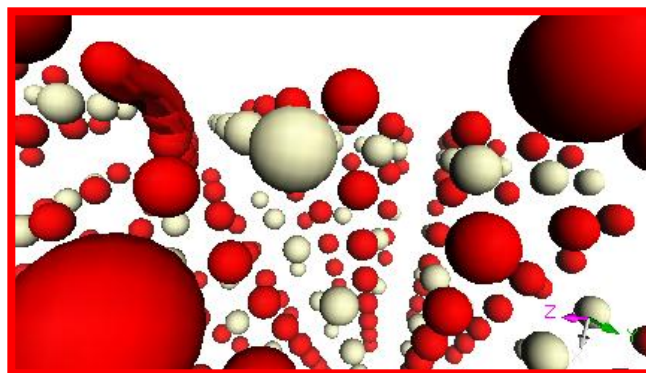




‘Unlocking the Oxygen Storage Capacity of Ceria’ – a research-linked learning resource

Dr Paul Martin

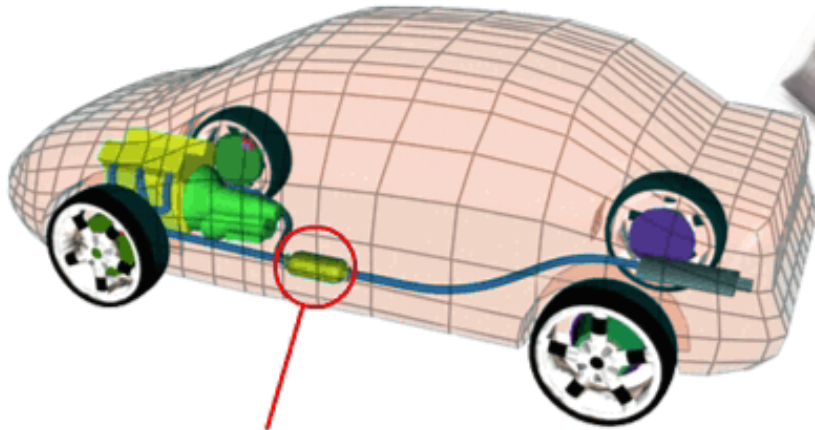
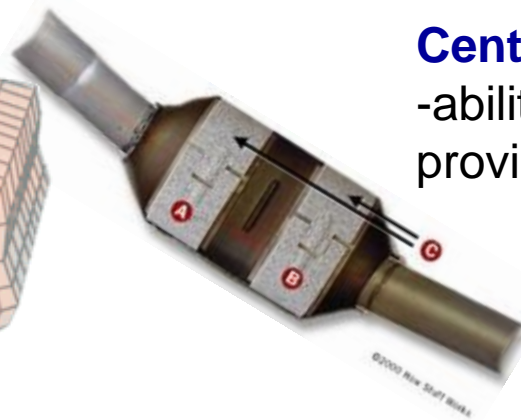


Why Ceria ?



Technological Uses:
Catalysis, Ionic Conductor
Gas Sensor, Fuel Cell
Component

Central reason for use:
-ability to store (OSC) and
provide oxygen for reactions



Typical Catalytic
Converter Location

Case Study Has potential to **Introduce** aspects and provide **background** knowledge of :

1. Surface Chemistry – Defect Chemistry
2. Environmental Chemistry
3. Catalysis and Kinetics
4. Thermodynamics
5. Solid State

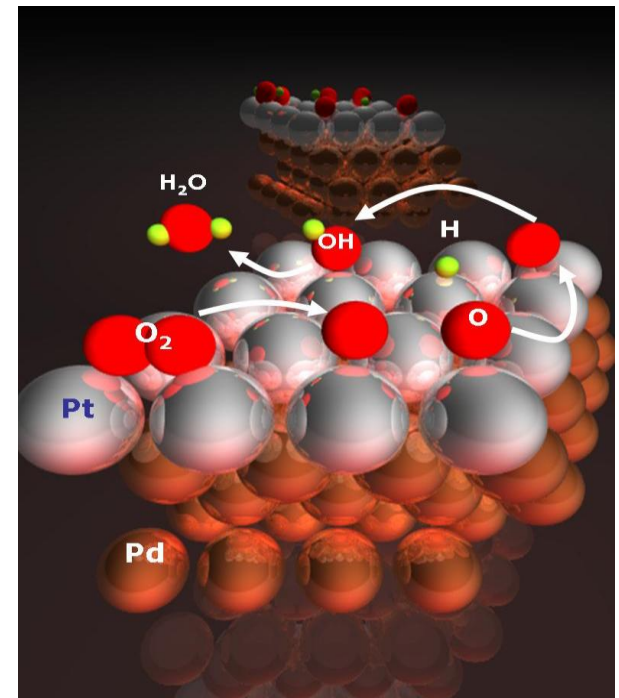
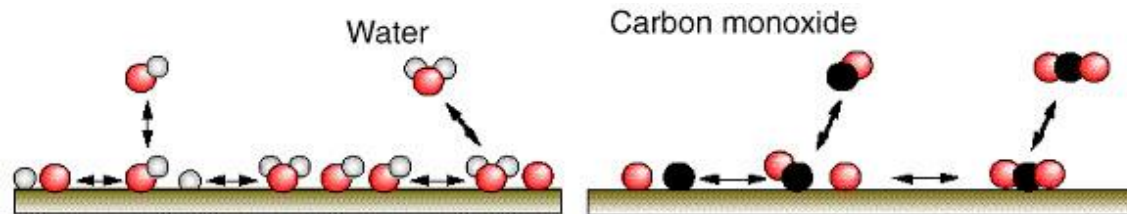
Introduce both Experimental (eg Microscopy {STM}) and Modelling & Simulation Approaches

Why Surfaces ?

Surfaces are like people, it is their defects that make them interesting

1951: (F.C. Frank – Materials Scientist) The Theory of Oriented Overgrowth of Crystals

1. Almost all of the industrial chemical processes involve heterogeneous catalysis and the **chemistry occurs at surfaces and involves adsorption of reactants.**
2. It is at surface defects where we get an active site where the chemistry occurs



Which Advanced Techniques ?

- Research/analysis of literature
- Experimental investigations of surfaces
- Experimental techniques
- Introduction to Chemo-informatics exercise
- Real example symbiosis between theoretical/experimental research and techniques
- Introduction to Computer Modelling and simulation – Building a model. Multi-scale modelling exercise.
- Blended approach: traditional lectures, computing lab slots, research-linked and PBL sessions

- **Research/analysis of literature**

VOLUME 79, NUMBER 21 P H Y S I C A L R E V I E W L E T T E R S

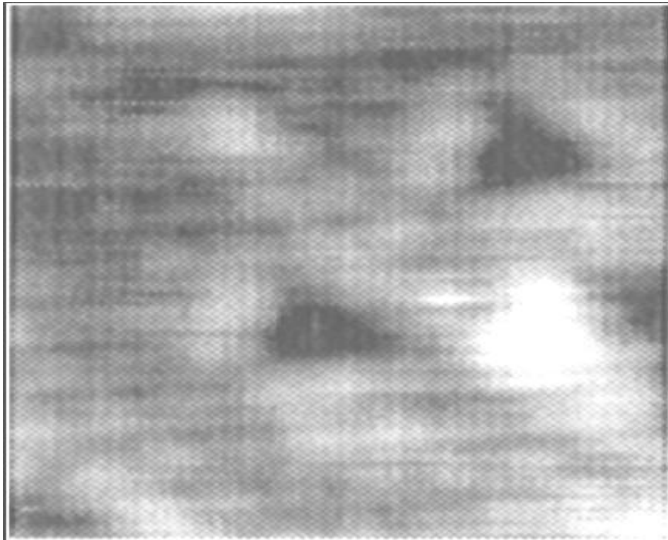
24 NOVEMBER 1997

**Defect Structure of Nonstoichiometric CeO₂ {111} Surfaces Studied
by Scanning Tunneling Microscopy**

H. Nörenberg* and G. A. D. Briggs

University of Oxford, Department of Materials, Parks Road, Oxford OX1 3PH, United Kingdom

(Received 23 July 1997)



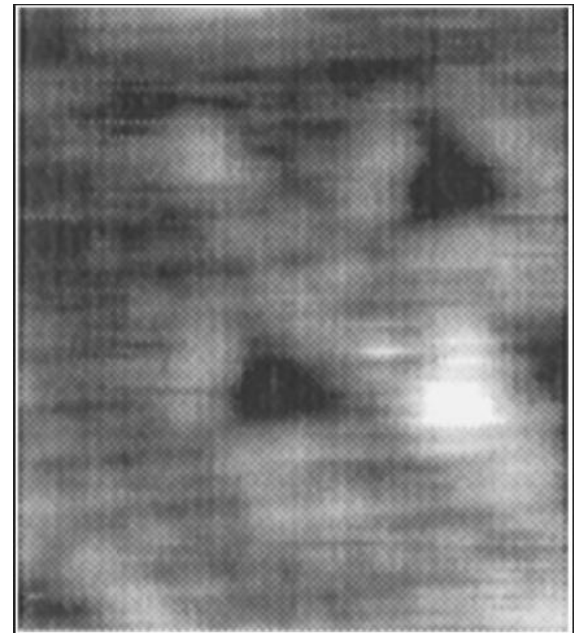
STM image of triangular defects on nonstoichiometric CeO₂ {111} showing enhanced brightness at the defect edges, image size 35 Å 3 40 Å, *U*_{bias} - 22.5 V, *I*_T - 10 pA, RT.

A Multidisciplinary Surface Science Project

You have been assigned to help investigate the possibility of the formation of potentially important catalytic sites on the surface of ceria.

Experimentalists have taken images of what they suspect are triangular vacancy clusters

As a respected chemist and materials modeller you are being contracted to collaborate with a multi-disciplinary surface science research group to investigate further these potentially important catalytic sites.



Your Expert Opinions are required: The 1st project decision

From what we know about molecular dynamics and from what we have seen from molecular dynamics studies of oxygen migration in ceria surfaces in the literature.

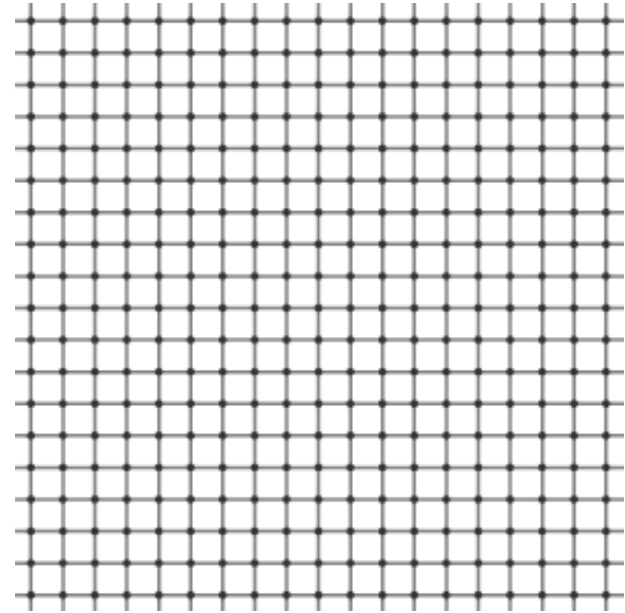
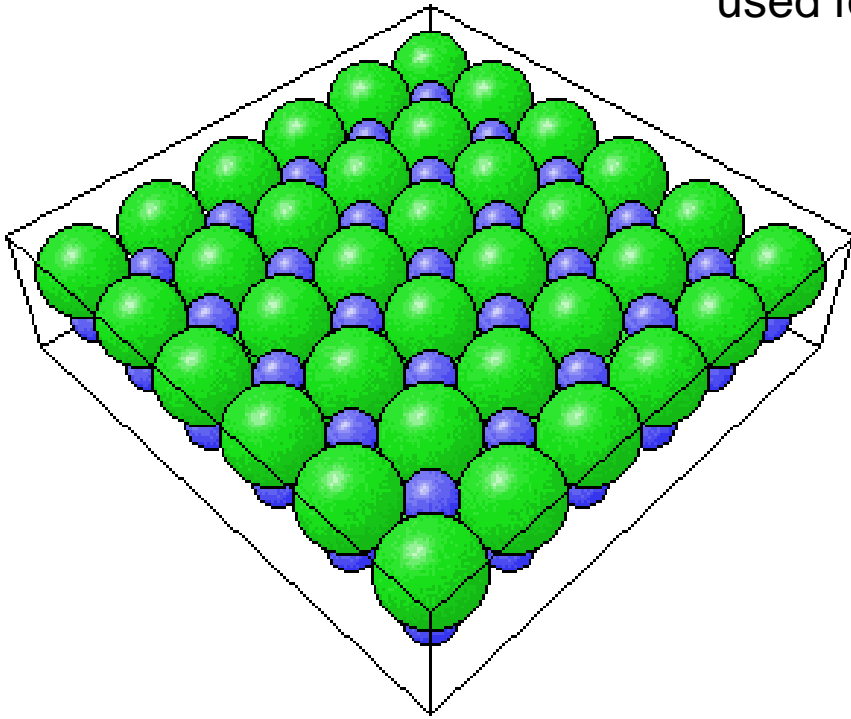
- Comment on what you think are the reasons behind a decision to go for a mesoscale approach, and not using a molecular dynamics simulations for a larger surface area model.

The Task

- You are being contracted to provide advice in computational solid state chemistry.
- 2 general areas of concern
- 1... Representing solid-state surface ion positions in computer memory.
- 2... Describing the anisotropic oxygen migration at the surface of ceria in terms of a logic table.
- The scientific programmers need this information to then write object-orientated code to simulate ceria surfaces at the mesotopic level

Co-ordinate systems.....

Project partners realise that we need to be able to describe the structure of a given surface in computer memory, that can be subsequently used for simulation experiments



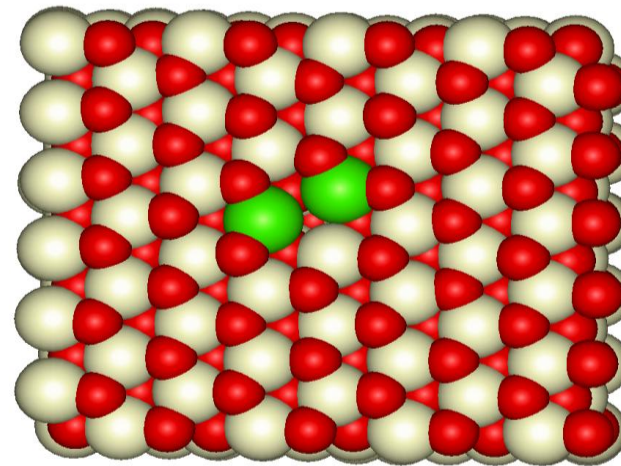
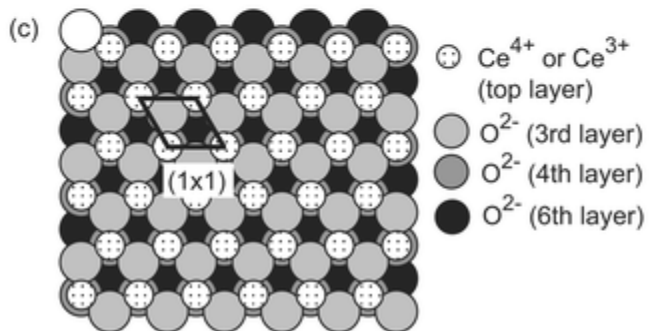
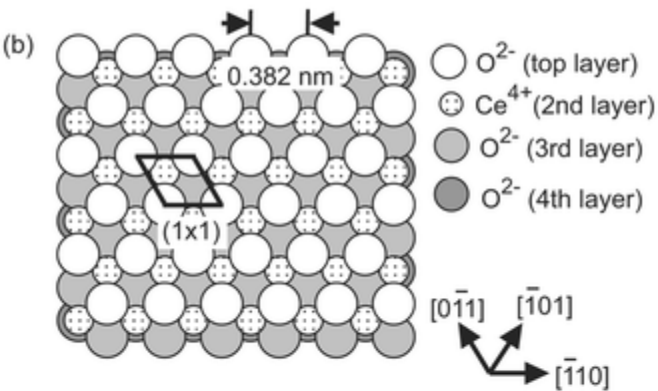
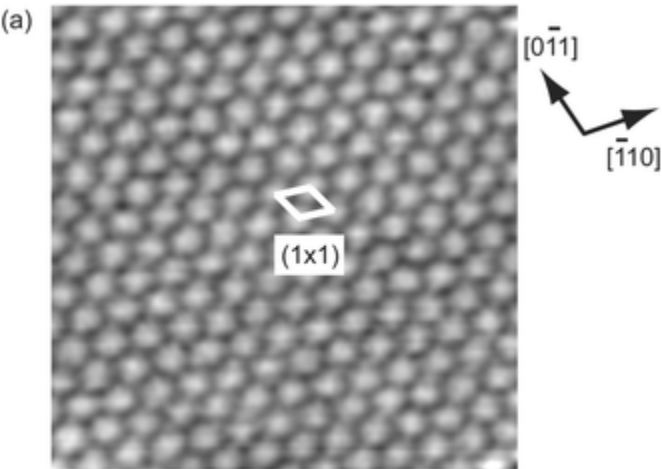
$$2D_Array = [x_0 \dots x_n] \cdot [y_0 \dots y_n]$$

And then each coordinate position is given a file with data about an ion in that position

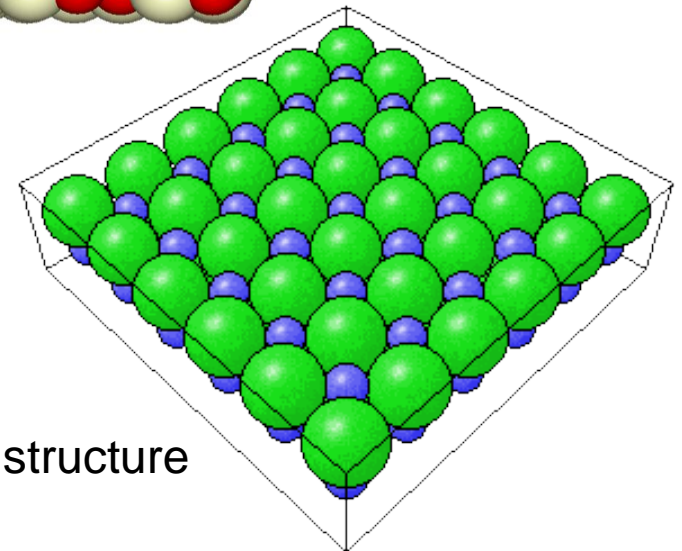
- What data/information about each respective ion would be needed ?

The Stable Surface of Ceria

STM Images



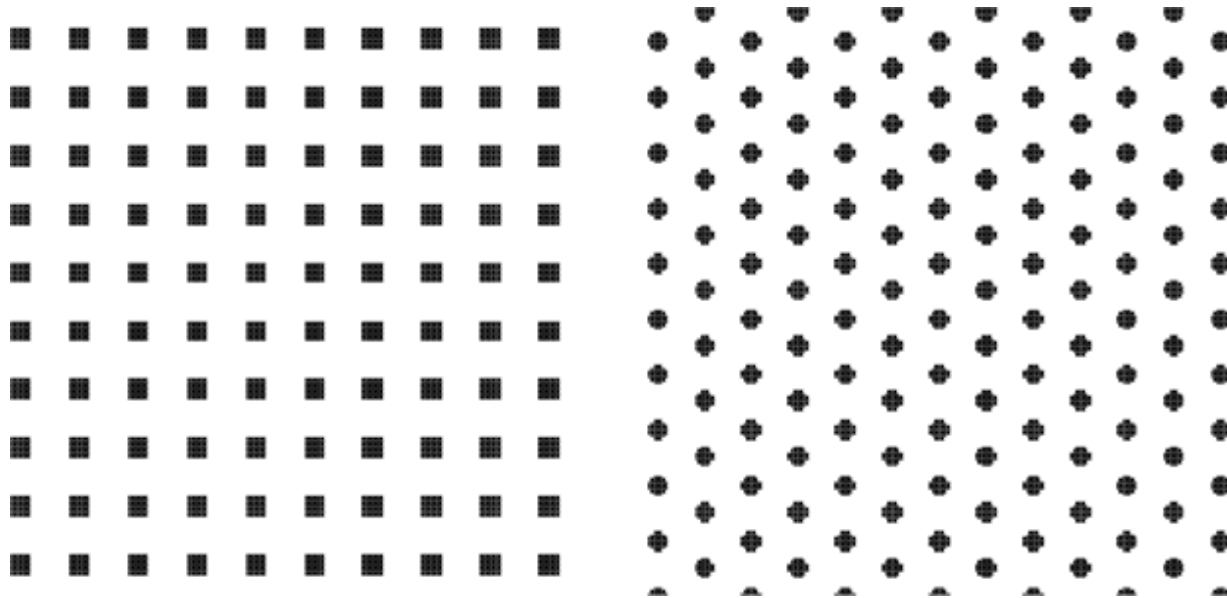
Hexagonal structure




Square lattice structure

- What are the differences in surface structure (square v hexagonal), describe them ?

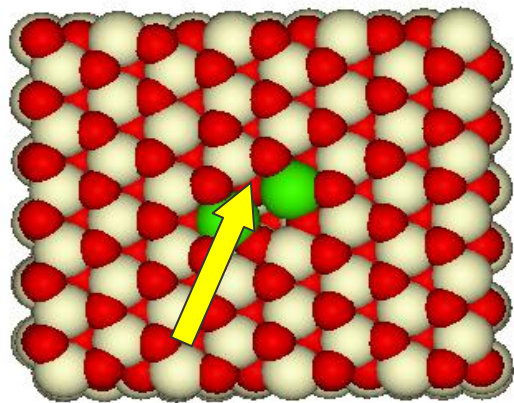
Lattice co-ordinate conversion



Square_2D_Array = $[x_0 \dots x_n] \cdot [y_0 \dots y_n]$  Hexagonal_2D_Array = $[x_0 \dots x_n] \cdot [y_0 \dots y_n]$

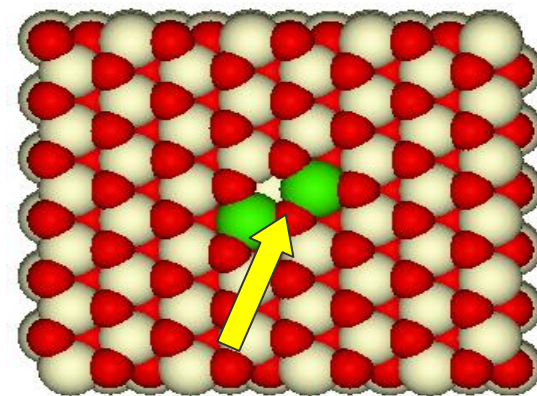
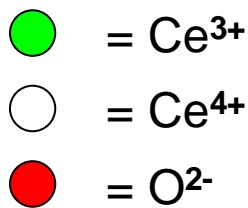
- 1...What are the operations and steps to go from one to the other
- 2...How would you do the same for a 3-D lattice coordinate system

Theoretical Case Study: Oxygen Migration at a Charge Compensating Surface Defect Cluster

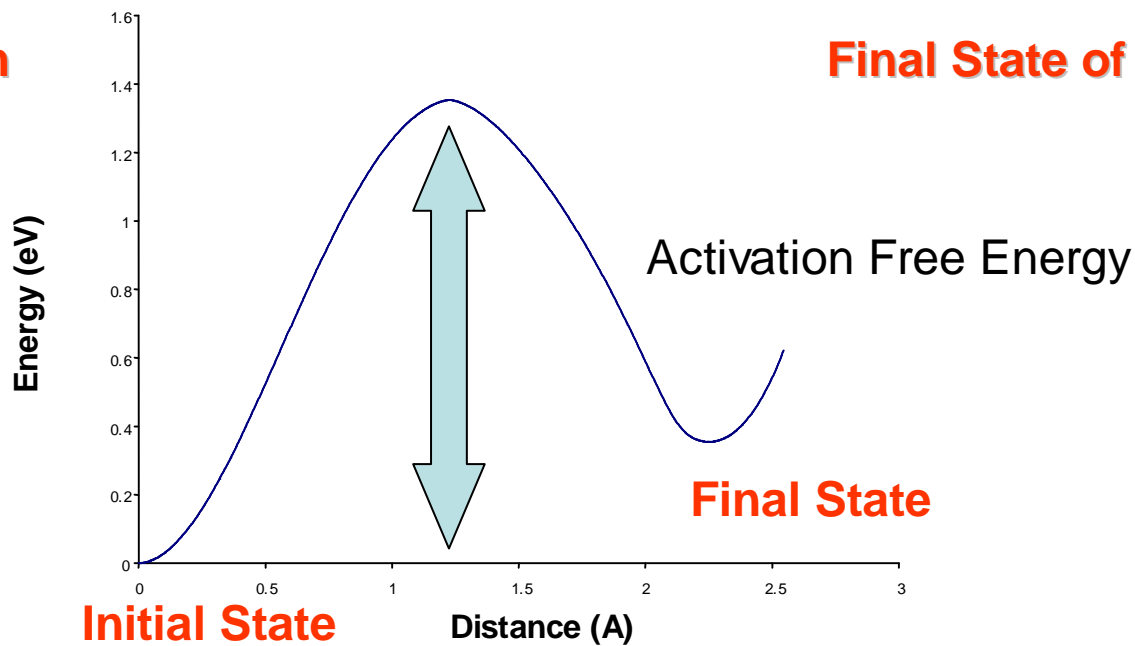


Initial State of System

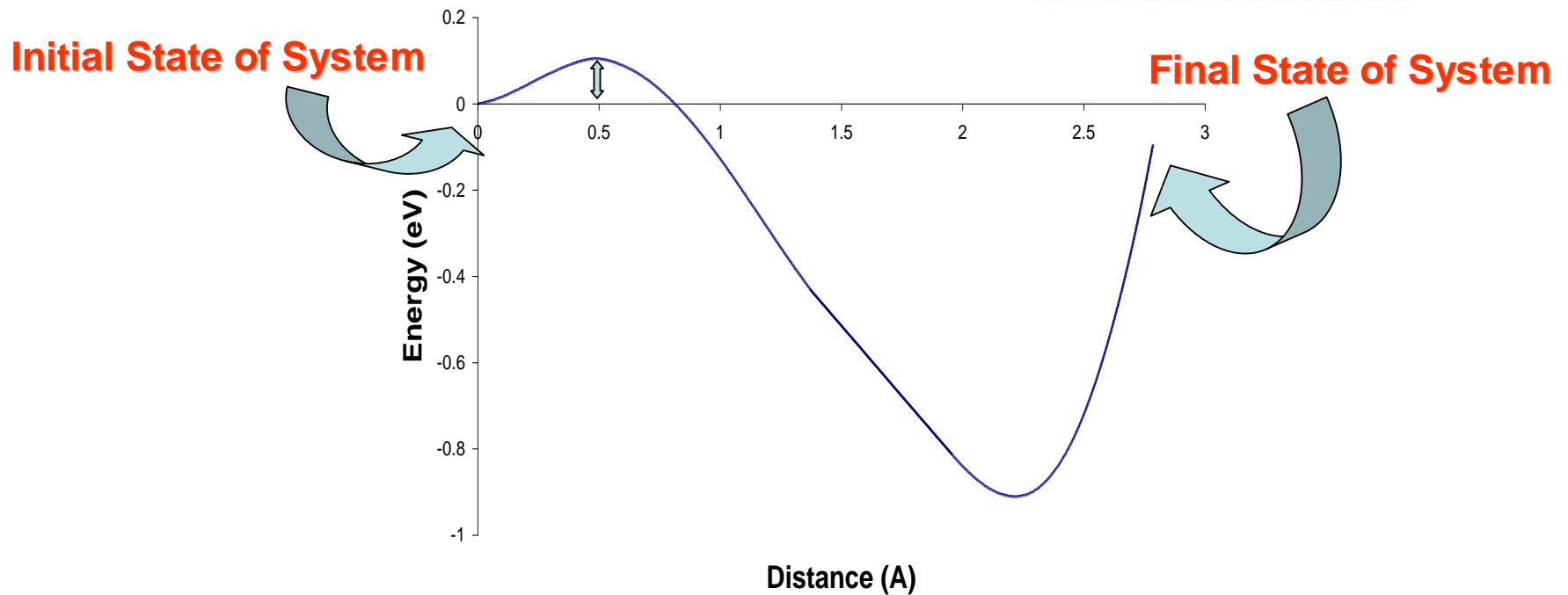
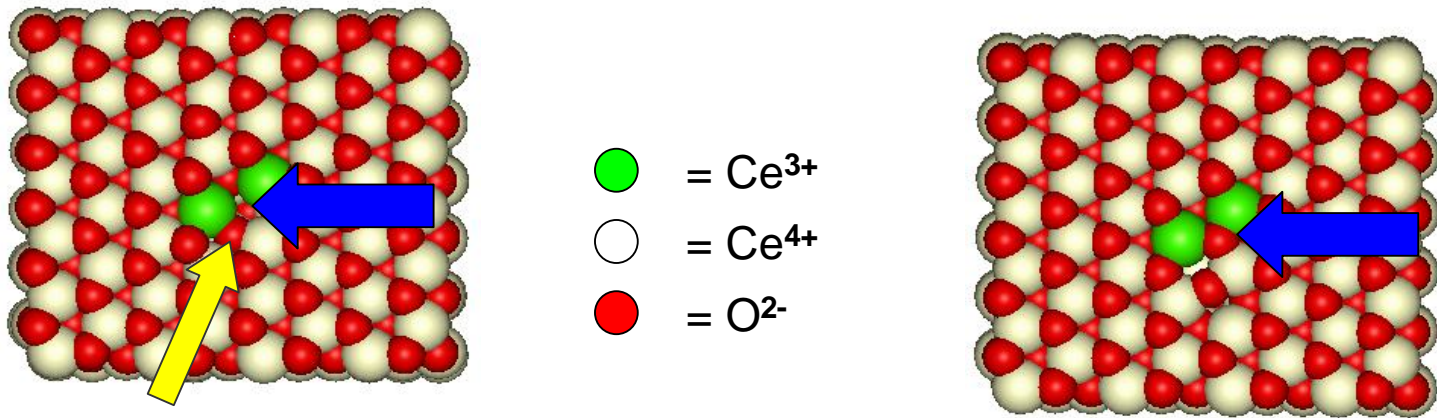
Treat the charge compensating defects as localised electrons on neighbouring cerium ions.



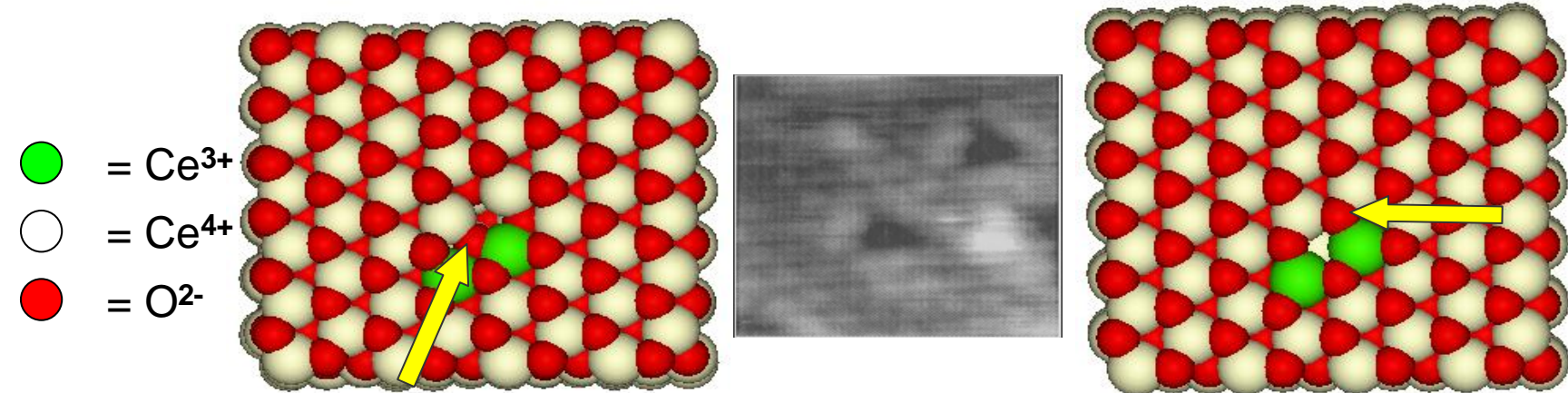
Final State of System



Large Anisotropic Effect on Migration

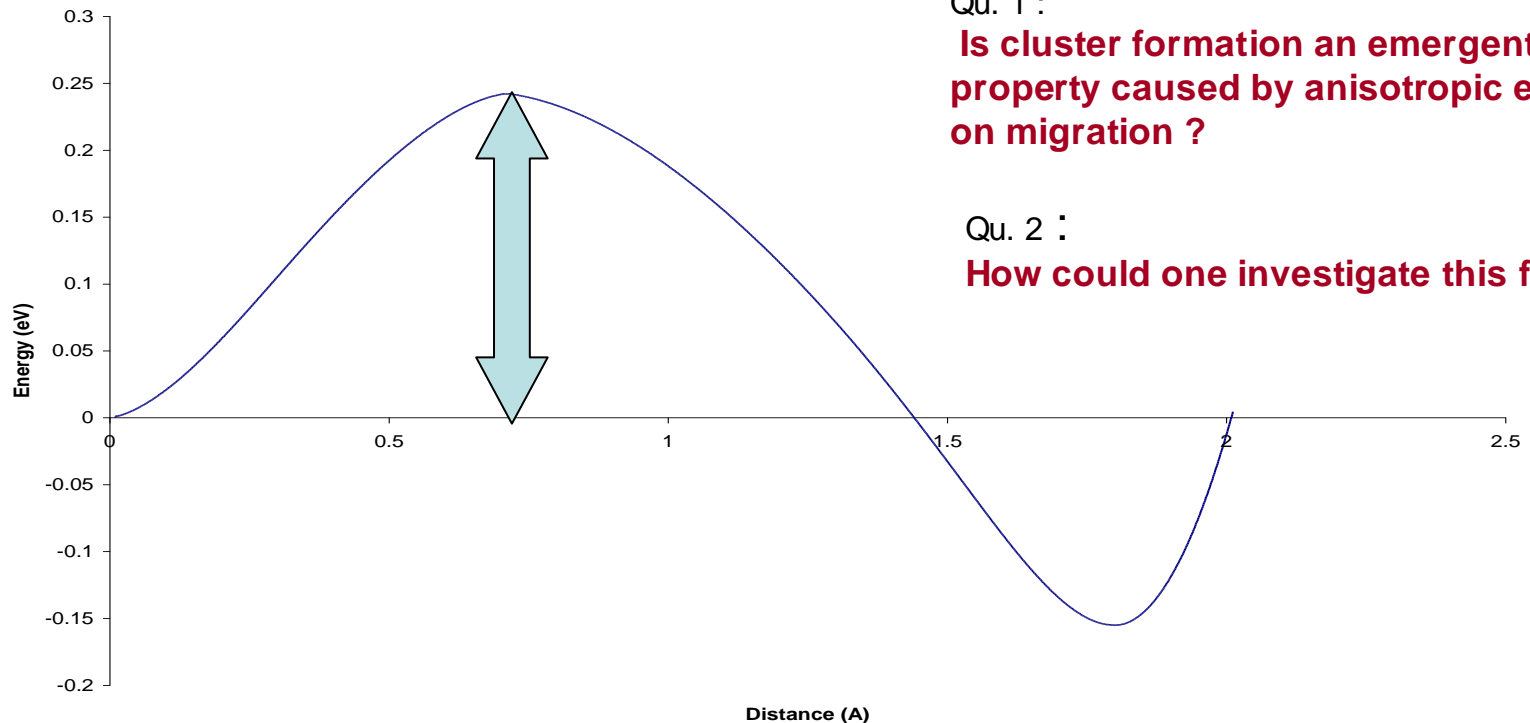


Large Anisotropic Effect on Migration



Initial State of System

Final State of System



Qu. 1 :

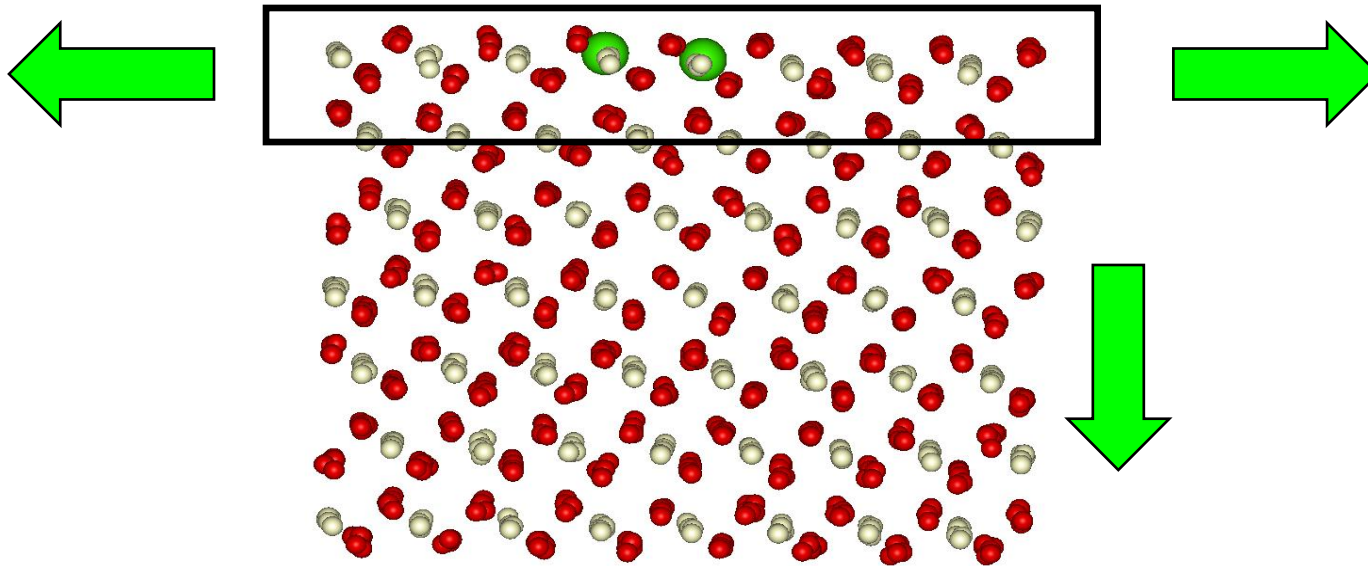
Is cluster formation an emergent property caused by anisotropic effect on migration ?

Qu. 2 :

How could one investigate this further ?

m.d. simulation Mesoscale

To simulate a large enough surface area, one would require a massive slab !

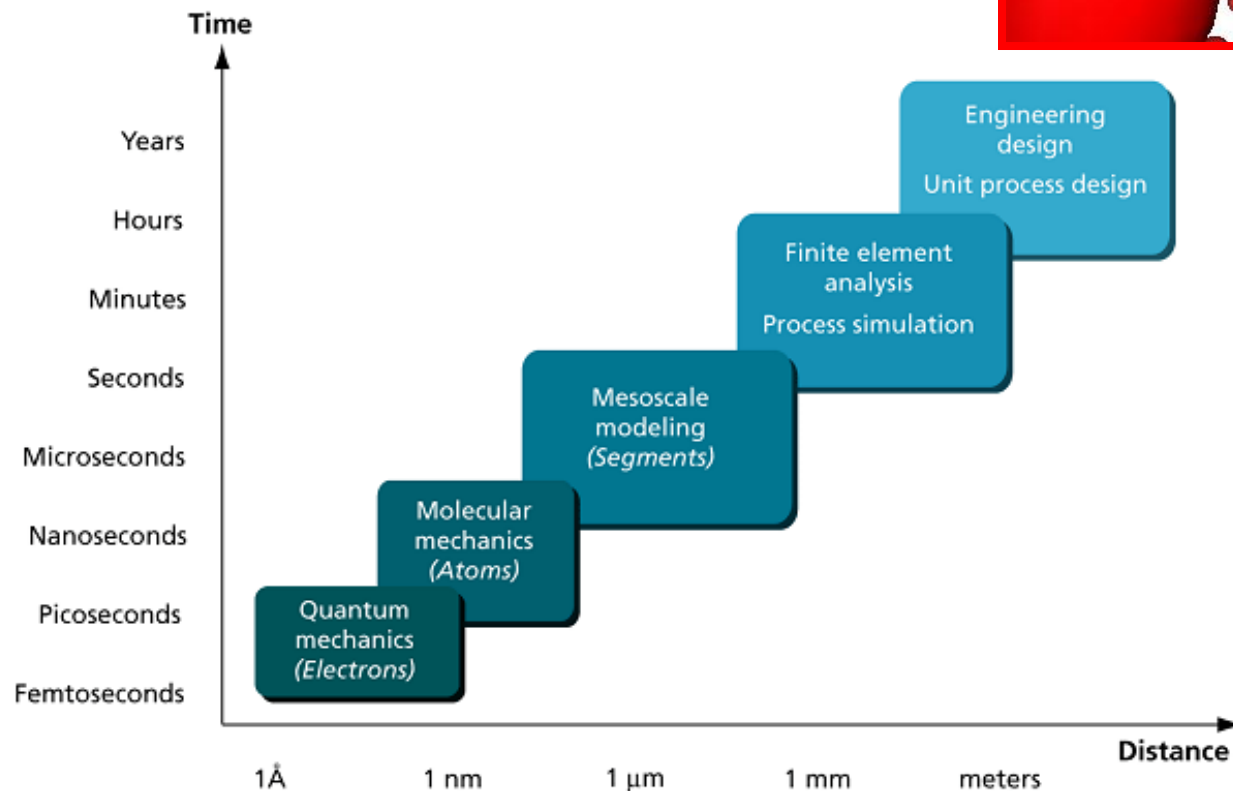
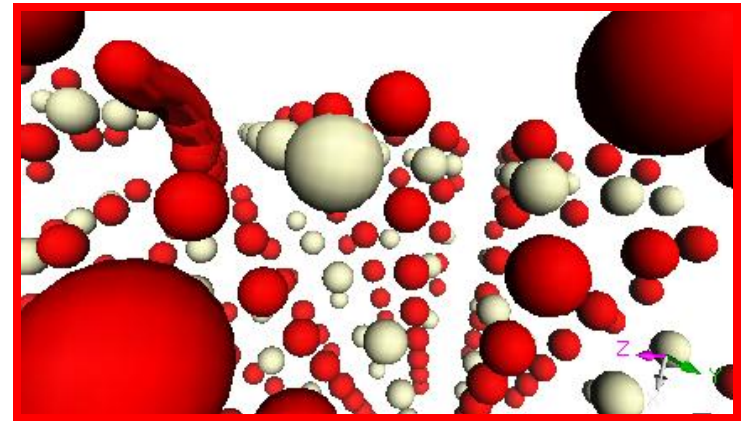


.....so, can we think of alternatives ?

Remember: Surface behaves differently to bulk material

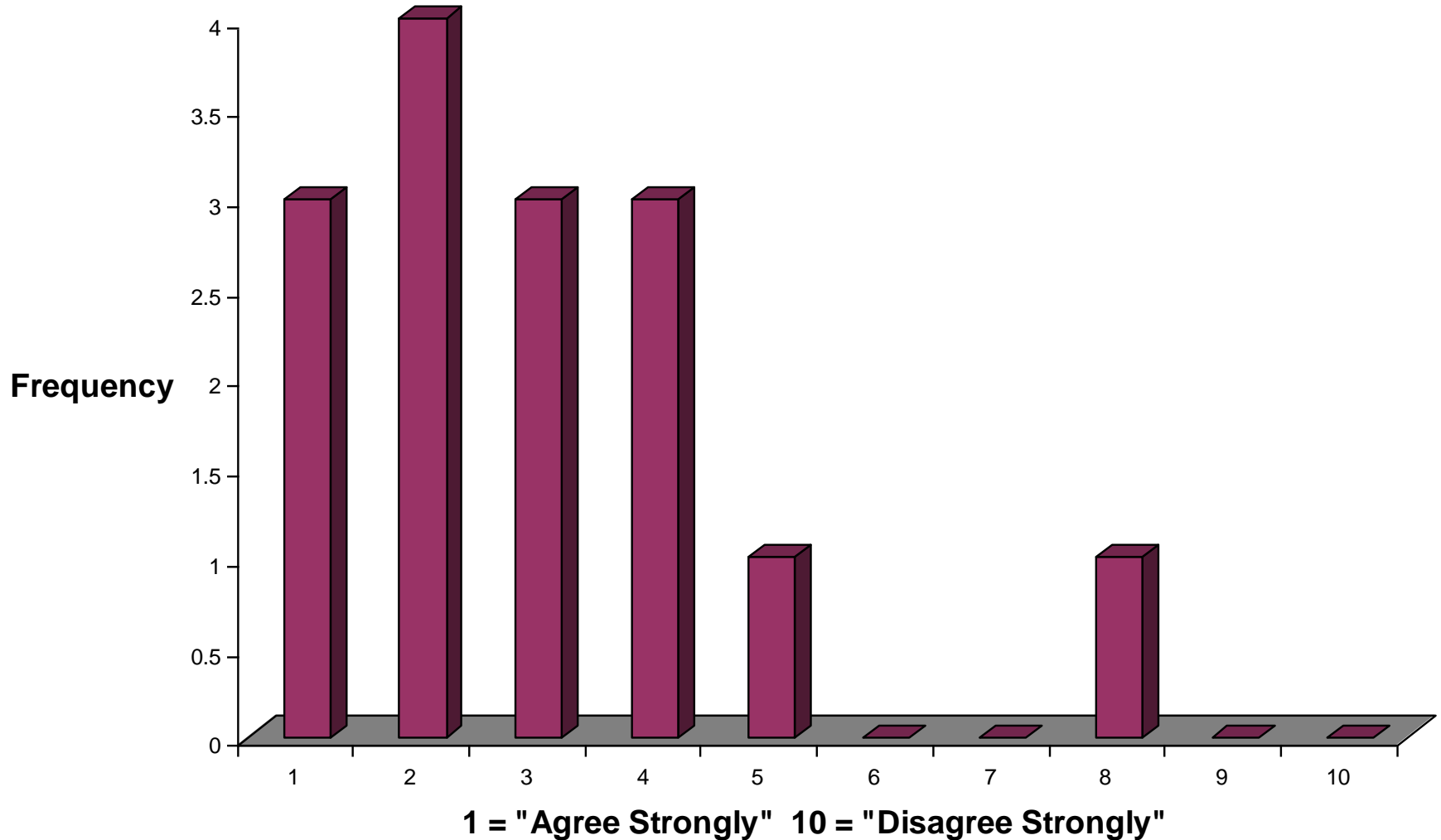
Solution: An Un-coupled, mesoscale surface simulation, based on anisotropic oxygen migration at surface.

A Multiscale simulation approach: Take atomistic model results and feed into a mesoscale model

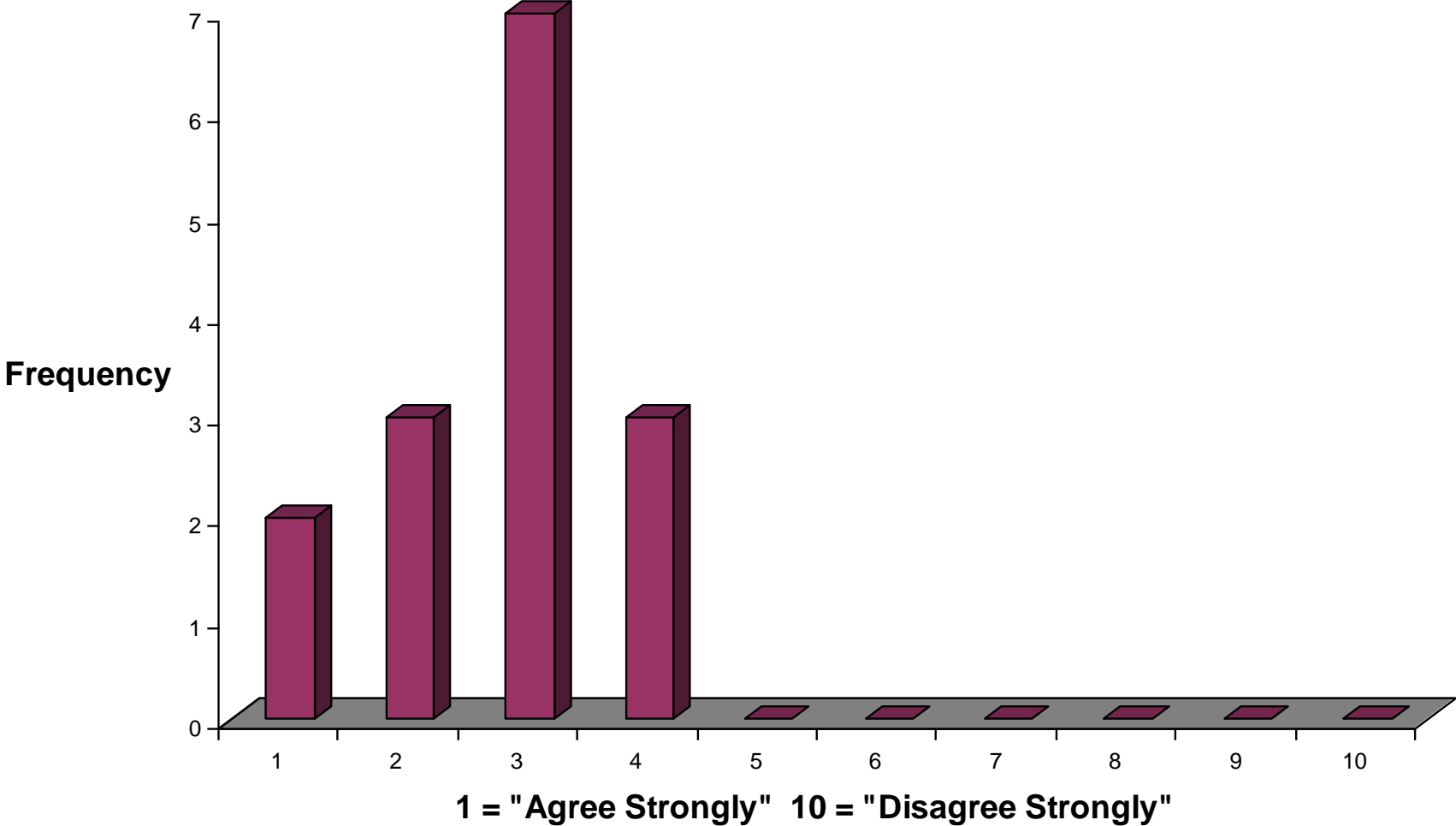


Samples of Student Feedback.....

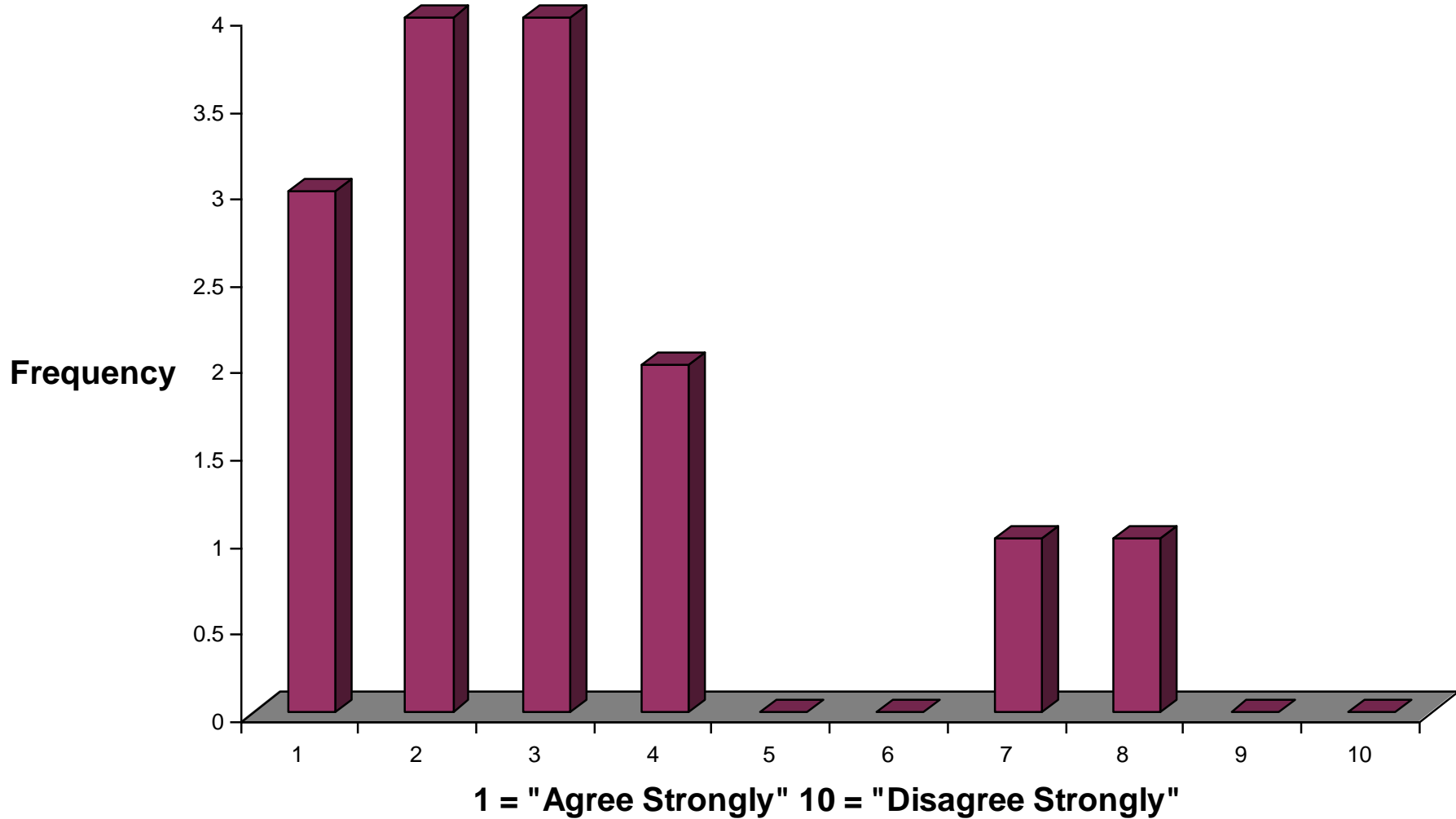
The case-study was interesting



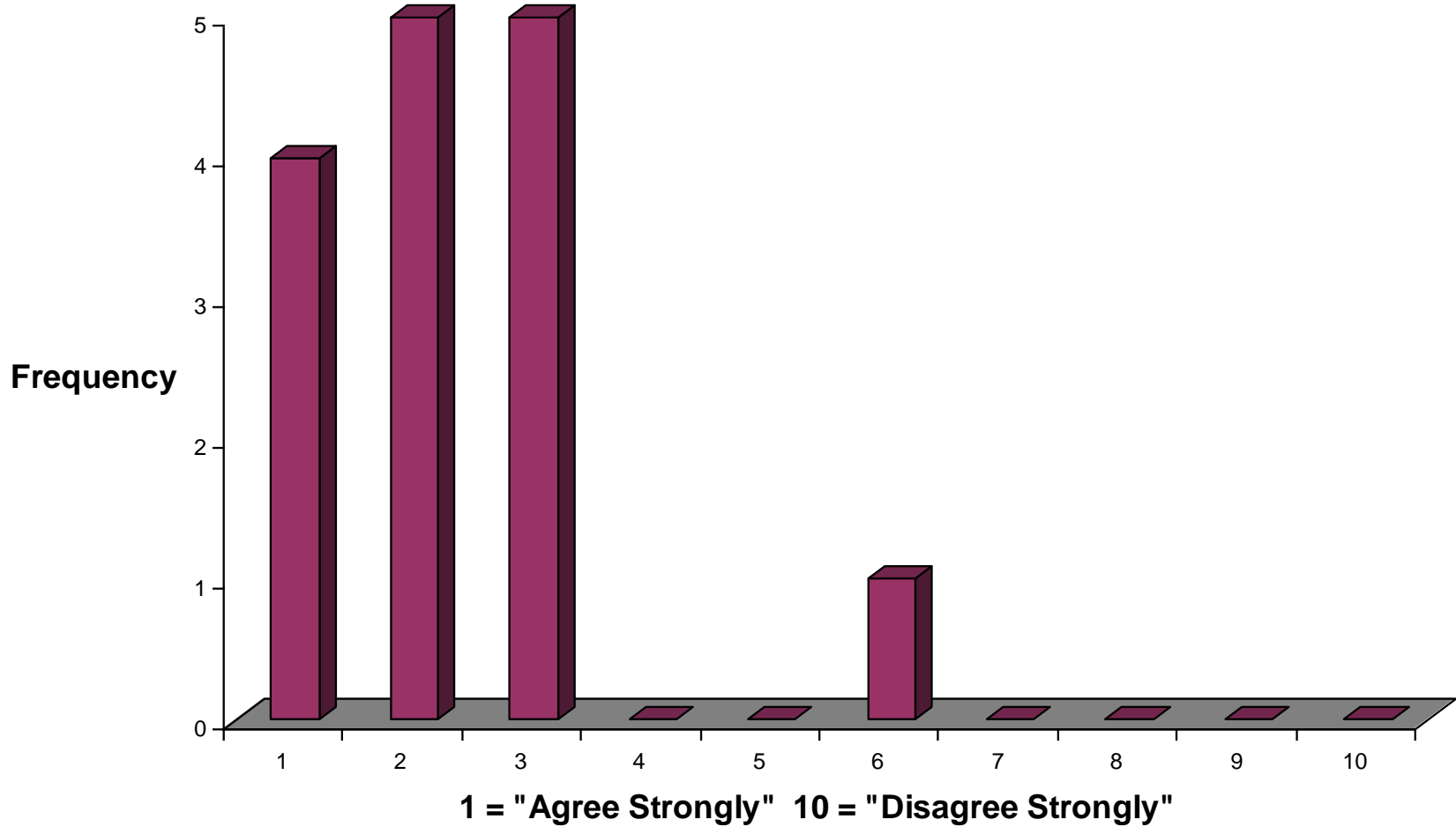
**The Case Study enabled me to make more sense of theory (eg
Thermodynamics)**



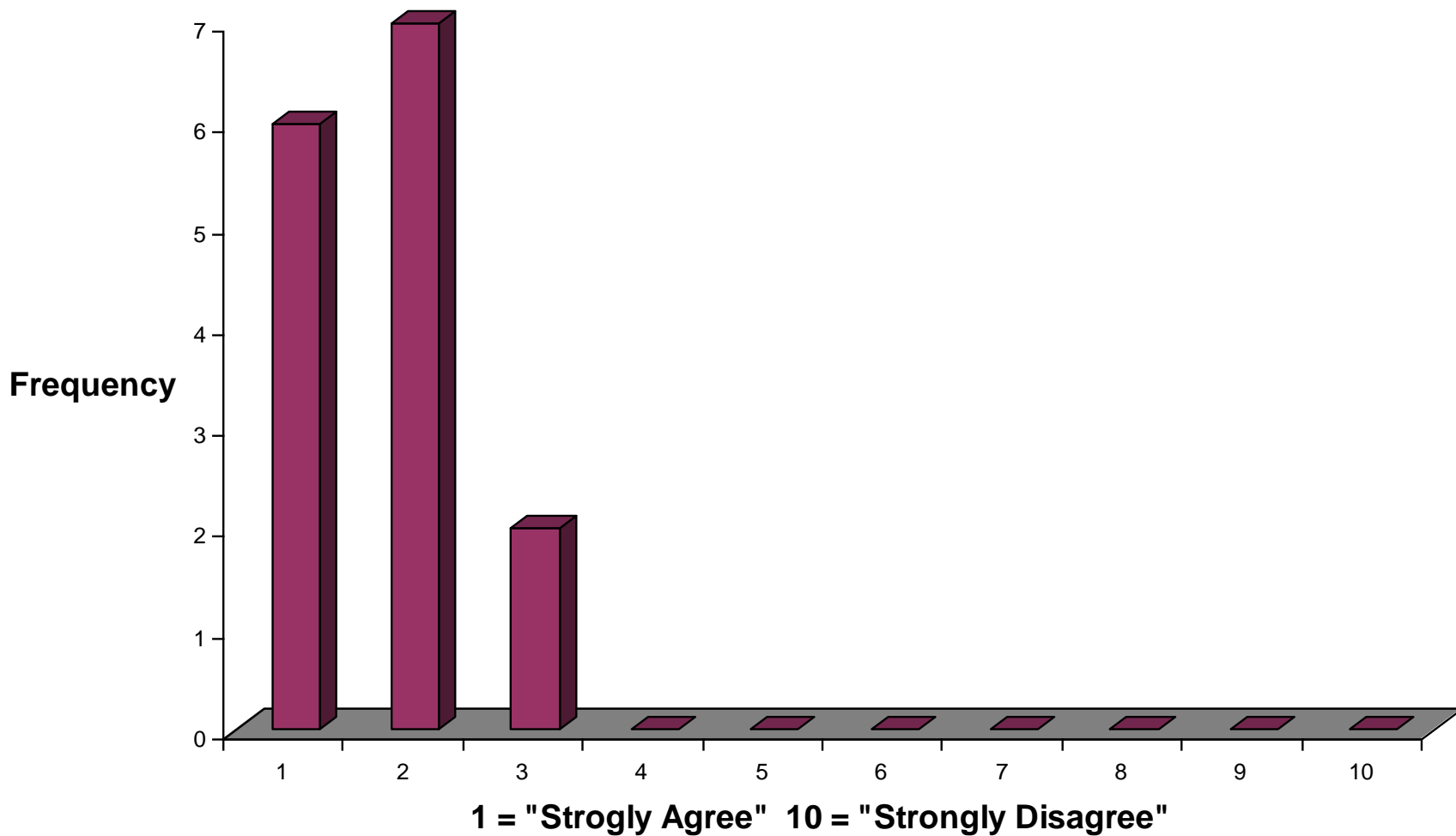
Activity was a good example of the symbiosis between experimental and theoretical/computational research



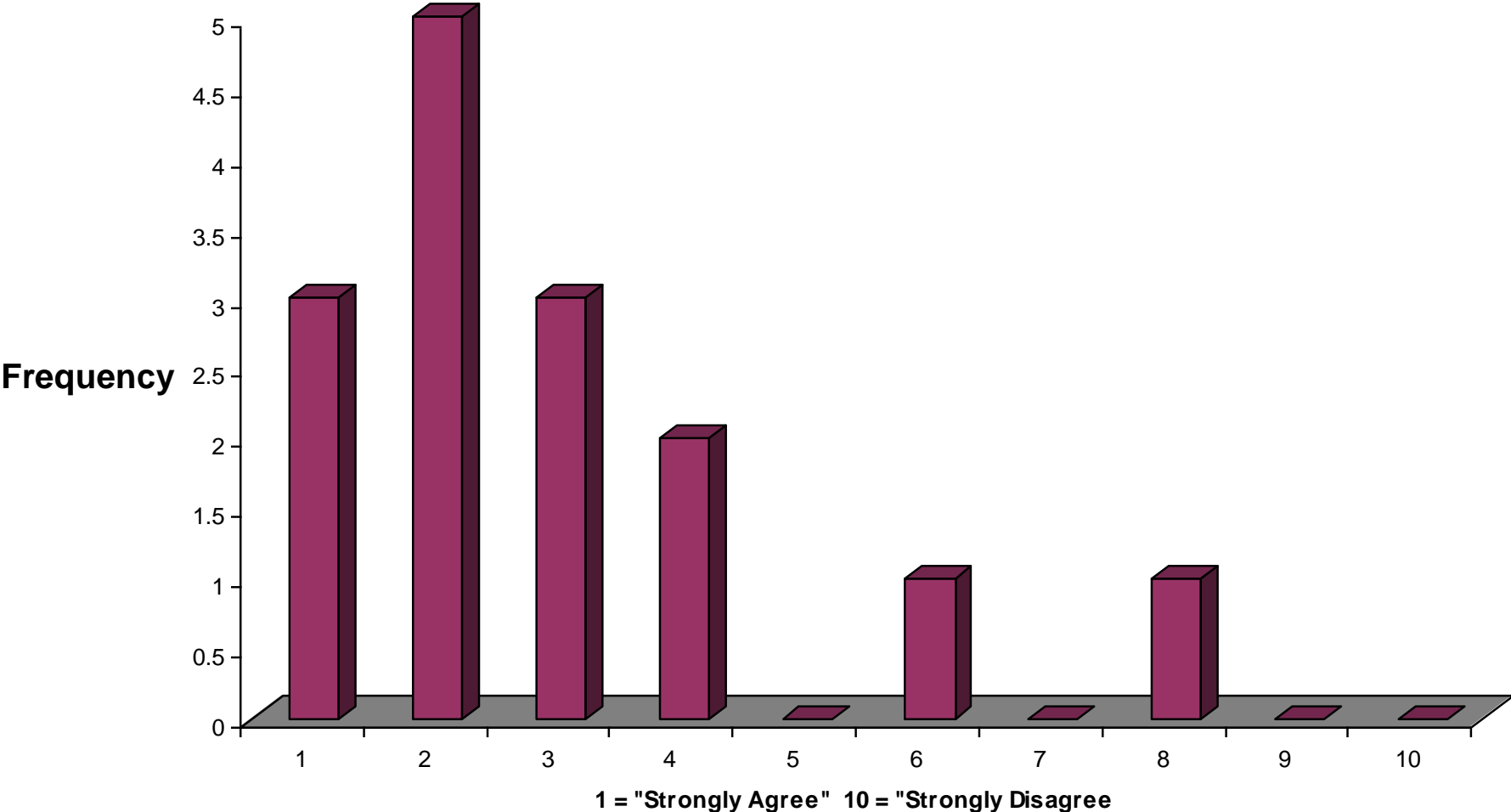
The work improved my understanding of how defects might form in surfaces



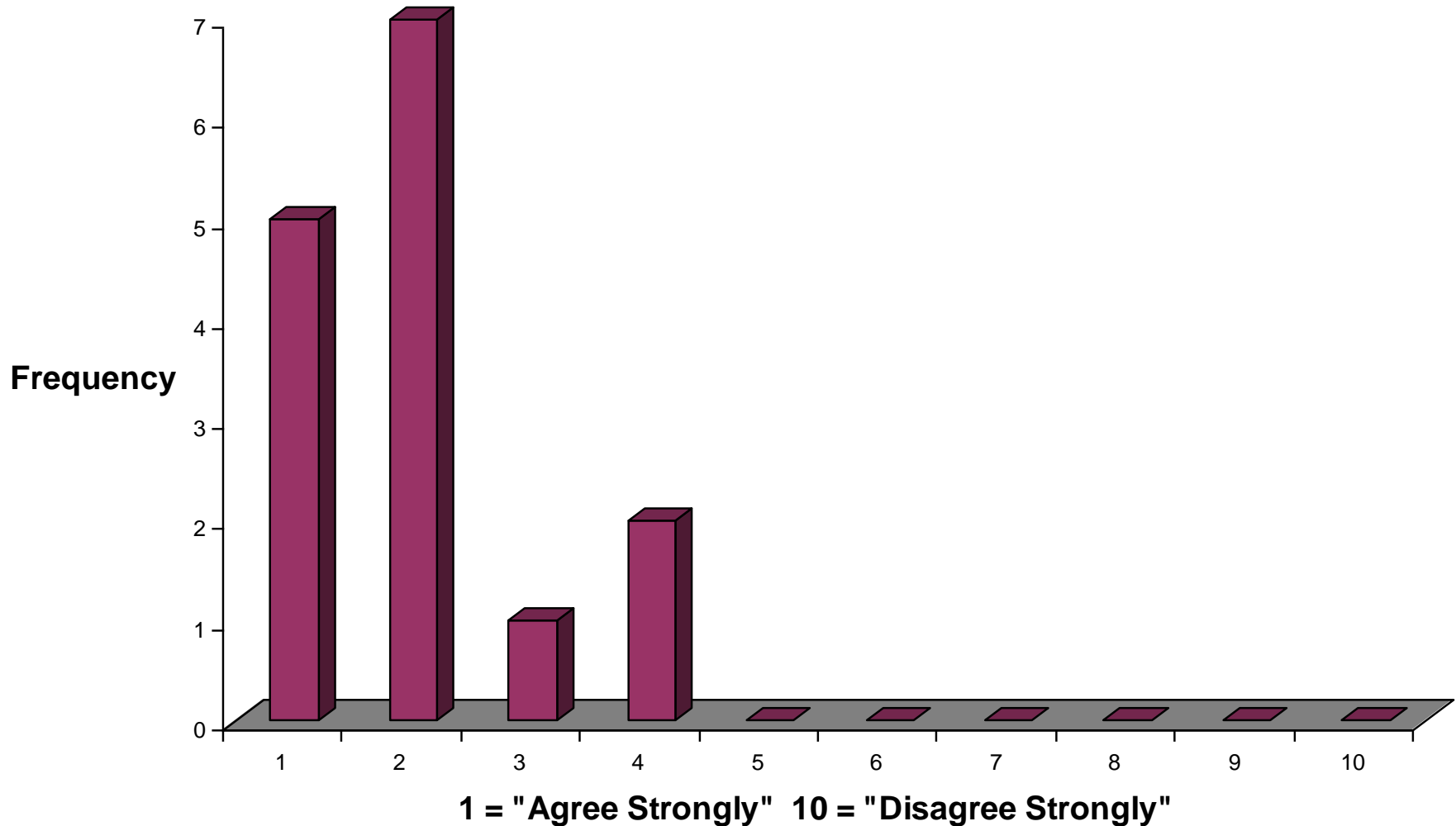
I understand better energy profiles and how they might be used to help understand oxygen migration at Ceria surfaces



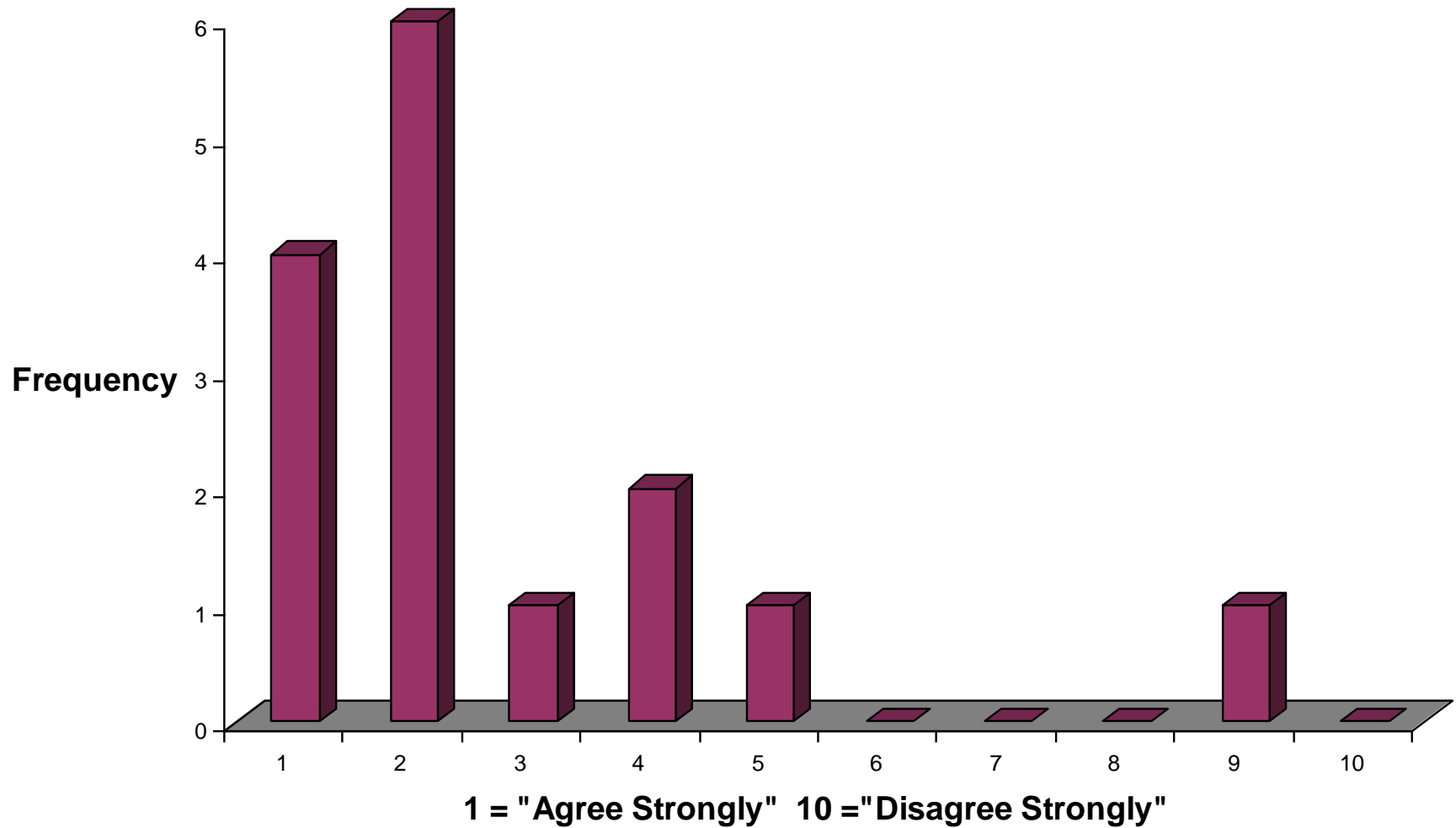
Activity allowed me to understand how results of an atomistic simulation can be used in a different meso-scale simulation on a larger scale to form a multi-scale surface simulation



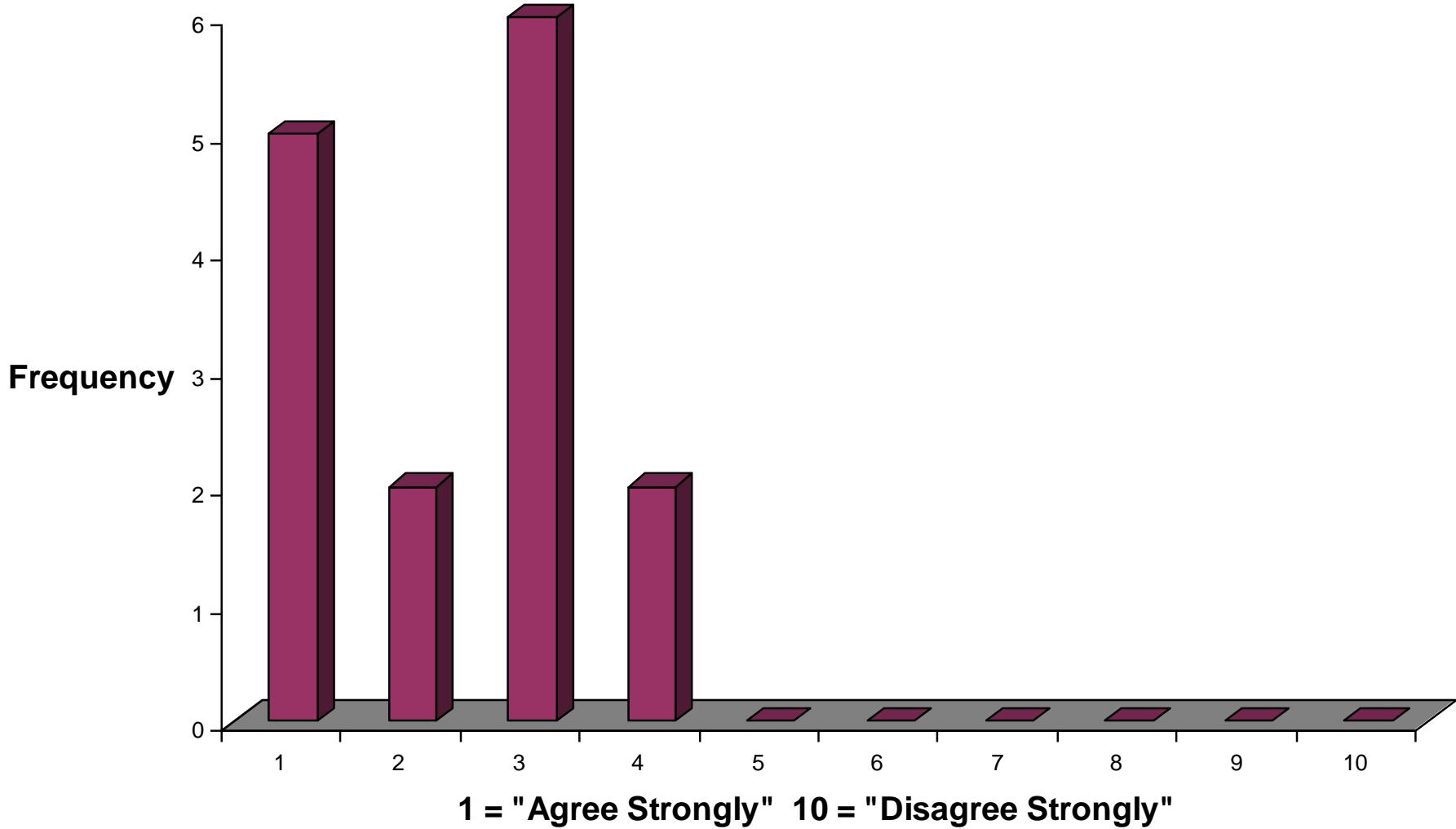
The work gave good examples of both experimental and theoretical techniques available for surface investigations.



The activity allowed me to improve my understanding of the importance of defects in catalysis and surface chemistry



The activity allowed me to improve understanding of how defects form



Conclusions/Lessons learnt:

- Novel science and educationally sound for module composition
- If activity involves a large amount of course-work – assessment scheduling
- Previous knowledge/experience: lots of new terminology – some students have better starting position than others.
- Need clear explanations of tasks/new info. throughout activity
- Computing labs :
 - **Potential for software licensing issues**
 - **Practical issues: room booking / type of room**

