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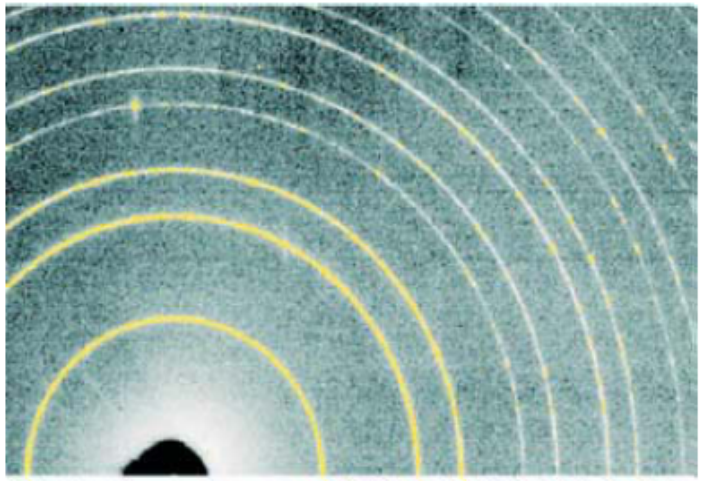
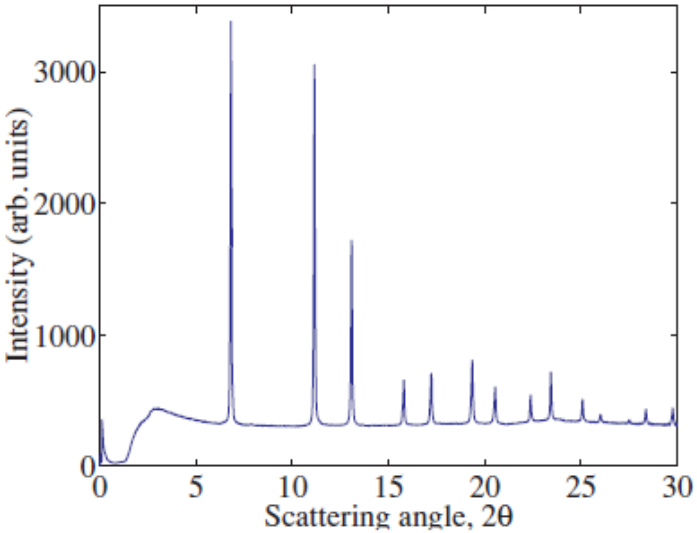
Homework Assignment #05:
Chapter 5: 1, 3, 7, 9, 10
due Thursday, April 02, 2015

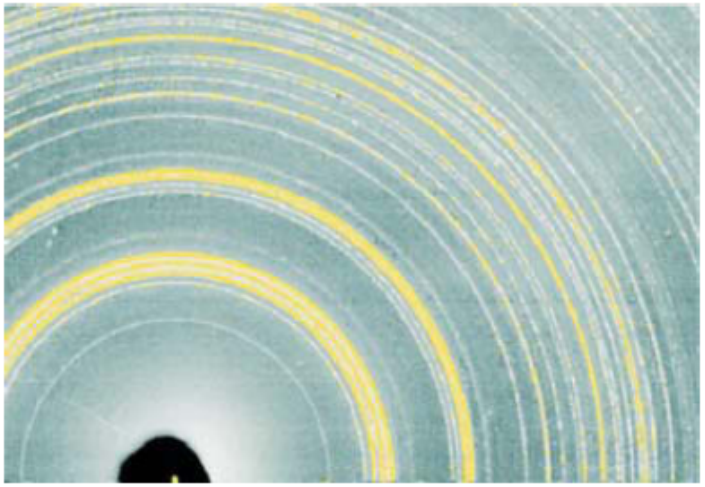
Powder diffraction

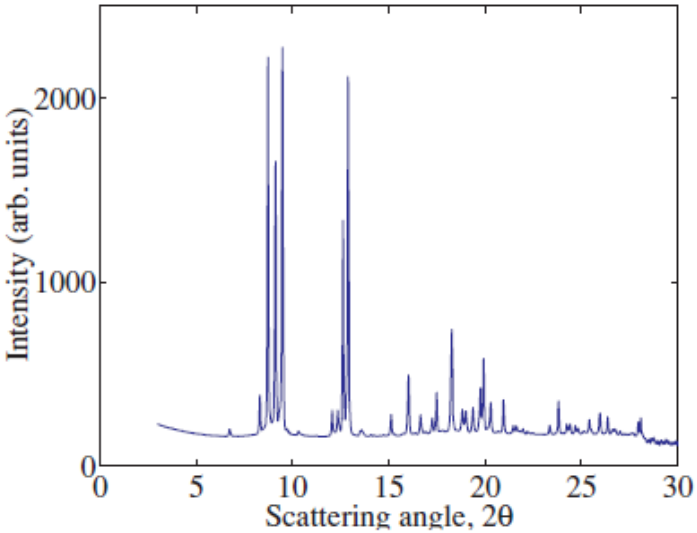
(a) Ambient pressure





(b) 4.9 GPa (49 kbar)





CaO-CaO_2 reaction kinetics

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A. Biasin, C.U. Segre, G. Salviulo, F. Zorzi, and M. Strumendo, *Chemical Eng. Sci.* **127**, 13-24 (2015)

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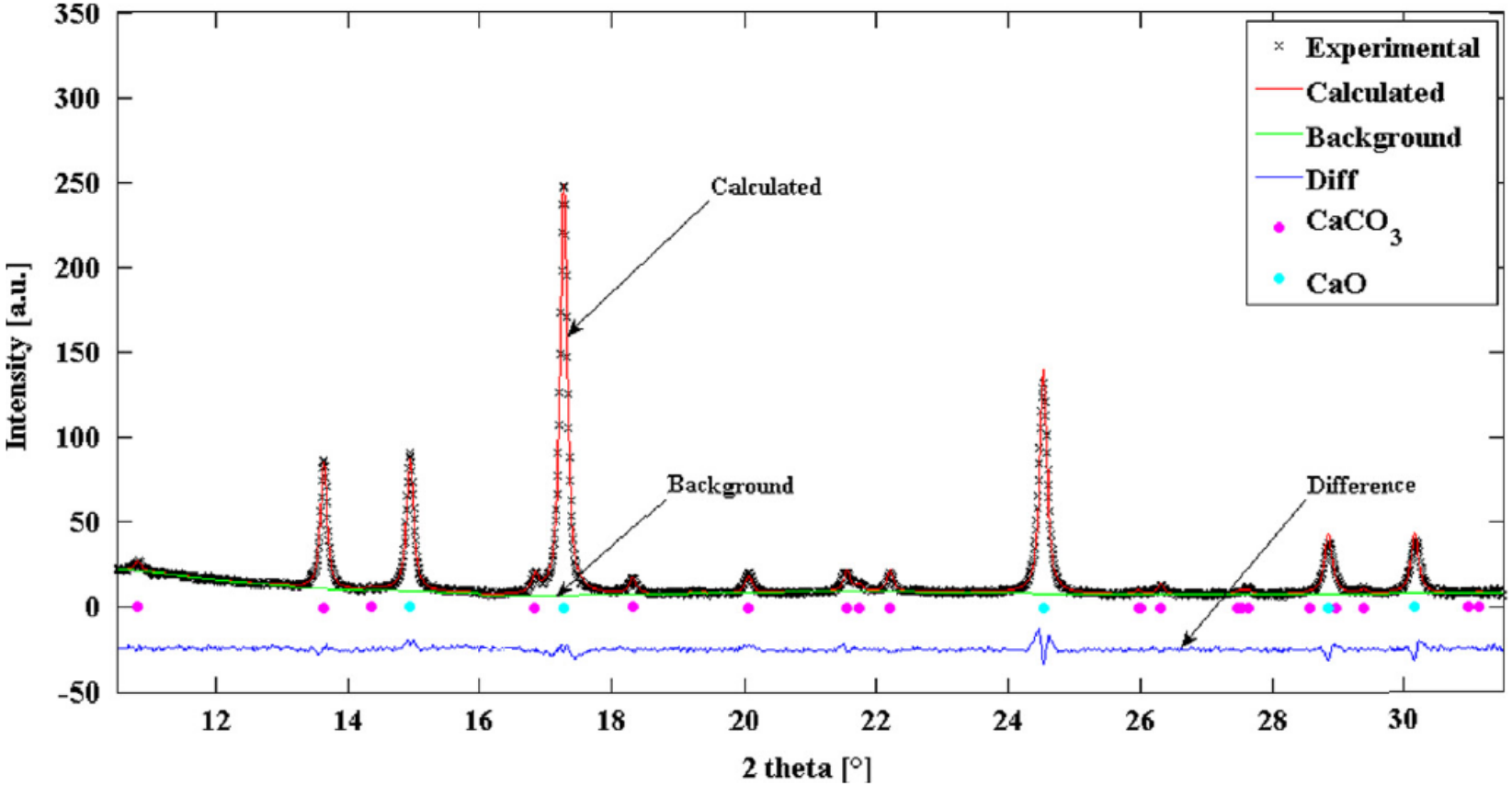

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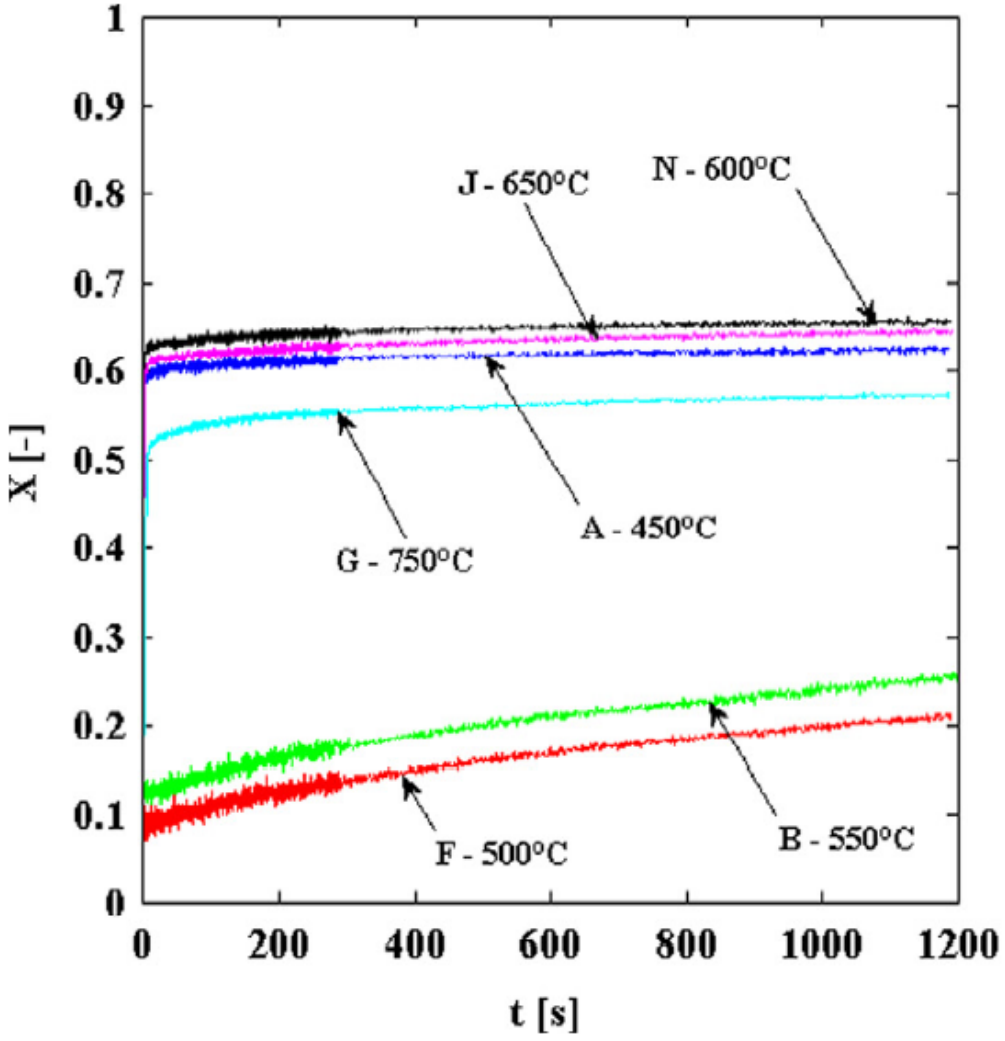
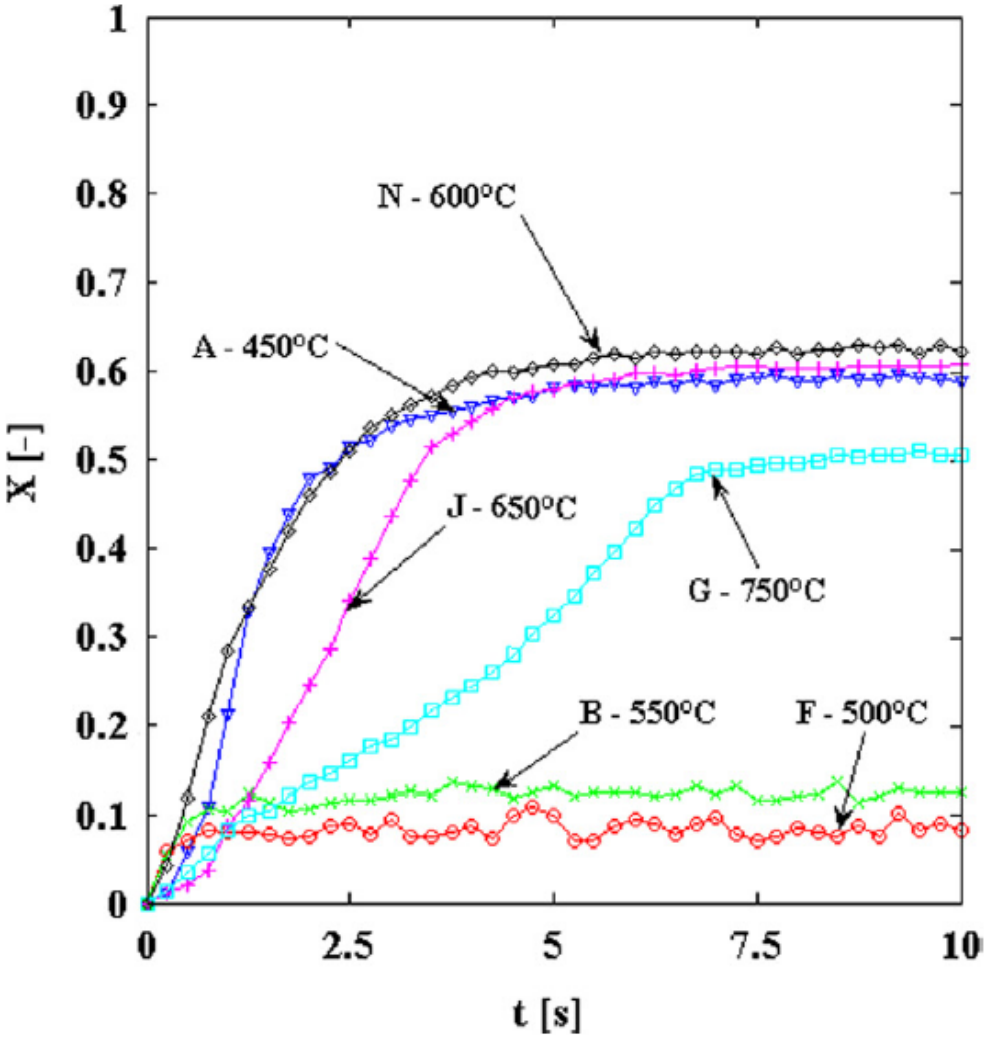


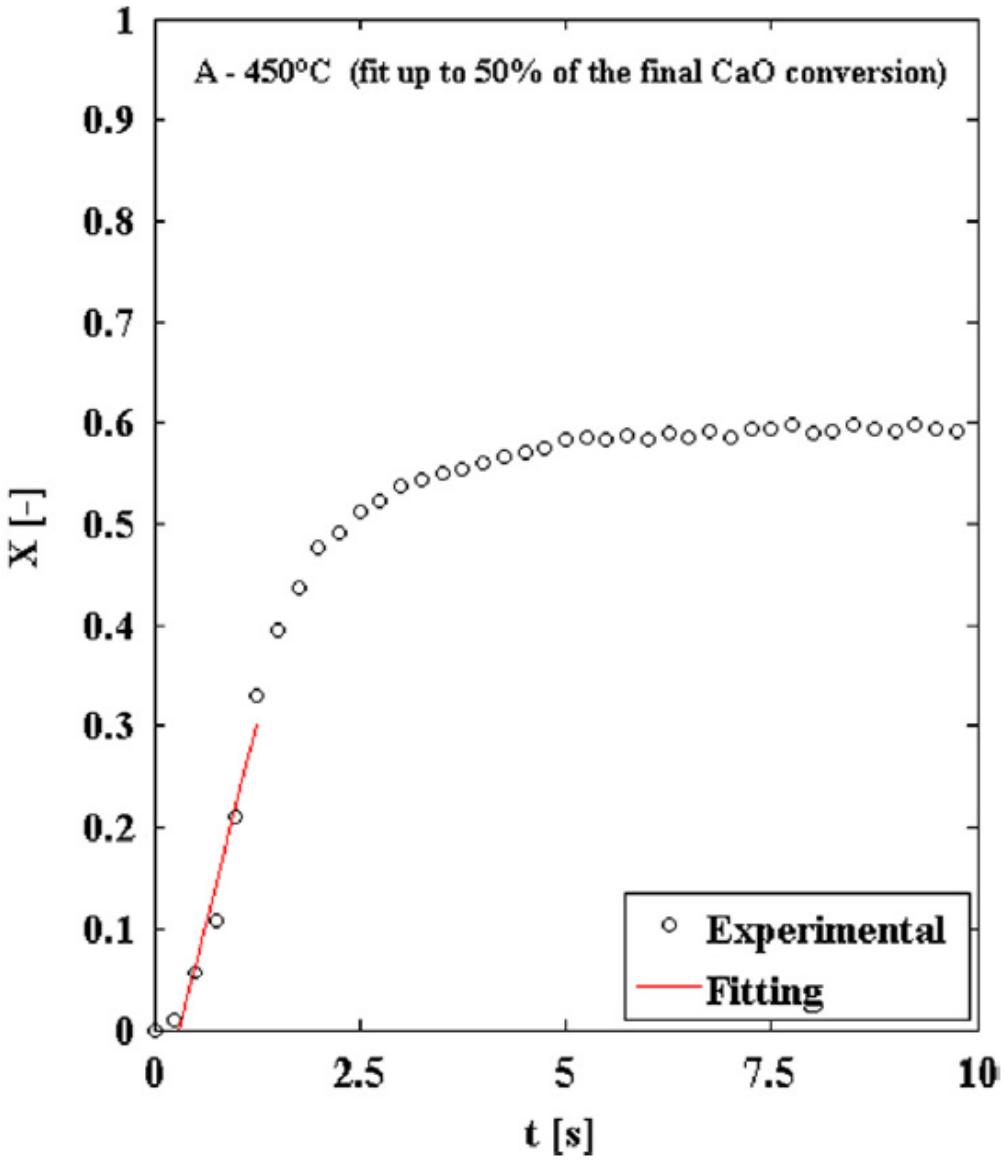
Final conversion fraction depends on temperature but also some other parameter (what?)

CaO-CaO_2 reaction kinetics



Reaction kinetics much faster than previously observed (0.28/s)

CaO-CaO_2 reaction kinetics



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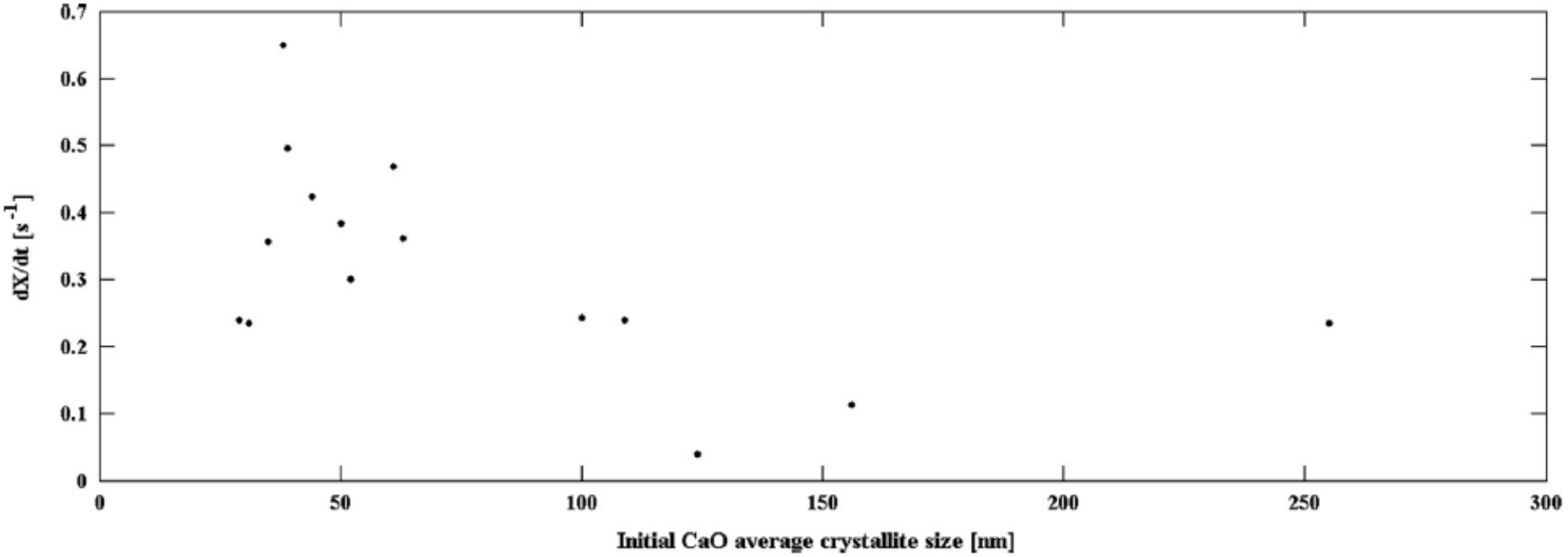
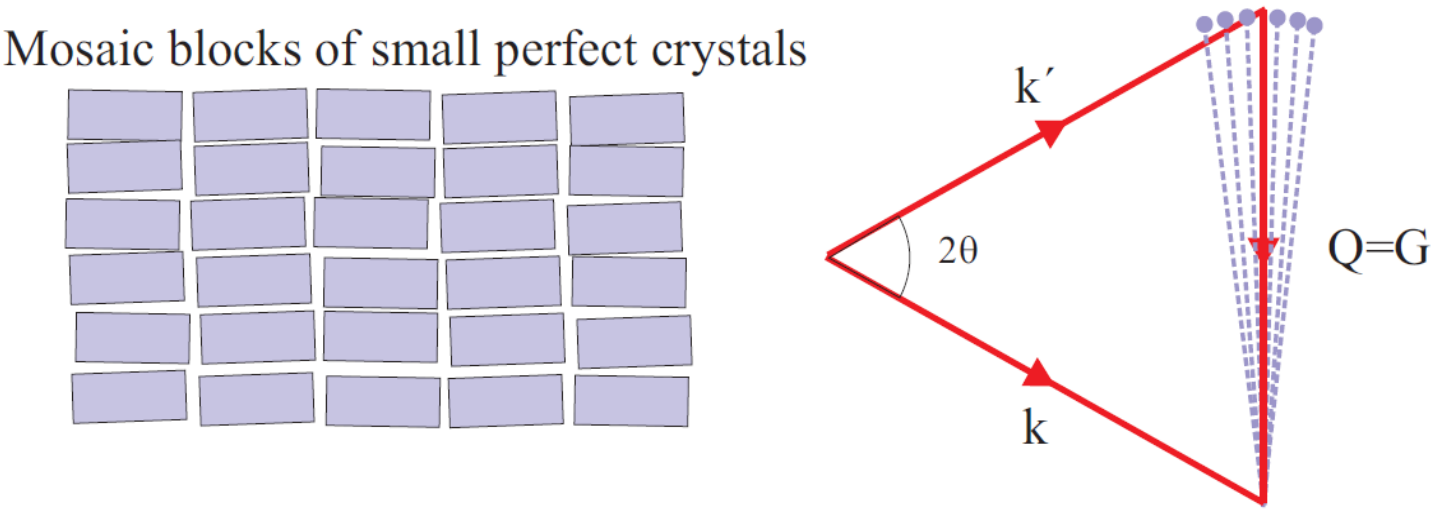


Initial crystallite size is one of the determining factors in inital rate of conversion and fraction converted.

CaO crystallite size can be related to porosity which is key to the conversion process.

Mosaic crystals



The kinematic approximation we have discussed so far applies to mosaic crystals. The size of the crystal is small enough that the wave field of the x-rays does not vary appreciably over the crystal.

For a perfect crystal, things are very different and we have to treat them specially using dynamical diffraction theory.

Bragg & Laue Geometries

Bragg

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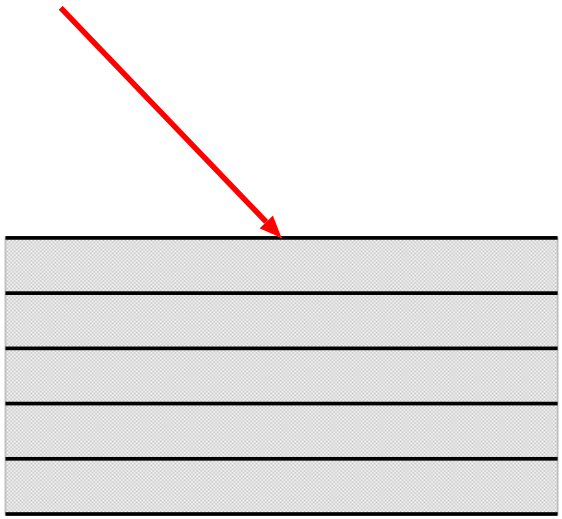

symmetric

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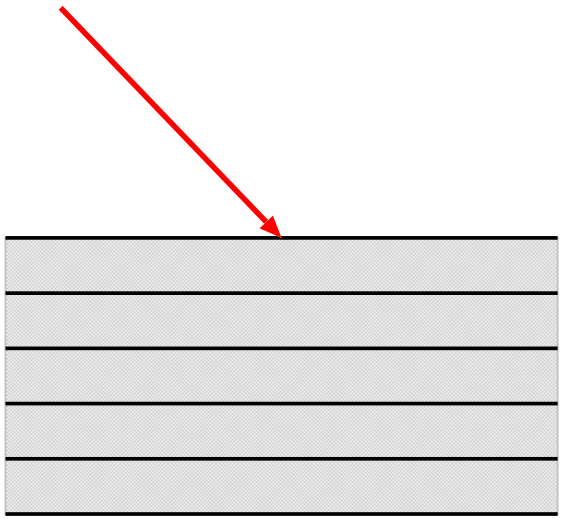

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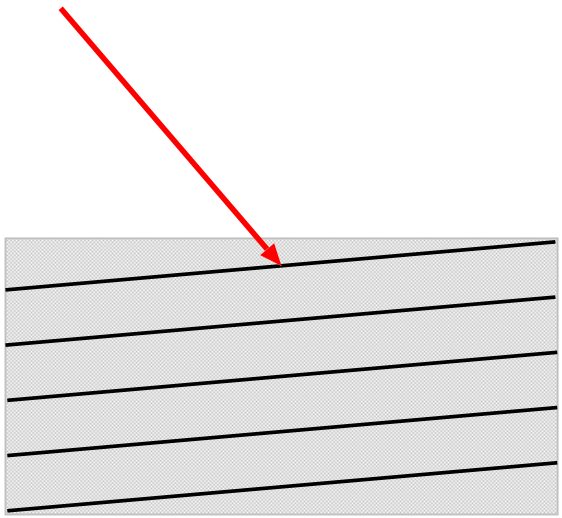

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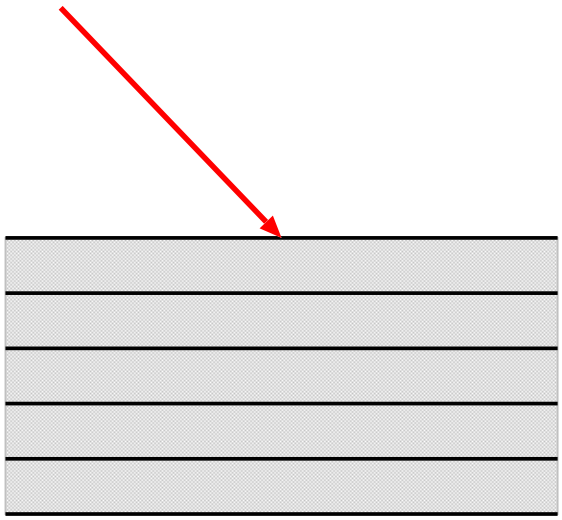

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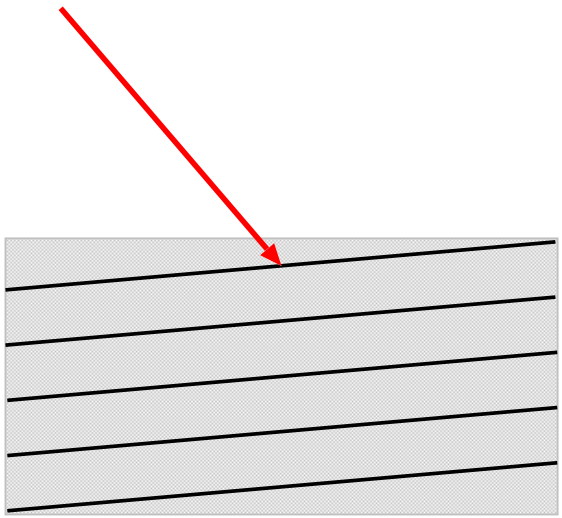

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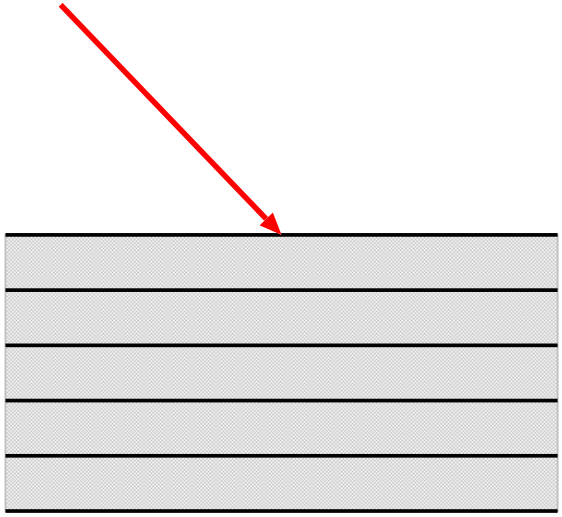

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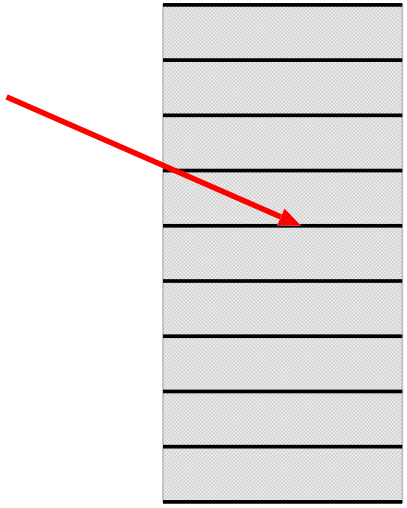

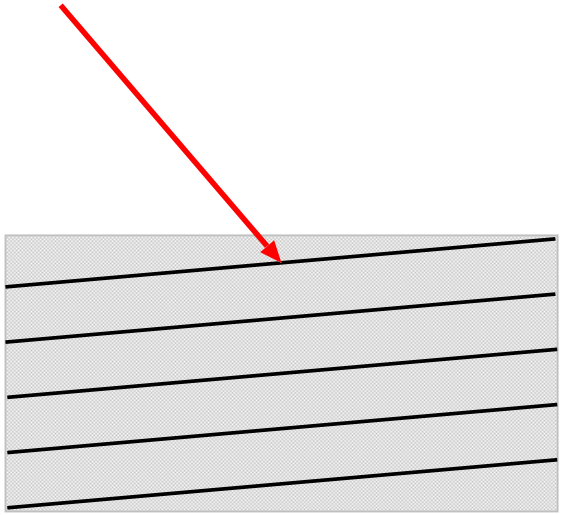

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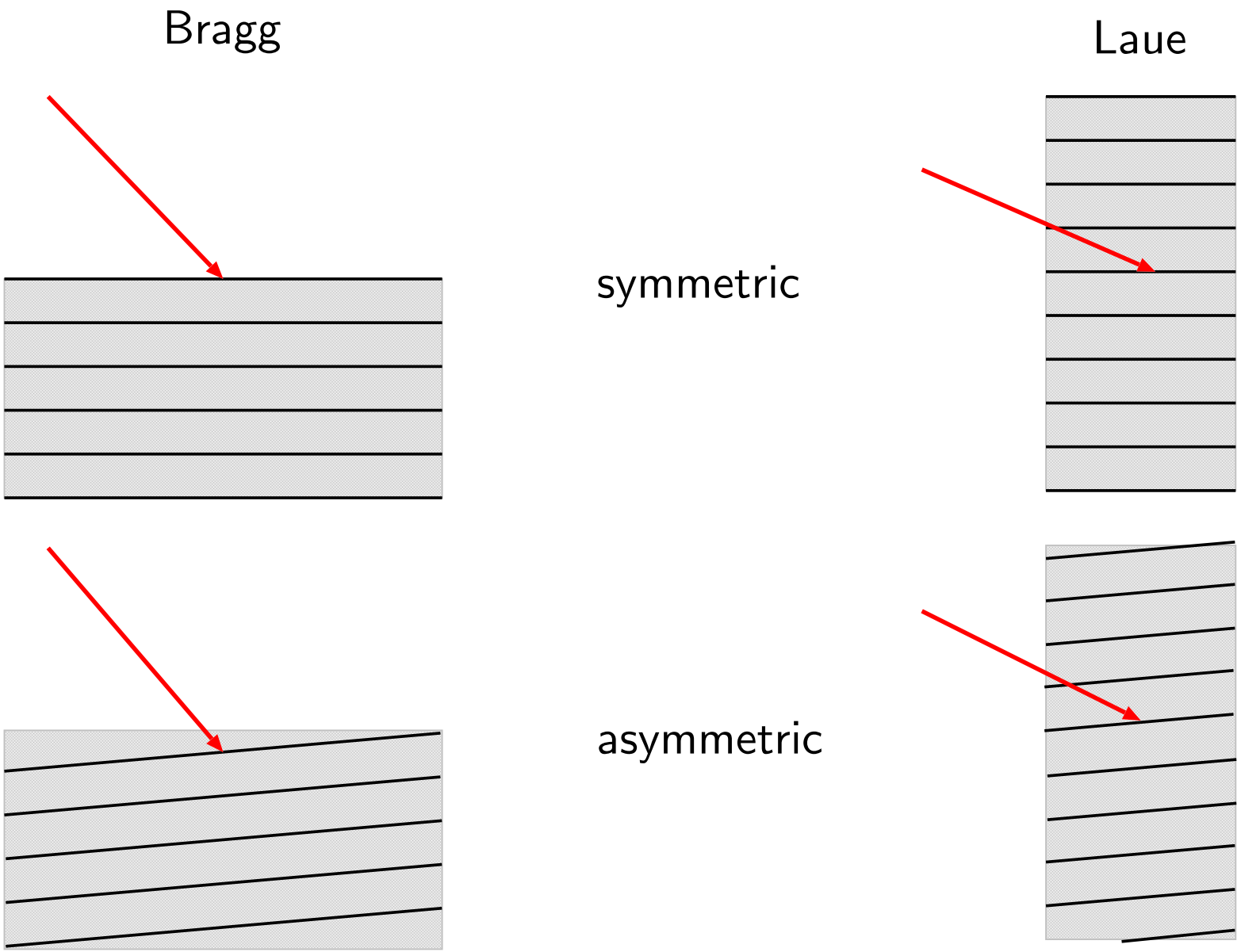

Scattering Geometry

Consider symmetric Bragg geometry

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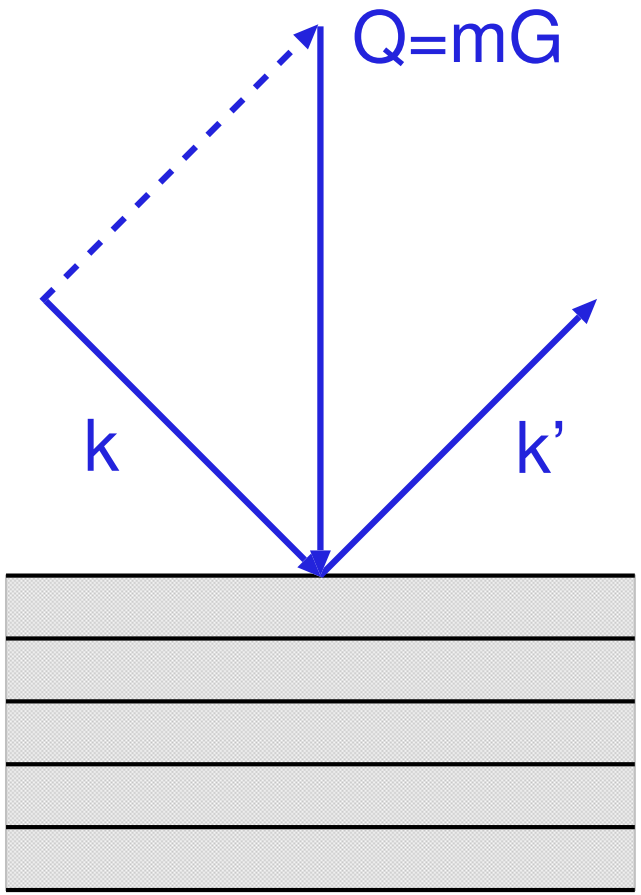

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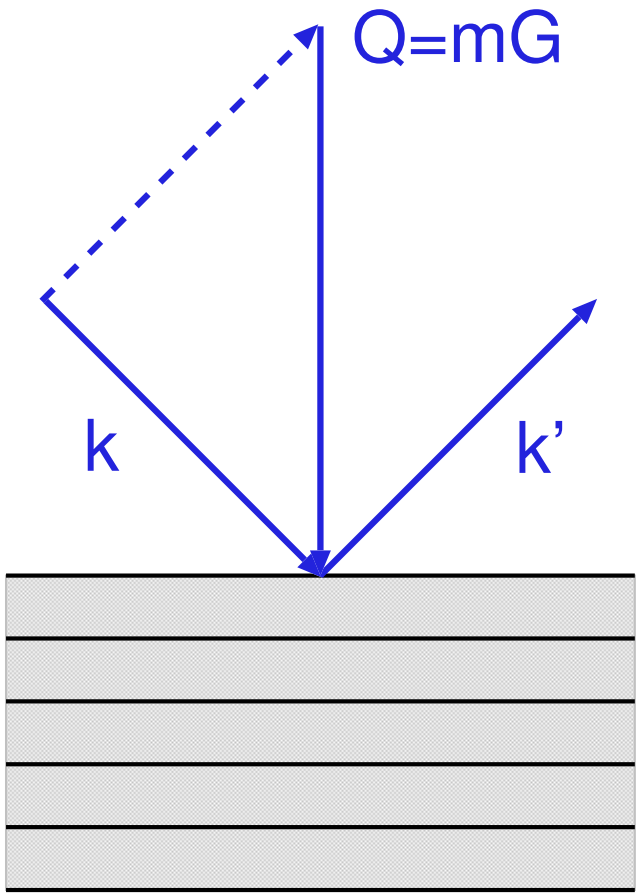

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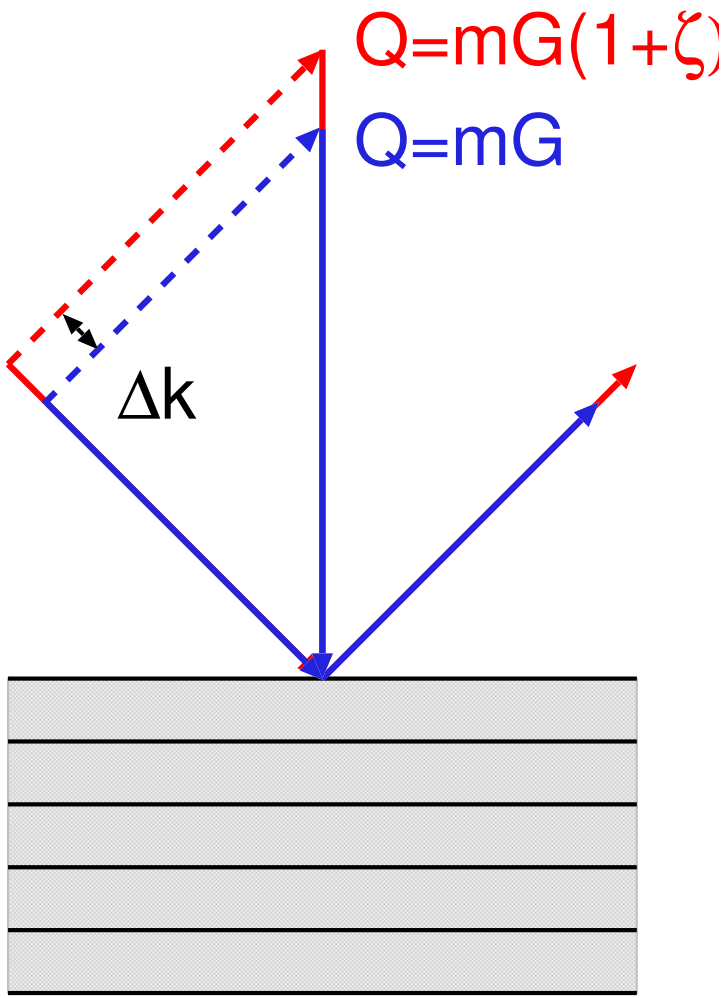
This defines a spread of scattering vectors such that

$$\zeta = \frac{\Delta Q}{Q} = \frac{\Delta k}{k}$$

called the relative energy or wavelength bandwidth



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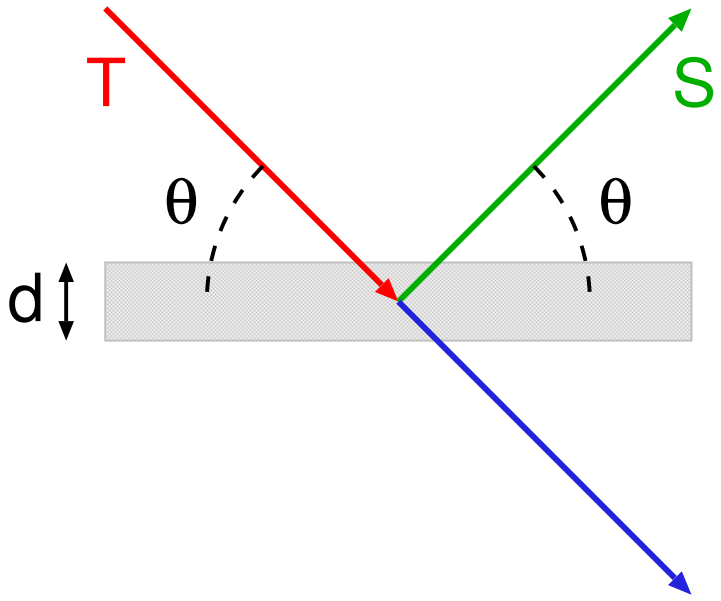

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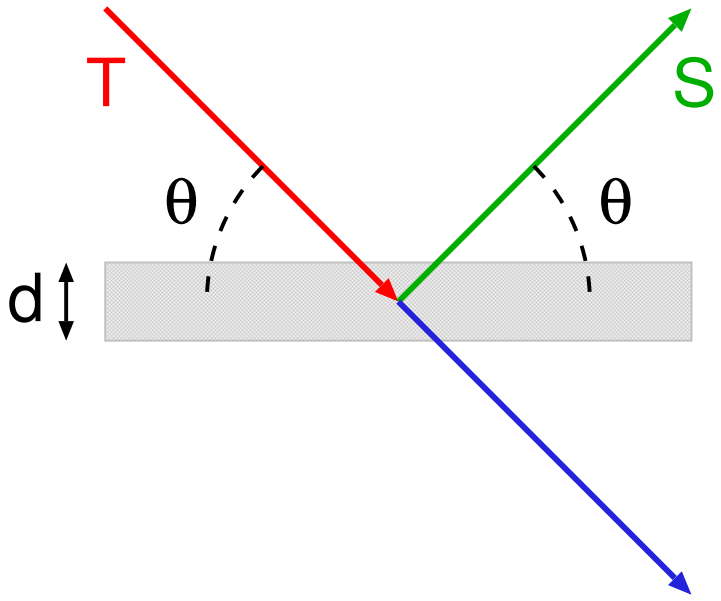

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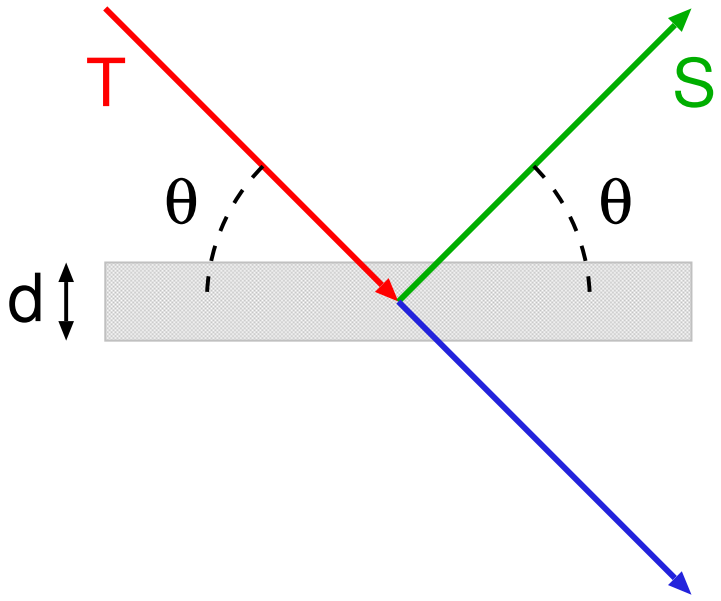

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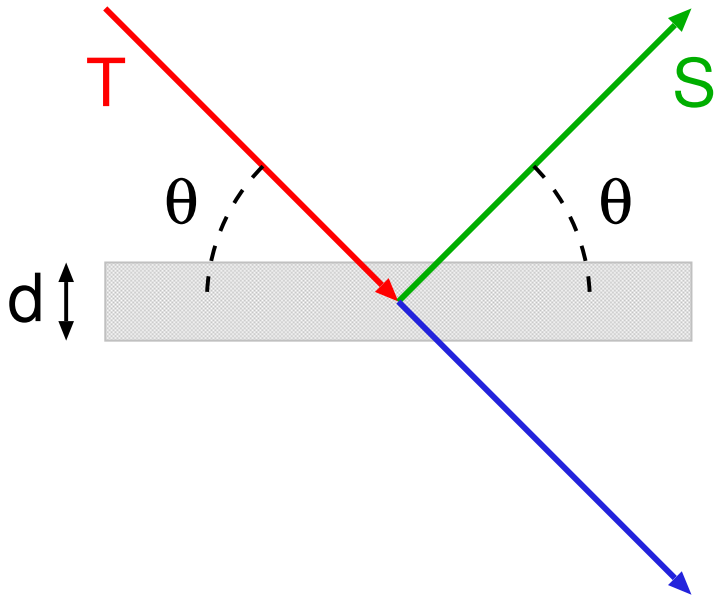

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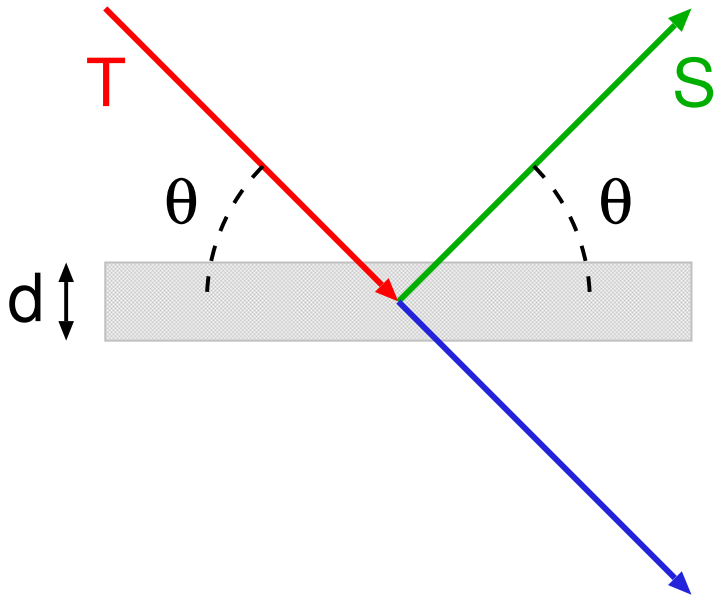

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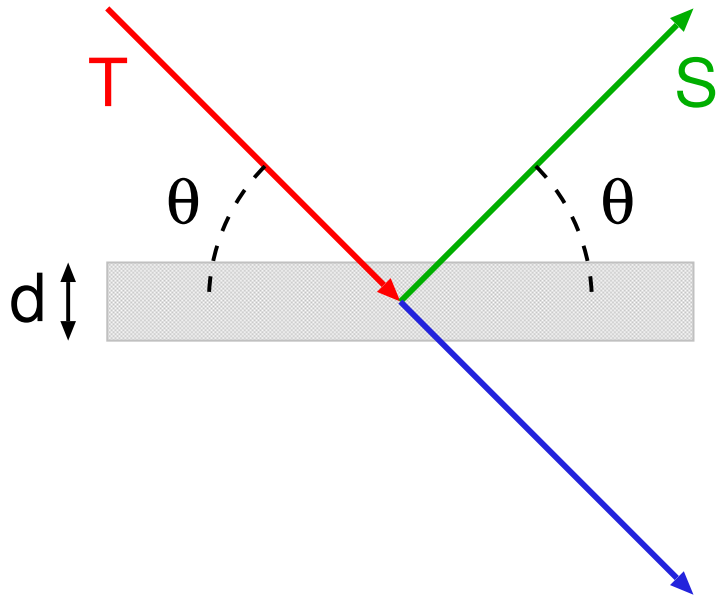

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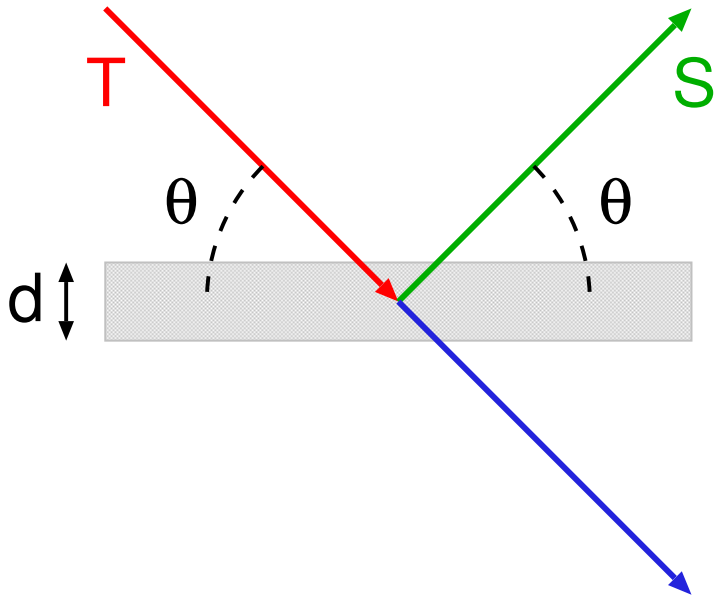

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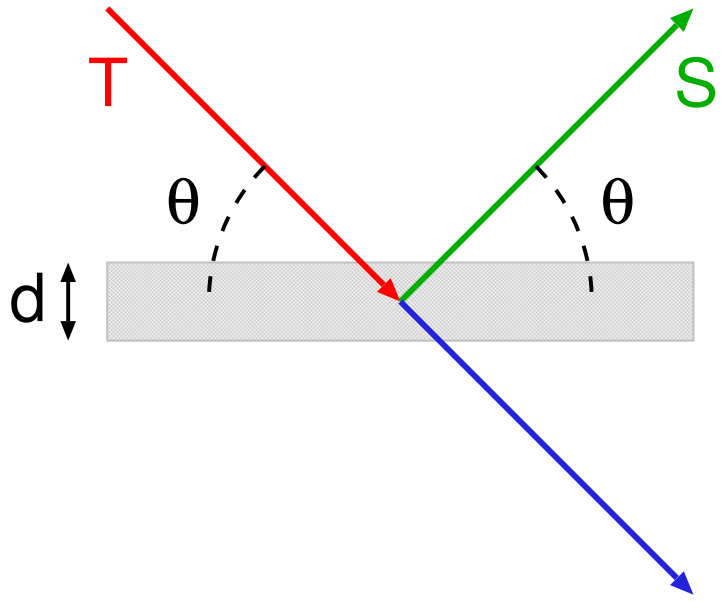

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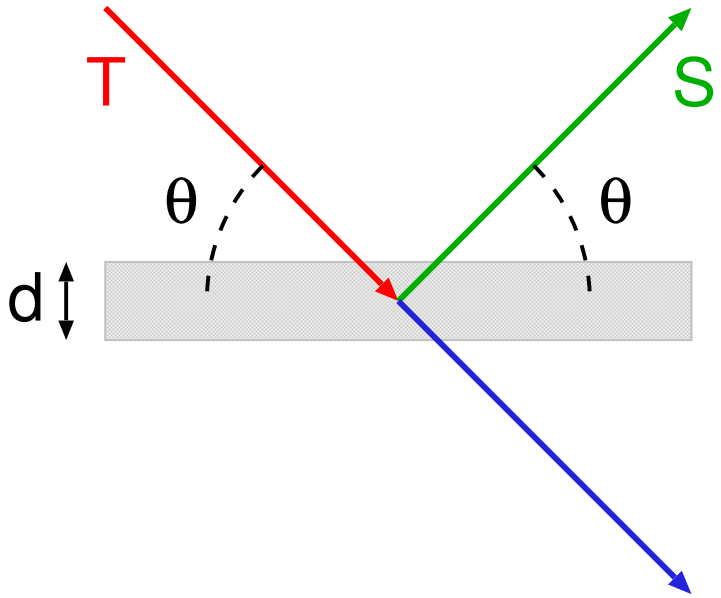

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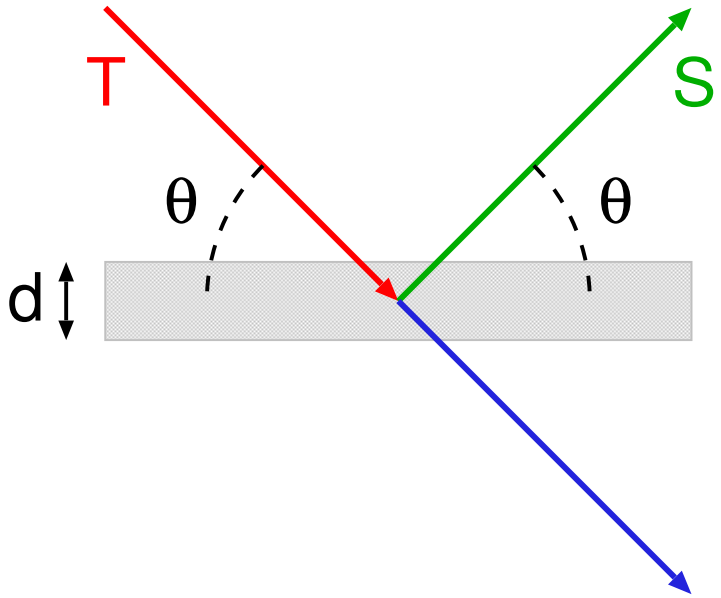

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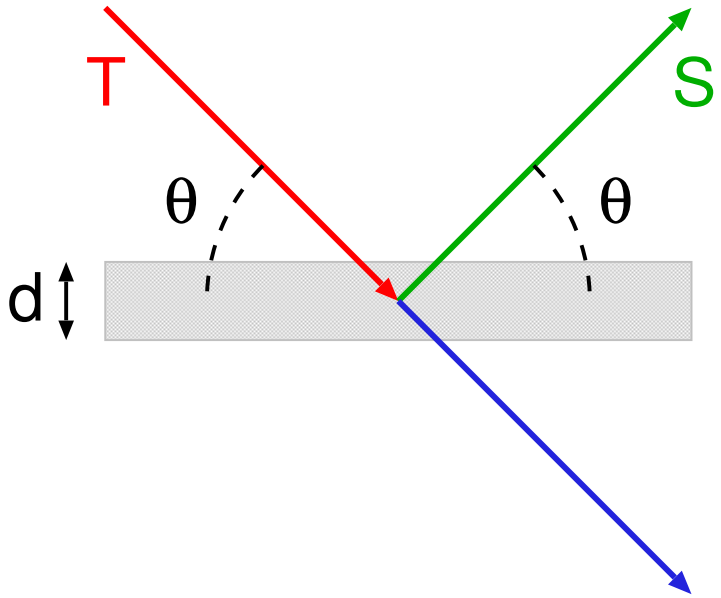

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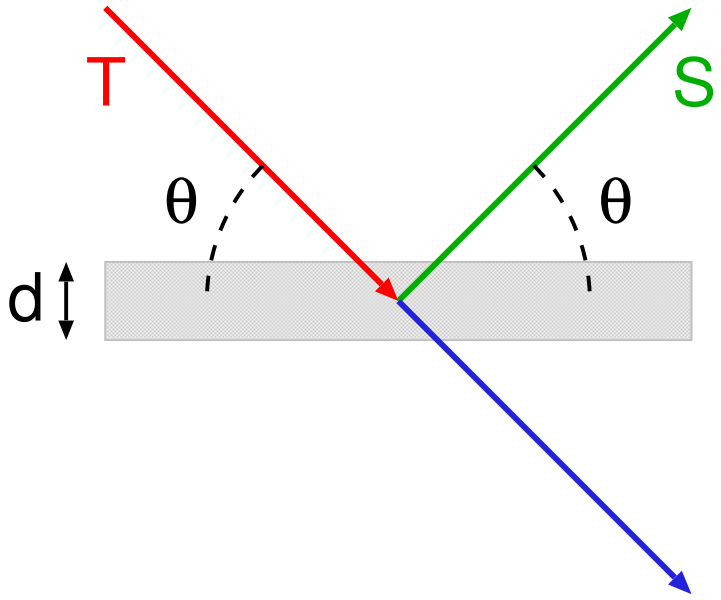

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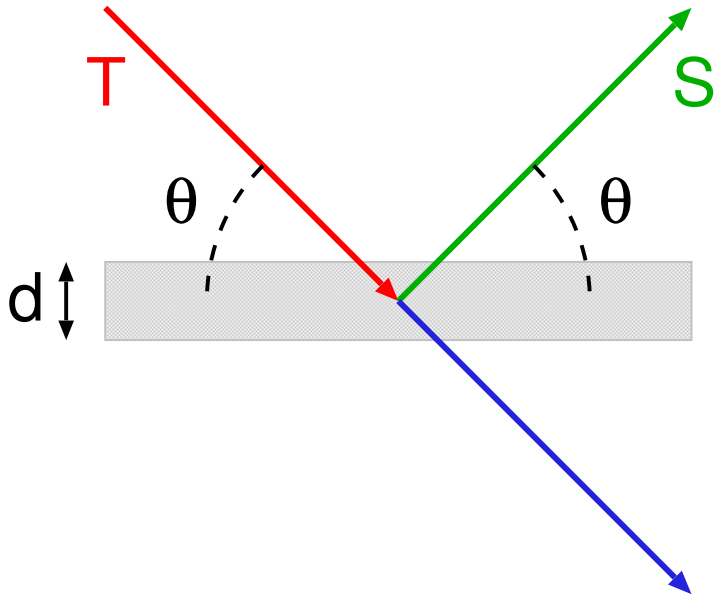

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these N unit cell layers will give a reciprocal lattice with points at multiples of $G = 2\pi/d$

Kinematical Reflection

If we now extend this model to N layers we can use this kinematical approximation if $Ng \ll 1$.

Proceed by adding reflectivity from each layer with the usual phase factor

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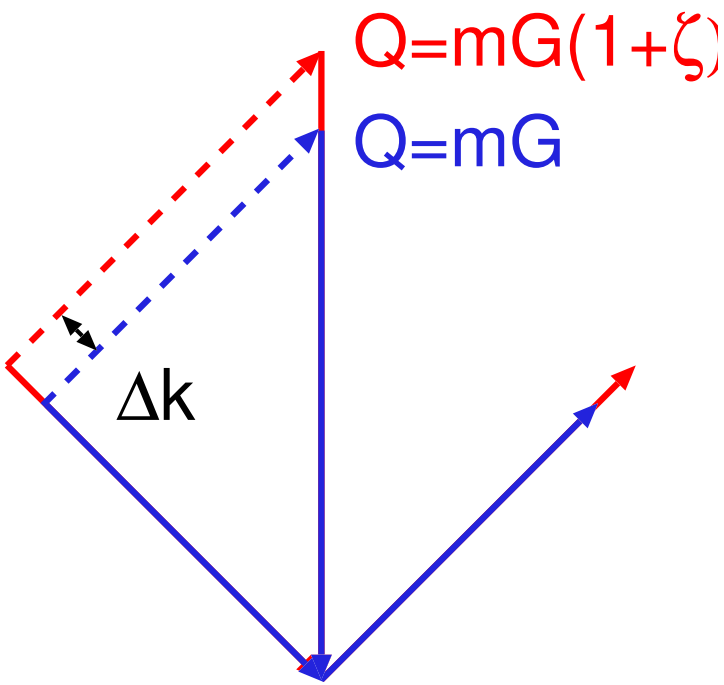

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these N unit cell layers will give a reciprocal lattice with points at multiples of $G = 2\pi/d$ we are interested in small deviations from the Bragg condition:

$$\zeta = \frac{\Delta Q}{Q} = \frac{\Delta k}{k} = \frac{\Delta \mathcal{E}}{\mathcal{E}} = \frac{\Delta \lambda}{\lambda}$$

Multiple Layer Reflection

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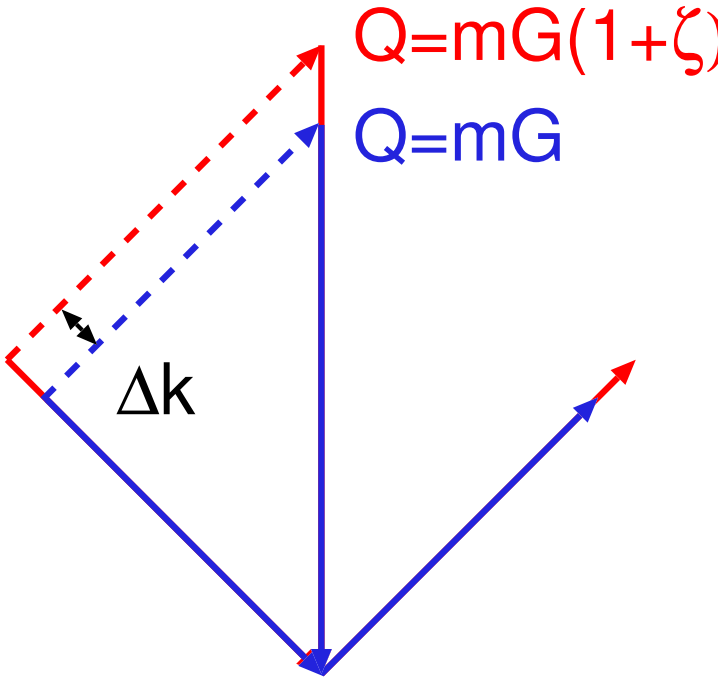

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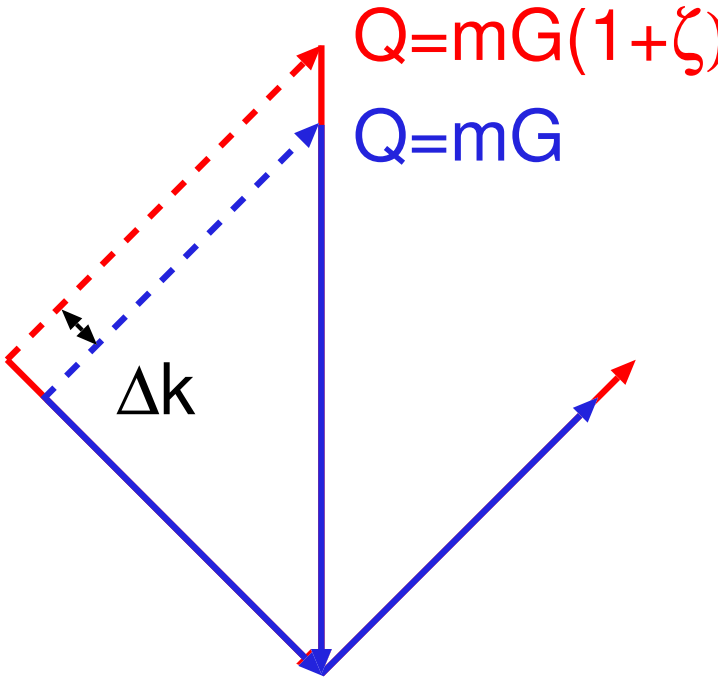

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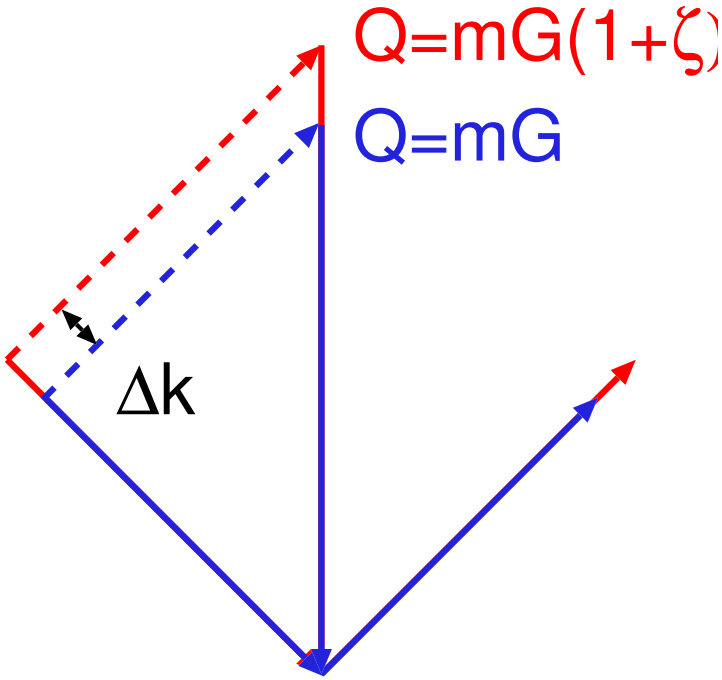

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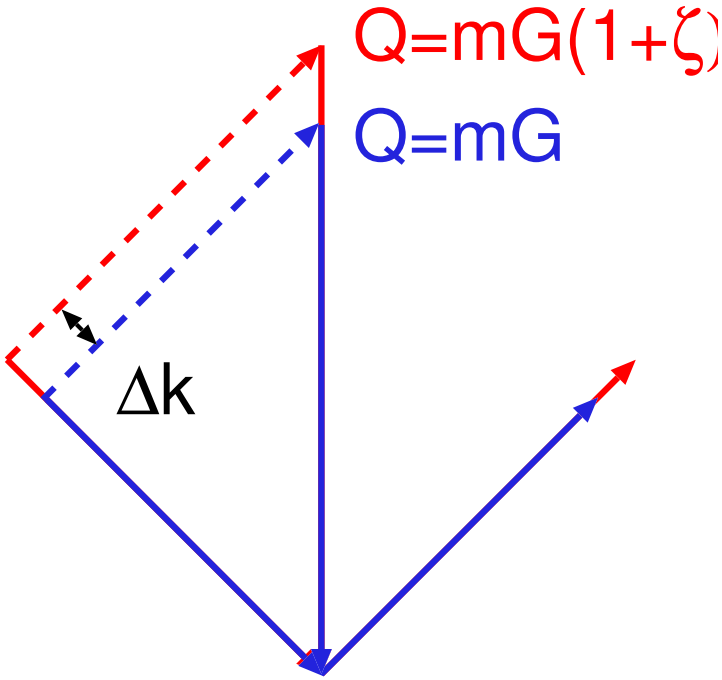

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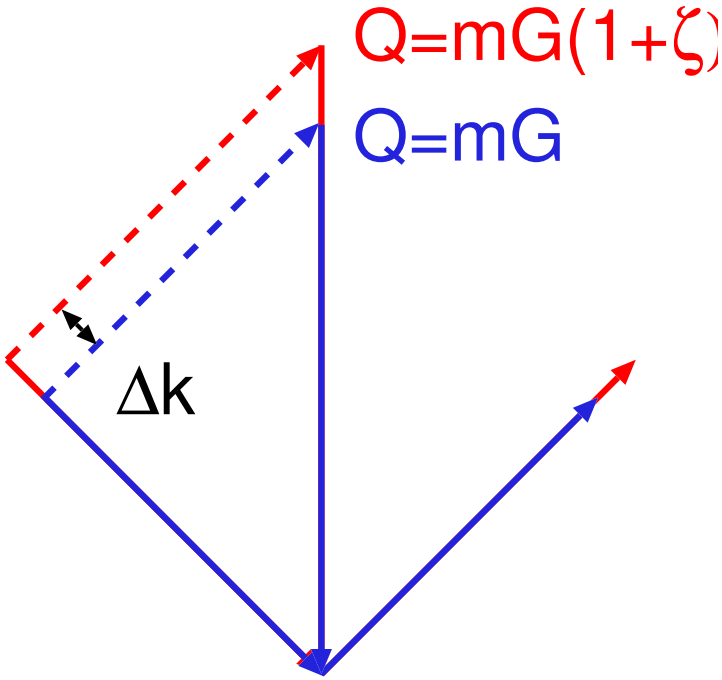

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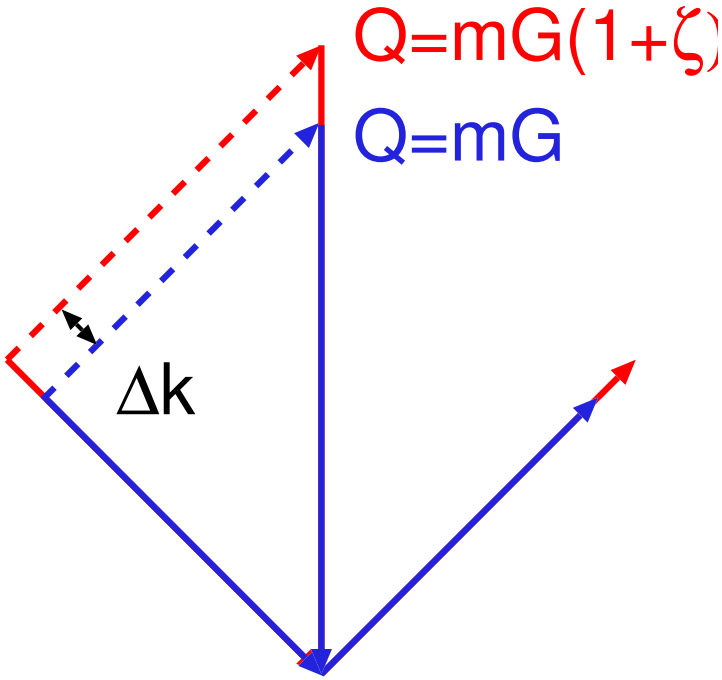

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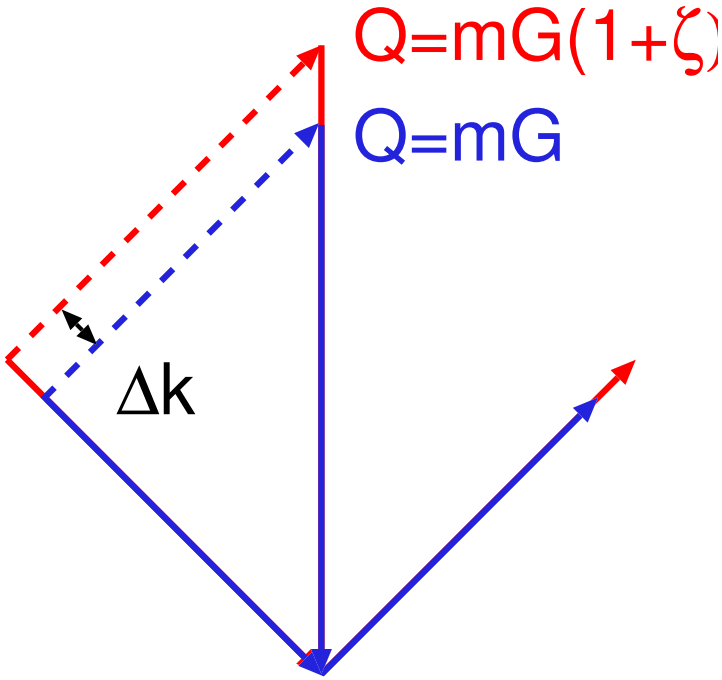

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This geometric series can be summed as usual

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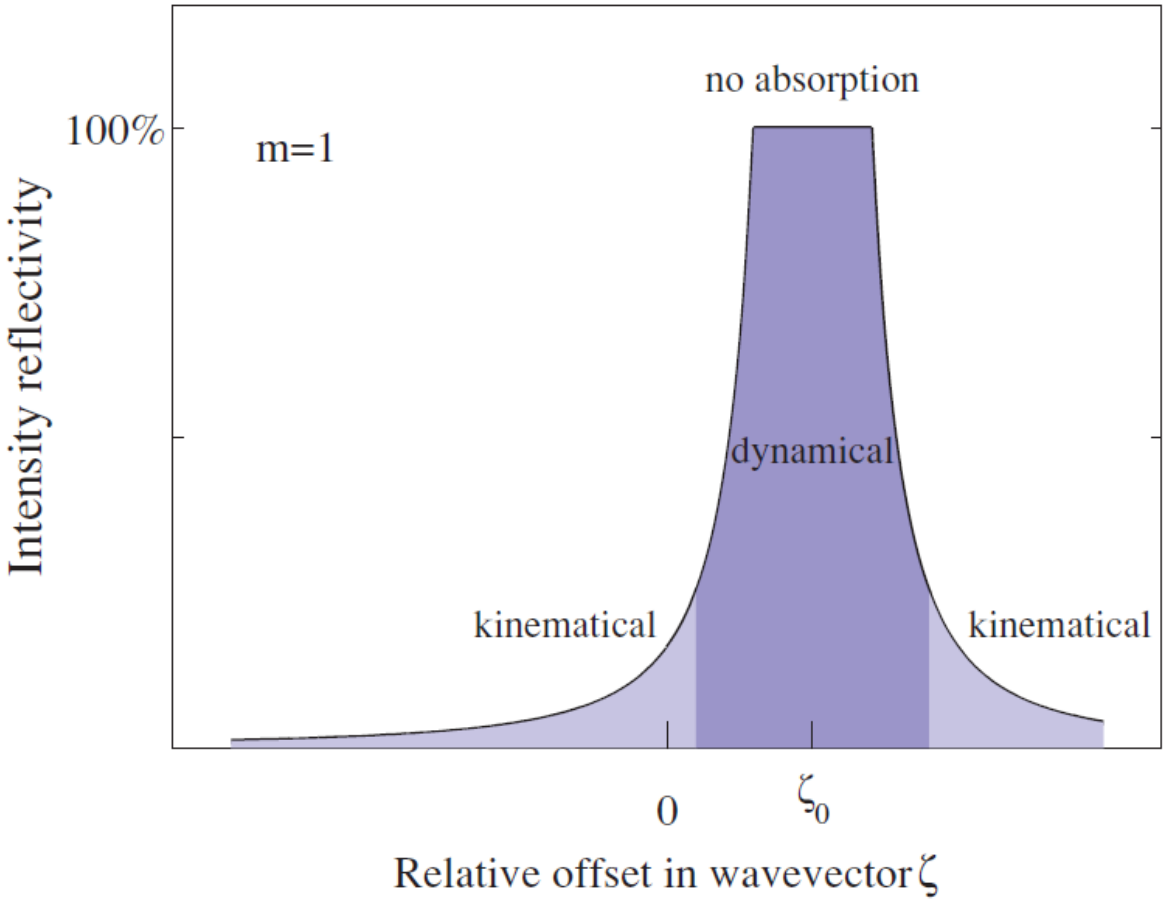
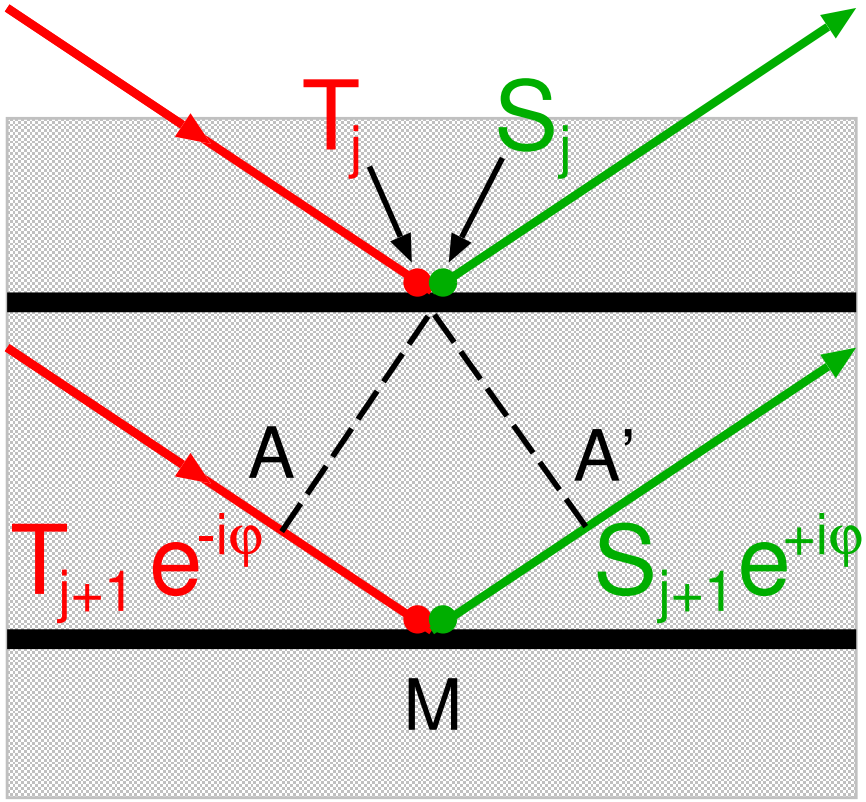


Difference Equation Review



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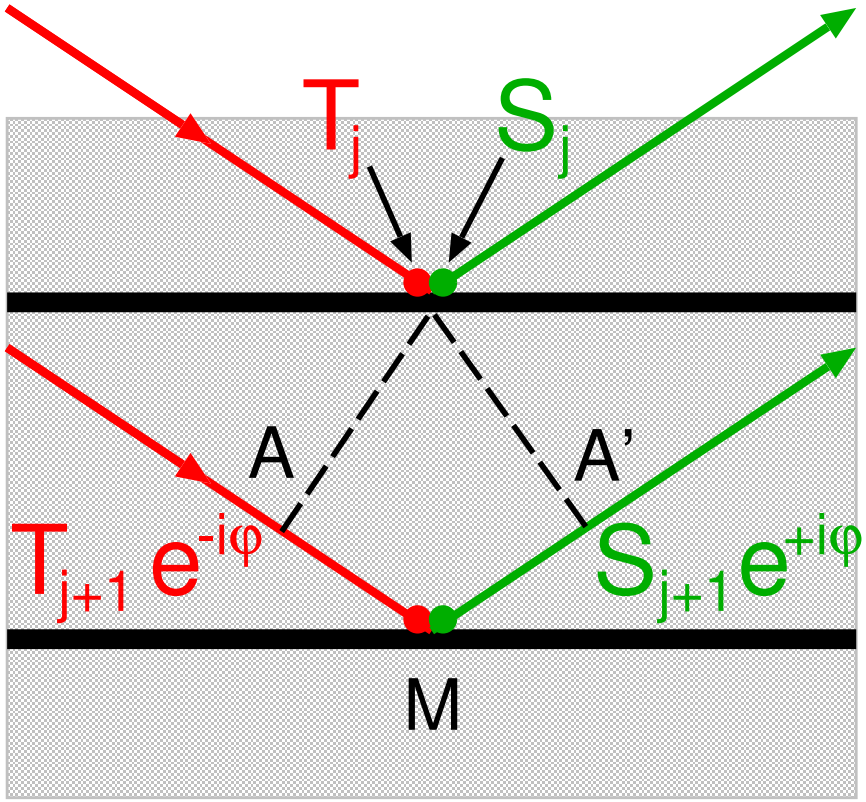

$$g = \frac{\lambda r_0 \rho d}{\sin\theta}, \qquad g_0 = \frac{|F_0|}{|F|} g$$

$$\Delta = m\pi\zeta, \qquad \zeta = \frac{\Delta\lambda}{\lambda}$$

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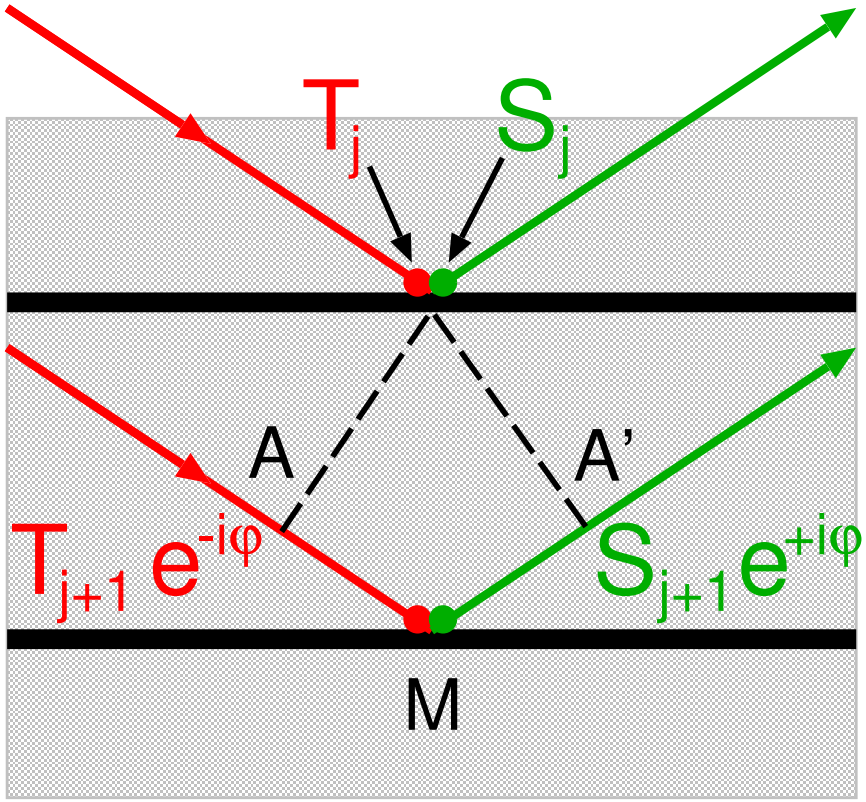

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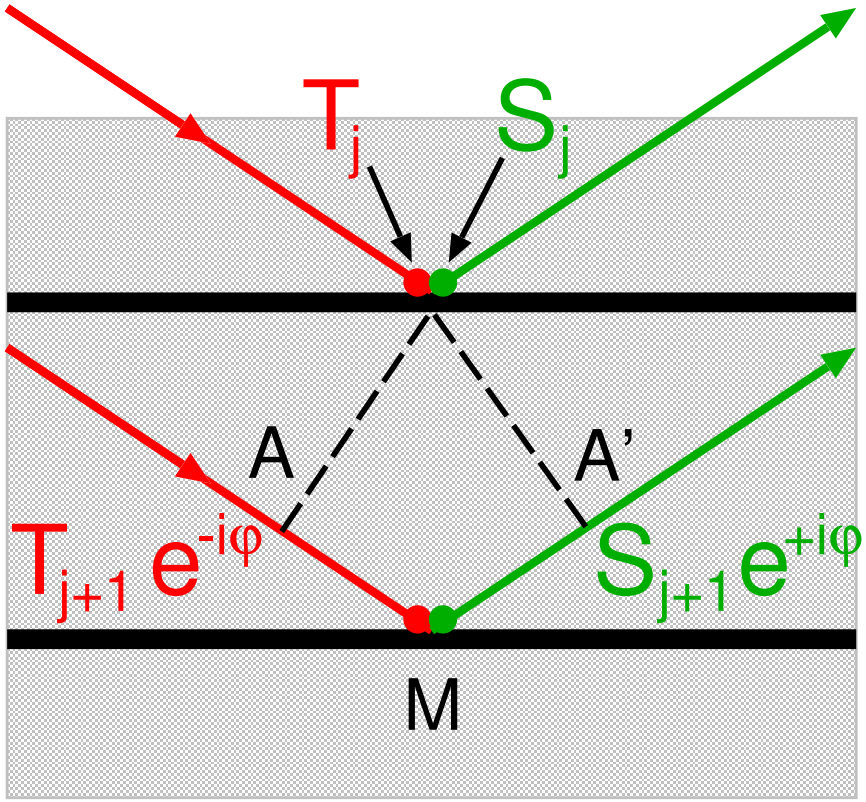

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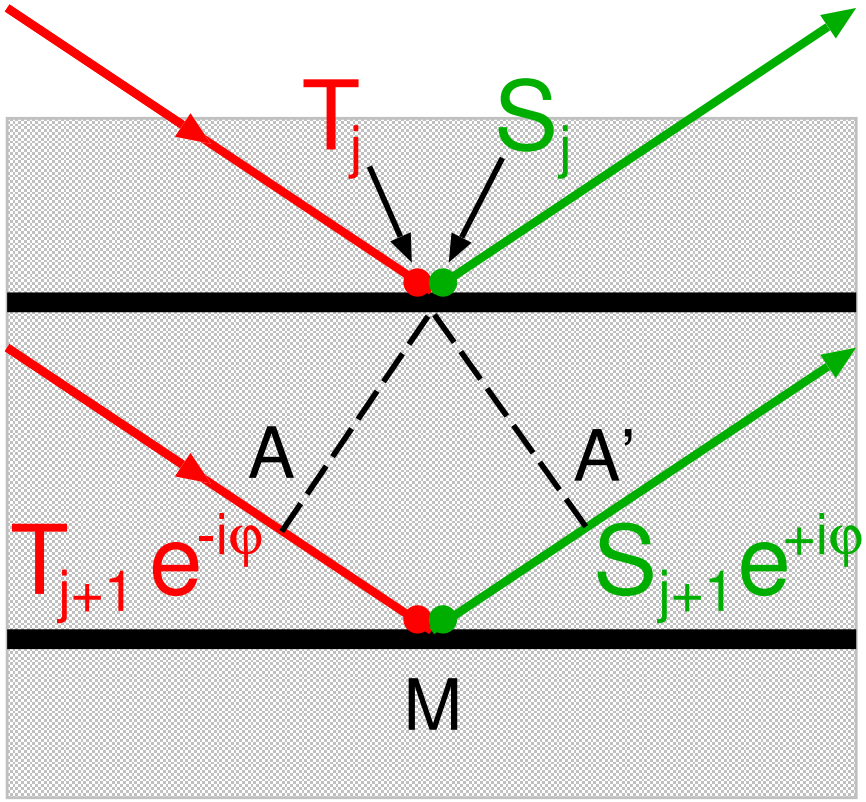

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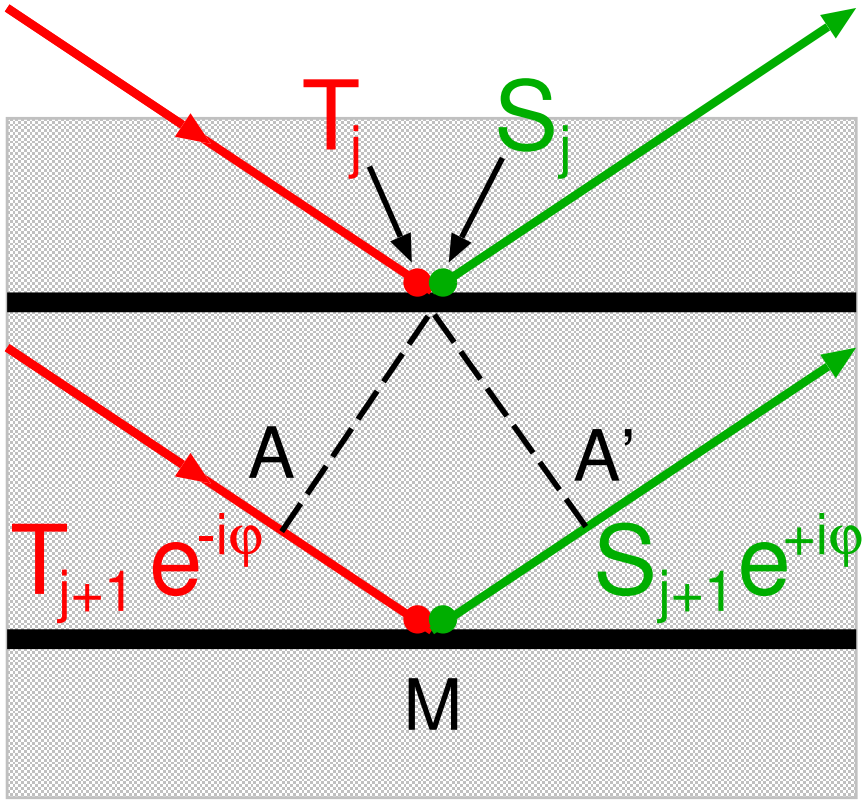

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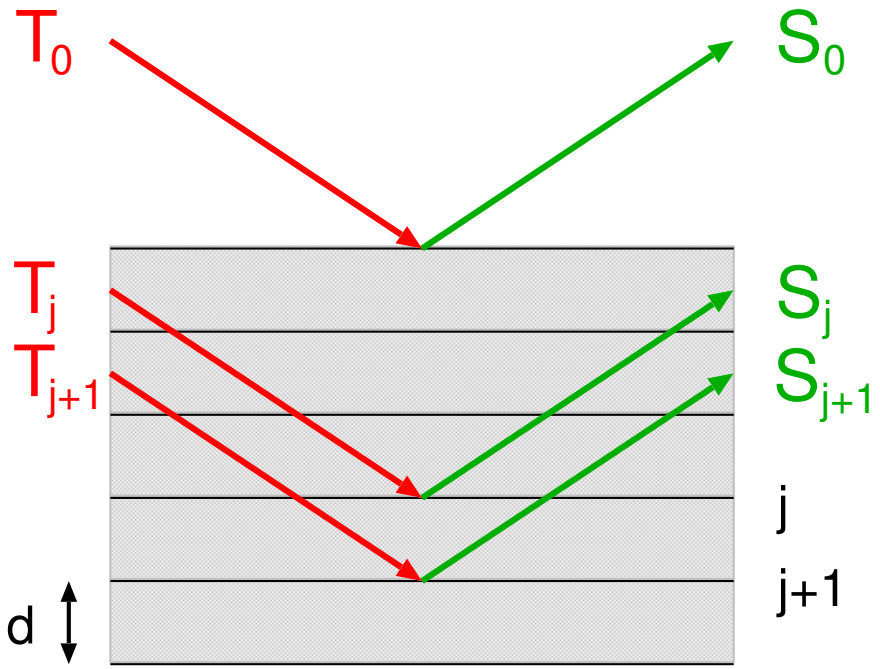
Reflectivity of a Perfect Crystal

In order to calculate the absolute reflectivity curve, solve for S_0 and T_0 using the solution and the recursive relations.



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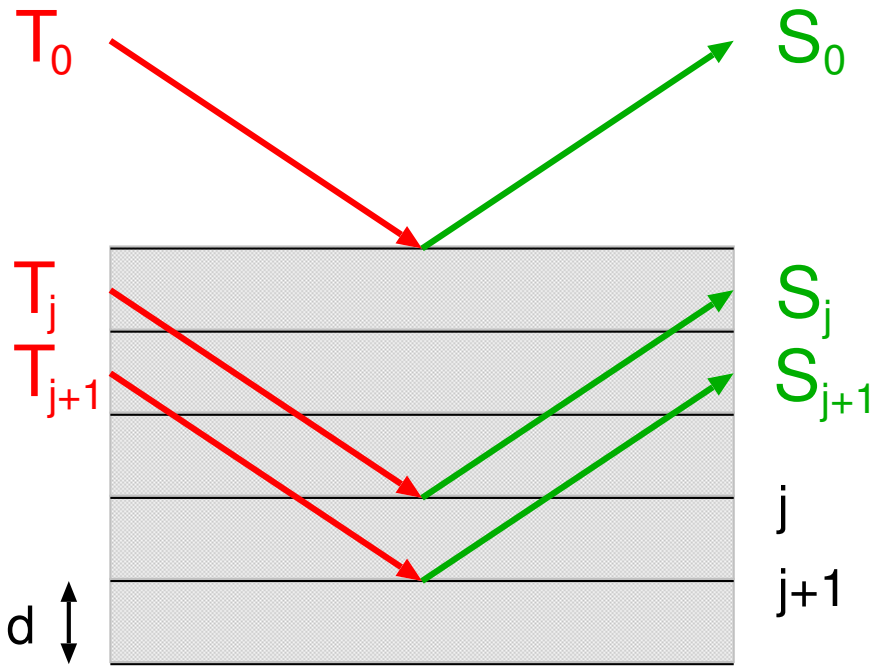

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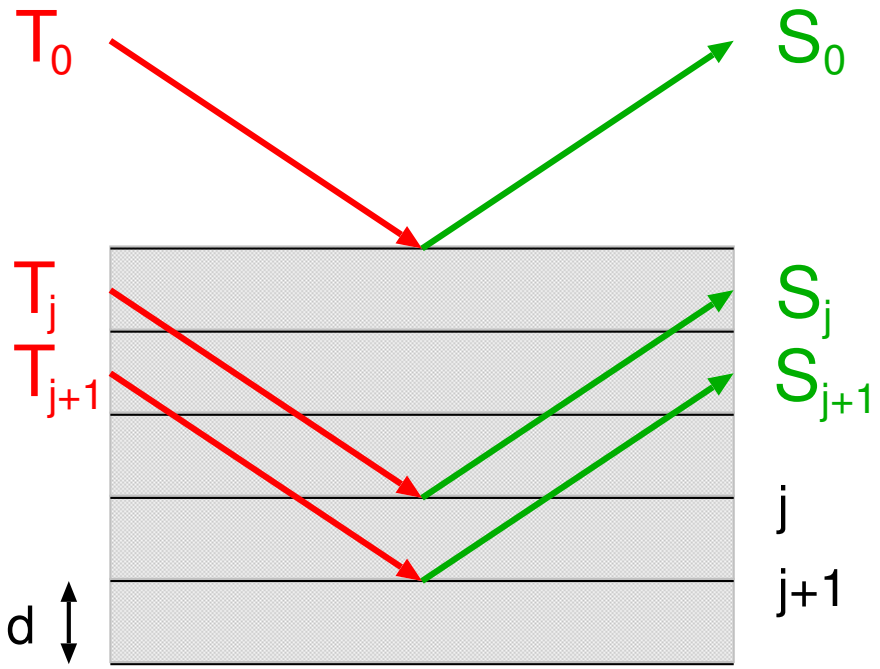

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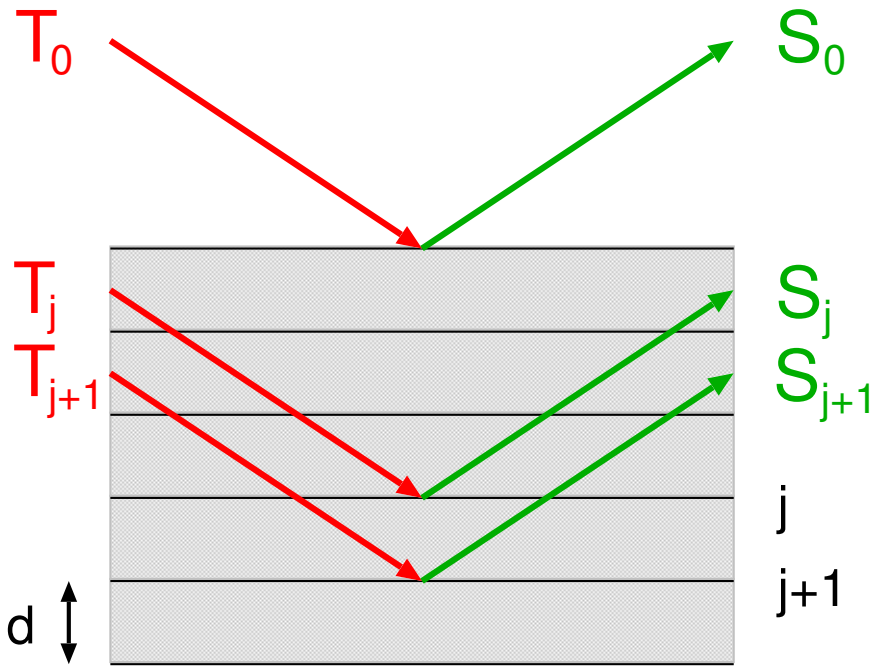

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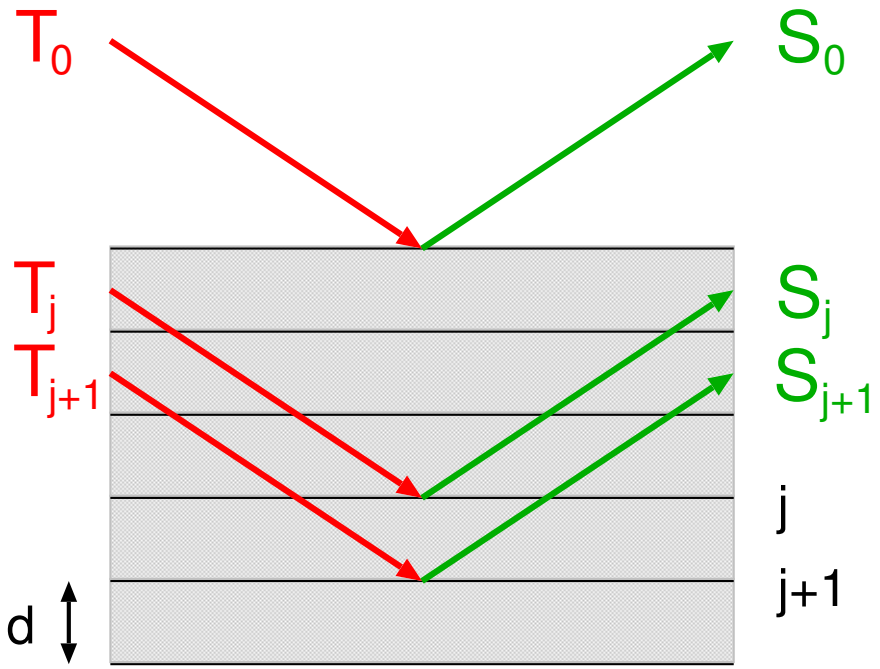

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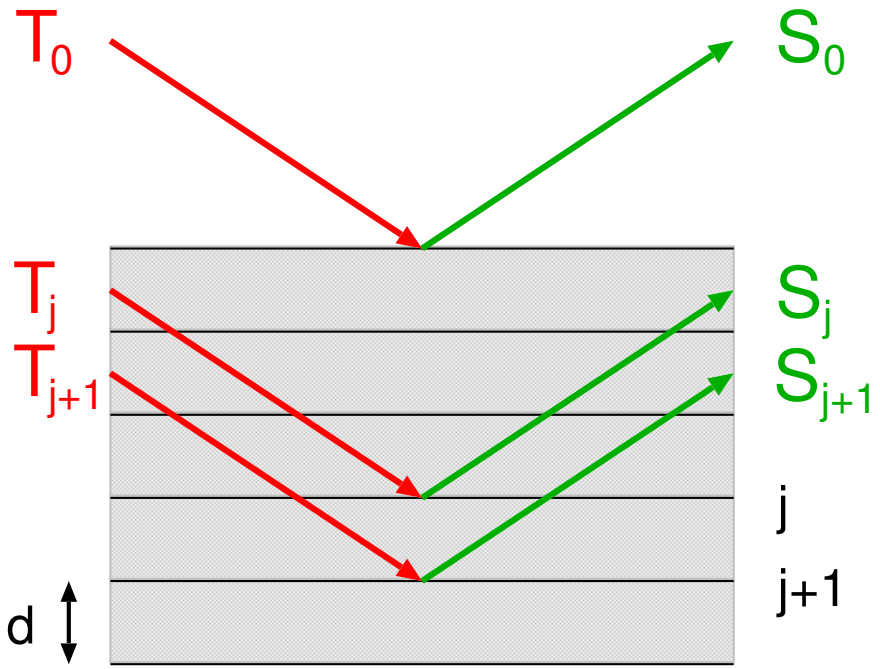

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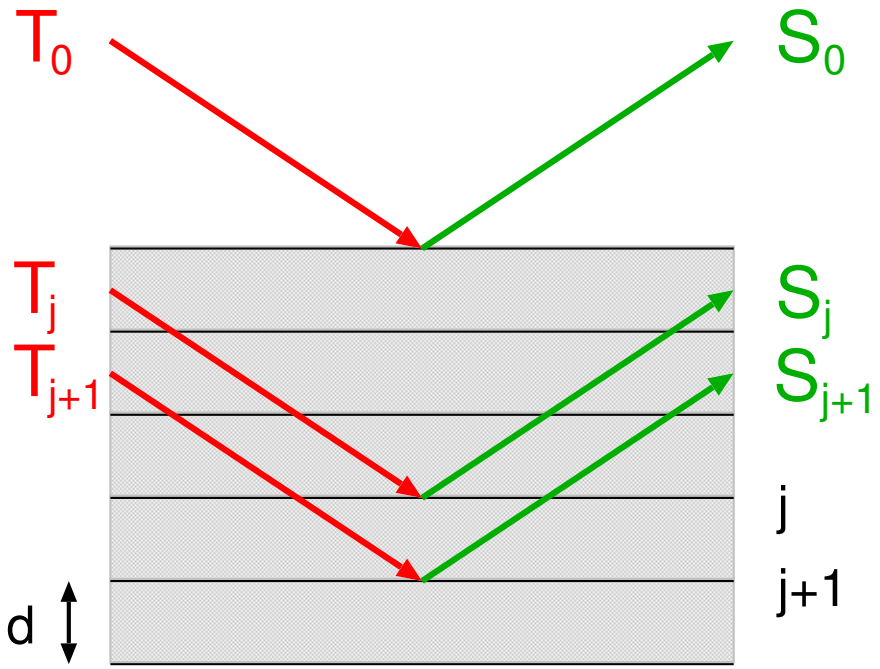

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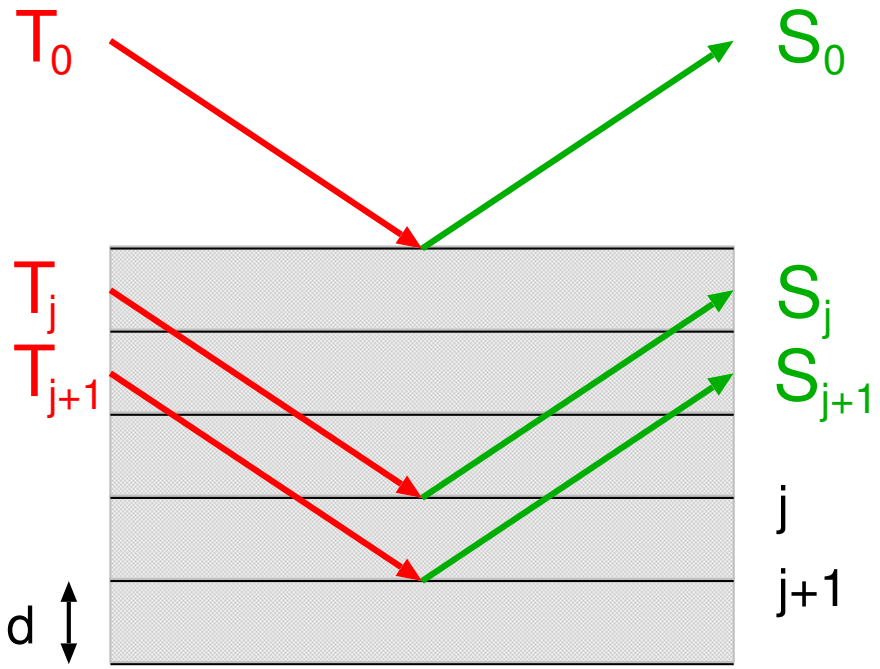

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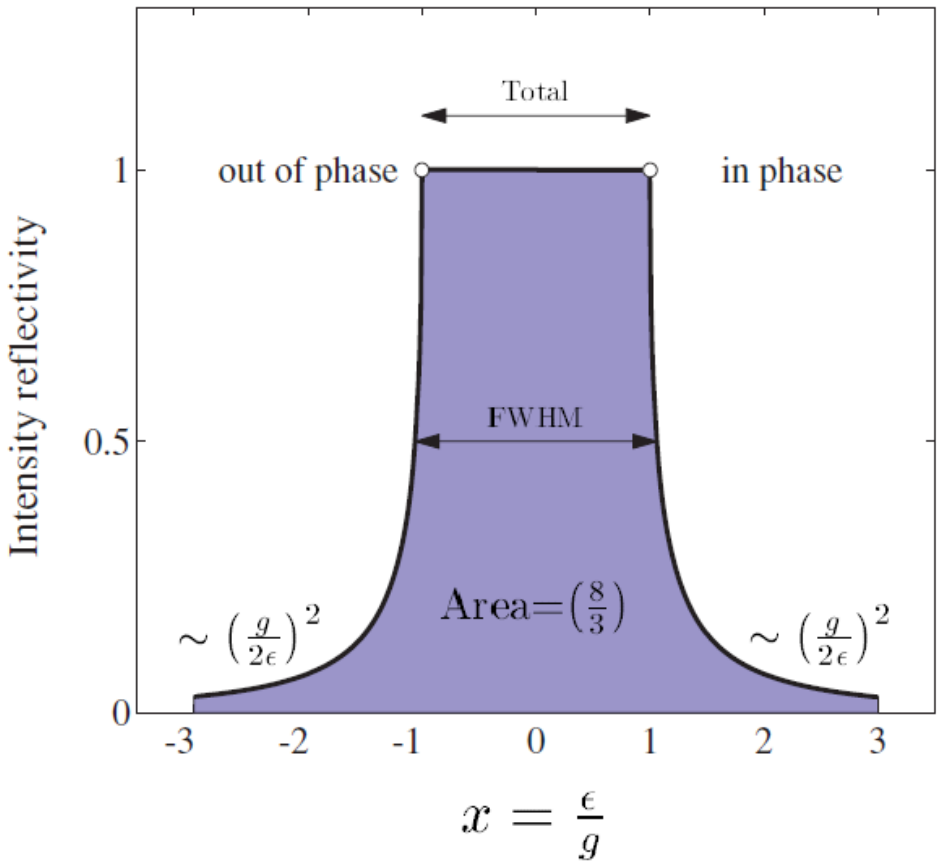
Darwin Reflectivity Curve

$$r = \frac{S_0}{T_0} = \frac{g}{i\eta + \epsilon} = \frac{g}{\epsilon \pm \sqrt{\epsilon^2 - g^2}}, \qquad \epsilon = \Delta - g_0 = m\pi\zeta - \pi\zeta_0$$



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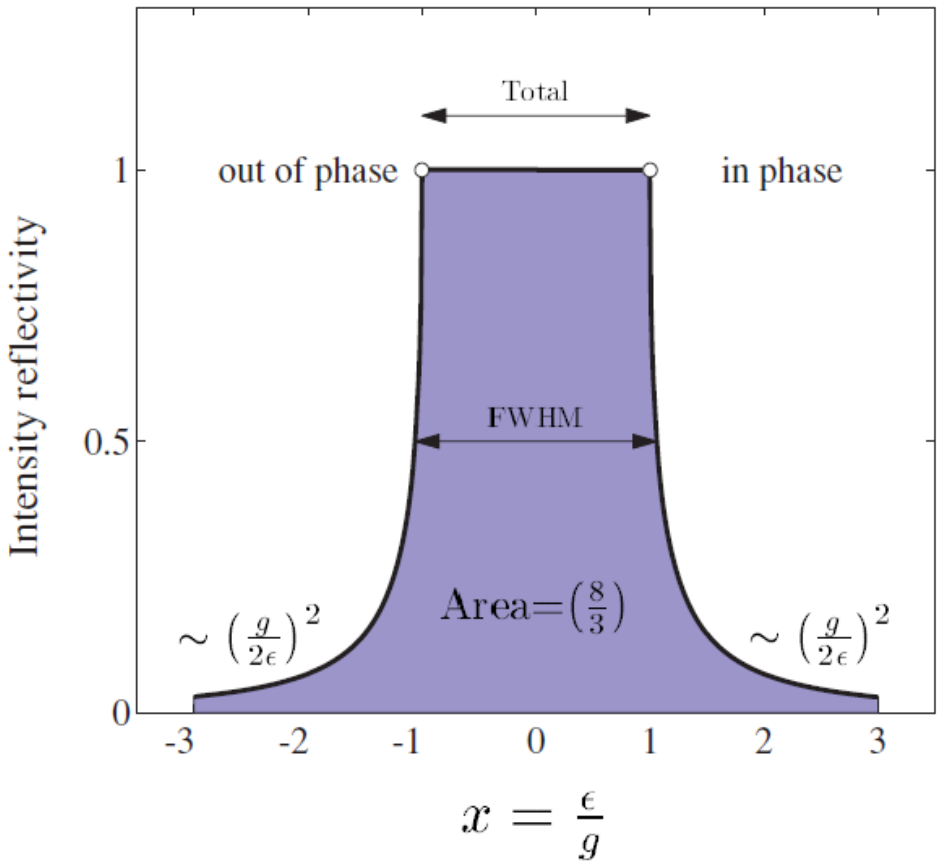
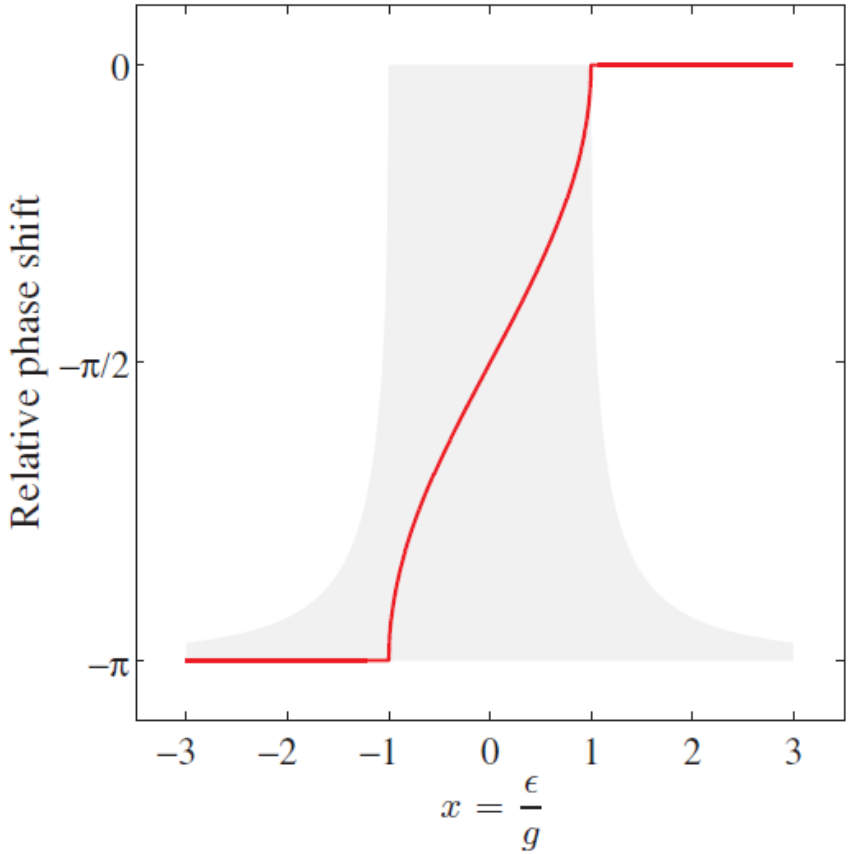
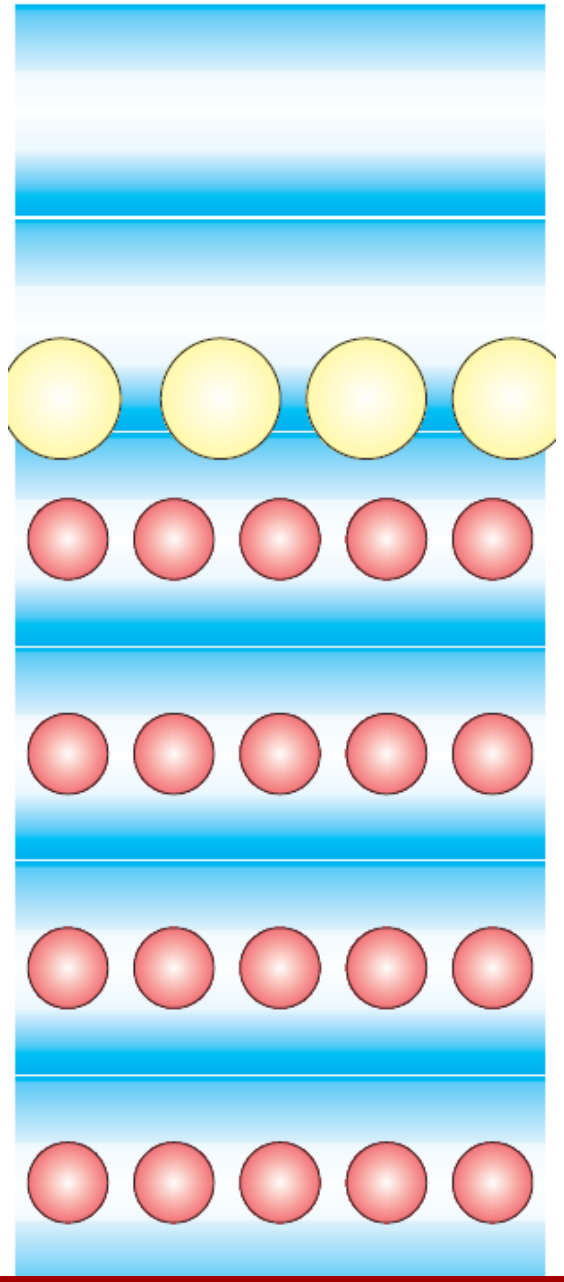




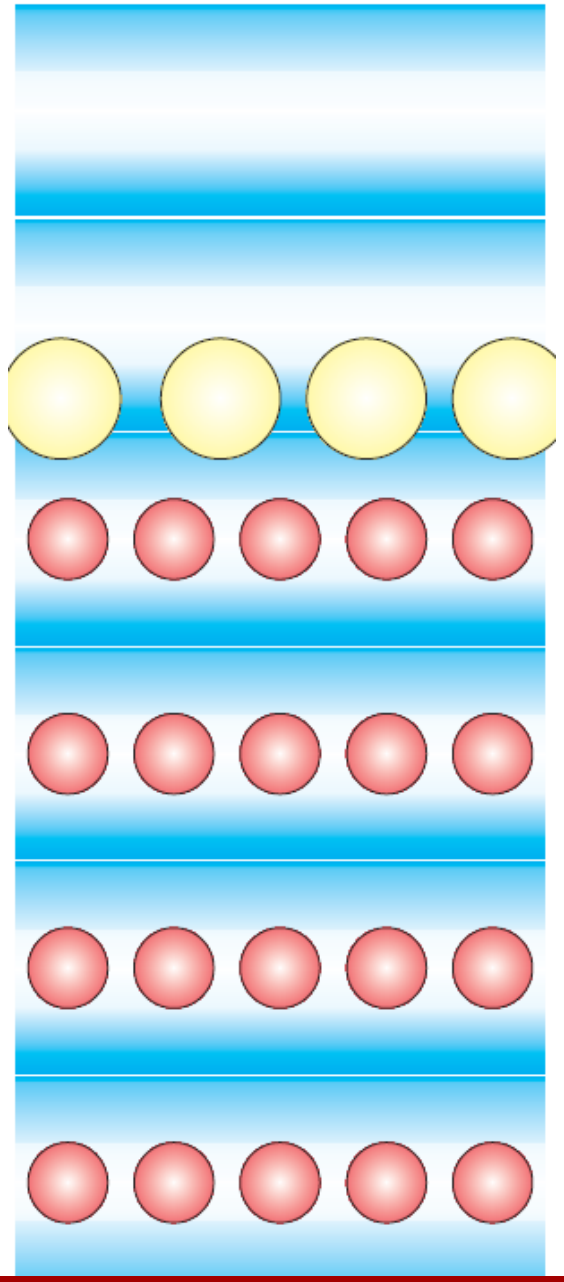
Standing Waves



$\longleftarrow x = -1$

out of phase

Standing Waves

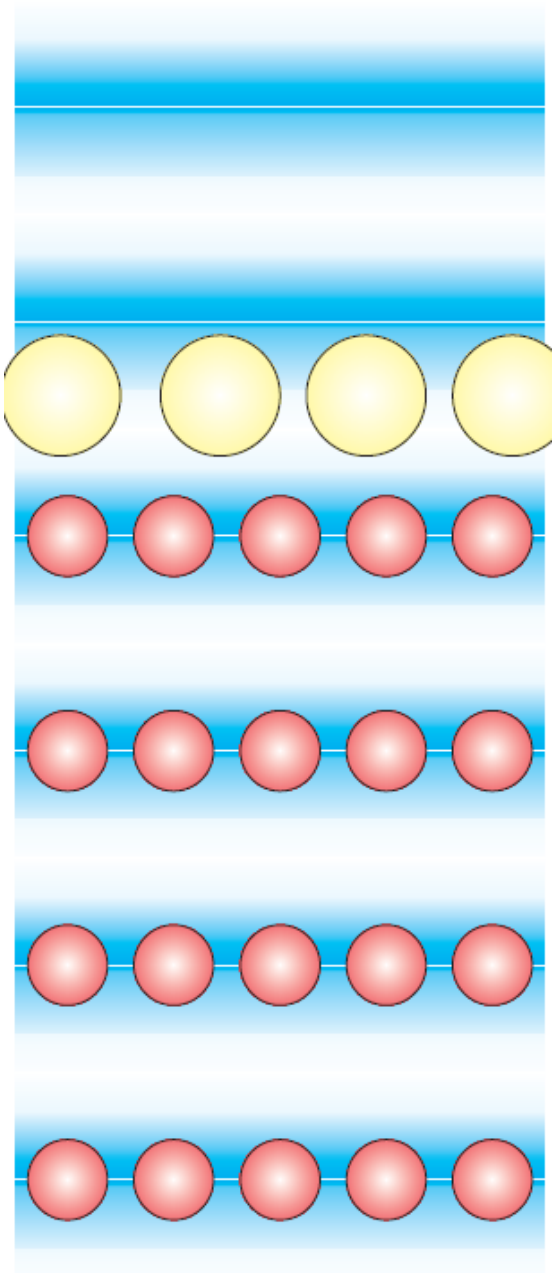


$\longleftarrow x = -1$

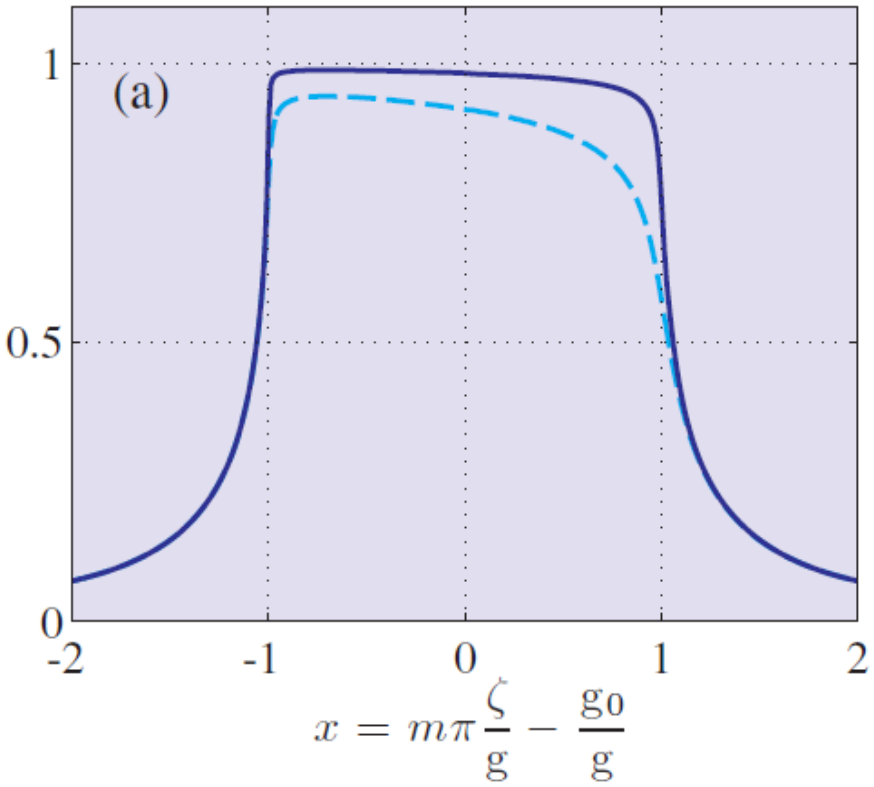
out of phase

$x = +1 \longrightarrow$

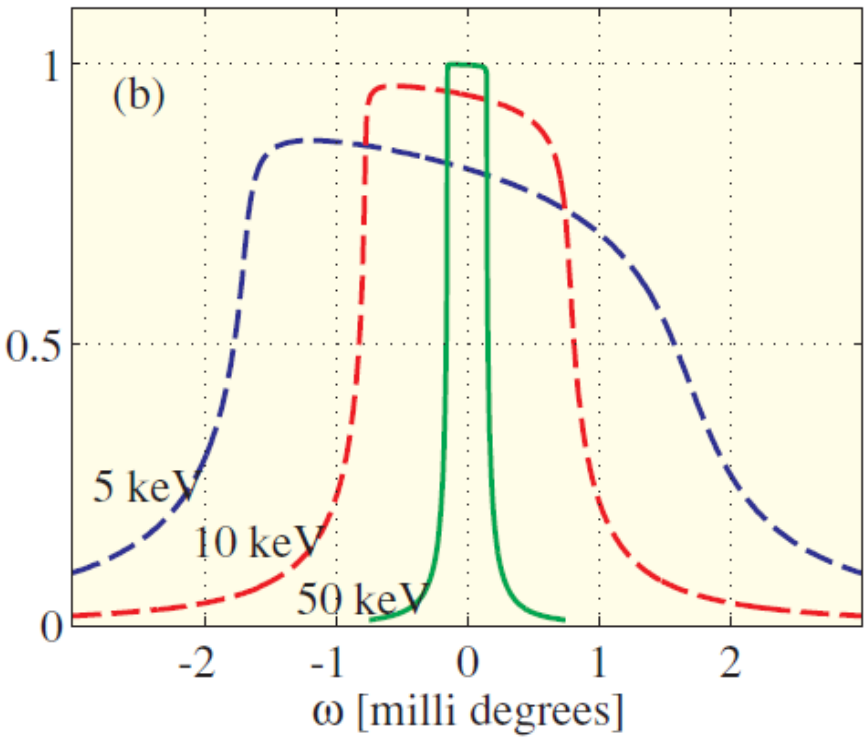
in phase



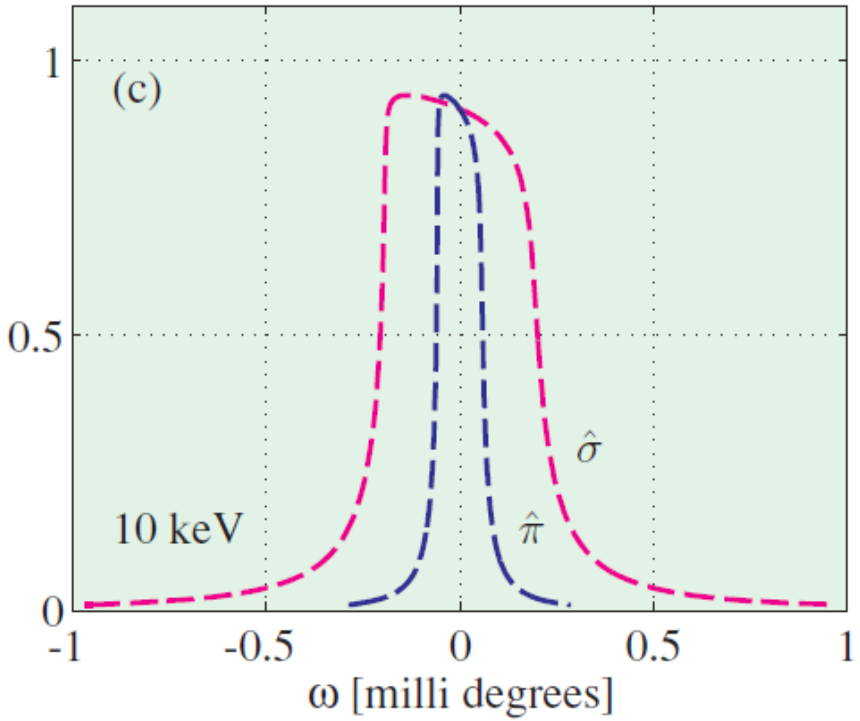
Absorption Effects



Energy Dependence

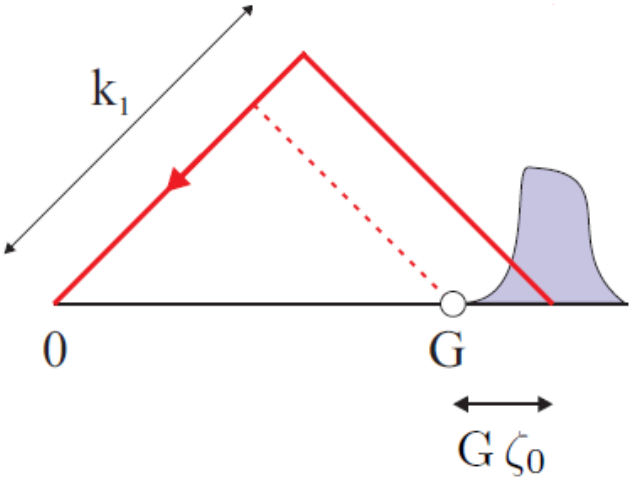


Polarization Dependence



Harmonic Suppression

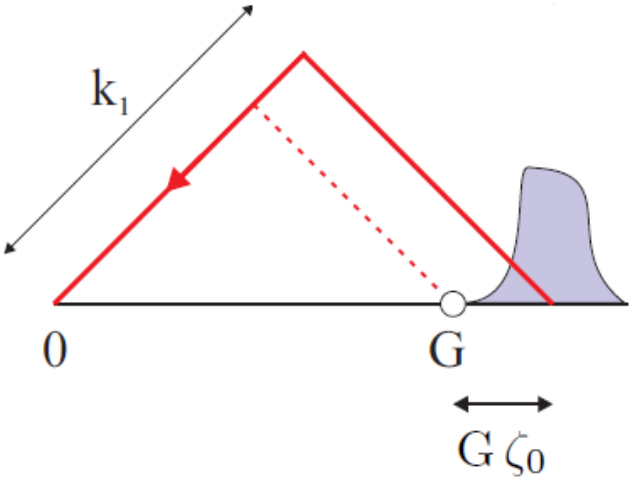
The displacement of the Darwin curve varies inversely as the order, m, of the reflection.



Harmonic Suppression

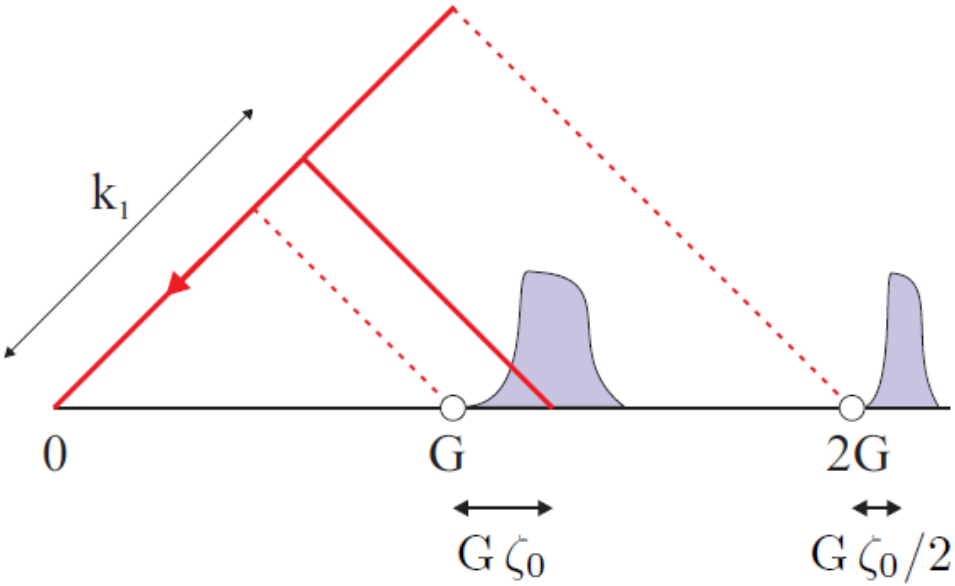
The displacement of the Darwin curve varies inversely as the order, m, of the reflection.

$$\zeta_0 = \frac{g_0}{\pi} = \frac{2d^2|F_0|r_0}{\pi m v_c}$$



Harmonic Suppression

The displacement of the Darwin curve varies inversely as the order, m, of the reflection. The width varies as the inverse squared.



$$\zeta_0 = \frac{g_0}{\pi} = \frac{2d^2|F_0|r_0}{\pi m v_c}$$

$$\zeta_D = \frac{2g}{m\pi} = \frac{4d^2|F|r_0}{\pi m^2 v_c}$$

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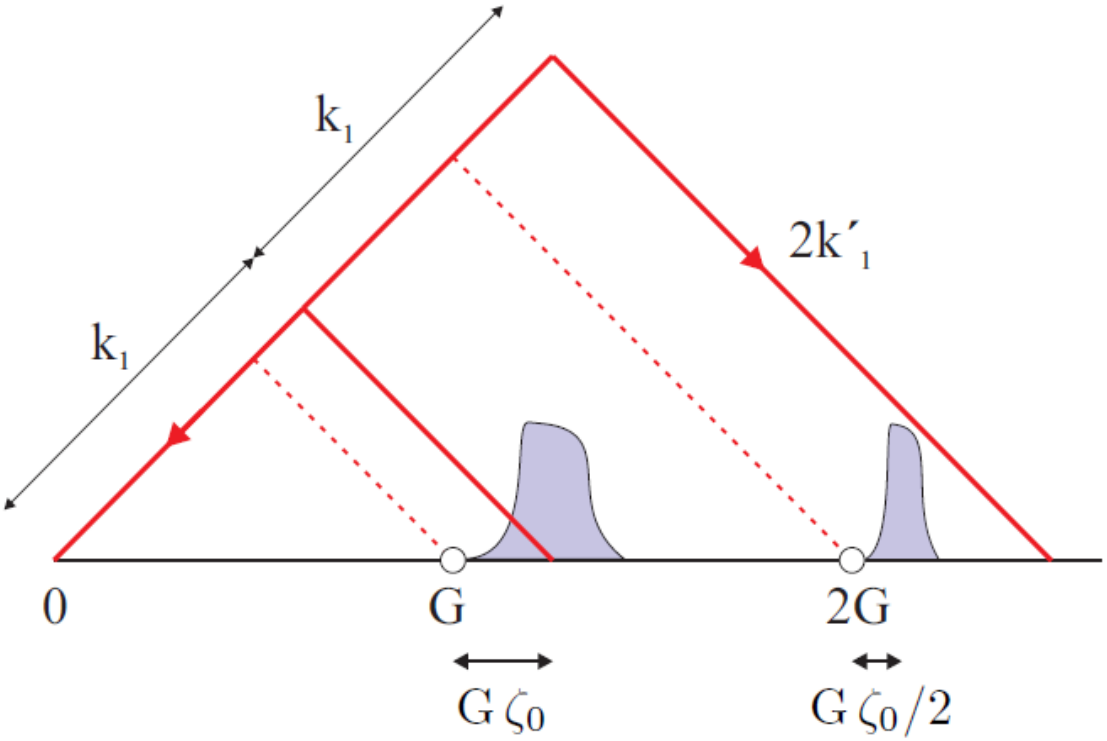

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By tuning to the center of a lower order reflection, the high orders can be effectively suppressed.

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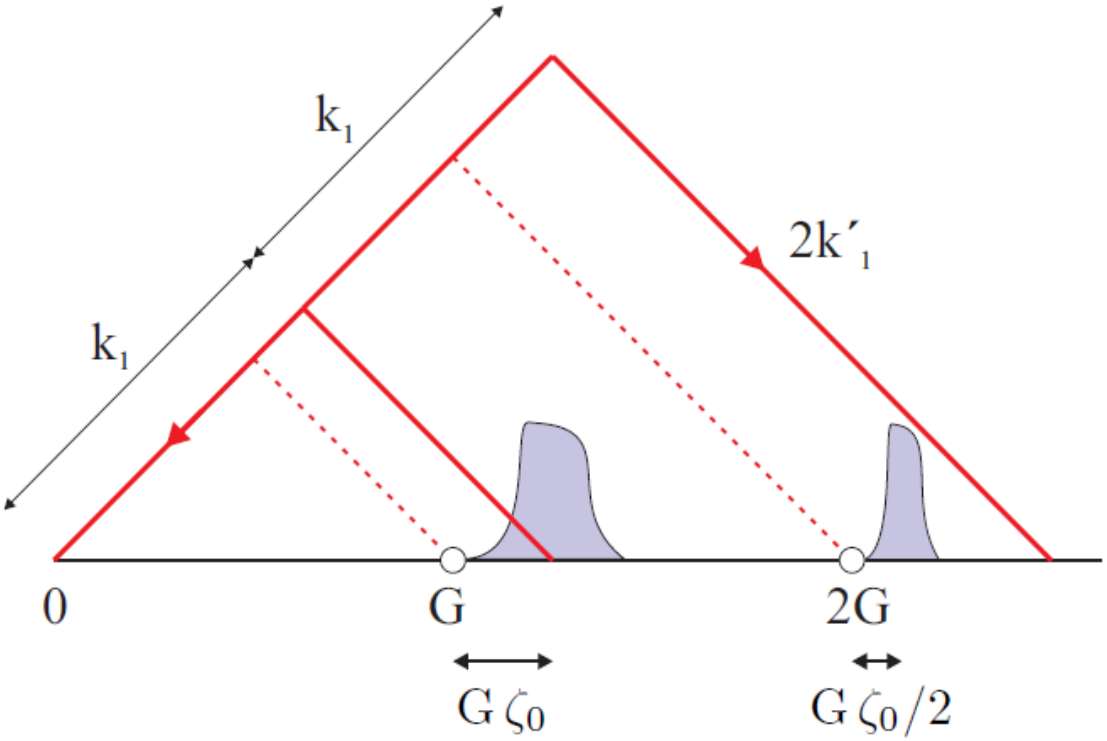

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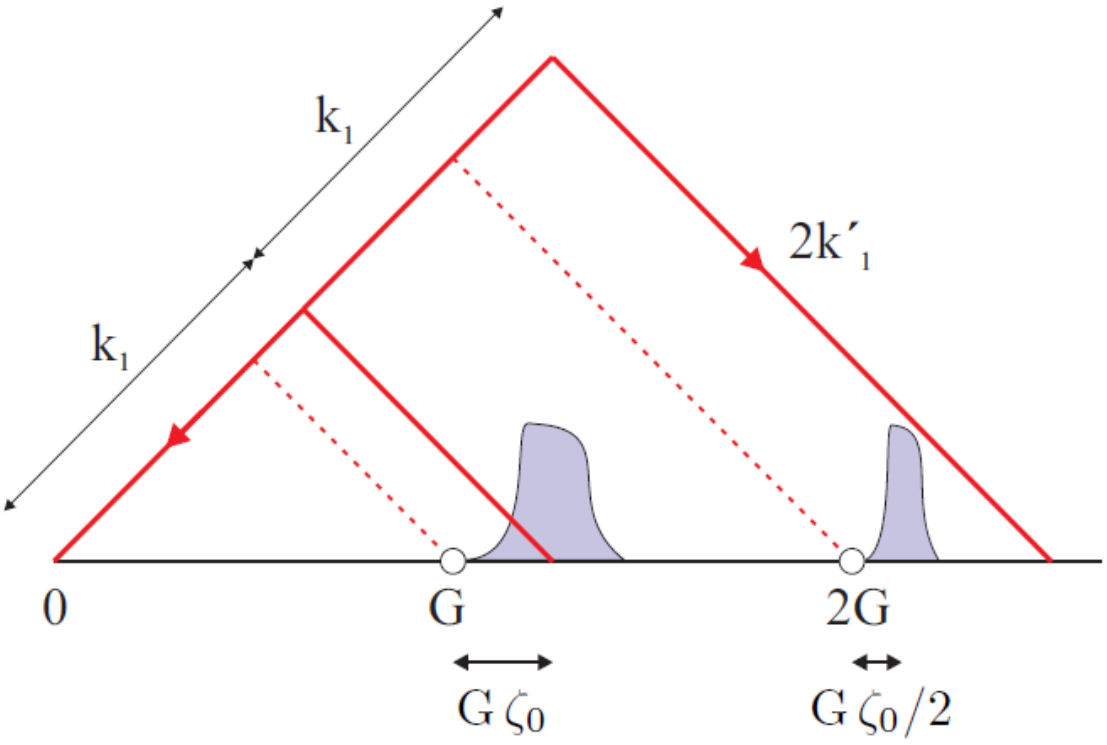
By tuning to the center of a lower order reflection, the high orders can be effectively suppressed.

By tuning a bit off on the "high" side we get even more suppression. This is called "detuning".

Angular Offset

We can calculate the angular offset by noting that the offset and width have many common factors.



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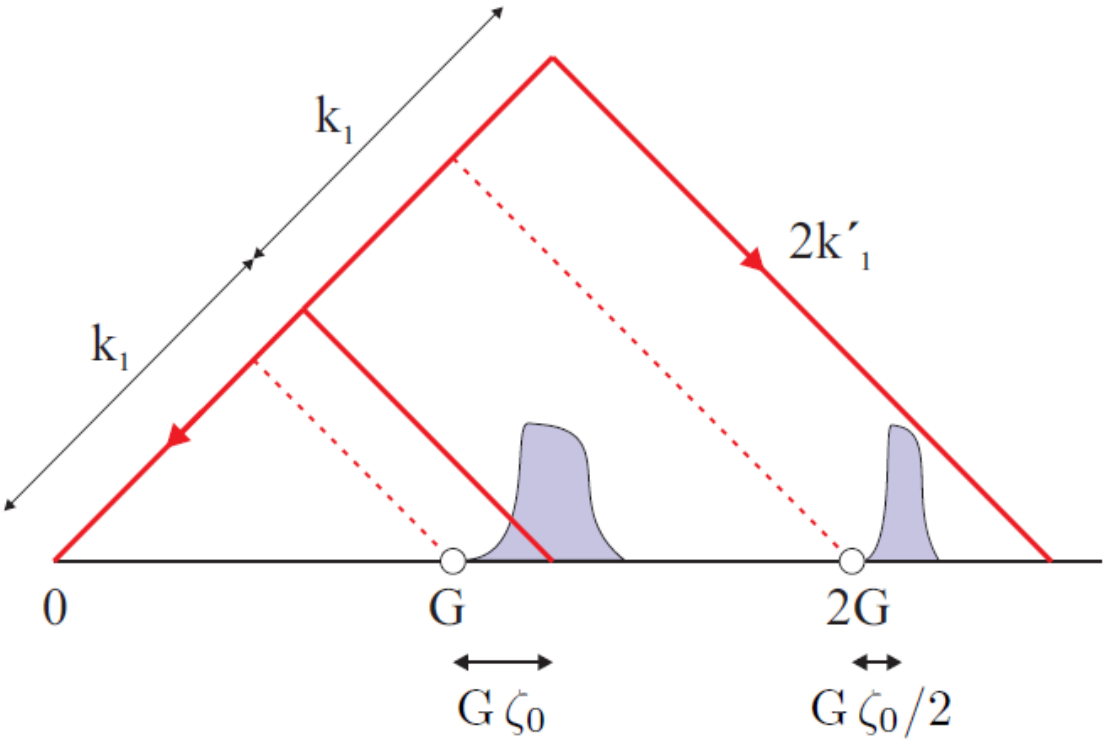

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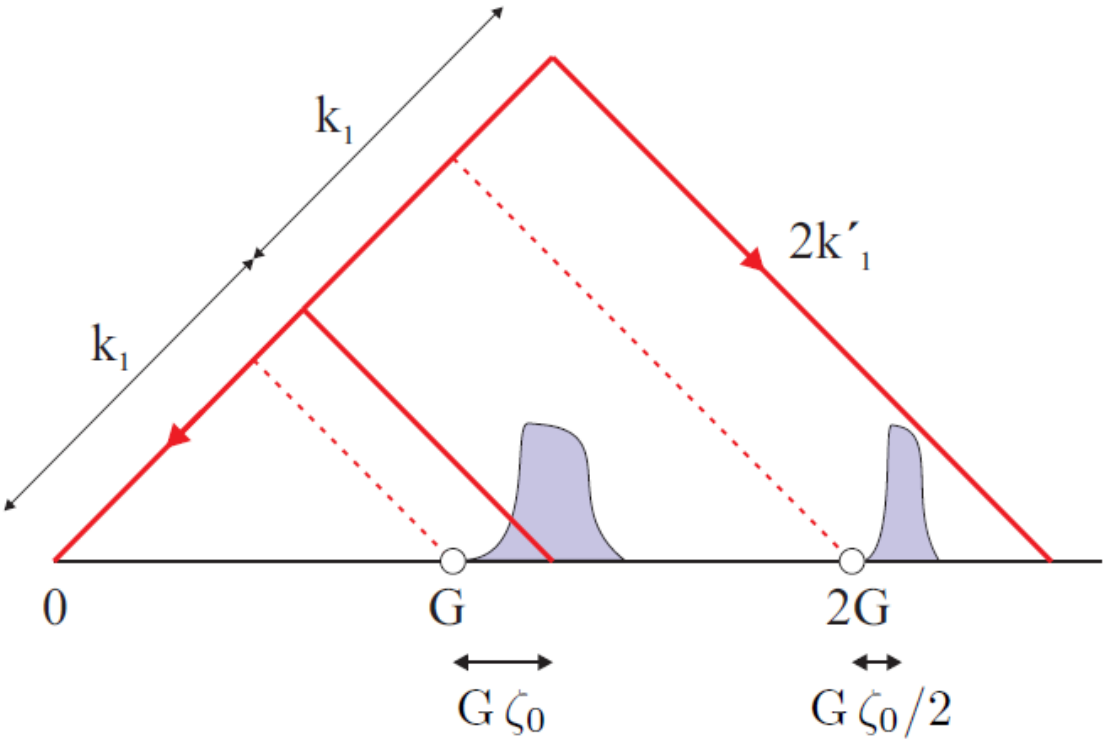
Angular Offset

We can calculate the angular offset by noting that the offset and width have many common factors. Converting this to an angular offset.



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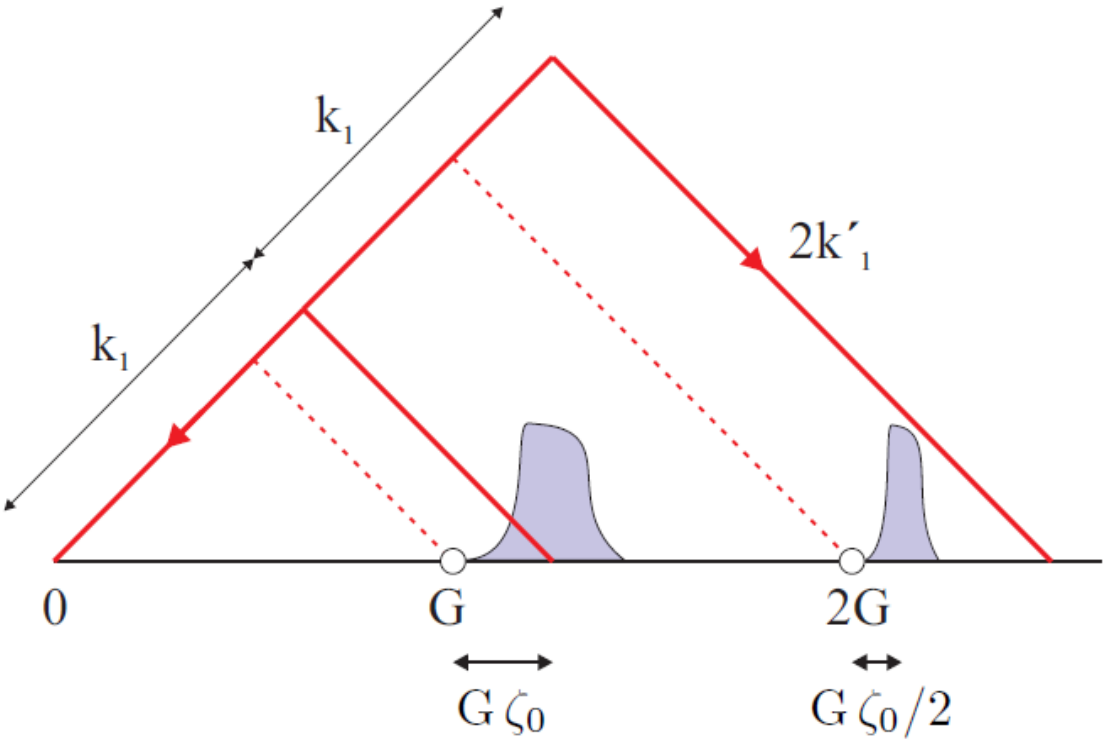

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For the Si(111) at $\lambda = 1.54056$Å

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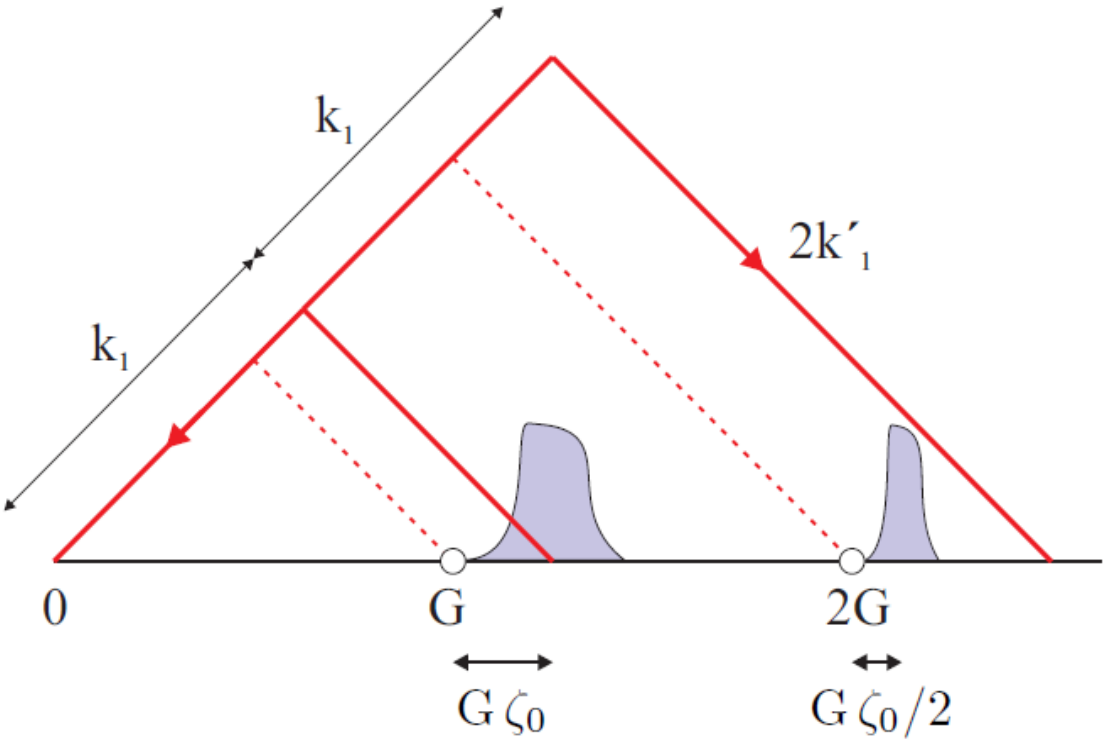

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For the Si(111) at $\lambda = 1.54056$Å

$$\omega_D^{total} = 0.0020^\circ$$

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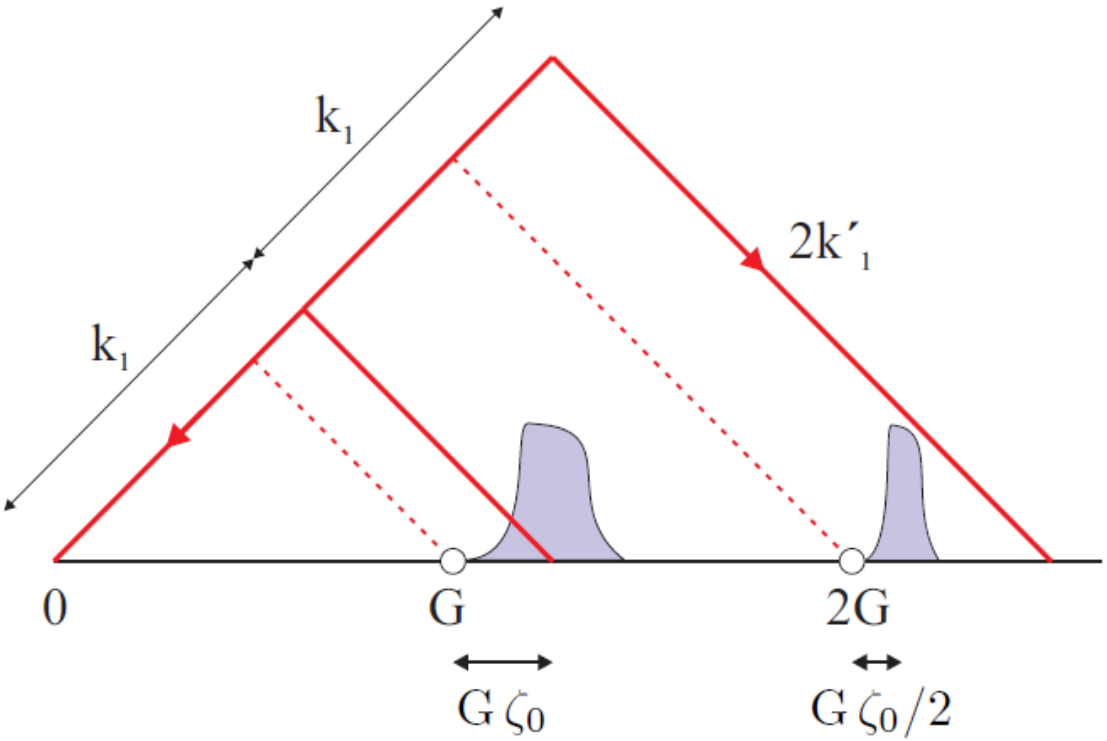

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$$\Delta\theta^{off} = \frac{\zeta_D}{2}\frac{|F|}{|F_0|}\tan\theta$$

For the Si(111) at $\lambda = 1.54056$Å

$$\omega_D^{total} = 0.0020^\circ \qquad \Delta\theta^{off} = 0.0018^\circ$$