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ECE695: Reliability Physics of Nano-Transistors

Lecture 5: Amorphous Material/Interfaces

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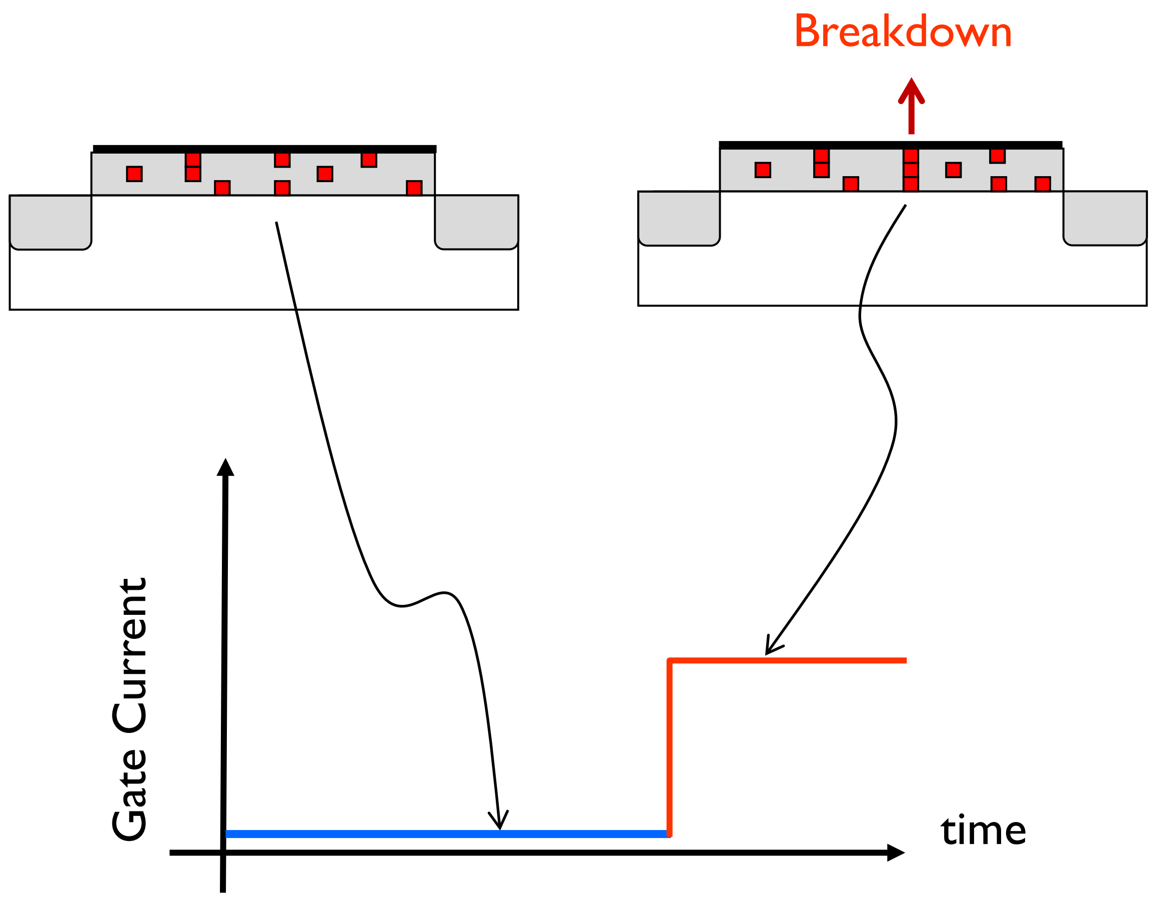
Outline of Lecture 5

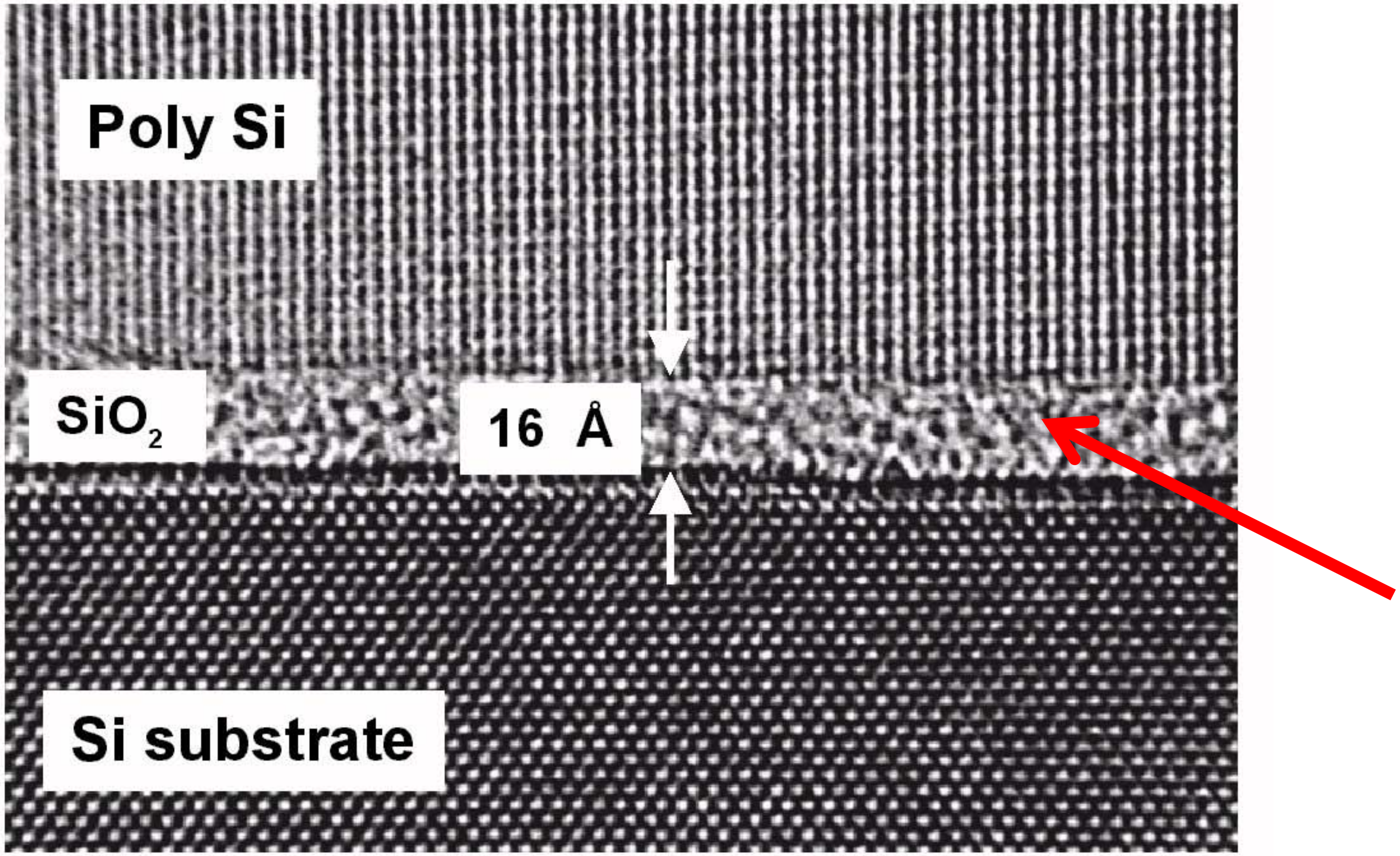
1. Amorphous vs. crystalline materials
2. Defect-free amorphous material
3. Origin of defects (Maxwell's relation)
4. Conclusions

Defects created during oxide breakdown

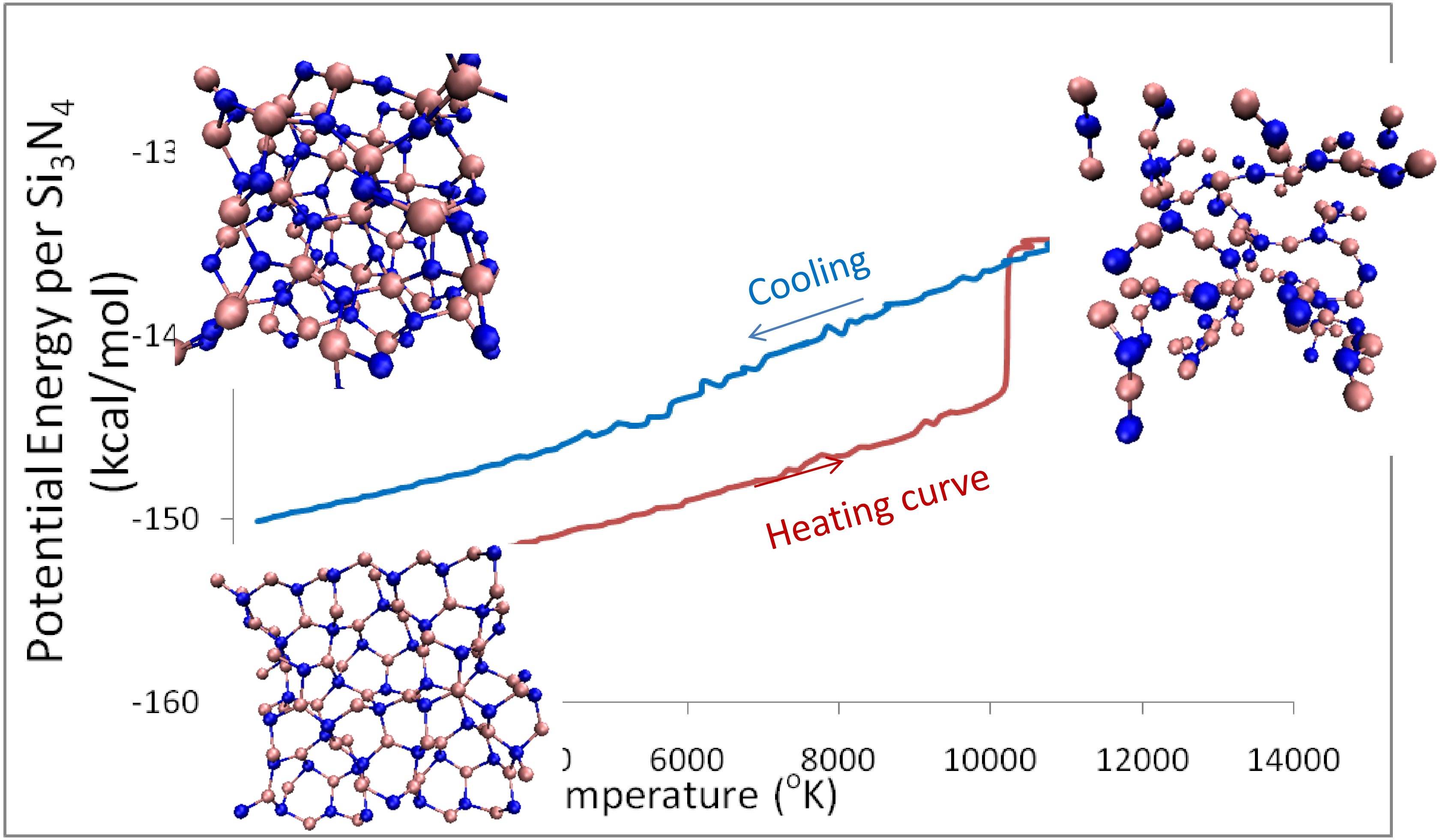


What do the red boxes represent physically?

Defects in amorphous materials

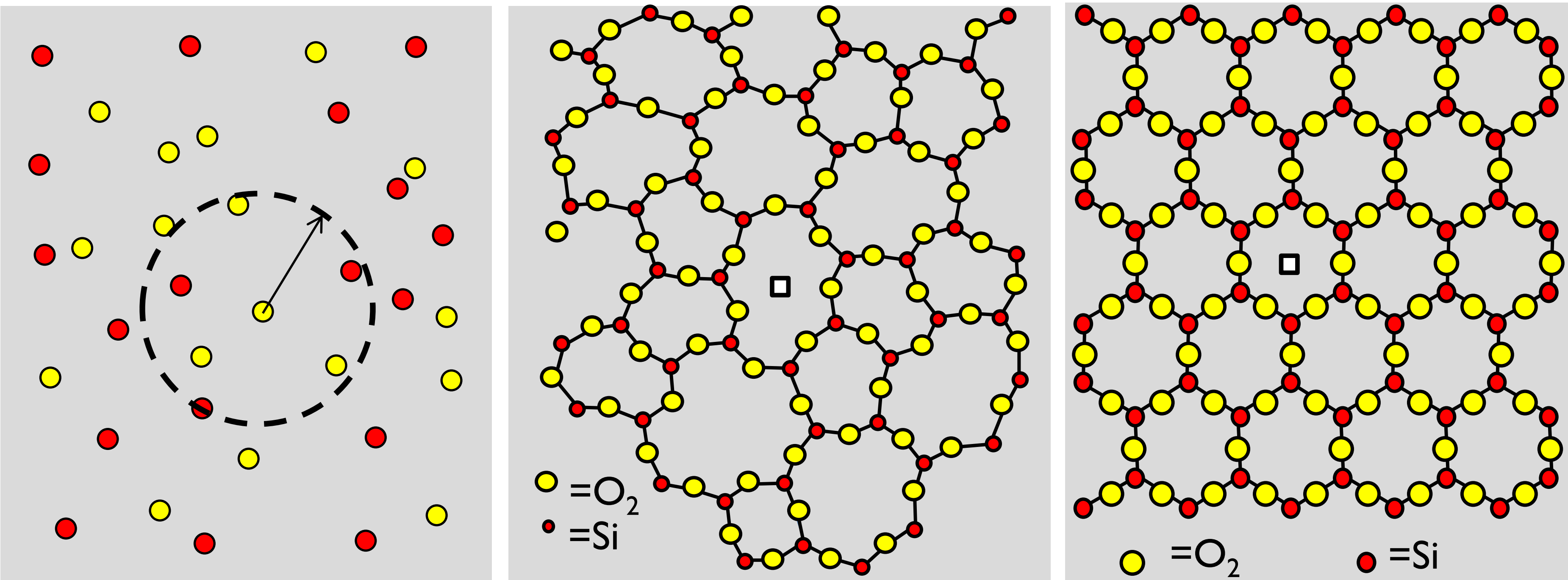


Creating amorphous structures

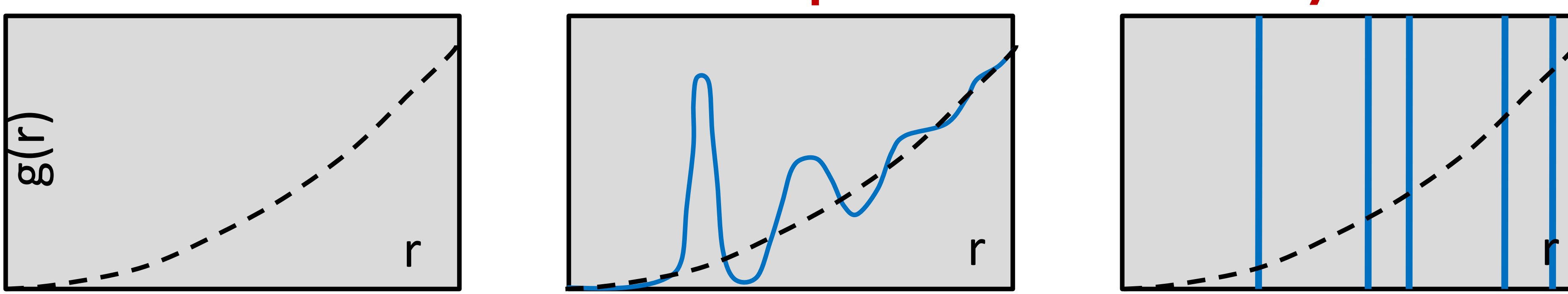


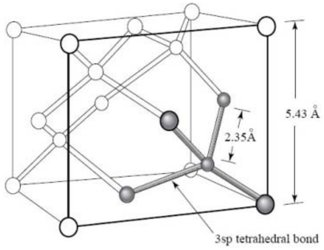
Molecular dynamics (LAMMPS) followed by DFT (Seaquest)

Crystalline, amorphous, and random materials

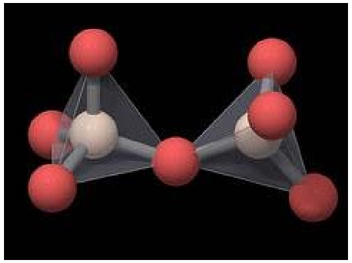


Random | **Amorphous** | **Crystalline**

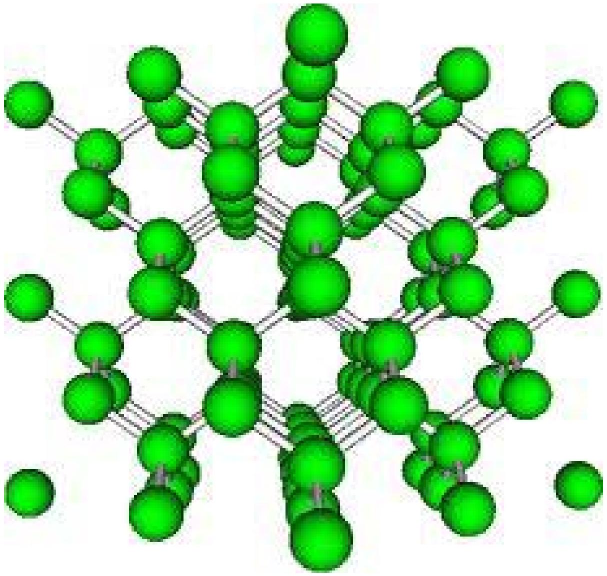




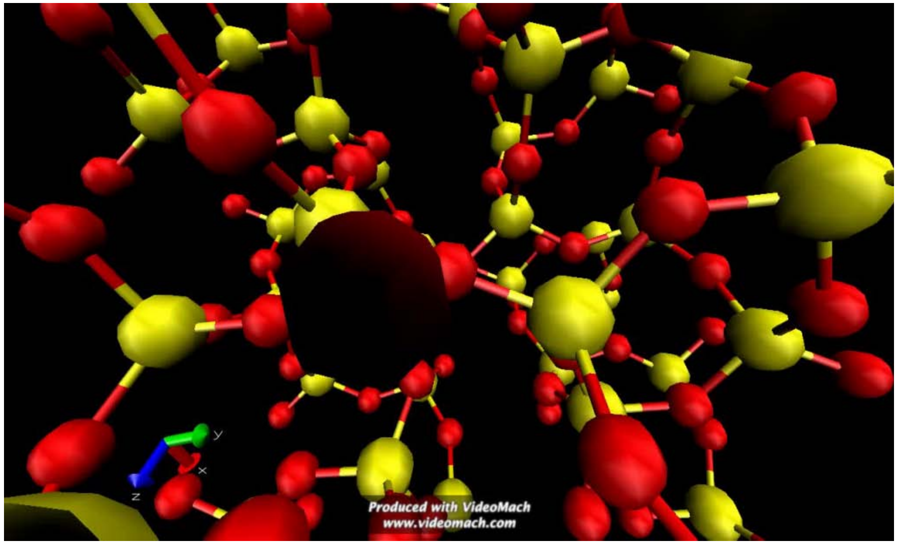
Crystalline Si and SiO_2



Crystalline Si

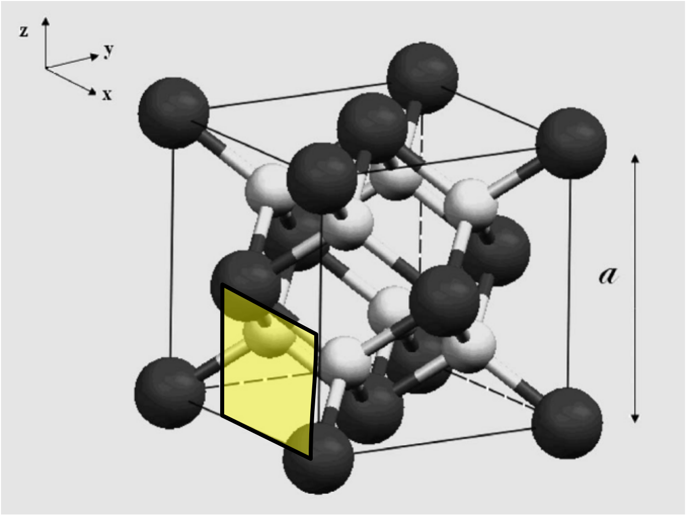


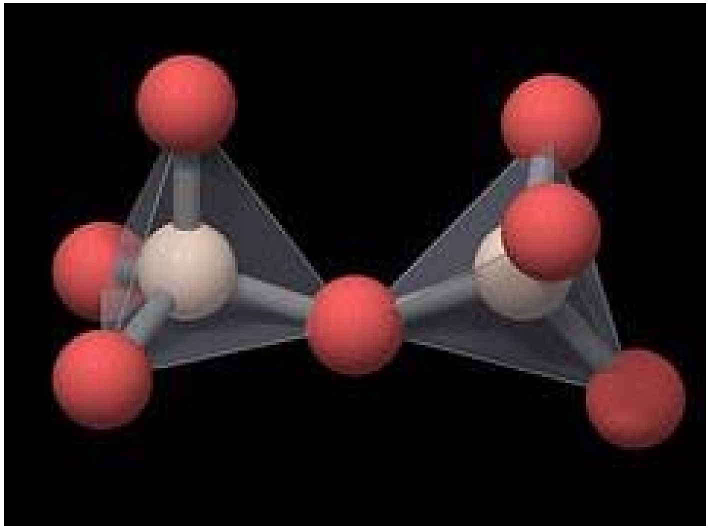
Amorphous SiO2



For a dynamic view of SiO2 see,
http://cst-www.nrl.navy.mil/lattice/struk.jmol/coesite.html

Composition vs. coordination





Structural unit of HfO_2

4 Hf atoms x 1/8 = ½

1 oxygen atom (white) = 1

$Hf_{1/2}O = HfO_2$

Oxygen coordination … 4
Hf coordination – 8

Structural unit of SiO_2

1 Si atoms (white)

4 oxygen atom x ½/cell = 2

SiO2 …..

Oxygen coordination … 2
Silicon coordination … 4

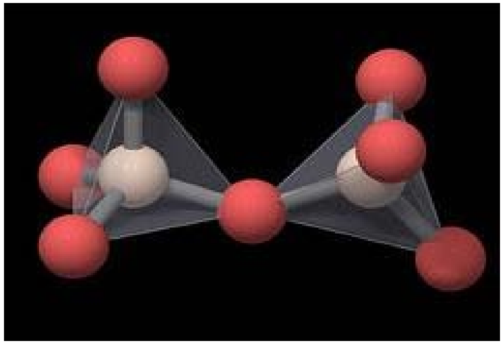
Outline

1. Amorphous vs. crystalline materials
2. Defect-free amorphous material
3. Origin of defects (Maxwell's relation)
4. Conclusions

Z=8-N Rule for amorphous structures

For elementary materials like: a-Si (*Polk, 1971*)

1. z(Si)=8-4=4
2. Constants: Bond lengths (within 1%)
3. Variables: Si-Si bond angles (< 10%)
4. No dangling bonds and no long range order

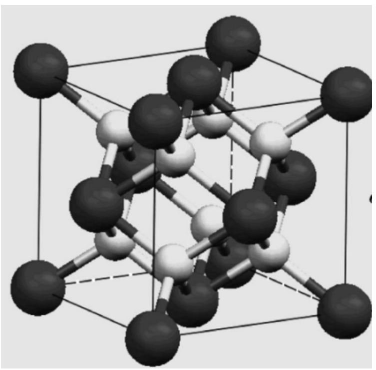


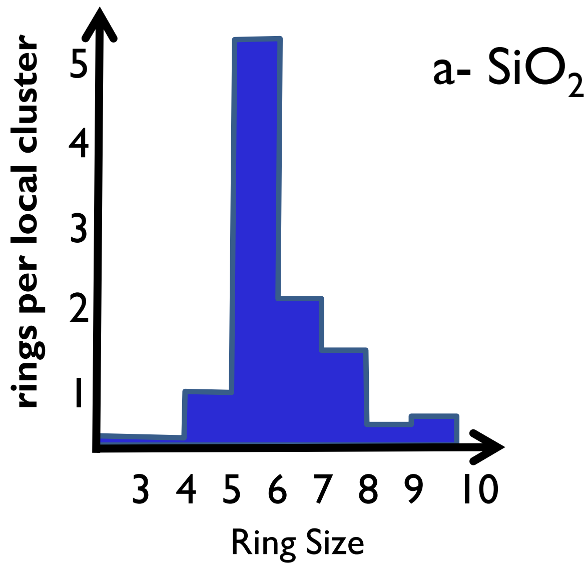
For Binary materials like: a-SiO2 (*Zachariasen, 1932*)

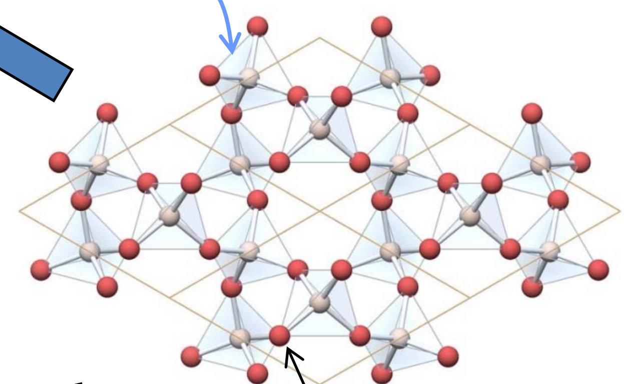
1. z(Si)=8-4=4, z(O)=6-2=2 coordination for silicon and oxygen
2. Presumed Constants:
   Bond lengths, O-Si-O bond angles (red-white-red)
3. Variables: Si-O-Si bond angles (white-red-white)
4. No dangling bonds and no long range order

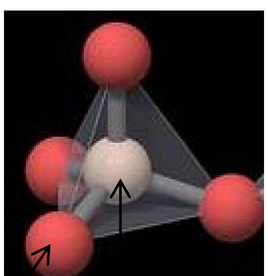
Unlike crystals, odd rings are possible – but the spread is limited

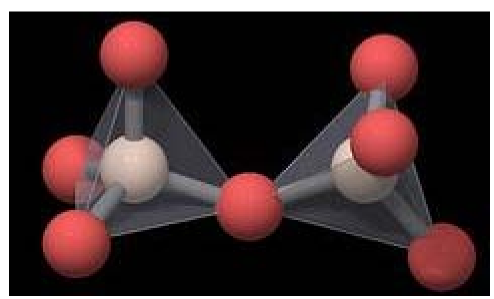
Crystalline vs. amorphous SiO_2/HfO_2







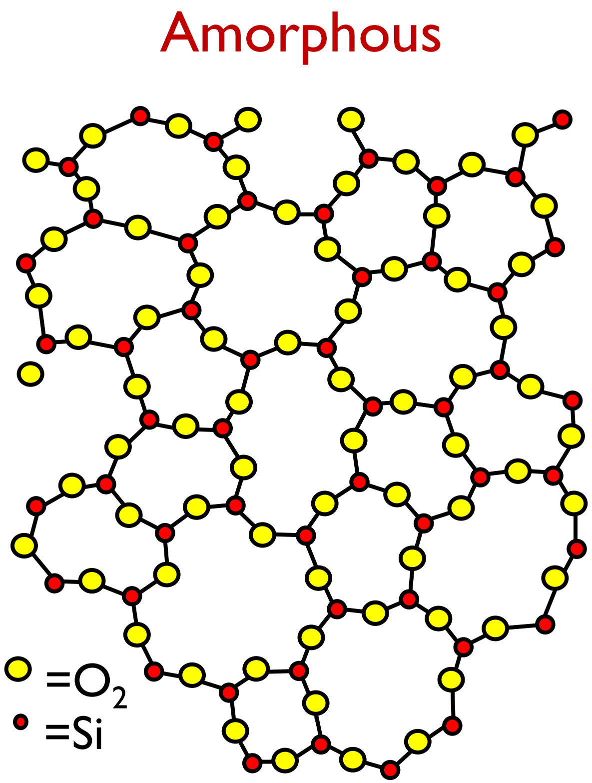


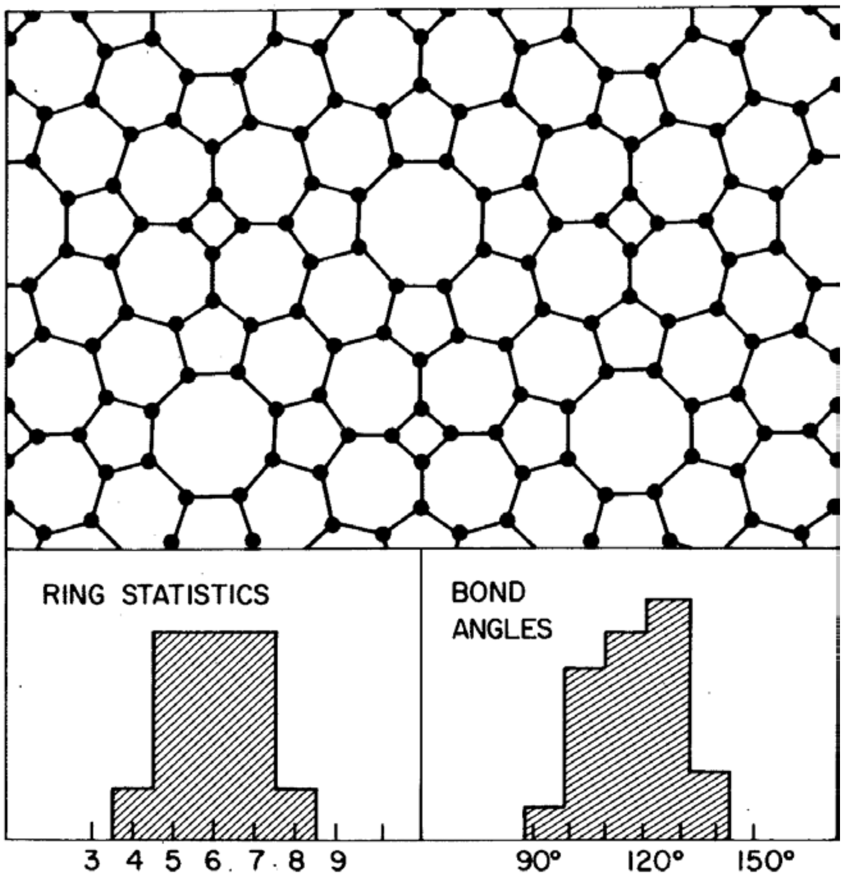


$$z_{Si} = 8 - N_{Si} = 4$$

$$z_O = 8 - N_o = 2$$

Amorphous is neither completely random, nor it is defective!



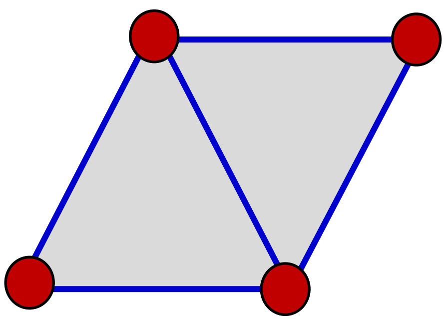


Topology of points and Euler relationship

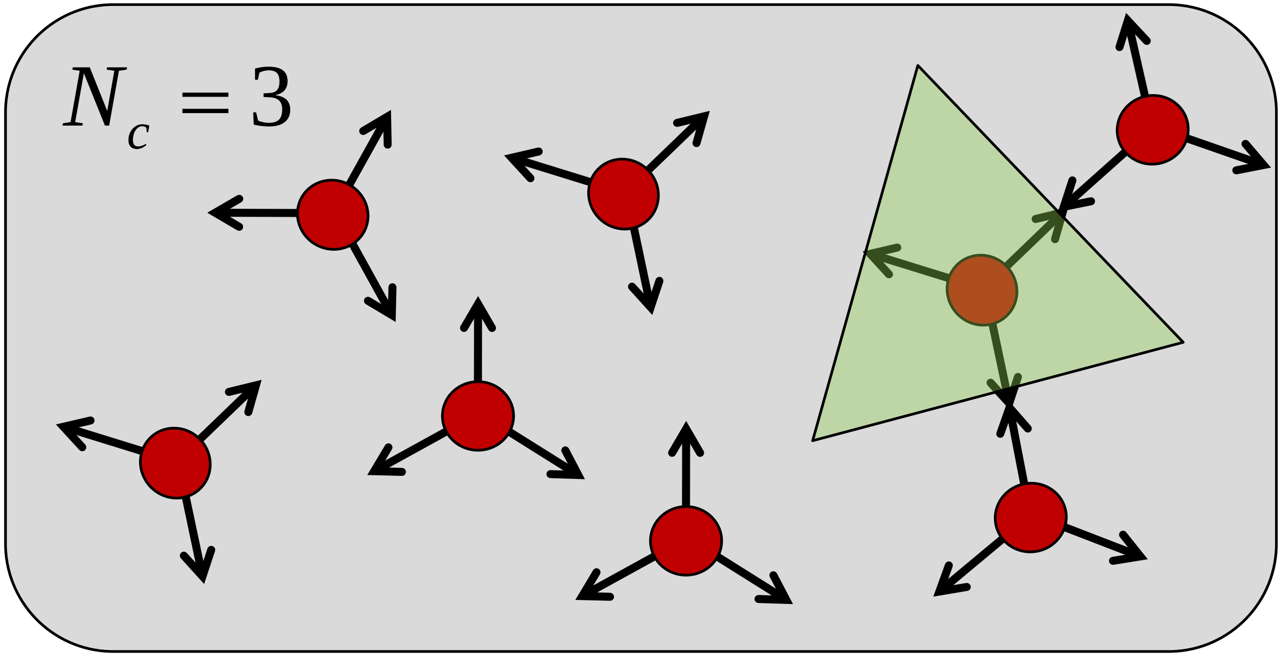
Euler relationship in 2D

$$V - E + N = 1$$

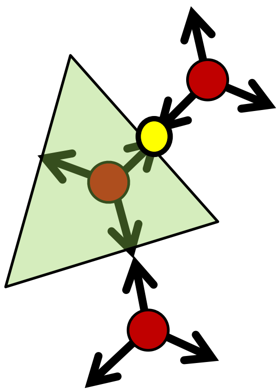
vertices　edges　cell number



$$\left.\begin{array}{l} V = 4 \\ E = 5 \\ N = 2 \end{array}\right] \Rightarrow 1$$

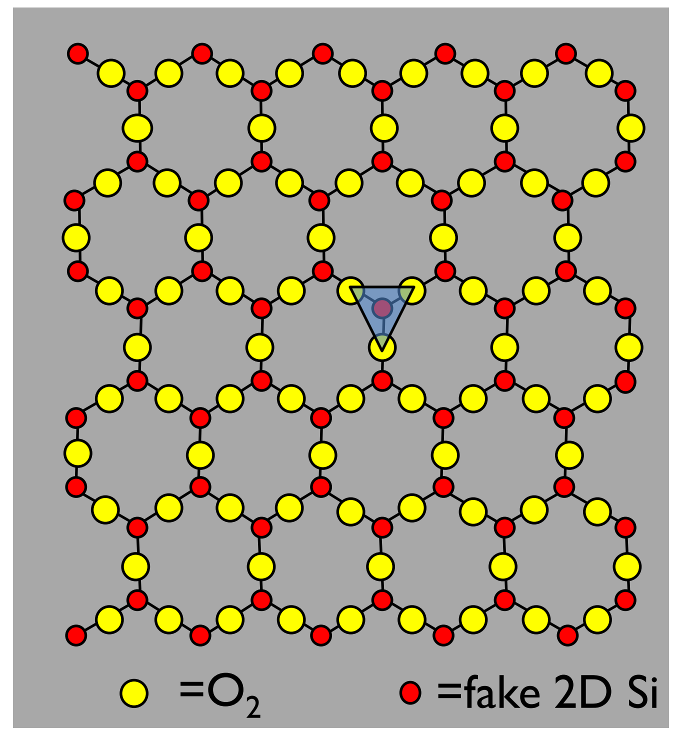


Recall: Euler anticipates *crystal* lattice

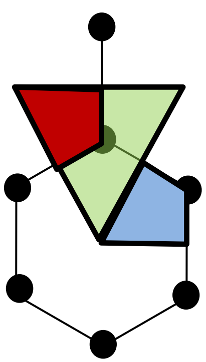


$$\left.\begin{aligned} V &= 1 \\ E &= \frac{3}{2} \end{aligned}\right\} 2E = 3V = N_p N$$

3 bonds/atoms to honeycomb lattice



$$V - E + N = 1$$



$$\frac{N_p N}{3} - \frac{N_p N}{2} + N \sim 0$$

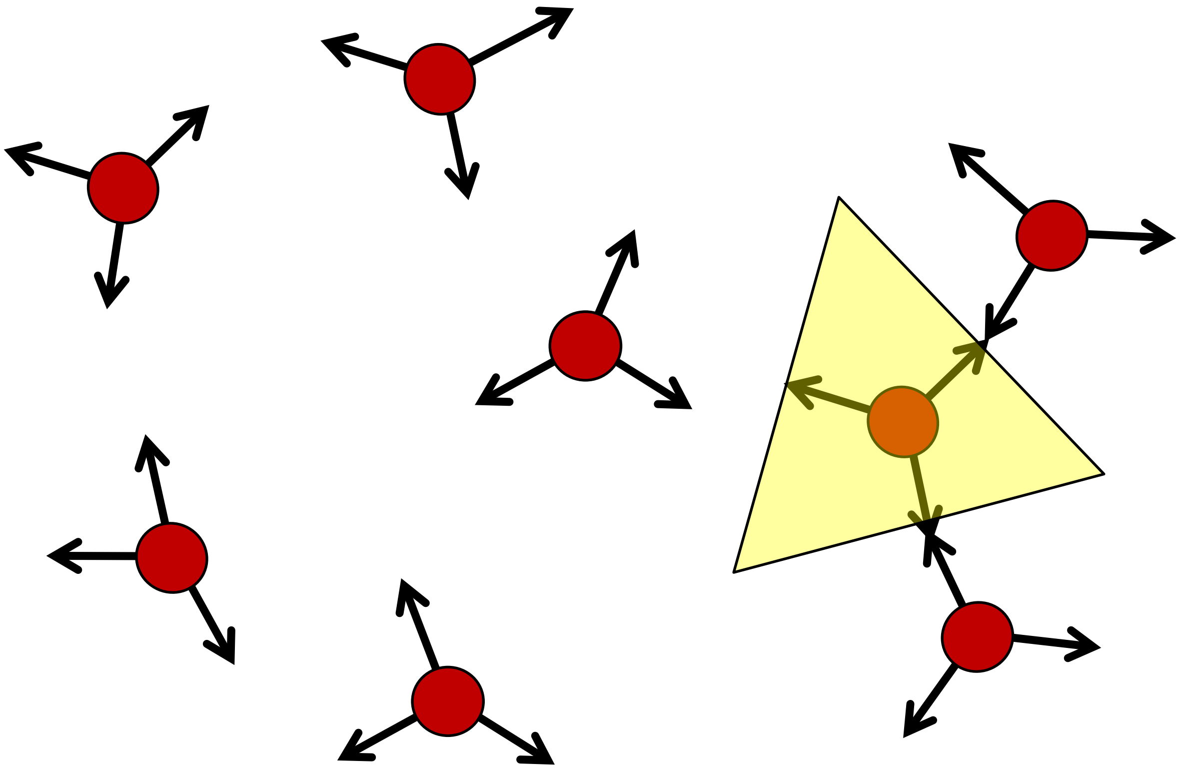
$N_p \cong 6 \longleftarrow$ edges/cell

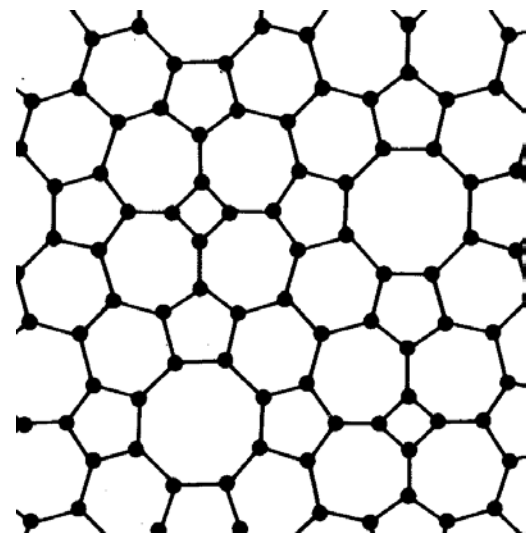
$$6N = 3V \Rightarrow N = \frac{1}{2}$$

1/2 of a cell; therefore each cell must have 6-sides!

Rings with hard vs. soft bonds

$$N_c = 3$$





Ring statistics in random structure

Euler relationship

$$V - E + N = 1$$

$$2E = 3V = \langle N_p \rangle N$$

Prob. of k-sided ring

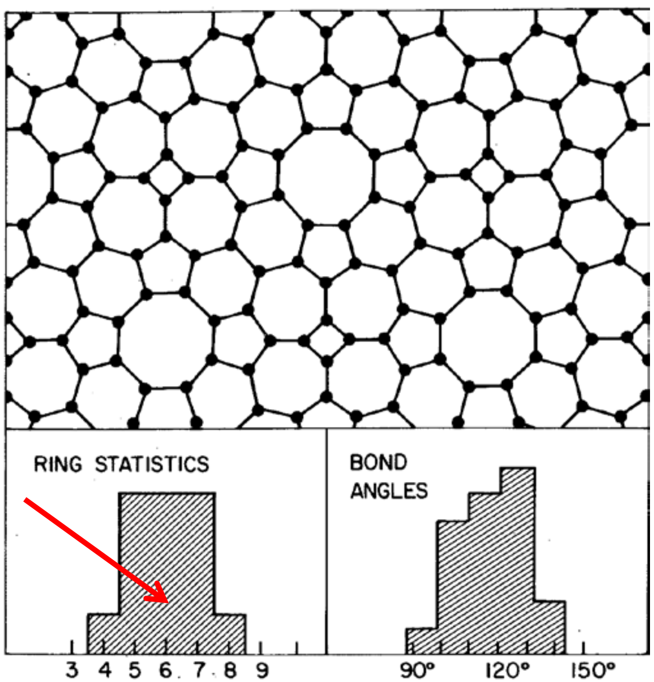
$$\langle N_p \rangle = 6 \quad = \sum_k k \times P_k$$

$$6 = 9P_9 + 8P_8 + 7P_7 + 6P_6 + 5P_5 + 4P_4 + 3P_3$$

$$\text{Ex. } P_9 = P_8 = P_4 = P_3 \equiv P$$

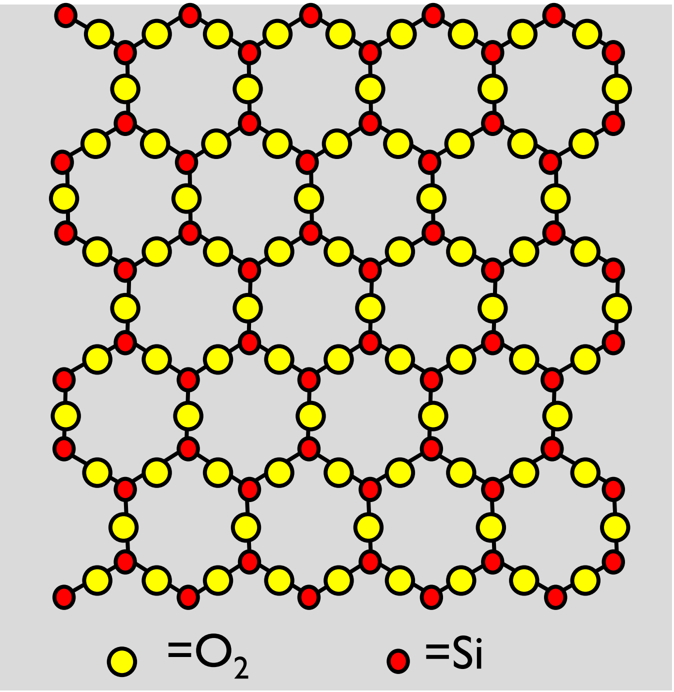
$$P_7 = P_6 = P_5 \equiv 3P$$

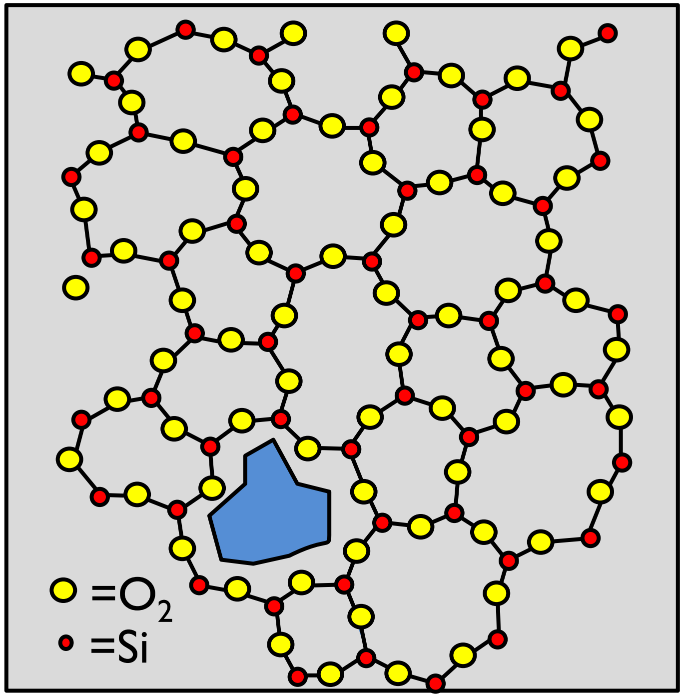
$$78P \approx 6 \Rightarrow P \sim 1/13$$

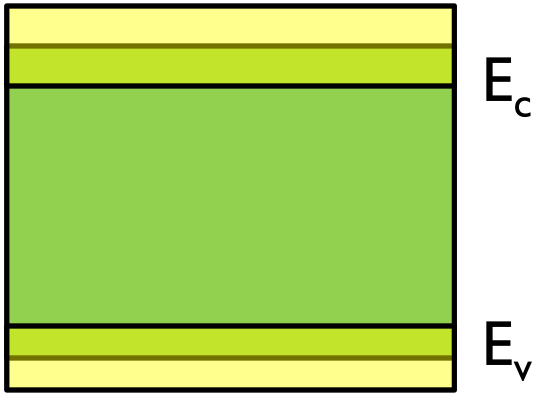


Large rings pay steric penalty and are therefore rare …

Amorphous material and band-tail states

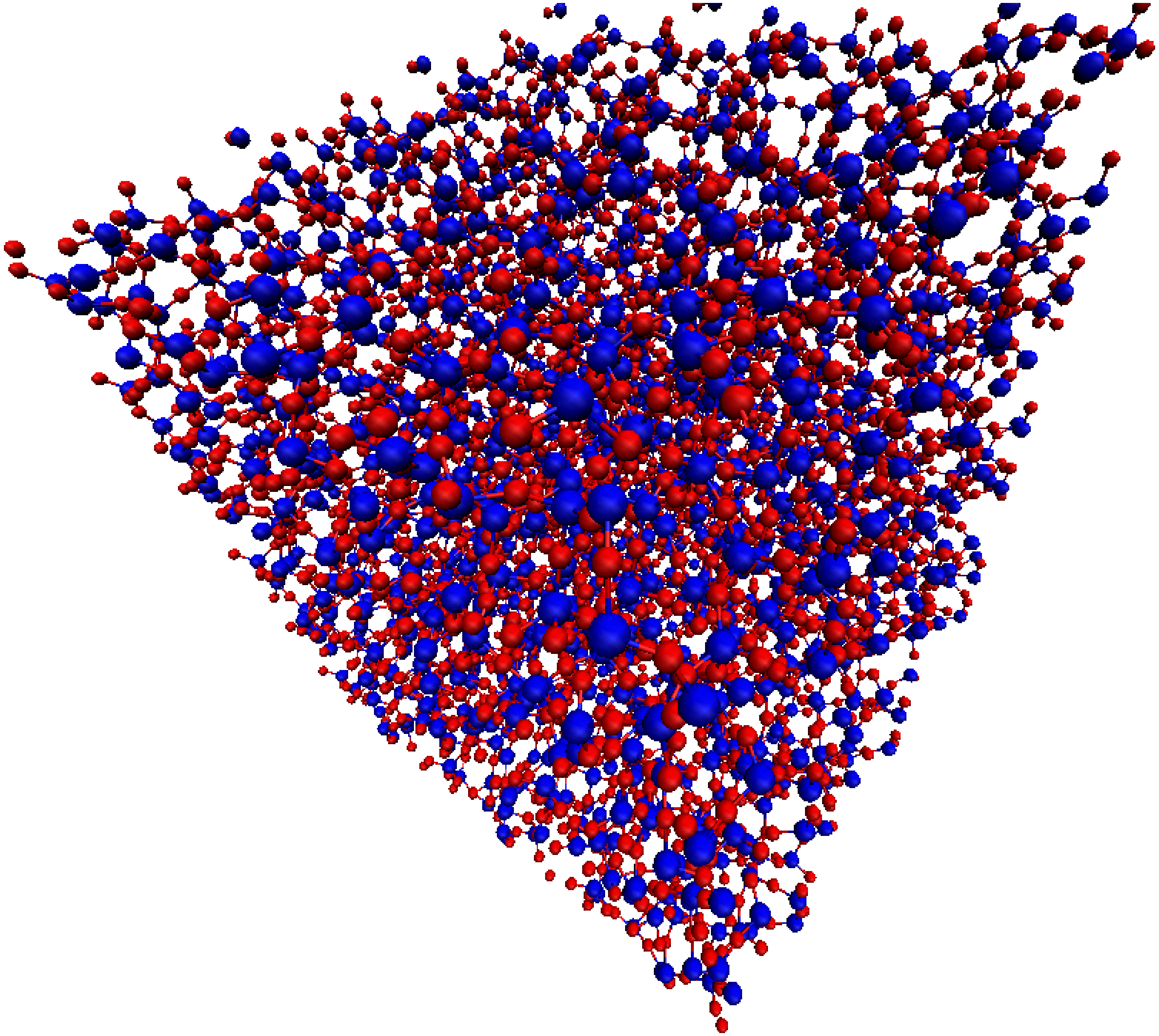




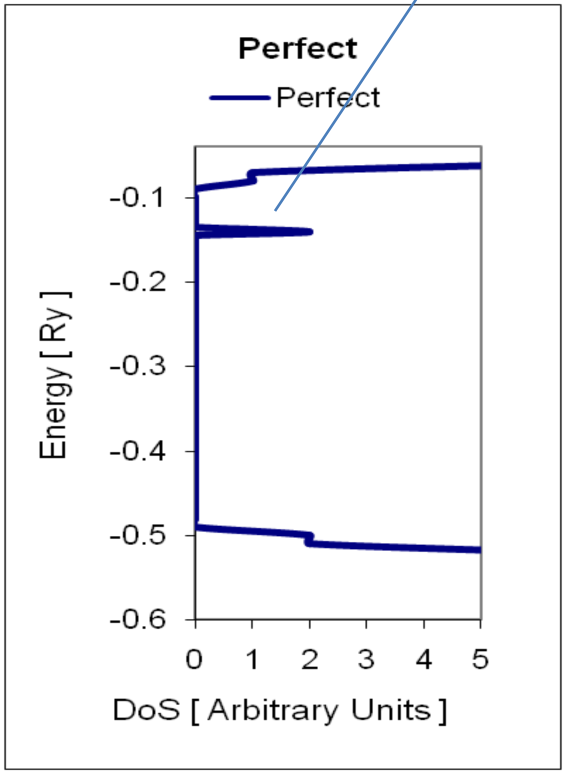


Resolves the puzzle why glass is transparent ….

Perfect amorphous structure



Band tail states



Credit: R.Vedula and A. Strachen

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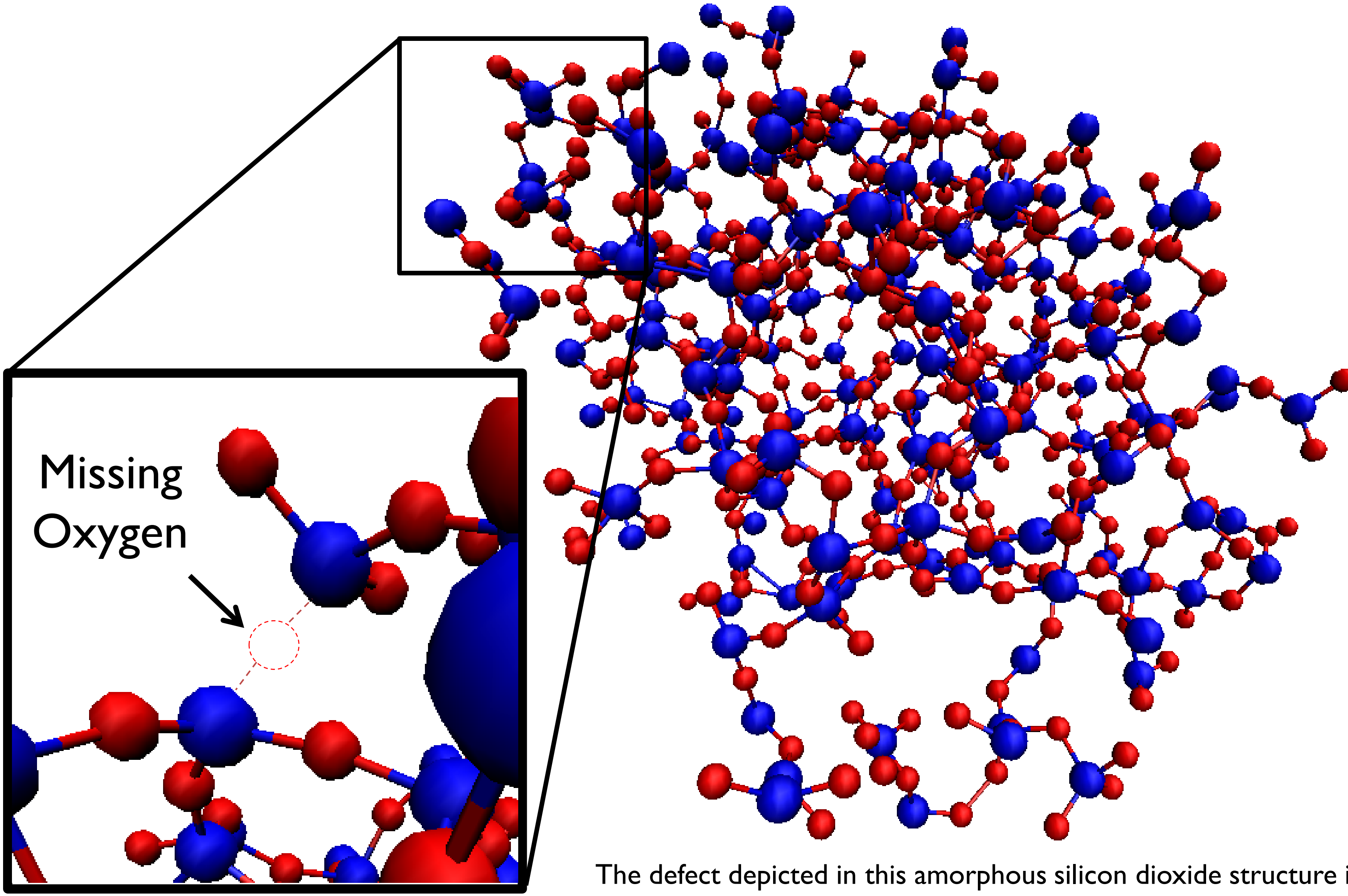
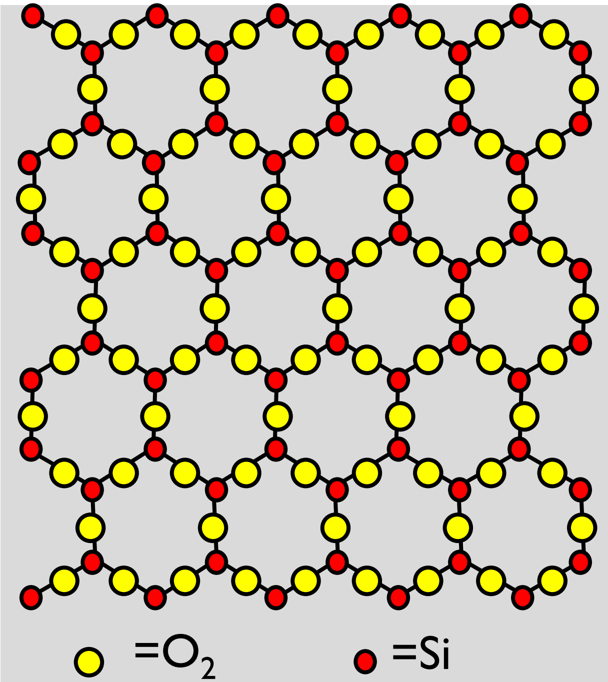
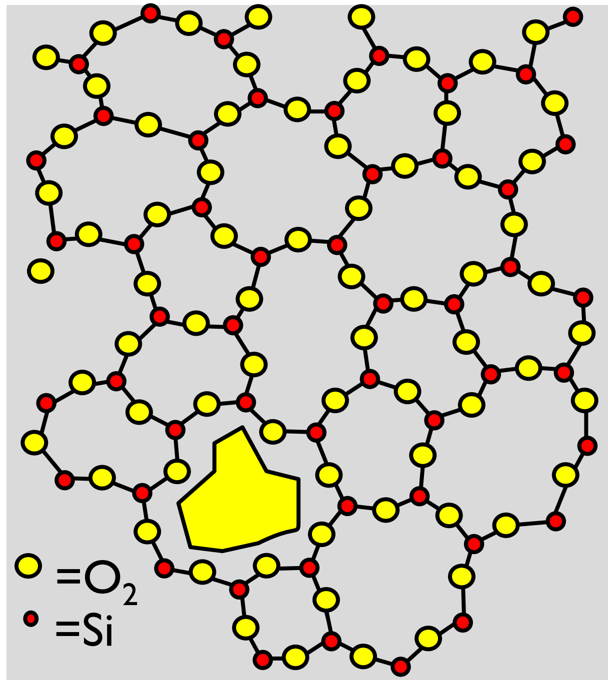


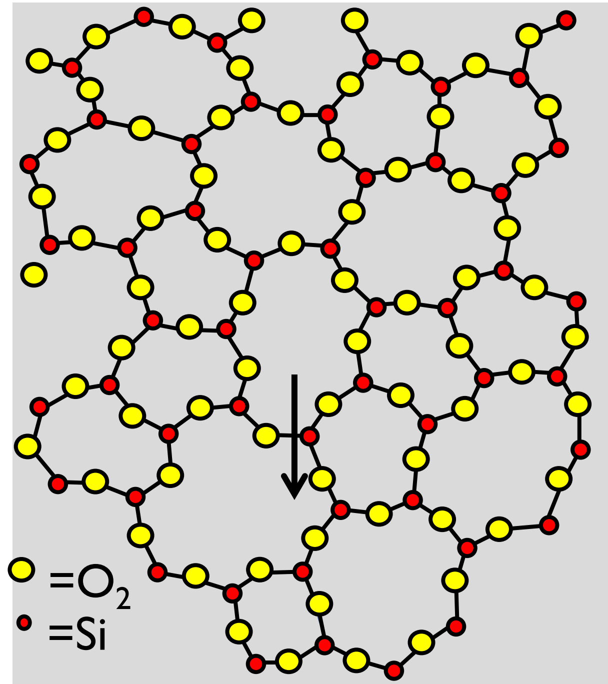
Credit: R. Vedula and A. Strachen

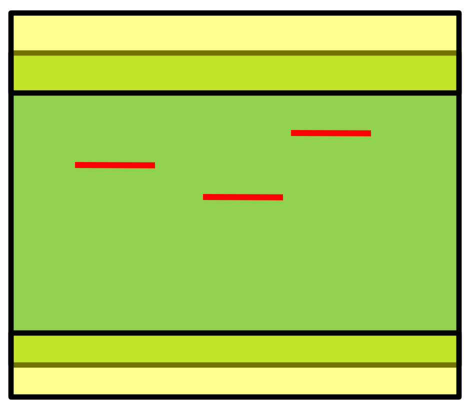
The defect depicted in this amorphous silicon dioxide structure is known as a neutral oxygen vacancy. It is one example of several defects being investigated that are believed to be associated with charged centers in dielectrics which contribute to the degradation of several different microelectronic devices.

Meaning of an oxide/nitride defect

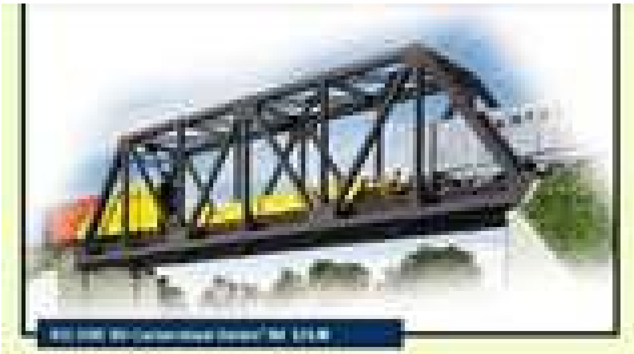








Why defects form:
Truss bridges vs. Maxwell relationship

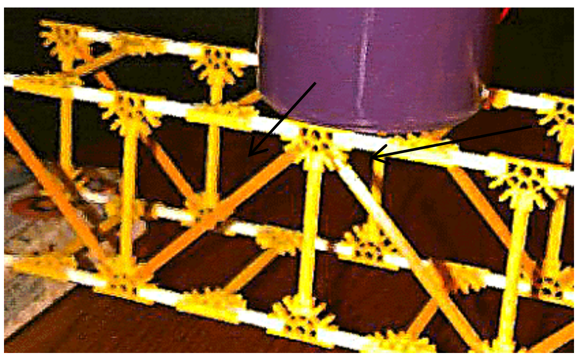


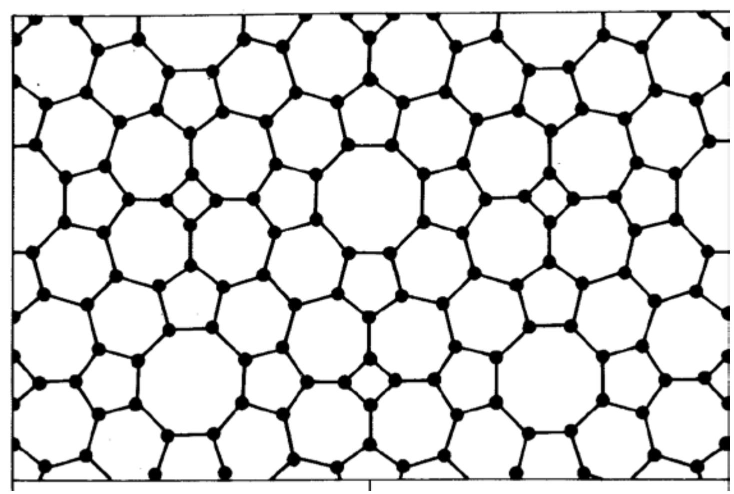
$$V = \frac{1}{2}\sum_{i,j} \alpha_{ij}(\Delta r_{ij})^2 + \frac{1}{2}\sum_{i,j,k} \beta_{ijk}(\Delta\theta_{ijk})^2$$

Zero T approximation

$$M_0 = DN - N_c - (D + \alpha)$$

$$M_0 > 0 \text{ unstable, } \; M_0 < 0 \text{ stable}$$





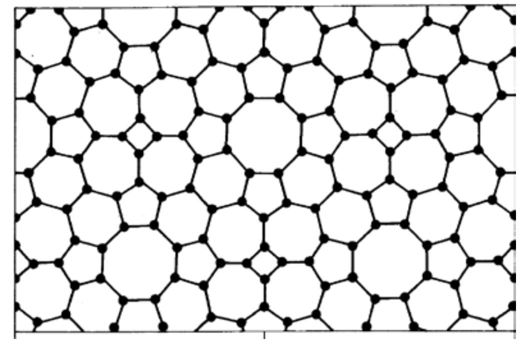
Origin of defects and Maxwell constraints

Dimensionality

Points to be stabilized

Constraints

$$M_0 = DN - N_c - (D + \alpha)$$



$$N \equiv \sum_{r=1}^{k} n_r$$

Types of atoms with different coordination

Number of atoms with coordination r

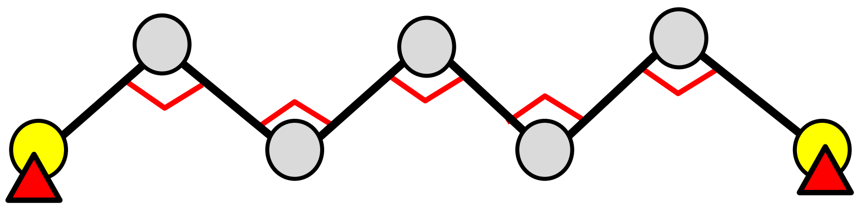
$$N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}\left(2r - D\right)\right]_{angle}$$

$M_0 > 0$ unstable, $M_0 < 0$ stable

Example: a bridge or a finite DNA …

$$M_0 = DN - N_c - (D+\alpha) \qquad M_0 > 0 \text{ unstable}, \quad M_0 < 0 \text{ stable}$$

$$N \equiv \sum_{r=1}^{k} n_r \qquad N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}(2r-D)\right]_{angle}$$



$$D=2 \quad r=2 \qquad n_1 = 2, \quad n_2 = (s-2) \qquad N = s$$

$$N_{c,bonds} = (s-1), \quad N_{c,angle} = (s-2) \quad \text{Just count!}$$

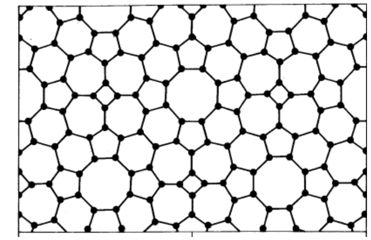
Unbounded at ends, plus a overall rotation: constraint lost … 3

$$M_0 = 2s - [(s-1)+(s-2)] - 3 = 0 \qquad \text{Stable!}$$

Homework: Show that unstable without angle constraints …

Example 2: Stability of molecules

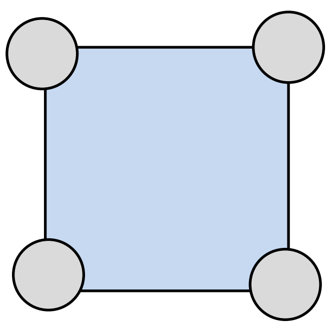
$$M_0 = DN - N_c - (D+\alpha)$$

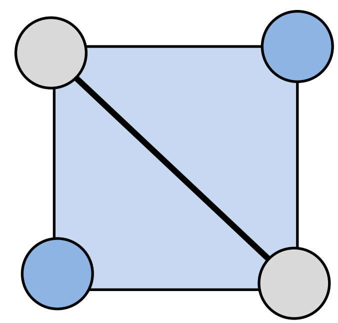


$$M_0 > 0 \text{ unstable}, \quad M_0 < 0 \text{ stable}$$

$$N \equiv \sum_{r=1}^{k} n_r \qquad N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \cancel{\left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}(2r-D)\right]_{angle}}$$

coordination





$r = 2 \quad n_{r=2} = 4 \quad N_c = 4$

$M_0 = (2\times 4) - 4 - 3 > 0$

$n_{r=2} = 2 \quad n_{r=3} = 2 \quad N_c = 5$

$M_0 = (2\times 4) - 5 - 3 = 0$

Exercise: honeycomb (unstable). triangular (stable)

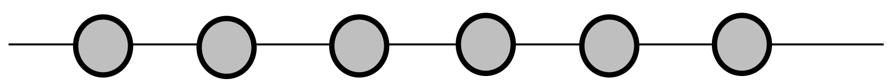
Illustrative example: 1D infinite polymer

$$\frac{M_0}{N} = D - \frac{N_c}{N} - \frac{(D+\alpha)}{N} \rightarrow D - \frac{N_c}{N}$$

$M_0 > 0$ unstable,

$M_0 < 0$ stable

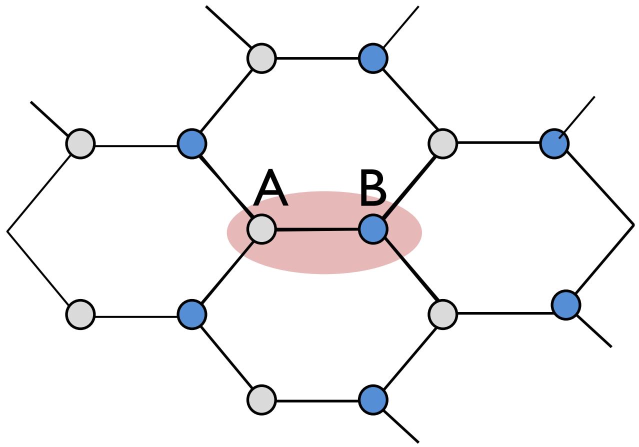
$$N \equiv \sum_{r=1}^{k} n_r \qquad N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \cancel{\left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}\left(2r-D\right)\right]_{angle}}$$



$$D = 1 \;\; r = 2 \qquad N_c = n_r \quad \Rightarrow \frac{M_0}{N} = 1 - \left(1 \times \frac{2}{2}\right) = 0$$

Stable system ..

Example 3: Two dimensional graphene



$$N \equiv \sum_{r=1}^{k} n_r = n_3 = N \qquad D = 2,\ r = 3$$

$$N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}(2r - D)\right]_{\theta}$$

$$= 1.5N + (N/2)(2\times 3 - 2) = 3.5N \text{ (with } \theta)$$

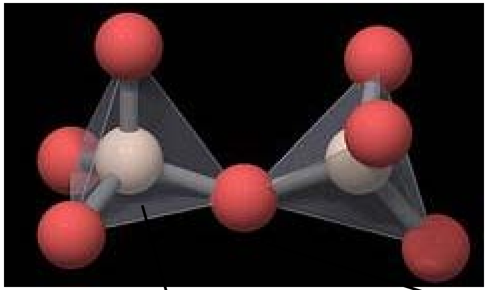
$$= 1.5N \text{ (without angle constraint)}$$

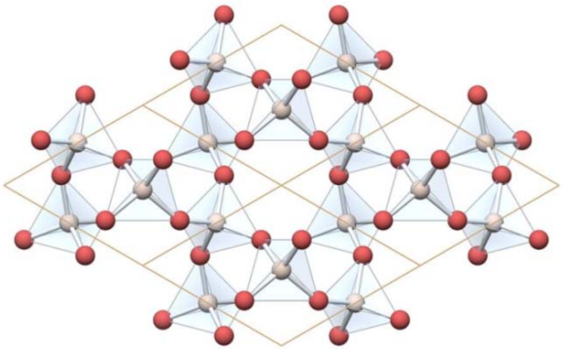
$$\frac{M_0}{N} = 2 - 3.5 = -1.5 \text{ (rigid, with } \theta)$$

$$= 2 - 1.5 = 0.5 \text{ (floppy, without angle)}$$

Example 4: 3D constraints for binary solids

$$N_c \equiv \left[\sum_{r=1}^{k} n_r \frac{r}{2}\right]_{bond} + \left[\sum_{r=1}^{k} n_r \frac{(D-1)}{2}(2r-D)\right]_{angle}$$





J.C. Phillips, 1979.
Thorpe, 1982.

$$N_c(Si) = \left.\frac{\langle N_{c,1}\rangle}{2}\right]_{r_{ij}} + \left(2\langle N_{c,1}\rangle - 3\right)\Big]_{\theta_{ijk}} \qquad N_c(O) = \left.\frac{\langle N_{c,2}\rangle}{2}\right] + 0$$

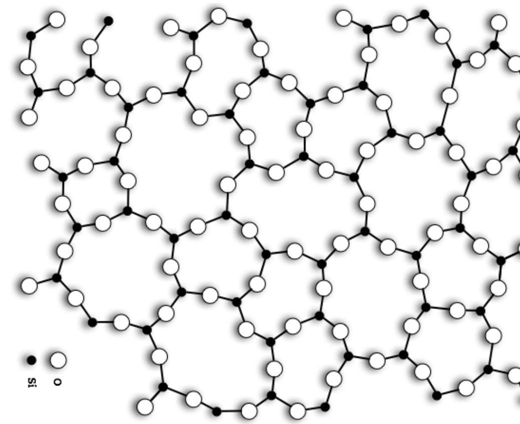
Average Si coordination … $\langle N_{c,1}\rangle$ Average O coordination … $\langle N_{c,2}\rangle$

Average coordination … $\langle N_c^{A_x B_{1-x}}\rangle = x\langle N_c^A\rangle + (1-x)\langle N_c^B\rangle$

Example 4: at what value of x is SiO strain-free?

$$\frac{M_0}{N} \approx 3 - x\left[\frac{\langle N_c^{Si}\rangle}{2} + (2\langle N_c^{Si}\rangle - 3)\right] + (1-x)\left[\frac{\langle N_c^{O}\rangle}{2} + 0\right]$$

$$= 3 - x\left[\frac{4}{2} + (2\times 4 - 3)\right] + (1-x)\times\frac{2}{2}$$



$$0 \Rightarrow 7x + (1-x) = 3 \quad x = \frac{1}{3}$$

$Si_{1/3}O_{1-1/3} = SiO_2$ stress-free optimally coordianted!

$$\langle N_c^{SiO_2}\rangle = 0.33 * \langle N_c^{Si}\rangle + 0.66 * \langle N_c^{O}\rangle$$

$$= 2.64$$

A very important number that arises in all good 3D ‘glass formers’

Conclusions

- Amorphous is neither completely random, nor it is defective. It lacks long range order (unlike crystalline) but has well defined short range order.
- Distribution in bond angles and size of rings are responsible for defect free amorphous structures.
- Maxwell relations help in defining the stable possible structures using only geometric relations. (i.e. T=0 approximation)
- Angular constraints are key to stability of systems.

References

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- A tutorial paper on constraint theory can be found in "Continuous deformation in random network", J of Non-Cryslline Solids, 57, (1983) 355-370. Also, "A topological-dynamical model of amorphycity" in the same Journal, 42, (1980), 87-96 is helpful. J.C. Phillips wrote the original paper (with some mistakes) J. Non-Crystal Solids, 34, 153, 1979.
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- A good introductory analysis of defects in noncrystalline semiconductor can be found in "Noncrystalline semiconductors", J. Fritzsche, Physics Today, 34, 1984. Has a good explanation of the Negative-U traps.
- For higher dimensions, V-E+F=2 … Vertex, edges, and faces … http://www.ics.uci.edu/~eppstein/junkyard/euler/charges.html Thurston's proof based on electrical charges.
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Review questions

G1: What is the difference between coordination and composition?

G2: Is periodicity essential for a defect-free structure?

G3: Why can't the amorphous material have arbitrary ring distribution?

G4: How does Temperature enter in Maxwell's relationship?

G5: Do you expect more or less defect for over-constrained systems?

G6: Is there a 3D version for Euler's relationship? What is it?

G7: Why is single stranded DNA floppy, while Graphene is so strong?