

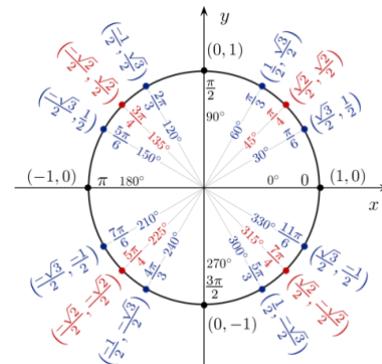
MSE 238 – Preliminary Exam sheet – status week 11

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: $\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$
 - $\mathbf{a} \cdot \mathbf{b} = \|\mathbf{a}\| \|\mathbf{b}\| \cos(\alpha)$ 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: $L = \left\{ \mathbf{M} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ such that } \exists \lambda \in \mathbb{R} \ \mathbf{AM} = \lambda \mathbf{AB} \right\}$
- **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: $P = \left\{ \mathbf{M} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \mathbf{AM} \cdot \mathbf{n} = 0 \right\}$
 - One can extract the linear equation: for $(a, b, c, d) \in \mathbb{R}^4$, $P = \left\{ \mathbf{M} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, ax + by + cz - d = 0 \right\}$
- **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 (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	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	 Trigonal or rhomboedric
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	
		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 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: $\rho = \frac{N_{\text{atoms per cell}} \times m_{\text{atoms}}}{V_{\text{cell}}}$
 - Packing fraction: c or $p = \frac{N_{\text{atoms per cell}} \times V_{\text{atoms}}}{V_{\text{cell}}}$
- 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:

$$\begin{array}{l} \overrightarrow{a^*} \cdot \overrightarrow{a} = 2\pi \\ \overrightarrow{a^*} \cdot \overrightarrow{b} = 0 \\ \overrightarrow{a^*} \cdot \overrightarrow{c} = 0 \end{array} \quad \begin{array}{l} \overrightarrow{b^*} \cdot \overrightarrow{a} = 0 \\ \overrightarrow{b^*} \cdot \overrightarrow{b} = 2\pi \\ \overrightarrow{b^*} \cdot \overrightarrow{c} = 0 \end{array} \quad \begin{array}{l} \overrightarrow{c^*} \cdot \overrightarrow{a} = 0 \\ \overrightarrow{c^*} \cdot \overrightarrow{b} = 0 \\ \overrightarrow{c^*} \cdot \overrightarrow{c} = 2\pi \end{array}$$

- 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 $ha^* + kb^* + lc^*$ in the reciprocal lattice.
- By construction, the distance between parallel crystal planes is given by: $d_{(hkl)} = \frac{2\pi}{\|N_{(hkl)}^*\|}$ where $N_{(hkl)}^*$ is a vector of coordinates (h, k, l) in the reciprocal basis $(0, \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$.
- 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: $d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \frac{a^2}{a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2}}}$
 - 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 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} : $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$. 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
- $$F(\mathbf{q}) = \sum_l^{\text{all atoms}} f_l(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_l} = \sum_{Rn+rj}^{\text{all atoms}} f_j(\mathbf{q}) e^{i\mathbf{q} \cdot (Rn+rj)} = \sum_n e^{i\mathbf{q} \cdot \mathbf{R}n} \sum_j f_j(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_j}$$
- 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}_l , 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.

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 \rightarrow 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 $f_l(q)$ of all atoms in their concentration c_l with

$$S(q) = \frac{I(q) - \sum c_l |f_l(q)|^2}{|\sum c_l f_l(q)|^2} + 1$$
- 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
 Weight 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 \rightarrow 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 $\mathbf{r} = \sum_{i=1}^N \mathbf{a}_i$ 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 monomer 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 -C₂H₄-) which forms a straight zigzag when stretched, most polymer chains when stretched are helically twisted due to steric constraints.
- 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(H₂O)_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 hydrophobic 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

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

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	1 H 1.00794	2	2 He 4.002602
3	4 Li 6.941	4 Be 9.012182	
11	12 Na 22.989770	12 Mg 24.3050	
	3	4	
	5	6	
	7	8	
	9	10	
	11	12	
	13	14	
	15	16	
	17		
	18		
5	6 B 10.811	7 C 12.0107	8 O 14.00674
13	14 Al 26.581538	9 F 15.9994	10 Ne 18.9984032
14	15 Si 28.0855	11 P 30.973761	12 S 32.066
15	16 Cl 35.4527	17 Ar 39.948	
16	17 He 4.002602		
17			
18			
19	20 Ca 44.955910	21 Ti 47.867	22 V 50.9415
K 39.0983	Sc 40.078	Ti 51.9961	Cr 54.938049
37	38 Sr 85.4678	39 Zr 88.90585	40 Nb 91.224
Rb 85.4678	Y 87.62	Zr 92.90638	Nb 95.94
42	43 Mo (98)	44 Ru 101.07	45 Rh 102.90550
43	42 Tc (98)	46 Pd 106.42	47 Ag 196.56655
44	45 Ru 101.07	48 Ag 112.411	49 Cd 114.818
45	46 Rh 102.90550	50 In 118.710	51 Sn 121.760
46	47 Pd 106.42	52 Sb 127.60	53 Te 127.60
47	48 Ag 196.56655	54 I 126.90447	54 Xe 131.29
48	49 Cd 112.411	55 Te 131.29	
49	50 In 114.818		
50	51 Sn 118.710		
51	52 Sb 121.760		
52	53 Te 127.60		
53	54 Xe 131.29		
54			
55	56 Ba 132.90545	71 Lu 137.327	72 Hf 174.967
56	57 Ba 132.90545	73 Ta 178.49	74 W 180.94.79
57	58 Ce 140.116	75 Re 183.84	76 Os 186.207
58	59 Pr 140.50765	77 Ir 190.23	78 Pt 192.217
59	60 Nd 144.24	79 Hg 195.078	80 Hg 196.56655
60	61 Pm (145)	81 Tl 200.59	82 Pb 204.3833
61	62 Sm 150.36	83 Bi 207.2	84 Po 208.58038
62	63 Eu 151.964	85 At (209)	86 Rn (210)
63	64 Gd 157.25	87 Tb 162.50	88 Dy 164.93032
64	65 Tb 158.92534	89 Ho 167.26	90 Er 168.93421
65	66 Dy 162.50	91 Tm 167.26	92 Yb 173.04
66	67 Ho 164.93032	93 Er 168.93421	
67	68 Er 167.26	94 Tm 173.04	
68	69 Tm 173.04	95 Er 173.04	
69	70 Yb 173.04	96 Er 173.04	
70		97 Bk (247)	
71		98 Cf (251)	
72		99 Es (252)	
73		100 Fm (257)	
74		101 Md (258)	
75		102 No (259)	
76			
77			
78			
79			
80			
81			
82			
83			
84			
85			
86			
87			
88			
89			
90			
91			
92			
93			
94			
95			
96			
97			
98			
99			
100			
101			
102			
103			
104			
105			
106			
107			
108			
109			
110			
111			
112			
113			
114			
115			
116			
117			
118			
119			
120			
121			
122			
123			
124			
125			
126			
127			
128			
129			
130			
131			
132			
133			
134			
135			
136			
137			
138			
139			
140			
141			
142			
143			
144			
145			
146			
147			
148			
149			
150			
151			
152			
153			
154			
155			
156			
157			
158			
159			
160			
161			
162			
163			
164			
165			
166			
167			
168			
169			
170			
171			
172			
173			
174			
175			
176			
177			
178			
179			
180			
181			
182			
183			
184			
185			
186			
187			
188			
189			
190			
191			
192			
193			
194			
195			
196			
197			
198			
199			
200			
201			
202			
203			
204			
205			
206			
207			
208			
209			
210			
211			
212			
213			
214			
215			
216			
217			
218			
219			
220			
221			
222			
223			
224			
225			
226			
227			
228			
229			
230			
231			
232			
233			
234			
235			
236			
237			
238			
239			
240			
241			
242			
243			
244			
245			
246			
247			
248			
249			
250			
251			
252			
253			
254			
255			
256			
257			
258			
259			
260			
261			
262			
263			
264			
265			
266			
267			
268			
269			
270			
271			
272			
273			
274			
275			
276			
277			
278			
279			
280			
281			
282			
283			
284			
285			
286			
287			
288			
289			
290			
291			
292			
293			
294			
295			
296			
297			
298			
299			
300			
301			
302			
303			
304			
305			
306			
307			
308			
309			
310			
311			
312			
313			
314			
315			
316			
317			