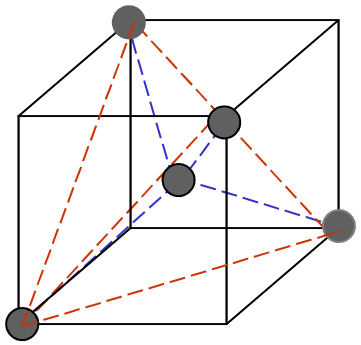
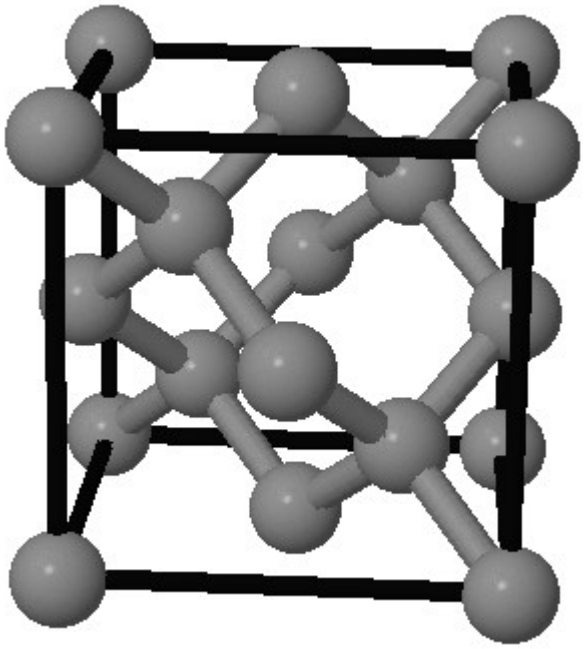
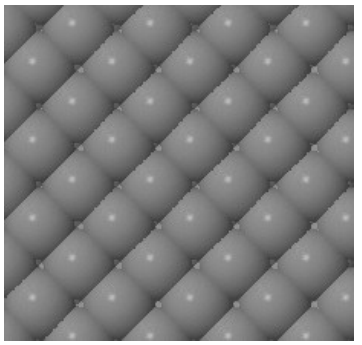
Diamond

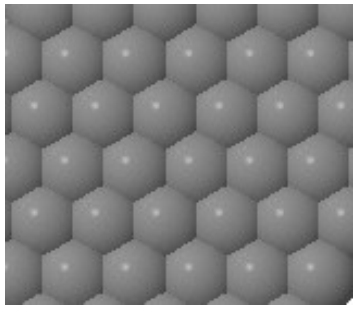


$$a = b = c, \quad \alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ$$





$$(100): \frac{2}{a^2}$$



$$(111): \frac{4}{\sqrt{3}a^2}$$

Space group: 227
point group: m3m

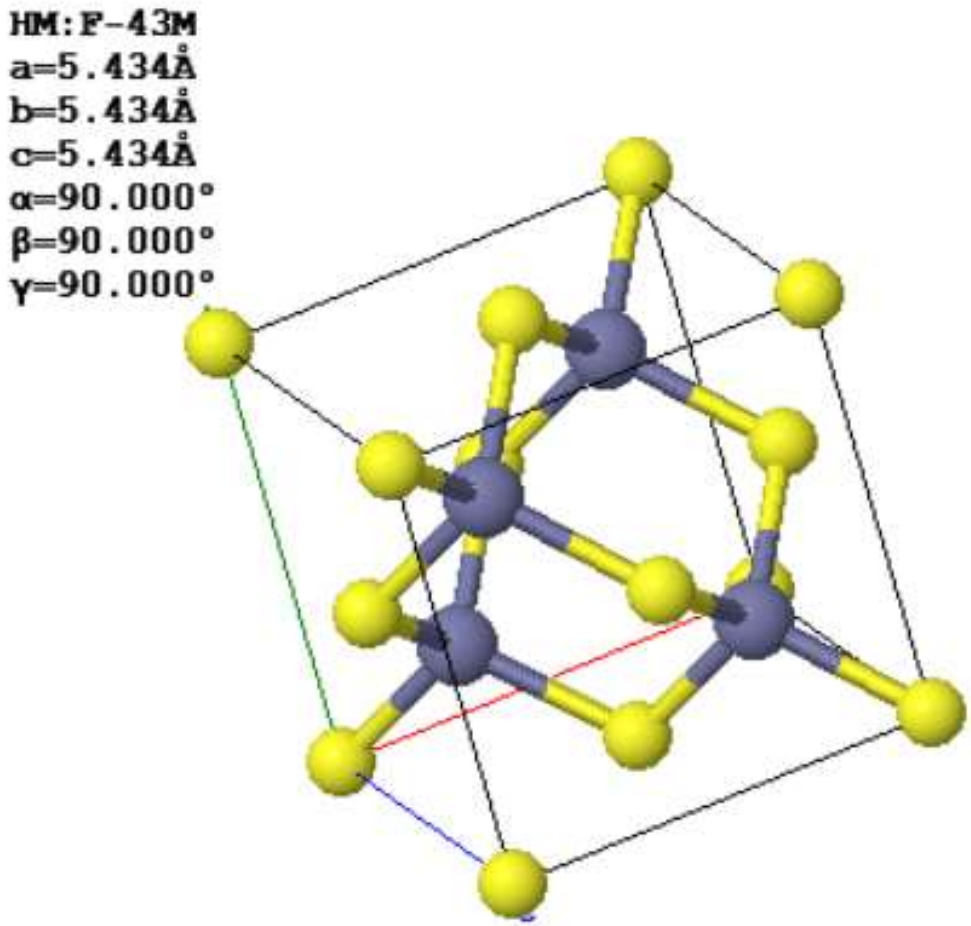
Primitive lattice vectors:

$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}, \qquad \vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}, \qquad \vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}.$$

Basis: $\vec{B}_1 = (0,0,0), \qquad \vec{B}_2 = (0.25, 0.25, 0.25).$

zincblende

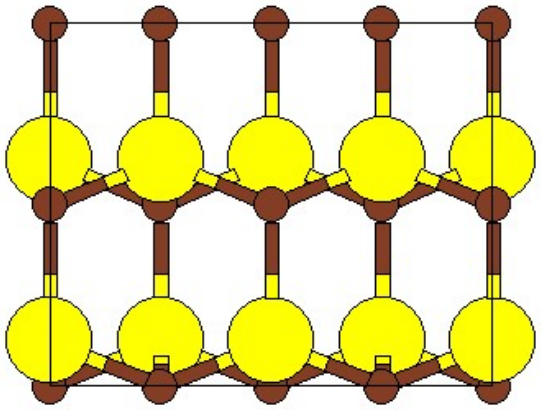
ZnS
GaAs
InP



space group 216
F$\bar{4}$3m

wurtzite

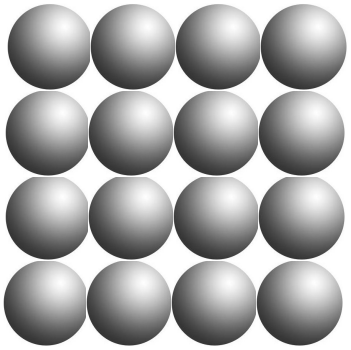
ZnS
ZnO
CdS
CdSe
GaN
AlN

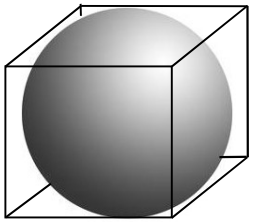


Number 186

There are 2 polytypes of ZnS: zincblende and wurtzite

atomic packing density



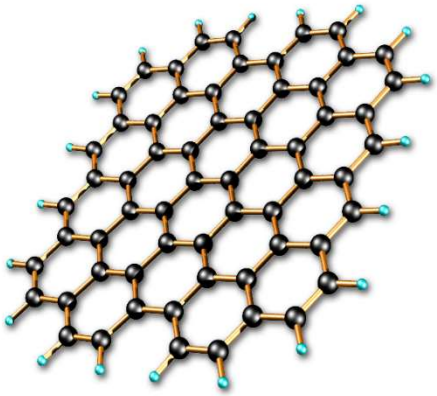


$$\frac{\frac{4}{3}\pi\left(L/2\right)^3}{L^3} = \frac{\pi}{6} \approx 0.52$$

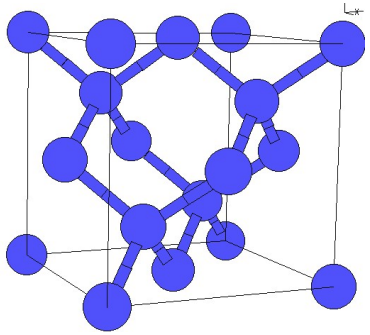
fcc, hcp = 0.74
random close pack = 0.64
simple cubic = 0.52
diamond = 0.34

Coordination number

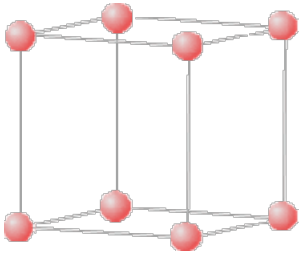
Number of nearest neighbors an atom has in a crystal



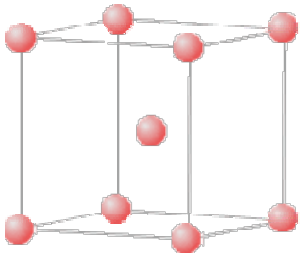
Graphene 3



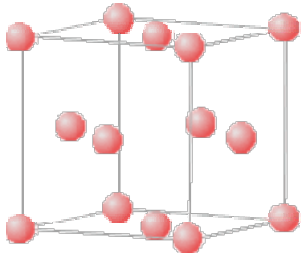
diamond 4



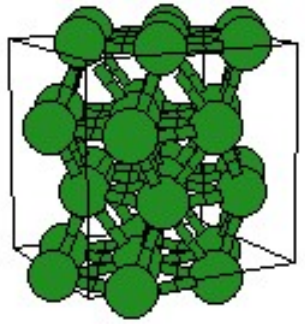
sc 6



bcc 8



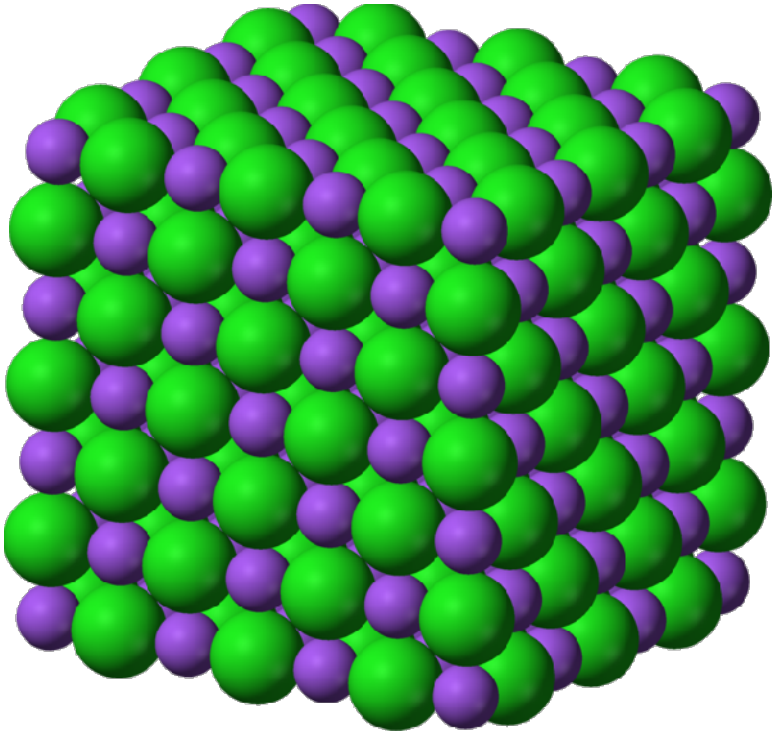
fcc 12



hcp 12

Ionic crystals

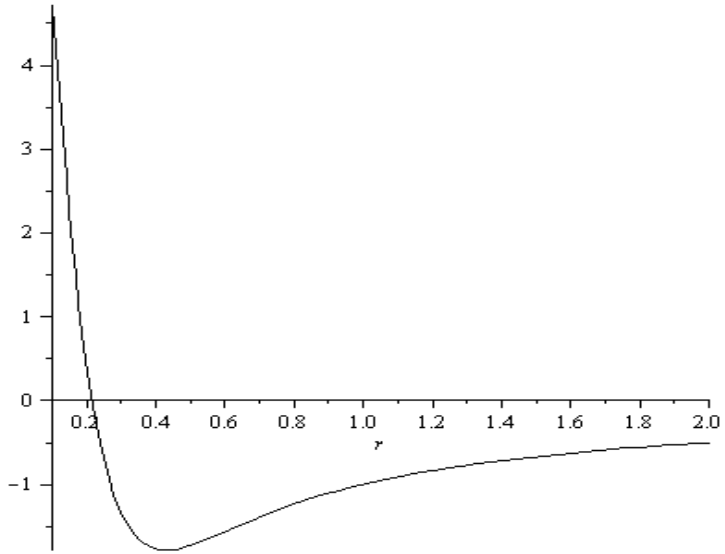
A crystal is a three dimensional periodic arrangement of atoms.



Read the first half of chapter 3 in Kittel

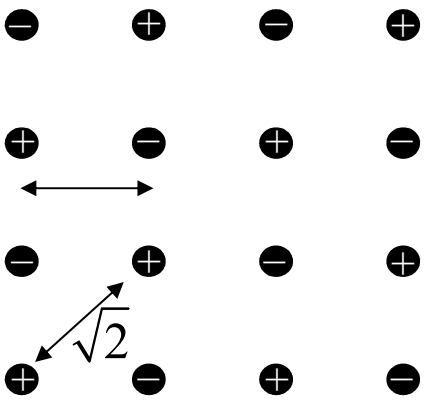
Ionic crystals

Nearest neighbors: $$U_{ij} = \lambda e^{-\frac{r_{ij}}{\rho}} - \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$



Distant neighbors: $$U_{ij} = \frac{\pm e^2}{4\pi\varepsilon_0 r_{ij}}$$

Ionic crystals



R = nearest neighbor separation

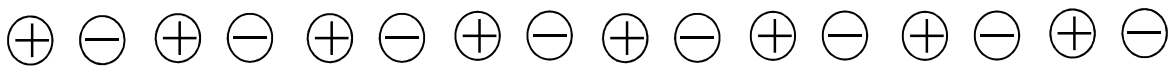
Ernst Madelung

$$U_{\text{ionic}} = -\frac{6e^2}{4\pi\epsilon_0 R} + \frac{8e^2}{4\pi\epsilon_0\sqrt{2}R} + \frac{6e^2}{4\pi\epsilon_0 2R} + \cdots$$

$$U_{\text{ionic}} = -\frac{e^2}{4\pi\epsilon_0 R}\left(6 - \frac{8}{\sqrt{2}} - 3 + \cdots\right)$$

α Madelung constant

Madelung constant in 1-D



$$\alpha = 2\left[1-\tfrac{1}{2}+\tfrac{1}{3}-\tfrac{1}{4}+\tfrac{1}{5}-\cdots\right]$$

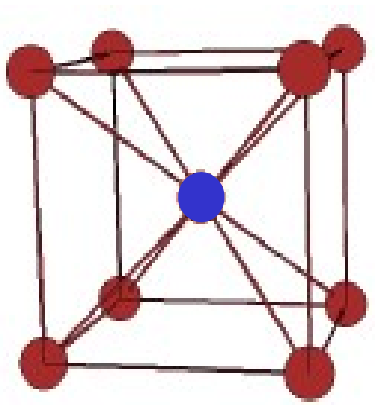
Taylor expansion: $\ln(1+x)=\left[x-\tfrac{x^2}{2}+\tfrac{x^3}{3}-\tfrac{x^4}{4}+\tfrac{x^5}{5}-\cdots\right]$

$$\ln(2)=\left[1-\tfrac{1}{2}+\tfrac{1}{3}-\tfrac{1}{4}+\tfrac{1}{5}-\cdots\right]$$

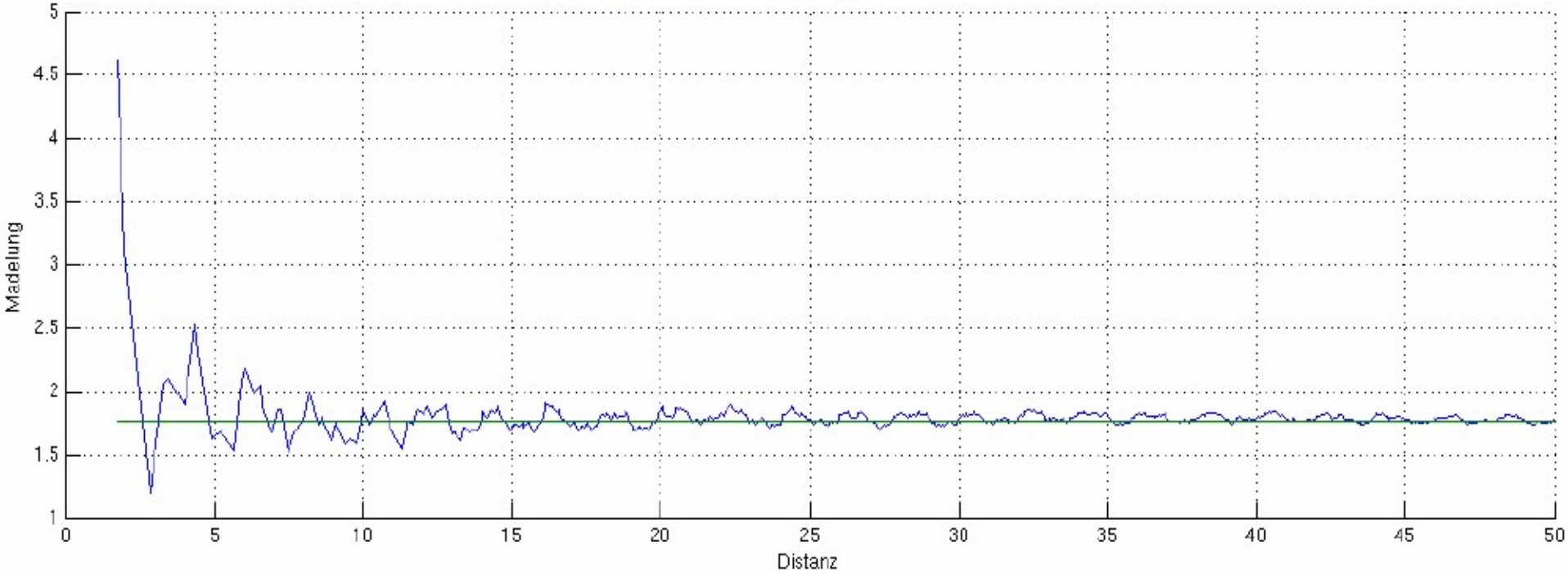
$$\alpha = 2\ln 2 = 1.38629436$$

Calculating the Madelung constant

CsCl
$z = 8$



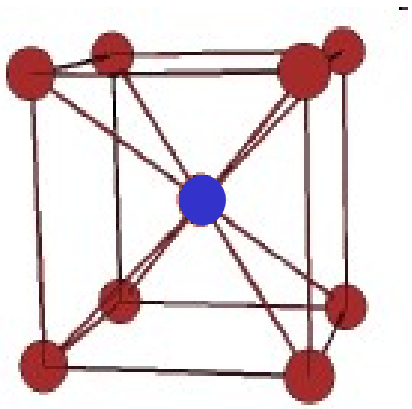
$\alpha = 1.767$



Iterative Bestimmung der Madelung-Konstante für CsCl - Yao Shan und Robert Krisper, 2010

Ionic Crystals

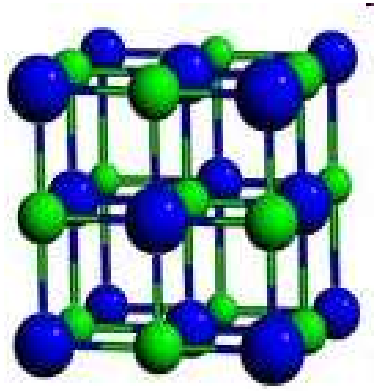
$\alpha = 1.767$



CsCl

$z = 8$

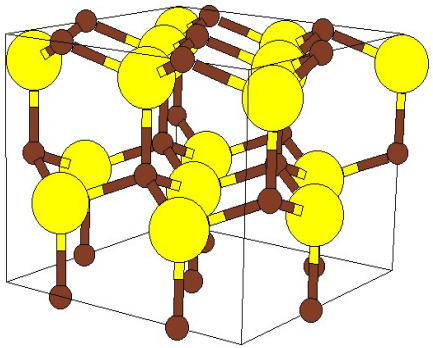
$\alpha = 1.747$



NaCl

$z = 6$

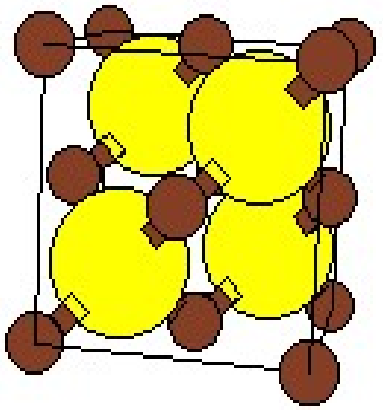
$\alpha = 1.641$



Wurtzite

$z = 4$

$\alpha = 1.638$

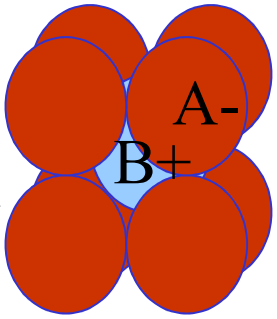


Zincblende

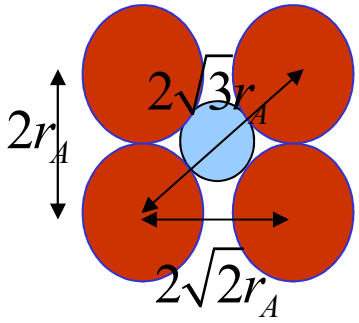
$z = 4$

Ionic radius

CsCl

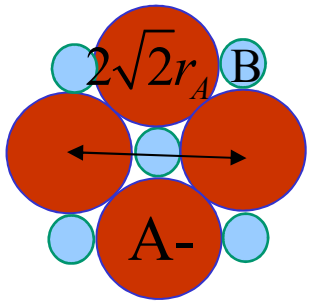


CsCl unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{3}-1} = 1.366$



CsCl 110 plane

NaCl



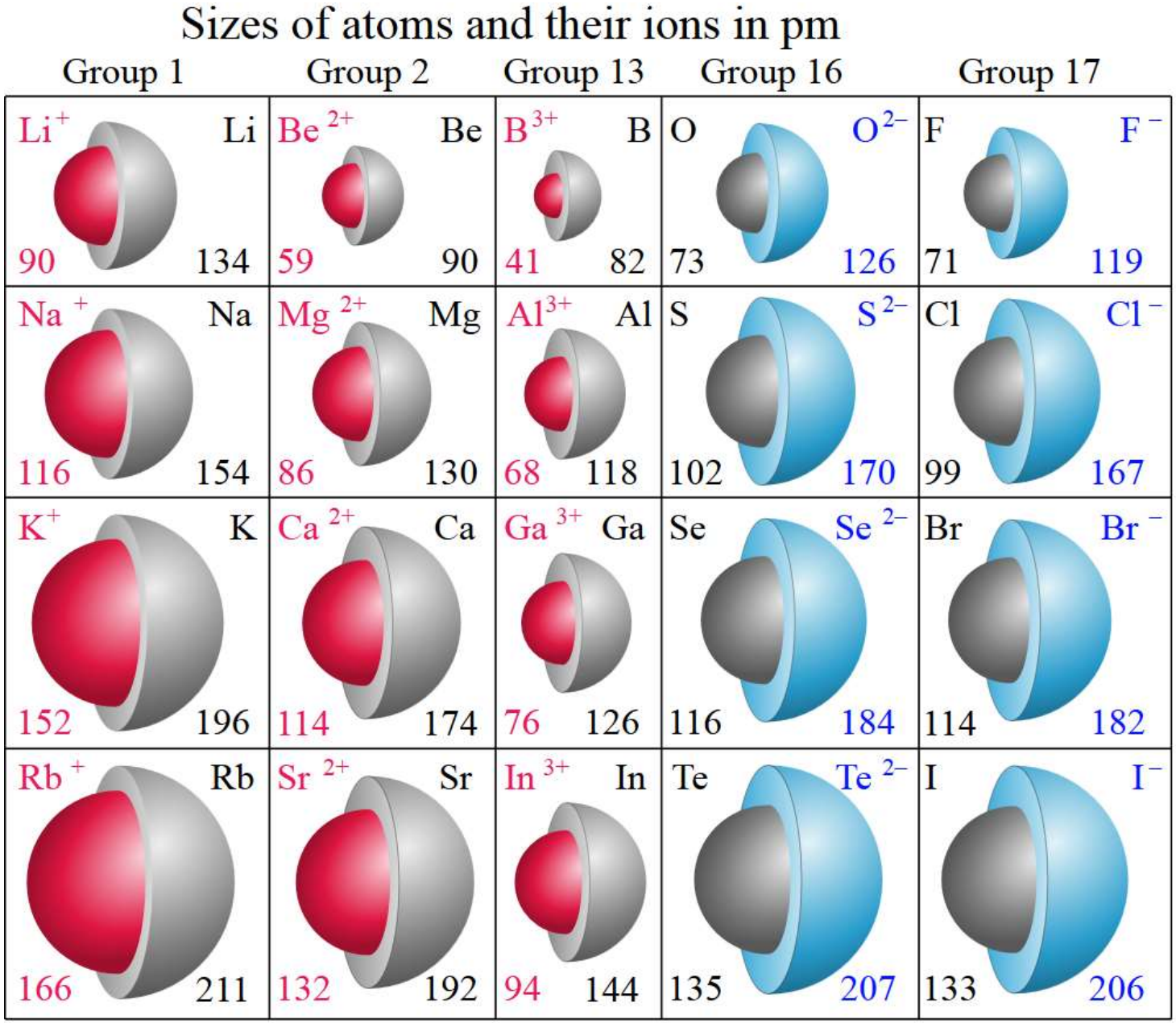
NaCl unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{2}-1} = 2.41$

NaCl 100 plane

CsCl:

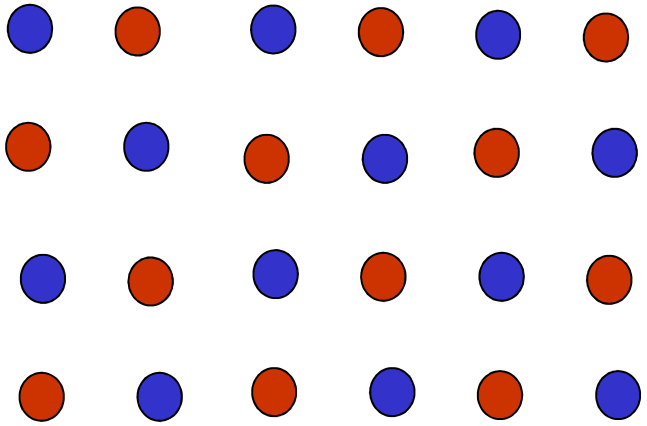
$\frac{r_A}{r_B} < 1.366$

$\frac{r_{Cl}}{r_{Na}} = 1.44$

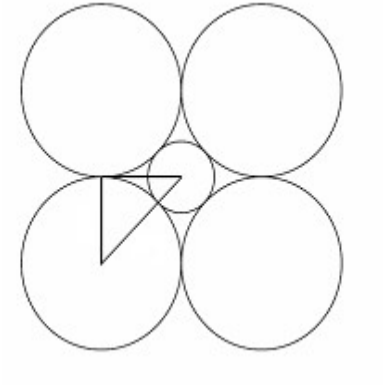


https://en.wikipedia.org/wiki/Ionic_radius#/media/File:Atomic_%26_ionic_radii.svg

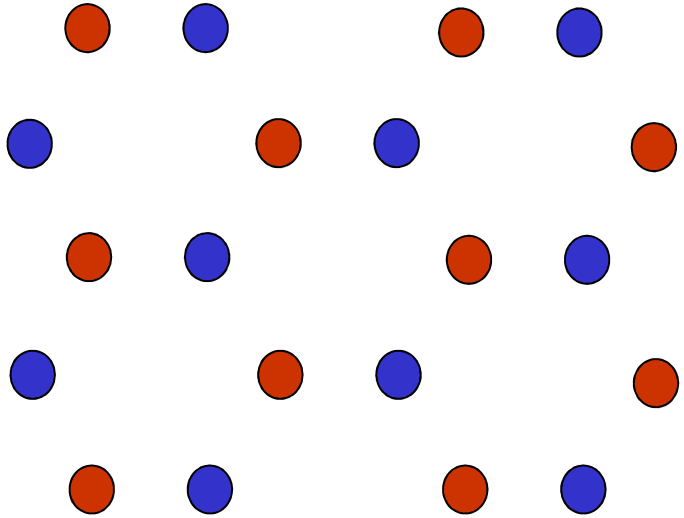
2-D crystals



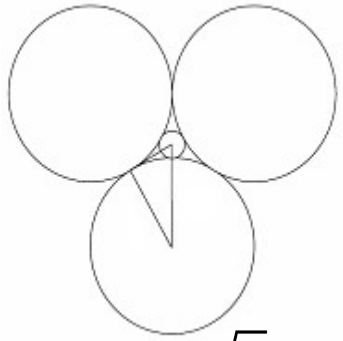
Checkerboard $\alpha = 1.616$



unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{2}-1} = 2.41$



Boron nitride $\alpha = 1.542$



unstable: $\frac{r_A}{r_B} > \frac{\sqrt{3}}{2-\sqrt{3}} = 6.464$

Fit the constants ρ and λ

$$U_{tot} = N\left(z\lambda e^{-\frac{R}{\rho}} - \frac{\alpha e^2}{4\pi\varepsilon_0 R} \right)$$

$$\frac{dU_{tot}}{dR} = N\left(-\frac{z\lambda e^{-\frac{R}{\rho}}}{\rho} + \frac{\alpha e^2}{4\pi\varepsilon_0 R^2} \right) = 0$$

R_0 is the equilibrium separation

$$R_0^2 e^{-\frac{R_0}{\rho}} = \frac{\alpha e^2 \rho}{4\pi\varepsilon_0 z\lambda}$$

x-ray determination of atomic spacing is accurate to 1 part in 10^5

Elastic constant

Near the minimum, the potential energy is approximately a parabola.

$$U_{tot} \approx \tfrac{1}{2} k \left(R - R_0 \right)^2$$

$$\frac{dU_{tot}}{dR} \approx k\left(R - R_0 \right) = -F$$

$$k = \left. \frac{d^2 U_{tot}}{dR^2} \right|_{R=R_0} = \left(\frac{z\lambda e^{-\frac{R_0}{\rho}}}{\rho^2} - \frac{\alpha e^2}{2\pi\varepsilon_0 R_0^3} \right)$$

spring constant of a bond

Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in square brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in square brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-neighbor separation R_0 in Å	Bulk modulus B, in 10^{11} dyn/cm^2 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

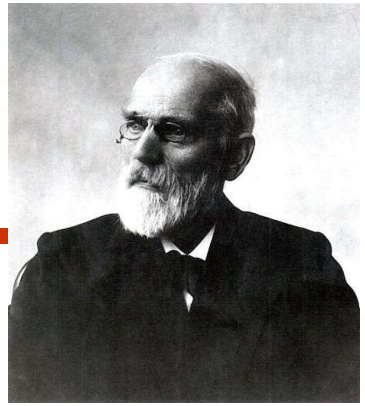
Data from various tables by M. P. Tosi, Solid State Physics **16**, 1 (1964).

$$B = \frac{1}{V}\frac{dp}{dV} = \frac{1}{\kappa}$$

κ is the compressibility

Kittel

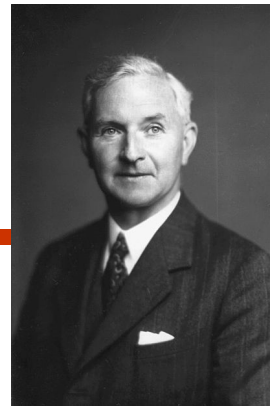
Van der Waals bonds



Johannes van der Waals

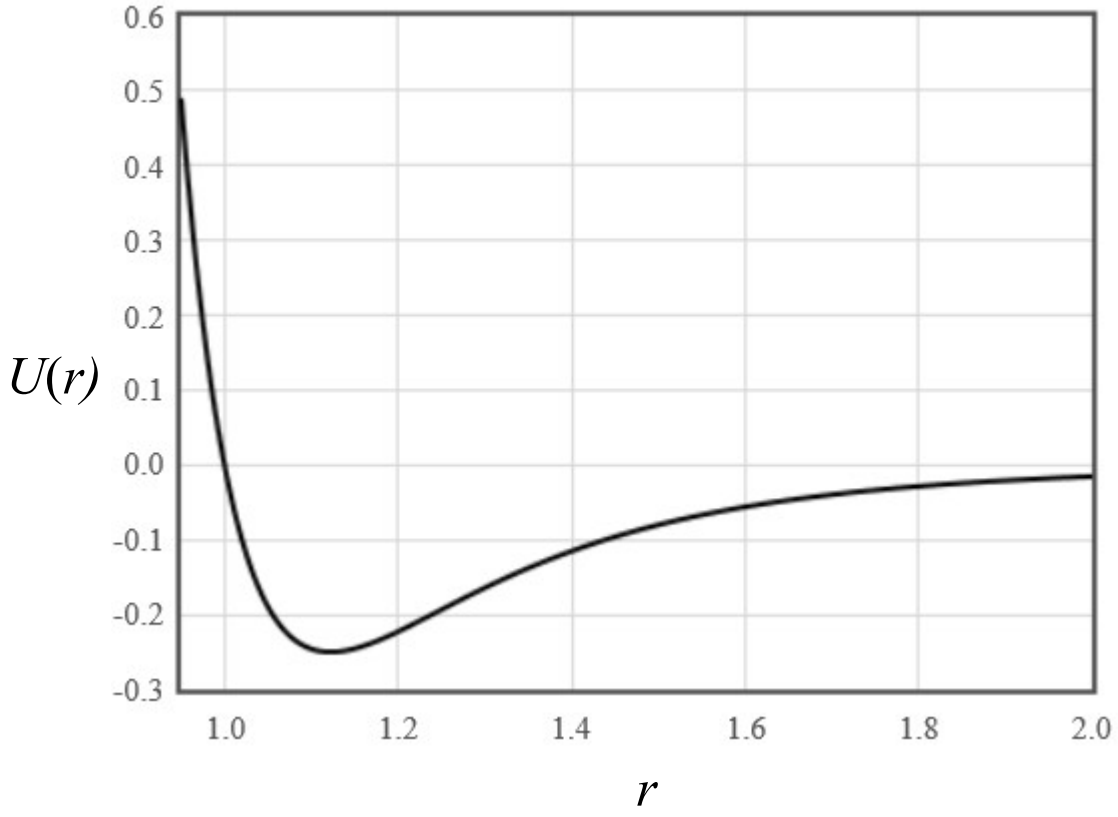
- Weak bonds ~ 0.01 eV
- Bonding due to fluctuations of the charge
- Responsible for crystals of ideal gasses (usually close -packed)
- Difficult to calculate

Lennard – Jones potential



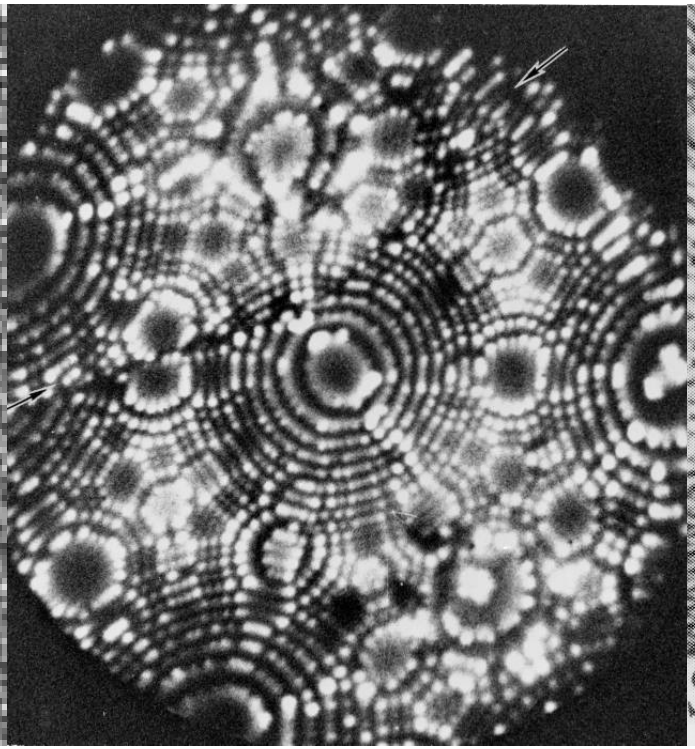
John Lennard-Jones

$$U(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

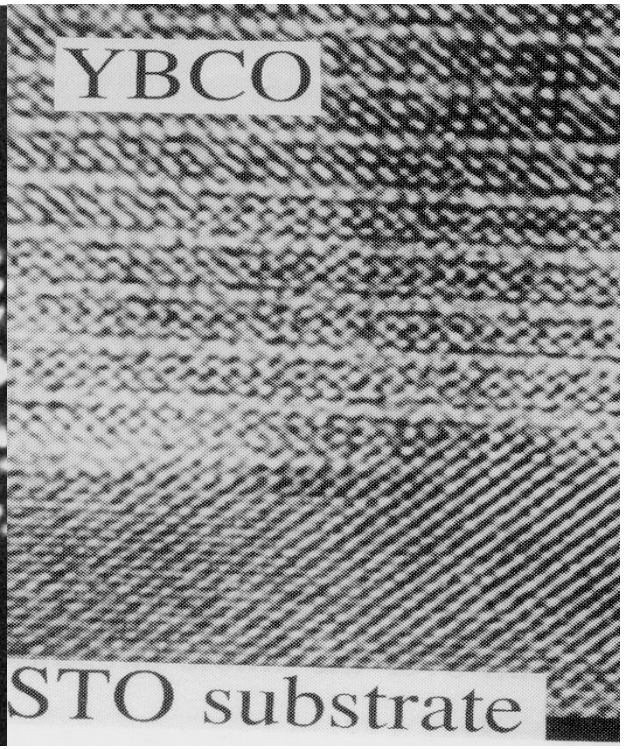


Crystal structure determination

Scanning tunneling microscope



Field ion microscope



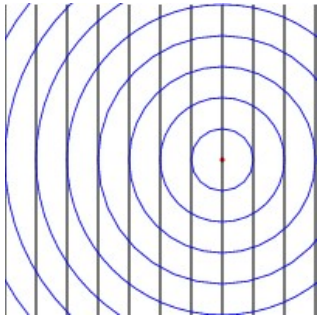
Transmission electron microscope

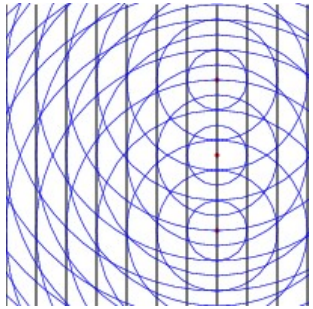
Usually x-ray diffraction is used to determine the crystal structure

Crystal diffraction (Beugung)

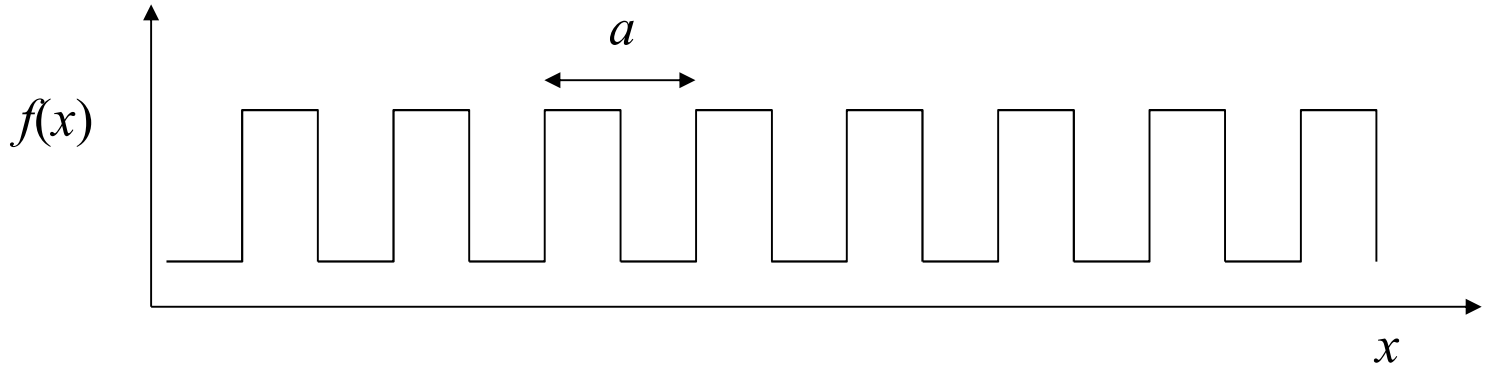
Everything moves like a wave but exchanges energy and momentum as a particle

light	photons
sound	phonons
electron waves	electrons
neutron waves	neutrons
positron waves	positrons
plasma waves	plasmons





Expanding a 1-d function in a Fourier series



Any periodic function can be represented as a Fourier series.

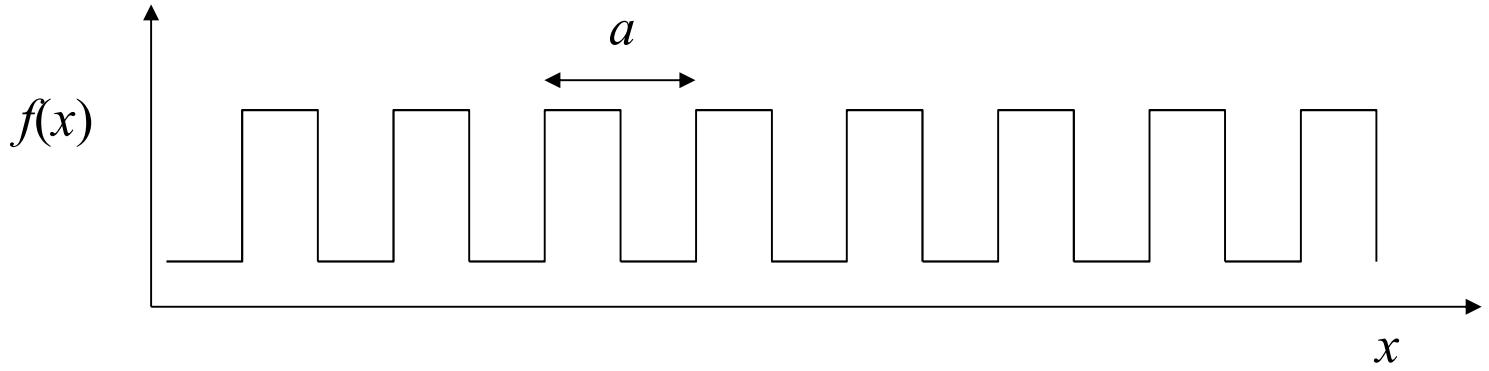
$$f(x) = f_0 + \sum_{p=1}^{\infty} c_p \cos(2\pi px/a) + s_p \sin(2\pi px/a)$$

multiply by $\cos(2\pi p'x/a)$ and integrate over a period.

$$\int_0^a f(x)\cos\left(2\pi p/a\right)dx = c_p \int_0^a \cos\left(2\pi p/a\right)\cos\left(2\pi p/a\right)dx = \frac{ac_p}{2}$$

$$c_p = \frac{2}{a}\int_0^a f(x)\cos\left(2\pi p/a\right)dx$$

Expanding a 1-d function in a Fourier series



Any periodic function can be represented as a Fourier series.

$$f(x) = f_0 + \sum_{p=1}^{\infty} c_p \cos(2\pi px/a) + s_p \sin(2\pi px/a)$$

$$\cos x = \frac{e^{ix} + e^{-ix}}{2} \qquad \sin x = \frac{e^{ix} - e^{-ix}}{2i}$$

$$f(x) = \sum_{G=-\infty}^{\infty} f_G e^{iGx} \qquad f_G = \frac{c_p}{2} - i\frac{s_p}{2} \qquad G = \frac{2\pi p}{a}$$

For real functions: $f_G^* = f_{-G}$

reciprocal lattice vector

Fourier series in 1-D, 2-D, or 3-D

In two or three dimensions, a periodic function can be thought of as a pattern repeated on a Bravais lattice. It can be written as a Fourier series

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vectors
(depend on the Bravais lattice)

Structure factors
(complex numbers)

In 1-D:

$$\vec{G} = v\vec{b} \qquad v = -\infty \ldots -1, 0, 1, \ldots \infty \qquad \left|\vec{b}\right| = \frac{2\pi}{a}$$

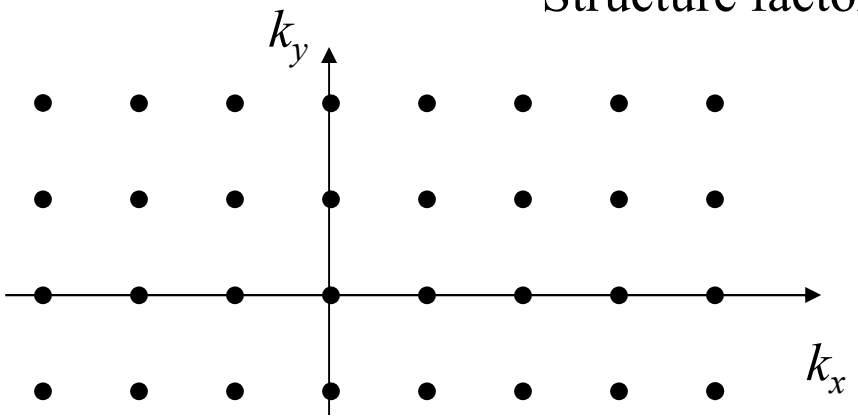
Reciprocal lattice (Reziprokes Gitter)

Any periodic function can be written as a Fourier series

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vector G

Structure factor



$$\vec{G} = \upsilon_1\vec{b}_1 + \upsilon_2\vec{b}_2 + \upsilon_3\vec{b}_3$$

v_i integers

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}, \qquad \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}, \qquad \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$