Today's Outline - March 24, 2015

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures
- Crystal Truncation Rods

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures
- Crystal Truncation Rods

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures
- Crystal Truncation Rods
- Diffuse Scattering

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures
- Crystal Truncation Rods
- Diffuse Scattering
- Debye-Waller factor

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures
- Crystal Truncation Rods
- Diffuse Scattering
- Debye-Waller factor

Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
due Thursday, April 2, 2015

Today's Outline - March 24, 2015

- Size exclusion chromatography SAXS
- Modulated Structures
- Crystal Truncation Rods
- Diffuse Scattering
- Debye-Waller factor

Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
due Thursday, April 2, 2015

No class on Thursday, March 26, 2015

Size exclusion chromatography SAXS

Size exclusion chromatography SAXS

SAXS of biological molecules is an excellent way of getting some information about the molecules as they exist in solution.

Size exclusion chromatography SAXS

SAXS of biological molecules is an excellent way of getting some information about the molecules as they exist in solution.

Obtaining information about R_g and the Porod region, combined with modeling and the known crystallographic structures can give a more complete picture of how these molecules function.

Size exclusion chromatography SAXS

SAXS of biological molecules is an excellent way of getting some information about the molecules as they exist in solution.

Obtaining information about R_g and the Porod region, combined with modeling and the known crystallographic structures can give a more complete picture of how these molecules function.

A major problem in these systems is aggregation and impurities. Pre-purification of samples is important but if they are left for some time before the SAXS mefasurement is performed, there can be decomposition.

Size exclusion chromatography SAXS

SAXS of biological molecules is an excellent way of getting some information about the molecules as they exist in solution.

Obtaining information about R_g and the Porod region, combined with modeling and the known crystallographic structures can give a more complete picture of how these molecules function.

A major problem in these systems is aggregation and impurities. Pre-purification of samples is important but if they are left for some time before the SAXS mefasurement is performed, there can be decomposition.

Even without any aggregation or decomposition, separation into a monodisperse molecule size is challenging.

Size exclusion chromatography SAXS

SAXS of biological molecules is an excellent way of getting some information about the molecules as they exist in solution.

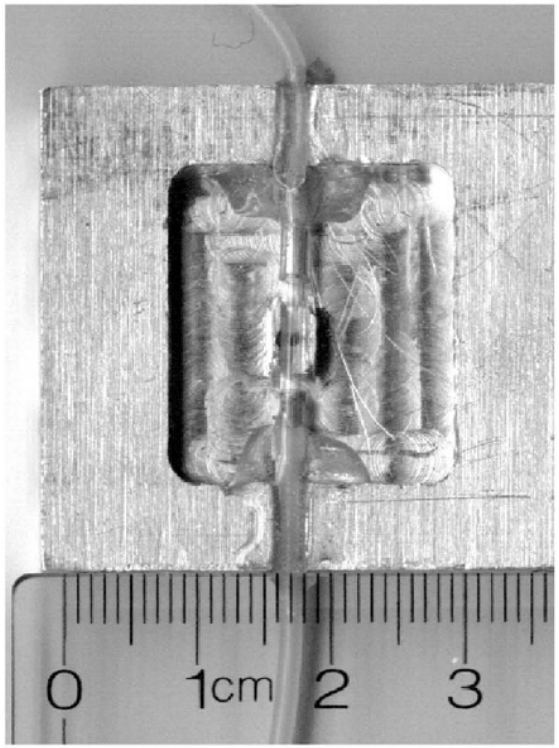
Obtaining information about R_g and the Porod region, combined with modeling and the known crystallographic structures can give a more complete picture of how these molecules function.

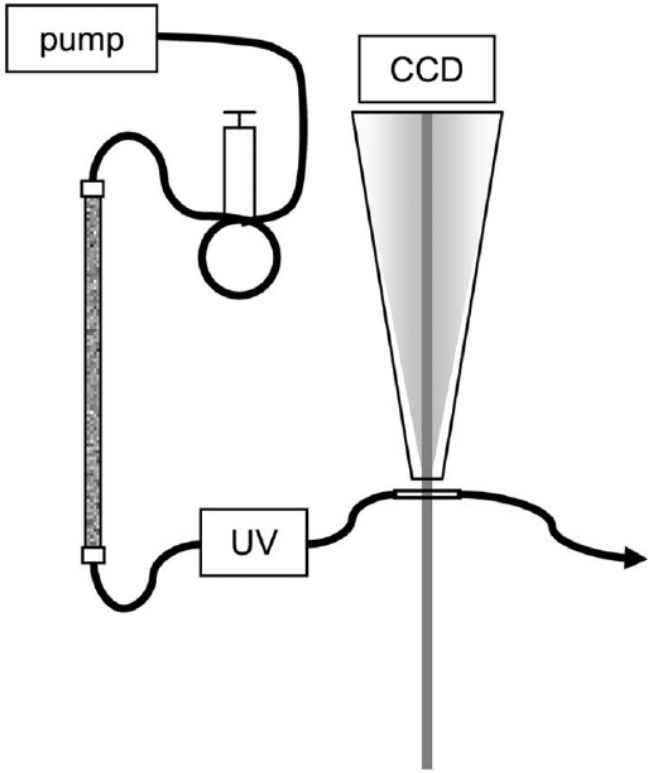
A major problem in these systems is aggregation and impurities. Pre-purification of samples is important but if they are left for some time before the SAXS mefasurement is performed, there can be decomposition.

Even without any aggregation or decomposition, separation into a monodisperse molecule size is challenging.

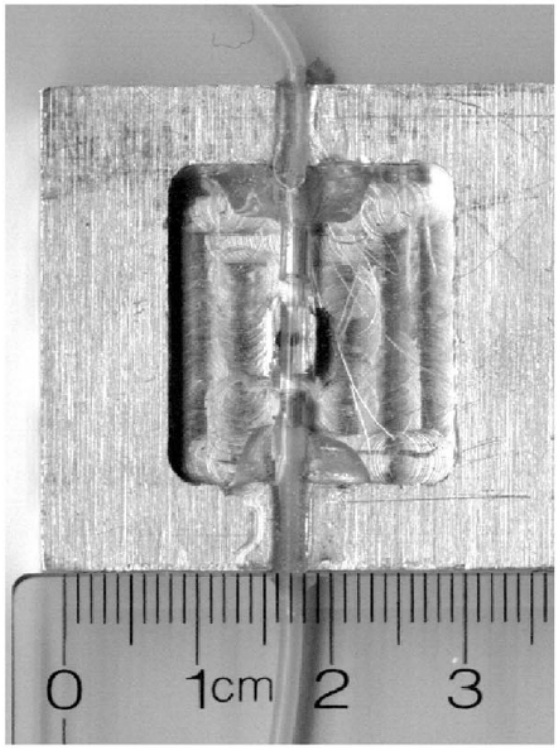
Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004) developed a technique which is now being used routinely in biological SAXS, called Size Exclusion Chromatography SAXS.

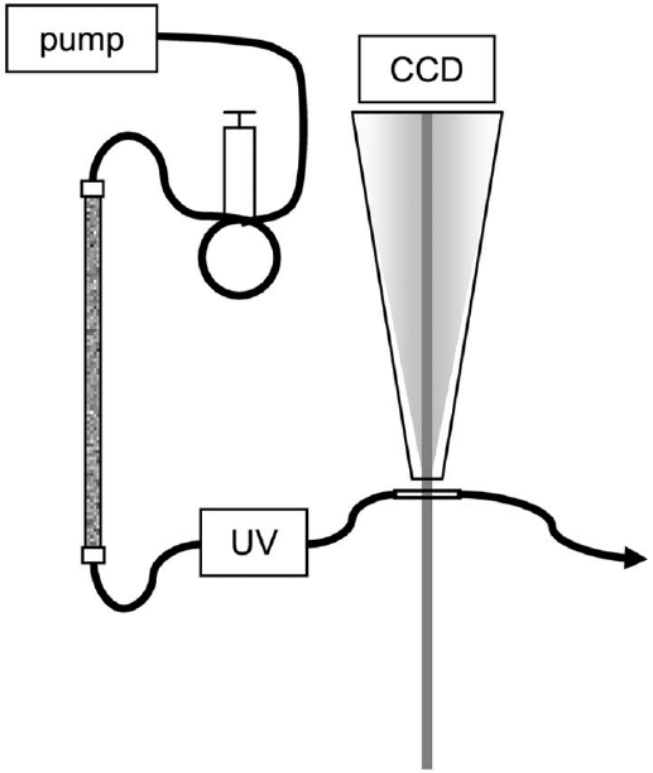
Size exclusion chromatography SAXS





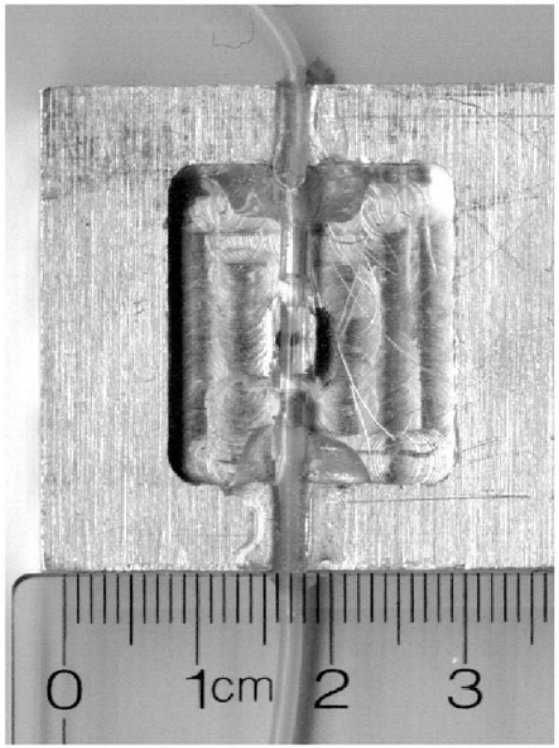
Size exclusion chromatography SAXS

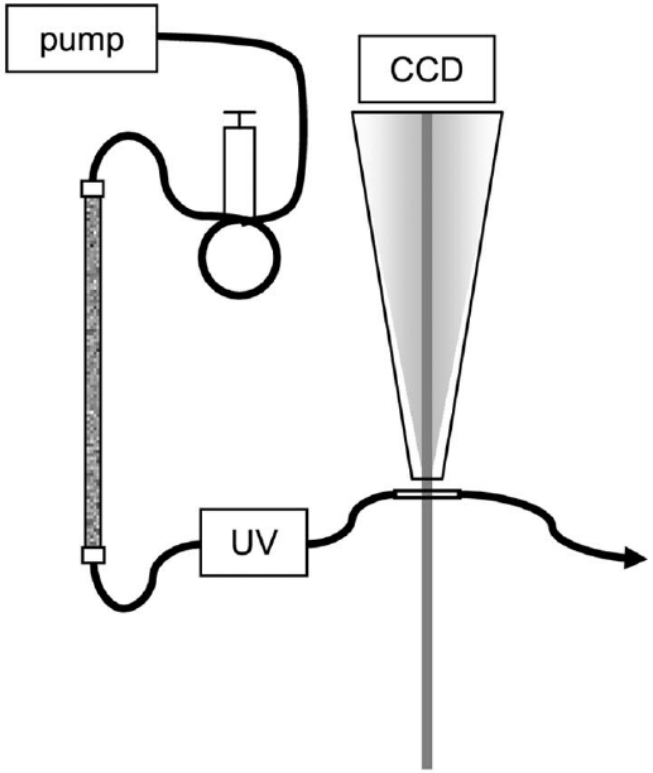




2m SAXS camera, 1.03Å(12 keV) x-rays were used

Size exclusion chromatography SAXS

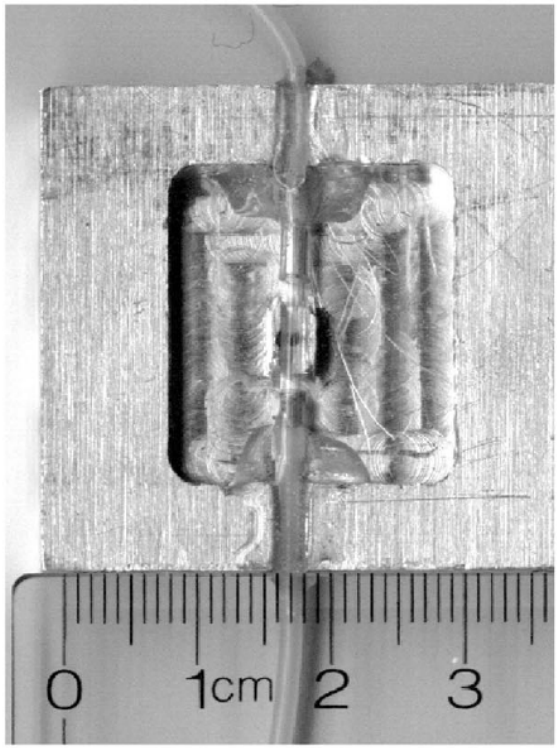


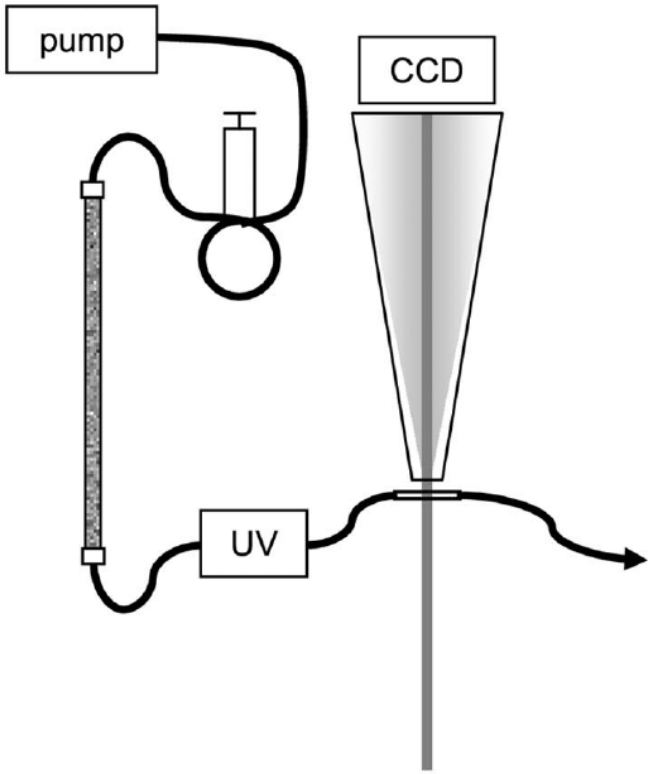


2m SAXS camera, 1.03Å(12 keV) x-rays were used

2s exposure times every 20s, with 0.25 ml/min flow rate

Size exclusion chromatography SAXS



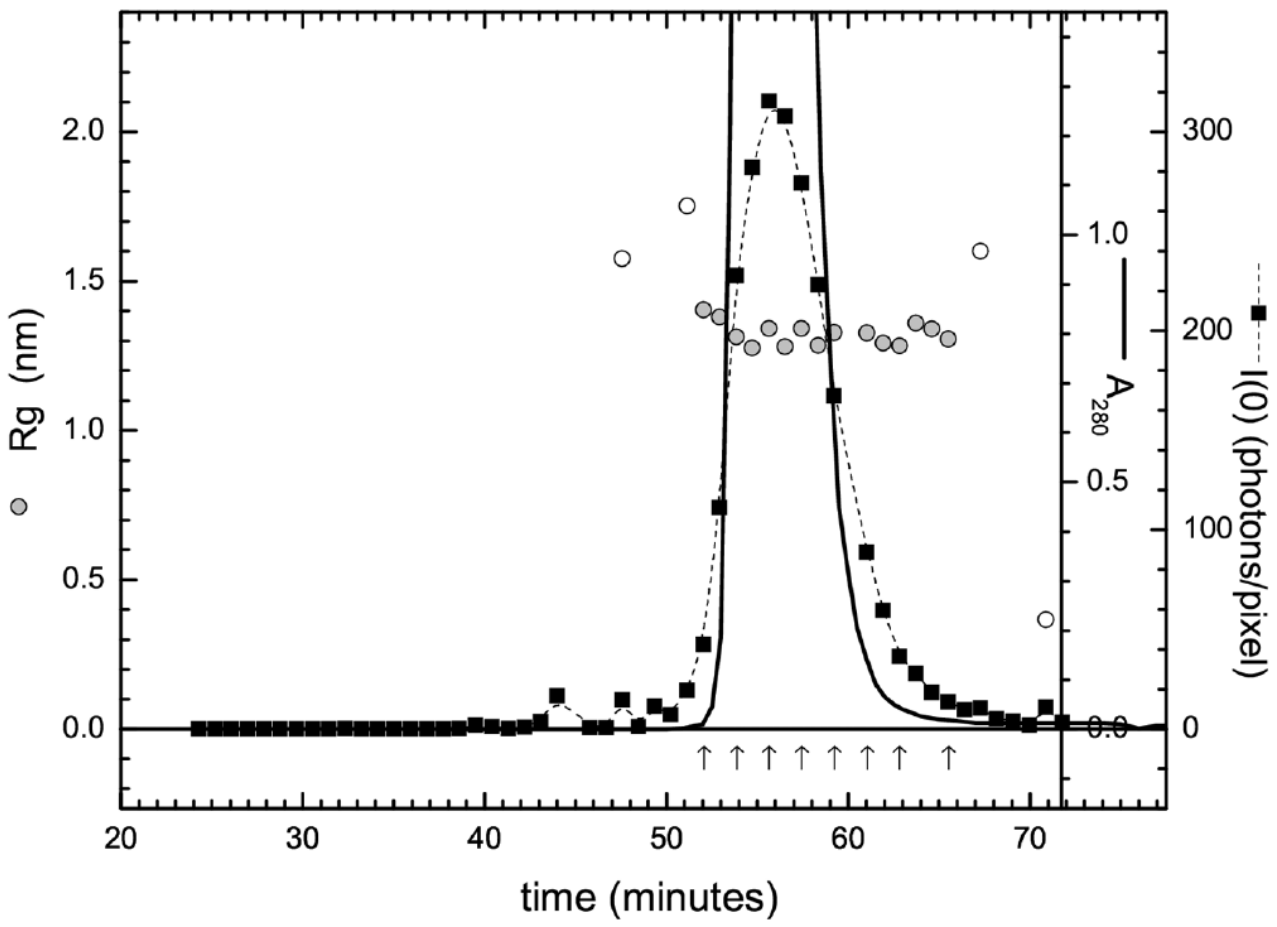


2m SAXS camera, 1.03Å(12 keV) x-rays were used

2s exposure times every 20s, with 0.25 ml/min flow rate

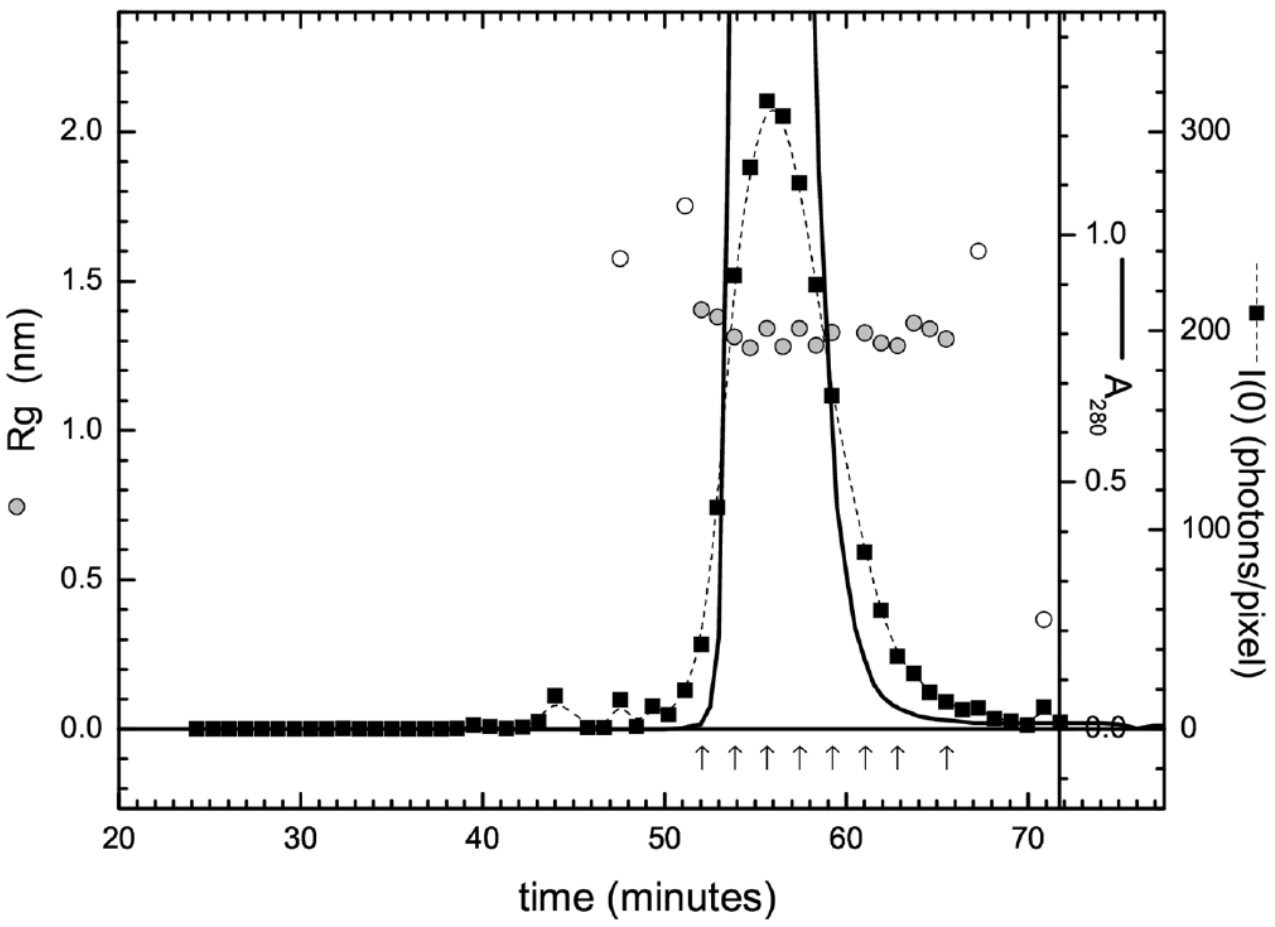
samples of (1) cytochrome c, (2) plasminogen, (3) mixture of cytochrome c bovine serum albumin, and blue dextran

SEC-SAXS experimental setup



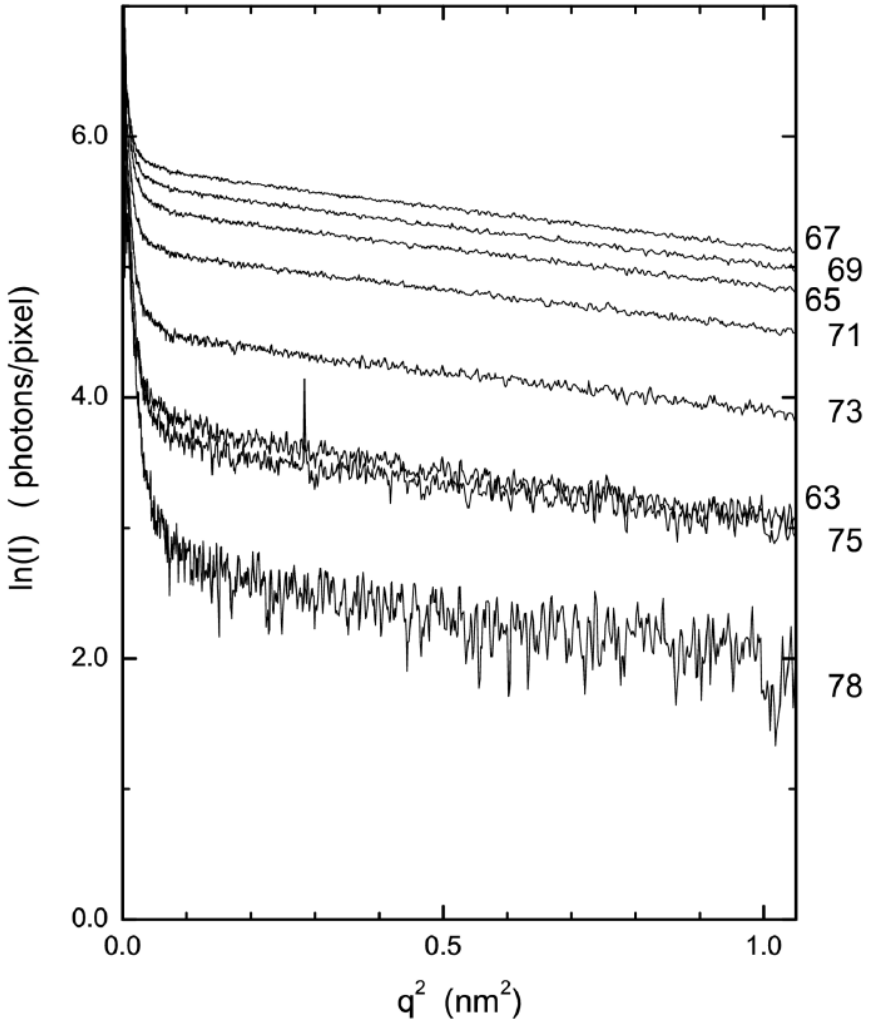
Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004).

Cytochrome c



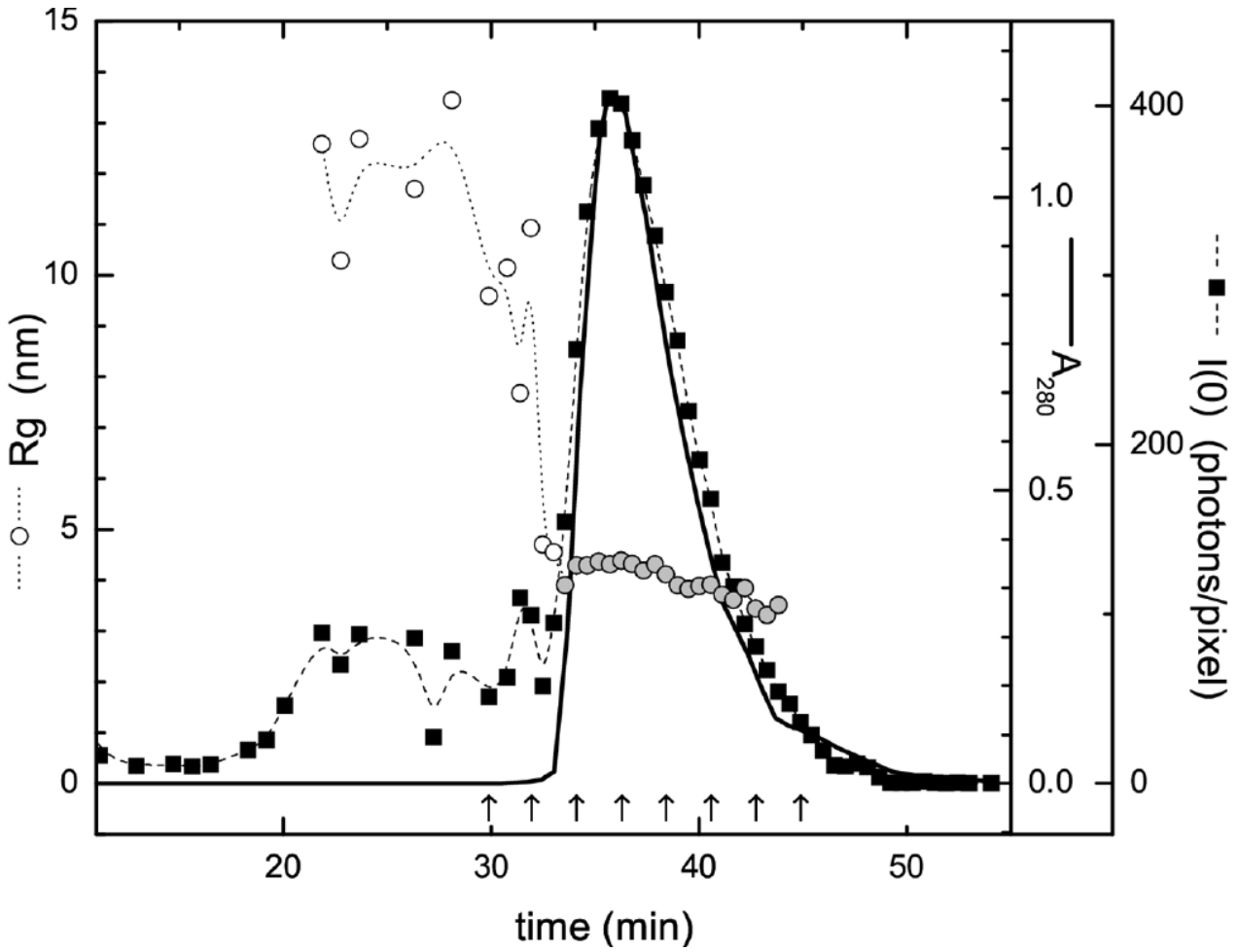
Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004).

Cytochrome c - Guinier plots



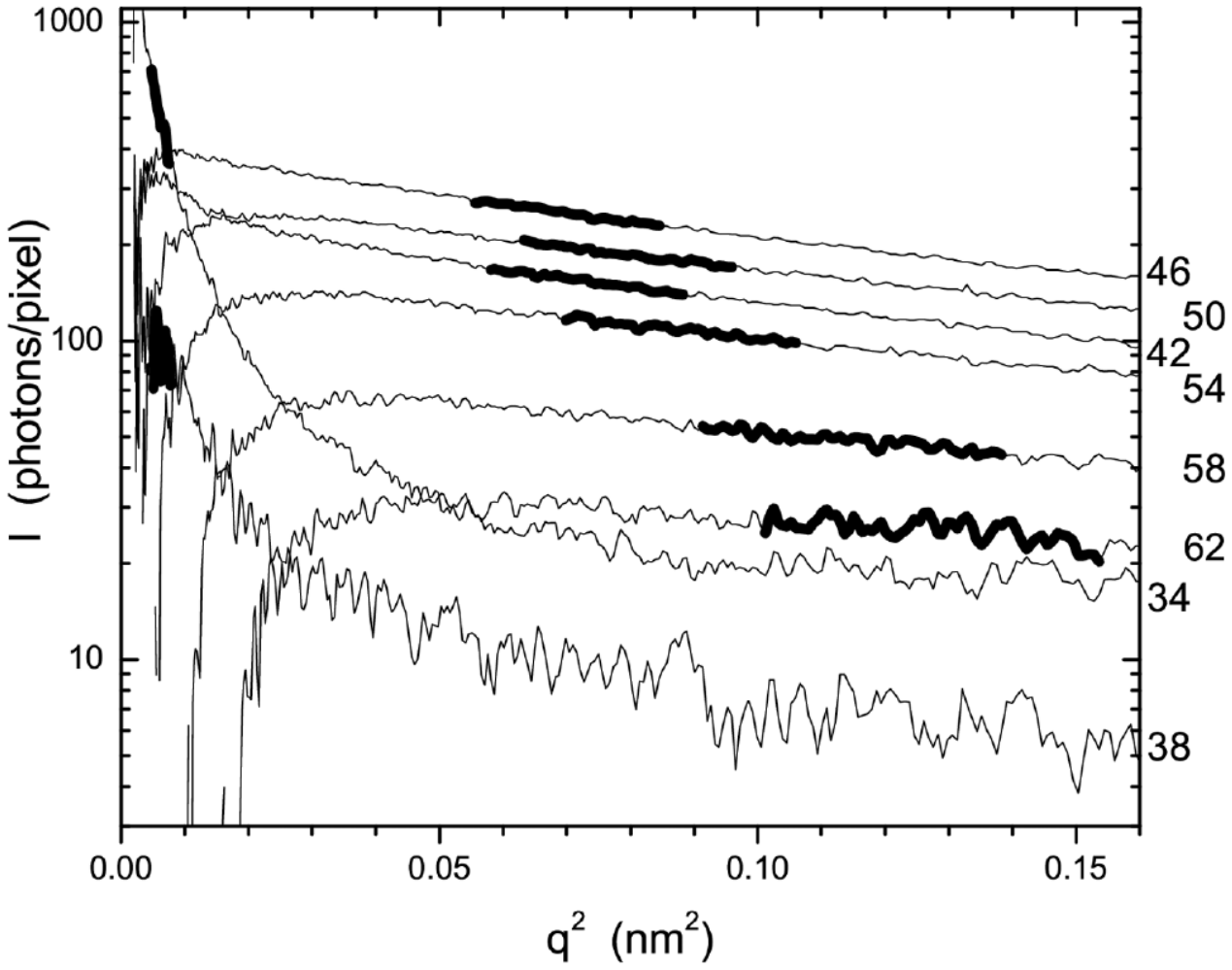
Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004).

Plasminogen



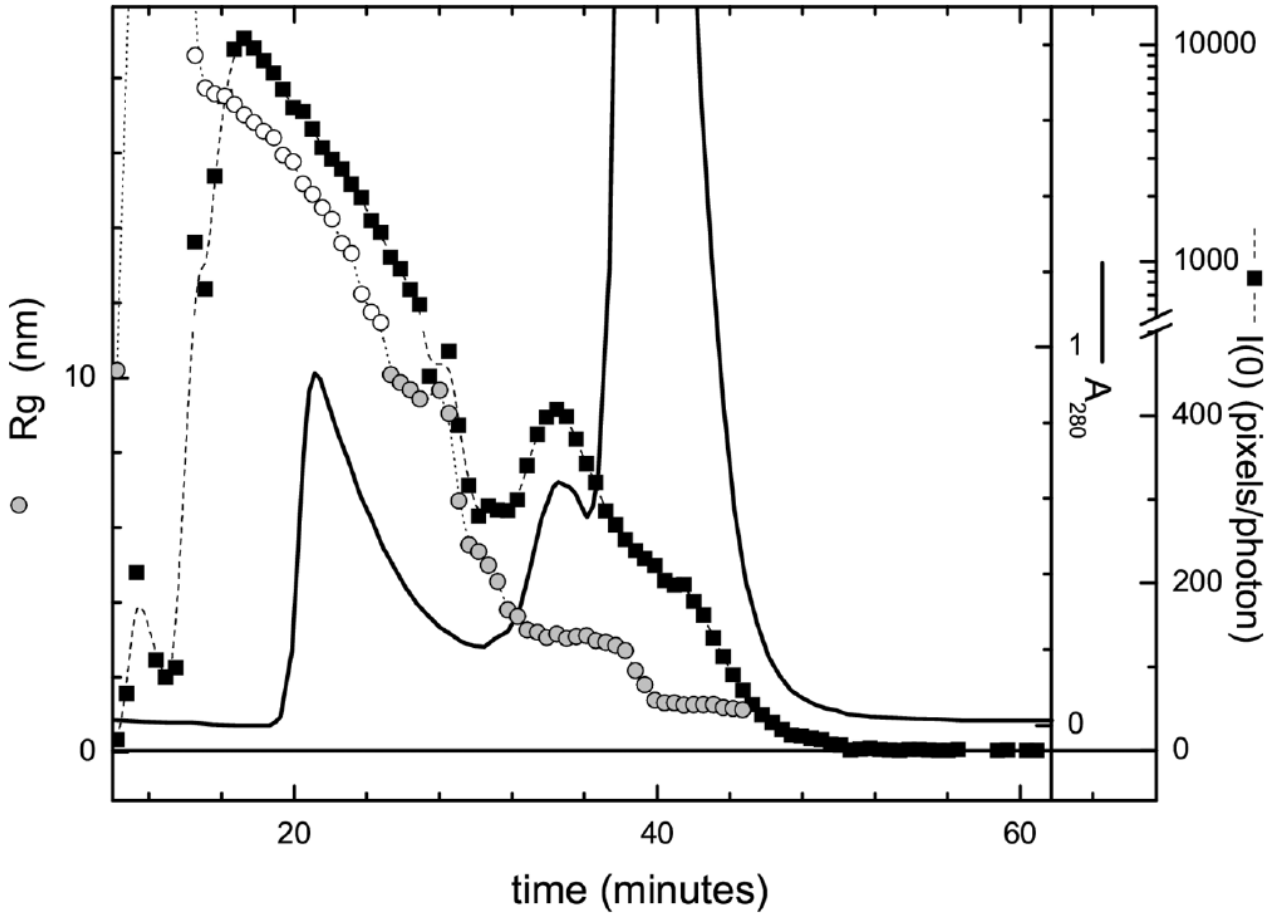
Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004).

Plasminogen - Guinier plots



Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004).

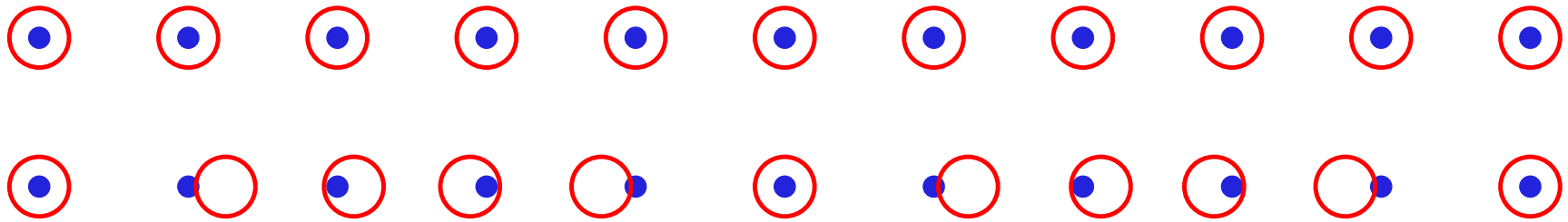
Three component mixture



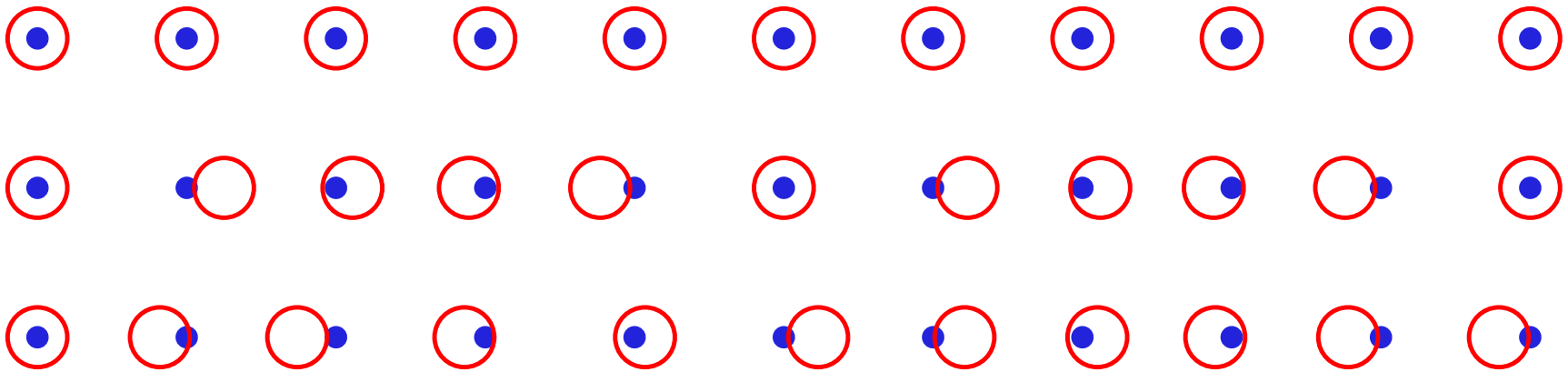
Matthew, Mirza & Menhart, "liquid-chromatography-coupled SAXS for accurate sizing of aggregating proteins," *J. Synchrotron Rad.* **11**, 314-318 (2004).

Periodic Lattice

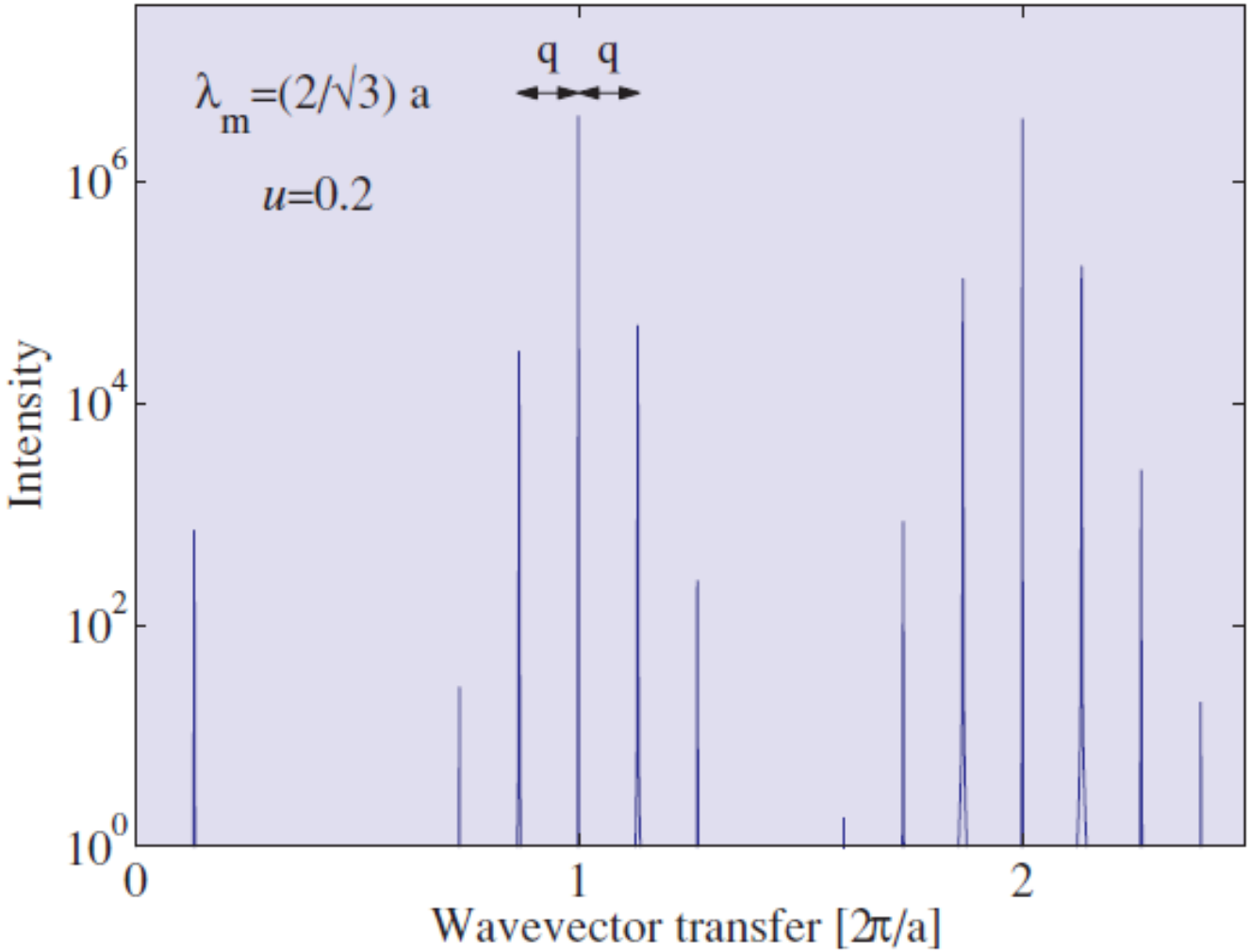
Commensurate Modulation



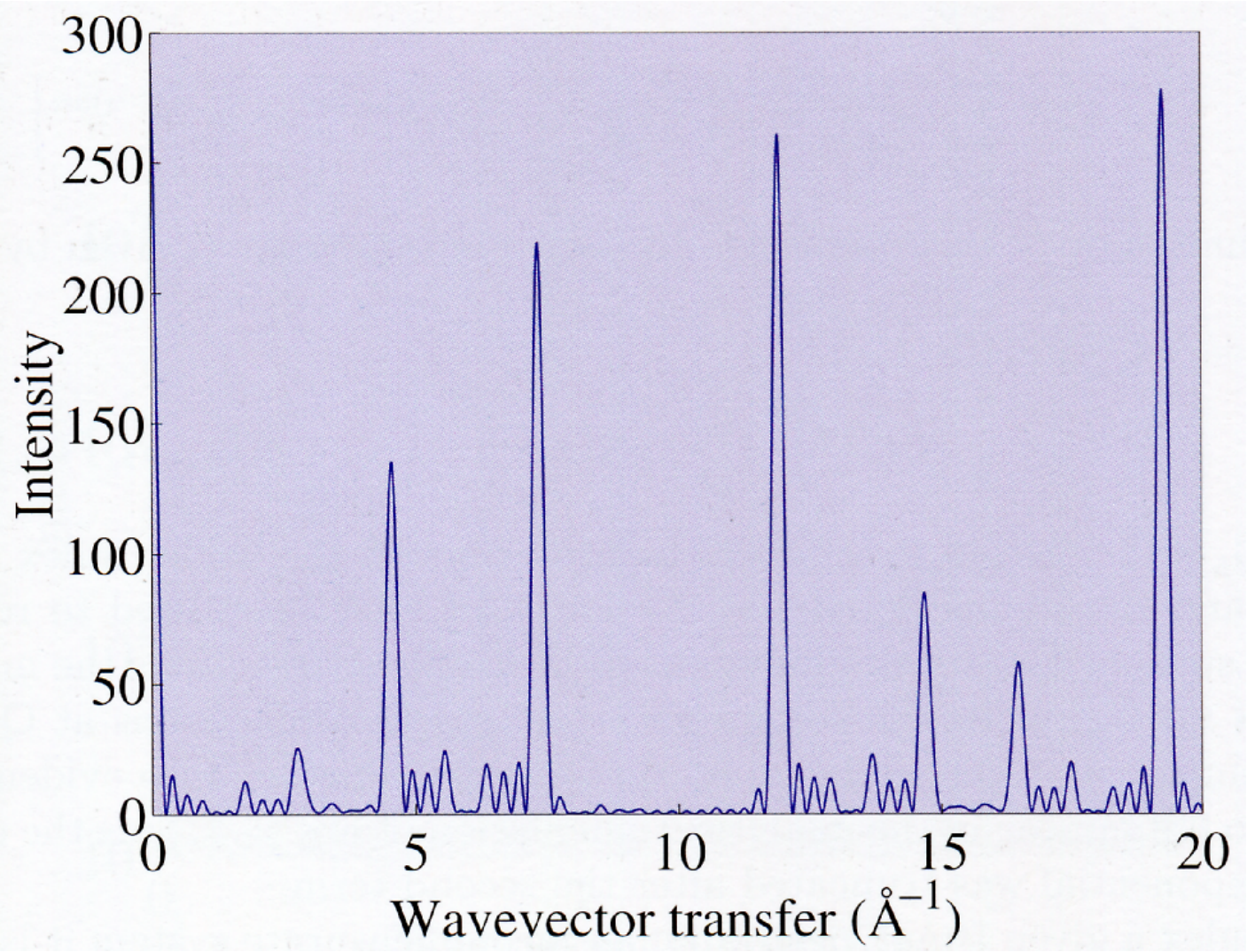
Incommensurate Modulation



Quasiperiodic Scattering



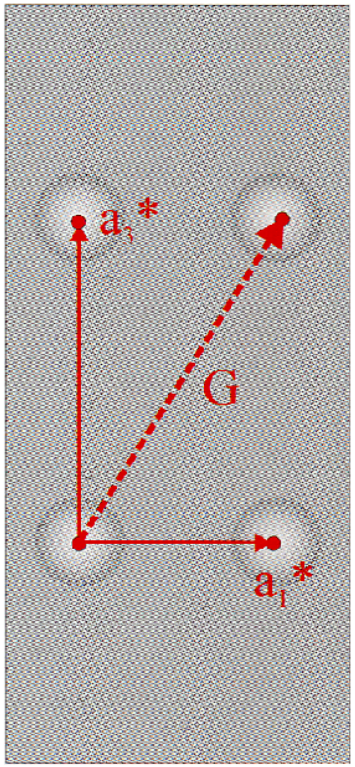
Fibonacci Sequence Intensity

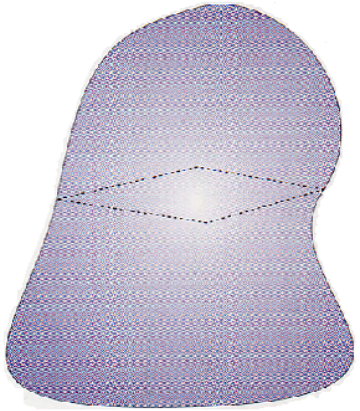


Diffraction from a Truncated Surface

For an infinite sample, the diffraction spots are infinitesimally sharp.

Diffraction from a Truncated Surface

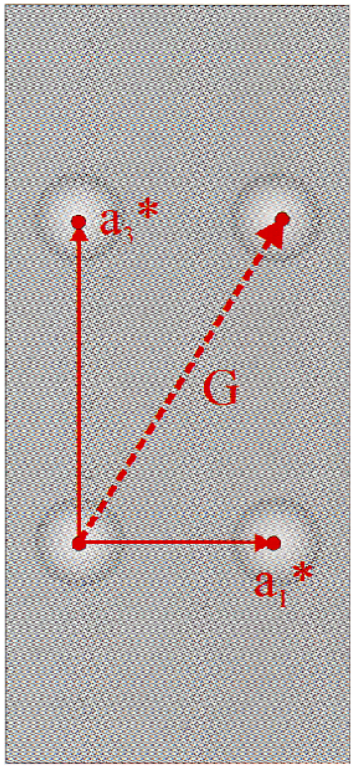


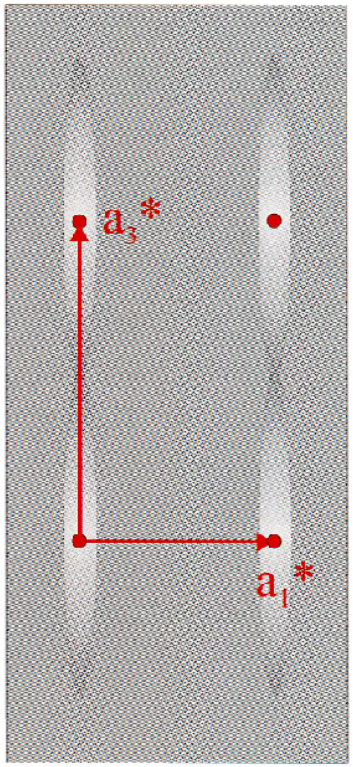


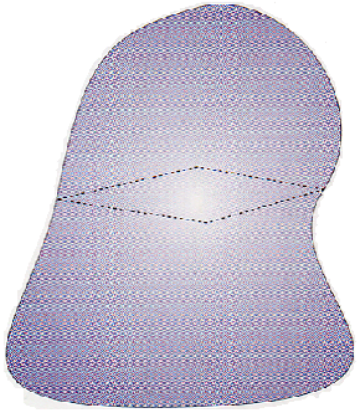
For an infinite sample, the diffraction spots are infinitesimally sharp.

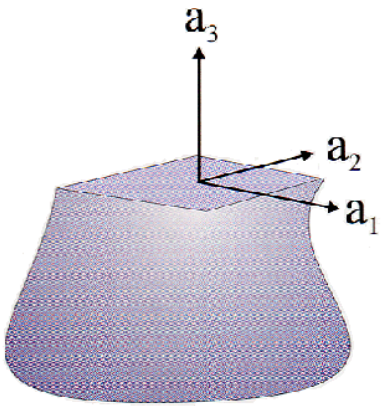
With finite sample size, these spots grow in extent and become more diffuse.

Diffraction from a Truncated Surface







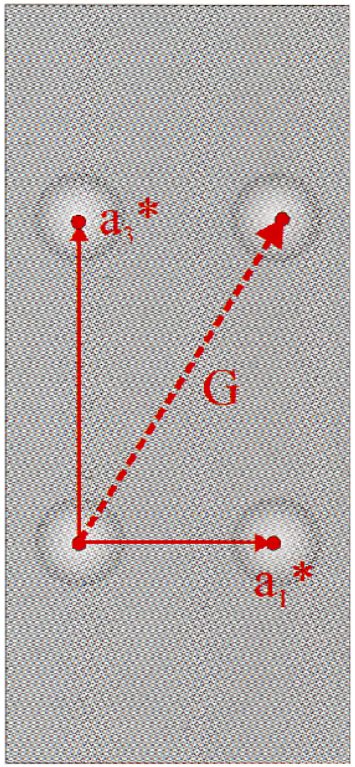


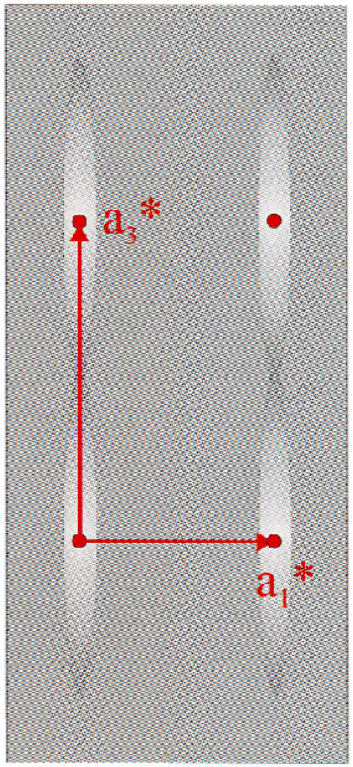
For an infinite sample, the diffraction spots are infinitesimally sharp.

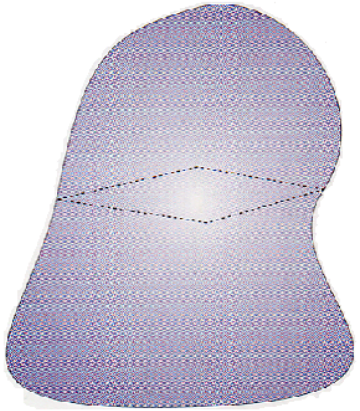
With finite sample size, these spots grow in extent and become more diffuse.

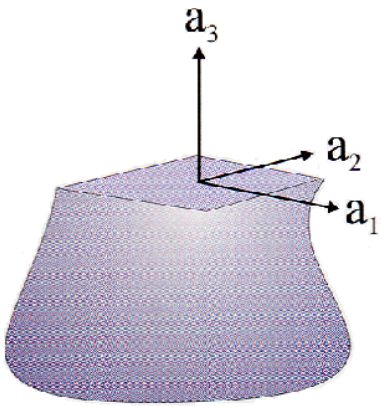
If the sample is cleaved and left with flat surface, the diffraction will spread into rods perpendicular to the surface.

Diffraction from a Truncated Surface









For an infinite sample, the diffraction spots are infinitesimally sharp.

With finite sample size, these spots grow in extent and become more diffuse.

If the sample is cleaved and left with flat surface, the diffraction will spread into rods perpendicular to the surface.

The scattering intensity can be obtained by treating the charge distribution as a convolution of an infinite sample with a step function in the z-direction.

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$

this sum has been discussed previously and gives

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$
$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3}}$$

this sum has been discussed previously and gives

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$

$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3}} = \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$

this sum has been discussed previously and gives

or, in terms of the momentum transfer along the z-axis, $Q_z = 2\pi l / a_3$

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$

$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3}} = \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$

this sum has been discussed previously and gives

or, in terms of the momentum transfer along the z-axis, $Q_z = 2\pi l / a_3$

since the intensity is the square of the scattering factor

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$

$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3}} = \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$

this sum has been discussed previously and gives

or, in terms of the momentum transfer along the z-axis, $Q_z = 2\pi l / a_3$

since the intensity is the square of the scattering factor

$$I^{CTR} = \left| F^{CTR} \right|^2 = \frac{\left| A(\vec{Q}) \right|^2}{\left(1 - e^{i2\pi l}\right)\left(1 - e^{-i2\pi l}\right)}$$

CTR Scattering Factor

The scattering amplitude F^{CTR} along a crystal truncation rod is given by summing an infinite stack of atomic layers, each with scattering amplitude $A(\vec{Q})$.

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$
$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3}} = \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$

this sum has been discussed previously and gives

or, in terms of the momentum transfer along the z-axis, $Q_z = 2\pi l / a_3$

since the intensity is the square of the scattering factor

$$I^{CTR} = \left|F^{CTR}\right|^2 = \frac{\left|A(\vec{Q})\right|^2}{\left(1 - e^{i2\pi l}\right)\left(1 - e^{-i2\pi l}\right)} = \frac{\left|A(\vec{Q})\right|^2}{4\sin^2(\pi l)}$$

Dependence on Q

When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

Dependence on Q

When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

$$I^{CTR} = \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(Q_z a_3/2\right)}$$

Dependence on Q

When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

$$
\begin{aligned}
I^{CTR} &= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(Q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(\pi l + q_z a_3/2\right)}
\end{aligned}
$$

Dependence on Q

When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

$$
\begin{aligned}
I^{CTR} &= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(Q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(\pi l + q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(q_z a_3/2\right)}
\end{aligned}
$$

Dependence on Q

When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

$$
\begin{aligned}
I^{CTR} &= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(Q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(\pi l + q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(q_z a_3/2\right)} \\
&\approx \frac{\left|A(\vec{Q})\right|^2}{4(q_z a_3/2)^2}
\end{aligned}
$$

Dependence on Q

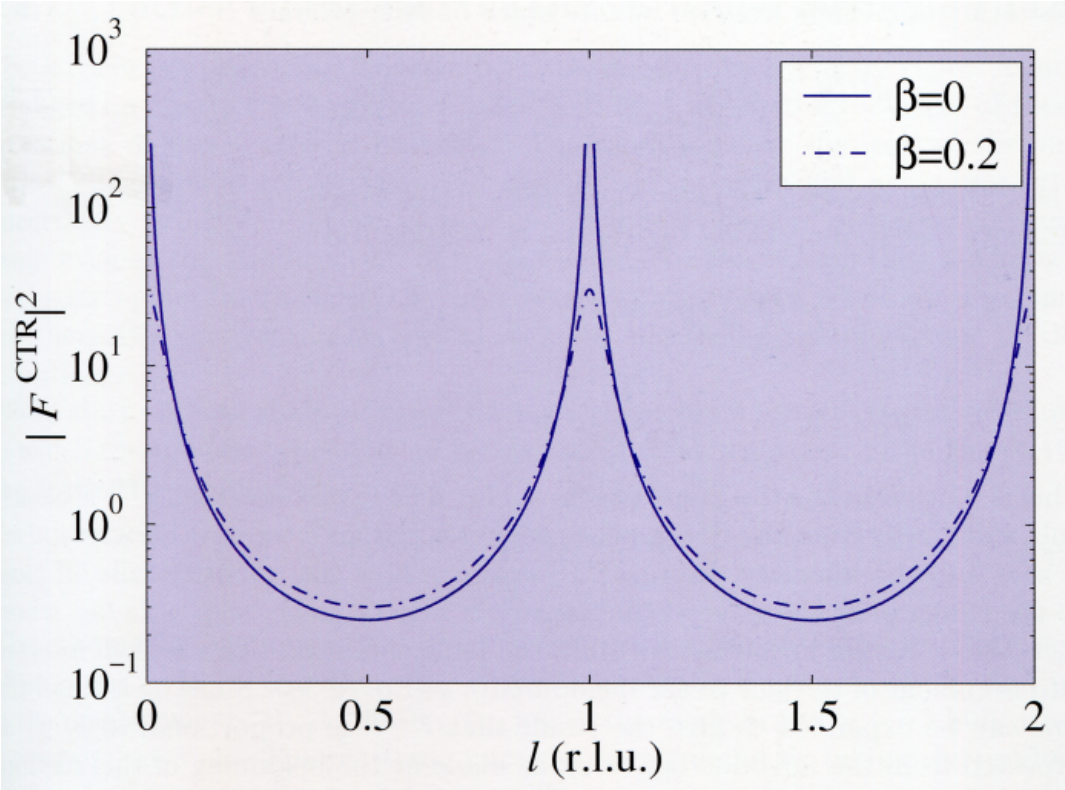
When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

$$
\begin{aligned}
I^{CTR} &= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(Q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(\pi l + q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(q_z a_3/2\right)} \\
&\approx \frac{\left|A(\vec{Q})\right|^2}{4(q_z a_3/2)^2} = \frac{\left|A(\vec{Q})\right|^2}{q_z^2 a_3^2}
\end{aligned}
$$

Dependence on Q

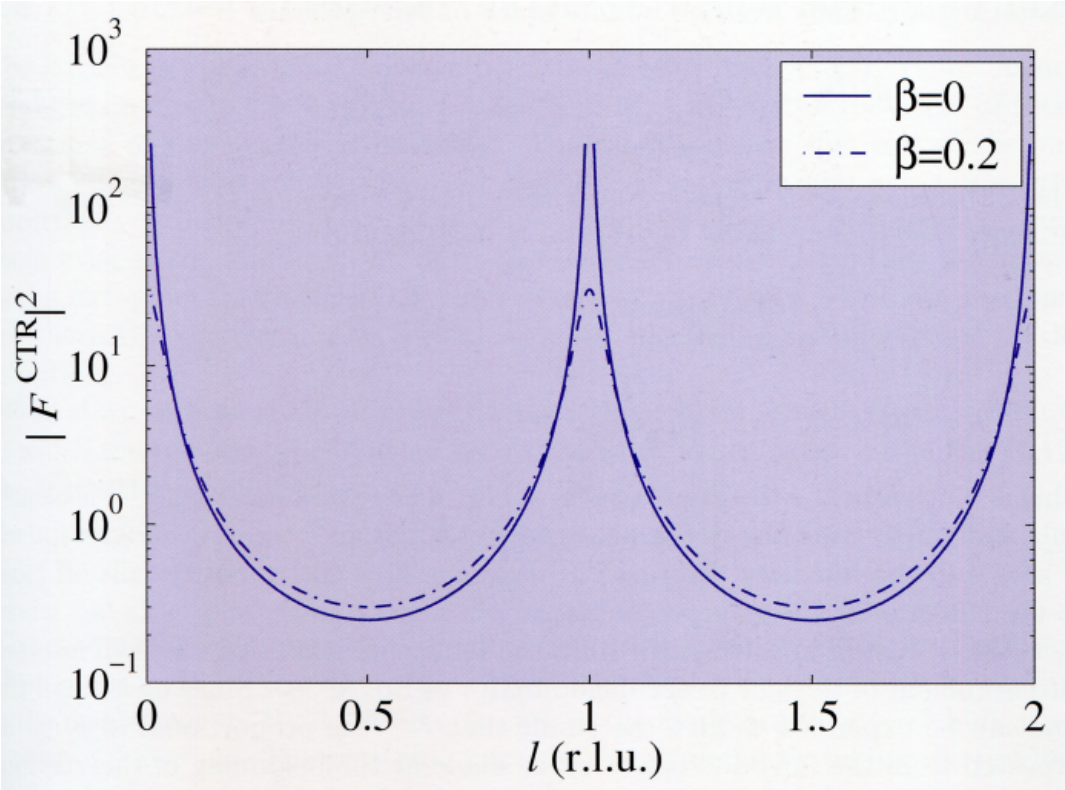
When l is an integer (meeting the Laue condition), the scattering factor is infinite but just off this value, the scattering factor can be computed by letting $Q_z = q_z + 2\pi/a_3$, with q_z small.

$$
\begin{aligned}
I^{CTR} &= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(Q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(\pi l + q_z a_3/2\right)} \\
&= \frac{\left|A(\vec{Q})\right|^2}{4\sin^2\left(q_z a_3/2\right)} \\
&\approx \frac{\left|A(\vec{Q})\right|^2}{4(q_z a_3/2)^2} = \frac{\left|A(\vec{Q})\right|^2}{q_z^2 a_3^2}
\end{aligned}
$$



Absorption Effect

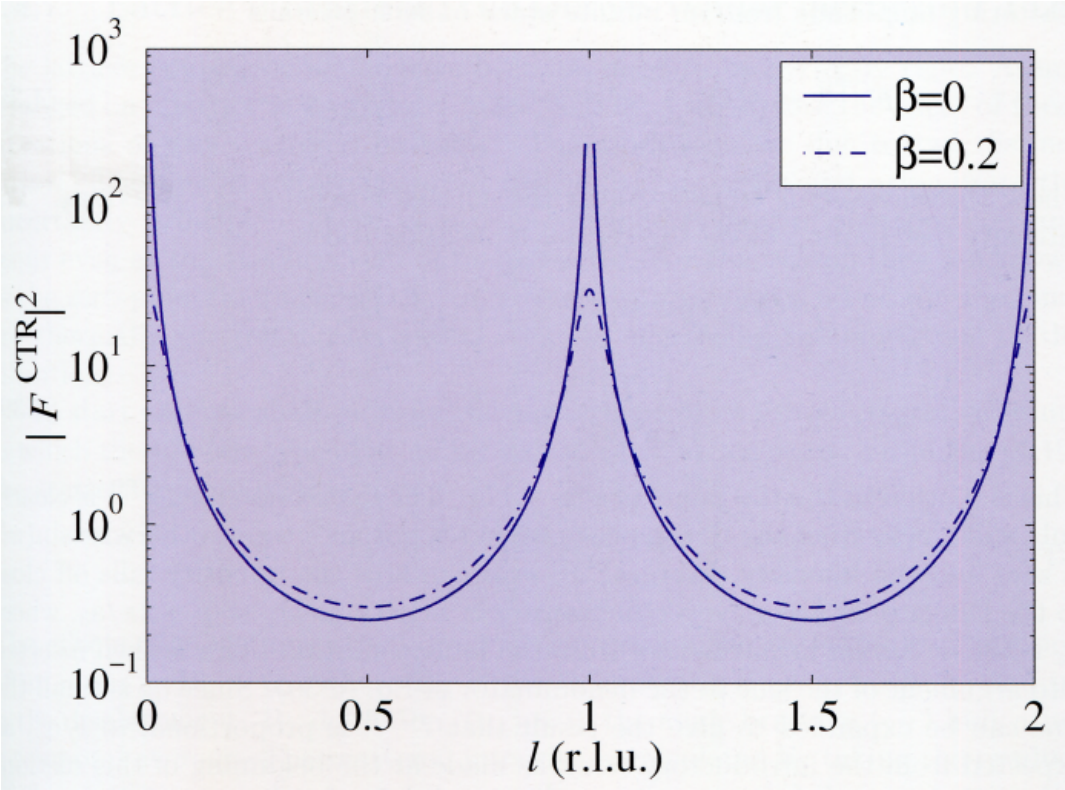
Absorption effects can be included as well



Absorption Effect

Absorption effects can be included as well

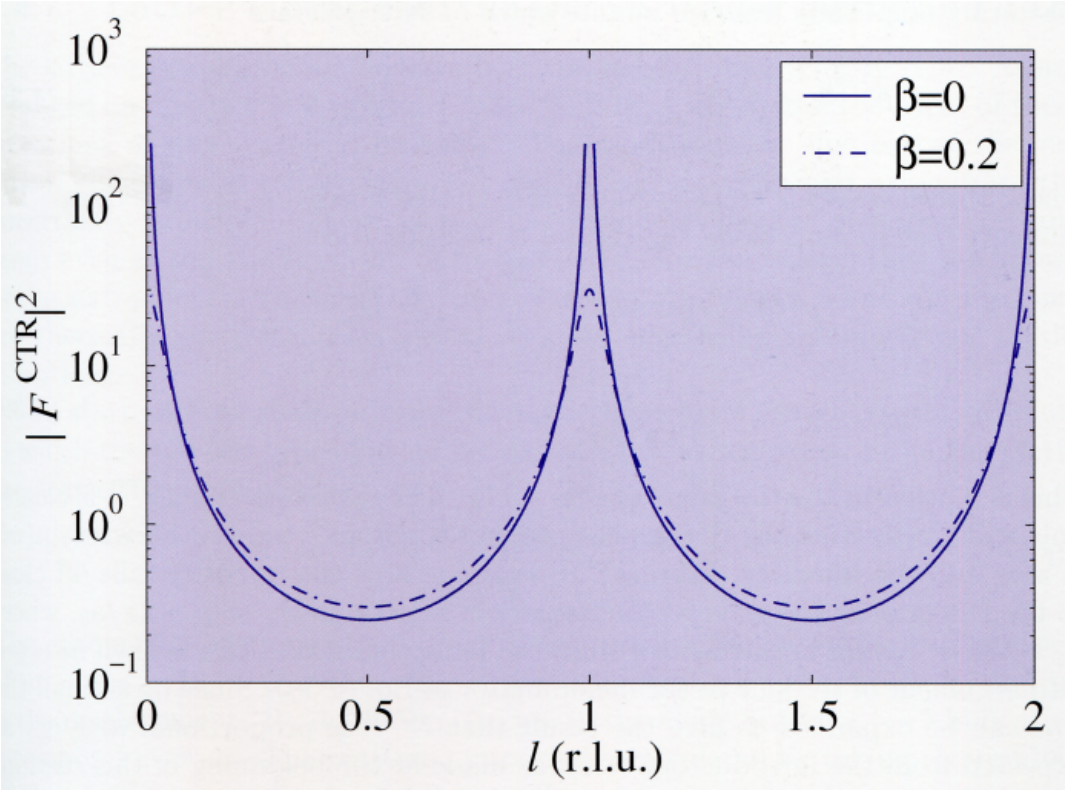
$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j}$$



Absorption Effect

Absorption effects can be included as well

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j} e^{-\beta j}$$

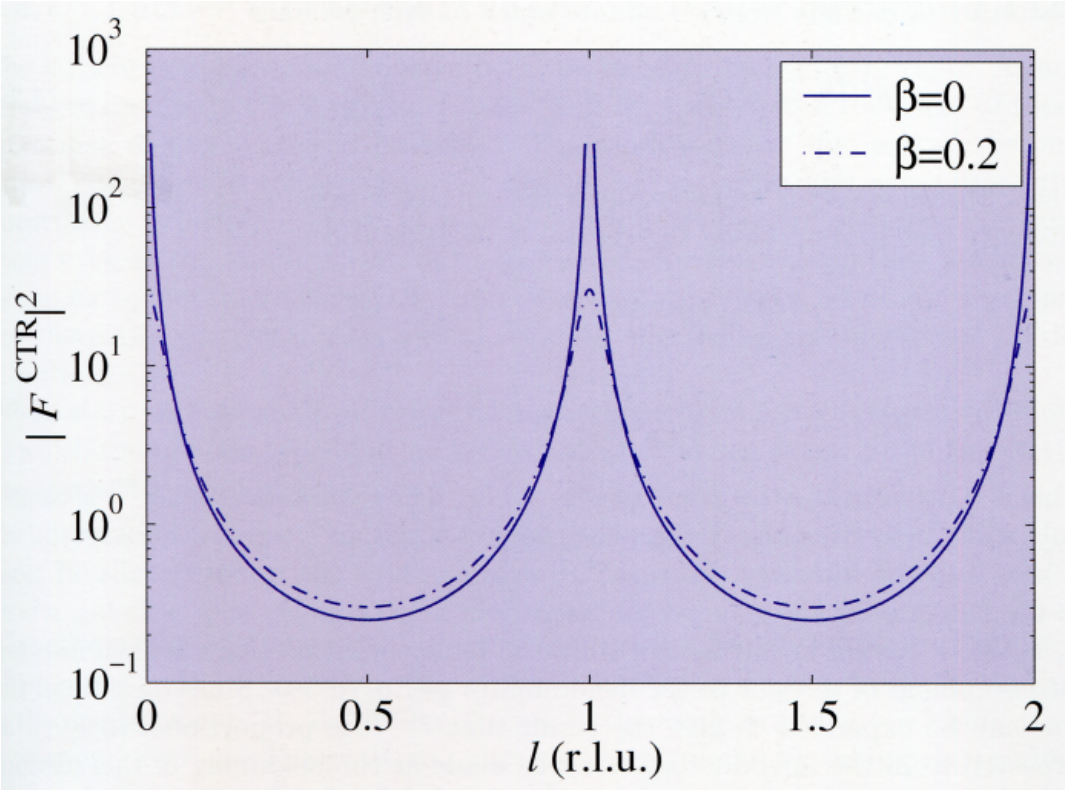


Absorption Effect

Absorption effects can be included as well

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j} e^{-\beta j}$$

$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3} e^{-\beta j}}$$



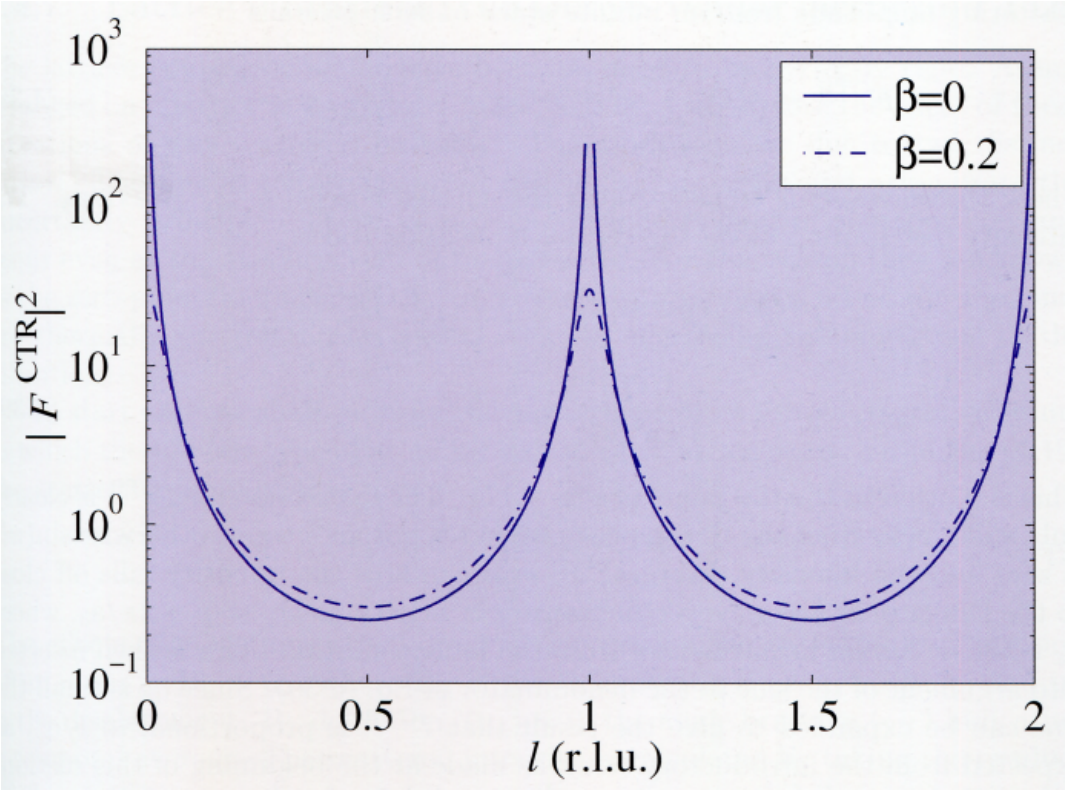
Absorption Effect

Absorption effects can be included as well

$$F^{CTR} = A(\vec{Q}) \sum_{j=0}^{\infty} e^{iQ_z a_3 j} e^{-\beta j}$$

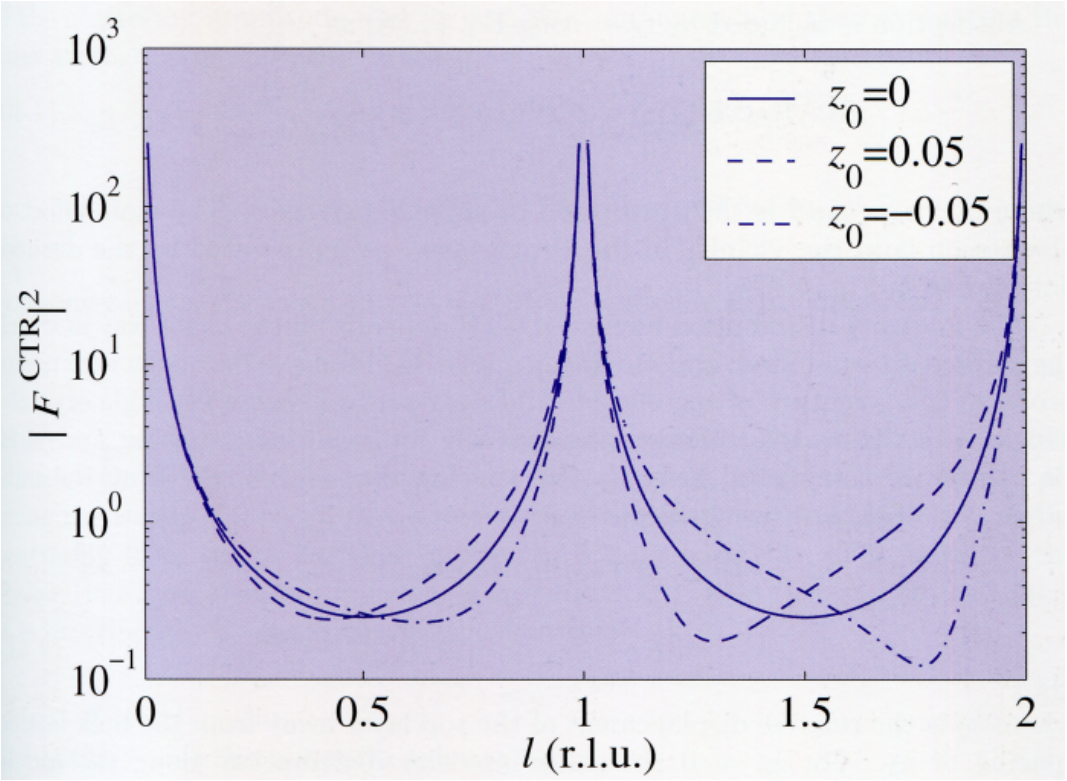
$$= \frac{A(\vec{Q})}{1 - e^{iQ_z a_3} e^{-\beta j}}$$

This removes the infinity and increases the scattering profile of the crystal truncation rod



Density Effect

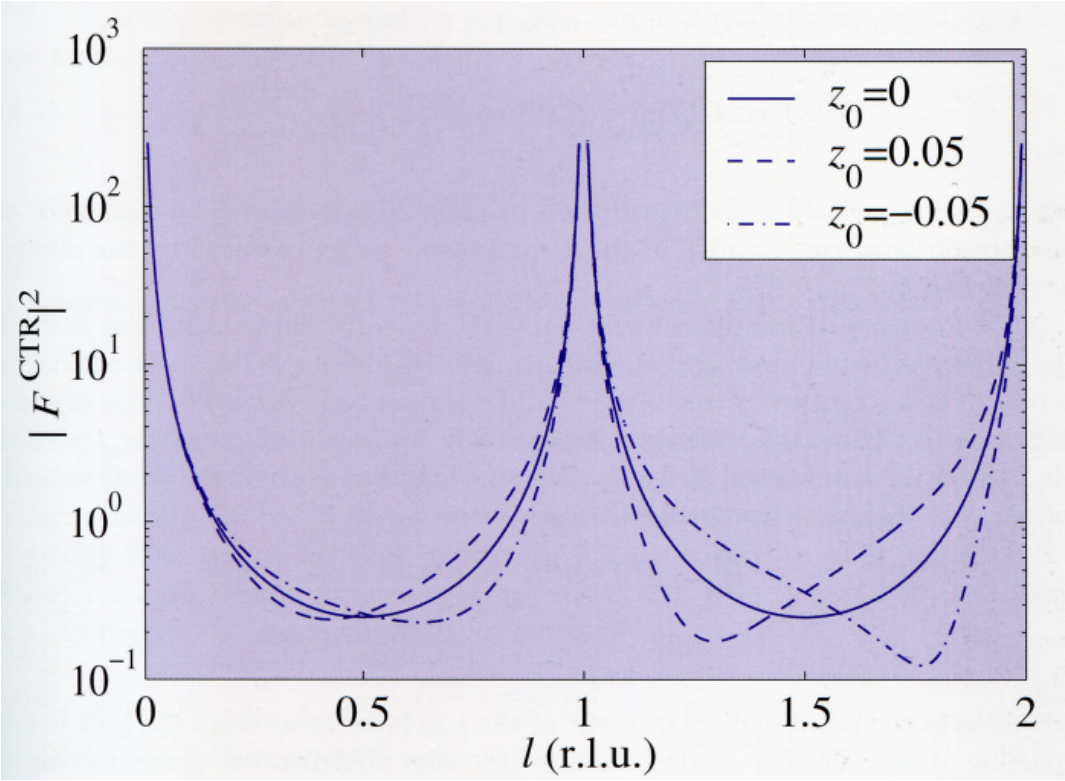
The CTR profile is sensitive to the termination of the surface. This makes it an ideal probe of electron density of adsorbed species or single atom overlayers.



Density Effect

The CTR profile is sensitive to the termination of the surface. This makes it an ideal probe of electron density of adsorbed species or single atom overlayers.

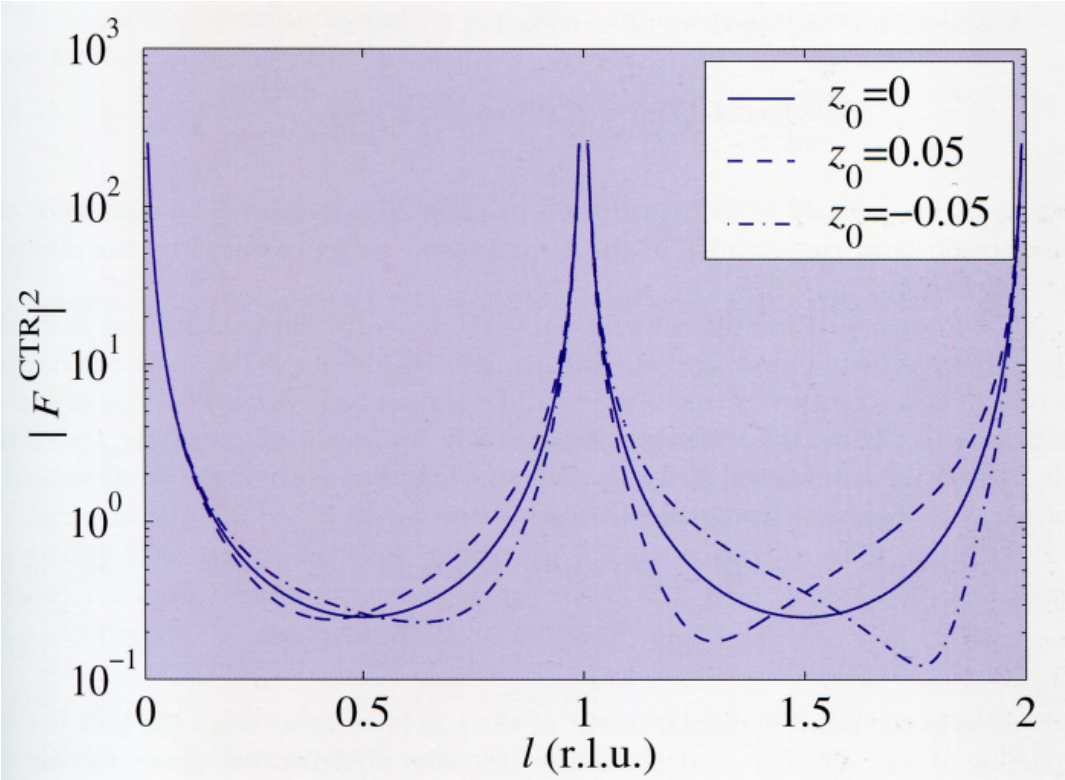
$$F^{total} = F^{CTR} + F^{top\ layer}$$



Density Effect

The CTR profile is sensitive to the termination of the surface. This makes it an ideal probe of electron density of adsorbed species or single atom overlayers.

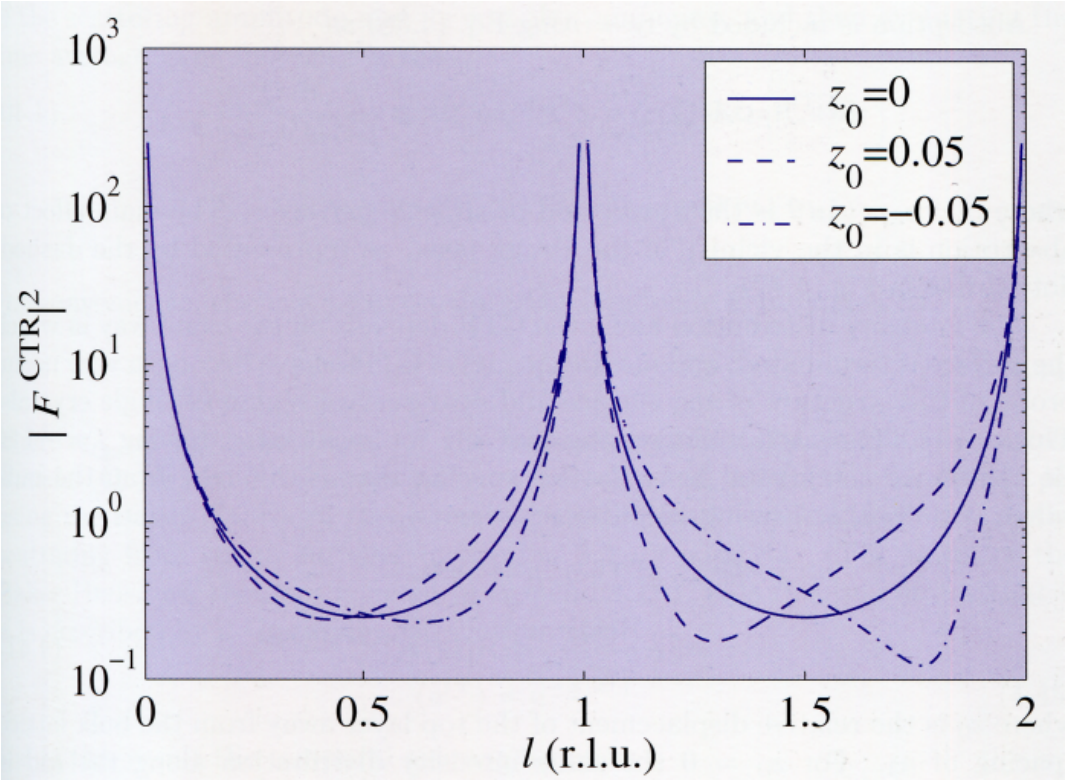
$$F^{total} = F^{CTR} + F^{top\ layer}$$
$$= \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$



Density Effect

The CTR profile is sensitive to the termination of the surface. This makes it an ideal probe of electron density of adsorbed species or single atom overlayers.

$$F^{total} = F^{CTR} + F^{top\ layer}$$
$$= \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$
$$+ A(\vec{Q})e^{-i2\pi(1+z_0)l}$$

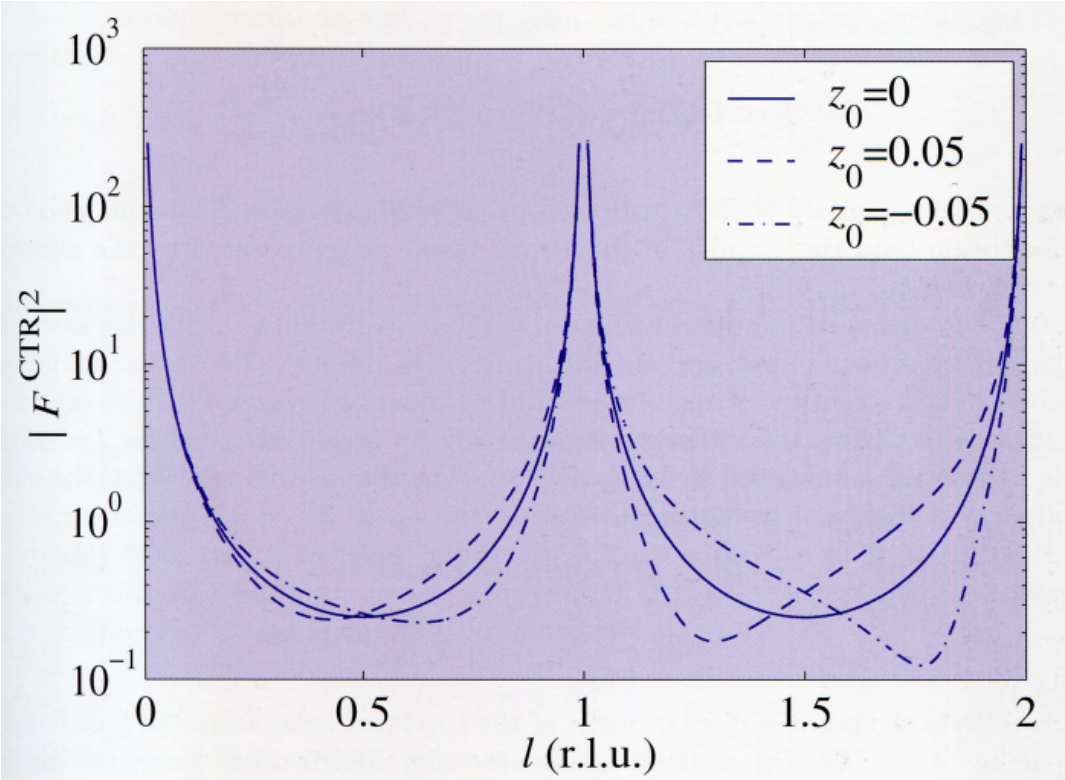


Density Effect

The CTR profile is sensitive to the termination of the surface. This makes it an ideal probe of electron density of adsorbed species or single atom overlayers.

$$F^{total} = F^{CTR} + F^{top\ layer}$$
$$= \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$
$$+ A(\vec{Q})e^{-i2\pi(1+z_0)l}$$

where z_0 is the relative displacement of the top layer from the bulk lattice spacing a_3



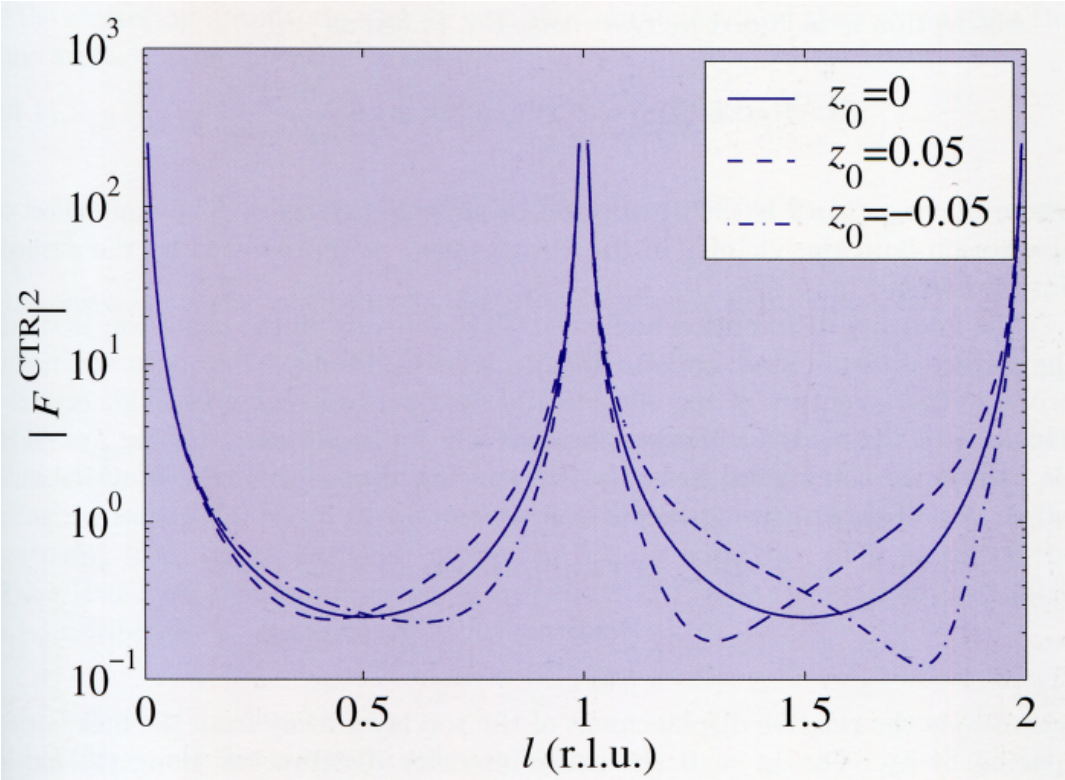
Density Effect

The CTR profile is sensitive to the termination of the surface. This makes it an ideal probe of electron density of adsorbed species or single atom overlayers.

$$F^{total} = F^{CTR} + F^{top\ layer}$$
$$= \frac{A(\vec{Q})}{1 - e^{i2\pi l}}$$
$$+ A(\vec{Q})e^{-i2\pi(1+z_0)l}$$

where z_0 is the relative displacement of the top layer from the bulk lattice spacing a_3

This effect gets larger for larger momentum transfers



Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$.

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$. Computing the intensity:

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$. Computing the intensity:

$$I = \left\langle \sum_m f(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m+\vec{u}_m)} \sum_n f^*(\vec{Q}) e^{-i\vec{Q}\cdot(\vec{R}_n+\vec{u}_n)} \right\rangle$$

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$. Computing the intensity:

$$
\begin{aligned}
I &= \left\langle \sum_m f(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m+\vec{u}_m)} \sum_n f^*(\vec{Q}) e^{-i\vec{Q}\cdot(\vec{R}_n+\vec{u}_n)} \right\rangle \\
&= \sum_m \sum_n f(\vec{Q}) f^*(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m-\vec{R}_n)} \left\langle e^{i\vec{Q}\cdot(\vec{u}_m-\vec{u}_n)} \right\rangle
\end{aligned}
$$

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$. Computing the intensity:

$$
\begin{aligned}
I &= \left\langle \sum_m f(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m+\vec{u}_m)} \sum_n f^*(\vec{Q}) e^{-i\vec{Q}\cdot(\vec{R}_n+\vec{u}_n)} \right\rangle \\
&= \sum_m \sum_n f(\vec{Q}) f^*(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m-\vec{R}_n)} \left\langle e^{i\vec{Q}\cdot(\vec{u}_m-\vec{u}_n)} \right\rangle
\end{aligned}
$$

The last term is a time average which can be simplified using the Baker-Hausdorff theorem, $\left\langle e^{ix} \right\rangle = e^{-\langle x^2 \rangle/2}$

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$. Computing the intensity:

$$\begin{aligned} I &= \left\langle \sum_m f(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m+\vec{u}_m)} \sum_n f^*(\vec{Q}) e^{-i\vec{Q}\cdot(\vec{R}_n+\vec{u}_n)} \right\rangle \\ &= \sum_m \sum_n f(\vec{Q}) f^*(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m-\vec{R}_n)} \left\langle e^{i\vec{Q}\cdot(\vec{u}_m-\vec{u}_n)} \right\rangle \end{aligned}$$

The last term is a time average which can be simplified using the Baker-Hausdorff theorem, $\left\langle e^{ix} \right\rangle = e^{-\langle x^2 \rangle/2}$

$$\left\langle e^{i\vec{Q}\cdot(\vec{u}_m-\vec{u}_n)} \right\rangle = \left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle$$

Lattice Vibrations

Atoms on a lattice are not rigid but vibrate. There is zero-point motion as well as thermal motion. These vibrations influence the x-ray scattering.

For a 1D lattice, we replace the position of the atom with its *instantaneous* position, $\vec{R}_n + \vec{u}_n$ where $\vec{u}_n$ is the displacement from the equilibrium position, $\vec{R}_n$. Computing the intensity:

$$\begin{aligned} I &= \left\langle \sum_m f(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m+\vec{u}_m)} \sum_n f^*(\vec{Q}) e^{-i\vec{Q}\cdot(\vec{R}_n+\vec{u}_n)} \right\rangle \\ &= \sum_m \sum_n f(\vec{Q}) f^*(\vec{Q}) e^{i\vec{Q}\cdot(\vec{R}_m-\vec{R}_n)} \left\langle e^{i\vec{Q}\cdot(\vec{u}_m-\vec{u}_n)} \right\rangle \end{aligned}$$

The last term is a time average which can be simplified using the Baker-Hausdorff theorem, $\left\langle e^{ix} \right\rangle = e^{-\langle x^2 \rangle/2}$

$$\left\langle e^{i\vec{Q}\cdot(\vec{u}_m-\vec{u}_n)} \right\rangle = \left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-\langle Q^2(u_{Qm}-u_{Qn})^2 \rangle/2}$$

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle} = e^{-M} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle} = e^{-M} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

$$= e^{-M}\left[1 + e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle} = e^{-M} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$

$$= e^{-M}\left[1 + e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

Substituting into the expression for intensity

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$
$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle} = e^{-M} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$
$$= e^{-M}\left[1 + e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

Substituting into the expression for intensity

$$I = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n}$$
$$+ \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$
$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle} = e^{-M} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$
$$= e^{-M}\left[1 + e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

Substituting into the expression for intensity

$$I = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n}$$
$$+ \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

The first term is just the elastic scattering from the lattice with the addition of the term $e^{-M} = e^{-Q^2\langle u_Q^2\rangle/2}$, called the Debye-Waller factor.

Lattice Vibrations

$$\left\langle e^{iQ(u_{Qm}-u_{Qn})} \right\rangle = e^{-Q^2\langle u_{Qm}^2\rangle/2} e^{-Q^2\langle u_{Qn}^2\rangle/2} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$
$$= e^{-Q^2\langle u_Q^2\rangle} e^{Q^2\langle u_{Qm}u_{Qn}\rangle} = e^{-M} e^{Q^2\langle u_{Qm}u_{Qn}\rangle}$$
$$= e^{-M}\left[1 + e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

Substituting into the expression for intensity

$$I = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n}$$
$$+ \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2\langle u_{Qm}u_{Qn}\rangle} - 1\right]$$

The first term is just the elastic scattering from the lattice with the addition of the term $e^{-M} = e^{-Q^2\langle u_Q^2\rangle/2}$, called the Debye-Waller factor.

The second term is the Thermal Diffuse Scattering and actually increases with mean squared displacement.

Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

The TDS has a width determined by the correlated displacement of atoms which is much broader than a Bragg peak.

Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

The TDS has a width determined by the correlated displacement of atoms which is much broader than a Bragg peak.

These correlated motions are just phonons.

Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

The TDS has a width determined by the correlated displacement of atoms which is much broader than a Bragg peak.

These correlated motions are just phonons.

A 0.5mm Si wafer illuminated by 28keV x-rays from an APS undulator were used to measure the phonon dispersion curves of silicon

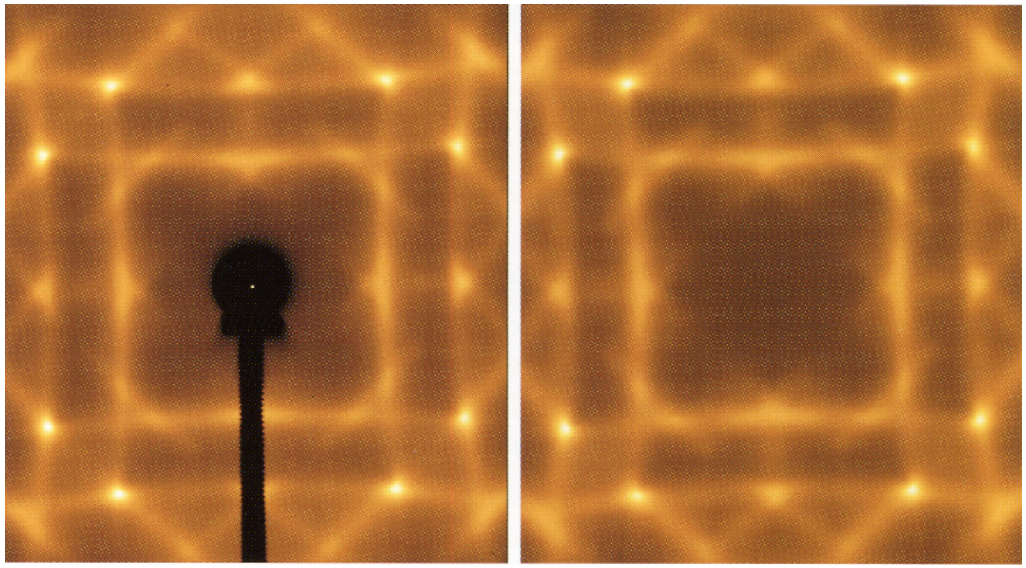
Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

The TDS has a width determined by the correlated displacement of atoms which is much broader than a Bragg peak.

These correlated motions are just phonons.

A 0.5mm Si wafer illuminated by 28keV x-rays from an APS undulator were used to measure the phonon dispersion curves of silicon



M. Holt, et al. *Phys. Rev. Lett.* **83**, 3317 (1999).

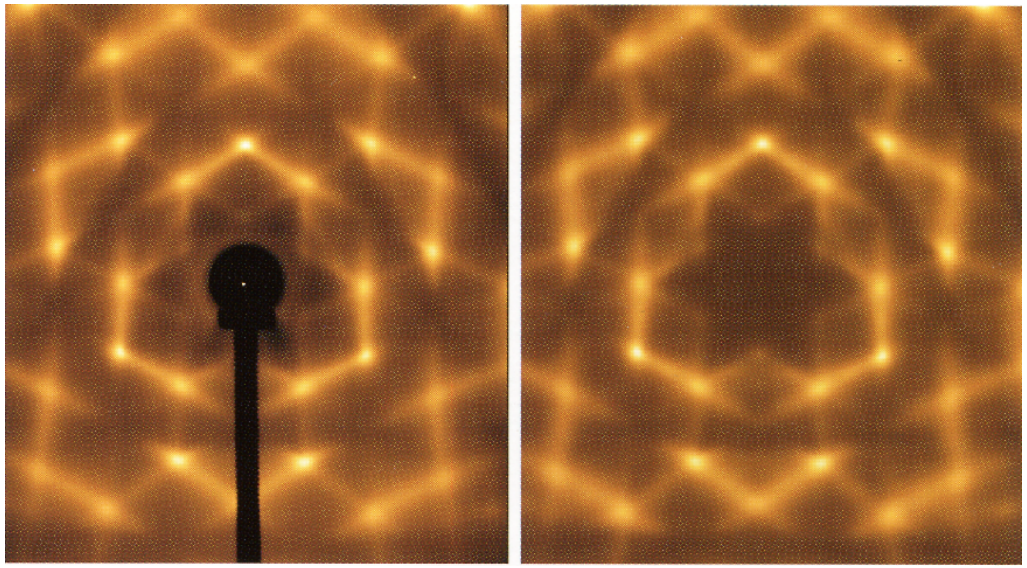
Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

The TDS has a width determined by the correlated displacement of atoms which is much broader than a Bragg peak.

These correlated motions are just phonons.

A 0.5mm Si wafer illuminated by 28keV x-rays from an APS undulator were used to measure the phonon dispersion curves of silicon



M. Holt, et al. *Phys. Rev. Lett.* **83**, 3317 (1999).

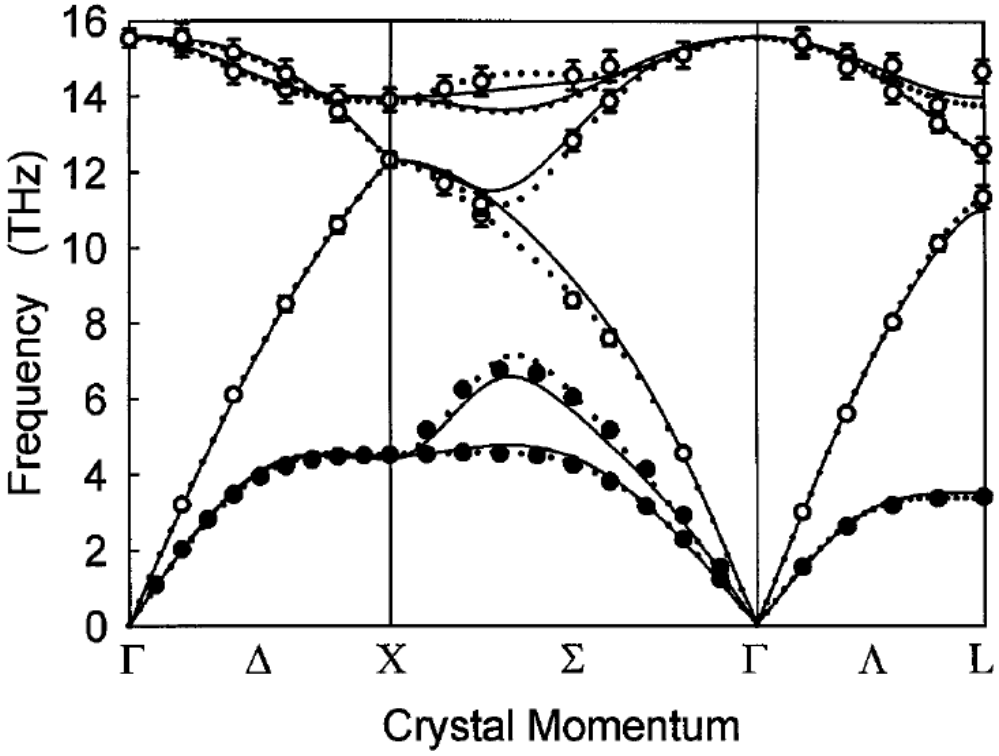
Thermal Diffuse Scattering

$$I^{TDS} = \sum_m \sum_n f(\vec{Q}) e^{-M} e^{i\vec{Q}\cdot\vec{R}_m} f^*(\vec{Q}) e^{-M} e^{-i\vec{Q}\cdot\vec{R}_n} \left[e^{Q^2 \langle u_{Qm} u_{Qn} \rangle} - 1 \right]$$

The TDS has a width determined by the correlated displacement of atoms which is much broader than a Bragg peak.

These correlated motions are just phonons.

A 0.5mm Si wafer illuminated by 28keV x-rays from an APS undulator were used to measure the phonon dispersion curves of silicon



M. Holt, et al. *Phys. Rev. Lett.* **83**, 3317 (1999).

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

$$M_j = \frac{1}{2} Q^2 \langle u_{Qj}^2 \rangle$$

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

$$M_j = \frac{1}{2} Q^2 \langle u_{Qj}^2 \rangle$$

$$= \frac{1}{2} \left(\frac{4\pi}{\lambda} \right)^2 \sin^2\theta \langle u_{Qj}^2 \rangle$$

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$B_T^j = 8\pi^2 \langle u_{Qj}^2 \rangle$$

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

$$M_j = \frac{1}{2} Q^2 \langle u_{Qj}^2 \rangle$$

$$= \frac{1}{2} \left(\frac{4\pi}{\lambda} \right)^2 \sin^2\theta \langle u_{Qj}^2 \rangle$$

$$M_j = B_T^j \left(\frac{\sin\theta}{\lambda} \right)^2$$

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$B_T^j = 8\pi^2 \langle u_{Qj}^2 \rangle$$

for isotropic atomic vibrations

$$\begin{aligned} \langle u^2 \rangle &= \langle u_x^2 + u_y^2 + u_z^2 \rangle \\ &= 3\langle u_x^2 \rangle = 3\langle u_Q^2 \rangle \end{aligned}$$

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

$$\begin{aligned} M_j &= \frac{1}{2} Q^2 \langle u_{Qj}^2 \rangle \\ &= \frac{1}{2} \left(\frac{4\pi}{\lambda} \right)^2 \sin^2\theta \langle u_{Qj}^2 \rangle \end{aligned}$$

$$M_j = B_T^j \left(\frac{\sin\theta}{\lambda} \right)^2$$

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$B_T^j = 8\pi^2 \langle u_{Qj}^2 \rangle$$

for isotropic atomic vibrations

$$\begin{aligned} \langle u^2 \rangle &= \langle u_x^2 + u_y^2 + u_z^2 \rangle \\ &= 3\langle u_x^2 \rangle = 3\langle u_Q^2 \rangle \end{aligned}$$

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

$$\begin{aligned} M_j &= \frac{1}{2} Q^2 \langle u_{Qj}^2 \rangle \\ &= \frac{1}{2} \left(\frac{4\pi}{\lambda} \right)^2 \sin^2\theta \langle u_{Qj}^2 \rangle \end{aligned}$$

$$M_j = B_T^j \left(\frac{\sin\theta}{\lambda} \right)^2$$

$$B_T^{iso} = \frac{8\pi^2}{3} \langle u^2 \rangle$$

Properties of the Debye-Waller Factor

For crystals with several different types of atoms, we generalize the unit cell scattering factor.

$$B_T^j = 8\pi^2 \langle u_{Qj}^2 \rangle$$

for isotropic atomic vibrations

$$\langle u^2 \rangle = \langle u_x^2 + u_y^2 + u_z^2 \rangle$$
$$= 3\langle u_x^2 \rangle = 3\langle u_Q^2 \rangle$$

$$F^{u.c.} = \sum_j f_j(\vec{Q}) e^{-M_j} e^{i\vec{Q}\cdot\vec{r}_j}$$

$$M_j = \frac{1}{2} Q^2 \langle u_{Qj}^2 \rangle$$
$$= \frac{1}{2}\left(\frac{4\pi}{\lambda}\right)^2 \sin^2\theta \langle u_{Qj}^2 \rangle$$

$$M_j = B_T^j \left(\frac{\sin\theta}{\lambda}\right)^2$$

$$B_T^{iso} = \frac{8\pi^2}{3}\langle u^2 \rangle$$

In general, Debye-Waller factors can be anisotropic

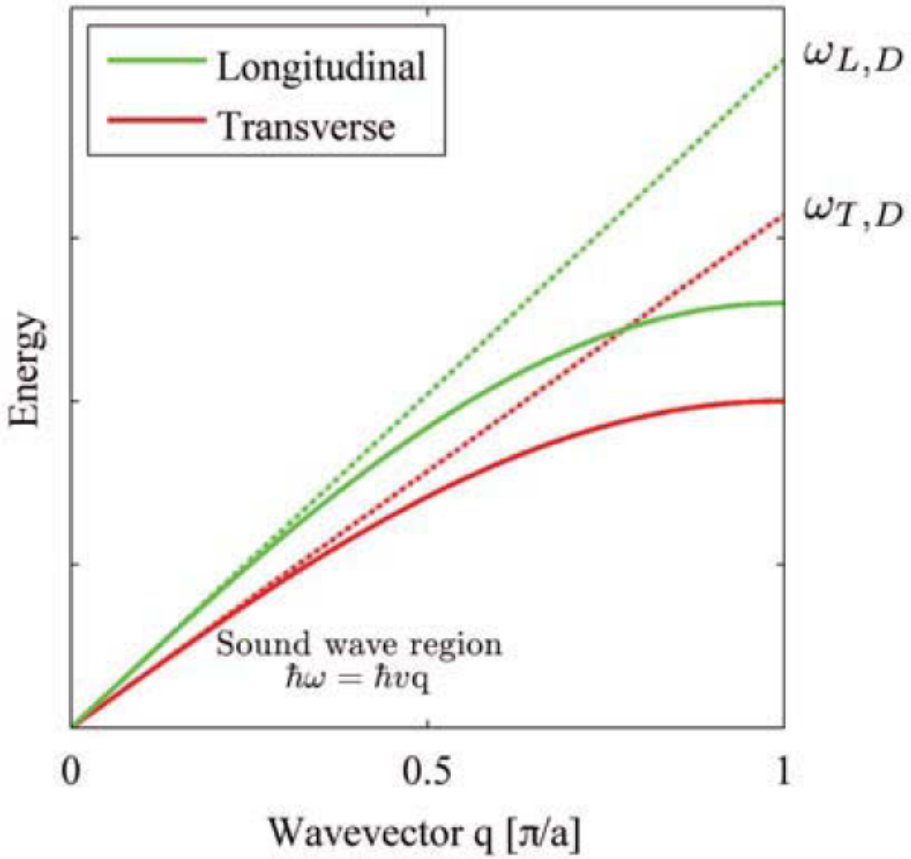
The Debye Model

The Debye model can be used to compute B_T by integrating a linear phonon dispersion relation up to a cutoff frequency, ω_D, called the Debye frequency.

The Debye Model

The Debye model can be used to compute B_T by integrating a linear phonon dispersion relation up to a cutoff frequency, ω_D, called the Debye frequency.

B_T is given as a function of the Debye temperature Θ.

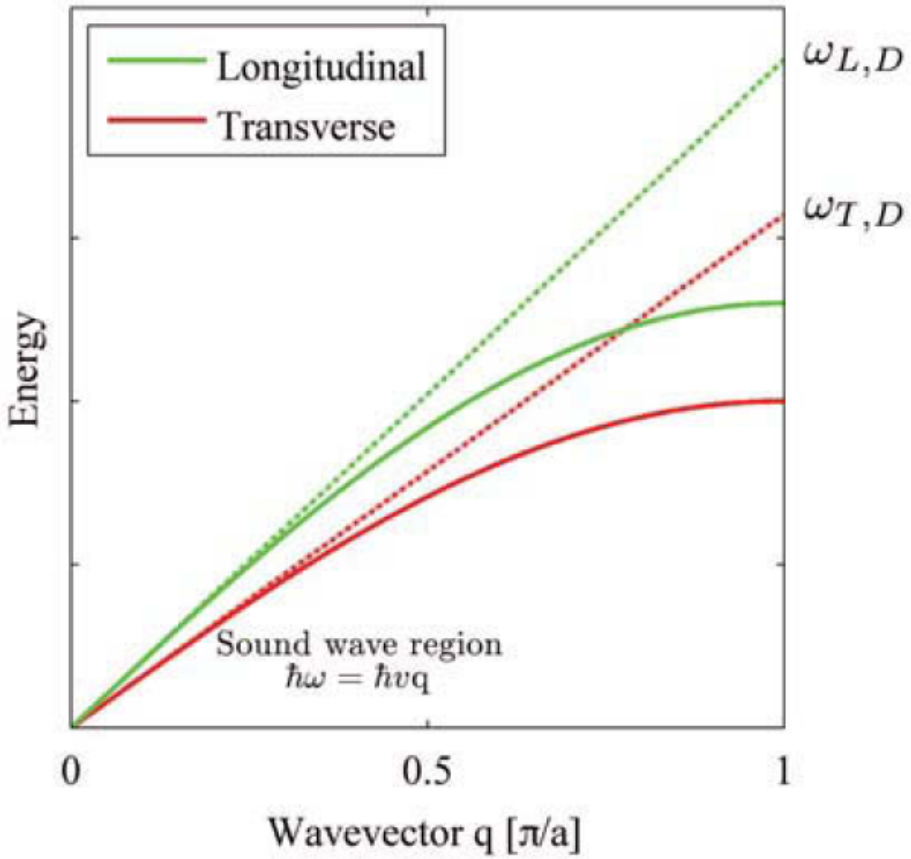


The Debye Model

The Debye model can be used to compute B_T by integrating a linear phonon dispersion relation up to a cutoff frequency, ω_D, called the Debye frequency.

B_T is given as a function of the Debye temperature Θ.

$$B_T = \frac{6h^2}{m_A k_B \Theta}\left[\frac{\phi(\Theta/T)}{\Theta/T} + \frac{1}{4}\right]$$



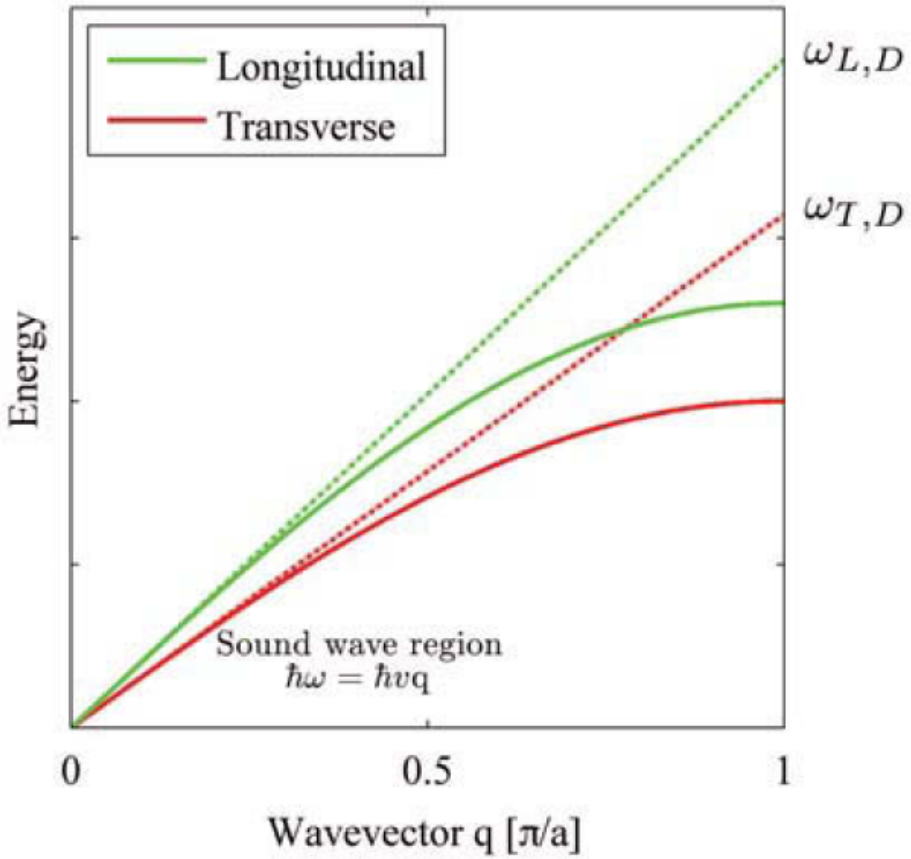
The Debye Model

The Debye model can be used to compute B_T by integrating a linear phonon dispersion relation up to a cutoff frequency, ω_D, called the Debye frequency.

B_T is given as a function of the Debye temperature Θ.

$$B_T = \frac{6h^2}{m_A k_B \Theta}\left[\frac{\phi(\Theta/T)}{\Theta/T} + \frac{1}{4}\right]$$

$$\phi(x) = \frac{1}{x}\int_0^{\Theta/T} \frac{\xi}{e^{\xi}-1} d\xi$$



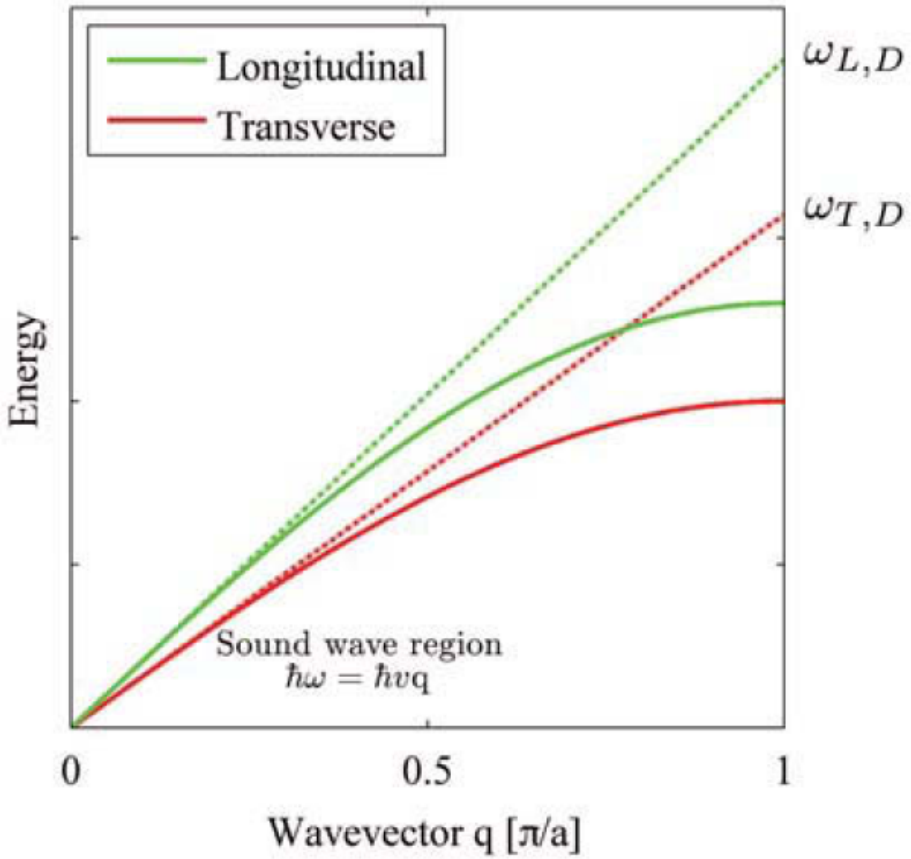
The Debye Model

The Debye model can be used to compute B_T by integrating a linear phonon dispersion relation up to a cutoff frequency, ω_D, called the Debye frequency.

B_T is given as a function of the Debye temperature Θ.

$$B_T = \frac{6h^2}{m_A k_B \Theta}\left[\frac{\phi(\Theta/T)}{\Theta/T} + \frac{1}{4}\right]$$

$$\phi(x) = \frac{1}{x}\int_0^{\Theta/T} \frac{\xi}{e^{\xi}-1} d\xi$$



$$B_T[\text{Å}^2] = \frac{11492\text{T}[\text{K}]}{\text{A}\Theta^2[\text{K}^2]}\phi(\Theta/\text{T}) + \frac{2873}{\text{A}\Theta[\text{K}]}$$

Debye Temperatures

$$B_T = \frac{11492\,T}{A\Theta^2}\phi(\Theta/T) + \frac{2873}{A\Theta}$$

	A	Θ (K)	$B_{4.2}$	B_{77} (Å^2)	B_{293}
C*	12	2230	0.11	0.11	0.12
Al	27	428	0.25	0.30	0.72
Cu	63.5	343	0.13	0.17	0.47

*diamond

Debye Temperatures

$$B_T = \frac{11492\,T}{A\Theta^2}\phi(\Theta/T) + \frac{2873}{A\Theta}$$

diamond is very stiff and Θ does not vary much with temperature

	A	Θ (K)	$B_{4.2}$	B_{77} (Å^2)	B_{293}
C*	12	2230	0.11	0.11	0.12
Al	27	428	0.25	0.30	0.72
Cu	63.5	343	0.13	0.17	0.47

*diamond

Debye Temperatures

$$B_T = \frac{11492\,T}{A\Theta^2}\phi(\Theta/T) + \frac{2873}{A\Theta}$$

	A	Θ (K)	$B_{4.2}$	B_{77} (Å^2)	B_{293}
C*	12	2230	0.11	0.11	0.12
Al	27	428	0.25	0.30	0.72
Cu	63.5	343	0.13	0.17	0.47

*diamond

diamond is very stiff and Θ does not vary much with temperature

copper has a much lower Debye temperature and a wider variation of thermal factor with temperature

Debye Temperatures

$$B_T = \frac{11492T}{A\Theta^2}\phi(\Theta/T) + \frac{2873}{A\Theta}$$

	A	Θ (K)	$B_{4.2}$	B_{77} (Å^2)	B_{293}
C*	12	2230	0.11	0.11	0.12
Al	27	428	0.25	0.30	0.72
Cu	63.5	343	0.13	0.17	0.47

*diamond

diamond is very stiff and Θ does not vary much with temperature

copper has a much lower Debye temperature and a wider variation of thermal factor with temperature