Negative Thermal Expansion in Zeolites
Lennard Jones Thermal Expansion Curve

Substances other than zeolites cannot shrink when given more energy from an increase in temperature as it has to overcome a large potential barrier caused by Pauli exclusion principle.

- Locus of mean separations
- Vibration amplitude at low temperature
- Not symmetrical changes in energy when separating, therefore it is easier to pull atoms apart than push them together.
Introduction

• What are Zeolites?
  – crystalline, porous aluminosilicate
  – related to phases of SiO$_2$
  – crystal structure
  – low density
  – widely used in industries for water purification and nuclear reprocessing
Open structure example; Zeolite ZSM-5

Pore space

H₂O molecule is released from here
Introduction

• Zeolites studied in this project
  – PHI

Composite building unit:
Introduction

• Zeolites studied in this project
  – NAB

Composite building unit:
Aim

• To determine if the zeolites selected show negative thermal expansion
Procedure

• Choose a zeolite from the database
• Create a virtual reality simulation
• Run the simulation for a wide range of temperatures
• Obtain the results and plot graphs
• Look out for negative thermal expansion or any other interesting results
Procedure

• Simulations
  – Operating System: Linux
  – Molecular Dynamics Program used is called DL_POLY
  – Download zeolite’s structure CIF file
  – Input files: CONFIG, FIELD, CONTROL
  – Output files: OUTPUT, STATIS, REVCON
  • To be viewed in a web browser
  • Relevant information extracted to be viewed in excel file
PHI’s structure

SiO$_4$ tetrahedra

Linked at corners (oxygen atoms)
Graph to show the change in average volume as temperature increases for Zeolite PHI
Graph to show the correlation between average volume and temperature in Zeolite PHI, excluding anomalous data.
Analysing the results...

PHI does not exhibit a strong positive correlation between volume and temperature. The results show the PHI is both shrinking at the same rate as it is expanding.

Explanation: The tetrahedra are moving into the gaps. However this is not fast enough to have enough of an overall shrinking effect on the framework structure.
The thermal expansion of the bonds is caused by an increase in temperature; when this occurs, the bond separation in the zeolite increases, causing its volume to expand. Bonds require less energy to expand than they need to contract, therefore it is more likely that most materials increase in volume when temperature is increased.
Zeolite NAB

The graph below shows the results from the simulation that I made; unfortunately, as seen below, it does not go through negative thermal expansion, as the volume of the zeolite and the increase in temperature has a positive correlation.
Result for Zeolite MFI
Zeolite MFI’s structure
Conclusion

NAB  PHI  MFI