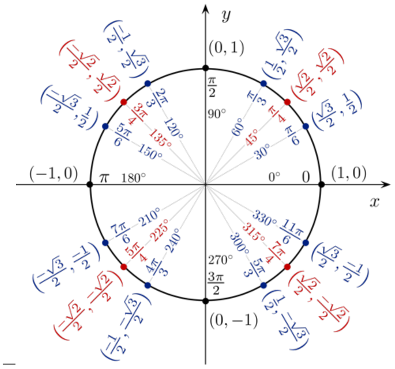
MSE 238 –Exam sheet

Reminder on Mathematics:

- Euclidean geometry
  - The following notation will be used: $\boldsymbol{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$
  - The magnitude (or norm) of a vector: $\|\boldsymbol{a}\| = \sqrt{{a_x}^2 + {a_y}^2 + {a_z}^2}$
  - Scalar (or dot) product: for two vectors in the **orthonormal basis** $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$, we have: $\boldsymbol{a}.\boldsymbol{b} = a_x b_x + a_y b_y + a_z b_z$ $\boldsymbol{a}.\boldsymbol{b} = \|\boldsymbol{a}\| \times \|\boldsymbol{b}\| \cos(\alpha)$ 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: $$\|\boldsymbol{a} \times \boldsymbol{b}\| = \|\boldsymbol{a}\|\,\|\boldsymbol{b}\| \sin(\alpha)$$
  - In an orthonormal basis (***i,j,k***), the Cross product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is: $$\boldsymbol{a} \times \boldsymbol{b} = (a_y b_z - a_z b_y)\boldsymbol{i} + (a_z b_x - a_x b_z)\boldsymbol{j} + (a_x b_y - a_y b_x)\boldsymbol{k}$$
- **Line**: Parametric equation of a line passing by two points A and B: $L = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \textit{such that } \exists \lambda \in \mathbb{R}\ \boldsymbol{AM} = \lambda \boldsymbol{AB} \right\}$
- **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 $\boldsymbol{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$
  - This can be expressed in a simple way as: $P = \left\{ M = \begin{pmatrix} x \\ y \\ z \end{pmatrix},\ \boldsymbol{AM}.\boldsymbol{n} = 0 \right\}$
  - 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 plan
  - Angle between two planes: Angle between their normals:
- Volume formed by three vectors: $V = \vec{a}.(\vec{b} \times \vec{c}) = \vec{b}.(\vec{c} \times \vec{a}) = \vec{c}.(\vec{a} \times \vec{b})$
- Complex Numbers
  - **Exponential form**: $z = r cos\theta + irsin\theta = re^{i\theta}$
  - For $z \in \mathbb{C}$, $z = re^{i\theta}$, $z^* = re^{-i\theta}$
  - $|e^{i\theta}| = 1 = \sqrt{x^2 + y^2}$, 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.

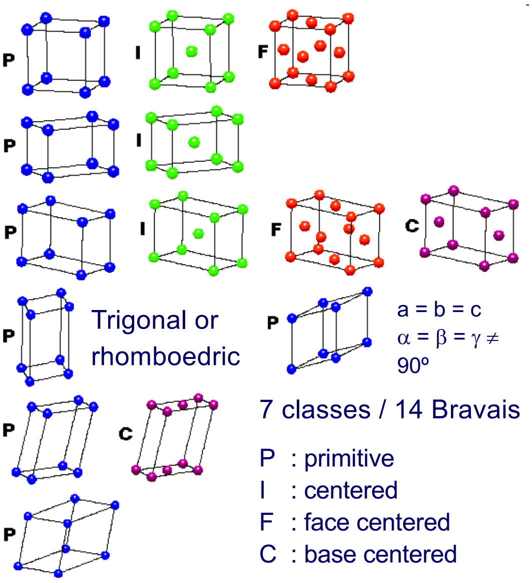
The Bravais lattice is expressed mathematically as an infinite set of points with translational symmetry along three axis that form a vector basis. Choosing an origin O, one can write

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

The vectors (a, b, 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 $\alpha = \beta = \gamma = 90°$
Tetragonal	a = b ≠ c $\alpha = \beta = \gamma = 90°$
Orthorhombic	a ≠ b ≠ c $\alpha = \beta = \gamma = 90°$
Hexagonal	a = b ≠ c $\alpha = \beta = 90°;\ \gamma = 120°$
Monoclinic	a ≠ b ≠ c $\alpha = \gamma = 90° \neq \beta$
Triclinic	a ≠ b ≠ c $\alpha \neq \beta \neq \gamma$



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 ioinc crystals, the coordiantion 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 $\mathrm{p} = \frac{N_{atoms\ per\ cell} \times V_{atoms}}{V_{cell}}$
- 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 ∈ G, x ∗ y ∈ 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 ∈ G, e ∗ x = x ∗ e = x
- Inverse – For every x in G there is an element y ∈ G such that x ∗ y = y ∗ x = e
- Associativity – The following identity holds for every x, y, z ∈ 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 $\mathcal{B}(O,\boldsymbol{x},\boldsymbol{y},\boldsymbol{z})$**,** 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 $(O,\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})$, we define the Reciprocal Lattice $(O,\boldsymbol{a}^*,\boldsymbol{b}^*,\boldsymbol{c}^*)$ such that:

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

- The reciprocal lattice, or reciprocal space, is the set of points: $\mathcal{R} = \{P,\ \boldsymbol{OP} = n_1\boldsymbol{a}^* + n_2\boldsymbol{b}^* + n_3\boldsymbol{c}^*, (n_1, n_2\ n_3) \in \mathbb{Z}^3\}$.
- The reciprocal basis, from these considerations, is constructed as follow: $\boldsymbol{a}^* = 2\pi\frac{\boldsymbol{b}\times\boldsymbol{c}}{V}$; $\boldsymbol{b}^* = 2\pi\frac{\boldsymbol{c}\times\boldsymbol{a}}{V}$; $\boldsymbol{c}^* = 2\pi\frac{\boldsymbol{a}\times\boldsymbol{b}}{V}$, where V is the volume formed by the $(\boldsymbol{a},\boldsymbol{b},\boldsymbol{c})$vectors: $V = \boldsymbol{a}.(\boldsymbol{b}\times\boldsymbol{c})$**.**

- A definition of Miller indices: Miller indices (hkl) represent the indices of the planes in the direct lattice that are orthogonal to the vector ha^*+kb^*+lc^* in the reciprocal lattice.

- By construciton, the distance between parallel crystal planes is given by: $d_{(hkl)} = \frac{2\pi}{\left\| \boldsymbol{N}^*_{(\boldsymbol{hkl})} \right\|}$ where $\boldsymbol{N}^*_{(\boldsymbol{hkl})}$ is a vector of coordinates (h,kl) in the reciprocal basis $(O, \boldsymbol{a}^*, \boldsymbol{b}^*, \boldsymbol{c}^*)$.
- The calculation can be made for other structures
  - – Monoclinic: $d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2\,hl}{a\,c}\cos\beta\right)\frac{1}{\sin^2\beta} + \frac{k^2}{b^2}}}$
  - – 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: $d_{hkl} = \frac{1}{\sqrt{\frac{4}{3\,a^2}(h^2 + k^2 + hk) + \frac{l^2}{c^2}}}$
  - – 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 interreference, and λ the wavelength of the incident beam.
- **Laue condition**: a condition for constructive interference where the difference of the diffracted wave vector $\boldsymbol{k_1}$ and the incident wave vector $\boldsymbol{k_0}$ verifies: $\boldsymbol{K} = \boldsymbol{k_1} - \boldsymbol{k_0} \in \mathcal{R}$ where $\mathcal{R}$ is the reciprocal space. In other words, for a given illumination direction given by k_0, interference peaks will be measured along directions (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 $\boldsymbol{k}$ is related to the wavelength of X-rays by: $\boldsymbol{k} = \frac{2\pi}{\lambda}$
- The scattering vector $\boldsymbol{q}$ (or $-\boldsymbol{K}$ as named above), is the vector difference between the incident $\boldsymbol{k_0}$ and scattered wave vector $\boldsymbol{k}$: $\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}$. For elastic scattering it follows the relationship between the scattering vector $\boldsymbol{q}$ and the scattering angle 2θ: $|\vec{q}| = q = \frac{4\pi\sin(\theta)}{\lambda}$
- 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: λ [Å] = 12.3984/E [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 |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≈ 1 and D is the diameter of the crystallite.

Structure factors

- The scattering from crystalline material can be calculated as
- $F(\boldsymbol{q}) = \sum_l^{all\,atoms} f_l(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}_l} = \sum_{\boldsymbol{Rn}+\boldsymbol{rj}}^{all\,atoms} f_j(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot(\boldsymbol{Rn}+\boldsymbol{rj})} = \sum_n e^{i\boldsymbol{q}\cdot\boldsymbol{Rn}} \sum_j f_j(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{rj}}$
- With the atomic form factor Atomic form factor $f_l(\boldsymbol{q}) = \int \rho(\boldsymbol{r}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} d\boldsymbol{r}$ of atom positioned at $\mathbf{r}_l$, and $\boldsymbol{r}_l = \boldsymbol{R}_n + \boldsymbol{r}_j$, $\boldsymbol{R}_n$ lattice vector, $\boldsymbol{r}_j$ position vector of the atoms in the unit cell
- The last term is called the structure factor. Considering Laue condition $\boldsymbol{q} = \boldsymbol{K} = \boldsymbol{k_0} - \boldsymbol{k}$
- $S(\boldsymbol{K}) = \sum_j f_j(\boldsymbol{K}) e^{i\boldsymbol{K}\cdot\boldsymbol{rj}}$
- 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.

Scattering

- For nanoparticle with well-defined size and shape, in analogy to diffraction a particle form factor P(q) can be defined, which is the Fourier transform of the electron density distribution at the nanoscale, and a particle structure factor S(q) which takes interference between neighboring particles into account resulting in a scattering intensity of $I(q) = (\rho_P - \rho_M)^2 N_P V_P^2 P(q) S(q)$, with $\rho_P - \rho_M$ the electron density difference between particle and matrix, N_P the number of particles, V_P the volume of particles, which can be used to mathematically model the scattering curves if pre-knowledge on the shape of the nanoparticles exist.
- Particle size can be extracted by the Guinier approximation $I(q) \approx I(0) e^{-(1/3) q^2 R_G^2}$ where R_G is the radius of gyration

- The radius of gyration R_G for some simple particle shapes is:
  - Solid sphere with radius R $R_G^2 = \frac{3}{5}R^2$
  - Thin rod with length L $R_G^2 = \frac{1}{12}L^2$
  - Thin disc with radius R $R_G^2 = \frac{1}{2}R^2$
  - Cylinder of height h and radius R $R_G^2 = \frac{R^2}{2} + \frac{h^2}{12}$
  - For a polymer coil with end to end distance *R* $R_G^2 = \frac{1}{6}R^2$

  - From the slope of the scattering curve at intermediate scattering vectors, the intensity varies with q^{-D} where D is the fractal dimension, i.e. how does the mass changes as a function of the size

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 arbitary 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 extractring the contribution of the atomic form factor $f_l(\boldsymbol{q})$ of all atoms in their concentration c_l with
  $S(q) = \frac{I(q) - \sum c_l |f_l(\boldsymbol{q})|^2}{|c_l f_l(\boldsymbol{q})|^2} + 1$
- For the atomic scale structure of amorphous solids different models exist:
  - Continous random-network model for covalently bonded glasses
  - Random coil-model for polymer chains
  - And random close-packing model for metallic glasses

Polymers:

- polymers are chain-like molecules where monomers covalently bond with each other repeat in either linear polymers, branched polymers (short and long side chains), star polymers or they form network of cross-linked polymer chains

- the tacticity describes the arrangement of side groups and is important to their ability to form crystals or glasses.
  - Isotactic: side groups on the same side of the chain
  - Syndiotactic: alternating side groups
  - Atactic: random arrangement of side groups

- Copolymers consist of different monomers and can appear in blocks, alternate regularly or in random sequence

- The polydispersity index is given by M_w/M_n with
  Weigth average $M_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i M_i}{\sum n_i M_i}$
  Where n_i and w_i are number and weight fractions of molecules/chains with molar mass M_i

- The contour length of a polymer is $r_{max} = Na$ with N the number of monomers and *a* the length of one monomer

- **Random coil model:** For freely jointed chain segments, at each connection point a new direction is acquired by random → random walk. To estimate the size of the coil: determination of end-to-end distance of the chain *r,* which is a random variable with the expected value *R*

- if each segment is equal to the chemical monomer with length *a* for one specific polymer chain, r is the vector sum of all monomers $\boldsymbol{r} = \sum_{i=1}^{N} \boldsymbol{a}_i$ for random walk the expected value *R* of this random walk is
    - $R = aN^{1/2}$
- In real chains it is the the statistical step length, called the **Kuhn length** *b* where the segments are freely jointed, the number of segments is *aN/b*
    - $R = b(Na/b)^{1/2} = (abN)^{1/2}$
    - $C_\infty = \frac{a^2}{b^2}$ is the Flory's characteristic ratio between the momomer length *a* and the Kuhn length *b*
- For very stiff polymers one considers the **worm-like chain model** of continuous bending chains, over even longer distances, there is still a loss of correlation, which is called the persistence length l_p and for long enough chains random walk still applies, but now with a statistical step size of the persistence length
    - $R = (2l_p aN)^{1/2}$
- In a solvent the interaction between the polymer chain and the solvent changes how much the coil expands
    - Poor solvent: segments attract each other, form a more compact structure $R = aN^{1/3}$
    - "theta solvent" repulsive and attractive forces are balanced: normal random walk $R = aN^{1/2}$
    - Good solvent: more repulsion between the chains resulting in an expanded coil $R = aN^{0.6}$

- Crystallinity in polymers: lamellar growth of crystalline domains, thickness usually around 10-20 nm, lateral extension much larger.

- Apart from the simple polyethylene chain (monomer $-C_2H_4-$) which forms a straight zigzag when stretched, most polymer chains when stretched are helically twisted due to steric constrains.

- Different microstructures form in semi-crystalline polymers
    - Spherulites: lamellae branches grow from a nucleation center spherically
    - If crystallization under influence of shear, more fibrillar structures are formed

- Main classes of biological materials

  Polymeric molecules
    - Nucleic acids: DNA stores genetic code, controlled sequence, double helix with complementary base pairs with specific hydrogen bonding which allows for exact copy in DNA replication, RNA slightly different chemical composition, single stranded, involved in transcription of information into proteins.
    - Proteins: monomers are 22 different amino acids, the amino acid sequence is the primary structure, determined by genetic code, some amino acids are hydrophobic (apolar), some are hydrophilic and either uncharged (polar) or charged (acidic or basic), these leads to specific interactions along the chain, fold into secondary structures (alpha-helix and beta-sheets) and assisted self-assembly into tertiary structures (and sometimes quaternary structures involving several molecules) forming the very specific functional three-dimensional structure
    - Polysaccharides, carbohydrates ($C_x(H_2O)_y$) monomers are various sugars, no defined sequence and branching

  Lipids:
    - Depending on double bonding present in the fatty acid chains (saturated or unsaturated fatty acids) they are in crystalline state at room temperature (fats) or in liquid state (oils)

  Amphiphilic molecules
    - Contain hydrophopic groups and hydrophilic groups in one molecule

      Self-assembly structures are formed, depending on the geometry of the molecules and they can form micelle (sphere), worm-like micelles (cylinders), bilayers (plane)
    - Packing parameter $\frac{v}{a_0 l_c}$ with l_C critical chain length, *v* chain volume and a_0 optimal headgroup area

      $\frac{v}{a_0 l_c} < \frac{1}{3}$ for spherical micelles, $\frac{v}{a_0 l_c} < \frac{1}{2}$ for cylinder, $\frac{v}{a_0 l_c} \approx 1$ for bilayer, $\frac{v}{a_0 l_c} > 1$ for inverted structures

  Biominerals
    - Calcium phosphate (eg hydroxyapatite in bone)
    - Calcium carbonate (eg aragonite and calcite in mollusk shells)
    - Silicates (diatoms)

- Hybrid materials are composites consisting of two constituents at the nanometer or molecular level
- Composite material consists of different materials/phases on the microscopic scale
- Composite materials
    - Reinforced composites: fiber, particulate or flake composites

      Properties are determined by properties of fiber and matrix, the ratio of fiber to matrix and the geometry and orientation of the fibers in the matrix
    - Sandwich structures: laminated sheets and shells, reduce material usage
    - Functional composites

B = Solids Hg = Liquids Kr = Gases Pm = Not found in nature

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
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)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uuo (277)

57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04
89 Ac 232.0381	90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)