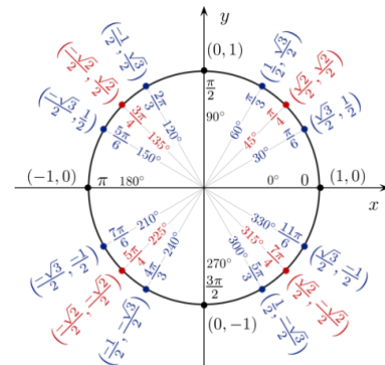


MSE 238 – Preliminary Exam sheet – status week 9

Reminder on Mathematics:

- Euclidean geometry
 - The following notation will be used: $\mathbf{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$
 - The magnitude (or norm) of a vector: $\|\mathbf{a}\| = \sqrt{a_x^2 + a_y^2 + a_z^2}$
 - Scalar (or dot) product: for two vectors in the **orthonormal basis** $\mathbf{i}, \mathbf{j}, \mathbf{k}$, we have: $\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$
 $\mathbf{a} \cdot \mathbf{b} = \|\mathbf{a}\| \times \|\mathbf{b}\| \cos(\alpha)$ where α is the angle between the two vectors.
 - The cross product of two vectors forming an angle α is a vector perpendicular to these vectors, with the magnitude:
 $\|\mathbf{a} \times \mathbf{b}\| = \|\mathbf{a}\| \|\mathbf{b}\| \sin(\alpha)$
 - In an orthonormal basis $(\mathbf{i}, \mathbf{j}, \mathbf{k})$, the Cross product of two vectors $\mathbf{a}$ and $\mathbf{b}$ is:

$$\mathbf{a} \times \mathbf{b} = (a_y b_z - a_z b_y) \mathbf{i} + (a_z b_x - a_x b_z) \mathbf{j} + (a_x b_y - a_y b_x) \mathbf{k}$$
- **Line:** Parametric equation of a line passing by two points A and B: $L = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ such that } \exists \lambda \in \mathbb{R} \mathbf{AM} = \lambda \mathbf{AB} \right\}$
- **Plane:**
 - A plane is defined by 3 points $A = \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix}$, $B = \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix}$ and $C = \begin{pmatrix} x_C \\ y_C \\ z_C \end{pmatrix}$ or a point A and a normal $\mathbf{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$
 - This can be expressed in a simple way as: $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \mathbf{AM} \cdot \mathbf{n} = 0 \right\}$
 - One can extract the linear equation: for $(a, b, c, d) \in \mathbb{R}^4$, $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, ax + by + cz - d = 0 \right\}$
- **Angles**
 - The angle between two vectors can be calculated from the dot or the cross products.
 - Angle between a line and a plane: Complementary of the angle between the line direction and the normal of the plane
 - Angle between two planes: Angle between their normals:
- Volume formed by three vectors: $V = \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$
- Complex Numbers
 - **Exponential form:** $z = r \cos \theta + i r \sin \theta = r e^{i\theta}$
 - For $z \in \mathbb{C}$, $z = r e^{i\theta}$, $z^* = r e^{-i\theta}$
 - $|e^{i\theta}| = 1 = \sqrt{x^2 + y^2}$, with $x = \cos \theta$ and $y = \sin \theta$
 - $\cos(x) = \frac{e^{ix} + e^{-ix}}{2}$ and $\sin(x) = \frac{e^{ix} - e^{-ix}}{2i}$
 - Unity circle is shown to the right.



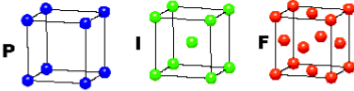
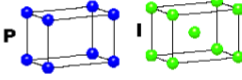
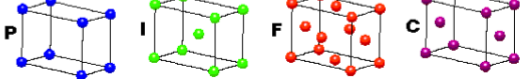
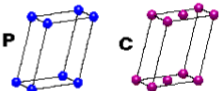
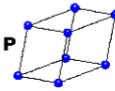
Crystalline State:

Materials in a crystalline state are organized into ordered arrangements of atoms. The chemical composition of the material forms a motif, that is placed at prescribed positions on a lattice called the Bravais Lattice. The Bravais lattice is expressed mathematically as an infinite set of points with translational symmetry along three axis that form a vector basis. Choosing an origin O, one can write

$$\mathcal{B} = \{P, \mathbf{OP} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, (n_1, n_2, n_3) \in \mathbb{Z}^3\}$$

The vectors $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ are the primitive vectors of the Bravais lattice.

One can distinguish **7 crystal systems**, that reflect the symmetry of the crystal. **14 Bravais lattices**:

Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	

Trigonal or rhomboedric

$a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$

7 classes / 14 Bravais

P : primitive
I : centered
F : face centered
C : base centered

Cells and basis

- To represent crystals, we use different types of unit cells. The conventional unit cell is the most commonly used as it exhibits the highest symmetry of the crystal. They can however contain several motifs.
- Primitive unit cells are cells with one motif.

Coordination Number

- Number of closest neighbors, ie when spheres are in contact in a hard sphere model.
- For crystals with different atoms in the motif and notably for ionic crystals, the coordination number counts the closest atoms of different nature.

Hard Sphere model

- A first intuitive representation of crystals can be obtained by considering atoms as hard spheres packed into 3D geometrical forms; From basic geometric and vectorial consideration of the unit cell, one can calculate key properties of materials such as density and packing fraction (of free volume).
 - Density: $\rho = \frac{N_{atoms\ per\ cell} \times m_{atoms}}{V_{cell}}$
 - Packing fraction: c or $p = \frac{N_{atoms\ per\ cell} \times V_{atoms}}{V_{cell}}$
- The number of atoms per cell must be evaluated carefully as each atom is shared with other neighboring cells.
- Direction and planes of high density are defined where atoms are organized in a dense manner where they are in contact with each other.

Interstitial sites and Ionic / covalent crystals

- The notion of interstitial sites in metals can be used to estimate what the crystal structure could be of ionic crystals.
 - First Pauling Rule: For two atoms (NaCl, ClCs, ZnS etc...), the first Pauling rule establishes a formula that defines the coordination number depending on the ratio of the radius of the cation to the one of the anion: $\rho = \frac{r_+}{r_-}$
 - Based on the hard sphere model, it predicts that if the cation is too small, anions get too close to each other which lead to an unstable structure due to repulsive forces.
 - At the limit of stability, geometric consideration can give a condition on the ratio to have a certain coordination, in other words a certain number of cations surrounding an anion (and vice versa).
 - The formula is given by : $\rho = \frac{r_+}{r_-} = \sqrt{\frac{12}{12-CN}} - 1$, where CN = coordination number
 - For $0.1547 < \rho < 0.2247$, $CN = 3$; Type of void: triangular planar
 - For $0.2247 < \rho < 0.4142$, $CN = 4$; Type of void: Tetrahedral
 - For $0.4142 < \rho < 0.7320$: $CN = 6$; Type of void: Octahedral
 - For $0.7320 < \rho < 1$: $CN = 8$; Type of void: Cubic

Crystal symmetries

- There are an infinite possibilities of Bravais lattices as the lattice parameters (vector norms and angles) can be chosen arbitrarily.
- The combination of the motif symmetry and the translational symmetry associated to the Bravais Lattice imposes restrictions on the type of symmetries a crystal (motif + Bravais lattice) can have.

- For a crystal to have a rotational symmetry of angle θ for example, translational symmetry indeed brings severe restrictions, as we can only have the following values for θ : $\frac{2\pi}{1}, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}$.
- A **symmetry operation** is an action that leaves an object unchanged.
- A **symmetry element** is a part of the object that doesn't move during the operation: a point, a line, a plane, an entire object.
- There are two kinds of symmetry operations:
 - Travel symmetry operations:**
 - Glide plane: *Action*: Reflect through a plane then translate parallel to it;
 - Screw axis: *Action*: Rotation by $360/N$ around an axis and translation along the axis
 - Point symmetry operations:**
 - Identity (1)**: *Action*: inversion through a point; *Symmetry element*: entire object
 - Inversion ($\bar{1}$)**: *Action*: inversion through a point; *Symmetry element*: a point
 - Rotation (N)**: *Action*: N-fold rotation around an axis ($360/N$); *Symmetry element*: a line
 - Mirror plane or reflection (m)**: *Action*: Reflection through a plane; *Symmetry element*: a plane
 - Rotoinversion ($\bar{N}$)**: *Action*: Rotation + Inversion; *Symmetry element*: a point

Point Group:

- Points group are a set of symmetries associated to a 2D object (or motif), that verifies certain rules.
- A *Group* is a very important mathematical construction. A set G of objects is a group if it is **closed under an operation $*$** : for any $x, y \in G$, $x * y \in G$.
- A Group is a mathematical construction that satisfies the following properties:
 - Identity (fixed point) – There is an element e in G , such that for every $x \in G$, $e * x = x * e = x$
 - Inverse – For every x in G there is an element $y \in G$ such that $x * y = y * x = e$
 - Associativity – The following identity holds for every $x, y, z \in G$: $x * (y * z) = (x * y) * z$
- Point Group Symmetry
 - Closure: The combination of symmetry operators is a symmetry operator in the group.
 - All symmetry operators have an inverse, some are their own inverse.
 - Identity is part of all the Point group symmetry.
 - Associativity is respected
- Order (or cardinal) of a group**: number of symmetry elements in the group.
- In 2D there are 10 point groups when we restrict to the 1,2,3,4 and 6 fold rotational symmetries. Combined with the 5 2D Bravais lattices, we obtain 17 “Plane groups” that characterize the possible symmetries of a 2D crystal.
- In 3D, there are 32 points group, and 14 possible Bravais Lattices. This results in 230 “Space groups”:
- For all crystals with one atom per motif, the space group corresponds to the point group of the conventional cell geometry. The atom being considered spherical, it conserves all other symmetries.

Crystal directions and planes, Miller indices

- Crystal directions are lines that pass through at least two lattice points. The direction can be defined by an origin (all lattice point can be an origin) and the coordinate of the other point in the lattice basis.
- The coordinates, which are relative integers, represent the Miller indices.
- Crystal planes pass through three lattice points and are also defined by Miller indices.
- Miller indices can vary depending on the basis used. Conventional cells are used by default to determine Miller indices.
- In the cubic system, in the orthonormal basis $\mathcal{B}(O, \mathbf{x}, \mathbf{y}, \mathbf{z})$, the equation of an (hkl) plane that intercepts the axis at points $A\left(\frac{a}{h}, 0, 0\right); B\left(0, \frac{a}{k}, 0\right); C\left(0, 0, \frac{a}{l}\right)$ where a is the edge of the cube, is given by:

$$\mathcal{P}^{(hkl)} = \{(x, y, z) \in \mathbb{R}^3 / hx + ky + lz = a\}$$

- In the cubic system, for a lattice parameter (or cube edge) a , the distance between parallel crystal planes $d_{(hkl)}$ is given by:

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Reciprocal space

- For a Direct lattice space $(O, \mathbf{a}, \mathbf{b}, \mathbf{c})$, we define the Reciprocal Lattice $(O, \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$ such that:

$$\begin{array}{lll} \vec{a}^* \cdot \vec{a} = 2\pi & \vec{b}^* \cdot \vec{a} = 0 & \vec{c}^* \cdot \vec{a} = 0 \\ \vec{a}^* \cdot \vec{b} = 0 & \vec{b}^* \cdot \vec{b} = 2\pi & \vec{c}^* \cdot \vec{b} = 0 \\ \vec{a}^* \cdot \vec{c} = 0 & \vec{b}^* \cdot \vec{c} = 0 & \vec{c}^* \cdot \vec{c} = 2\pi \end{array}$$

- The reciprocal lattice, or reciprocal space, is the set of points: $\mathcal{R} = \{P, \mathbf{OP} = n_1 \mathbf{a}^* + n_2 \mathbf{b}^* + n_3 \mathbf{c}^*, (n_1, n_2, n_3) \in \mathbb{Z}^3\}$.

- The reciprocal basis, from these considerations, is constructed as follow: $\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{V}$; $\mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{V}$; $\mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{V}$, where V is the volume formed by the $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ vectors: $V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$.
- A definition of Miller indices: Miller indices (hkl) represent the indices of the planes in the direct lattice that are orthogonal to the vector $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ in the reciprocal lattice.
- By construction, the distance between parallel crystal planes is given by: $d_{(hkl)} = \frac{2\pi}{\|\mathbf{N}_{(hkl)}^*\|}$ where $\mathbf{N}_{(hkl)}^*$ is a vector of coordinates (h, k, l) in the reciprocal basis $(\mathbf{O}, \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$.
- The calculation can be made for other structures

– Monoclinic:

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl}{ac} \cos\beta\right) \frac{1}{\sin^2\beta} + \frac{k^2}{b^2}}}$$

– Orthorhombic:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

– Tetragonal:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$

– Hexagonal:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2}}}$$

– Cubic:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

Diffraction

- Interference phenomena can occur when a X-ray beam is shun upon a crystal. Crystal planes act as scatterers and a Bragg law can be obtained that linked the angle of incidence, the wavelength and the distance between crystal planes, in order to observe a peak of interference.
- Bragg law**: $2d_{(hkl)} \sin(\theta) = n\lambda$, where $\frac{\pi}{2} - \theta$ is the angle of incidence with the normal to the plane, n is an integer defining the order of the interference, and λ the wavelength of the incident beam.
- Laue condition**: a condition for constructive interference where the difference of the diffracted wave vector $\mathbf{k}_1$ and the incident wave vector $\mathbf{k}_0$ verifies: $\mathbf{K} = \mathbf{k}_1 - \mathbf{k}_0 \in \mathcal{R}$ where $\mathcal{R}$ is the reciprocal space. In other words, for a given illumination direction given by $\mathbf{k}_0$, interference peaks will be measured along directions $(\mathbf{k}_1)$ for which the vector representing the difference between the two wave vectors belongs to the reciprocal space.
- We consider elastic scattering (Thompson scattering)
- The wave vector $\mathbf{k}$ is related to the wavelength of X-rays by: $\mathbf{k} = \frac{2\pi}{\lambda}$
- The scattering vector $\mathbf{q}$ (or $-\mathbf{K}$ as named above), is the vector difference between the incident $\mathbf{k}_0$ and scattered wave vector $\mathbf{k}$: $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$. For elastic scattering it follows the relationship between the scattering vector $\mathbf{q}$ and the scattering angle 2θ : $|\mathbf{q}| = q = \frac{4\pi \sin(\theta)}{\lambda}$
- Since the X-ray energy is often given in kilo electron Volts keV, the following simplified equation can be used to transform to the wavelength: $\lambda [\text{\AA}] = 12.3984/E [\text{keV}]$
- In order to measure a diffraction peak, the Bragg points (000) , which is at the position of the direct incoming beam and the Bragg point (hkl) from the reciprocal space lattice must lie on a sphere of radius equal $|\mathbf{k}|$ (the wave vector of the experiment) in reciprocal space $\mathcal{R}$, the so called Ewald sphere.
- Scherrer equation $B = \frac{K\lambda}{D \cos \theta}$ where B is the broadening of the diffraction line at half maximum (after correction for instrument broadening), K is a constant depending on the crystal structure, $K \approx 1$ and D is the diameter of the crystallite.

Structure factors

- The scattering from crystalline material can be calculated as
- $F(\mathbf{q}) = \sum_l^{\text{all atoms}} f_l(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_l} = \sum_{\mathbf{R}_n + \mathbf{r}_j}^{\text{all atoms}} f_j(\mathbf{q}) e^{i\mathbf{q} \cdot (\mathbf{R}_n + \mathbf{r}_j)} = \sum_n e^{i\mathbf{q} \cdot \mathbf{R}_n} \sum_j f_j(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_j}$
- With the atomic form factor Atomic form factor $f_j(\mathbf{q}) = \int \rho(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}$ of atom positioned at $\mathbf{r}_1$, and $\mathbf{r}_l = \mathbf{R}_n + \mathbf{r}_j$, $\mathbf{R}_n$ lattice vector, $\mathbf{r}_j$ position vector of the atoms in the unit cell
- The last term is called the structure factor. Considering Laue condition $\mathbf{q} = \mathbf{K} = \mathbf{k}_0 - \mathbf{k}$
- $S(\mathbf{K}) = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}_j}$
- The sum is over the j atoms of a motif.
- To explain diffraction, one can view non-primitive crystal structures as being defined by the conventional cell, and a motif with a number of atoms equal to the number of atoms per conventional cell. For example, a BCC structure can be seen as a simple cubic structure with two atom (one atom on cube corner, one in the center) as the motif.
- That way, a structure factor can be calculated for materials with different atoms in its motif, but also for crystals with the same atom in the motif.

Amorphous materials: glasses

- Whereas crystalline materials have long-range order, the exact location from an atom can be interfered relative to a chosen atom at the origin → atomistic structure description in crystallography
- amorphous materials only exhibit short-range order over some atomic/molecular diameters, still a certain periodicity in the distribution of atoms exist, over longer distance the correlation gets lost, due to that randomness in the position, structure can only be described statistical
- liquid crystals exhibit long range order and either only orientational symmetry (nematic) or orientational and translational symmetry (smectic)
- **pair distribution function** (PDF) describes the probability $g(r)$ of finding an atom/molecule at a certain distance r normalized over the overall density, and thus describes the local density in the structure surrounding an atom with radius R_0
- $g(r) = \frac{dn(r,r+dr)}{dv(r,r+dr)} \frac{1}{\rho_0} = \frac{\rho(r)}{\rho_0}$ with dn the number of atoms in a spherical shell with volume dv in distance r from an arbitrary atom selected as the origin, with the atomic pair density $\rho(r)$ in the shell and ρ_0 the average particle density
- PDF is related to the measured X-ray (or neutron) powder diffraction through a Fourier transform
$$g(r) = (2/\pi) \int_{q=0}^{q_{max}} q[S(q) - 1] \sin(qr) dq$$
where $S(q)$ is the liquid (or glass) structure factor. In analogy with the discussion in diffraction and scattering, $S(q)$ is the interaction term of the scattering, and can be extracted from the measured and corrected intensity $I(q)$ by extracting the contribution of the atomic form factor $f_i(q)$ of all atoms in their concentration c_i with
$$S(q) = \frac{I(q) - \sum c_i |f_i(q)|^2}{|\sum c_i f_i(q)|^2} + 1$$
- For the atomic scale structure of amorphous solids different models exist:
 - Continuous random-network model for covalently bonded glasses
 - Random coil-model for polymer chains
 - And random close-packing model for metallic glasses

B = Solids																		Hg = Liquids																		Kr = Gases																		Pm = Not found in nature																		18																																																																																																																																																																																											
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37 Rb 85.4678		38 Sr 87.62																39 Y 88.90585																40 Zr 91.224																41 Nb 92.90638																42 Mo 95.94																43 Tc (98)																44 Ru 101.07																45 Rh 102.90550																46 Pd 106.42																47 Ag 196.56655																48 Cd 112.411																49 In 114.818																50 Sn 118.710																51 Sb 121.760																52 Te 127.60																53 I 126.90447																54 Xe 131.29	
55 Cs 132.90545		56 Ba 137.327																71 Lu 174.967																72 Hf 178.49																73 Ta 180.94.79																74 W 183.84																75 Re 186.207																76 Os 190.23																77 Ir 192.217																78 Pt 195.078																79 Au 196.56655																80 Hg 200.59																81 Tl 204.3833																82 Pb 207.2																83 Bi 208.58038																84 Po (209)																85 At (210)																86 Rn (222)	
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