Scattering and Diffraction

Adventures in k-space, part 1

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Outline

Elastic Scattering
• Review / overview and terminology
• Form factors

Diffraction
• Crystalline arrangements
• Structure factors
• Approximations in practice
Elastic Scattering
Introduction and terms

Incident light:
Approximate plane-wave E-field

\[ E(\mathbf{r}, t) = E_0 \exp(i(\omega t - \mathbf{k} \cdot \mathbf{r})) \]

Incoming light
- Source wavelength: \( \lambda \)
- Wavevector \( \mathbf{k} \): photon momentum
  \[ ||\mathbf{k}|| = \frac{2\pi}{\lambda} \]
- E-field frequency: \( \omega = \frac{2\pi c}{\lambda} \)
- Incident field accelerates the charged particle
- Charged particle acceleration radiates a new \textit{scattered} E-field

Scattered light
- Accelerating charged particle radiates E-fields in all transverse directions
- E-fields are transverse: no radiation is emitted parallel to acceleration vector
- Scattered field amplitude is modulated by charge, mass, and geometric factors
Elastic Scattering
introduction and terms

Incident light:
Approximate plane-wave E-field

\[ E(\mathbf{r}, t) = E_0 \exp(i(\omega t - \mathbf{k} \cdot \mathbf{r})) \]

Multiple scatterers
- Scattered fields from multiple scatterers superimpose
- Superposition of scattered waves → interference
- The interference pattern is related to the positions of the scatterers
Elastic Scattering
introduction and terms

Incident light:
Approximate plane-wave E-field

\[ E(\mathbf{r},t) = E_0 \exp(i(\omega t - \mathbf{k} \cdot \mathbf{r})) \]

Distribution of scatterers
- The entire distribution of charge density, \( \rho(\mathbf{r}) \), simultaneously scatters the light
- Scattered fields from different parts of the distribution interfere
- The interference pattern is directly related to the distribution of charge
- How can we use the real-space pattern to interrogate \( \rho(\mathbf{r}) \)?

Subject of this talk

Same distribution, different wavelength

Multiple scatterers
Single scatterer

Position of measurement
Scattered amplitude
Elastic Scattering
introduction and terms

Incident light:
Approximate plane-wave E-field

\[ E(r,t) = E_0 \exp(i(\omega t - k \cdot r)) \]

Detector measurement:
scattered light at a chosen \( k' \)

Scattered light

- Scattering vector \( q = k' - k \) describes momentum transfer
- Detector placement selects a scattering vector
- Elastic scattering: momentum transfer occurs without energy absorption
  \[ \rightarrow ||k'|| = ||k|| = k \]

\[ E_{\text{det}}(t) \propto E_0 \exp(i(\omega t - k \cdot R)) \]
Elastic Scattering
introduction and terms

Scattered field (for an electron):

\[
E_{\text{det}}(t) = \frac{E_0 e^2 \cos(\alpha)}{4 \pi R \epsilon_0 m_e c^2} \exp(i(\omega t - kR))
\]

\[= E_0 \frac{r_e}{R} \cos(\alpha) \exp(i(\omega t - kR))\]

The scattered intensity is (typically) much smaller than the incident intensity.

Scattered field amplitude factors:
- \( m_e \) – particle mass
- \( e \) – particle charge
- \( 4\pi R \) – spherical dissipation
- \( \cos(\alpha) \) – \( \alpha \) is the complement of the angle between the scattering path \( \mathbf{k}' \) and the charge acceleration vector
- \( c \) – speed of light
- \( \epsilon_0 \) – permittivity of vacuum
- \( r_e \) – electron radius
Snattered field from one particle with $\cos(\alpha)=1$:

$$E(\mathbf{q}) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right)$$

(Not a function of $\mathbf{q}$)

Multiple particles:
(assumption: distance between scatterers is much less than distance to the detector)

$$E(\mathbf{q}) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right) \sum_n \exp\left(i \mathbf{q} \cdot \mathbf{r}_n\right)$$

(Sum over particles at positions $\mathbf{r}_n$)

Distribution of particles:

$$E(\mathbf{q}) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right) \int d^3 \mathbf{r} \rho(\mathbf{r}) \exp\left(i \mathbf{q} \cdot \mathbf{r}\right)$$

(Integrate the particle distribution over $\mathbf{r}$)

\[ \ldots \text{we just found the Fourier transform of } \rho(\mathbf{r}) \]

The scattering pattern of a charge distribution is its Fourier transform, in the space of $\mathbf{q}$ (elastic momentum transfer) vectors
Elastic Scattering
form factors

\[ E = E_0 \frac{r_e}{R} \exp \left( i (\omega t - k R) \right) \int d^3 r \rho(r) \exp \left( i q \cdot r \right) \]

This Fourier transform is the form factor of \( \rho(r) \)

- Form factor \( f(q) = F[\rho(r)] \)
- This is powerful: it is very difficult to solve or measure \( \rho(r) \), but we can interrogate it by (much easier) measurements of \( f(q) \)
- Atom cores have fairly repeatable \( \rho(r) \)
  \( \rightarrow \) atomic form factors are well documented
- Materials also have repeatable \( \rho(r) \)
  \( \rightarrow \) scattering form factors are known for many different shapes of material

\[ f(q) \equiv \int d^3 r \rho(r) \exp \left( i q \cdot r \right) \]
Elastic Scattering
form factors

\[ f(q) \equiv \int d^3 r \rho(r) \exp(iq \cdot r) \]

Atomic species:

\[ f(q) = Z - 41.78214 s^2 \sum_k a_k \exp(-s^2 b_k) \]

\[ s \equiv q / (4 \pi) \]

Empirical parameters
Elastic Scattering
form factors

Spheres:

\[ f(q) = \frac{3 \sin(q r_{\text{sph}}) - q r_{\text{sph}} \cos(q r_{\text{sph}})}{(q r_{\text{sph}})^3} \]

\[ f(q) \equiv \int d^3 r \, \rho(r) \exp(i q \cdot r) \]
Scattering measurements
non-dilute / condensed arrangements

\[
E(q) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right)f(q)
\]

Non-dilute arrangement: condensed formation of identical scatterers

- Add (superimpose) the scattered amplitudes from all scattering centers in the material (scatterer location: \(R_p\))
- Form the scattered intensity
- The main ingredient is the square of the form factor
- An additional pair summation appears: this is the scattering structure factor

\[
I(q) = |E(q)|^2 = E'(q)E(q)
\]

\[
= \left(E_0 \frac{r_e}{R}\right)^2 f(q)^2 \sum_p \left(\exp\left(-i q \cdot R_p\right)\right) \sum_m \left(\exp\left(i q \cdot R_m\right)\right)
\]

\[
= N \left(E_0 \frac{r_e}{R}\right)^2 f(q)^2 \left(1 + \frac{1}{N} \sum_p \sum_{m \neq p} \exp\left(i q \cdot (R_m - R_p)\right)\right)
\]

Relative interparticle positions modulate the scattered intensity according to the structure factor

\[
S(q) \equiv 1 + \frac{1}{N} \sum_p \sum_{m \neq p} \exp\left(i q \cdot (R_m - R_p)\right)
\]
Scattering measurements
structure factors for condensed arrangements

\[ I(q) = N \left( E_0 \frac{r_e}{R} \right)^2 f(q)^2 S(q) \]

\[ S(q) \equiv 1 + \frac{1}{N} \sum_p \sum_{m \neq p} \exp(iq \cdot (R_m - R_p)) \]

Non-dilute scattering structure factor
- Interacting particles will exhibit characteristic interparticle spacings
- The pair summation in \( S(q) \) is directly related to the pair correlation function \( g(r) \) (isotropic case)

\[ S(q) = 1 + N \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin(qr)}{qr} dr \]

- Pair correlation functions are analytical for some simple inter-particle potentials
- Hard sphere potential:
  \[ V(r) = \begin{cases} 0, & r \geq r_{\text{sph}} \\ \infty, & r < r_{\text{sph}} \end{cases} \]

- Hard sphere structure factor: (big nasty equations)
Scattering measurements
dilute / diffuse arrangements

\[ E(q) = E_0 \frac{r_e}{R} \exp \left( i(\omega t - k R) \right) f(q) \]

Dilute arrangement: dispersed formation of non-interacting identical scatterers

- The vast majority of scattering events will be from single scatterers
- The pair summation in the structure factor is assumed to average out to zero, over all pairs
- The structure factor reduces to 1

\[ E(q) = E_0 \frac{r_e}{R} \exp \left( i(\omega t - k R) \right) \sum_p \left[ f(q) \exp(i q \cdot R_p) \right] \]

\[ I(q) = |E(q)|^2 = E'(q) E(q) \]

\[ = N \left( E_0 \frac{r_e}{R} \right)^2 f(q)^2 \left( 1 + \frac{1}{N} \sum_p \sum_{m \neq p} \exp\left(i q \cdot (R_m - R_p)\right) \right) \]

\[ \approx N \left( E_0 \frac{r_e}{R} \right)^2 f(q)^2 \]

... dilute scattering directly probes the square of the form factor

Assumption: uncorrelated positions

\[ \frac{1}{N} \sum_p \sum_{m \neq p} \exp\left(i q \cdot (R_m - R_p)\right) \approx 0 \]
Scattering measurements
diffuse intensity profiles

\[ I(q) = N \left( E_0 \frac{r_e}{R} \right)^2 f(q)^2 S(q) \]

Dilute scattering Intensity

- \( S(q) = 1 \)
- Directly probe the square of the form factor
- Shown here:

  Guinier-Porod spheroids
  \( r_g = 10A\sqrt{3/5} \)
  \( D = 4 \)

  Identical spheres
  \( r = 10A \)

  Spheres with gaussian size distribution
  \( r_0 = 10A \)
  \( \sigma = 0.1 \)
Scattering measurements
condensed intensity profiles

\[ I(q) = N \left( \frac{E_0 r_e}{R} \right)^2 f(q)^2 S(q) \]

Non-dilute scattering Intensity

- Product of form factor (squared) and structure factor
- Only valid for isotropic form factors
- Shown here: hard sphere structure factor
  characteristic radius: 10A
  volume fraction: 0.3
From Scattering to Diffraction
scattering of crystalline arrangements

\[ E(q) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right)f(q) \]

Crystalline arrangement: repeating lattice of identical charge distributions
- Just like scattering, superimpose amplitudes from all scattering centers in the crystal (scatterer location: \( R_p \))
- Separate the sum over scatterers:
  1. Outer **crystal summation** over all unit cells in the crystal (unit cell position: \( R_m \))
  2. Inner **form factor-weighted sum** over all species in the unit cell basis: the **crystalline structure factor** (specie position: \( r_n \))

\[
E(q) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right) \sum_{p} \left[ f_p(q) \exp\left(i q \cdot R_p\right) \right]
\]

\[
= E_0 \frac{r_e}{R} \exp\left(i(\omega t - k R)\right) \sum_{m} \exp\left(i q \cdot R_m\right) \sum_{n} f_n(q) \exp\left(i q \cdot r_n\right)
\]

\[
F(q) \equiv \sum_{n} f_n(q) \exp\left(i q \cdot r_n\right)
\]
From Scattering to Diffraction
scattering of crystalline arrangements

Effects of crystal summation

- Crystal lattice vectors (spatial units of repetition): \(a_1, a_2, a_3\)
- Scattering vector components in crystal basis: \(q_1, q_2, q_3\)
- Analytical solution (lattice of \(N_1, N_2, N_3\) repeating units):

\[
E(q) = E_0 \frac{r_e}{R} \exp(i(\omega t - k R)) F(q) \sum_m \exp(i q \cdot R_m)
\]

\[
\sum_m \exp(i q \cdot R_m) = \prod_{j=1}^{3} \exp \left( i(N_j - 1) \frac{q_j a_j}{2} \right) \frac{\sin \left( N_j \frac{q_j a_j}{2} \right)}{\sin \left( \frac{q_j a_j}{2} \right)}
\]

- Peaks occur at \(q_j a_j / 2 = n\pi\) for any integer \(n\) \(\rightarrow\) Bragg’s Law
- Off-peak: crystal summation is approximately zero for large \(N_j\)
- Higher \(N_j\) \(\rightarrow\) sharper peaks; crystal defects \(\rightarrow\) broader peaks
From Scattering to Diffraction
scattering of crystalline arrangements

\[ E(q) = E_0 \frac{r_e}{R} \exp\left(i(\omega t - k \cdot R)\right) F(q) \sum_m \exp\left(i q \cdot R_m \right) \]

Effects of structure factor

- Recall, the crystal summation leads to Bragg’s Law: Peaks occur at \( q_j a_j / 2 = n \pi \) for all \( j \), for any integer \( n \)
- Define the reciprocal lattice basis vectors: \( b_1, b_2, b_3 \)
- General reciprocal lattice vector \( G_{hkl} \equiv h b_1 + k b_2 + l b_3 \) (corresponds to lattice plane with Miller indices \( h,k,l \))
- Equivalent statement of Bragg’s Law: crystal summation selects \( q \)-values that satisfy \( q_{pk} = 2\pi G_{hkl} \), for integers \( h,k,l \)
- It is common to evaluate the structure factor only at reciprocal lattice points \( q = 2\pi G_{hkl} \) for some \( \{h,k,l\} \) of interest
- The structure factor can systematically amplify, attenuate, or eliminate a given peak, depending on its \( h,k,l \) values
- Different crystal structures exhibit different elimination or amplification patterns

\( F(q) \equiv \sum_n f_n(q) \exp(i \cdot q \cdot r_n) \)
Diffraction Profiles  
common practices and approximations

$E(q) = E_0 \frac{r_e}{R} \exp(i(\omega t - k R)) F(q) \sum_m \exp(i q \cdot R_m)$

$\approx c \epsilon_0 \left( \frac{E_0 r_e}{R} \right)^2 \sum_{h,k,l} \left[ F(q_{hkl}) \right]^2 P_{hkl}(q)$

Typical approach:

1. Evaluate structure factor at $2\pi G_{hkl}$, for some $\{h,k,l\}$ of interest

(simple)

2. We generally do not have the necessary information to evaluate the crystal summation: instead, apply an empirical broadening function (Gauss, Lorentz, Voigt)

(ambitious)

3. Or, if available, use physical parameters to incorporate crystal disorder ("FPA": Full Parameterization Approach)

4. Sum the (broadened) peak profiles for all $\{h,k,l\}$ of interest
Diffraction Profiles
common practices and approximations

\[ I(q) = c \epsilon_0 |E(q)|^2 \]

\[ \approx c \epsilon_0 \left( \frac{E_0 r_e}{R} \right)^2 \sum_{h,k,l} |F(q_{hkl})|^2 P_{hkl}(q) \]

Consider:

- The broadening function creates non-zero intensities for \( q \)-values near (but not equal to) \( q_{hkl} \)
- Is it a good idea to apply \( F(q_{hkl}) \) to the entire \( P_{hkl}(q) \)?
- This tends to be okay when the form factors are slowly varying
- This could be a mistake when the form factors are sharply featured
- One safe alternative: compute the whole structure factor

\[ I(q) \approx c \epsilon_0 \left( \frac{E_0 r_e}{R} \right)^2 |F(q)|^2 \sum_{h,k,l} P_{hkl}(q) \]
Isotropic intensity examples

- fcc Aluminum powder
- Spherical particle close-packed superlattice with same dimensions as fcc Aluminum
- Spherical form factor has sharper features, which disrupt the \{200\} peak
The end – thank you!

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Reference materials:

- **Scattering and diffraction theory:**
  (course reader for Stanford University Materials Science 205)
  Available at Stanford bookstore

- **Computation and plotting of scattering and diffraction patterns:**
  xrsdkit (X-Ray Scattering and Diffraction toolKIT)
  https://github.com/scattering-central/xrsdkit
What do we get from the detector?

- Detector position selects a \( q \) value
- Detector has finite size: a given position integrates a small, finite range of \( q \)
- Detector has finite speed: the measured intensity is integrated over time
- We measure the “integrated intensity” pattern \( l(q) \), proportional to the time-averaged square of \( E(q) \)
- Exact (non-integrated) intensity profiles are not generally feasible to measure
Area detectors

- Most modern experiments employ area detectors (see Tim Dunn’s talk at 11:15)
- Essentially, thousands or millions of detectors operating simultaneously in parallel
- Each pixel selects a different range of \( q \) values
- Each pixel requires different geometric corrections
- Analysis is no less complicated, but the experiment happens faster and the \( q \)-range is measured concurrently