

Week 8

Crystal Structure and Surface Chemistry

8.1 X-Ray Diffraction Fundamentals

5/16:

- Final exam next Wednesday in class.
 - 50 minutes.
 - Questions like the midterm.
 - We can bring our notes and textbook, but cannot search online.
 - Can we bring notes on a computer, like mine, or do we have to print?
 - 1 computation problem.
 - We will write answers on paper.
- Review of last lecture.
- Tian goes through some examples of naming crystallographic planes from pictures of them intersecting a unit cell.
 - The first example is a 111 plane.
 - If asked to identify a 111 plane, it is enough to identify it as a 111 plane; we do not have to identify it as a possible 222 plane, too.
 - Consider a plane intersecting the **a**, **b**, and **c** axes at $a' = 2a/5$, $b' = b/2$, and $c' = c/5$, respectively.
 - Then $h = \frac{5}{2}$, $k = 2$, and $l = 5$.
 - An easier way to show this, however, is with $h = 5$, $k = 4$, and $l = 10$. Aren't these planes spaced twice as close together, though?
 - Consider a plane intersecting the **a**, **b**, and **c** axes at $a' = a/2$, $b' = b/2$, and $c' = -c/4$, respectively.
 - A convenient point to use as the origin in this case is the upper-left corner.
 - Thus, the plane is $(2, 2, -4)$.
 - The question of could we denote the plane by $(1, 1, -2)$: These two sets of planes are parallel, but the spacing of $(1, 1, -2)$ would skip every plane like $(2, 2, -4)$. Thus, we need $(2, 2, -4)$ for the spacing.
- Rules.
 1. If you see a fraction, convert to integers.
 2. But do not reduce a ratio.

- The fundamentals of X-ray diffraction.

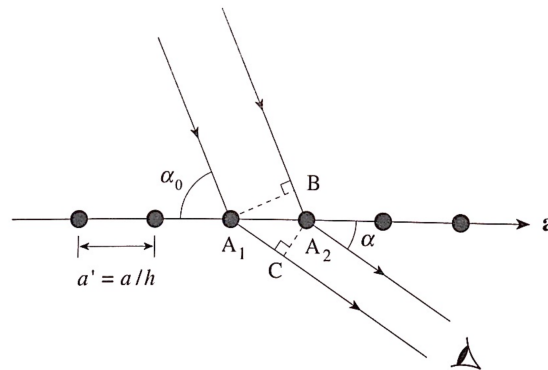


Figure 8.1: Deriving the von Laue equations.

- An X-ray diffraction pattern is a collection of spots of varying intensity.
 - The arrangement of the spots provides a great deal of information on the crystal structure, as we will soon see.
- We define

$$\Delta = \overline{A_1C} - \overline{A_2B}$$

- Imagine two parallel rays of light incident on points A_1 and A_2 in a crystal lattice.
- $\overline{A_1C}$ is the distance that the bottom beam travels after being scattered at A_1 and before the top beam is scattered at A_2 .
- Symmetrically, $\overline{A_2B}$ is the distance that the top beam travels after the bottom beam is scattered at A_2 and before being scattered at A_2 .
- Either way, Δ represents a kind of phase offset that occurs upon scattering. Say, for instance, that the two waves are in phase before scattering. Then from the perspective of the top wave, the bottom wave gets offset by Δ relative to it during the scattering process, and vice versa from the perspective of the bottom wave.
- If the distance Δ is equal to an integral multiple of the wavelength of the X-ray radiation, the two diffracted beams will interfere constructively. Mathematically, since

$$\overline{A_1C} = a' \cos \alpha \qquad \overline{A_2B} = a' \cos \alpha_0$$

as we may readily read from Figure 8.1, we require

$$\begin{aligned} n\lambda &= \Delta \\ &= \overline{A_1C} - \overline{A_2B} \\ &= a'(\cos \alpha - \cos \alpha_0) \\ nh\lambda &= a(\cos \alpha - \cos \alpha_0) \end{aligned}$$

- **First-order reflection:** A diffraction spot that corresponds to $n = 1$ in the above equation.
- **Second-order reflection:** A diffraction spot that corresponds to $n = 2$ in the above equation.
- **n^{th} -order reflection:** A diffraction spot that corresponds to n in the above equation.
- **von Laue equations:** The following three equations, which relate the quantities involved in a first-order reflection. *Given by*

$$a(\cos \alpha - \cos \alpha_0) = h\lambda \qquad b(\cos \beta - \cos \beta_0) = k\lambda \qquad c(\cos \gamma - \cos \gamma_0) = l\lambda$$

where $\alpha_0, \beta_0, \gamma_0$ are the angles of incidence of the X-ray radiation with respect to the **a**, **b**, and **c** axes of the crystal, respectively, and α, β , and γ are the corresponding diffraction angles.

- An example of how to use the von Laue equations.
 - Consider the diffraction pattern obtained when an X-ray beam is directed at a crystal whose unit cell is primitive cubic.
 - Orient the crystal such that the incident X-rays are perpendicular to the **a** axis of the crystal.
 - Then the relevant von Laue equation reduces to $a \cos \alpha = h\lambda$.
 - It follows that discrete angles will yield discrete spots?
- A more general situation.
 - For an arbitrary hkl plane, the direction of diffraction with respect to the **a** axis is the same as that for the $h00$ planes. But there is also diffraction with respect to the **b** and **c** axes.
 - The diffraction spots from an hkl plane (with fixed h) will lie along the surface of a cone that makes an angle α with respect to the **a** axis of the crystal.
- The Bragg diffraction.
 - We have

$$\lambda = 2 \left(\frac{d}{n} \right) \sin \theta$$

where θ is the angle of incidence (and reflection) of the X-rays with respect to the lattice plane, λ is the wavelength of the X-ray radiation, and $n = 1, 2, \dots$ is the order of the reflection.
 - d in terms of the Miller indices for a cubic unit cell gives

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$
 - Tian will not go through the details, but there will be a homework problem in which we will explore this.
- Rotating the sample vs. rotating the incident beam in an X-ray diffraction experiment.
 - In most cases, we fix the incident beam orientation and rotate the sample on the sample stage.
- Midterms back today or tmw.
- The grade distribution in the course.
 - A or A- is typically 65-70%.

8.2 The Scattering Factor and Intensity

5/18:

- Reviews the Bragg diffraction.
 - There is no such thing as a 222 or a 333 lattice plane; rather, there are 111 lattice planes with higher order diffractions.
 - Tian says something about higher order reflections?
- **Scattering factor** (of an atom): The following quantity, where $\rho(r)$ is the spherically symmetric electron density (number of electrons per unit volume) of the atom and $k = 4\pi \sin(\theta)/\lambda$. In turn, θ is the scattering angle and λ is the wavelength of the X-radiation. *Denoted by **f**. Given by*

$$f = 4\pi \int_0^\infty \rho(r) \frac{\sin kr}{kr} r^2 dr$$

- The integral $4\pi \int_0^\infty \rho(r) r^2 dr$ gives the total number of electrons in the atom.

- The total scattering intensity is related to the periodic structure of the electron density in the crystal.
 - If the crystal is oriented such that the von Laue equation governing scattering from atoms along the a axis is satisfied, then

$$\Delta_{11} = \Delta_{22} = \frac{a}{h}(\cos \alpha - \cos \alpha_0) = \lambda \qquad \Delta_{12} = x(\cos \alpha - \cos \alpha_0)$$

- Combining these two equations, we learn that

$$\Delta_{12} = \frac{\lambda h x}{a}$$

- The difference in path length corresponds to a phase difference between the diffracted beams from successive 1 and 2 atoms of

$$\phi = 2\pi \frac{\Delta_{12}}{\lambda} = 2\pi \frac{\lambda h x / a}{\lambda} = \frac{2\pi h x}{a}$$

- The amplitude of the light scattered from successive 1 and 2 atoms is then

$$\begin{aligned} A &= f_1 \cos \omega t + f_2 \cos(\omega t + \phi) \\ &= f_1 e^{i\omega t} + f_2 e^{i(\omega t + \phi)} \end{aligned}$$

- The detected intensity is proportional to the square of the magnitude of the amplitude.

$$\begin{aligned} I \propto |A|^2 &= [f_1 e^{i\omega t} + f_2 e^{i(\omega t + \phi)}][f_1 e^{-i\omega t} + f_2 e^{-i(\omega t + \phi)}] \\ &= f_1^2 + f_1 f_2 e^{i\phi} + f_1 f_2 e^{-i\phi} + f_2^2 \\ &= f_1^2 + f_2^2 + 2f_1 f_2 \cos \phi \end{aligned}$$

- The first two terms reflect the constructive interference of the X-rays scattered from the set of parallel planes through the 1 atoms and 2 atoms, respectively.
 - The third term takes into account the interference of the scattering from these two sets of parallel planes.
- We can therefore ignore the $e^{i\omega t}$ term and define

$$F(h) = f_1 + f_2 e^{i\phi} = f_1 + f_2 e^{2\pi i h x / a}$$

- The intensity is then proportional to $|F(h)|^2$.
- Generalizing to three dimensions for a unit cell that contains atoms of type j located at points x_j, y_j, z_j gives

$$F(hkl) = \sum_j f_j e^{2\pi i (hx_j/a + ky_j/b + lz_j/c)} = \sum_j f_j e^{2\pi i (hx'_j + ky'_j + lz'_j)}$$

where $x'_j = x_j/a$, $y'_j = y_j/b$, and $z'_j = z_j/c$.

- An analysis of the CsCl body-centered cubic lattice, where we take the unit cell to have eighth chloride atoms at every corner and one cesium ion in the center.
 - Taking f_+ to be the scattering factor of the Cs^+ cations and f_- to be the scattering factor of the Cl^- anions, we get

$$\begin{aligned} F(hkl) &= 1 \times f_- e^{\pi i (h+k+l)} + \frac{1}{8} \times f_+ \left[e^0 + e^{2\pi i h} + e^{2\pi i k} + e^{2\pi i l} + e^{2\pi i (h+k)} + e^{2\pi i (k+l)} + e^{2\pi i (h+l)} + e^{2\pi i (h+k+l)} \right] \\ &= f_- (-1)^{h+k+l} + \frac{1}{8} f_+ [8] \\ &= \begin{cases} f_+ + f_- & h+k+l \text{ is even} \\ f_+ - f_- & h+k+l \text{ is odd} \end{cases} \end{aligned}$$

where we substitute $e^{\pi i} = -1$ and $e^{2\pi i} = 1$ to get from the first line to the second.

8.3 Continuous Structure Factors and Adsorption

5/20:

- More on the CsCl example today.
 - We simplify $e^{i\pi(h+k+l)}$ to $(-1)^{h+k+l}$ by expanding to $\cos[\pi(h+k+l)]$, ignoring the imaginary part to get $\cos[\pi(h+k+l)]$, the sign of which does depend on whether the natural number $h+k+l$ is even or odd exactly like $(-1)^{h+k+l}$.
- CsI example.
 - Cs^+ and I^- are **isoelectronic**.
 - We have that

$$f_+(\text{Cs}^+) = f_-(\text{I}^-)$$

- The structure factor and the electron density are related by a Fourier transform.
 - In both atomic and molecular crystals, the electron density is not localized at individual points within the unit cell.
 - We should consider the unit cell of the crystal to have a continuous electron density distribution $\rho(x, y, z)$.
 - The structure factor is no longer simply a sum over discrete atoms but now becomes an integral over the continuous electron density distribution in the unit cell, as follows.

$$F(hkl) = \int_0^a \int_0^b \int_0^c \rho(x, y, z) e^{2\pi i(hx/a + ky/b + lz/c)} dx dy dz$$

- For the entire crystal, we have the following.

$$F(hkl) \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z) e^{2\pi i(hx/a + ky/b + lz/c)} dx dy dz$$

- $F(hkl)$ is related to $\rho(x, y, z)$ by a **Fourier transform**.

$$\rho(x, y, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) e^{-2\pi i(hx/a + ky/b + lz/c)}$$

- If we let $F(hkl) = A(hkl) + iB(hkl)$, then it follows that the intensity is

$$I(hkl) \propto |F(hkl)|^2 = [A(hkl)]^2 + [B(hkl)]^2$$

- An electron-density map of a benzoic acid molecule.

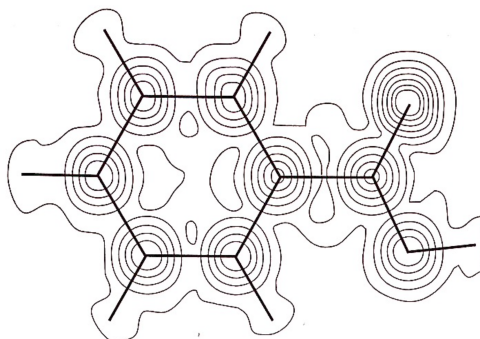


Figure 8.2: The electron density of benzoic acid.

- An electron-density map of a benzoic acid molecule determined from the X-ray diffraction pattern of a benzoic acid crystal.
- Each contour line corresponds to a constant value of the electron density.
- The location of the nuclei are readily deduced from this electron-density map and are represented by the vertices of the solid lines.
- A gas molecule can physisorb or chemisorb to a solid surface.

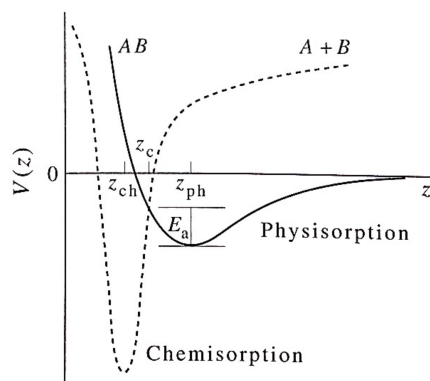
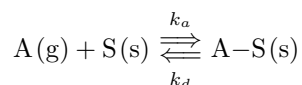


Figure 8.3: Comparing physisorption and chemisorption.

- Figure 8.3 shows one-dimensional potential-energy curves for the physisorption of molecule AB (solid line) and the dissociative chemisorption of AB (dashed line).
- The quantity z is the distance from the surface.
- In the physisorbed state, the molecule AB is bound to the surface by van der Waals forces.
- In the chemisorbed state, the A–B bond is broken, and the individual atoms are bound covalently or ionically on the surface.
 - As such, chemisorbed molecules are bound more strongly, are held closer to the surface.
 - As $z \rightarrow \infty$, V approaches a value greater than zero because AB is dissociated here. The asymptote is the bond dissociation energy (BDE).
 - Additionally, while A + B may be at zero, what we have here is $A^+ + B^-$. As such, we have the Coulomb potential, and the charged ions are unstable to be apart.
- The points z_{ch} and z_{ph} are the surface-molecule bond lengths for a chemisorbed and physisorbed molecule, respectively. The length of the substrate-adsorbate bond is shorter for a chemisorbed molecule than for a physisorbed molecule.
- The two potential curves cross at z_c . The activation energy for the conversion from physisorption to chemisorption is measured from the bottom of the physisorbed potential and is E_a .
- **Adsorption isotherm:** A plot of surface coverage as a function of gas pressure at constant temperature.
- Langmuir's assumptions.
 - The adsorbed molecules do not interact with one another.
 - The enthalpy of adsorption was independent of surface coverage.
 - There are a finite number of surface sites where a molecule can adsorb.

- The process of adsorption and desorption is depicted by the reversible elementary process



with equilibrium constant

$$K_c = \frac{k_a}{k_d} = \frac{[\text{A-S}]}{[\text{A}][\text{S}]}$$

where k_a and k_d are the rate constants for adsorption and desorption, respectively.

- The fact that k_a and k_d are constants independent of the extent of surface coverage implies that adsorbed molecules do not interact with one another.
- An analysis of surface coverage.
 - Let σ_0 be the concentration of surface sites in units of m^{-2} .
 - If the fraction of surface sites occupied by an adsorbate is θ , then σ (the adsorbate concentration on the surface) is $\theta\sigma_0$ and the concentration of empty surface sites is given by $\sigma_0 - \theta\sigma_0 = (1 - \theta)\sigma_0$.
 - We have that

$$v_d = k_d\theta\sigma_0$$

$$v_a = k_a(1 - \theta)\sigma_0[\text{A}]$$

where v_d is the rate of desorption, v_a is the rate of absorption, and $[\text{A}]$ is the number density or the concentration of A (g) .

- It follows that at equilibrium,

$$k_d\theta = k_a(1 - \theta)[\text{A}]$$

$$\frac{1}{\theta} = 1 + \frac{1}{K_c[\text{A}]}$$

- Additionally, since

$$[\text{A}] = \frac{P_{\text{A}}}{k_{\text{B}}T}$$

the Langmuir adsorption isotherm is

$$\frac{1}{\theta} = 1 + \frac{1}{bP_{\text{A}}}$$

where we have defined $b = K_c/k_{\text{B}}T$.

- For different materials, the same mass may correspond to orders of magnitude different surface areas (consider MOFs for instance).
- Langmuir adsorption isotherm for the case in which a diatomic molecule dissociates upon adsorption to the surface.
 - This reaction can be written as



- Two surface sites are involved in the adsorption and desorption process.

$$v_a = k_a[\text{A}_2](1 - \theta)^2\sigma_0^2$$

$$v_d = k_d\theta^2\sigma_0^2$$

- At equilibrium, these rates are equal, i.e.,

$$k_a[A_2](1 - \theta)^2 = k_d\theta^2$$
$$\theta = \frac{K_c^{1/2}[A_2]^{1/2}}{1 + K_c^{1/2}[A_2]^{1/2}}$$

- Having defined $[A] = P_A/k_B T$ and $b = K_c/k_B T$, we have

$$\theta = \frac{b_{A_2}^{1/2} P_{A_2}^{1/2}}{1 + b_{A_2}^{1/2} P_{A_2}^{1/2}}$$
$$\frac{1}{\theta} = 1 + \frac{1}{b_{A_2}^{1/2} P_{A_2}^{1/2}}$$