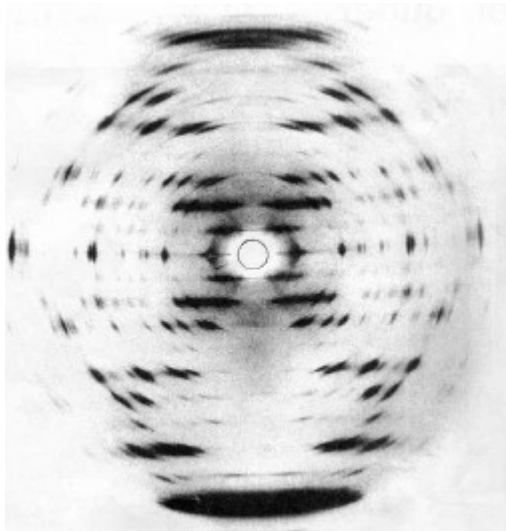


# Diffraction

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# crystal structure solution



"Guess" the crystal structure

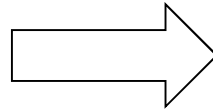
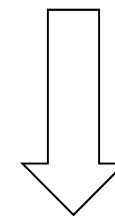


Table 4.3.2.2 | pdf |

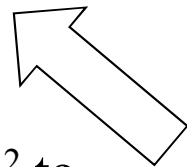
Elastic atomic scattering factors of electrons for neutral atoms and s up to  $2.0 \text{ \AA}^{-1}$

Element	Z	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$b_1$	$b_2$	$b_3$
H	1	0.0349	0.1201	0.1970	0.0573	0.1195	0.5347	3.5867	12.3471
He	2	0.0317	0.0838	0.1526	0.1334	0.0164	0.2507	1.4751	4.4938
Li	3	0.0750	0.2249	0.5548	1.4954	0.9354	0.3864	2.9383	15.3829
Be	4	0.0780	0.2210	0.6740	1.3867	0.6925	0.3131	2.2381	10.1517
B	5	0.0909	0.2551	0.7738	1.2136	0.4606	0.2995	2.1155	8.3816
C	6	0.0893	0.2563	0.7570	1.0487	0.3575	0.2465	1.7100	6.4094
N	7	0.1022	0.3219	0.7982	0.8197	0.1715	0.2451	1.7481	6.1925
O	8	0.0974	0.2921	0.6910	0.6990	0.2039	0.2067	1.3815	4.6943
F	9	0.1083	0.3175	0.6487	0.5846	0.1421	0.2057	1.3439	4.2788
Ne	10	0.1269	0.3535	0.5582	0.4674	0.1460	0.2200	1.3779	4.0203
Na	11	0.2142	0.6853	0.7692	1.6589	1.4482	0.3334	2.3446	10.0830
Mg	12	0.2314	0.6866	0.9677	2.1882	1.1339	0.3278	2.2720	10.9241
Al	13	0.2390	0.6573	1.2011	2.5586	1.2312	0.3138	2.1063	10.4163
Si	14	0.2519	0.6372	1.3795	2.5082	1.0500	0.3075	2.0174	9.6746
P	15	0.2548	0.6106	1.4541	2.3204	0.8477	0.2908	1.8740	8.5176
S	16	0.2497	0.5628	1.3899	2.1865	0.7715	0.2681	1.6711	7.0267
Cl	17	0.2443	0.5397	1.3919	2.0197	0.6621	0.2468	1.5242	6.1537
Ar	18	0.2385	0.5017	1.3428	1.8899	0.6079	0.2289	1.3694	5.2561



From the atomic form factors, calculate the structure factors  $n_G$ .

Compare  $|n_G|^2$  to the measurements



$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$$

**Primitive lattice vectors:**

$$\vec{a}_1 = 4.12\text{E-}10 \hat{x} + 0 \hat{y} + 0 \hat{z} \text{ [m]}$$

$$\vec{a}_2 = 0 \hat{x} + 4.12\text{E-}10 \hat{y} + 0 \hat{z} \text{ [m]}$$

$$\vec{a}_3 = 0 \hat{x} + 0 \hat{y} + 4.12\text{E-}10 \hat{z} \text{ [m]}$$

**Basis:**  
The positions of the atoms are given in fractional coordinates between -1 and 1.

Cs1+	0	$\vec{a}_1 +$	0	$\vec{a}_2 +$	0	$\vec{a}_3$
Cl1-	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2 +$	0.5	$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$

submit

**Primitive reciprocal lattice vectors**

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 1.525\text{e+}10 \hat{k}_x + 0.000 \hat{k}_y + 0.000 \hat{k}_z \text{ [m}^{-1}\text{]}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000 \hat{k}_x + 1.525\text{e+}10 \hat{k}_y + 0.000 \hat{k}_z \text{ [m}^{-1}\text{]}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000 \hat{k}_x + 0.000 \hat{k}_y + 1.525\text{e+}10 \hat{k}_z \text{ [m}^{-1}\text{]}$$

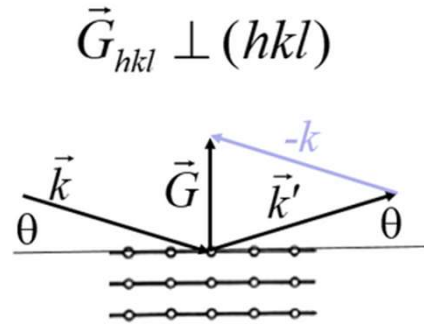
**Structure factors**

The value of  $|n_{\vec{G}}|$  for the 000 diffraction peak is the total number of electrons in the primitive unit cell. The intensities of the peaks in an x-ray diffraction experiment

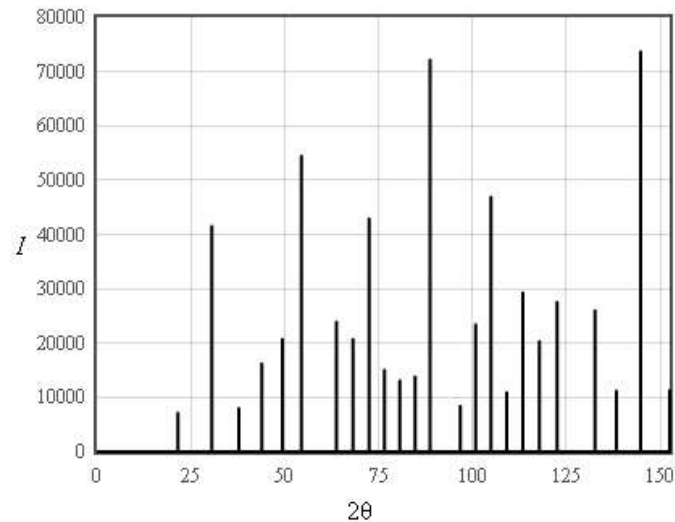
$hkl$	$ \vec{G}  \text{ \AA}^{-1}$	$ n_{\vec{G}} $	$ n_{\vec{G}} ^2$	$\text{Re}\{n_{\vec{G}}\}$	$\text{Im}\{n_{\vec{G}}\}$
000	0.000	72.00	5184	72.00	0.000
-100	1.525	34.43	1185	34.43	5.333e-8
0-10	1.525	34.43	1185	34.43	5.333e-8
00-1	1.525	34.43	1185	34.43	5.333e-8
001	1.525	34.43	1185	34.43	-5.333e-8

## Powder diffraction

For powder diffraction, a crystal is ground into a fine powder so that there are many small crystals with random orientations. X-rays strike the surface of the sample at an angle  $\theta$  and an x-ray detector is placed at an angle  $\theta$  to the surface. Only planes parallel to the surface will diffract x-rays to the detector.



Since there are many small crystals with random orientations in the sample, all possible crystal planes that can diffract the x-rays will contribute to the measured signal when  $\theta$  satisfies the Bragg condition. The form below can calculate the powder diffraction pattern for any crystal with up to five atoms per primitive unit cell. Some buttons are provided that load the form with the data for certain crystals.



### Primitive lattice vectors:

$$\begin{aligned} \vec{a}_1 &= 4.12\text{E-}10 \hat{x} + 0 \hat{y} + 0 \hat{z} \text{ [m]} \\ \vec{a}_2 &= 0 \hat{x} + 4.12\text{E-}10 \hat{y} + 0 \hat{z} \text{ [m]} \\ \vec{a}_3 &= 0 \hat{x} + 0 \hat{y} + 4.12\text{E-}10 \hat{z} \text{ [m]} \end{aligned}$$

### Basis:

The positions of the atoms are given in fractional coordinates between -1 and 1.

Cs1+	0	$\vec{a}_1 +$	0	$\vec{a}_2 +$	0	$\vec{a}_3$
Cl1-	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2 +$	0.5	$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$

X-ray wavelength  $\lambda$  [Å] = 1.540598 Cu K $\alpha$

submit

Al (fcc)

NaCl (fcc)

CsCl (sc)

SrTiO<sub>3</sub> (perovskite, sc)

GaAs (Zincblend, fcc)

GaN (Wurtzite, hex)

# Powder diffraction

---

## **Phase identification**

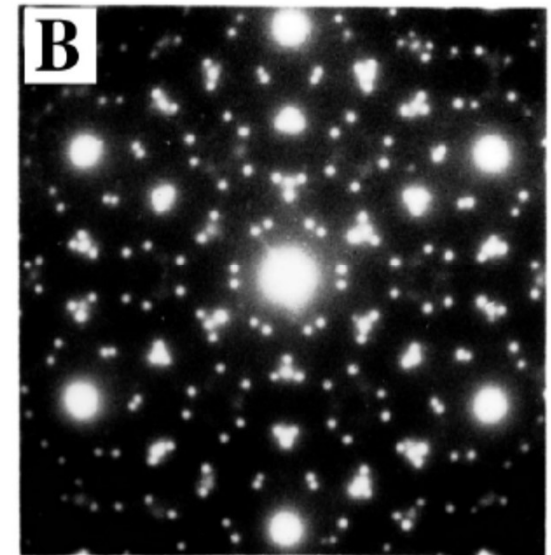
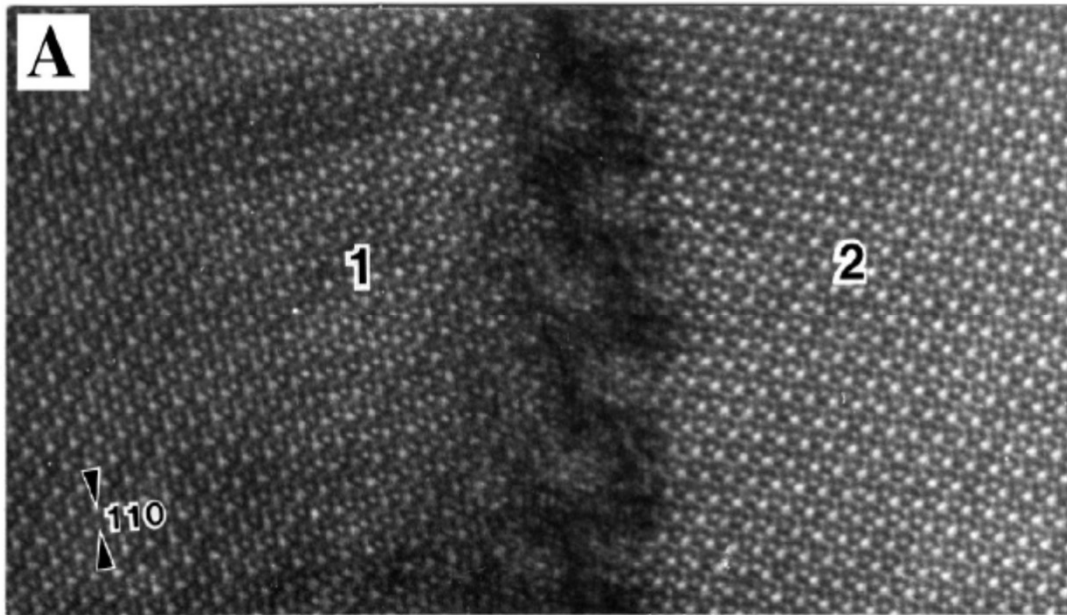
Every crystal has a specific "fingerprint" given by the positions and intensities of the diffraction peaks. The composition of a multi-phase specimen can be determined by fitting its diffraction pattern to the diffraction patterns of pure crystals which can be looked up in a database.

**International Centre for Diffraction Data** [www.icdd.com](http://www.icdd.com)  
1143236 (2022) reference materials

Phase transitions, thermal expansion, piezoelectricity, piezomagnetism, bulk modulus, compliance tensor can be measured.

# Electron diffraction in a TEM

---



The wavelength of the electrons is typically much smaller than the lattice spacing. The diffraction peaks in the plane perpendicular to  $k$  are observed.

## Electron diffraction

In electron diffraction, the intensity of a diffraction peak at reciprocal lattice vector  $\vec{G}$  is the square of the structure factor,  $n_{\vec{G}}$ .

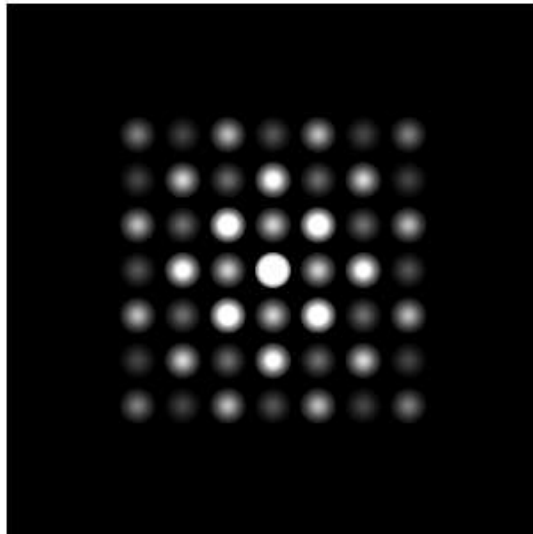
$$n_{\vec{G}} = \frac{1}{V} \sum_j f_j(\vec{G}) e^{-i\vec{G} \cdot \vec{r}_j} = \frac{1}{V} \sum_j f_j(\vec{G}) \left( \cos(\vec{G} \cdot \vec{r}_j) - i \sin(\vec{G} \cdot \vec{r}_j) \right)$$

Here  $V$  is the volume of the primitive unit cell,  $j$  sums over the atoms in the basis,  $\vec{r}_j$  are the positions of the atoms in the basis, and  $f_j(\vec{G})$  are the electron atomic form factors evaluated at  $\vec{G}$ .

The form below calculates the electron structure factors based on this formula. The crystal structure is specified by providing the primitive lattice vectors and the positions of the atoms in the basis. A basis of up to five atoms can be calculated. The script first calculates the primitive reciprocal lattice vectors and from them calculates the reciprocal lattice vectors  $\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ .

On this page, the direction of the incoming electrons is given in terms of the primitive lattice vectors in reciprocal space,  $H\vec{b}_1 + K\vec{b}_2 + L\vec{b}_3$ . Usually the direction of the incoming electrons are given in terms of the conventional lattice vectors. Be aware that the [100] is a (usually) different direction if primitive lattice vectors are used than if conventional lattice vectors are used.

H:  K:  L:



[010] →

**Primitive lattice vectors:**

$$\begin{aligned} \vec{a}_1 &= 4.12\text{E-}10 \hat{x} + 0 \hat{y} + 0 \hat{z} \text{ [m]} \\ \vec{a}_2 &= 0 \hat{x} + 4.12\text{E-}10 \hat{y} + 0 \hat{z} \text{ [m]} \\ \vec{a}_3 &= 0 \hat{x} + 0 \hat{y} + 4.12\text{E-}10 \hat{z} \text{ [m]} \end{aligned}$$

**Basis:**

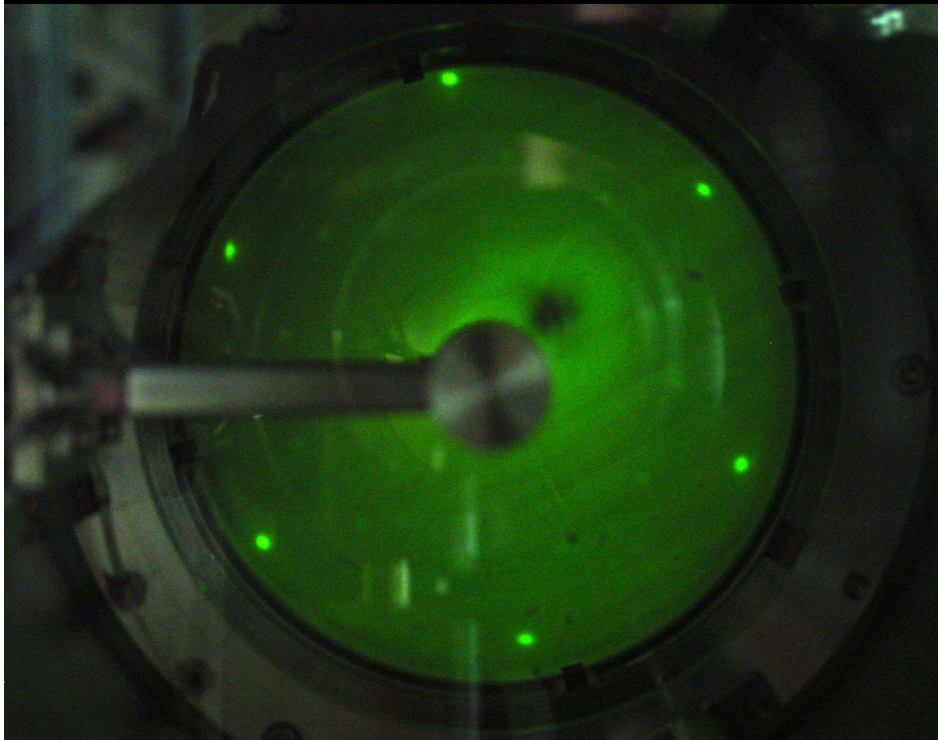
The positions of the atoms are given in fractional coordinates between -1 and 1.

Cs	<input type="text" value="0"/>	$\vec{a}_1 +$	<input type="text" value="0"/>	$\vec{a}_2 +$	<input type="text" value="0"/>	$\vec{a}_3$
Cl	<input type="text" value="0.5"/>	$\vec{a}_1 +$	<input type="text" value="0.5"/>	$\vec{a}_2 +$	<input type="text" value="0.5"/>	$\vec{a}_3$
<input type="text"/>	<input type="text"/>	$\vec{a}_1 +$	<input type="text"/>	$\vec{a}_2 +$	<input type="text"/>	$\vec{a}_3$
<input type="text"/>	<input type="text"/>	$\vec{a}_1 +$	<input type="text"/>	$\vec{a}_2 +$	<input type="text"/>	$\vec{a}_3$
<input type="text"/>	<input type="text"/>	$\vec{a}_1 +$	<input type="text"/>	$\vec{a}_2 +$	<input type="text"/>	$\vec{a}_3$

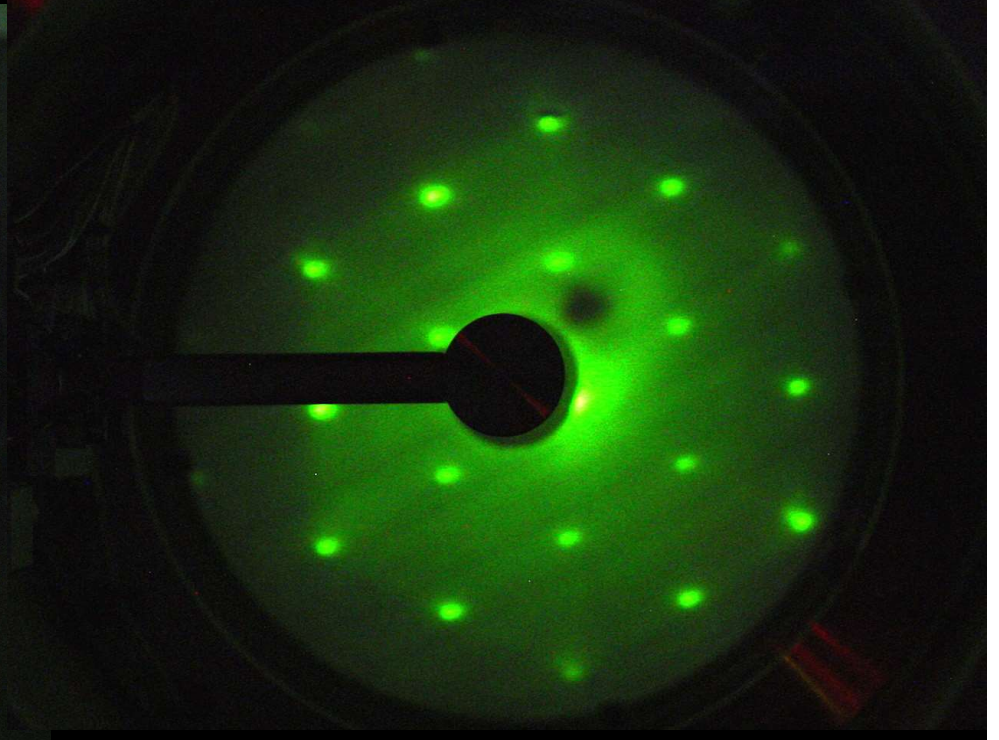
# LEED

Low Energy Electron Diffraction

$$100 \text{ V} \rightarrow k \sim 5 \times 10^{10} \text{ m}^{-1}$$



Clean Pd (111)



Pd (111) + 0.3 ML VO<sub>x</sub>

LEED is surface sensitive



# LEED

Energy of the electron beam:  [eV]






Primitive lattice vectors:

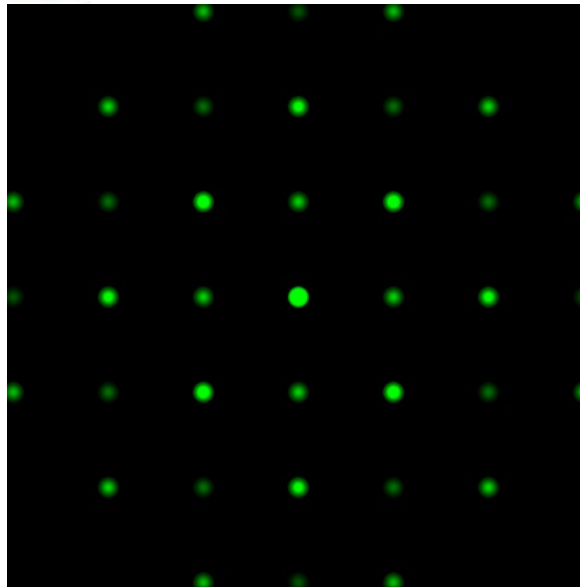
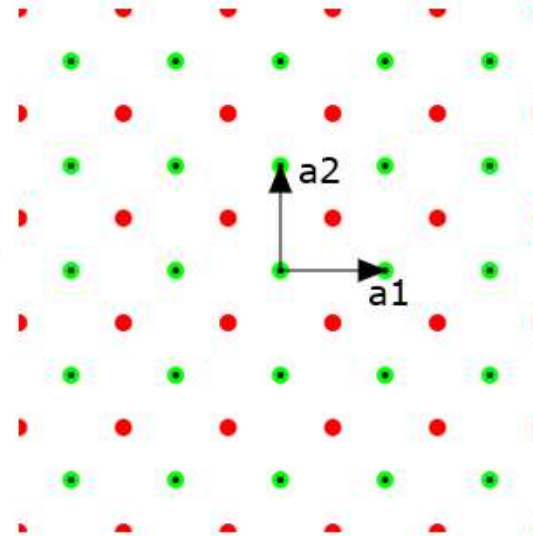
$$\vec{a}_1 = \begin{matrix} 4.12\text{E-}10 & \hat{x} + 0 \\ 0 & \hat{y} \end{matrix} \text{ [m]}$$

$$\vec{a}_2 = \begin{matrix} 0 & \hat{x} + 4.12\text{E-}10 \\ 0 & \hat{y} \end{matrix} \text{ [m]}$$

Basis:

The positions of the atoms are given in fractional coordinates between -1 and 1.

Cs	<input type="text" value="0"/>	$\vec{a}_1 +$	<input type="text" value="0"/>	$\vec{a}_2$	
Cl	<input type="text" value="0.5"/>	$\vec{a}_1 +$	<input type="text" value="0.5"/>	$\vec{a}_2$	
	<input type="text"/>	$\vec{a}_1 +$	<input type="text"/>	$\vec{a}_2$	
	<input type="text"/>	$\vec{a}_1 +$	<input type="text"/>	$\vec{a}_2$	
	<input type="text"/>	$\vec{a}_1 +$	<input type="text"/>	$\vec{a}_2$	



# Forbidden reflections

Primitive lattice vectors:

$$\vec{a}_1 = 4.12\text{E-}10 \hat{x} + 0 \hat{y} \text{ [m]}$$

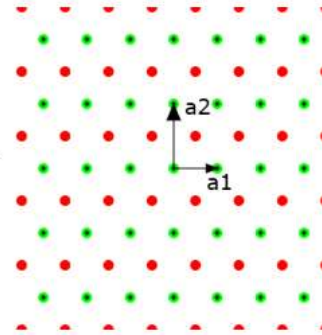
$$\vec{a}_2 = 0 \hat{x} + 6.12\text{E-}10 \hat{y} \text{ [m]}$$

Basis:

The positions of the atoms are given in fractional coordinates between -1 and 1.

C	0	$\vec{a}_1 + 0$	$\vec{a}_2$	
C	0.5	$\vec{a}_1 + 0.5$	$\vec{a}_2$	
	0.2	$\vec{a}_1 + 0.3$	$\vec{a}_2$	
		$\vec{a}_1 +$	$\vec{a}_2$	
		$\vec{a}_1 +$	$\vec{a}_2$	

submit



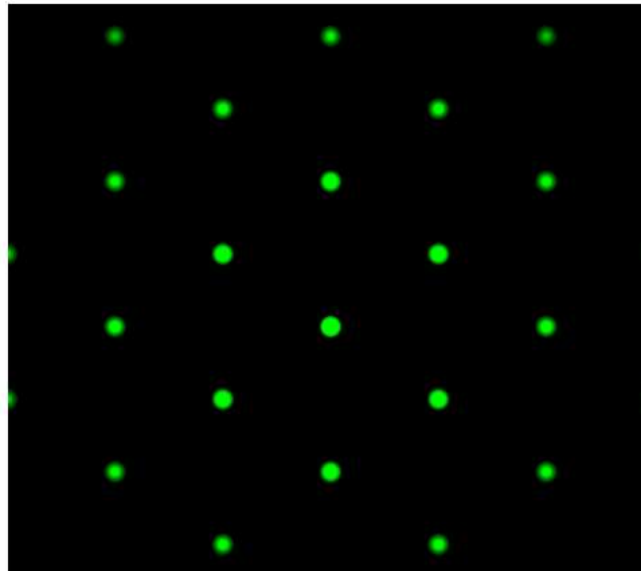
Primitive reciprocal lattice vectors

$$\vec{b}_1 = 2\pi \frac{R \vec{a}_2}{\vec{a}_1 R \vec{a}_2} = 1.525\text{e+}10 \hat{k}_x + 0.000 \hat{k}_y \text{ [m}^{-1}\text{]}$$

$$\vec{b}_2 = 2\pi \frac{R \vec{a}_1}{\vec{a}_1 R \vec{a}_2} = 0.000 \hat{k}_x + -1.027\text{e+}10 \hat{k}_y \text{ [m}^{-1}\text{]}$$

with  $R = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$

Low Energy  
Electron Diffraction



# Forbidden reflections

$$n_{u.c.}(\vec{r}) = \sum_j Z_j \delta(\vec{r} - \vec{r}_j)$$

## Primitive reciprocal lattice vectors

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 3.939 \hat{k}_x + -2.275e+10 \hat{k}_y + 0.000 \hat{k}_z [\text{m}^{-1}] \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 3.939 \hat{k}_x + 2.275 \hat{k}_y + 0.000 \hat{k}_z [\text{m}^{-1}] \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = 0.000 \hat{k}_x + 0.000 \hat{k}_y + 1.212e+10 \hat{k}_z [\text{m}^{-1}] \end{aligned}$$

$$n_{\vec{G}} = \sum_j Z_j \exp(-i\vec{G} \cdot \vec{r}_j)$$

## Structure factors

The value of  $|n_{\vec{G}}|$  for the 000 diffraction peak is the total number of electrons in the primitive unit cell. The intensities of the peaks in an x-ray diffraction experiment are proportional to  $|n_{\vec{G}}|^2$ . Note that elements with more electrons produce stronger diffraction intensities.

$hkl$	$ \vec{G}  \text{ \AA}^{-1}$	$ n_{\vec{G}} $	$ n_{\vec{G}} ^2$	$\text{Re}\{n_{\vec{G}}\}$	$\text{Im}\{n_{\vec{G}}\}$
000	0.000	75.94	5767	75.94	0.000
0-10	4.549e-10	37.87	1434	-37.87	0.02201
010	4.549e-10	37.87	1434	-37.87	-0.02201
0-20	9.098e-10	38.17	1457	-38.17	0.04379
020	9.098e-10	38.17	1457	-38.17	-0.04379
0-30	1.365e-9	75.94	5767	75.94	-0.1318
030	1.365e-9	75.94	5767	75.94	0.1318
0-3-1	1.212	0.3909	0.1528	0.02780	0.3899
0-31	1.212	0.3914	0.1532	-0.02727	0.3904
0-2-1	1.212	42.85	1836	-7.648	42.16
0-21	1.212	42.74	1827	7.551	42.07
0-1-1	1.212	43.01	1850	7.610	-42.33
0-11	1.212	42.96	1845	-7.561	-42.29
00-1	1.212	8.896e-8	7.914e-15	-1.573e-8	8.756e-8
001	1.212	8.896e-8	7.914e-15	-1.573e-8	-8.756e-8
01-1	1.212	42.96	1845	-7.561	42.29
011	1.212	43.01	1850	7.610	42.33
02-1	1.212	42.74	1827	7.551	-42.07
021	1.212	42.85	1836	-7.648	-42.16
03-1	1.212	0.3914	0.1532	-0.02727	-0.3904

# Neutron diffraction

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Typically a nuclear reactor is used as the neutron source

There are different atomic form factors for neutrons than for x-rays.

Determine the positions of H in biological samples.

Can for example distinguish between Fe and Co which have similar atomic form factors for x-rays.

## Structure factor for neutrons

The structure factor for neutrons can be calculated with the following formula,

$$F_{\vec{G}} = \sum_j b_j e^{-i\vec{G}\cdot\vec{r}_j} = \sum_j b_j \left( \cos(\vec{G}\cdot\vec{r}_j) - i \sin(\vec{G}\cdot\vec{r}_j) \right).$$

where  $\vec{r}_j$  defines the position of the atom  $j$  and  $\vec{G}$  is the reciprocal lattice vector.  $b_j$  is called the neutron scattering length, it depends on the spin-state of the neutron-nucleus system and the isotope the neutron is scattered from. The scattering lengths can be looked up at the [NIST Center for Neutron Research](http://www.nsl.jrnl.gov/Research/Structure_Factors/).

The form below calculates the neutron structure factors. The script first calculates the reciprocal lattice vectors and from them calculates the reciprocal lattice vectors  $\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ . The structure factors are calculated for a few reciprocal lattice vectors and listed in a table.

### Primitive lattice vectors:

$$\begin{aligned} \vec{a}_1 &= 4.12\text{E-}10 \hat{x} + 0 \hat{y} + 0 \hat{z} \text{ [m]} \\ \vec{a}_2 &= 0 \hat{x} + 4.12\text{E-}10 \hat{y} + 0 \hat{z} \text{ [m]} \\ \vec{a}_3 &= 0 \hat{x} + 0 \hat{y} + 4.12\text{E-}10 \hat{z} \text{ [m]} \end{aligned}$$

### Basis:

The positions of the atoms are given in fractional coordinates between -1 and 1.

Pb	▼	0	$\vec{a}_1 +$	0	$\vec{a}_2 +$	0	$\vec{a}_3$
Ti	▼	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2 +$	0.5	$\vec{a}_3$
O	▼	0	$\vec{a}_1 +$	0.5	$\vec{a}_2 +$	0.5	$\vec{a}_3$
O	▼	0.5	$\vec{a}_1 +$	0	$\vec{a}_2 +$	0.5	$\vec{a}_3$
O	▼	0.5	$\vec{a}_1 +$	0.5	$\vec{a}_2 +$	0	$\vec{a}_3$
	▼		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
	▼		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$
	▼		$\vec{a}_1 +$		$\vec{a}_2 +$		$\vec{a}_3$

submit

# Atomic beams

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Hydrogen and Helium are used for diffraction studies

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

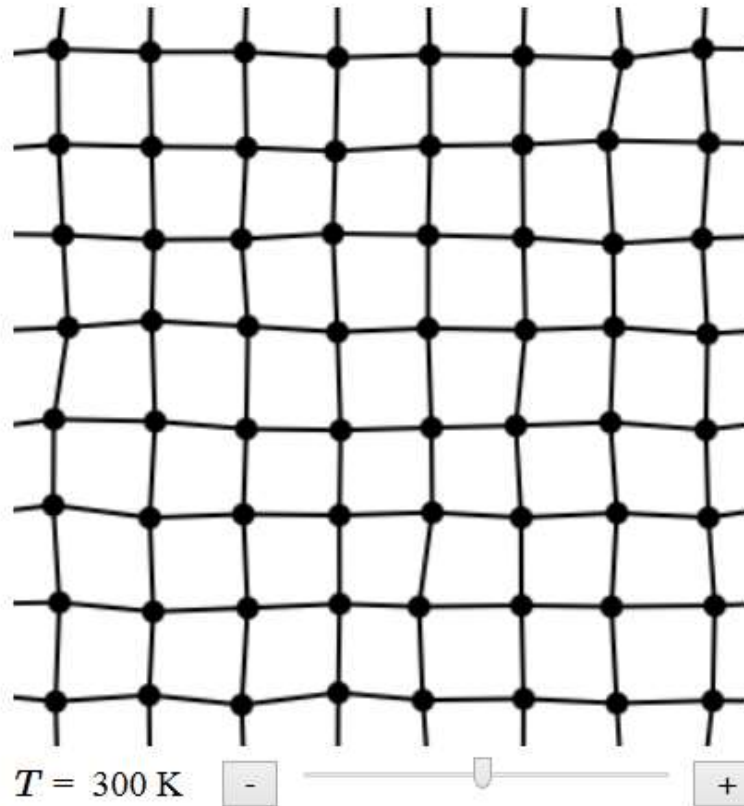
Low energies can be used for delicate samples.  
Measure the surface like LEED.

# Phonons

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## Normal Modes and Phonons

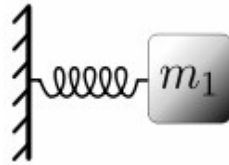
At finite temperatures, the atoms in a crystal vibrate. In the simulation below, the atoms move randomly around their equilibrium positions.





# Vibrations of a mass on a spring

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$$m \frac{d^2 x}{dt^2} = -Cx$$

The solution has the form

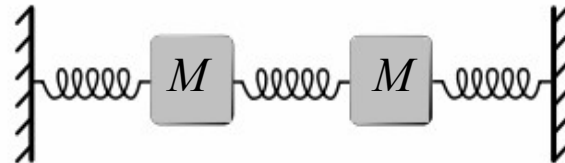
$$x = Ae^{-i\omega t}$$

$$-\omega^2 mAe^{-i\omega t} = -CAe^{-i\omega t}$$

$$\omega = \sqrt{\frac{C}{m}}$$

# Coupled masses

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Newton's law

$$M \frac{d^2 x_1}{dt^2} = -Cx_1 + C(x_2 - x_1)$$

$$M \frac{d^2 x_2}{dt^2} = -Cx_2 + C(x_1 - x_2)$$

assume harmonic solutions

$$x_1(t) = A_1 \exp(i\omega t)$$

$$x_2(t) = A_2 \exp(i\omega t)$$

$$-\omega^2 M A_1 e^{i\omega t} = -2C A_1 e^{i\omega t} + C A_2 e^{i\omega t}$$

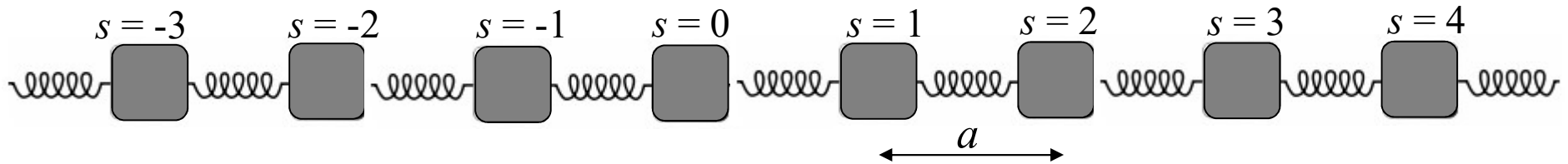
$$-\omega^2 M A_2 e^{i\omega t} = -2C A_2 e^{i\omega t} + C A_1 e^{i\omega t}$$

$$-\omega^2 M \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} -2C & C \\ C & -2C \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix}$$

Find the eigenvectors of this matrix

The masses oscillate with the same frequency but different phases

# Linear Chain



$$m \frac{d^2 u_s}{dt^2} = C(u_{s+1} - u_s) - C(u_s - u_{s-1}) = C(u_{s+1} - 2u_s + u_{s-1})$$

Assume every atom oscillates with the same frequency  $u_s = A_s e^{-i\omega t}$

$$\begin{bmatrix} 2C - \omega^2 m & -C & 0 & 0 & 0 & -C \\ -C & 2C - \omega^2 m & -C & 0 & 0 & 0 \\ 0 & -C & 2C - \omega^2 m & -C & 0 & 0 \\ 0 & 0 & -C & 2C - \omega^2 m & -C & 0 \\ 0 & 0 & 0 & -C & 2C - \omega^2 m & -C \\ -C & 0 & 0 & 0 & -C & 2C - \omega^2 m \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{bmatrix} = 0$$

$$\left[ (2C - \omega^2 m) \mathbf{I} - C(\mathbf{T} + \mathbf{T}^{-1}) \right] \vec{A} = 0.$$

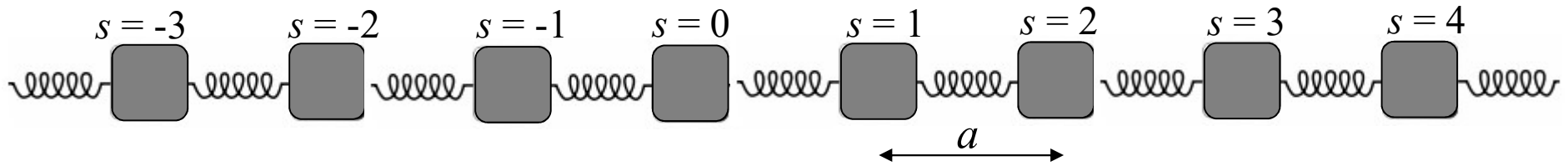
# Eigen vectors of the translation operator

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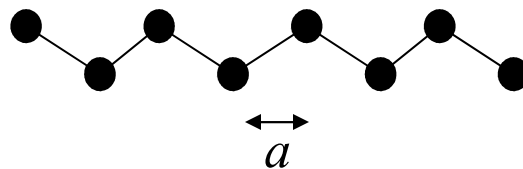
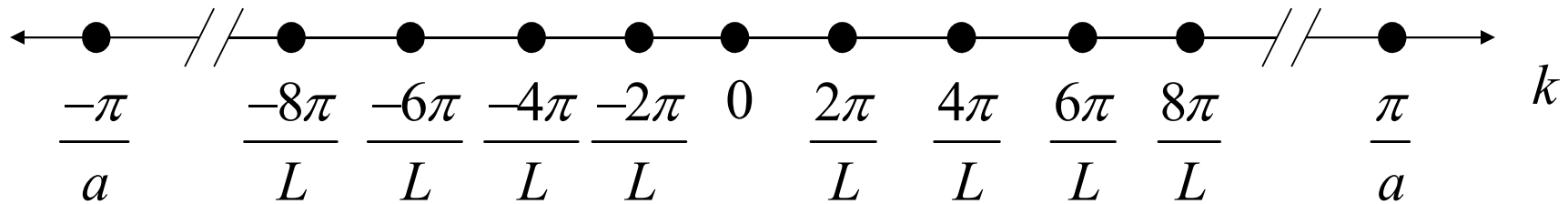
$$T = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ e^{i2\pi j/N} \\ e^{i4\pi j/N} \\ e^{i4\pi j/N} \\ \vdots \\ e^{i2\pi(N-1)j/N} \end{bmatrix} \quad j = 1, \dots, N$$

$$\begin{bmatrix} 1 \\ e^{ika} \\ e^{i2ka} \\ e^{i3ka} \\ \vdots \\ e^{-ika} \end{bmatrix} \quad k = 0, \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \dots$$

# Linear Chain

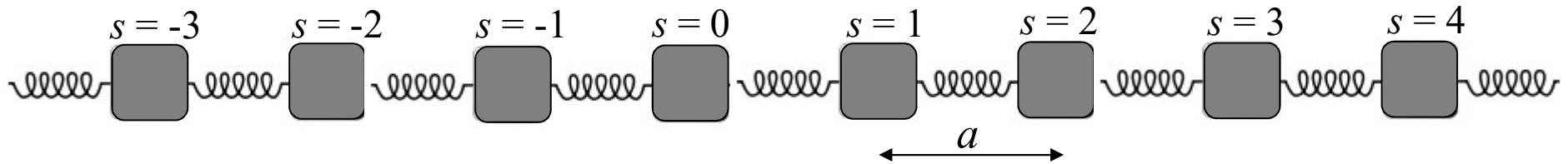


solution:  $u_s = A_k e^{i(ksa - \omega t)} = A_k e^{iksa} e^{-i\omega t}$



# Normal modes are eigen functions of T

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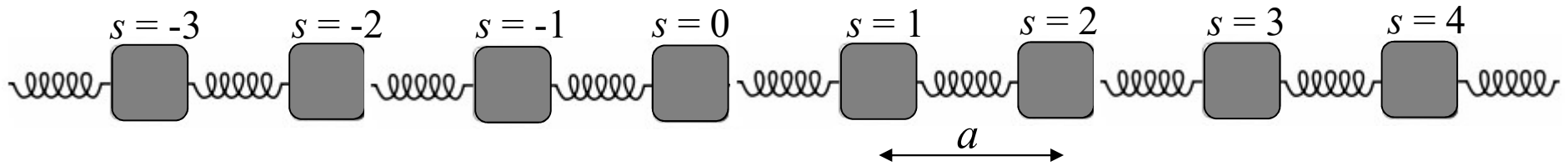
solutions are eigenfunctions of the translation operator

$$u_s = A_k e^{iksa} e^{-i\omega t} = A_k e^{i(ksa - \omega t)}$$

$$T u_s = A_k e^{i(k(s+1)a - \omega t)} = e^{ika} A_k e^{i(ksa - \omega t)} = e^{ika} u_s$$

$N$  atoms,  $N$  normal modes,  $N$  eigenvectors of the translation operator,  $N$  allowed values of  $k$  in the first Brillouin zone

# Linear Chain



$$m \frac{d^2 u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$$

solutions:  $u_s = A_k e^{i(ksa - \omega t)}$

$$-\omega^2 m e^{i(ksa - \omega t)} = C(e^{i(k(s+1)a - \omega t)} - 2e^{i(ksa - \omega t)} + e^{i(k(s-1)a - \omega t)})$$

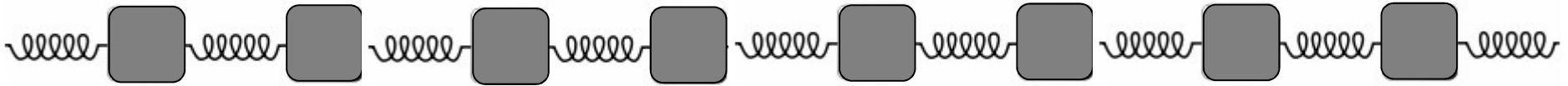
$$-\omega^2 m = C(e^{ika} - 2 + e^{-ika})$$

$$\omega^2 m = 2C(1 - \cos(ka))$$

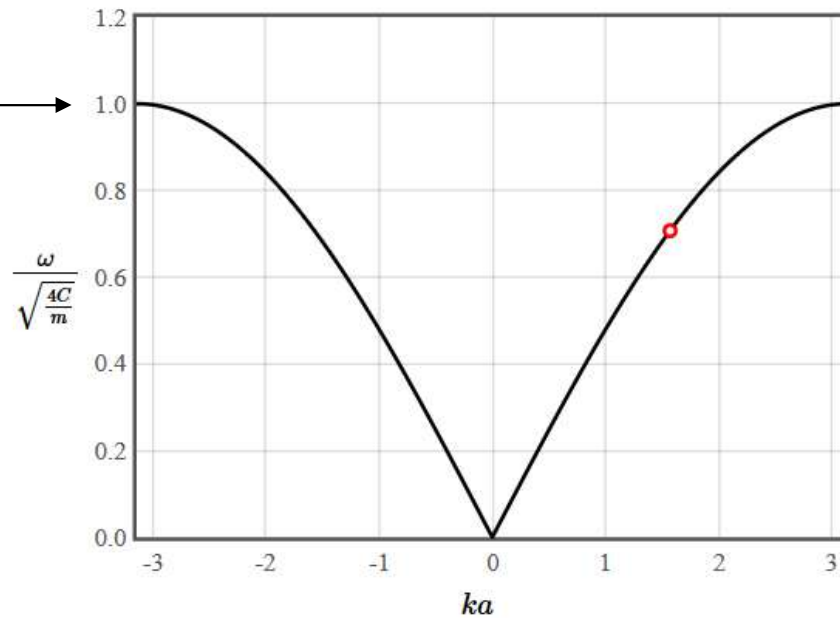
$$\sin^2 \frac{ka}{2} = \frac{1}{2}(1 - \cos ka)$$

$$\omega = \sqrt{\frac{4C}{m}} \left| \sin \left( \frac{ka}{2} \right) \right|$$

# Linear Chain - dispersion relation



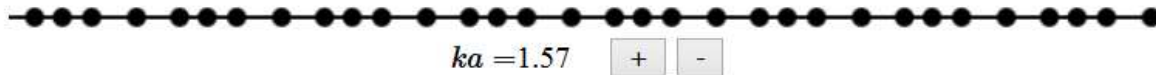
Max. freq. →



$$m \frac{d^2 u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$$

$$u_s = A_k e^{i(ksa - \omega t)}$$

$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$



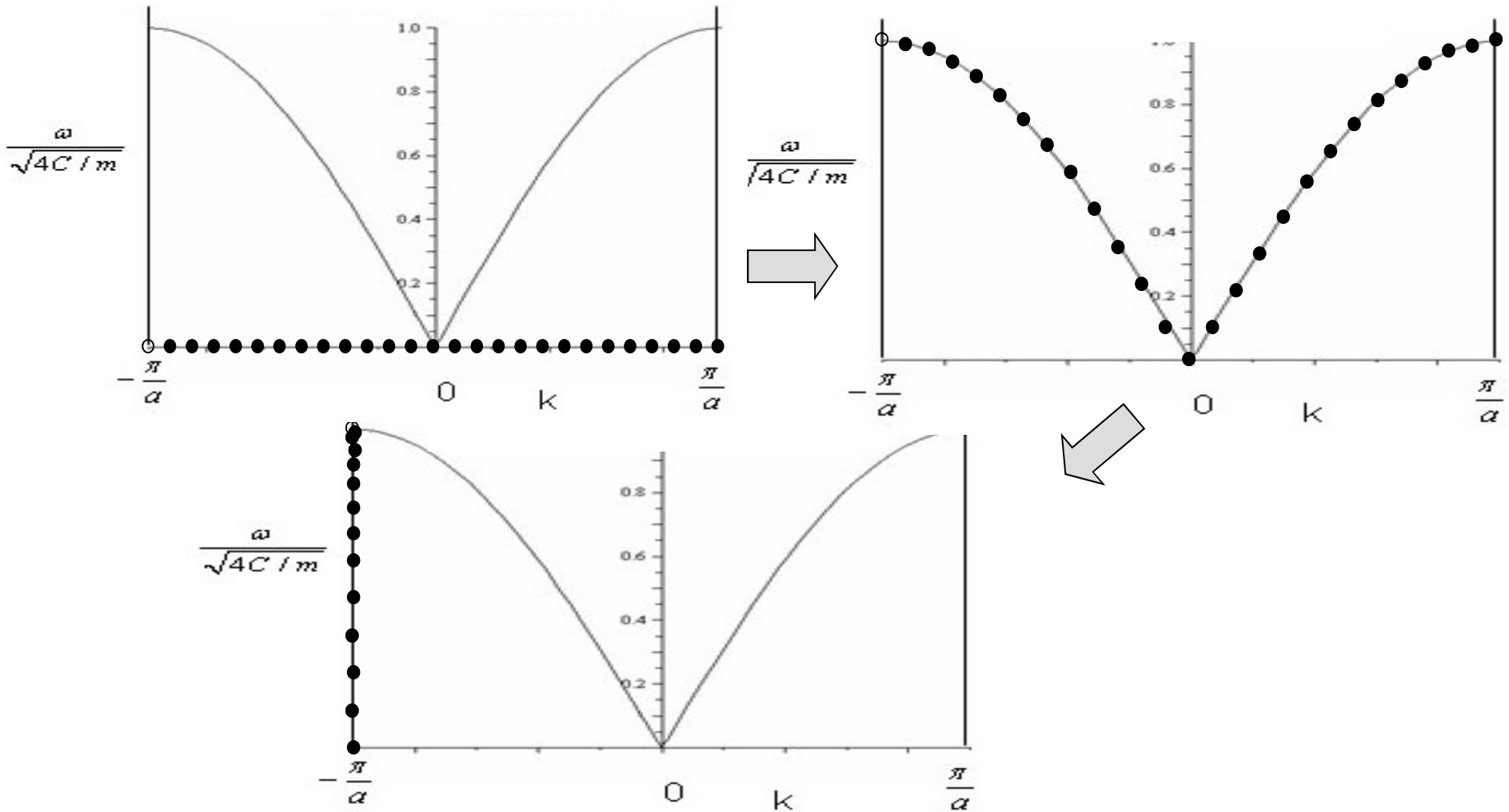
$$\text{speed of sound} = \sqrt{\frac{C}{m}} a$$



# Linear Chain - density of states

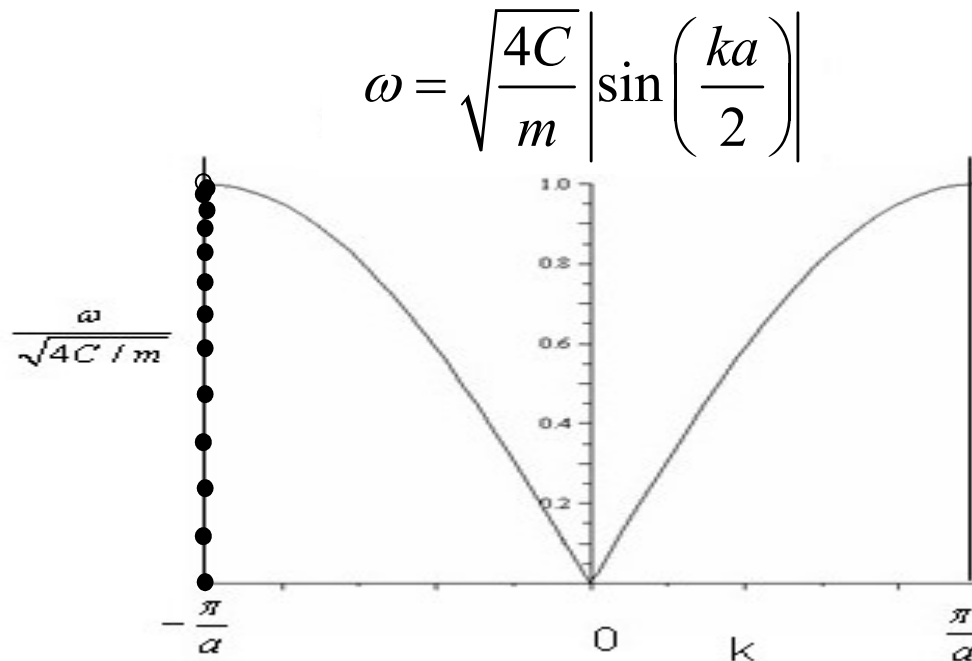
Determine the density of states numerically

$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$



# Linear Chain - density of states

This case is an exception where the density of states can be determined analytically.



for every  $k$  calculate the frequency

$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

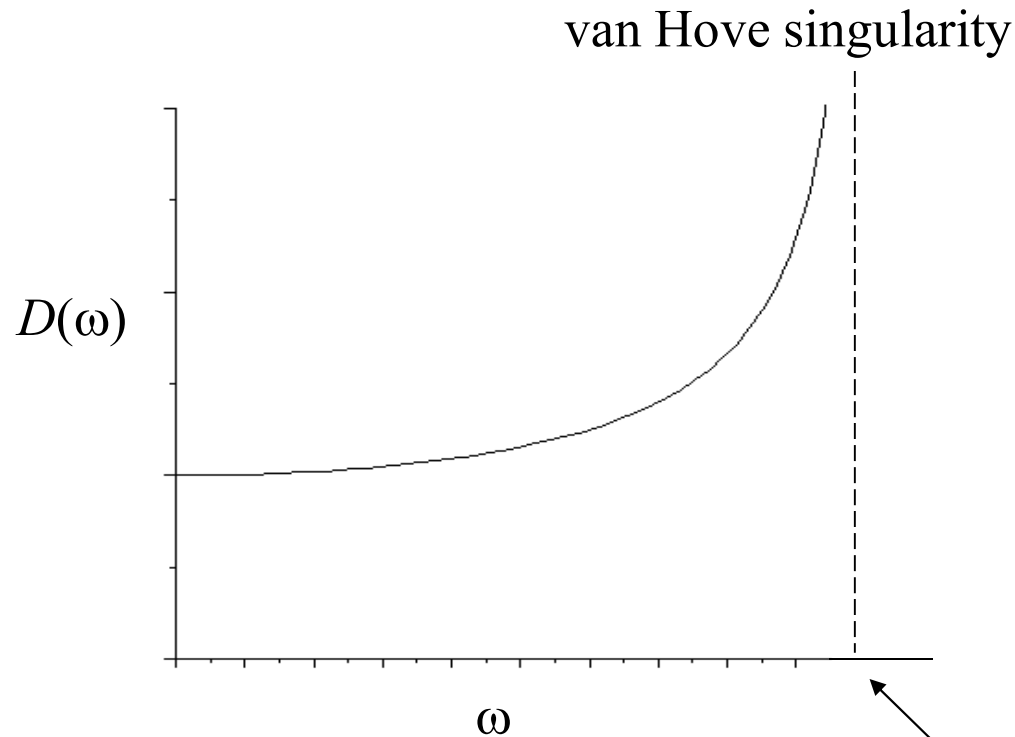
$$D(k) = \frac{1}{\pi}$$

$$D(\omega) = D(k) \frac{dk}{d\omega}$$

$$d\omega = a \sqrt{\frac{C}{m}} \cos\left(\frac{ka}{2}\right) dk$$

$$D(\omega) = \frac{1}{\pi a \sqrt{\frac{C}{m}} \sqrt{1 - \frac{\omega^2 m}{4C}}}$$

# density of states



$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

$$D(k) = \frac{1}{\pi}$$

$$D(k)dk = D(\omega)d\omega$$

$$d\omega = a \sqrt{\frac{C}{m}} \cos\left(\frac{ka}{2}\right) dk$$

$$D(\omega) = \frac{1}{\pi a \sqrt{\frac{C}{m}} \sqrt{1 - \frac{\omega^2 m}{4C}}}$$

maximum frequency