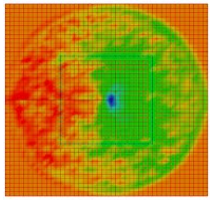
October 2013-January 2014

ESP900: Atomistic/Molecular Simulation:

Lecture 7: Analyzing inhomogeneous systems



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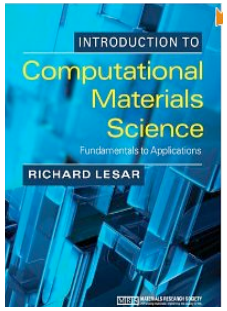

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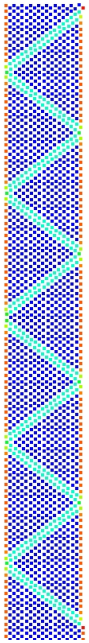
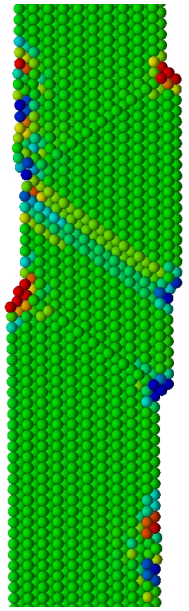


Outline

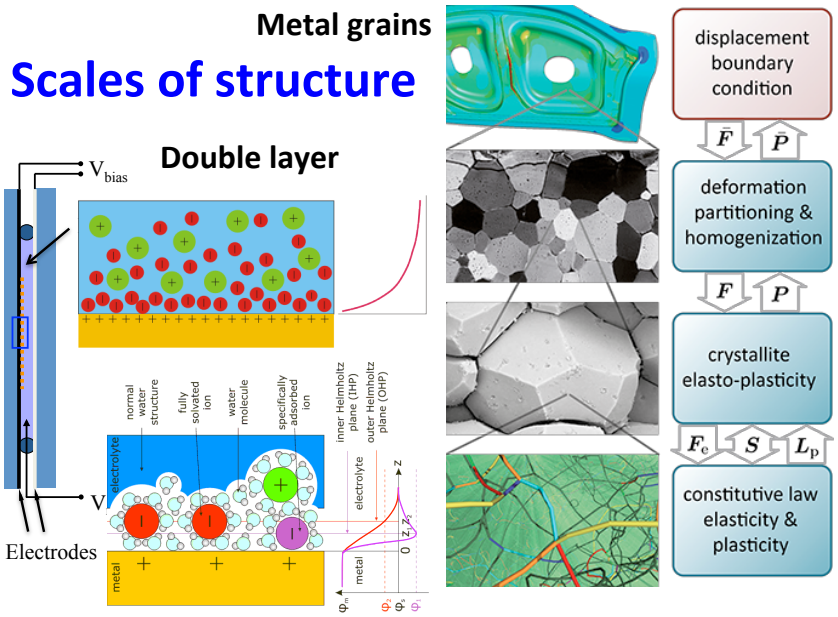
- Fluids: solvation shells & double layers
  - Radial distribution function/ spatial correlation
  - Molecules: radius of gyration
- Solids: lattice defects
  - Centrosymmetry
  - Common neighbor analysis
  - Slip vector
- Dense systems:
  - Kinematic measures
  - Continuum field estimation



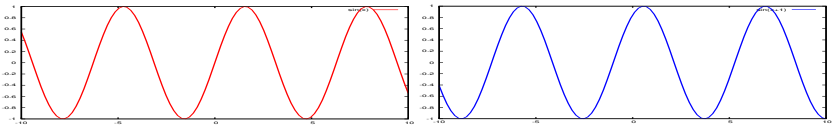
Scales of structure

Metal grains

Double layer



Correlation



Given a function of space v(x) the correlation C(x,y) is an indication of how, e.g. motion if v is velocity, is coordinated as a function of distance or time

$$C_v(x,y) = \langle v(x)v(y)\rangle = \langle v(0)v(x-y)\rangle = C_v(x-y)$$

If all the atoms are statistically equivalent, then (x,y) -> x-y
In discrete time dynamics, a time correlation is approximated by :

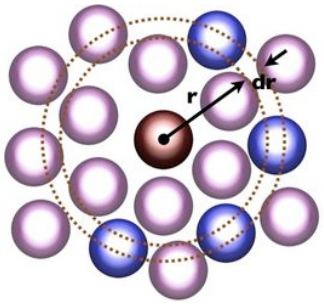
$$C_v(j\Delta t) \approx \frac{1}{n}\sum_{i,\alpha} v_\alpha(i\Delta t)\, v_\alpha((i+j)\Delta t)$$

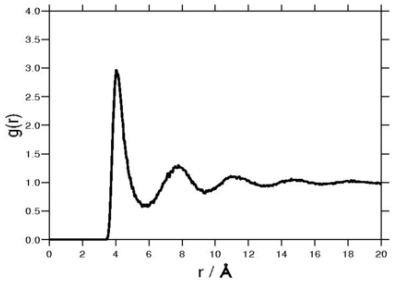
Radial Distribution Function

Radial **distribution** function (RDF) is also known as the pair **correlation** function, g. The RDF describes how atomic density varies as a function of distance from any particular atom in group a to group b. It can be approximated using, e.g. kernel density estimation, where Δ_h is a bell-shaped function with width h.

$$g_{ab}(r) = \frac{1}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \langle \delta(|\mathbf{r}_{ij}| - r) \rangle$$

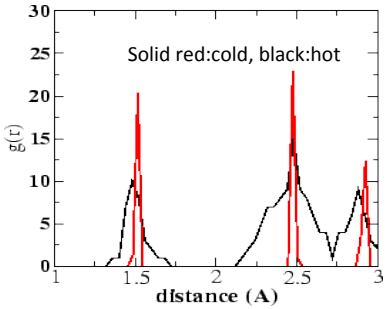
$$\approx \frac{1}{N_a N_b} \sum_{i,j} \Delta_h(\|\mathbf{r}_{ij}\| - r)$$

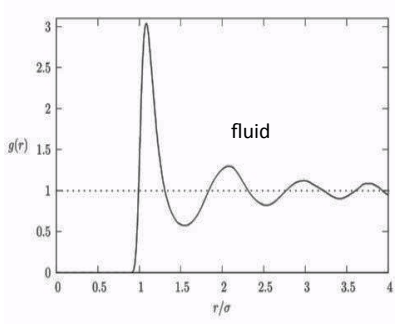




RDF as a phase discriminator

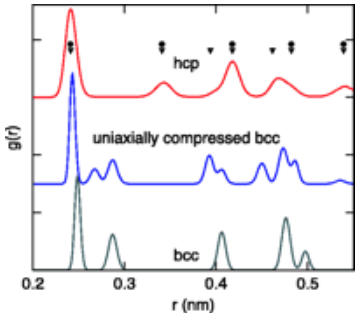
The widths of the peaks of the RDF (or the lack of peaks) can be used to identify whether a given substance is in a amorphous fluid/crystalline solid phase. As a crystalline solid heats and melts the peaks denoting atomic shells broaden and merge.

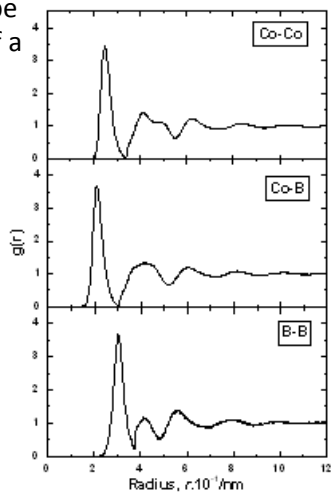




RDF as a structure discriminator

- The locations of peaks in the RDF can be used to identify the crystal structure of a solid material (as in X-ray diffraction)
- For alloys/mixtures, multiple RDFs can be constructed to provide information about the structure of the alloy.





Common Neighbor Analysis

Common neighbor analysis (CNA) is a **classifie**r of local atomic structure based on the coordination of any particular atom and the patterns of typical crystalline structures (FCC, BCC, HCP etc) With CNA a structure is classified by topologically. Starting with a pair of atoms, *α* ar *β*, a diagram is created with a set of four indices

(i) indicates that *α* and *β* are nearest-neighbors

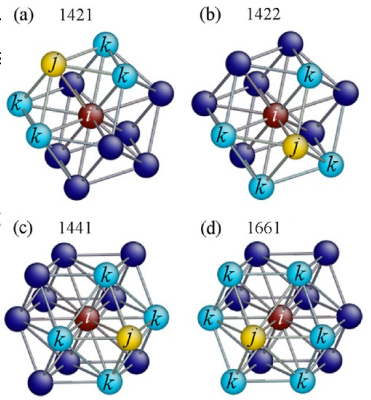
(ii) indicates the number of nearest neighbors shared by the pair

(iii) indicates the number of bonds among the common neighbors

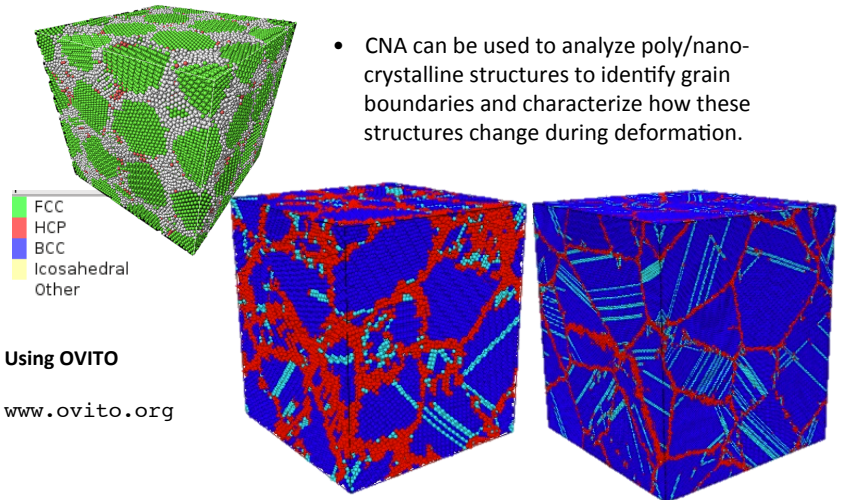
(iv) differentiates diagrams with same (i), (ii), and (iii) indexes and different bonding among common neighbors.

Relative presence of different CNA diagrams in the fcc, bcc, and hcp crystal structures

CNA diagram	fcc	bcc	hcp
1421	1	0	0.5
1422	0	0	0.5
1441	0	3/7	0
1661	0	4/7	0



CNA visualization of grain structures



- CNA can be used to analyze poly/nano-crystalline structures to identify grain boundaries and characterize how these structures change during deformation.

Using OVITO

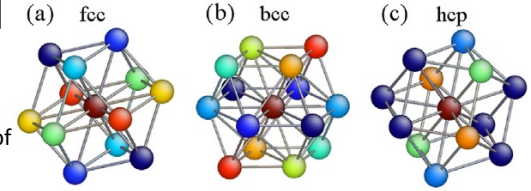
www.ovito.org

Centrosymmetry

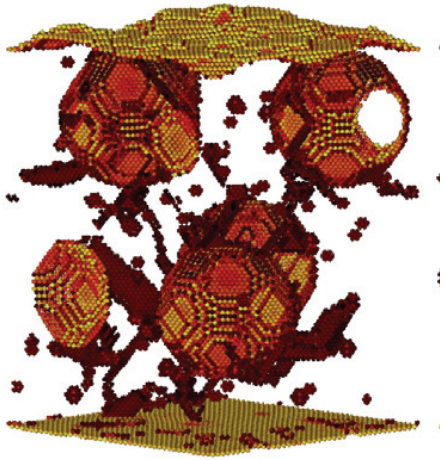
- CNA is useful for discriminating various structured phases of bulk materials. But, what if surfaces are present?
- One way to isolate surfaces is to filter atoms according to values of potential energy; however, this tends to "drown-out" defect structures like stacking faults and dislocation cores.
- The centrosymmetry parameter can be used for **radially-symmetric crystal structures** (e.g. FCC, BCC) to **detect regions where symmetry has been lost** such as surfaces, dislocation cores and stacking faults.

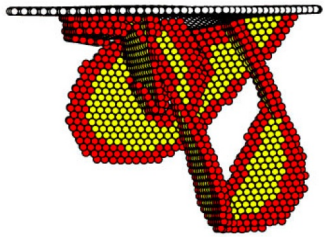
$$c_k = \min_{N_k} \sum_{i,j \in N_k} \left\| \mathbf{x}_{ik} + \mathbf{x}_{jk} \right\|$$

Here N_k is one of the 1/2n(n-1) unique pairings of the n neighbors of k



Centrosymmetry





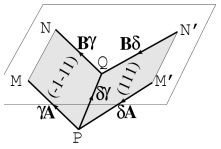
CSP produces the highest values for

1. surfaces vacancies
2. stacking faults
3. dislocation cores
4. highly-stretched regions.

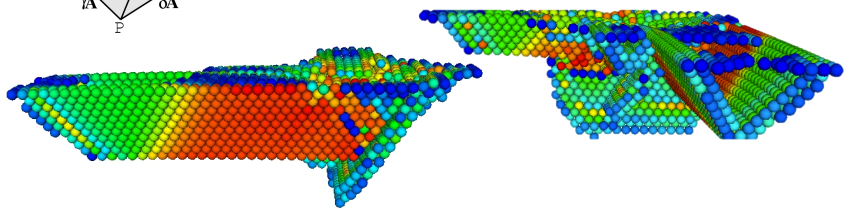
Atoms in bulk configuration have CSP equal to zero.

Slip Vector

- CNA and the centrosymmetry parameter are useful for discriminating and visualizing surfaces, defects, etc.
- Another piece of desired information are **crystallographic** details regarding these defects, e.g. **Burgers vectors**.
- The slip vector **s** is the "slip" for atoms that lie on planes that border these discontinuities relative to **reference positions** X

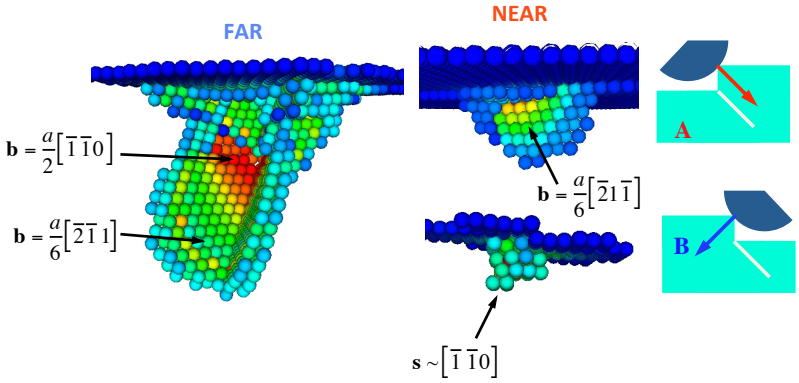


$$\mathbf{s}^{\alpha} = -\frac{1}{n_s} \sum_{\beta \neq \alpha}^{n} \left(\mathbf{x}^{\alpha\beta} - \mathbf{X}^{\alpha\beta} \right).$$

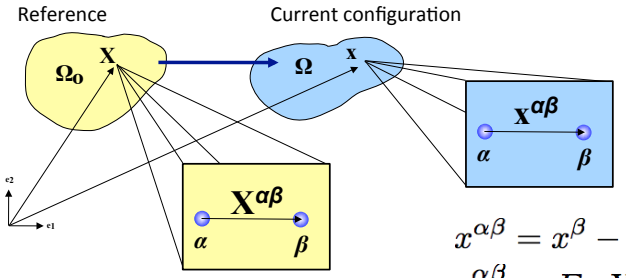


Example: dislocation nucleation during nanoindentation

Using the slip vector, dislocation structure can be determined in terms of specific Burgers vectors .



Atomic-scale deformation gradient



$$x^{\alpha\beta} = x^{\beta} - x^{\alpha}$$
$$x_i^{\alpha\beta} = F_{iI} X_I^{\alpha\beta}$$

A single atom-neighbor pair is insufficient to completely determine F.

Multiple neighbors are used employing a least-squares mean:

$$\min_{\mathbf{F}} \sum_{\beta=1}^{n} \left(x_i^{\alpha\beta} X_M^{\alpha\beta} - F_{iI}^{\alpha} X_I^{\alpha\beta} X_M^{\alpha\beta}\right)^2$$

Atomic-scale deformation gradient

Minimization leads directly to: $F_{iI}^{\alpha} = \omega_{iM}^{\alpha} (\eta^{\alpha})_{MI}^{-1}$

where:

$$\omega_{iM}^{\alpha} = \sum_{\beta=1}^{n} x_i^{\alpha\beta} X_M^{\alpha\beta} \quad \text{and} \quad \eta_{IM}^{\alpha} = \sum_{\beta=1}^{n} X_I^{\alpha\beta} X_M^{\alpha\beta}$$

Polar decomposition gives a rotation and stretch $\mathbf{F} = \mathbf{RU}$

From the rotation tensor a rotation vector can be form that can discriminate grain texture $\phi_k = -\frac{1}{2}\epsilon_{ijk}(R_{skew})_{ij}$

Atomic-scale velocity gradient

A similar minimization gives a velocity gradient

$$\mathbf{L} = \frac{\partial \mathbf{v}}{\partial \mathbf{x}} \longrightarrow v_i^{\alpha\beta} = L_{ik} x_k^{\alpha\beta} \longrightarrow \boxed{L_{ik}^{\alpha} = \rho_{im}^{\alpha} \left(\tau_{km}^{\alpha}\right)^{-1}}$$

where

$$\rho_{im}^{\alpha} = \sum_{\beta=1}^{n} v_i^{\alpha\beta} x_m^{\alpha\beta} \qquad \tau_{km}^{\alpha} = \sum_{\beta=1}^{n} x_k^{\alpha\beta} x_m^{\alpha\beta}$$

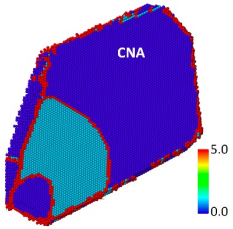
The usual symmetric + skew decomposition leads to

$$\mathbf{L} = \mathbf{D} + \mathbf{W} \qquad \mathbf{W} = \frac{1}{2}\left(\mathbf{L} - \mathbf{L}^T\right)$$

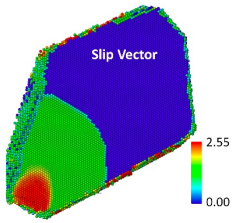
And a vorticity vector $\omega_k = -\frac{1}{2}\epsilon_{ijk} W_{ij}$

Correlating multiple metrics

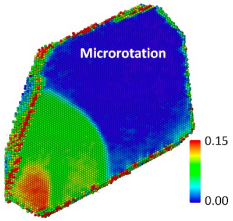
CNA



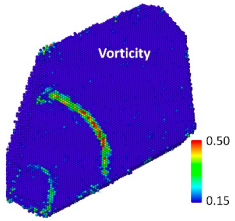
slip



rotation



vorticity



Estimating continuum fields

In 1950 Irving and Kirkwood provided a direct connection between continuum and atomic mechanics.

Three basic fields are postulated:

Mass density $\rho(x,t) = \sum m_\alpha \, \Delta(x - x_\alpha(t))$

Momentum density $p(x,t) = \sum m_\alpha v_\alpha(t) \Delta(x - x_\alpha(t))$

Energy density $\varepsilon(x,t) = \sum e_\alpha(t) \, \Delta(x - x_\alpha(t))$

Using a kernel function Δ that is normalized $\int \Delta(x) dV = 1$

Estimating continuum fields

The velocity is derived $v(x) = \dfrac{p(x,t)}{\rho(x,t)}$

And the per-atom energy e is somewhat arbitrary due to the potential energy being based on bonds

$$e_\alpha = \frac{1}{2} m_\alpha v_\alpha^2 + \frac{1}{2n} \sum_\beta \phi(x_{\alpha\beta})$$

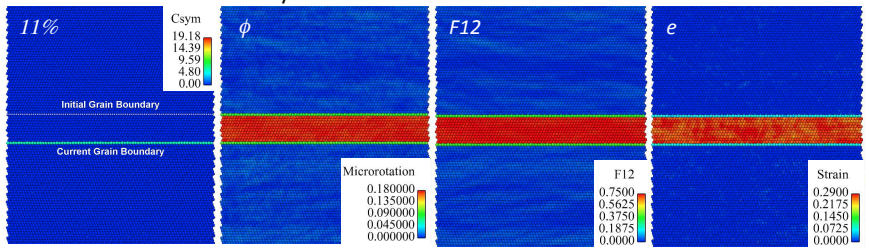
Substituting the primitive fields in the continuum balance of mass, momentum, and energy results in formulae for the continuum fluxes, e.g. stress

$$\dot{p} = \frac{d}{dt} \sum m_\alpha v_\alpha(t) \Delta(x - x_\alpha(t)) = \sum f_\alpha(t) \Delta(x - x_\alpha(t)) + m_\alpha v_\alpha \otimes v_\alpha \nabla \cdot \Delta(x - x_\alpha(t))$$

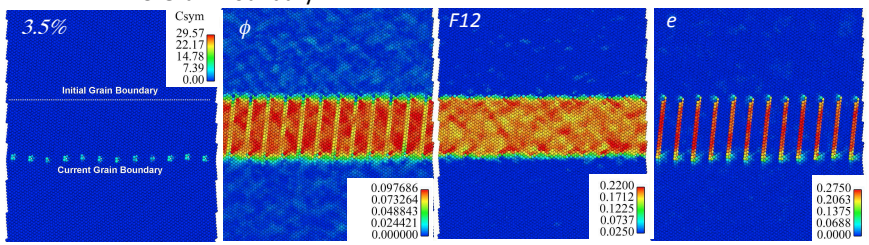
$$= \nabla \cdot \sum f_{\alpha\beta} \otimes x_{\alpha\beta} B(x - x_\alpha, x - x_\beta) + m_\alpha v_\alpha \otimes v_a \, \Delta(x - x_\alpha(t)) = \nabla \cdot \sigma$$

Example: Grain Boundary Migration

- Σ3 Grain Boundary

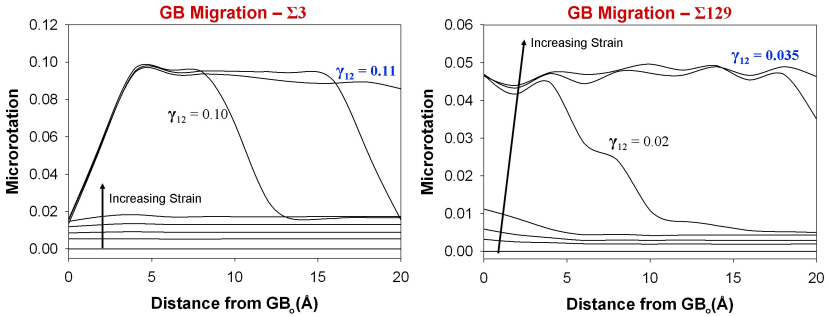


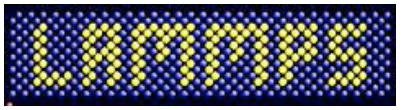
- Σ129 Grain Boundary



Think beyond visualization

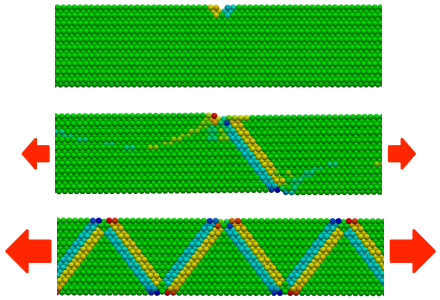
While all of these metrics and tools make lovely pictures and provide visual insight on deformation phenomena, the longer-term goal to use this information to construct models at larger scales…

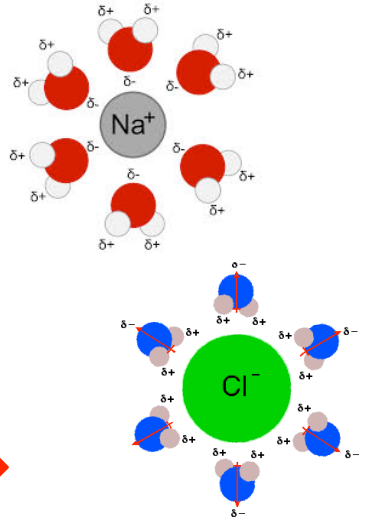




"Homework"

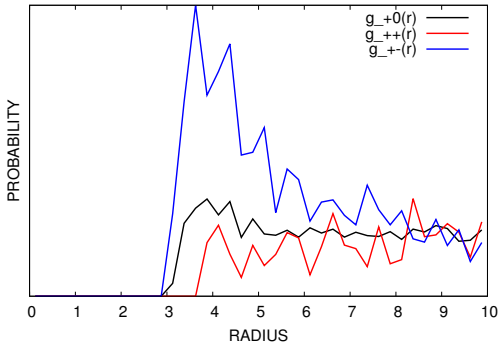
- Two choices:
  - Radial distribution function for an ionic fluid
  - Centrosymmetry & CNA for a defected solid system





INPUT-RDF

```
pair_style lj/cut/coul/cut 10.
dielectric 80.0
read_data       relax.data
group NEUTRAL  type 1
group POSITIVE type 2
group NEGATIVE type 3
pair_coeff * * 0.2381 3.405
pair_modify shift yes
mass       * 39.948
timestep       1.0
fix     NVE all nve
thermo 100
thermo_style custom step temp pe
compute RDF all rdf 40 2 1 2 2 2 3
fix RDF all ave/time 1000 1 1000 c_RDF file rdf.dat mode vector
run 100000
```



- Do these distributions make sense?
- Why is there a gap?
- Why is the blue curve peaked?
- Why are the curves ordered the way they are?
- Is this data converged?
- Does the system size matter?

INPUT-CNA/CS

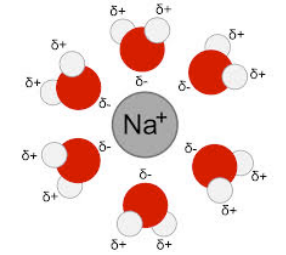
```
boundary      p s p
atom_style    atomic
lattice       fcc 3.52 origin 0.001 0.001 0.001 orient x 1 1 0 orient y 0 0 1 orient z 1 -1 0
region        SYSTEM block -25 25 -5 5 0 3 units lattice
create_box    1 SYSTEM
create_atoms  1 region SYSTEM
mass          1 58.70
region        STEP block 0 0.5 4.5 5 0 3 units lattice
group         step region STEP
delete_atoms  group step
pair_style    eam/alloy
pair_coeff    * * ni1.set Ni
neighbor      0.3 bin
thermo        20
thermo_style  custom step pe
compute       CEN all centro/atom 12
compute       CNA all cna/atom 3.0
dump          D all custom 100000 nanobeam.dmp id type x y z c_CEN c_CNA
variable n equal 10
variable i loop $n
label loop_i
  change_box all x scale 1.01
  minimize 1.e-10 1.e-10 10000 100000
next i
jump SELF loop_i
```

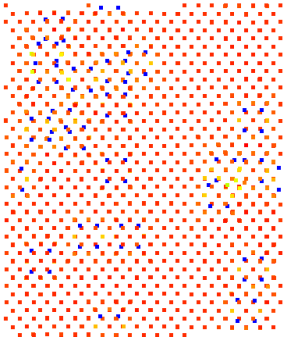
- What are the green colored regions?
- When do they appear?
- Why do they appear?
- What does the "step" do in the deformation process?
- Does the pattern depend on loading? E.g. step size, tension/ compression

BONUS

- Change the neutral species in the fluid system for a water model like TIP4P and observe the differences in the solvation structure
- Make a fluid confined by two walls. Will the RDF change? Will it be uniform?

- Observe the differences in point defect structures obtained using a Stillinger-Weber potential vs Tersoff
- Reverse the loading of the nanobeam , will the response change?
- Add stress as an output does it tell you anything?





Lecture 8

Week 7: **Analyzing Inhomogeneous Systems**

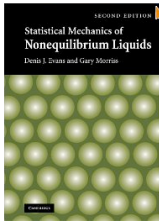
- Identification and visualization of defects and structures
- Metrics, e.g. radial distribution function, common neighbor analysis, centrosymmetry
- Available tools
- Homework: Calculation of centrosymmetry and slip vector around a defect

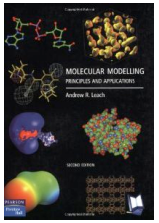
Week 8 : **Molecular Dynamics**

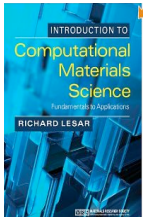
- Newton's 2nd Law
- Time integration algorithms (Verlet, SHAKE, Gear)
- Conserved quantities
- Ensembles (NVE, NVT, NPT, NPH) & equations of motion
- Thermostats, e.g. Nose-Hoover
- Initial conditions and velocity distributions
- *Homework*: NVT average of pressure.

Reading Suggestions for Lec. 8

- Chapter 6 of LeSar
- Chapter 4 of Frenkel & Smit
- Chapter 3 & 6 of Evans & Morriss
- http://en.wikipedia.org/wiki/Molecular_dynamics
- http://lammps.sandia.gov/







Additional slides

Calculating Centrosymmetry within LAMMPS

```
compute ID group-ID centro/atom lattice
```

* ID, group-ID are documented in compute command
* centro/atom = style name of this compute command
* lattice = fcc or bcc or N = # of neighbors per atom to include

Examples:

```
compute 1 all centro/atom fcc
compute 1 all centro/atom 8
```

Typical centro-symmetry values, from a nanoindentation simulation into gold (FCC):

```
Bulk lattice = 0
Dislocation core ~ 1.0 (0.5 to 1.25)
Stacking faults ~ 5.0 (4.0 to 6.0)
Free surface ~ 23.0
```

Calculating CNA within LAMMPS

```
compute ID group-ID cna/atom cutoff
```

* ID, group-ID are documented in compute command
* cna/atom = style name of this compute command
* cutoff = cutoff distance for nearest neighbors (distance units)

Examples:

```
compute 1 all cna/atom 3.08
```

Currently, there are five kinds of CNA patterns LAMMPS recognizes:

* fcc = 1 * hcp = 2 * bcc = 3
* icosohedral = 4 * unknown = 5

The value of the CNA pattern will be 0 for atoms not in the specified compute group. Note that normally a CNA calculation should only be performed on mono-component systems.

Calculating RDF within LAMMPS

```
compute ID group-ID rdf Nbin itype1 jtype1 itype2 jtype2 ...
```

* ID, group-ID are documented in compute command
* rdf = style name of this compute command
* Nbin = number of RDF bins
* itypeN = central atom type for Nth RDF histogram (see asterisk form below)
* jtypeN = distribution atom type for Nth RDF histogram (see asterisk form below)

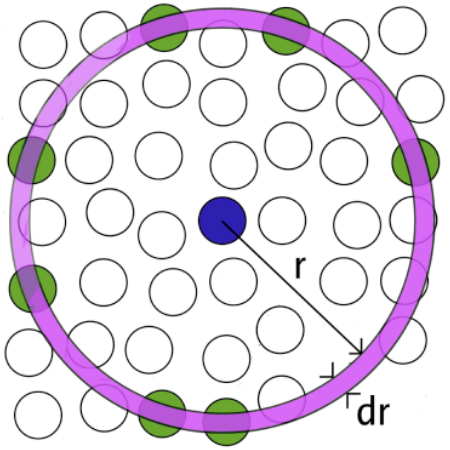
Examples:

```
compute 1 all rdf 100
compute 1 all rdf 100 1 1
compute 1 all rdf 100 * 3
compute 1 fluid rdf 500 1 1 1 2 2 1 2 2
compute 1 fluid rdf 500 1*3 2 5 *10

compute myRDF all rdf 50
fix 1 all ave/time 100 1 100 c_myRDF file tmp.rdf mode vector
```

Radial distribution function

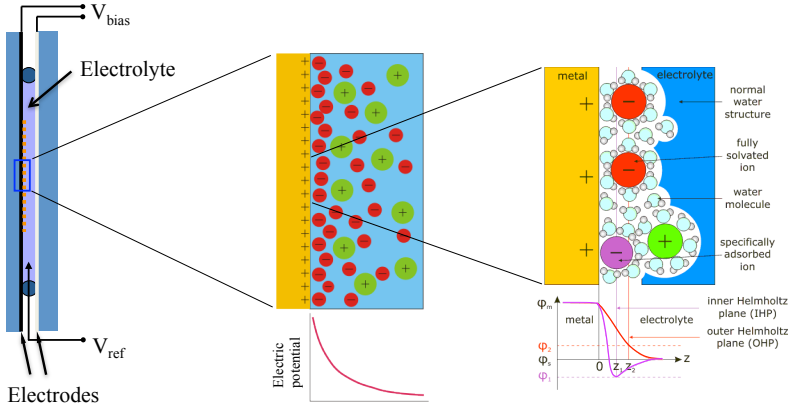
Assume circumeferential variation unintersing



Structure of electrochemical interfaces

The importance of the electric double layer

The electric double layer is where extreme gradients in electrical and chemical potentials provide the driving force for electrochemical reactions



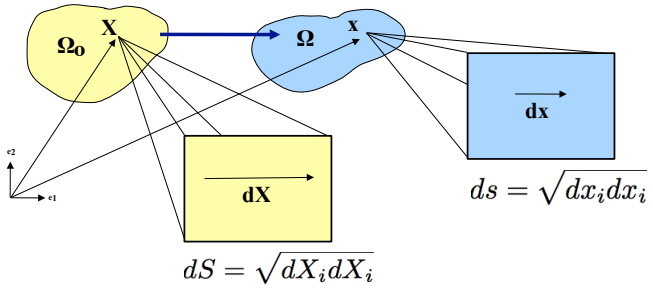
Most electrochemical devices have ion conducting electrolytes between two electrodes

The operating voltage drop occurs across an interfacial layer a few molecules thick. This results in extremely high fields and large interfacial capacitance.

Complex interface structure depends on surface structure, ion size, ion charge and applied voltage

Continuum-based Kinematic Metrics

- Continuum Mechanics



$ds = \sqrt{dx_i dx_i}$

$dS = \sqrt{dX_i dX_i}$

Deformation Gradient (F): $F_{iI} = \frac{\partial x_i}{\partial X_I}$ $dx_i = F_{iI} dX_I$

$$\mathbf{F} = \mathbf{RU}$$