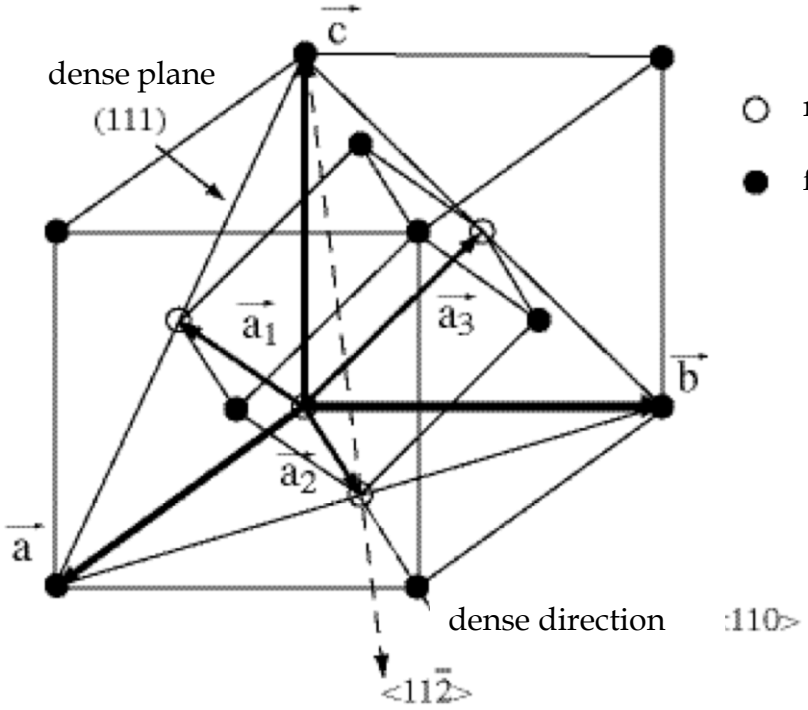
PHYSICS OF MATERIALS

Physics School Autumn 2024

Series 2 - Solution **27 September 2024**

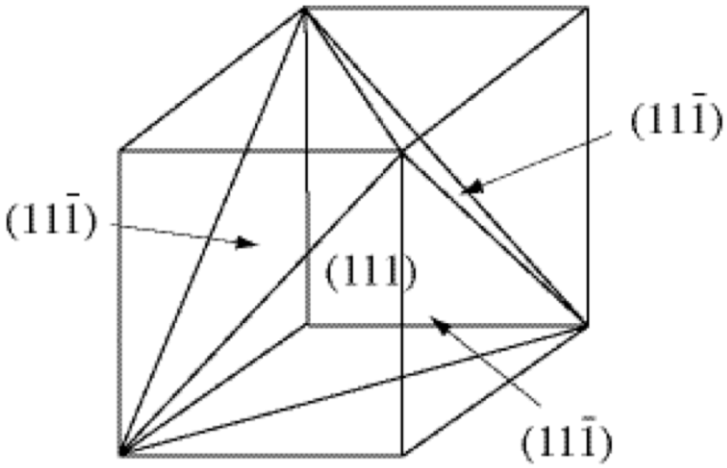
Exercise #1

1.1-1.4



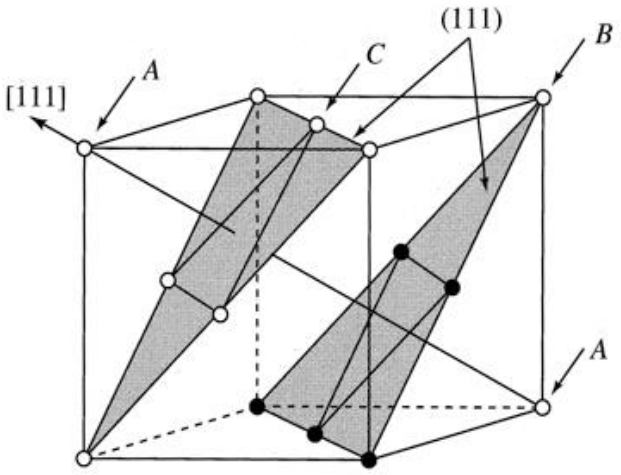
rear atom

front atom



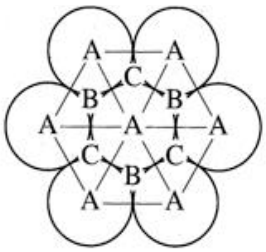
dense plane tetrahedron

To calculate the distance between dense planes, we can graphically deduce that three series of dense planes exist on the cube's diagonal. It is a stacking where atoms find themselves at the same position every three planes (stacking ABC, ABC...).



Face-centered cubic structure

A..B..C.. stacking



We can calculate the distance between planes by taking the norm of the normal (111) to the dense planes.

$$\left\|\vec{r}^{\,*}_{hkl}\right\| = \frac{1}{d_{hkl}}$$

$$(111) = \vec{a}_1^{\,*} + \vec{a}_2^{\,*} + \vec{a}_3^{\,*}$$

Base vectors of the primitive cell:

$$\vec{a}_1 = \begin{pmatrix} a/2 \\ 0 \\ a/2 \end{pmatrix} \quad \vec{a}_2 = \begin{pmatrix} a/2 \\ a/2 \\ 0 \end{pmatrix} \quad \vec{a}_3 = \begin{pmatrix} 0 \\ a/2 \\ a/2 \end{pmatrix}$$

The volume of the primitive cell is 1/4th of that of the centered cell, as we can easily verify by the triple product. The primitive cell thus contains one atom per cell. We can calculate the distance between planes (111) by choosing the base vectors of the primitive cell. We carry out calculations in the orthogonal base [100], [010], [001].

$$\vec{a}_1^{\,*} = \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \begin{pmatrix} a^2/4 \\ -a^2/4 \\ a^2/4 \end{pmatrix} \frac{4}{a^3} = \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix} \frac{1}{a} \qquad d_{111} = \frac{a}{\sqrt{3}} = \frac{1}{3}\sqrt{3}a$$

1.5

The Atomic Packing Factor (APF) is the fraction of the volume of the unit cell that is occupied by atoms. For an FCC structure, the APF can be calculated as:

$$APF = \frac{Volume\ of\ atoms\ in\ unit\ cell}{Volume\ of\ unit\ cell} =$$

Assuming each atom is a sphere, and that FCC unit cell has 4 atoms:

$$Volume\ of\ atoms = 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$$

For FCC, the close directions are <110>, and thus, atom radius (r) and lattice parameter (a) are related as,

$$a = 2\sqrt{2}r$$

$$volume\ of\ cubic\ crystal\ unit\ cell = a^3 = (2\sqrt{2})^3 r^3$$

As such, APF is,

$$APF = \frac{{}^{16}/_{3}\,\pi r^3}{16\sqrt{2}} = \frac{\pi}{3\sqrt{2}} \approx 0.74$$

The mathematical proof that the highest possible packing efficiency for hard spheres is approximately 0.74 was first rigorously established in 1998 by American mathematician Thomas Hales. This proof confirmed what is known as the Kepler Conjecture, a problem that had been posed over 300 years earlier by the astronomer Johannes Kepler in 1611.

Kepler conjectured that the densest possible arrangement of equal-sized spheres was the face-centered cubic (FCC) or hexagonal close-packed (HCP) arrangements, both of which have a packing efficiency of approximately 74% (or 0.74). However, this conjecture remained unproven for centuries, and although it was widely believed to be true, it required a formal mathematical proof.

Hales' proof used a combination of traditional geometric methods and extensive computer calculations to rigorously establish that no other arrangement of spheres could surpass this packing density. The proof was highly complex, involving the examination of numerous possible configurations, and was one of the first significant mathematical proofs to rely heavily on computational methods.

In 2014, Hales and a team of collaborators produced a formal verification of the proof using computer proof-checking software, fully confirming the result with a higher level of rigor than the original 1998 proof. This development ensured that the 0.74 packing efficiency is the mathematically proven highest possible for hard spheres.

1.6

The coordination number is the number of nearest-neighbor atoms surrounding a given atom.In an FCC structure, each atom has 12 nearest neighbors: 4 in the same plane, 4 in the plane above, and 4 in the plane below. Therefore, the coordination number of the FCC structure is 12. Most metals have compact crystal structures due to their electronic structure and bonding, and thus, they tend to have high coordination numbers.

1.7

The density (ρ) of a material can be calculated using the formula:

$$\rho = \frac{Z \times M}{N_A \times V}$$

where:

- Z is the number of atoms per unit cell (4 atoms for FCC),
- M is the molar mass (atomic weight),
- N_a is Avogadro's number (6.022×10^{23}),
- V(a^3) is the volume of the unit cell.

1.8

For copper (Cu):

- r = 0.128×10^{-7} cm,
- $a = 2\sqrt{2}r = 0.361 \times 10^{-7}\text{cm}$,
- M = 63.55 g/mol
- Z = 4, N_A = 6.022×10^{23} atoms/mol
- V= $a^3 = 4.70 \times 10^{-23}$

$$\rho = \frac{4 \times 63.55}{6.022 \times 10^{23} \times 4.7 \times 10^{-23}} = 8.96\ \text{g/cm}^3$$

Exercise #2

The volume of a tetragonal cell is given by.

$$V = a^2 c = (5.094)^2 (5.304) = 137.6\ \mathring{A}^3$$

The volume of a monoclinic cell is given by:

$$V_m = abc\sin(\beta) = (5.156)(5.191)(5.304)\sin(98.9°) = 140.25\ \mathring{A}^3$$

There is thus an expansion when the cell transforms from the tetrahedral structure to the monoclinic structure. This expansion is 1.9%.

Most ceramics cannot stand volume changes larger than 0.1%. Thus, when the zirconium dioxide transforms, it cracks. To use the ZrO_2 in mechanical applications, we must stabilize the tetrahedral or cubic phase with additives such as Y_2O_3. Conversely, the phase transformations of ZrO_2 can make the ceramics tougher (resistant to rupture). We can introduce, e.g., particles of ZrO_2 in aluminum oxide (Al_2O_3). When a crack propagates in the aluminum oxide, it releases internal stresses that maintain ZrO_2 in the tetrahedral phase, which is metastable at ambient temperature. As a result, the ZrO_2 particles expand and close the crack.

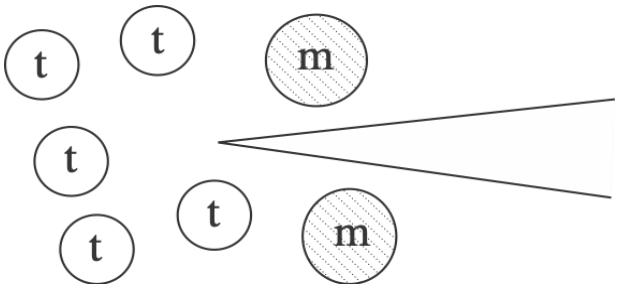
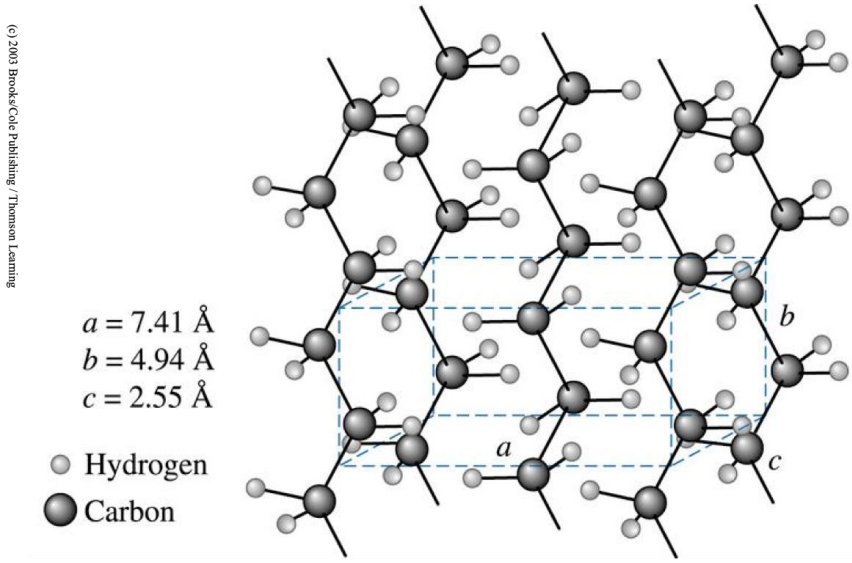


Fig. 2.1 Crack propagating through a matrix containing particulates of ZrO_2.

Exercise 3 Crystalline polyethylene

Polyethylene crystallizes in a tetragonal structure. How many carbon (and hydrogen) atoms will there be in one cell knowing that the PE's density is ρ=0.9972 g/cm^3?



So for orthorhombic crystal, the volume of the unit cell V= a*b*c. If we assume that each carbon atom is bonded with two H atoms, we can calculate the rough number of those molecules within the unit of the given cell (a=0.741nm, b=0.494 nm, and c=0.255 nm) using the density ρ=0.9972 g/cm^3. The volume of this orthorhombic unit cell is 9.33 x10^{-23} cm^{-3}

So, C^{12}+2H= 14 AMU= 14g/mol and divided by Avogadro's number 6.022 x10^{23} molecules/mol, then the CH_2 molecule in the polyethylene crystal has 2.32 X10^{-23} g/molecule.The number of molecules in the unit cell would be

= (9.33 x10^{-23} cm^{-3}) * (0.9972 g/cm^3) /(2.32 X10^{-23} g/molecule)~ 4 molecules, or 4 carbons and 8 Hydrogen atoms