Molecular static study on voids in UO_2

Wei-Ying Chen

MSE 485 Final Project

Introduction

1. Voids are widely observed in irradiated materials
2. Voids are important for mechanical property
3. Voids are places for fission gas storage
4. Hard to investigate the early stages of the formation process

Goal

- Should there be a limit size for voids?
- How does the voids evolve as growing in size?

Approach

Using GULP(J. D. Gale[1])

1. Construct perfect UO2 lattice
2. Put Schottky defects into the perfect lattice
3. Relax to find the configuration that minimize energy locally.
4. Calculate formation energy per pair
5. Analyze data and conclude

Constructing voids

- Schottky defect cluster is void
- Schottky defect is fixed on [111] direction
- Voids is built to 3 categories:

1. Line: lies in [110] direction
2. Disk:lies on (111) & (11-1) plane
3. 3D

Potential

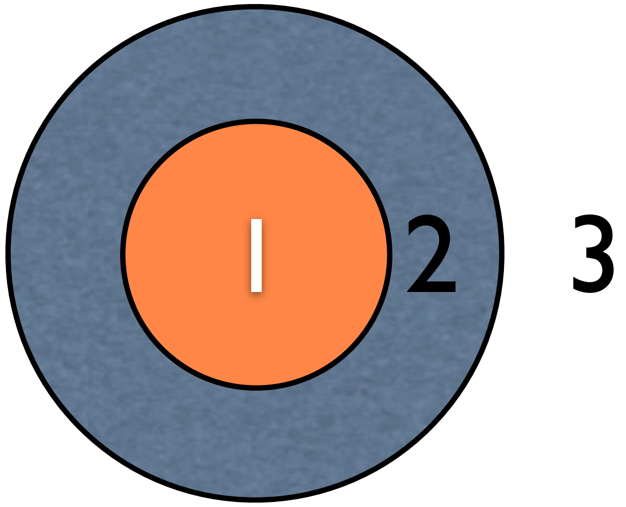
- General Buckingham form
- Ewald[2] method for Coulomb term
- Grimes[3] potential for short range term

$$U_{ij}(r) = \frac{q_i q_j e^2}{4\pi r} + A_{ij} \exp\left(-\frac{r}{\varrho_{ij}}\right) - \frac{C_{ij}}{r^6}$$

Energy Minimization Strategy

- Periodic Boundary Condition
- Mott-Littleton method

1. Fully relaxed
2. Weakly perturbed
3. Di-electric medium

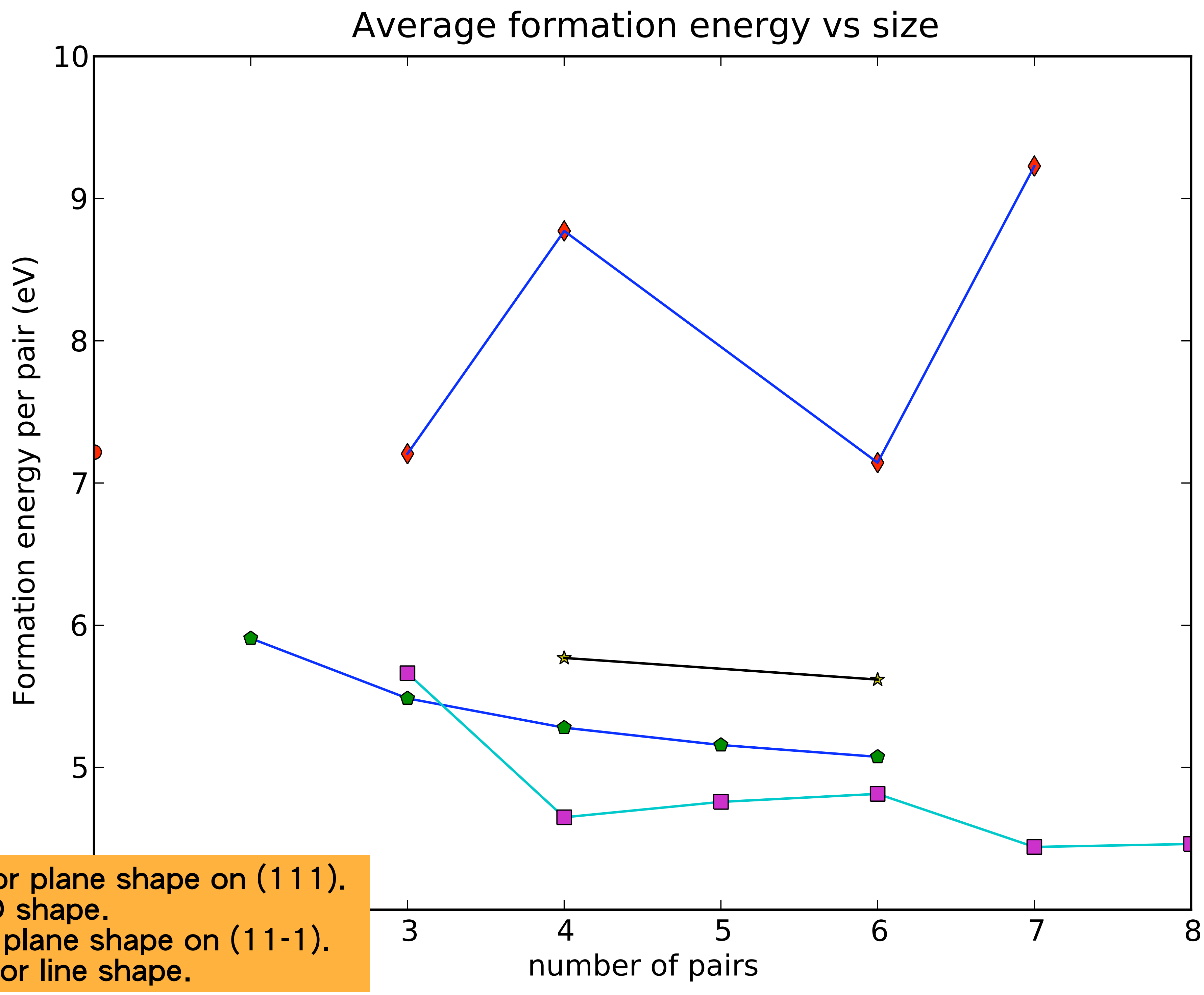


Energy minimization

- Local minimum
  1. Conjugate gradient
  2. Newton-Raphson
- Newton-Raphson is faster for small system, but Hessian become too large for large system

$$U(x+dx) = U(x) + \frac{dU}{dx}dx + \frac{1}{2!}\frac{d^2U}{dx^2}\cdot(dx)^2 + \ldots$$

Results



Diamond mark is for plane shape on (111).
Star mark is for 3D shape.
Square mark is for plane shape on (11-1).
Pentagon mark is for line shape.

Discussion

- For Line shape, the average formation decreases as length increases, implying that cluster can always lower system enthalpy by lengthening itself.
- Binding energy is also calculated to be around 2.5 eV and keep steady as size grows.
- There is no limit on the length of line shape voids.(do not consider entropy)

Discussion

- Average formation energy for (11-1) act like line shape. So it has a tendency to grow.
- Average formation energy for (111) does no decline and is beyond 7.1 eV. This is because it has higher strain energy.
- Bulge on (11-1) curve reflects the broken symmetry

Discussion

- line shape is the most stable shape for size 1 to 3.
- Starting from size 4, plane shape on (11-1) takes place as most stable configuration.
- A transition happens between size 3 and 4. Another transition from disk shape to 3D shape is expected to happen for larger size.
- Voids can always grow as long as there is sufficient Schottky defect supply.

Reference

[1]J. D. Gale, A. L. Rohl, Mol. Simul. 29 (2003) 291

[2]P.P. Ewald. Die Berechnung optischer und elektrostatisher gitterpotentiale *Ann. Phys.*, 64:253–287, 1921.

[3] N.F. Mott, M.J. Littleton, Trans. Faraday Soc. 34(1938)

[7]K. Govers, S. Lemehov, M. Hou, M. Verwerft, J. Nucl. Mater. 366 (2007) 161