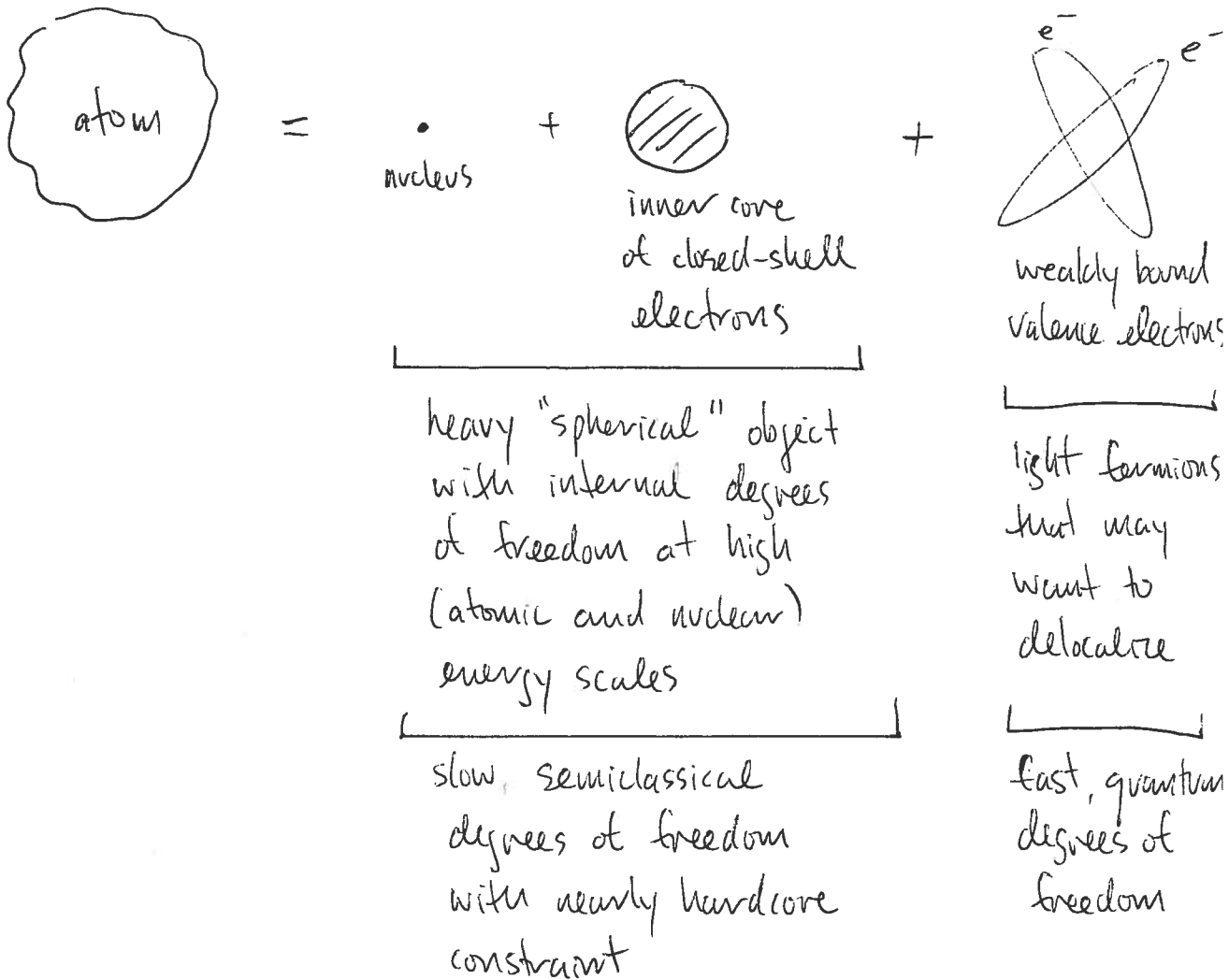


SOLIDIFICATION

\* What turns a fluid into a solid — and in particular a regular solid?

\* Model a large collection of atoms

→ clear separation of energy and time scales



→ from the point of view of the valence electrons, the ionic cores are frozen in position; from the point of view of the ionic cores, the valence electrons constitute an instantaneously-reacting smeared cloud of charge

→ Born-Oppenheimer approximation

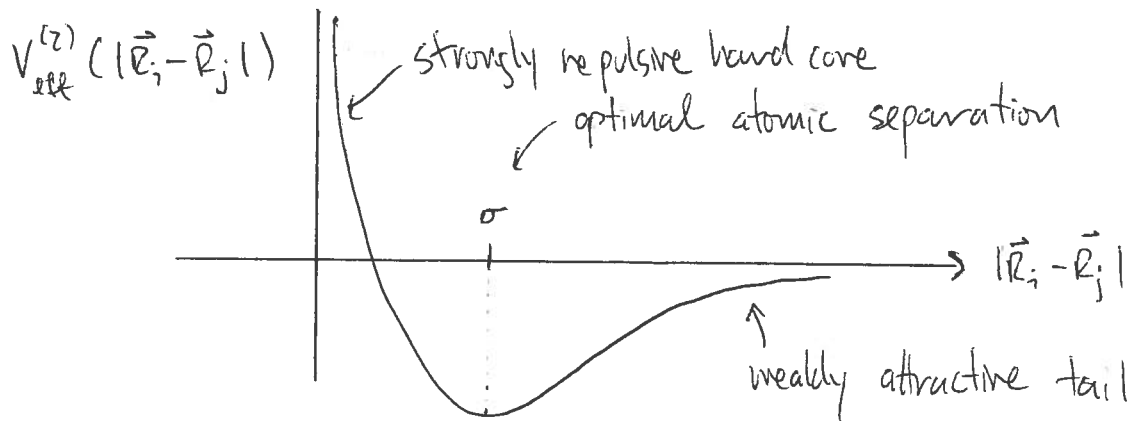
$$\Psi_{\text{tot}} = \Psi_{\text{ionic}} \times \Psi_{\text{electronic}} \quad (\text{w.f. is a product state})$$

\* "Integrating out" the fast d.o.f. leaves an effective model for the ionic cores (each at position  $\vec{R}_i$ )

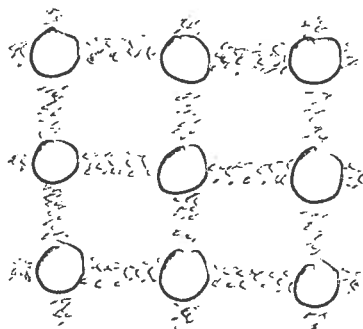
$$H = \sum_i \frac{\mathbf{P}_i^2}{2M} + \sum_{i < j} V_{\text{eff}}^{(2)}(\vec{R}_i, \vec{R}_j) + \dots$$

(where the ellipses ~~might~~ might include effective interactions that are 3-body or higher)

→ typical form

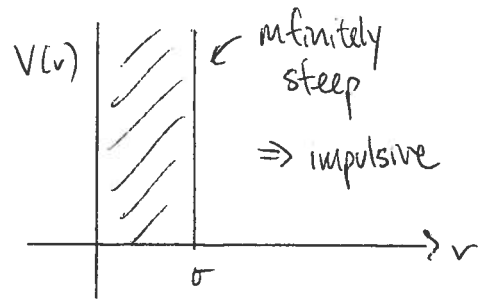


→ 2-body terms not enough to describe directional bonding; e.g. covalent network

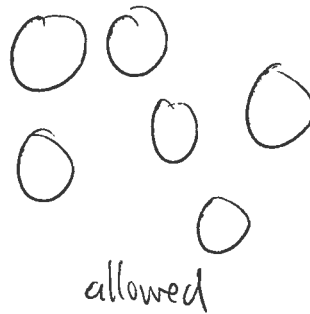
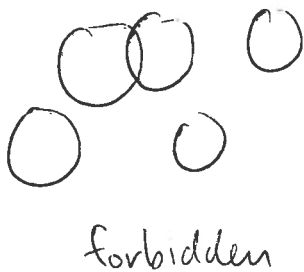


\* Consider a system of hard spheres:

$$V(r) = \begin{cases} \infty & \text{if } r < \sigma \\ 0 & \text{otherwise} \end{cases}$$



→ so-called "excluded volume" interaction

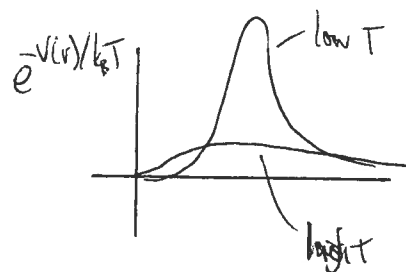
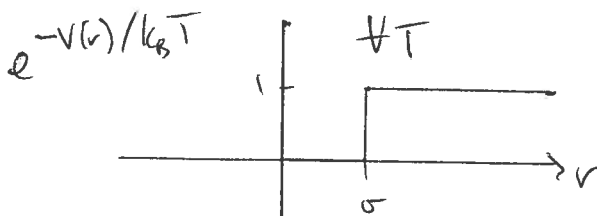
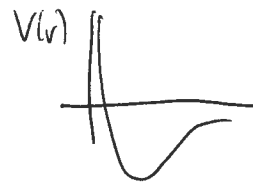
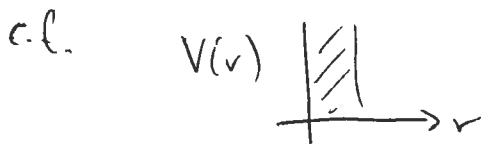


\* Boltzmann weight

$$e^{-\beta V(r)} = e^{-V(r)/k_B T} = \begin{cases} 0 & \text{if } r < \sigma \\ 1 & \text{otherwise} \end{cases}$$

→ no weight for any configuration that includes overlapping spheres

→ athermal: no T dependence



\* Structural and thermal properties depend only on the density of spheres  $\rho$

→ two extremes:

(1)  $\rho = \frac{N}{V} \equiv \frac{1}{v}$  is small, with typical

separation  $L = \left(\frac{N}{\rho}\right)^{1/3} = (Nv)^{1/3} \gg \sigma$

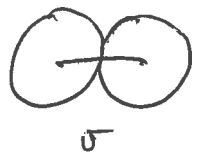
i.e. each sphere is effectively point-like and governed by the ideal gas limit

(2) packing fraction of close-packed spheres

is  $\eta_{cp} = \frac{\pi}{3\sqrt{2}} \approx 0.74$

general fraction is  $\eta = \frac{4}{3}\pi \left(\frac{\sigma}{2}\right)^2 \rho$

$$= \frac{\pi \rho \sigma^3}{6}$$



Hence,  $\rho = \frac{6\eta}{\pi\sigma^3}$

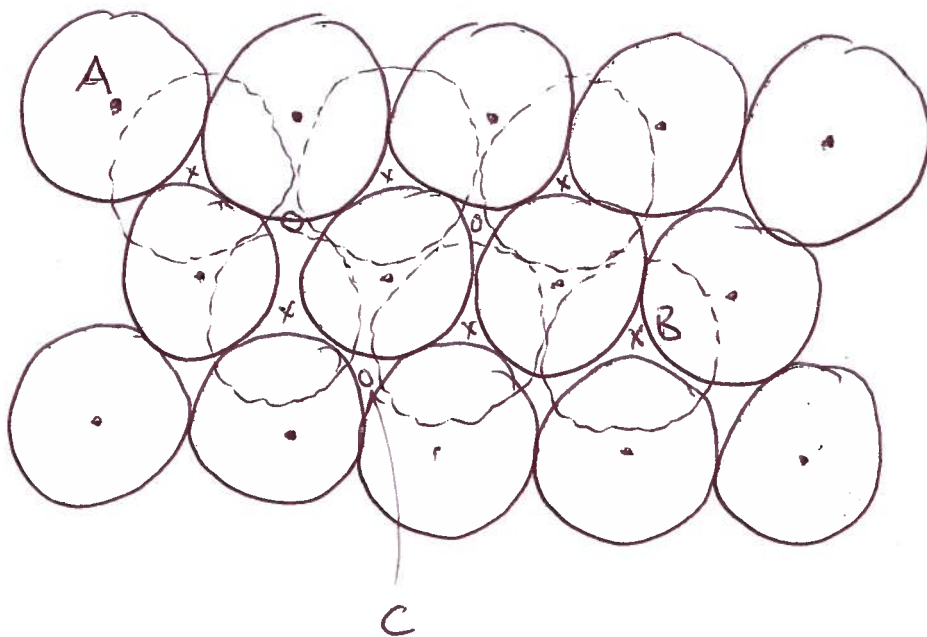
and  $\rho_{max} = \frac{6\eta_{cp}}{\pi\sigma^3} = \frac{6}{\pi\sigma^3} \left(\frac{\pi}{3\sqrt{2}}\right) = \frac{2}{\sqrt{2}\sigma^3} = \frac{\sqrt{2}}{\sigma^3}$

## \* Close packing in 3D

→ tightest regular arrangement is grocer's packing

→ first layer is a coplanar set of touching spheres in a triangular lattice, which defines a set of "A" positions

→ the next layer is also triangular, but shifted to settle into the local depression where 3 spheres meet; this defines a set of "B" positions



→ there remains one additional set of triangular positions "C"

\* Since there's no potential energy in this problem ( $\langle V \rangle = 0$ ), the stacking arrangement is highly degenerate

→ regular arrangements

A  
B  
A  
B  
A  
B  
A  
B

hexagonal  
close-packed  
(hcp)



A  
B  
C  
A  
B  
C  
A  
B  
C

face-centred  
cubic  
(fcc)

A  
B  
A  
C  
A  
B  
A  
C

So-called  
double-hcp

→ or purely random ones!

\* For hard spheres, there must be a phase transition in the range of densities  $0 < \eta < \eta_{cp}$   
 $0 < \rho < \rho_{max}$

\* Since potential energy vanishes for all allowed configurations, the free energy scales linearly with  $T$ ,

$$\begin{aligned}
 F &= \langle H_{kin} \rangle - TS \\
 &= \frac{3}{2} N k_B T - TS \quad (\text{by classical equipartition}) \\
 &= \left( \frac{3}{2} N k_B - S \right) T
 \end{aligned}$$

↑ trivial constant
 ↑ overall rescaling

→ so for any  $T > 0$ , the free energy is minimized by maximizing the entropy

i.e. hard spheres are an entropic system

\* But this is counterintuitive:

→ our first thought is "high entropy = low order"

→ this leads us to draw an incorrect phase diagram

↑  
increasing  
entropy

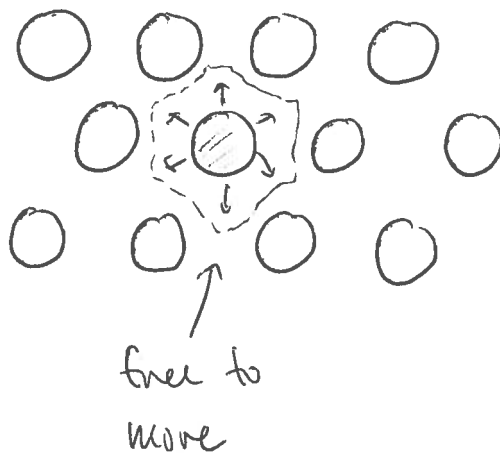
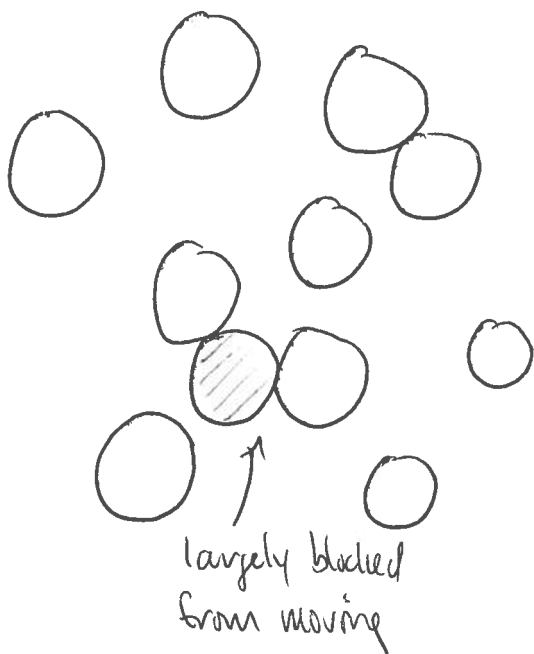
disordered phase is favoured  
~~~~~  
ordered phase is favoured

\* More careful thinking leads to the following

→ there are two qualitatively different contributions to the entropy

(1) overall configurational entropy

(2) entropy corresponding to placement within the local "free volume" of each cell





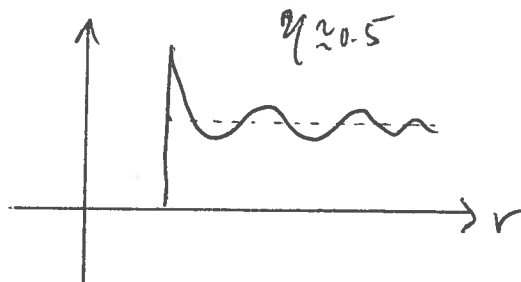
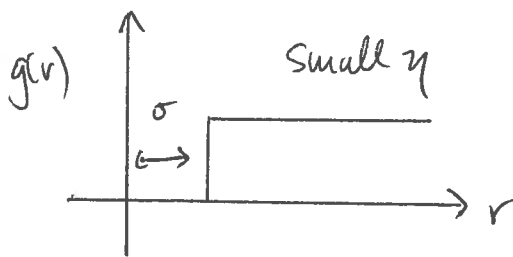
→ regular order favours the second type (dominant at high density)

→ randomness favours the first type (dominant at low density)

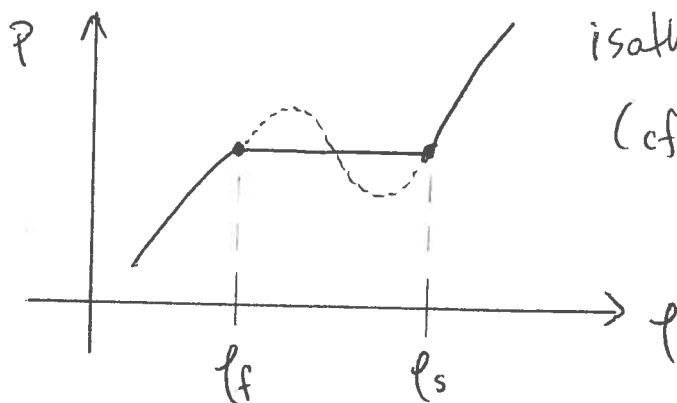
→ transition is driven by competition between the two types of entropy

\* The transition to a crystal is visible in the pair distribution function

$$g(r) = \frac{1}{\rho^2 N} \left\langle \sum_{i,j} \delta(r - |\vec{R}_i - \vec{R}_j|) \right\rangle$$



\* Transition is 1<sup>st</sup> order



isothermal eq. of state  
(cf.  $P = \rho k_B T$ )

→ possible to describe  $m$  various ensembles

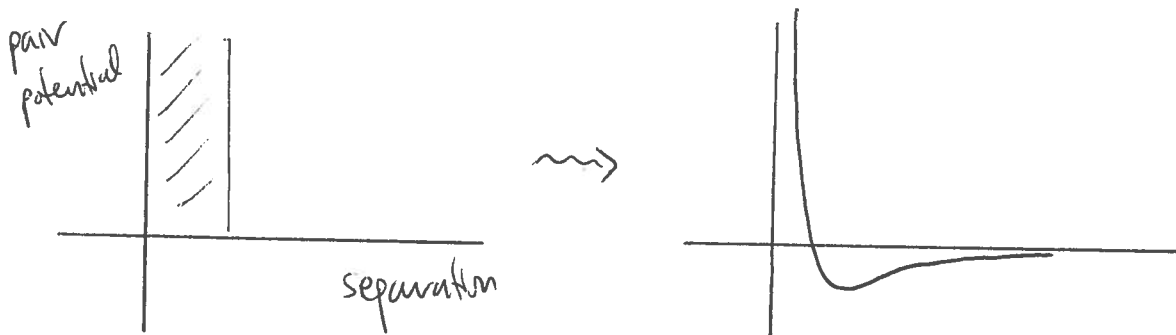
$$F(T, N, V) \rightarrow G(T, \mu) = F - \mu N$$



$$G(T, P) = F - PV$$

→ but always externally driven since the model includes no cohesion

→ a real crystal has to come together on its own; hence, there must be some weak long range attraction



# Crystalline Solids

\* Def<sup>n</sup> of a solid is vague:

## Properties

hardness

keep shape indefinitely

## Exceptions

- very soft alkali metals do not keep their shape when deformed (plastic deformation)

- amorphous solids change shape over long times (decades)

- glasses are more like semi-frozen liquids

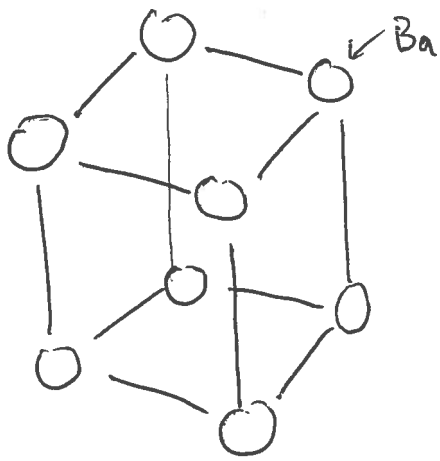
\* But it is clear what we mean by a crystal

→ the atoms form a regular array

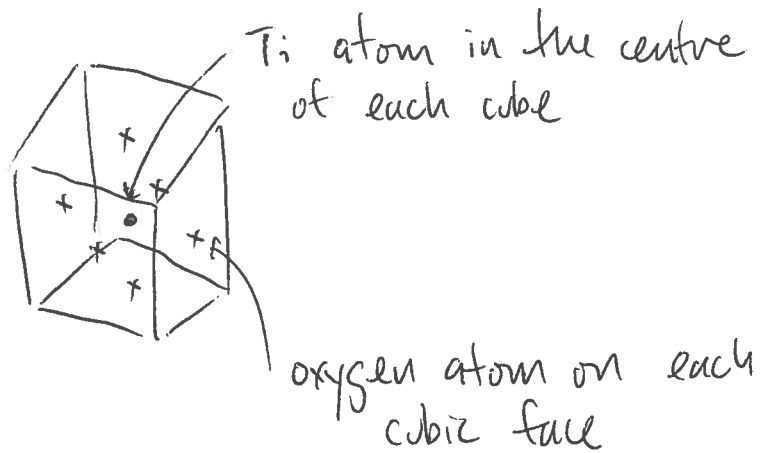
→ knowing the positions of a handful of atoms is enough to predict the positions of all the rest

→ long-range correlation over macroscopic distances

\* Building block is the unit cell (basic repeating unit), and materials are generally named after the atoms appearing in each unit cell



Simple cubic arrangement of Ba atoms



→ avoiding double counting, we conclude that each unit cell has

1 Ba

1 Ti

3 O

5 atoms

Hence  $\text{BaTiO}_3$  (Barium Titanate)

\* Formally, Crystal = Bravais lattice + basis of atoms in the unit cell

\* Bravais lattice is an infinite set of points

$\mathbb{Z}\vec{a}_1 + \mathbb{Z}\vec{a}_2 + \mathbb{Z}\vec{a}_3$  defined by a linearly independent set of lattice vectors  $\{\vec{a}_i\}$

→ there are exactly 5 unique Bravais lattices in 2D

→ and 14 in 3D

→ each lattice site is of the form

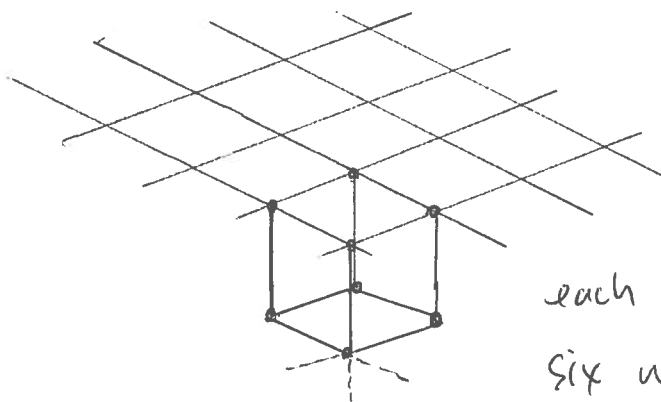
$$\vec{R} = \vec{R}_{l,m,n} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

for some triplet of integers  $(l, m, n)$

→ the set  $\{\vec{a}_i\}$  define the discrete translational symmetries of the lattice

→ a very simple construction is to identify the ~~closest~~ vectors to the closest equivalent atoms and to choose from those any 3 that are non-coplanar

e.g.



each Ba in  $\text{BaTiO}_3$  has six nearest neighbour Ba atoms

we're free to choose  $\vec{a}_i$  vectors coincident with the cartesian axes

$$\vec{a}_1 = a(1, 0, 0) \quad \vec{a}_2 = a(0, 1, 0) \quad \vec{a}_3 = a(0, 0, 1)$$

\* In that example, each Ba is at a position

$$R_{l,m,n} + \tau_{Ba} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 + 0$$

each Ti is at a position

$$R_{l,m,n} + \tau_{Ti} = R_{lmn} + \frac{a}{2}(1,1,1)$$

and the three inequivalent oxygens are at sites

$$R_{l,m,n} + \tau_0^{(j)} \quad (\text{for } j=1,2,3)$$

$$\text{with } \tau_0^{(1)} = \frac{a}{2}(1,1,0)$$

$$\tau_0^{(2)} = \frac{a}{2}(1,0,1)$$

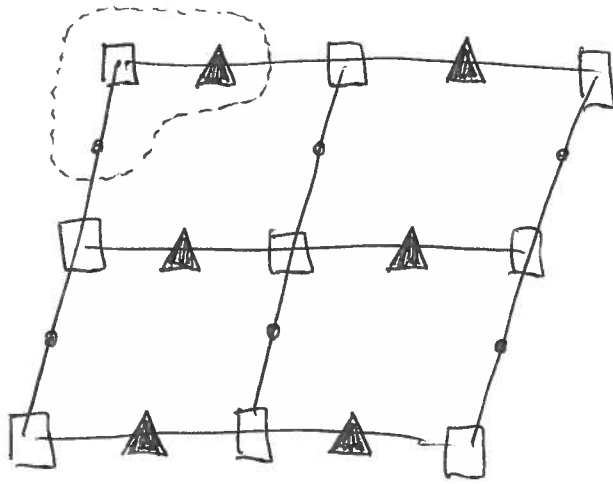
$$\tau_0^{(3)} = \frac{a}{2}(0,1,1)$$

→ the set of  $\vec{\tau}$  vectors constitutes the basis

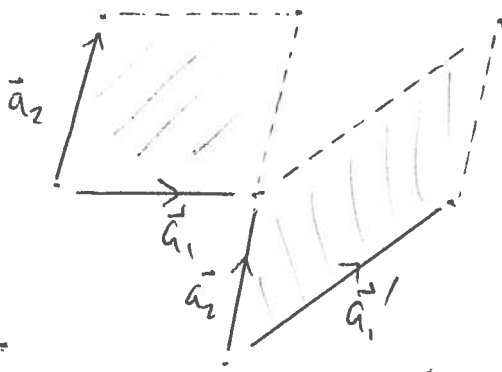
→ here, there are  $\dim \{ \tau_{Ba}, \tau_{Ti}, \tau_0^{(j)} \} = 5$   
atoms in each unit cell of volume

$$\Omega_0 = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3$$

basis



e.g. in this crystal, there are 3 basis elements per unit cell



but the  $\det^v$  of the  $\{\vec{a}_i\}$  is not unique

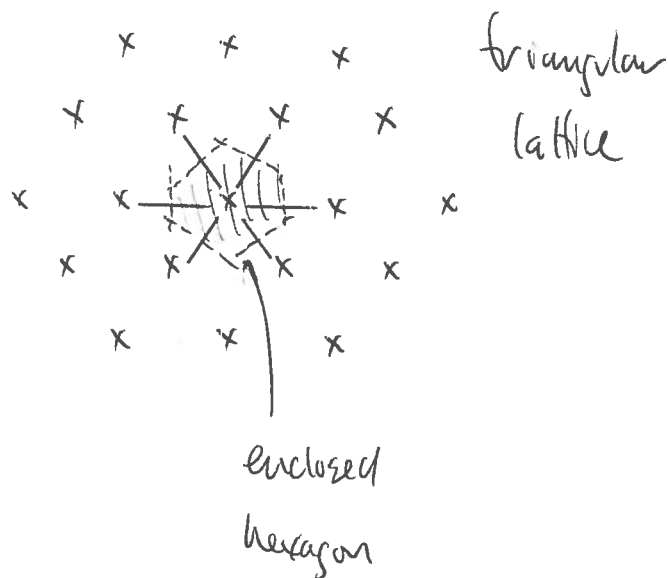
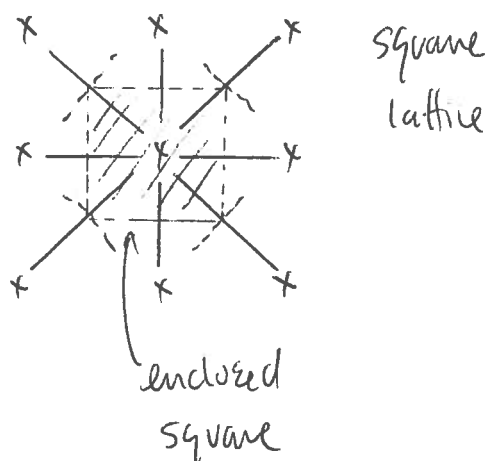
$$Z\vec{a}_1 + Z\vec{a}_2 = Z\vec{a}_1' + Z\vec{a}_2'$$

→ a useful unique cell arises from the Wigner-Seitz construction:

- (1) bisect all vectors emerging from a lattice point
- (2) take unit cell to be the smallest enclosed volume

(more often used in Fourier space than real space)

2D examples



→ but in general, any non-overlapping, space-filling repeating unit of volume  $\Omega_0$  will do

\* Consider the set of vectors dual to the lattice positions

→ this set  $\{\vec{G}\}$  of reciprocal lattice vectors obeys  $e^{i\vec{G}\cdot\vec{R}} = 1 \quad \forall \vec{G} \text{ and } \vec{R}$

→ achieved when  $\vec{G}\cdot\vec{R}$  is an integer multiple of  $2\pi$

→ hence  $\vec{G}$  is of the form

$$\vec{G}_{\alpha\beta\gamma} = \alpha\vec{g}_1 + \beta\vec{g}_2 + \gamma\vec{g}_3$$

for integers  $(\alpha, \beta, \gamma)$



$$\text{with } \vec{g}_1 = \frac{2\pi}{a_0} \vec{a}_2 + \vec{a}_3 \quad (1,2,3)$$

$$\vec{g}_2 = \frac{2\pi}{a_0} \vec{a}_3 + \vec{a}_1 \quad (2,3,1)$$

$$\vec{g}_3 = \frac{2\pi}{a_0} \vec{a}_1 + \vec{a}_2 \quad (3,1,2)$$

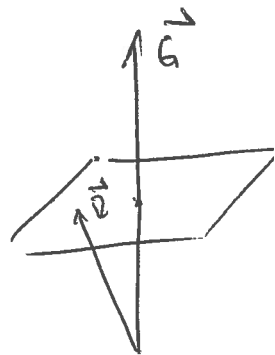
cyclic permutation  
pattern to the  
definitions

\* reciprocal lattice vectors obey the identity

$$\vec{g}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$$

$$\vec{G} \cdot \vec{R} = \vec{G}_{\alpha\beta\gamma} \cdot \vec{R}_{lmn} = 2\pi (\alpha l + \beta m + \gamma n)$$

$$e^{i\vec{G} \cdot \vec{R}} = \exp(2\pi i (\alpha l + \beta m + \gamma n)) = 1$$



equation of  
a Bragg plane

→ we'll often drop the triplet of integer labels and write sums of the form

$$\sum_{\vec{R}} = \sum_{l=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \delta(\vec{R} - \vec{R}_{l,m,n})$$

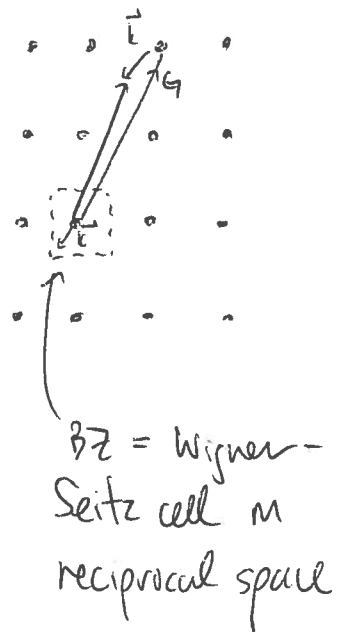
$$\sum_{\vec{G}} = \sum_{\alpha=-\infty}^{\infty} \sum_{\beta=-\infty}^{\infty} \sum_{\gamma=-\infty}^{\infty} \delta(\vec{G} - \vec{G}_{\alpha,\beta,\gamma})$$

\* Any function  $f(\vec{r})$  (in real space) that shares the periodicity of the lattice (i.e.  $f(\vec{r}) = f(\vec{r} + \vec{R})$  for any lattice vector  $\vec{R}$ ) has a Fourier expansion in reciprocal lattice vectors

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

\* Any arbitrary function defined pointwise on the lattice sites can be written as a sum over  $\vec{k}$  vectors in the Brillouin Zone

$$\begin{aligned} f(\vec{r}) &= \frac{1}{N} \sum_{\vec{k}} \tilde{f}_{\vec{k}} e^{i\vec{k} \cdot \vec{R}} \\ &= \frac{1}{N} \sum_{\vec{G}} \sum_{\vec{k} \in \text{BZ}} \tilde{f}_{\vec{k} + \vec{G}} e^{i(\vec{k} + \vec{G}) \cdot \vec{R}} \\ &= \sum_{\vec{k} \in \text{BZ}} \underbrace{\left( \frac{1}{N} \sum_{\vec{G}} \tilde{f}_{\vec{k} + \vec{G}} \right)}_{\equiv f_{\vec{k}}} e^{i\vec{k} \cdot \vec{R}} \end{aligned}$$



→ for a finite crystal of  $N$  unit cells, there are exactly  $N$   $k$ -points in the BZ

→ for the infinite crystal, the wavevectors become continuous and

$$\sum_{\vec{k}} \xrightarrow{N \rightarrow \infty} V \int \frac{d^3k}{(2\pi)^3}$$