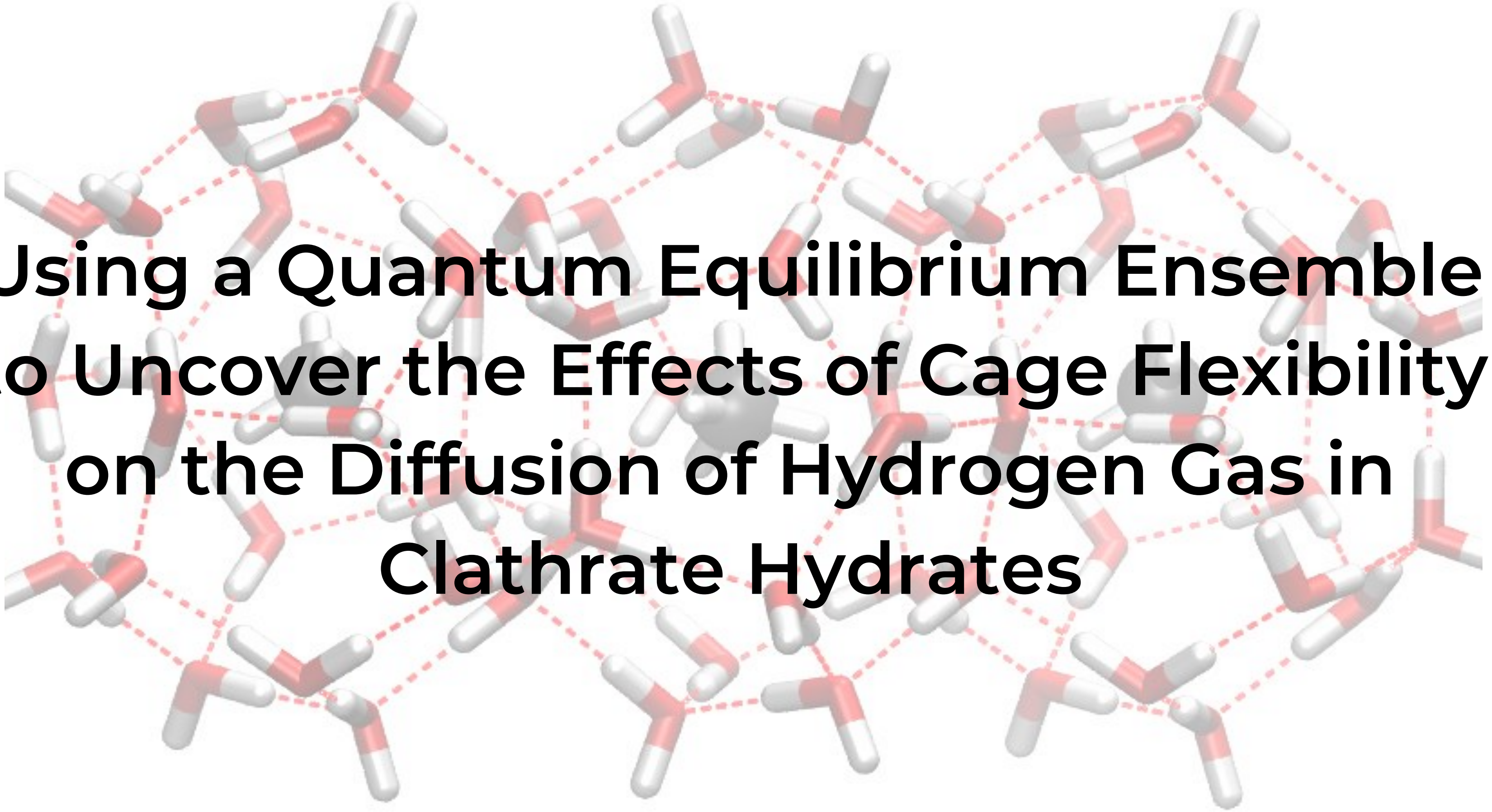

Using a Quantum Equilibrium Ensemble to Uncover the Effects of Cage Flexibility on the Diffusion of Hydrogen Gas in Clathrate Hydrates

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Abstract

Alternative energy research is turning towards hydrogen as a means of storing renewable sources, such as solar energy, and of providing clean fuel to motor vehicles. Scientists have expressed interest in clathrate hydrates in the past twenty years for their potential to efficiently store hydrogen, a task which turns out to be quite difficult. The goal is to eventually create a marketable product, but before this can be done, accurate data on clathrate hydrates must be obtained in order to prove their worth. Until the cage-to-cage diffusion mechanism of hydrogen within the crystal lattice is fully understood, such data cannot be obtained. The flexibility of the clathrate cages has been theorized to play a role in diffusion, but this has yet to be verified numerically. This study provides an answer to this problem, also providing some direction on where clathrate research should go next. Using the theory of driven adiabatic free energy dynamics, programs were written to obtain the free energy profile for diffusion at several temperatures, assuming rigid cages. Using quantum transition state theory, rates were also obtained. Observation of the differences between the results of this study and a prior study, which obtained the same results but with flexible cages, led to the conclusion that flexibility does indeed play a role in diffusion. This indicates that scientists must take into account flexibility as a factor in their simulations in the future.

Background

- **Use of Hydrogen**: Alternative Energy researchers want to use hydrogen as a means of storing renewable energy sources → renewable energy economy
- **Problems with Hydrogen Storage**: Hydrogen storage is difficult since conditions to maintain it in a dense form demand a large amount on money and energy
- **Benefits of Clathrate Hydrates:** Clathrate hydrates could solve these problems since it's energy dense, stable at higher temperatures, and made of water, one of the cheapest resources
- **Barriers to Clathrate Hydrate Technology**: To market this product, accurate data about how well it retains hydrogen is a necessity
- **Current Research**: Through simulation, scientists want to understand the processes involved in diffusion, which will help them calculate data when they scale up simulations

Literature Review (part 1)

1) Initial study found size of clathrates and initial cage occupation data experimentally

- Limitations: experimental studies can’t find accurate data on cage occupation
- 2005 Study finds that small cages are singly occupied

2) Another study found data on migration rates at different temperatures

- Model was inaccurate

3) Experimental study provided more accurate cage-to-cage migration data

- Data was still inaccurate because it only examined ortho-hydrogen, and not para-hydrogen

Literature Review (part 2)

4) 2015 study → investigated large-to-small and large-to-large diffusion as well

- Limitations: failed to account for quantum effects
- However, it did suggest flexibility as a possible factor that affects diffusion

5) 2016 study → investigated quantum effects, finding them clearly present around lower temperatures and deeming them significant at most temperatures

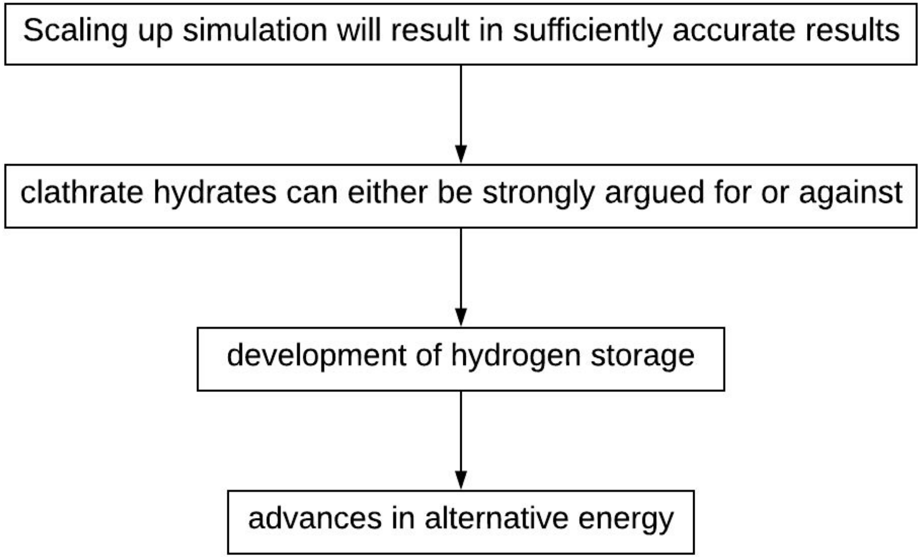
- Limitations: still hasn't considered flexibility

Research Problem

- Flexibility is an issue that has yet to be addressed but could have a large effect on the results.
- Now that quantum effects are known to be important, especially at low temperatures, a much more accurate picture can be drawn by testing the effects of flexibility in a quantum system

Significance

- Once the issue of flexibility is resolved, diffusion data at the small scale will be closer if not at the point where simulation can be scaled up



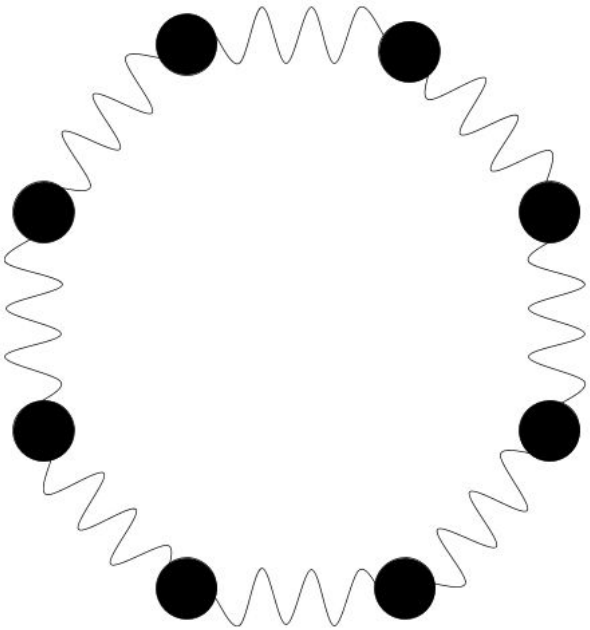
Prior Methodologies (part 1)

Path Integral Molecular Dynamics

- Feynman's path integral formulation → particles act like necklaces made of springs and beads
- Centroid is commonly taken before quantities such as free energy are calculated → efficiency (yet in some cases leads to

$$Q_P(N,V,T) = \prod_{i=1}^{N}\left(\frac{m_i P}{2\pi\beta\hbar^2}\right)^{dP/2}\int\prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i^{(1)}\cdots \mathrm{d}\mathbf{r}_i^{(P)} \mathrm{d}\mathbf{p}_i^{(1)}\cdots \mathrm{d}\mathbf{p}_i^{(P)}$$

$$\times\exp\left\{-\beta\sum_{k=1}^{P}\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^{(k)^2}}{2m_i'}+\sum_{i=1}^{N}\frac{1}{2}m_i\omega_P^2\left(\mathbf{r}_i^{(k+1)}-\mathbf{r}_i^{(k)}\right)^2+\frac{1}{2}U\left(\mathbf{r}_1^{(k)},\ldots,\mathbf{r}_N^{(k)}\right)\right]\right\}$$



Prior Methodologies (part 2)

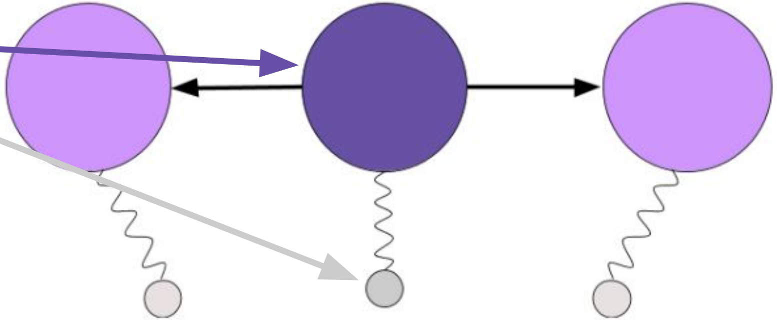
Driven Adiabatic Free Energy Dynamics

- Employs a massive high energy virtual particle which couples to the physical particles → it drags the physical particles around the accessible phase space, allowing for a faster sampling of rare events (points of high free energy)

$$\tilde{\mathcal{H}}(\mathbf{r},\mathbf{p},s,p) = \mathcal{H}(\mathbf{r},\mathbf{p}) + \sum_{\alpha=1}^{n}\left[\frac{p_\alpha^2}{2\mu_\alpha} + \underbrace{\frac{1}{2}\kappa_\alpha \left(q_\alpha(\mathbf{r}) - s_\alpha\right)^2}_{\textbf{Coupling}}\right]$$

$$F_\alpha(s) = \langle \kappa_\alpha \left(q_\alpha(\mathbf{r}) - s_\alpha\right)\rangle$$

$$A(s_1,\ldots,s_\alpha) = -\int \prod_{\alpha=1}^{n} F_\alpha(s)\mathrm{d}s_\alpha$$



Prior Methodologies (part 3)

Quantum Transition State Theory

- First, calculate the probability of the collective variable hitting the transition state:

$$P(q_c^\ddagger) = \frac{e^{-\beta A(q_c^\ddagger)}}{\int_{q_0}^{q^\ddagger} e^{-\beta A(q_c)} \mathrm{d}q_c}$$

- Then, calculate the “static” quantum rate:

$$k_{\mathrm{QTST}} = \frac{1}{\sqrt{2\pi\beta\mu}} P(q_c^\ddagger)$$

Computational Methods

Equations

$$F_\alpha(s) = \langle \kappa_\alpha \left(q_\alpha(\mathbf{r}) - s_\alpha\right)\rangle$$

$$A(s_1, \ldots, s_\alpha) = -\int \prod_{\alpha=1}^{n} F_\alpha(s)\mathrm{d}s_\alpha$$

$$P(q_c^\ddagger) = \frac{e^{-\beta A(q_c^\ddagger)}}{\int_{q_0}^{q^\ddagger} e^{-\beta A(q_c)}\mathrm{d}q_c}$$

$$k_{\mathrm{QTST}} = \frac{1}{\sqrt{2\pi\beta\mu}}P(q_c^\ddagger)$$

Computational Phases

Parameters were chosen based on previous studies and inputted into the PINY_MD package. The resultant output of the simulations was set to be a list of q_c -values versus κ(q(r)-s))

The data was filtered into a histogram with a specific bin length, and the average of κ(q(r)−s) was taken in each bin, which is equal to the mean force at the point q

The mean force was numerically integrated by means of the midpoint rectangular approximation method

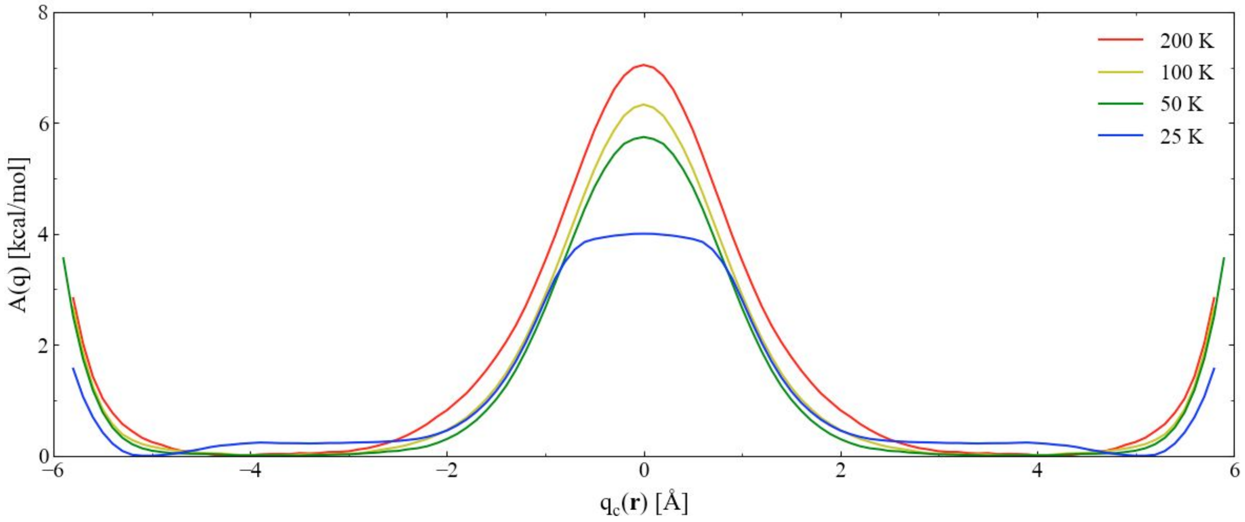
The free energy profiles were made symmetric by averaging each +q and −q, and the graphs were shifted to intersect the q

The static quantum transition state rates of diffusion were calculated using the equations of QTST and the numerical integration scheme employed was the trapezoidal method.

Results (part 1): Temperature Comparison

A temperature comparison indicates that, as expected, tunneling is more present at lower temperatures

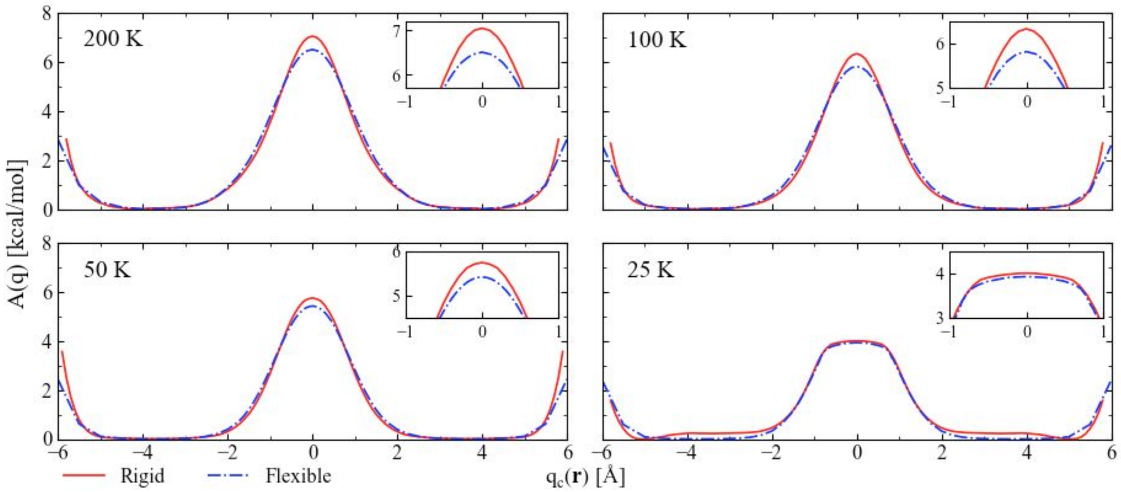
Also, the dip in the 25 K curve is due to simulation error (discussed later)



Results (part 2): Free Energy Comparison

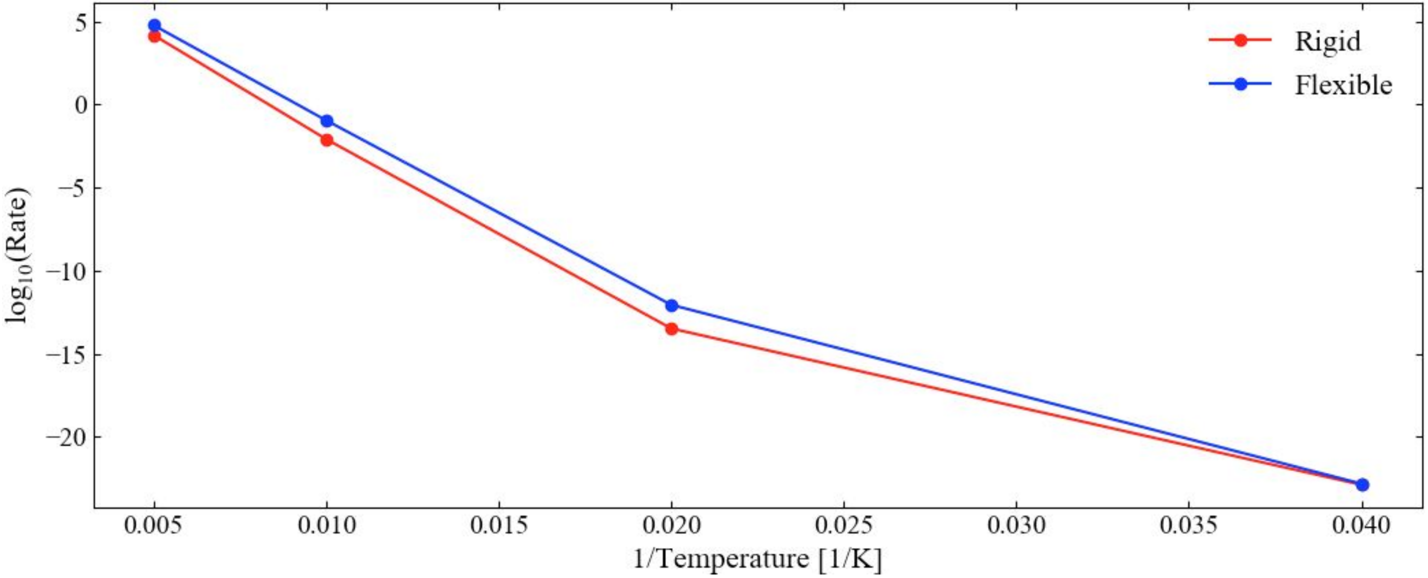
Flexibility vs Rigid graphs at each temperature indicate that flexible cages have lower free energies (as hypothesized)

Also, as temperature decreases, the curves get closer together, since flexible cages can't expand at low temperatures even if there is no constraint imposed



Results (part 3): Diffusion Rate Comparison

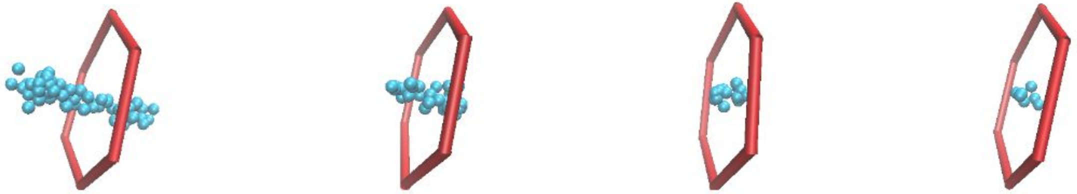
Rates graphed on a log scale show that, as expected from the previous graphs, the flexible rates are higher than the rigid rates at each point, and the rates move closer together at the low temperatures



Results (part 4): An Interesting Result

The table of rates along with the graph on the previous slide indicate that the mid-range temperatures have larger differences between the rates. This is likely due to the shape of the bead spring necklace

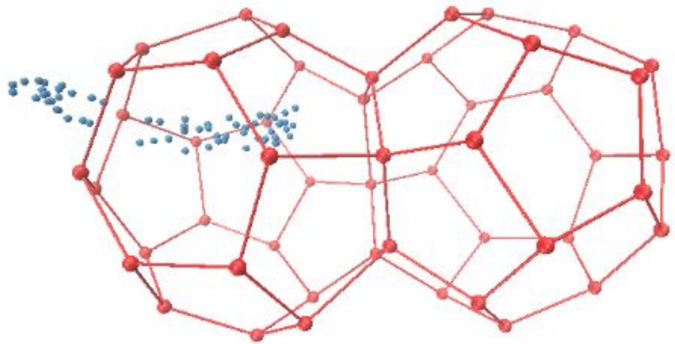
Temperature	Rigid Rate	Flexible Rate	Factor of Increase
200 K	$1.517 \cdot 10^{4}$	$5.960 \cdot 10^{4}$	$3.928 \cdot 10^{0}$
100 K	$8.343 \cdot 10^{-3}$	$1.124 \cdot 10^{-1}$	$1.348 \cdot 10^{1}$
50 K	$3.327 \cdot 10^{-14}$	$8.921 \cdot 10^{-13}$	$2.648 \cdot 10^{1}$
25 K	$1.319 \cdot 10^{-23}$	$1.523 \cdot 10^{-23}$	$1.155 \cdot 10^{0}$

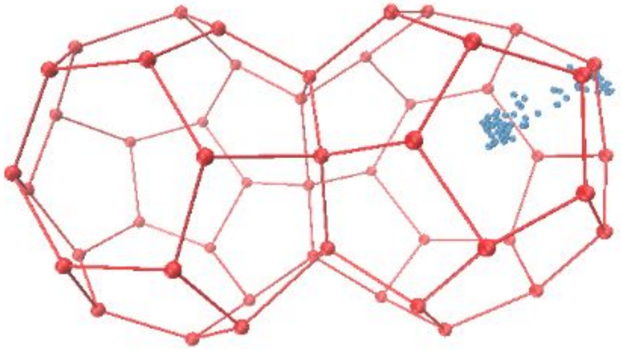


(a) 25K (b) 50K (c) 100K (d) 200K

Results (part 5): Error Points

Due to the use of a soft harmonic barrier, some of the beads poked out of the walls, and this ended up causing the dip in the 25 K data. This however, doesn't change the conclusions from the results because the expected results still occurred, and either way, the main temperatures scientists care about are around 100 K anyway.





Conclusion

- It is without doubt that flexibility of the cages affects the free energy and diffusion rates of hydrogen → simulations in the future must not assume cage rigidity
- The next steps are either to expand simulation scale or to look further into the effects of cage occupancy
    - This study is crucial for those next steps so that sufficient accuracy is maintained throughout simulation
- In time, hopefully clathrate hydrate researchers can use these results to put forth an efficient and elegant solution to hydrogen storage, promoting the switch to alternative energy

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