# QM PART B: NNP MD Simulations of H2 in ZIF-8
## Advanced Practical Course in Theoretical Chemistry

Lukas Meinschad (lukas.meinschad@student.uibk.ac.at), 12104730

universität innsbruck

## Introduction

Metal-organic frameworks (MOF) are porous extended structures made from metal ions and organic linkers [1]. MOFs provide potential applications in clean energy, providing a storage media for gases such as hydrogen, methan or carbon dioxide.

In this part of the practical course **ZIF-8**, which crystalizes in a cubic unit cell with 12 $Zn^{2+}$ ions coordinated by 24 methylimidazole linkers, was simulated using the **MACE-MP** neural network [2].
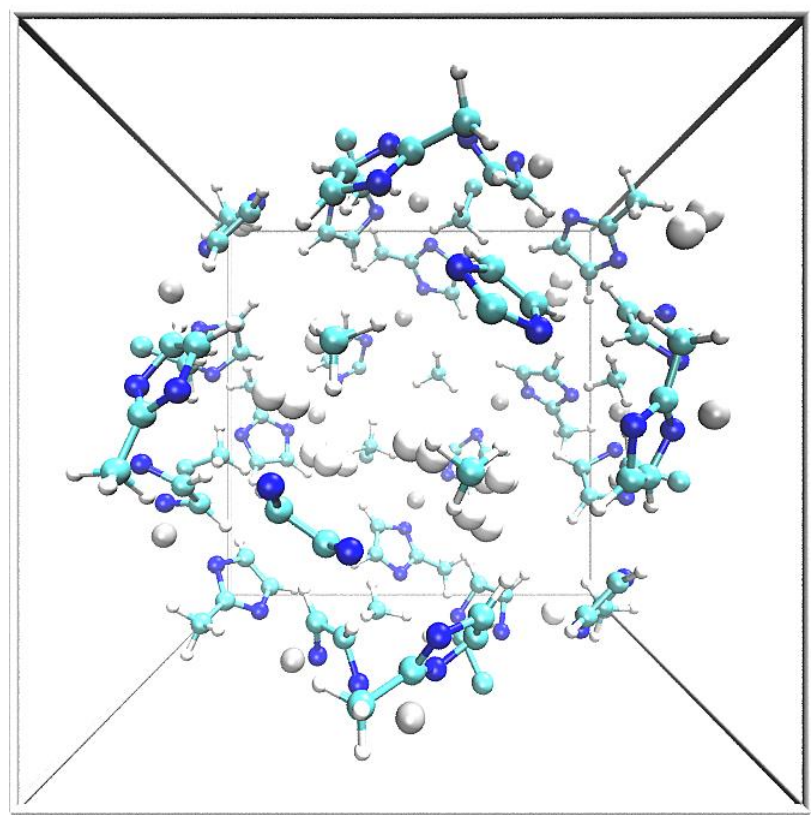


**Fig 1:** Structure of ZIF-8, in lightblue, blue the methylimidazole linkers, in grey the zink atoms and in white the hydrogen that was loaded into the framework.

## Equilibration

In order to calculate the thermal expansion coefficient, a 500 ps NPT run of the empty ZIF-8 framework was performed. With the data one can calculate the average lattice parameter $<a>$ and the average volume of the unit cell $V$.
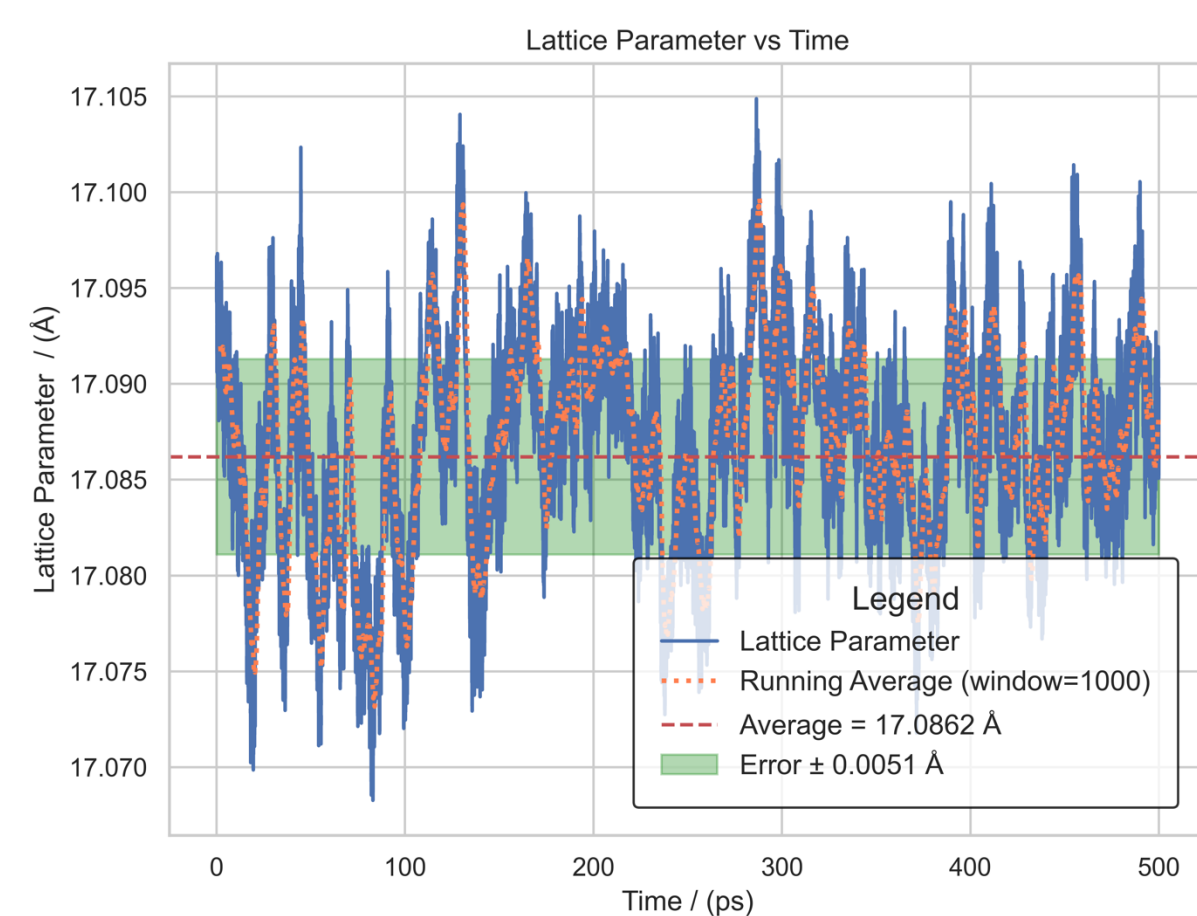


**Fig 2:** Lattice parameter $a$ of the cubic unit cell against the temperature. The dashed red line shows the average over the whole simulation together with the error. A running average (orange dotted points) with a window size of 1000 datapoints was determined to better visualize fluctuations inside the system.

Fig 1. shows that after 500 ps fluctuations in terms of the lattice parameters are still present. Literature X-Ray experiments give a lattice constant of 16.992 Å [3].

## Radial Distribution Function

The radial distribution functions allows to measure structural information of the ZIF-8 system.

It describes the probability of finding a target particle (H or Zn) in a distance to a reference particle:

$$P_{ab}(r) = \int_0^{r'} 4\pi r'^2 \, g_{ab}(r') dr'$$

In Fig 3. (top) the H-H pairs show a sharp peak at low distances, suggesting they are close to each other during the simulation. The Zn-H pairs (bottom) indicate the most probable distance is located around 6 Å.
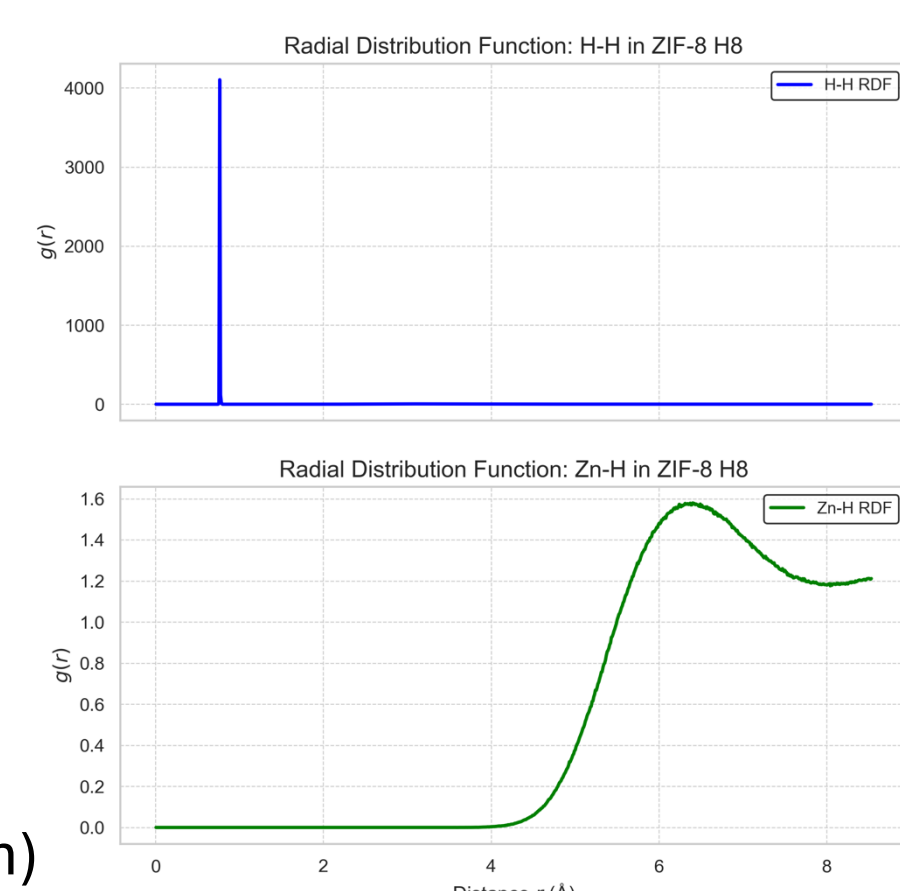


**Fig 3:** Radial Distribution Function for both H-H (top) and Zn-H in ZIF-8 H8 (bottom)

## Gas Diffusion

### Einstein Relation

For the calculation of the activation energy $E_a$, the self-diffusion coefficient $D_s$ needs to be determined. This can be calculated as the slope of the mean-squared displacement (MSD) over time origins $\tau$:

$$D_s = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} MSD(\tau)$$

The MSD describes the temporally displacement of a particle from a time origin averaged over the time interval $\tau$.

$$MSD(\tau) = \left\langle \frac{1}{N} \sum_{i=1}^{N} |\vec{r_i}(t) - \vec{r_i}(t_0)|^2 \right\rangle$$
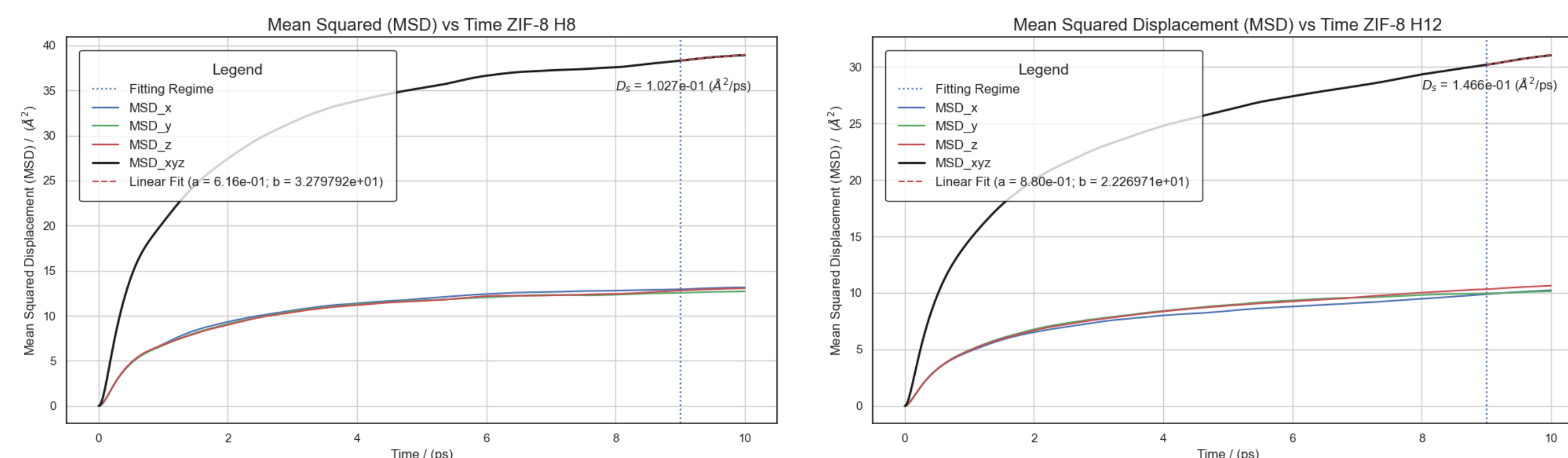


**Fig 4:** Mean Square Displacment against the simulation time for ZIF-8 with eight $H_2$ (left) and twelve $H_2$ (right). The blue, green and red lines represent the MSD in respect to the x,y,z coordinates, the black line is the total MSD summed over all components. A linear fit (dotted red line) in the Regime (dotted blue line)was used calculate $D_s$.

From Fig 4. it comes apparent that for both systems the MSD deviates from linear behaviour in the fitting regime. A reason and bottleneck for the prediction of $D_s$ is the simulation time. As $D_s$ is determined by the limit $t \to \infty$ longer simulations thus allow for a more precise determination. A linear trend in the MSD plot indicates a diffusive movement best described by a random walk. At the beginning of the simulation, the steep increase proposes a directed motion.

### Green Kubo Relation

The Green-Kubo relations express transport coefficients like the diffusion coefficient in terms of time integrals of correlation functions. Thus, to calculate the self-diffusion coefficient $D_s$ one needs to integrate the velocity-autocorrelation function $VACF(t)$:

$$D_s = \frac{1}{d} \int_0^\infty VACF(t) dt$$

The velocity autocorrelation function measures how the velocity of a particle at time $t$ is correlated with a later time $t_0$

$$VACF(\tau) = \left\langle \frac{1}{N} \sum_{i=1}^{N} |\vec{v_i}(t) \, \vec{v_i}(t_0)|^2 \right\rangle$$
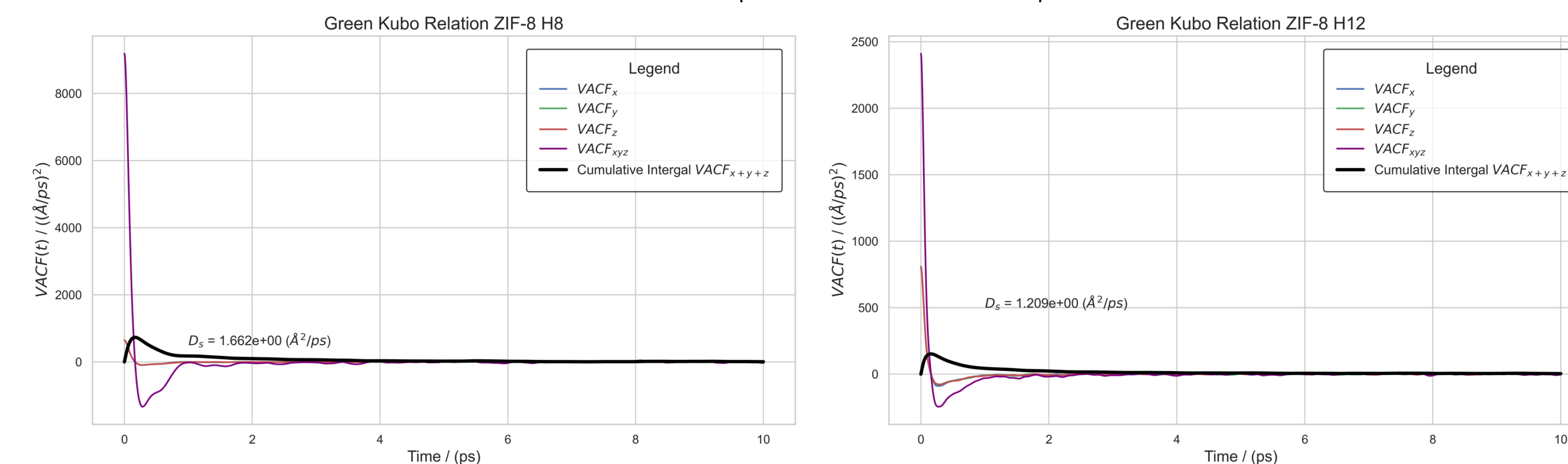


**Fig 5:** VACF plotted against the simulation time for ZIF-8 with eight $H_2$ (left) and twelve $H_2$ (right). The blue, green and red line display the individual x,y,z components, the magenta line shows the total VACF summed over all components. The black line shows the cumulative integral.

Initially, the VACF is a high value, the fast decay indicates a rapid loss of correlation in the velocities, suggesting faster diffusion rates. As also the cumulative integral flattens out, this indicates that further time integration does not change the value of $D_s$. This is not in correspondence with the MSD because Fig 4. shows, that in the proposed fitting regime still fluctuations from diffusive movement are present.

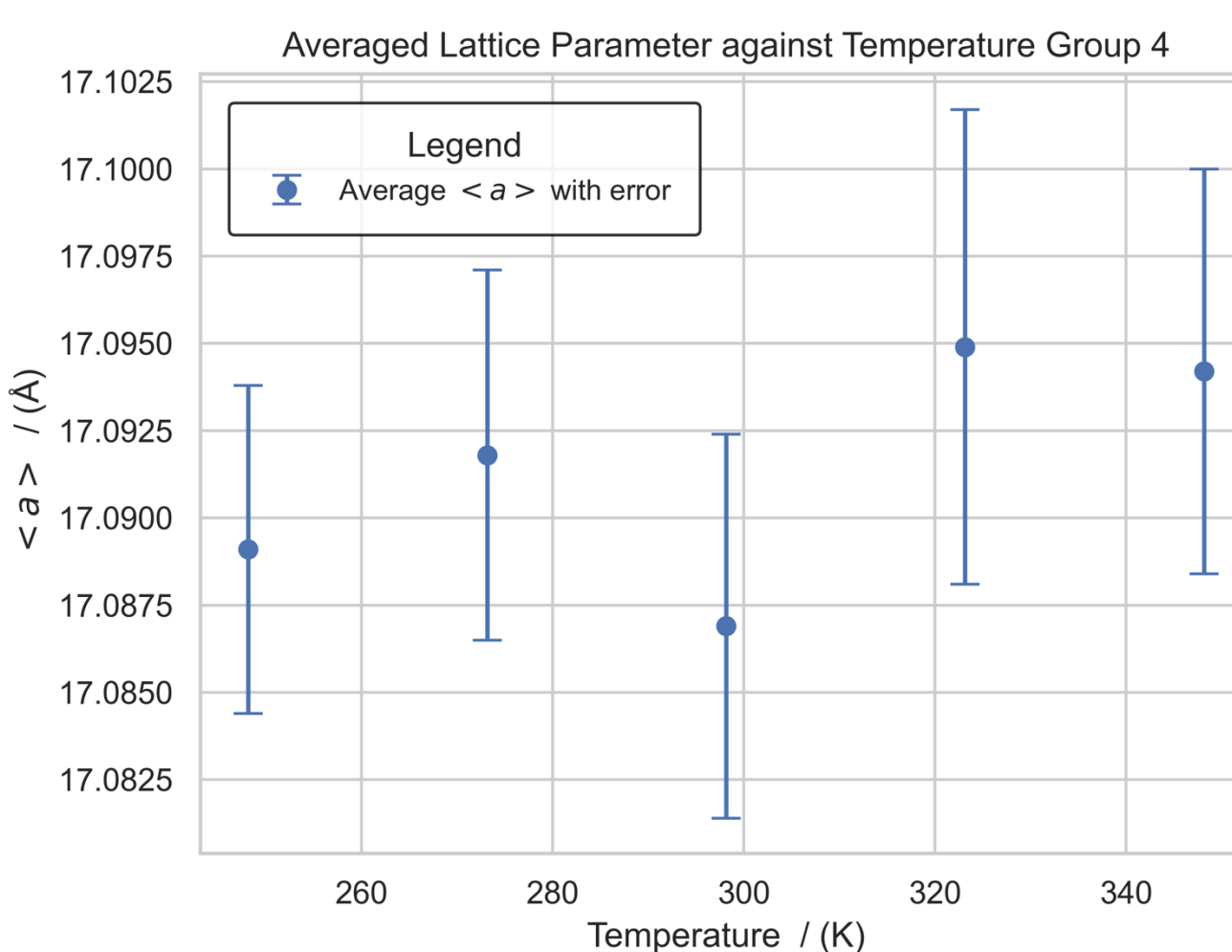## Group Work

### Thermal Expansion Coefficient



**Fig 6:** Average Lattice Parameter against the Temperature for ZIF-8.

As also studied in literature, [4] the unit cell of ZIF-8 becomes larger with increasing temperature. The Thermal expansion coefficient $\alpha$ can be calculated by using a 5-point stencil:

$$\alpha = \frac{\partial x}{\partial T} \approx \frac{\langle x_{248\,K}^T \rangle - 8 \langle x_{273\,K}^T \rangle + 8 \langle x_{323\,K}^T \rangle - \langle x_{348\,K}^T \rangle}{12 \Delta T} = 1.642E\text{-}05 \text{ Å/K}$$

The data in Fig 4. indicates an increase of the average lattice constant with the temperature, but no linear relationship can be derived from the measured datapoints.
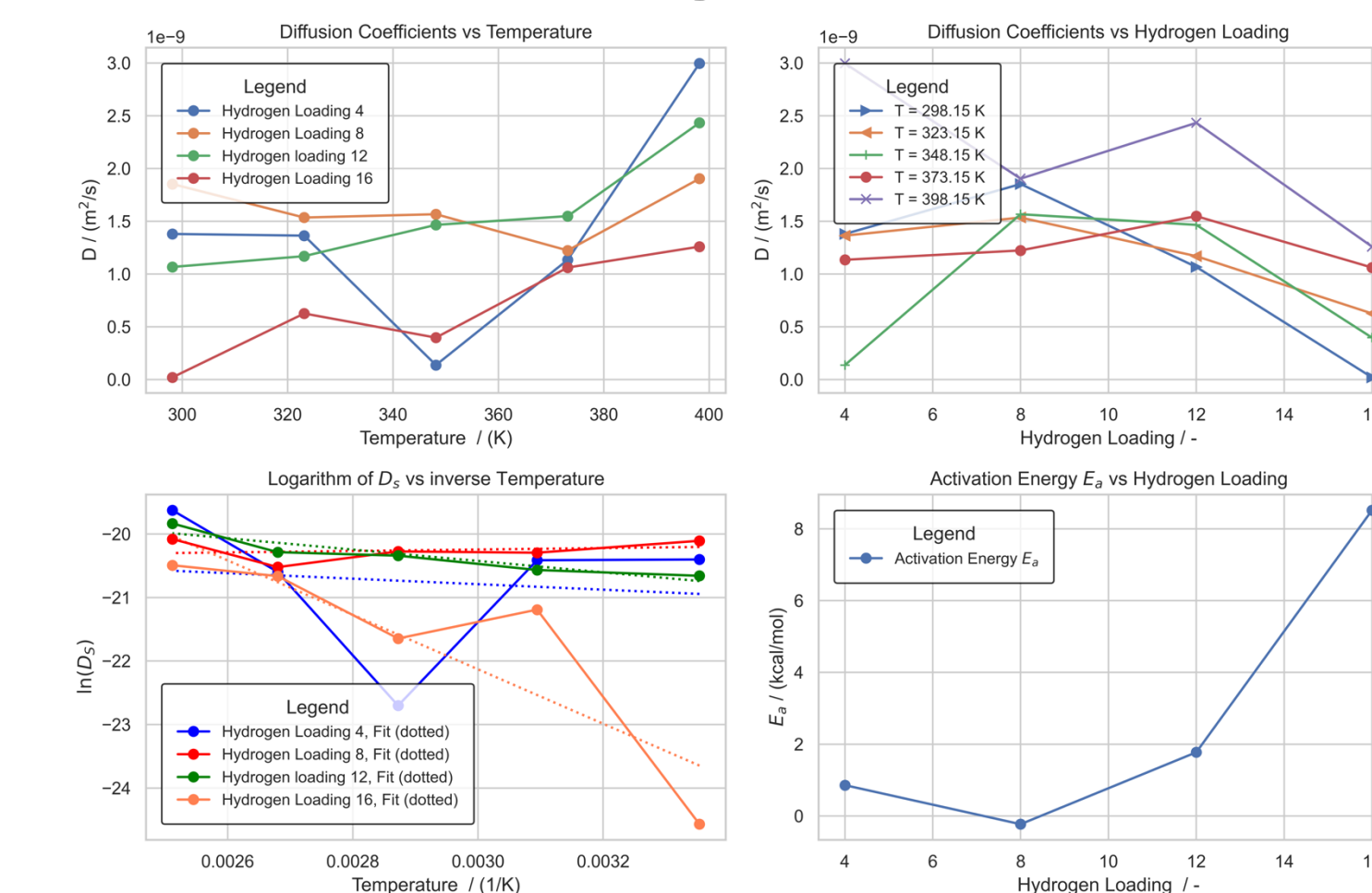
### Activation Energy Einstein-Relation



**Fig 7:** (Top Left) Self-Diffusion $D_s$ against Temperature for four different hydrogen loadings. (Top Right) Self-Diffusion $D_s$ against hydrogen loading. (Bottom Left) Arrhenius Equation and linear regression (dotted lines) for the four different hydrogen loadings. (Bottom Right) Activation Energy calculated from the slope of the Arrhenius equation.

The diffusion should increase with temperature, which is only partially visible in Fig 5. The top right figure here shows that the hydrogen loading has a mixed effect on the diffusion, with higher loadings (n=16) having overall lower values for $D_s$. In the Arrhenius plot, one can see a mixed behaviour where higher loadings (n=16) deviate from a linear relationship, indicating maybe more complex interaction between $H_2$ and the ZIF-8 framework. Lastly, one may note the increase in Activation energy at higher loadings.
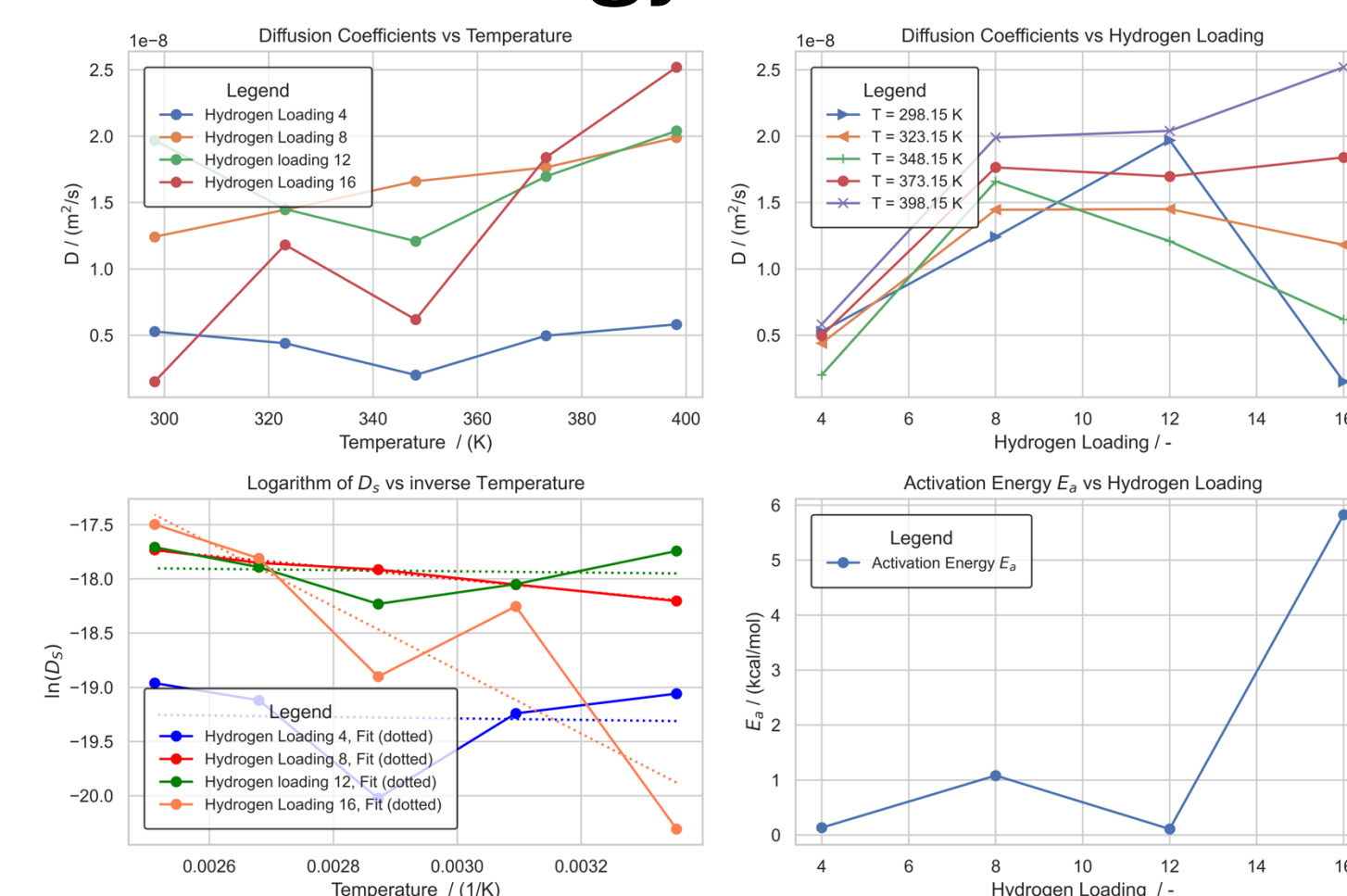
### Activation Energy Green Kubo-Relation



**Fig 8:** (Top Left) Self-Diffusion $D_s$ against Temperature for four different hydrogen loadings. (Top Right) Self-Diffusion $D_s$ against hydrogen loading. (Bottom Left) Arrhenius Equation and linear regression (dotted lines) for the four different hydrogen loadings. (Bottom Right) Activation Energy calculated from the slope of the Arrhenius equation.

Fig 8. shows for $D_s$ against T ,that irrespective of the hydrogen loading $D_s$ increases with temperature. The Arrhenius plot for higher loadings (n=16) deviates strongly from a linear relationship, reflecting similar trends to Fig 5. Here one may note, that large errors are present and especially the fits show almost no linear correlation of the data. Hence a precise interpretation of the obtained data is difficult, for deriving a clear conclusion further temperature points and longer simulations are needed.

**References:**
[1] Introduction to Metal–Organic Frameworks, Hong-Cai Zhou et al. (2012), doi: https://doi.org/10.1021/cr300014x
[2] MACE: Higher Order Equivariant Message Passing Neural Networks for Fast and Accurate Force Fields, Batatia et al. (2023) doi: https://doi.org/10.48550/arXiv.2206.07697
[3] A review of the features and applications of ZIF-8 and its derivatives for separating CO2 and isomers of C3- and C4- hydrocarbons, Bergaoi et al., doi: https://doi.org/10.1016/j.jngse.2021.104289
[4] Evaluation of ZIF-8 flexible force fields for structural and mechanical propertie, Acuna-Yeomans et al. (2023), doi: https://doi.org/10.1016/j.micromeso.2022.112406