

5. STRUCTURES AND DEFECTS IN AMORPHOUS SOLIDS

5.1 Review/Background:

In Chapter 4, we discussed the origin of crystal structures and Bravais lattices based on Euler relationship. In this chapter, we will discuss a number of related questions and concepts: Simply because amorphous solid does not have periodicity, does it mean its spatial arrangement is completely random? What is the geometrical essence of an amorphous structure? Can amorphous structure be defect free? Can the defects in amorphous solids be classified and can the propensity of defect formation be predicted? Given the ubiquity of random materials, many have thought about the problem of geometry, structure, and function of amorphous solid deeply. We will use some of the tools developed to answer the questions.

5.2 Amorphous vs. Crystalline Structures:

Given any material to characterize its structure, we look at the radial distribution functions or structural factor functions obtained from Neutron Diffraction or X-ray diffraction

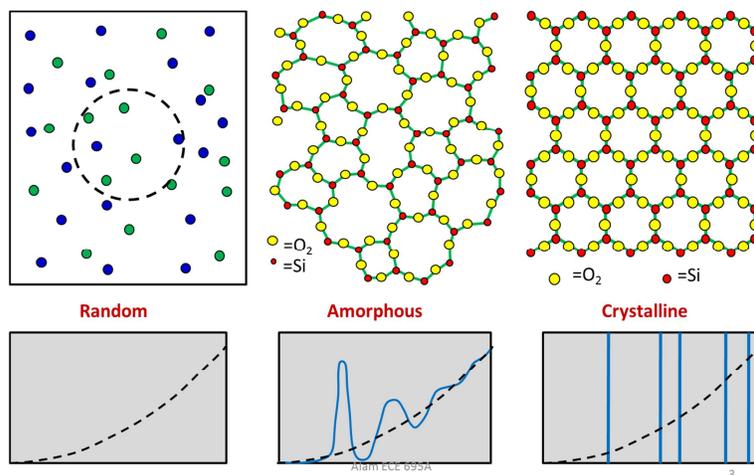


Fig. 5.1 (top row) Representative figures of Random, Amorphous and Crystalline structures and (bottom row) their respective structural functions.

experiments to determine the Radial Distribution Function, $g(r)$. The RDF is defined as the probability of finding an atom in a spherical shell of very small thickness dr at a distance r from a chosen center atom. In other this defines the average density of atoms at a particular position r . In Fig. 5.1, we show the structure function ($r * g(r)$) for random, amorphous and crystalline materials. In leftmost of the figure, we see that the number of atoms, in $r * g(r)$ function, increases as function of radius cubed (r^3). This is the indication of a random structure. In the middle, for amorphous structure we see that there are well defined peaks at short distances and the radial distribution function goes as radius cubed (r^3) at longer distances r from the center. This indicates that amorphous structure is not random and has a well-defined short range order, but no long range order. In contrast, in the rightmost figure, we observe only delta functions as distance from center (r) increases indicating fixed distances between nearest neighbors and fixed ring size. This is indicative of a crystalline structure.

5.3 Amorphous Structures do not have vacancies/interstitials, but they have coordination defects

The structure of various amorphous defect free oxide structures was first proposed by W. H. Zachariasen in his famous 1932 paper “The atomic structure in glass”. The condition for the formation of a glass is expressed as the substance that can form extended 3D networks lacking periodicity with an energy comparable with that of the corresponding crystal network. If the energy of a glass is to be comparable with that of the crystal, we must require that oxygen polyhedral arrangement in glass and crystal are essentially the same. That means we should have the same structural unit. Therefore, in vitreous SiO_2 , we expect to find tetrahedra of oxygen atoms around silicon. If silicon were surrounded by three or by five or any other number of oxygen atoms (instead of typical 4), the potential energy would be much greater. In view of the above arguments, he proposed that vitreous SiO_2 glass is made up of a continuous network of connected structured tetrahedral units consisting of one Silicon surrounded by four oxygen [3].

The rules for formation of glass oxides like SiO_2 proposed by Zachariasen are

1. $z(\text{Si})=4$, $z(\text{O})=2$ coordination for silicon and oxygen
2. Presumed Constants: Bond lengths and O-Si-O bond angles
3. Variables: Si-O-Si bond angles
4. No dangling bonds and no long range order

Using the above defined rules a glass can be created by tiling a network of connected SiO₂ structural units beside each other. This gives rise to a spread in Si-O-Si bond angle and variable ring size with each atom being completely coordinated. Hence a glass structure similar to one shown in Fig. 5.2 below.

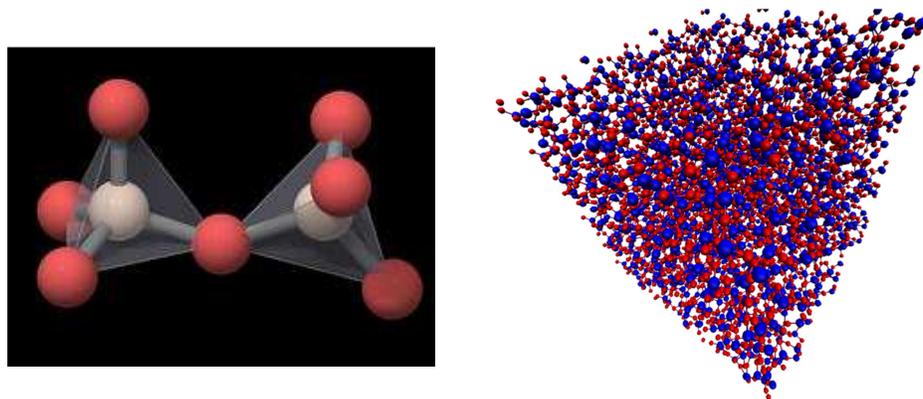


Fig. 5.2 (left) Structural Unit of SiO₂, (right) amorphous SiO₂.

5.4 Ring Statistics explains the structure of a random material

Although an amorphous solid may appear completely random, it is anything but. Let me show that in a 2D defect free random solid shown in Fig. 5.3, rings of sizes 5-7 are most probable, large rings or very small rings are possible, but rare. Recall from Chapter 4 that in 2D, Euler relationship for large system is given by

$$V - E + N \sim 0 \quad 5.1$$

where V is the number of vertices, E is the number of edges, and N is the number of cells.

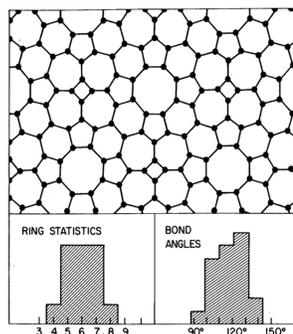


Fig. 5.3 Ring Statistics and Bond angle distribution of amorphous network

For atom in a random structure made of atoms with soft bonds,

$$2E = 3V = \langle N_p \rangle N \quad 5.2$$

Here, $\langle N_p \rangle$ is the average number of bonds per-ring in a unit cell. Since atoms with soft bonds can form rings of arbitrary sizes, as opposed to atoms with hard bonds which essentially make fixed six sided rings, $N_p=6$. For a random structure average ring size should be

$$\langle N_p \rangle = 6 = \sum_{i=3}^{\infty} iP_i = \dots + 9P_9 + 8P_8 + 7P_7 + 6P_6 + 5P_5 + 4P_4 + 3P_3 \quad 5.3$$

The requirement that the rhs sum to 6 requires suggests that the probability of finding large ring is greatly reduced. For example, if the probability of finding a size 9 ring is P , based on Fig. 5.3, it is 1/3 less probable than finding a ring of size 6, we find

$$\begin{aligned} P_9 &= P_8 = P_4 = P_3 \equiv P \\ P_7 &= P_6 = P_5 \equiv 3P \\ 78P &\approx 6 \Rightarrow P \sim 1/13 \end{aligned} \quad 5.4$$

that is only 1 in 13 rings (less than 8%) will have rings of size 9. Consider the probability of having a ring of 21 sides, i.e.,

$$\begin{aligned} P_{21} &= P_8 = P_9 \equiv P \\ P_7 &= P_6 = P_5 \equiv 5P \\ P_3 &= P_4 = P_2 = 15P \\ P &\sim 1/263 \end{aligned} \quad 5.5$$

It is virtually impossible to find a ring of size 21. The value of P_i considered here is arbitrary, but you can come to very similar conclusion no matter the weight you use. For example, if you assumed that probability of all rings upto size m are the same, then $6 = P \sum_{i=1}^m i = m * (m + 1)/2$. If $m=21$, then $P \sim 2.5\%$. From the above example we see that to form large rings we will need a very large number of small rings surrounding the larger ring. This can be understood using simple law of averages. Since large rings have to pay large steric penalty by bending many bonds, they are extremely rare.

Hence due to presence of large number of rings very close to average number six, amorphous structure has a well defined band-gap, close to the bandgap of solid, see Fig. 5.4. The presence of the band-gap enables glass to be transparent and the locality of the gap often makes it direct. The variation in the ring size explains the presence of band tail states close to conduction and valence band edges. In other words, when we solve the Schrodinger equation for a crystals, we will get discrete energy levels (bands) for electron. For the amorphous materials, however, we have rings of different sizes, so if we solve Schrodinger equation, all the rings of different sizes will not be at the same energy level rather at different place in the E_g , as shown in the figure below. And finally, all the bonds are fully coordinated, therefore, an amorphous material – despite its randomness and lack of long range order – can be defect free.

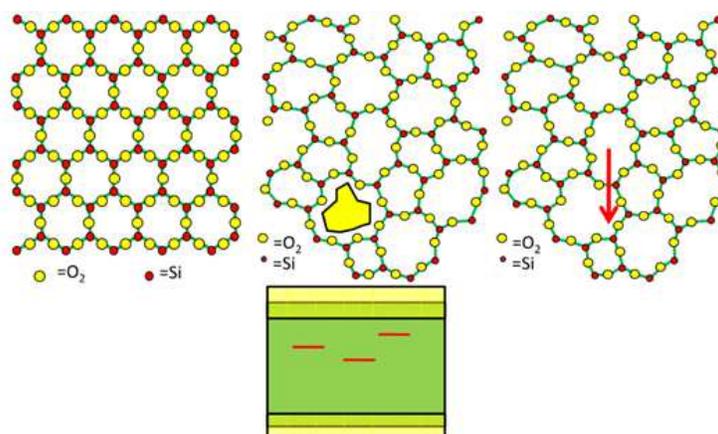


Fig. 5.4 Crystalline and amorphous Si. The bottom panel shows E_g states in the amorphous material.

5.5 Defects in Amorphous Solids

5.5.1 A defect in amorphous solid involves faulty coordination

As opposed to crystalline structures where various kinds of defects can be classified, coordination defects are the only main type of defects existent in amorphous structures. A coordination defect is defined as atom having a different coordination compared to the atoms of similar type in the structure. For example, all the red atoms in Fig. 5.4 are 3-coordinated. If a bond is broken (see red arrow), the corresponding red-atom will become 2-coordinated and the oxygen (yellow) atom will have a dangling bond. Similarly in a 3D solid, if a oxygen vacancy is

created, then the neighboring silicon will have coordination 3 (instead of typical 4, see white atom in Fig. 5.2). The dangling bonds is known as neutral oxygen vacancy and would cause states to appear within the band gap.

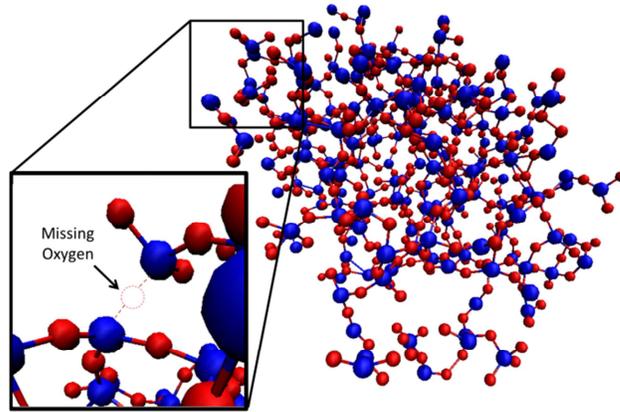


Fig. 5.5 Defect in an amorphous structure (Neutral Oxygen Vacancy)[4]

5.5.2 Maxwell rules for defect formation (and yes, this is the Maxwell!)

Can we tell how many coordination defects might form in a given amorphous solid or if one solid is more prone to defect formation compared to others? The answer is Yes and can be understood as follows. Consider the potential energy of a set of atoms connected by chemical bonds

$$V = \frac{1}{2} \sum_{i,j} \alpha_{i,j} (\Delta r_{i,j})^2 + \frac{1}{2} \sum_{i,j,k} \beta_{i,j,k} (\Delta \theta_{ijk})^2 \quad 5.6$$

The first term defines the energy penalty associated with changing the bond length (compression or tension) and the second reflects the penalty associated with changing the bond angle (torsion). The energy minima defines the preferred configuration of the solid. At zero temperature Eq. 5.5 can be approximated as

$$M_0 = D \times N - N_C - (D + \alpha) \quad 5.7$$

where $D = 1, 2, 3$ is the dimension of the solid, n_r is the coordination of bonds, $N = \sum_{r=1}^k n_r$ is the number of points to be stabilized, N_c is the number of constraints (angle/position) involved, and is given by

$$N_{cx} = \left[\sum_{r=1}^k n_r \left(\frac{r}{2} \right) \right]_{bond} + \left[\sum_{r=1}^k n_r \left(\frac{D-1}{2} \right) (2r - D) \right]_{angle} \quad 5.8$$

In general, Maxwell proved that

$M_0 > 0$ system is unstable

$M_0 < 0$ system is stable

M_0 is optimally stable

While an unstable system is floppy, it need not be defect; the optimally stable system is rigid and yet has sufficient flexibility to accommodate stress (flat potential profile); and finally, the stable system is rigid, so much so that this over-coordinated system could be prone to defect formation.

Let us consider the stability of the four structures shown below:

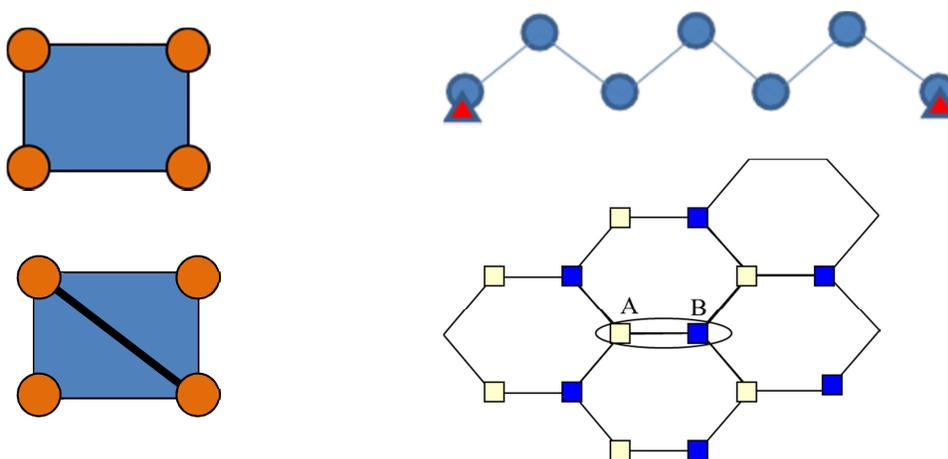


Fig. 5.6 Top left: Four atoms without angle constraints, Bottom left: Four atoms with diagonal constraints, Top right: A DNA bridge, Bottom right: 3-coordinated graphene.

Example 1: Finite system with 4-atoms

In Fig. 5.6 (top left), we have $D = 2$, $\alpha = 1$, $N = 4$, $n_{r=2} = 4$ (number of atoms with 2 arms), $N_c = 4$ (number of bond length constraints, because the angles are not constrained). Therefore, $M_0 = (2 \times 4) - 4 - 3 > 0$. Maxwell predicts that the system is unstable, but then you do not need a Maxwell to tell you that – if you ever made a bookrack without angle support (as I have done), the results are obvious.

Example 2: Finite system with 4-atoms with diagonal constraints

Here, $D = 2$, $\alpha = 1$, $N = 4$, $n_{r=2} = 2$ (number of atoms with 2 arms), $n_{r=3} = 2$ (number of atoms with 3 arms), $N_c = 5$ (number of bond constraints), therefore, $M_0 = (2 \times 4) - 5 - 3 = 0$ and the system is stable.

Examples 3: A finite DNA bridge

The finite bridge has $N = s (= 7)$ points, $s - 1$ bond constraints, and $s - 2$ angle constraints and 3 degrees of freedom (two translational, 1 rotational), i.e. $\alpha = 1$. Substituting in the Maxwell's relationship we find that the system is optimally stable.

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

In practice, a single DNA bridge does not have any angle constraint, therefore $M_0 > 0$ and single DNA is floppy. Only when the second DNA provides the structural rigidity by fixing the bonds angles is the structural stability possible. This rigidity transition is a great feature of biology, and Maxwell would have predicted it just by analyzing the structural stability of bridges and trusses.

Example 4: Graphene is stable only with angle constraints

In Graphene, every atom is connected to 3 neighbors ($n_{r=3} = N$) so that the angle between the bonds is 120 degrees. Number of bond constraints is $1.5N$ since each point can make three bonds ($3N$) and each bond is shared by 2 points ($3N/2$). Similarly the angle constraints are $2N$, since the angle at each point is constrained by the positions of two other points to obtain a bond angle of 120. Same results are also obtained by evaluating the right hand side of Eq. 5.8. Substituting these values in the Maxwell relationship we get $M_0/N = -1.5$. Hence grapheme is a stable structure. If the angle constraints are removed, if the bonds were flexible as is the case for many polymers, M_0/N turns out to 0.5. Maxwell would predict that the structure is floppy and under any compressive load, the structure will collapse.

5.6 Conclusions

Amorphous structure is neither completely random, nor it is intrinsically defective. It has a well-defined short range order defined by the simple structural units. It lacks long range order as can be seen from the distribution of ring size and angle distributions. The application of Maxwell relation and Euler relations explain the defect free amorphous structures and the reasons for their stability. In the next chapter, we will use these powerful techniques to explore the potential of defect formation in various materials. I should emphasize, however, that these zero temperature approximate relationships and only provide a basic geometrical basic understanding to the structures. To understand the effect of temperature and thermodynamics more involved models accounting for the different forces need to be used. The origin of these defects and their evolution are important to understand the various concerns of physical reliability in devices.

5.6 REFERENCES:

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