MSE6701H Multiscale Materials Modeling and Simulation

Lecture 05

Property Evaluation and Result Analysis

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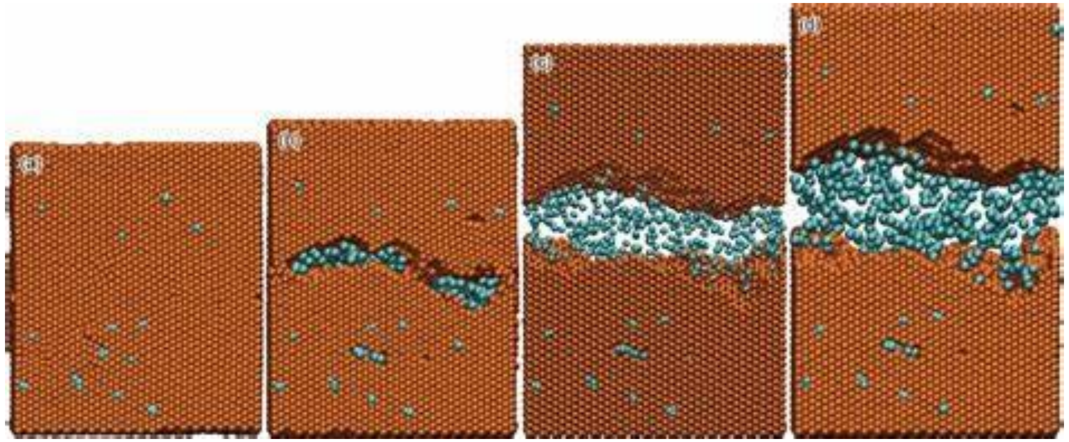
Outline

- Property Evaluation
  - Readily available quantities
  - Derived/measured quantities
- Structure Analysis
  - Global structure
  - Local atomic order
  - Defects

Readily Available Quantities



- N, V, E_P, E_K, M, ρ
- $c_i = n_i/N$
- $U = E_P + E_K, \quad H = U + PV$
- T, P

$$E_K = \sum_{i,\alpha} \frac{1}{2} m_i v_{i,\alpha}^2 = \frac{3}{2} N k_B T$$

$$T = \frac{2}{3 N k_B} \sum_{i,\alpha} \frac{1}{2} m_i v_{i,\alpha}^2$$

$$P_{\alpha,\beta} = \frac{1}{V} \left(\sum_i m_i v_{i,\alpha} v_{i,\beta} + \sum_{i>j} r_{ij,\alpha} \cdot f_{ij,\beta} \right)$$

$$P = \frac{1}{3} \sum_{\alpha} P_{\alpha,\alpha}$$

Derived/measured quantities

- Elastic constants $$C_{ij} = \frac{1}{V}\left[\frac{\partial^2 E}{\partial \varepsilon_i \varepsilon_j}\right]_0$$

- Constant pressure heat capacity C_p

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N}$$

$$C_p = \frac{H(p, T + \Delta T) - H(p, T - \Delta T)}{2\Delta T}$$

$$C_p = \frac{1}{V k_B T^2}\langle \sigma_H^2 \rangle$$

$$\langle \sigma_H^2 \rangle = \frac{1}{N_t}\sum_{i=1}^{N_t}(H_{t_i} - \bar{H})^2$$

https://docs.lammps.org/Howto_elastic.html

Derived/measured quantities

- Isothermal compressibility $\beta = 1/B$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

$$\beta = -\frac{1}{V(p,T)}\frac{V(p+\Delta p,T)-V(p-\Delta p,T)}{2\Delta p}$$

$$\beta = \frac{1}{Vk_BT}\langle\sigma_V^2\rangle$$

- Thermal expansion coefficient α

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{N,T}$$

$$\alpha = \frac{1}{V(p,T)}\frac{V(p,T+\Delta T)-V(p,T-\Delta T)}{2\Delta T}$$

$$\alpha = \frac{1}{Vk_BT^2}\langle\sigma_{V,H}\rangle$$

Mean Squared Displacement and Diffusion Coefficient

Assuming 1D diffusion, Fick's 2nd Law:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} \qquad n(x,t) = \frac{N}{2\sqrt{\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right)$$

Mean Squared Displacement:

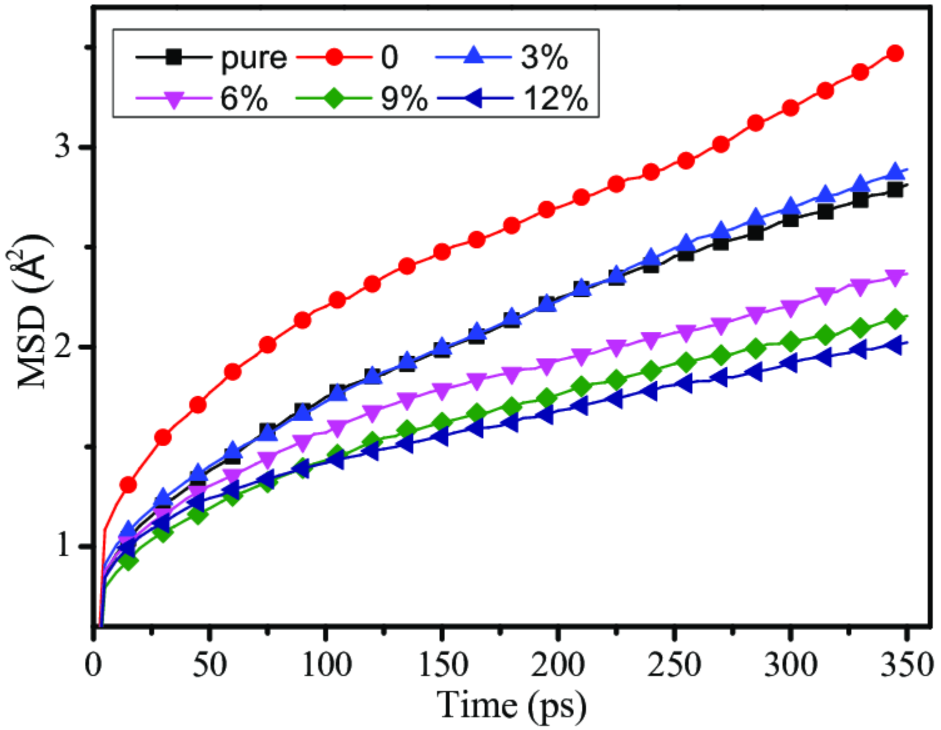
$$\langle x^2(t)\rangle = \frac{\int_{-\infty}^{\infty} x^2 \cdot n(x,t)\mathrm{d}x}{\int_{-\infty}^{\infty} n(x,t)\mathrm{d}x} = 2Dt$$

For 3D case (Einstein Relation):

$$\langle \Delta r^2(t)\rangle = 6Dt$$

MSD can be measured from MD:

$$\langle \Delta r^2(t)\rangle = \langle |\mathrm{r}_i(t) - \mathrm{r}_i(0)|^2\rangle$$



Kinematic viscosity & thermal conductivity

- Viscosity η

$$\eta_{\alpha,\beta} = \frac{1}{Vk_BT}\int_0^\infty \langle p_{\alpha,\beta}(t)p_{\alpha,\beta}(0)\rangle \mathrm{d}t$$

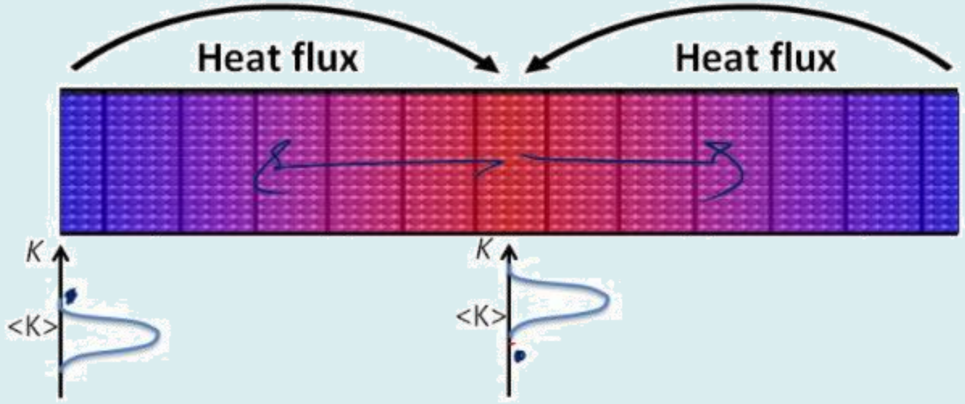
- Thermal conductivity κ

$$\kappa = \frac{1}{Vk_BT^2}\int_0^\infty \langle J(t)J(0)\rangle \mathrm{d}t$$

Autocorrelation function

$$C(t) = \langle p(t_0+t)p(t_0)\rangle$$

Alternative:
reverse Non-equilibrium MD

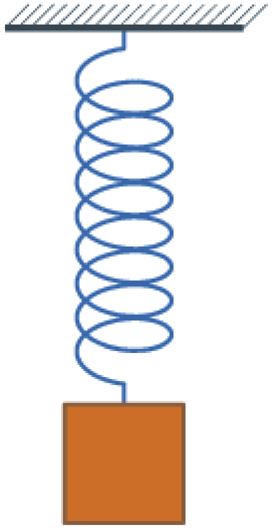


$$\kappa = -\frac{J}{\mathrm{d}T/\mathrm{d}x}$$

Phonons

- Finite difference based method (static)
- Velocity autocorrelation function based

$$g(\omega) = \int \mathrm{e}^{i\omega t} \frac{\langle v(t)v(0)\rangle}{\langle v(0)v(0)\rangle} \mathrm{d}t = \int \mathrm{e}^{i\omega t} C(t) \mathrm{d}t$$



- Fluctuation-dissipation based method

Harmonic oscillator

$$\frac{1}{2}k\langle \Delta x^2\rangle = \frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_B T,$$

$$k = \frac{k_B T}{\langle \Delta x^2\rangle}.$$

Real materials

$$G_{lk_\alpha, l'k'_\beta} = \langle u_{lk_\alpha} u_{l'k'_\beta}\rangle,$$

$$\mathbf{\Phi} = k_B T \mathbf{G}^{-1}.$$

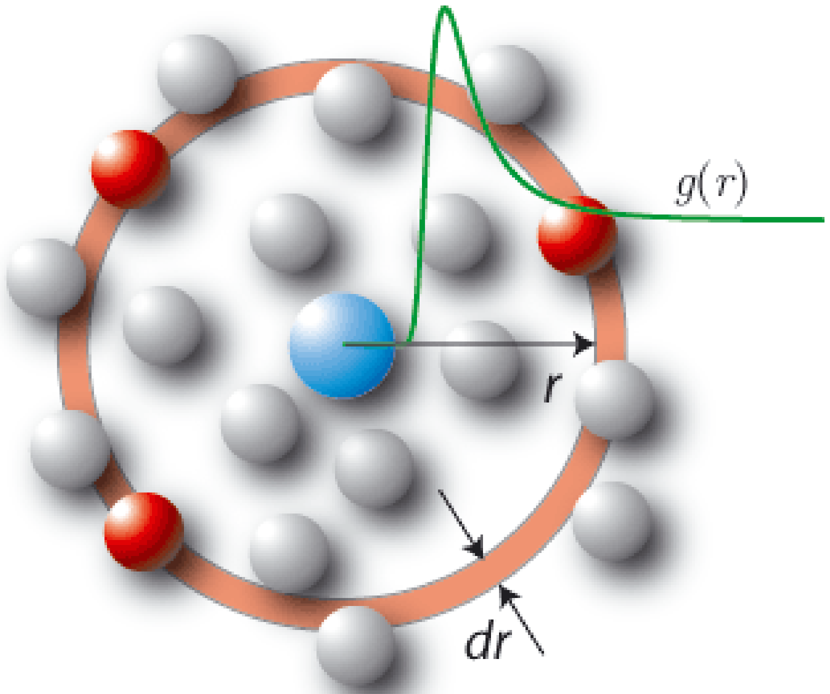
https://docs.lammps.org/fix_phonon.html

Structure Analysis: pair correlation function

Pair correlation function

$$g(r) = \frac{\rho(r)}{\rho_0}$$

$$\rho_0 = \frac{N}{V} \qquad \rho(r) = \frac{n(r)}{\Delta V_r} = \frac{n(r)}{4\pi r^2 \Delta r}$$

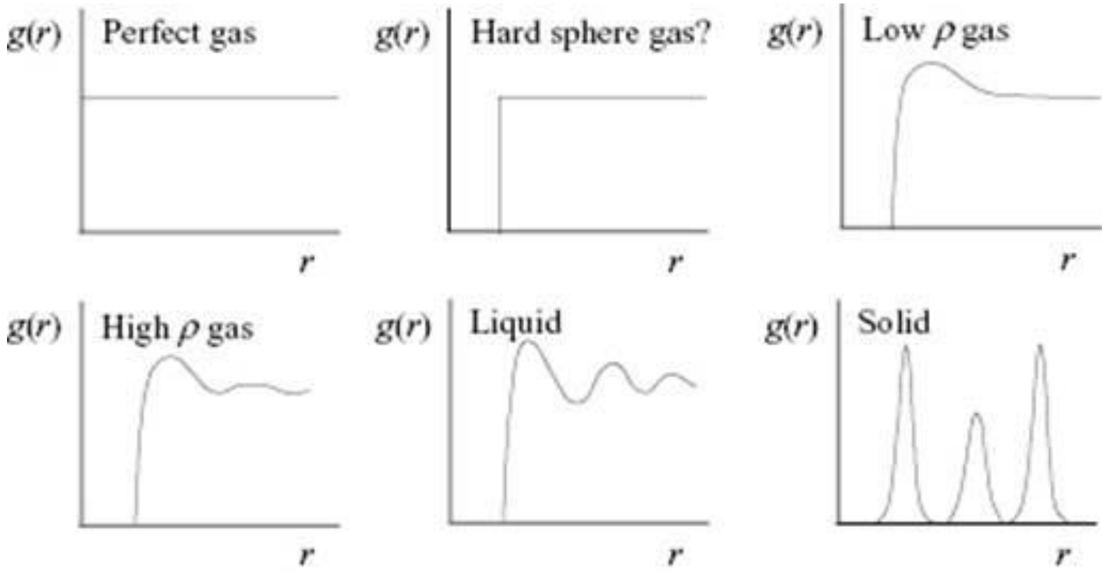


$$\begin{aligned} g(r) &= \frac{V}{4\pi r^2 N^2} \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \\ &= \frac{V}{4\pi r^2 N^2} \sum_i \sum_{j \neq i} \frac{n_{r_{ij} \in [r - \frac{\Delta r}{2}, r + \frac{\Delta r}{2}]}}{\Delta r} \end{aligned}$$

Partial pair correlation function

$$g_{\alpha\beta}(r) = \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \frac{V \delta(r_{ij} - r)}{4\pi r^2 N_\alpha N_\beta} = g_{\beta\alpha}(r)$$

Structure Analysis: pair correlation function



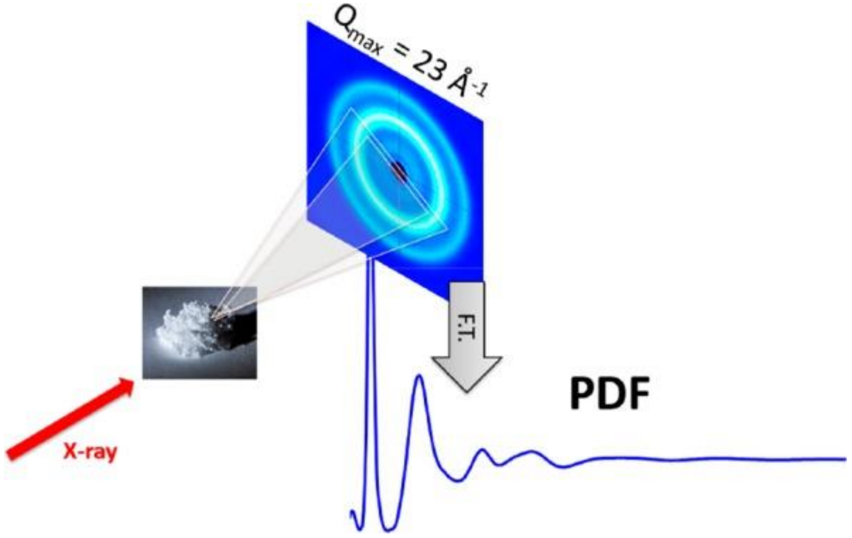
- r_1, r_2, r_3…
- **Coordination number**
- **Medium range order**

For pair potential *u(r)*:

$$p = \frac{Nk_BT}{V} - \frac{N^2}{6V^2}\int r\frac{\mathrm{d}u(r)}{\mathrm{d}r}g(r)\mathrm{d}r$$

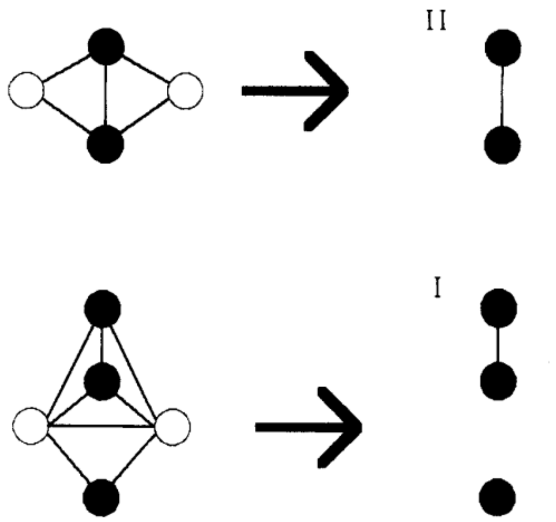
Structure Factor *S(k)*:

$$S(k) = 1 + \frac{N}{V}\int [g(r) - 1]e^{i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}\mathbf{r} \qquad k = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$



https://doi.org/10.1021/acs.jpcb.8b04823

Structure Analysis: Honeycutt-Andersen Index

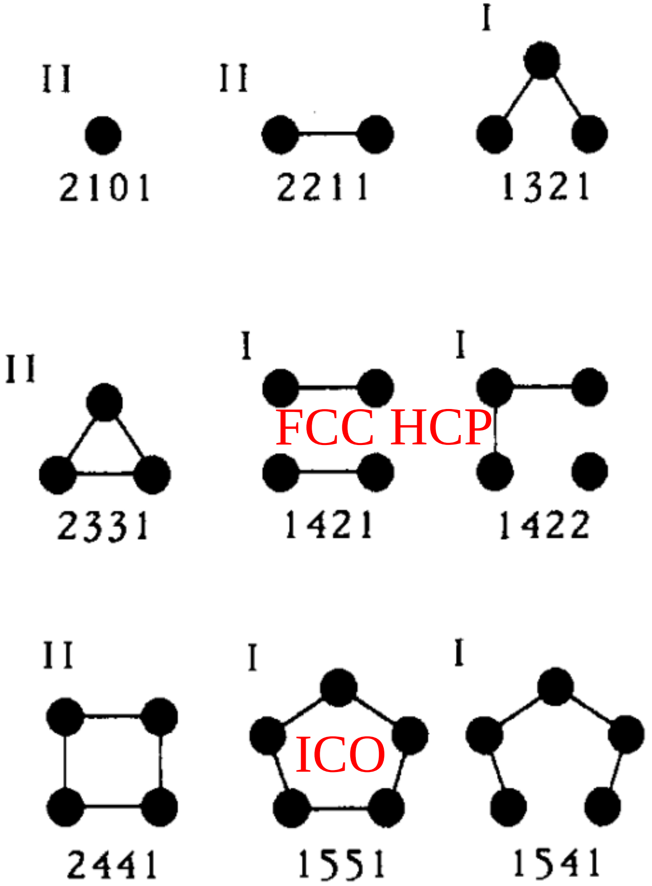


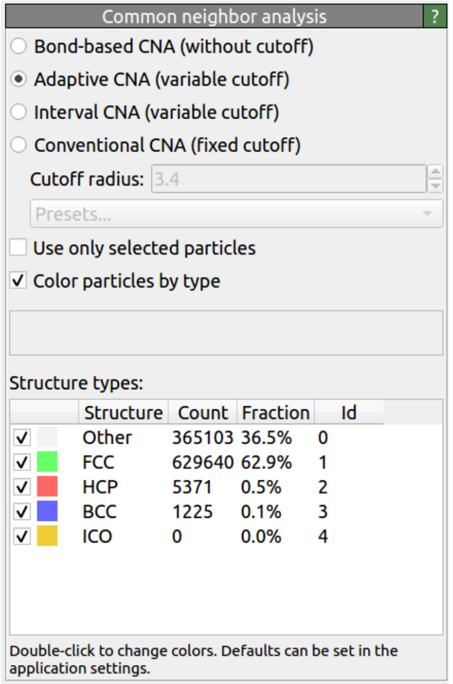
1 1-bonded; 2-non-bonded

2 # of common neighbors

3 # of bonds among neighbors

4 ID of similar environment



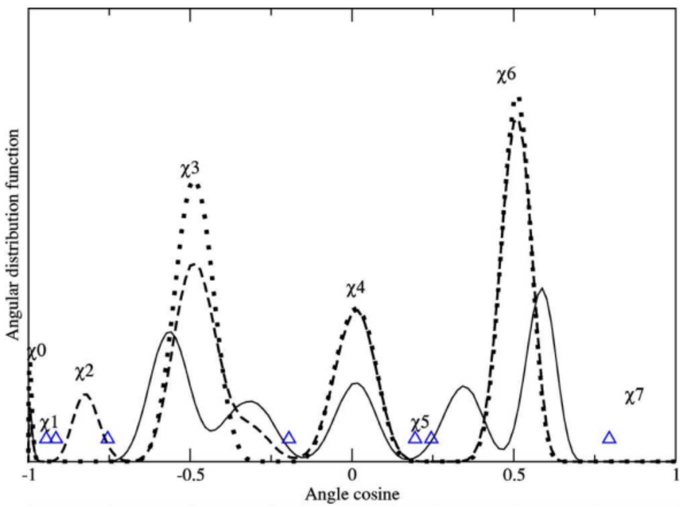


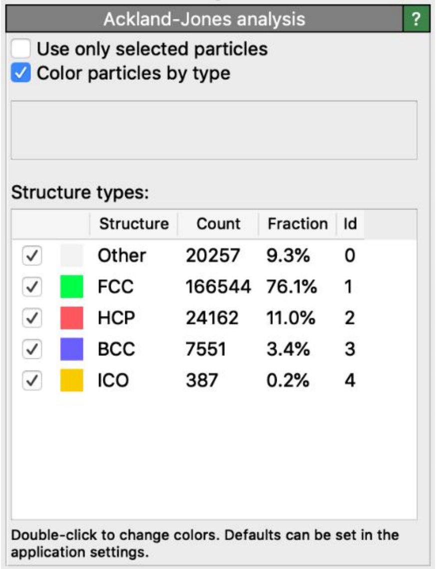
https://pubs.acs.org/doi/pdf/10.1021/j100303a014

https://www.ovito.org/docs/current/reference/pipelines/modifiers/common_neighbor_analysis.html

Structure Analysis: Ackland-Jones Parameter

(i)	Evaluate mean squared separation $r_0^2=\sum_{j=1}^{6} r_{ij}^2/6$ for nearest six particles to i.
(ii)	Find N_0 near neighbors with $r_{ij}^2<1.45r_0^2$ and N_1 with $r_{ij}^2<1.55r_0^2$.
(iii)	Evaluate bond angle cosines (Ref. 14) $\cos\theta_{jik}$ between all $N_0(N_0-1)/2$ neighbor pairs of atom i.
(iv)	From bond angle cosines, determine χ_i (Table I).
(v)	Assign any atom with $N_0<11$ or $\chi_0>0$ as an unknown.
(vi)	If $\chi_0=7$, particle is bcc, if $\chi_0=6$, particle is fcc, if $\chi_0=3$, particle is hcp.
(vii)	From the angle cosines, define deviations from the expected angular distribution δ (Table I).
(viii)	If no $\delta<0.1$, then structure is unassigned.
(ix)	If $\delta_{bcc}<\delta_{CP}$ and $10<N_1<13$ assign bcc.
(x)	If $N_0>12$ the structure is unassigned, otherwise $\delta_{hcp}<\delta_{fcc}$ implies hcp and $\delta_{fcc}<\delta_{hcp}$ gives fcc.



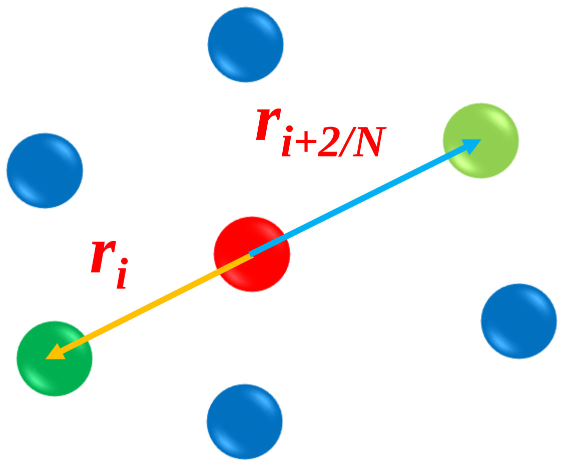


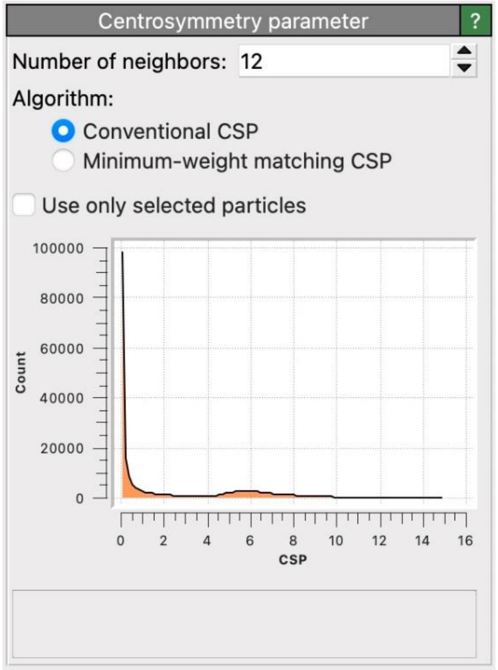
	Minimum $\cos\theta_{jik}$	Maximum $\cos\theta_{jik}$	bcc	Ideal fcc	hcp
χ_0	−1.0	−0.945	7	6	3
χ_1	−0.945	−0.915	0	0	0
χ_2	−0.915	−0.755	0	0	6
χ_3	−0.755	−0.705	36	24	21
χ_4	−0.195	0.195	12	12	12
χ_5	0.195	0.245	0	0	0
χ_6	0.245	0.795	36	24	24
χ_7	0.795	1.0	0	0	0
δ_{bcc}	$0.35\chi_4/(\chi_5+\chi_6+\chi_7-\chi_4)$				
δ_{CP}	$0.61\vert 1-\chi_6/24\vert$				
δ_{fcc}	$0.61(\vert\chi_0+\chi_1-6\vert+\chi_2)/6$				
δ_{hcp}	$(\vert\chi_0-3\vert+\vert\chi_0+\chi_1+\chi_2+\chi_3-9\vert)/12$				

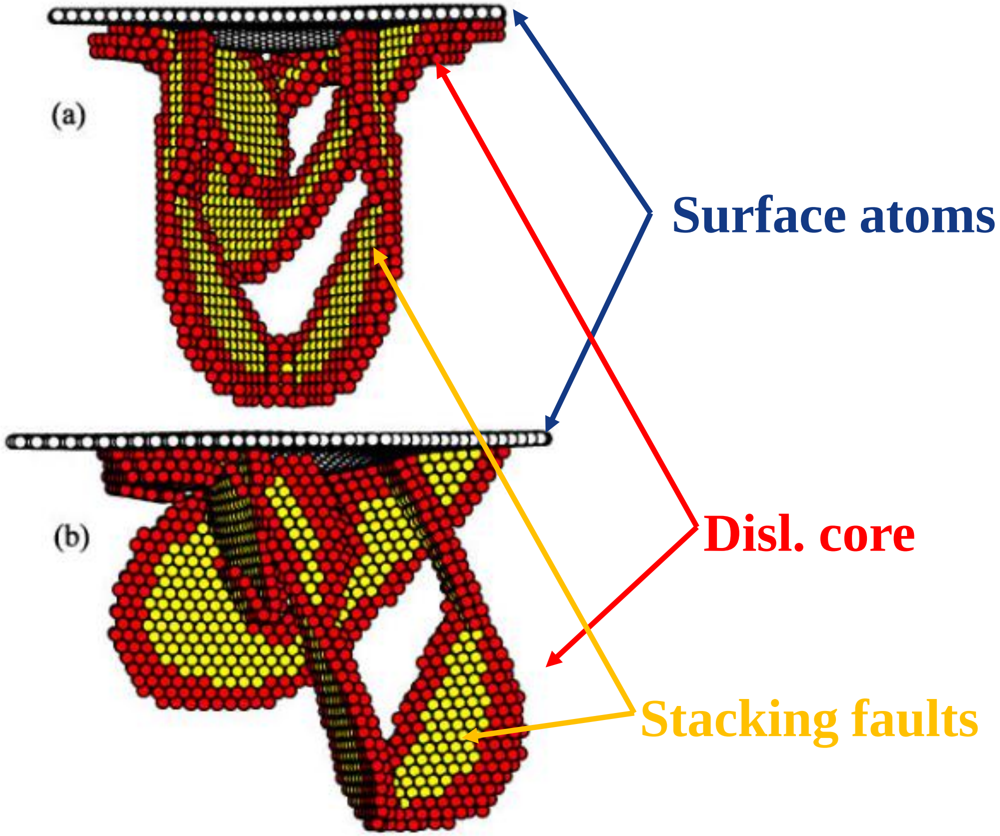
https://www.ovito.org/docs/current/reference/pipelines/modifiers/bond_angle_analysis.html#particles-modifiers-bond-angle-analysis

https://journals.aps.org/prb/pdf/10.1103/PhysRevB.73.054104

Structure Analysis: Centro-Symmetry Parameter







$$P = \sum_{i=1}^{N/2} \left| \mathbf{r}_i + \mathbf{r}_{i+2/N} \right|^2$$

Bulk lattice = 0 a_0^2

Dislocation core ~ 0.06 (0.03 to 0.075) a_0^2

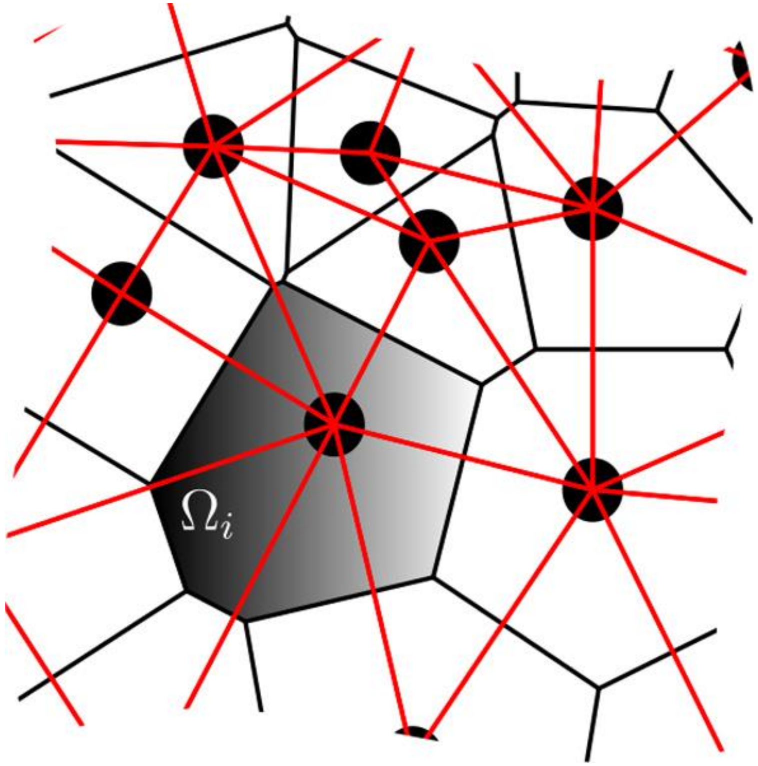
Stacking faults ~ 0.3 (0.24 to 0.36) a_0^2

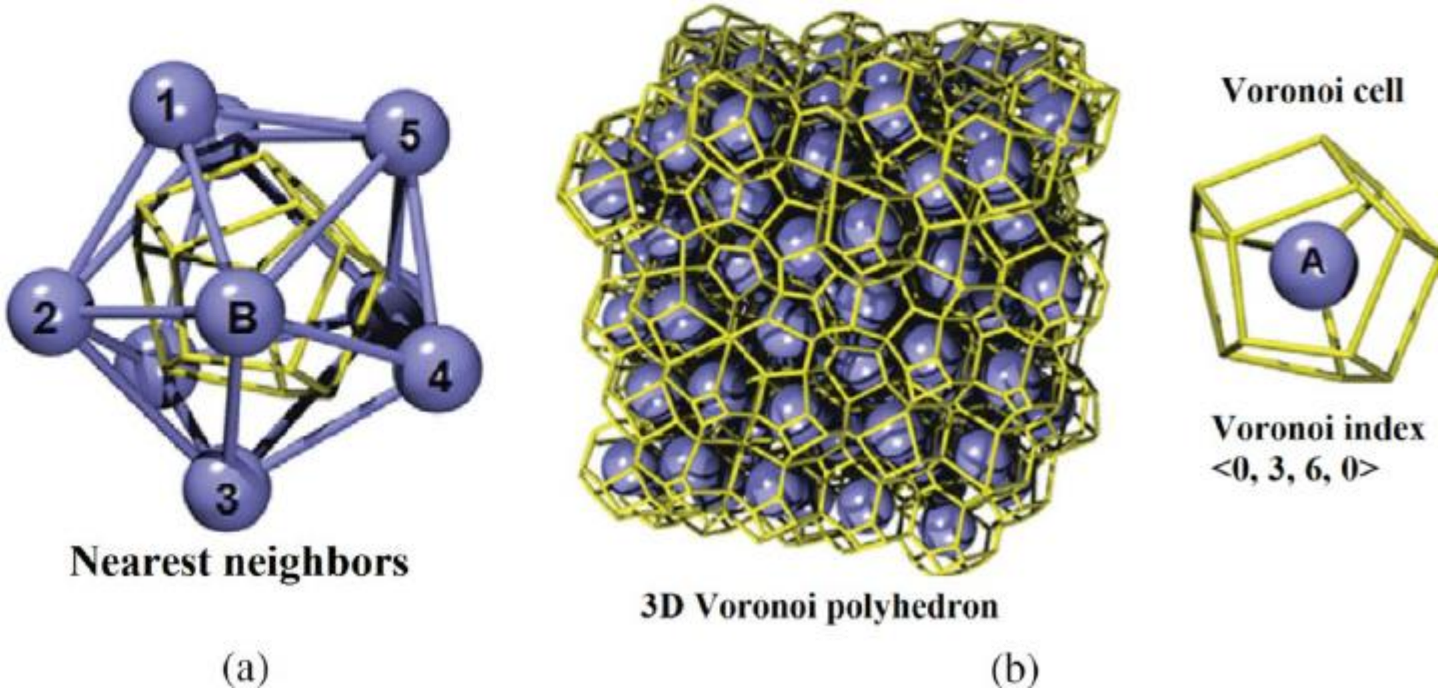
Free surface ~ 1.38 a_0^2

https://www.ovito.org/docs/current/reference/pipelines/modifiers/centrosymmetry.html#particles-modifiers-centrosymmetry

https://docs.lammps.org/compute_centro_atom.html

Structure Analysis: Voronoi Tessellation





(a) (b)

Voronoi Index

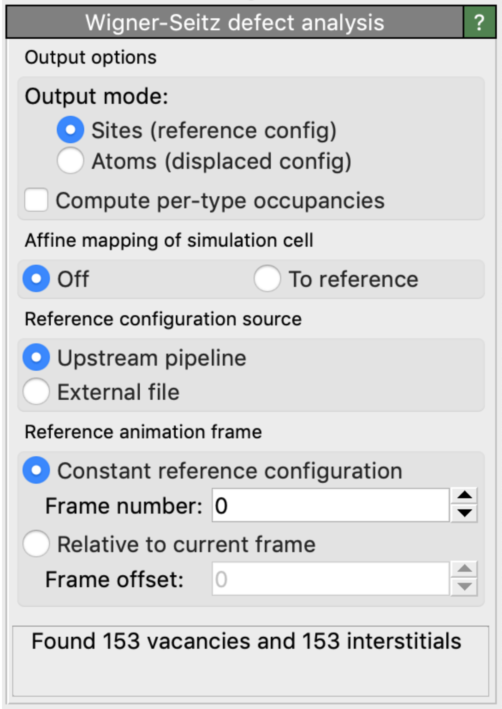
$<n_3,n_4,n_5,n_6>$

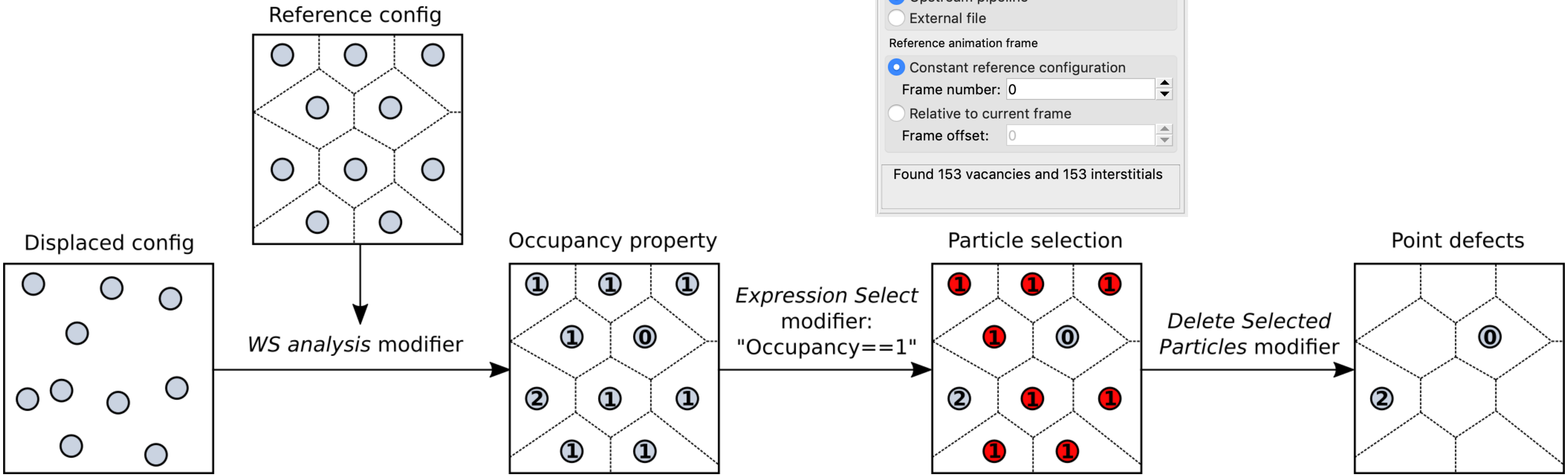
- FCC: <0,12,0,0>
- BCC: <0,6,0,8>
- HCP: <0,12,0,0>
- ICOs: <0,0,12,0>

✓ Nearest neighbors
✓ Coordination number
✓ Atomic volume
✓ Local environment
✓ Atomic stress

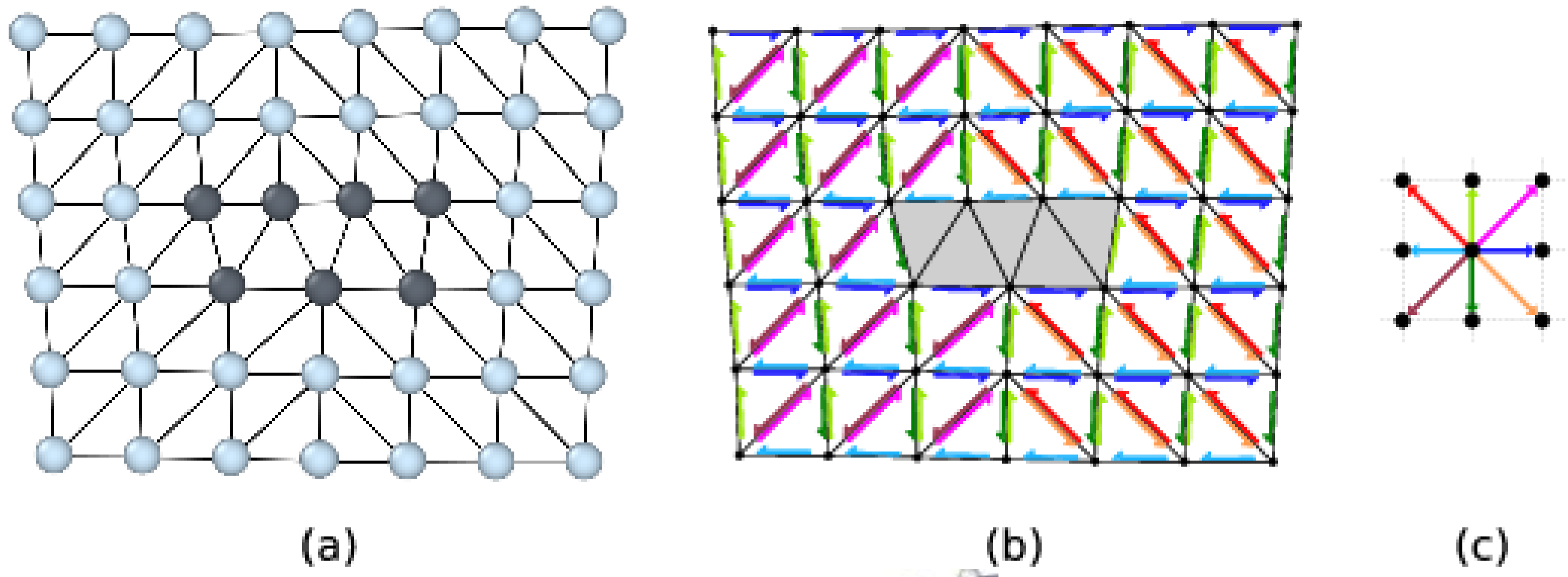
https://math.lbl.gov/voro++

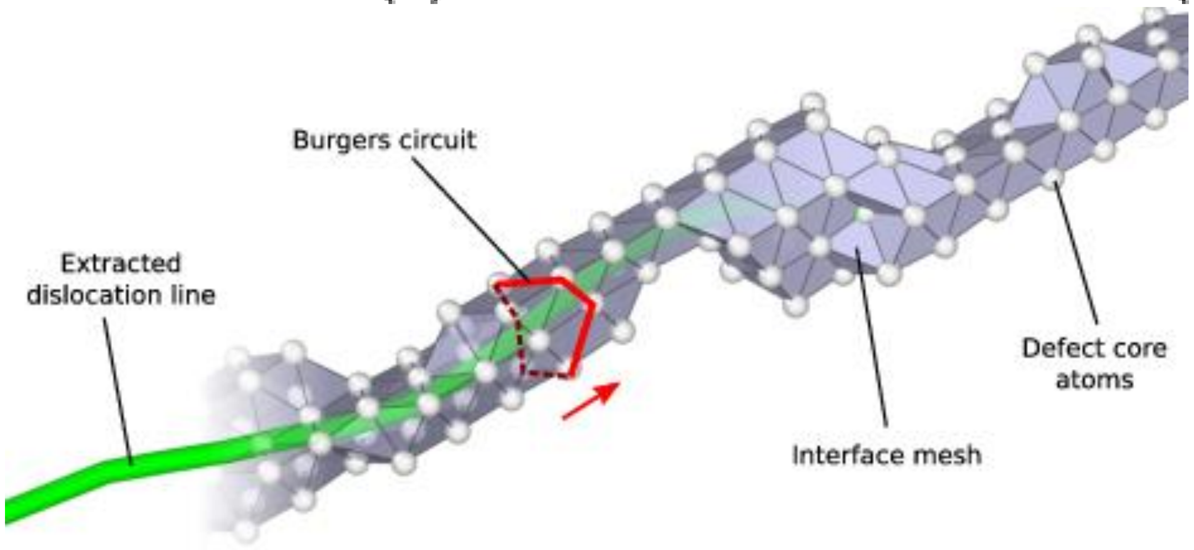
Structure Analysis: Wigner-Seitz defect analysis

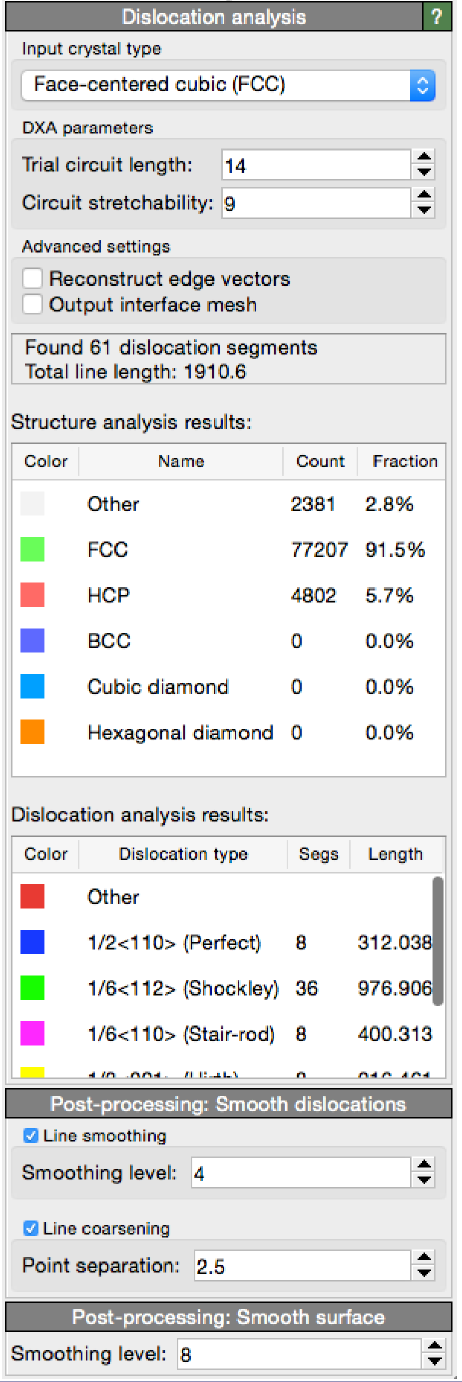




Structure Analysis: Dislocation Analysis







https://www.ovito.org/docs/current/reference/pipelines/modifiers/dislocation_analysis.html

Next Lecture：

Brief Introduction to Density Functional Theory

Homework

- Complete the MD Course Project as described on the hands-on manual
- Due: Nov 9, 2022

5. MD Course Project

This will be your first course project. The due is: Nov 9th, 2022.
The files needed to complete the MD course project are located in:

```
cd ~/MSE6701H/2-MolecularDynamics/7-experiments/
```

To update the files in this directory, one should run:

```
git pull
```

anywhere within the MSE6701H directory.

These are the experiments that you are expected to carry out. Please refer to the instructions above to accomplish your task and write a comprehensive epxerimental report for all the calculations.

```
.
├── 1-LatticeConstants
├── 2-SurfaceEnergy
├── 3-PointDefectFormationEnergy
└── 4-Dislocation-mobility
```

The **first three** are required for all students, while the last (*4-Dislocation-mobility*) is *optional* and for advanced learners only. For the last task, the DXA tool within *ovito* software is recommended to analyze the dislocation.

https://notes.sjtu.edu.cn/K7Bi_n0YQ2K7UIh6bxhGaA