Fast and Accurate Modelling of Harmonic and Anharmonic Motions in Molecular Crystals from Classical Molecular Dynamics

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1. PROBLEM

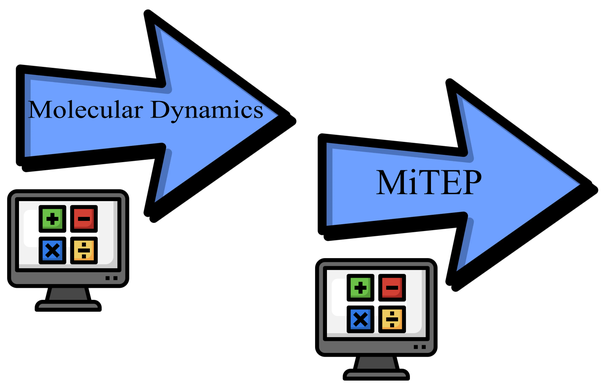
- Harmonic atomic displacement parameters (ADPs) provide useful information about the magnitudes and the directions of average atomic vibrations
- However, anharmonic effects may be far from negligible, especially above cryogenic temperatures
- Estimating the relative weight of anharmonic and harmonic displacements is experimentally challenging, as it requires diffraction data at high resolution
- A new cheap method to calculate ADPs and the Grüneisen parameterusing Molecular Dynamics (MD) is proposed

2. METHODS

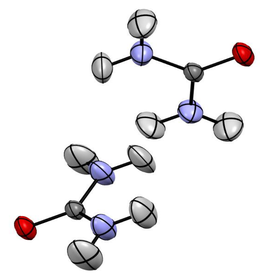
MD methods available MiCMoSv2.4 [1] to sample atomic probability density functions (pdfs) in form I of crystalline urea [2] as a function of temperature and pressure

Input

Molecular Topology
Simulation Box
MD instructions
(T, P, FF, etc..)



ADP



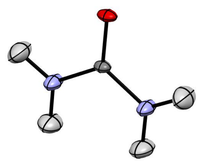
MiTEP (Milano Thermal Ellipsoid Program) operates by:

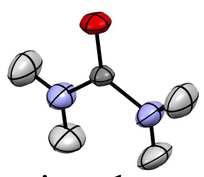
1) Puts the molecules back in the original cell position
2) Calculates the ADPs for each molecule
3) Calculates the average of the ADPs for each molecule over time taking symmetry in consideration

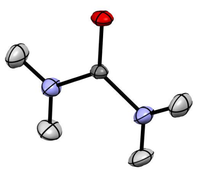
3. RESULTS

Best results obtained with the LJC (Lennard-Jones-Coulomb) Force Field, here shown results in comparison with experimental data [3] at 123 K and 293 K

123 K


Experimental


Computational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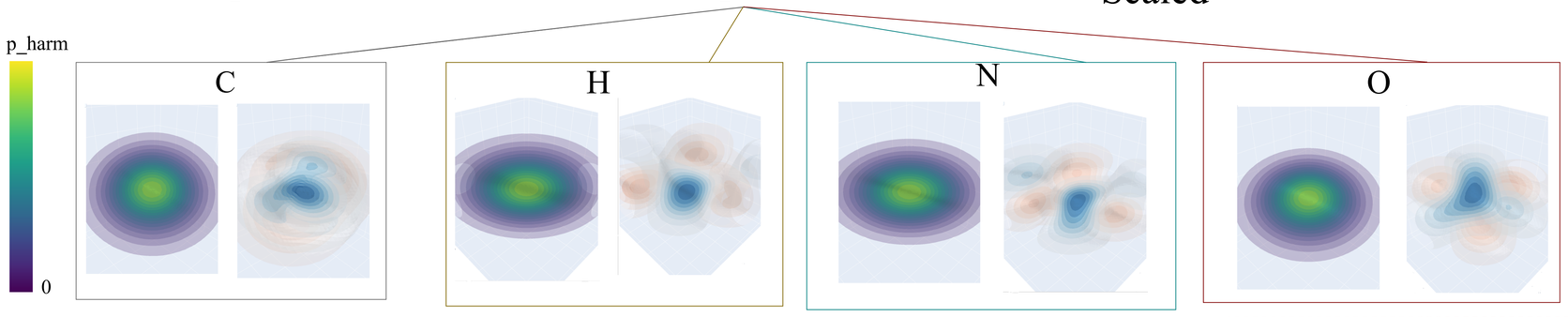
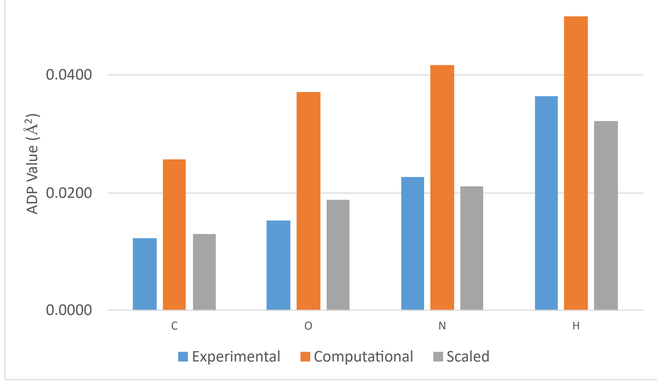
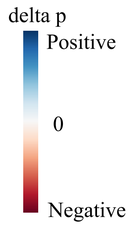
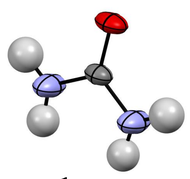
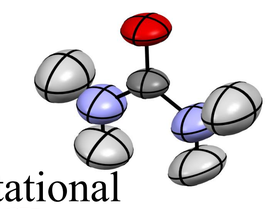


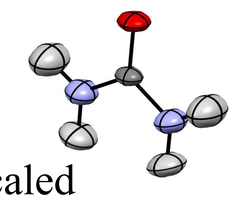


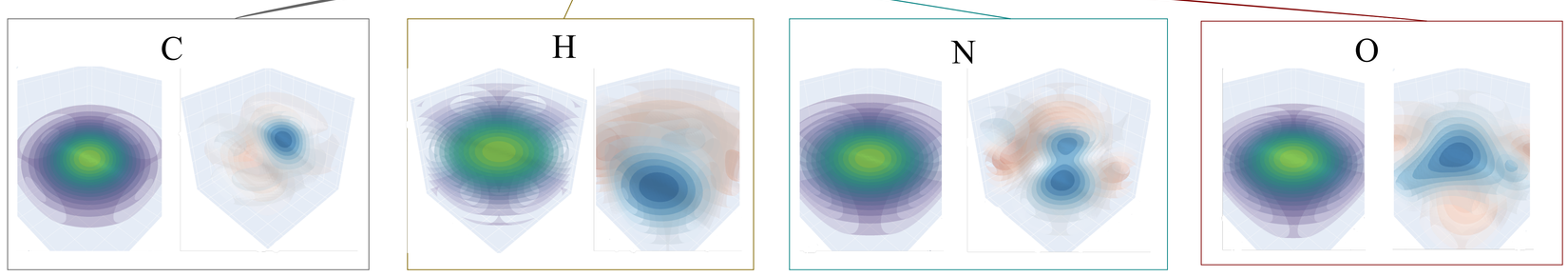


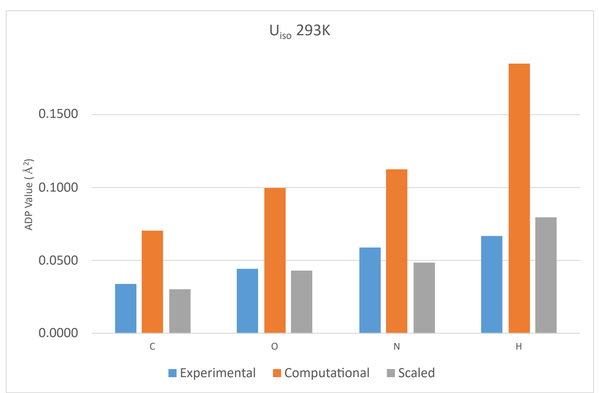
293 K


Experimental


Computational


Scaled





4. FINAL TASK

- We want to use this model to calulate the Grüneisen parameter (γ_G): it quantifies the anharmonic contribution of the system [4]
- This correction factor can account entirely fo anharmonicity in the temperature range 100-300K [5]
- It's common to find this value for inorganic materials, but not for molecular crystals

$$B = B^h(1 + 2\gamma_G\chi T)$$

B = B-factor
B^h = totally harmonic B-factor
χ = volume coeffcient of expansion
T = temperature

5. CONCLUSIONS

- The proposed method is computationally cheap and effective at a semi-quantitative level
- It's possible to distinguish the harmonic and anharmonic contributions at various temperatures and pressures also for H atoms
- The calculation of γ_G is still a work in progress
- In the future this model can be tested on other molecular crystals

6. REFERENCES

[1] Lo Presti, L. et al., Compreh. Comput. Chem., 2024, 3, 777-803
[2] Lo Presti, L. et al., Cryst. Growth Des., 2013, 13, 10, 4571–4582
[3] Schwarzenbach, D. et al., Acta Cryst., 2004, A60, 371 - 381
[4] Coppens, P., Acta Cryst. A, 1975, 31, 879-879
[5] Nicklow R.M. et al., Phys. Rev., 1966, 143, 487