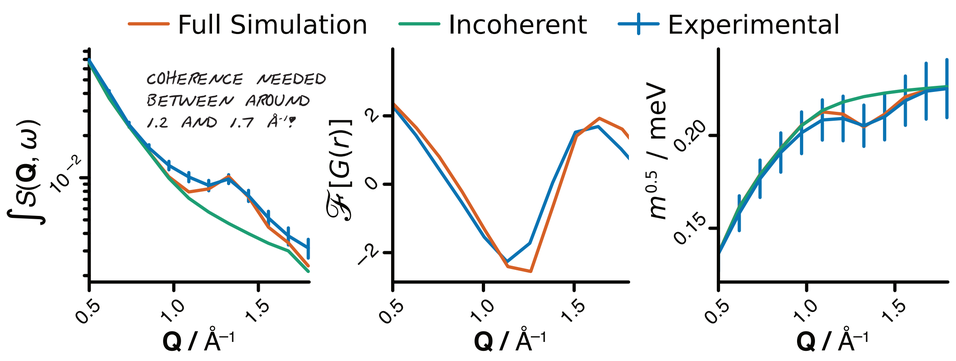
The force field accuracy limits the ability for direct comparison. But simulations can be used as a qualitative model.



Can simulation provide a model prior for Bayes equation for model comparison, $p(m)$?

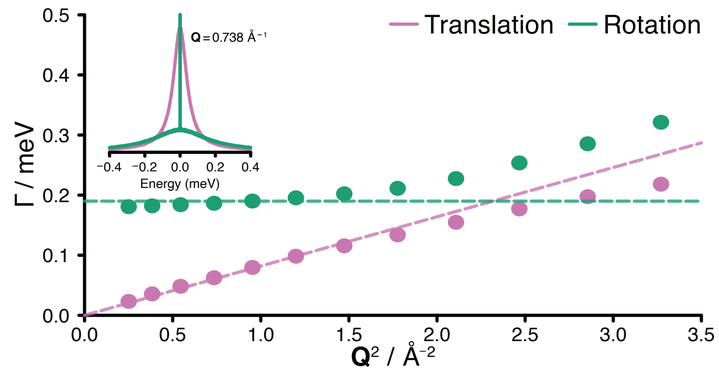
RESULTS: WHAT DOES THE SIMULATION TELL US FOR OUR TEST SYSTEM OF BENZENE?

Structure[2] and dynamics can be well reproduced.



But even for something as hydrogenous as benzene, we need to consider coherent signals.

The simulation can be decomposed to give pure translational and rotational signal.



Using this decomposition approach, we find that:
- Not just a single isotropic rotation.
- Translation deviates from Fickian at high-Q.

SEE FINAL COLUMN IN TABLE, WHERE WE USE THIS AS THE MODEL PRIOR.

The model with the highest evidence for the decomposed simulation, $p(D \mid m_{sim})$, has two rotational models and a single Hall-Ross translational model.

RESULTS: WHAT DOES THE EXPERIMENT TELL US, USING THE SIMULATION AS PRIOR MODEL KNOWLEDGE?

Bayesian evidences from nested sampling. Showing models that best describe both the data and simulation (using Bayes equation).

	MODEL	ln[p(m_{exp} | D)]	ln[p(D | m_{exp})]	ln[p(D | m_{sim})]
No Coherence	1R + FICKIAN	-11145	-10963	-182
	1R + HALL-ROSS	-10526	-10347	-179
	2R + FICKIAN	-7919	-7742	-177
	2R + HALL-ROSS	-7775	-7601	-174
Coherence	1R + FICKIAN	-7574	-7392	-182
	1R + HALL-ROSS	-7488	-7309	-179
	2R + FICKIAN	-7217	-7040	-177
	2R + HALL-ROSS	-7204	-7030	-174

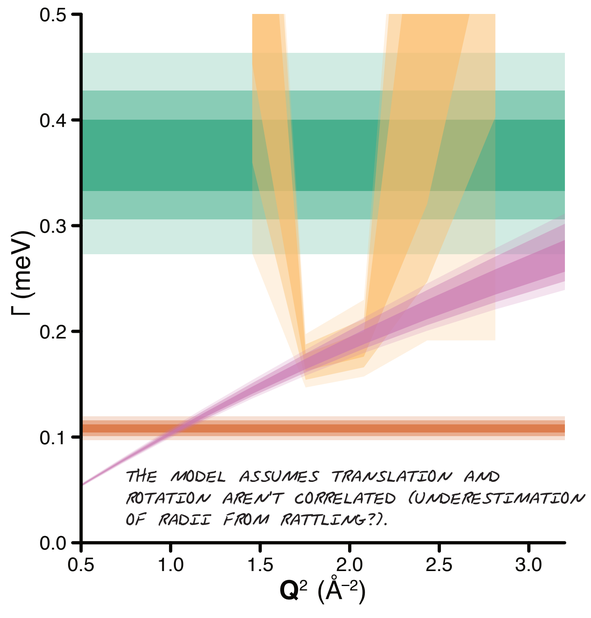
LESS NEGATIVE VALUES, MEAN MORE EVIDENCE FOR GIVEN MODEL.

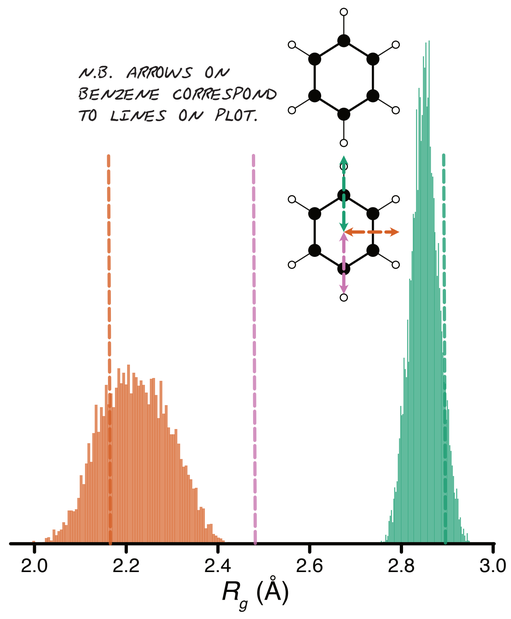
The simulation informed Bayesian evidence provides a rational comparison metric between different models. This tool is powerful for understanding information sparse data, like QENS.

The best model for the experimental data:

$$S_i(\mathbf{Q},\omega) = \left[e^{-\mathbf{Q}^2\langle u^2\rangle/3}\left[\frac{1}{\pi}\frac{\Gamma_T(\mathbf{Q})}{\omega^2+\Gamma_T(\mathbf{Q})^2}\right]\right] \otimes \sum_{n=1}^{2}\left[j_0^2(\mathbf{Q}R_{g,n}) + 3j_1^2(\mathbf{Q}R_{g,n})\left[\frac{1}{\pi}\frac{\Gamma_{R,n}}{\omega^2+\Gamma_{R,n}}\right]\right].$$

And it is necessary to include additional coherent signals between Q of 1.2 and 1.7 Å⁻¹.





Simulations can be used as a qualitative model to inform our experimental QENS analysis, helping to maximise the information density. In this example, this approach allows, for the first time, the decomposition of two distinct rotations in benzene from QENS. The translational Fickian diffusion coefficient agrees well with PFG-NMR measurements.[3]

REFERENCES

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