Introduction

What is Condensed matter physics?
Where does it stand in physics?

* Condensed matter physics : field that deals with the macroscopic and microscopic physical properties of matter ; in particular, it deals with the "condensed" phases that appear whenever # of constituents in a system is thermodynamically large. It includes both solids & liquids.

* History : grew out of solid state physics
The name was coined by P.W. Anderson & Volker Heine (renamed their research group in Cavendish lab. from "Solid-State theory" to "Theory of Condensed Matter.)

In 1978, Division of Solid State physics of APS was renamed as the Division of Condensed Matter Physics.

* Feature of successful contributions :
Feynman: "We are not trying to explain and predict everything about the Solid".
for instance, when predicting superconductivity, one knows that certain phenomena "such as e^+e^- annihilation" are not going to be relevant.

Therefore, even though the full Hamiltonian for condensed matter is known:

$$H = \sum_{i=\text{ions}} \frac{p_i^2}{2m_i} + \sum_{j=\text{electrons}} \frac{p_j^2}{2m_j} + \sum_{ij} U_{ij} + \sum_{ii'} U_{ii'} + U_{jj'}$$

, the Hamiltonians that are considered for different problems vary. These Hamiltonians are only part of full H; they are extracted to be revalent ~~the~~ to individual problem.

Finding the appropriate Hamiltonian is usually important in condensed matter physics and is considered as an "insight" to the problem.

Where does it stand in physics ?

V. F. Weisskopf

(i) Gravitational Matter ($\sim 10^{50}$ atoms)

galaxies, solar systems, "quasi-stellar" sources, ..

inter-"particle" interaction = gravity

(ii) Plasma matter : gas of charged particles

* (iii) atomic matter : atoms are intact (basic "unit")

3 States { solid, liquid, gas

(iv) Nuclear matter : nucleus — neucleons

(v) Mesonic Matter : substance of neucleons, HEP

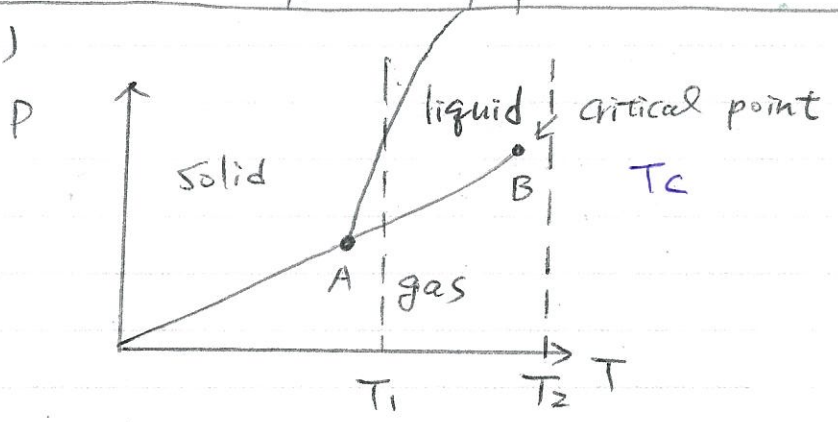
(vi) Leptonic matter : weakly interacting particles

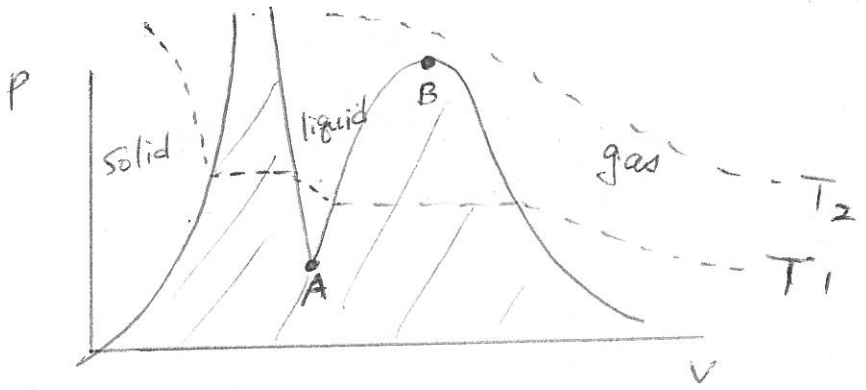
e^-, μ^-

Global

Phase diagram of a typical symple atomic matter

(e.g. water)





/// = coexistent area.

Inside → more phases

Solid : 

can't flow

- Crystalline state (Crystals)
- liquid crystal, quasi-crystal
- amorphous solids, (glass)
- others (ceramics, wood, polymers ...)

+ Quantum liquids (He) + LCD + polymers ⇒ Condensed Matter

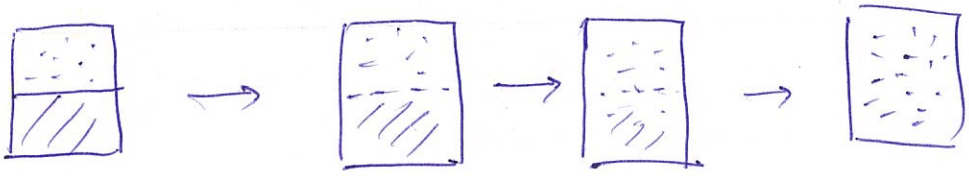
liquid / gas > can flow, viscosity η is finite

gas — η is smaller, more compressible.

liquid — η is larger, less " .

On the isotherm, liquid → gas, dis continuous change of volumes!!

✡ Beyond the critical point, no real distinction between liquids and gases!!



The theory that explains the vapor-liquid critical point is the renormalization group theory.

Orders, order parameter & broken symmetry

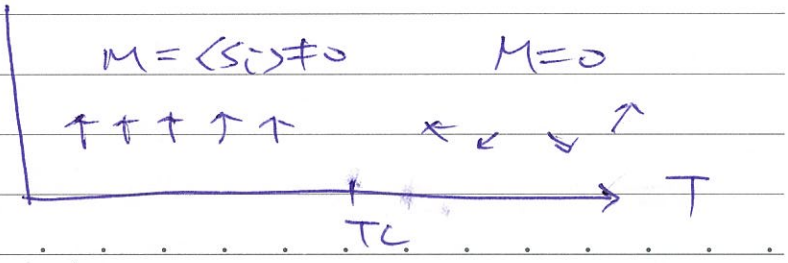
Most materials we experience daily are not crystals. However, in condensed matter, we are more interested in materials with orders. Landau is the first person to realize that to describe macroscopic materials, in addition to the usual macroscopic variables such as P, V, T, one also needs to introduce the order parameter ψ so that in so-called ordered phase (such as crystalline), $\psi \neq 0$, otherwise $\psi = 0$

$\psi = 0$ & $\psi \neq 0$ are terms as different phases and the transition is the phase transition.

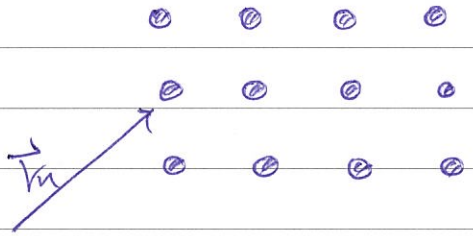
$\psi = 0$ & $\psi \neq 0$ are often resulted from symmetry broken (i.e. phases $\psi = 0$ & $\psi \neq 0$ correspond to materials in different symmetry.

Examples:

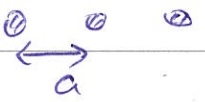
Ferromagnetism



Crystals



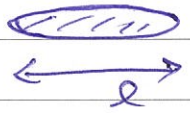
$$\rho(\vec{r}) = \sum_n \delta(\vec{r} - \vec{r}_n)$$

1D $\quad \rho(x) = \sum_n \delta(x - na) = \rho(x+a)$ ⇒ 

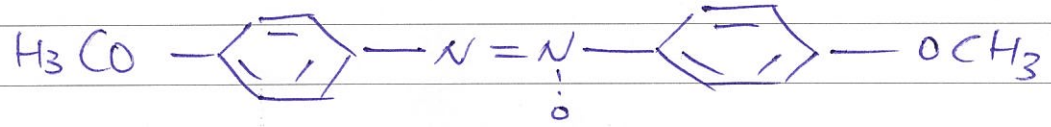
$\rho(g) = \int dx\, e^{ig\cdot x}\rho(x)$ is non-vanishing

only when $g = \frac{2\pi}{a} \times n$ $\quad \rho(x) = \sum_g e^{igx}\rho(g)$

$\therefore \rho(\frac{2\pi n}{a})$ = order parameter.

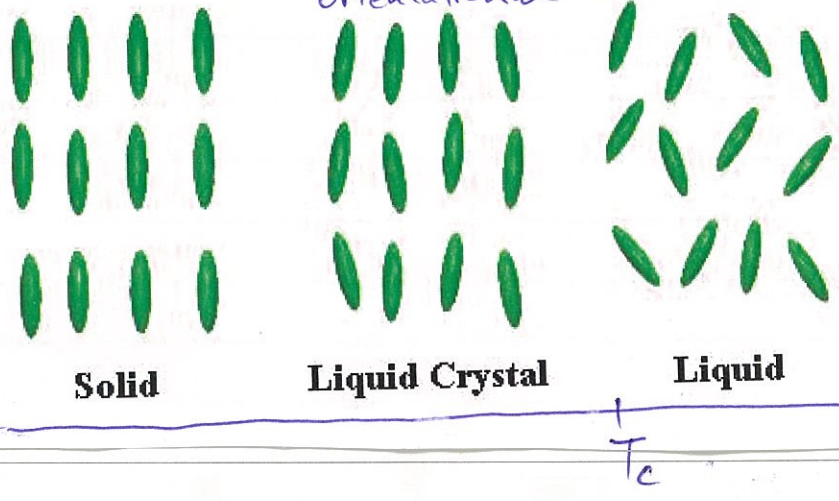
Liquid crystals : molecules 

$\ell > a$

e.g. 

position & orientation

orientational order

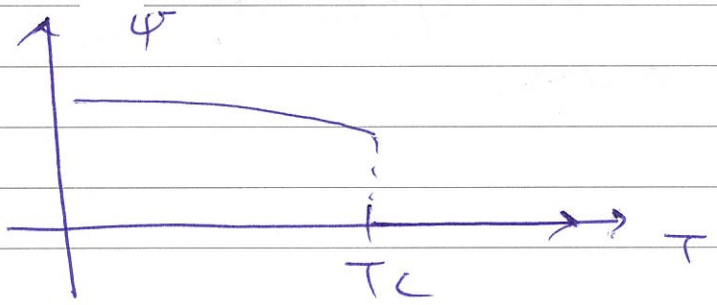


isotropic

isotropic

$\langle \cos^2\theta \rangle = \frac{1}{3}$

order parameter $\equiv \psi = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$



The order parameter corresponds to a symmetry, but what is a symmetry? (see over)

Spontaneous symmetry broken

$$\hat{H} = \sum_i \frac{1}{2m_i}\hat{P}_i^2 + V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

$[x, p_x] \neq 0$ → $[\hat{H}, e^{iax_i}] \neq 0$ (translate x_i by a is not a symmetry)

$\therefore [\hat{H}, \vec{r}_i] \neq 0$ $\hat{H}$ & $\vec{r}_i$ can't be diagonalized simultaneously

Crystalline order:

$\hat{H}|\psi_0\rangle = E_0|\psi_0\rangle$ $|\psi_0\rangle$ = ground state

but $\langle \psi_0 | \vec{r}_i | \psi_0 \rangle = na \neq 0$ (translational symmetry is broken)

In general, if $[\hat{O}, \hat{H}] = 0$, $\langle \hat{O} \rangle_0 \neq 0$ ($\hat{O}$ = order parameter)

This is termed as spontaneous symmetry broken (Anderson, P.W.).

Note that not all systems are crystals at $T=0$ (i.e. ^4He), we shall see many examples in condensed matter system (proteins, ---)

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* Up to now, there is no rigorous proof that for a given $V(r_1, r_2, r_3, \ldots r_N)$, the ground state is a crystal.

Hence,
Prediction of crystal structure also has limited success.

* Symmetry

Symmetry is summarized in "Symmetry operations" that so the system in consideration is invariant under these symmetry operations. $[\hat{O}, \hat{H}] = 0$ (H is invariant)

The collection of the symmetry operations $G \equiv \{A, B, \ldots\}$ with rules

(i) natural combination rules & close
AB = operation B followed by A
$A \& B \in G$, $AB \in G$

(ii) exist $I \in G$ $IA = AI = A$

(iii) reversible $A^{-1} \in G$. $A^{-1}A = AA^{-1} = I$

(iv) $(AB)C = A(BC)$ $\Rightarrow$ group

Therefore; for each order parameter O, there will be a corresponding subgroup $g \subset G$ so that O is invariant.

Crystalline is the symmetry that we most often encounter in condensed matter.

Classification of crystals

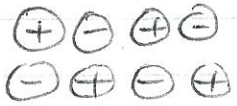
2-4

Crystals formed by other particles are also observed such as wigner crystals (electrons) and Coulomb crystals (伊林's expt.).

We will not discuss these crystals.

Interactions are essential for forming crystals. Hence, we may classify crystals in terms of the type of bonding between atoms

(i) Ionic Crystals : e.g. NaCl, KCl, ~ 10 eV/at



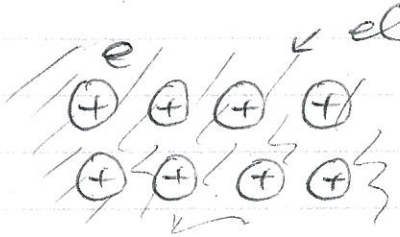
Coulomb attraction = binding force

electrons are localized at ⊖. no free electrons

⇒ poor electrical, thermal conductivity

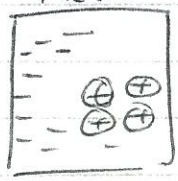
high melting point (凝結解)

(ii) Metals, Cohesive energy ~ 1-5 eV/atom



→ The difference between the energy per atom of a system of free atoms at rest far apart from each other and the energy of solid

Screening ⊕⊕ repulsion by electrons.



⇒ binding force weak ∴ low melting point, softness, malleability high.

free electrons (can't absorpt optical E.M.) ⇙ reflect optical light. shining, high σ, thermal conductivity

(iii) Covalent Crystals : diamond, silicon, etc. ~ 10 eV/atom

Valence electrons are shared between atoms.

⇒ Therefore, poor cleavability and great hardness

(iv) Molecular Crystals : Ar, He, O_2, H_2, CH_4, many other inorganic compounds.

The constituent atoms are very stable and not likely to share their electrons with others, i.e., they are neutral

The inter-particle is therefore very weak, due to van der Waals forces. ($\sim 1/r^6$) (dipolar distortions). Cohensive energy ~ 0.1 eV/molecule

∴ The melting temperature is very low.

(v) Hydrogen bonded (氫鍵) Crystals : KH_2PO_4, H_2O, ...

$O-H\cdots O$: Sharing protons

$^{+}\quad\ ^{-}$

Cohesive energy ~ 0.5 eV / molecule

measured from an assembly of seperate atoms

Note that cohensive energy in ionic crystals comes from electrostatic attraction of ions, not from the formations of bonds.

※ No clear cut between ionic & covalent crystals!

Crystal lattices

* Bravais lattice & its description

Bravais lattice:

∞ mathematical points : $\{\vec{R} \mid \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3\}$

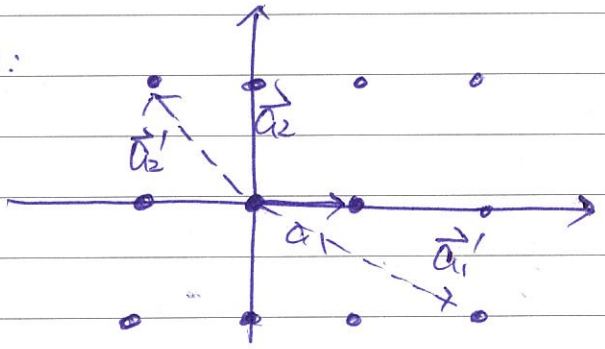
that are periodic

n_i run through all $\mathbb{Z}$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ any three linearly independent vectors

$\vec{a}_i$: primitive vectors

example:



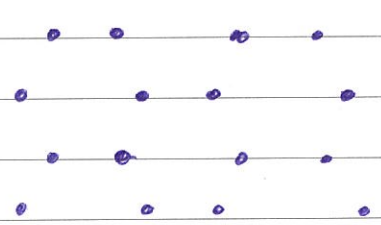
The parallelepiped formed by $\vec{a}_1$, $\vec{a}_2$ & $\vec{a}_3$

= primitive (unit) cell

= a volume of space, when translated by $\vec{R}$, fills all space without overlapping or leaving voids

$\Leftrightarrow$ this is called tiling.

example: non Bravais lattice



2D honeycomb lattice

(1) $\vec{a}_i$ are not unique

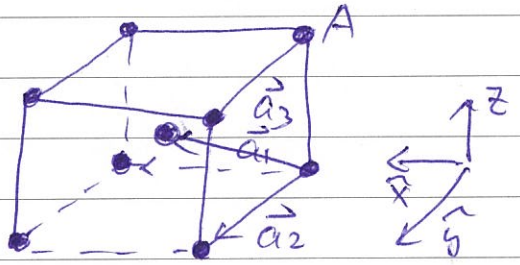
for instance, in the above example, $\vec{a}_1', \vec{a}_2'$ are also primitive vectors

$$\left.\begin{aligned}\vec{a}_1' &= 2\vec{a}_1 - \vec{a}_2 \\ \vec{a}_2' &= -\vec{a}_1 + \vec{a}_2\end{aligned}\right\} \quad \left.\begin{aligned}\vec{a}_1 &= \vec{a}_1' + \vec{a}_2' \\ \vec{a}_2 &= \vec{a}_1' + 2\vec{a}_2'\end{aligned}\right.$$

$$\therefore \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 = \overbrace{(n_1 + n_2)}^{n_1'}\vec{a}_1' + \overbrace{(n_1 + 2n_2)}^{n_2'}\vec{a}_2'$$

(iii) Some lattices are periodic by looking but it is not straight forward to show its Bravais lattice

example : body-centered cubic (BCC)



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

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

$\vec{a}_3 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

$\vec{A} = (0, 0, 1)$

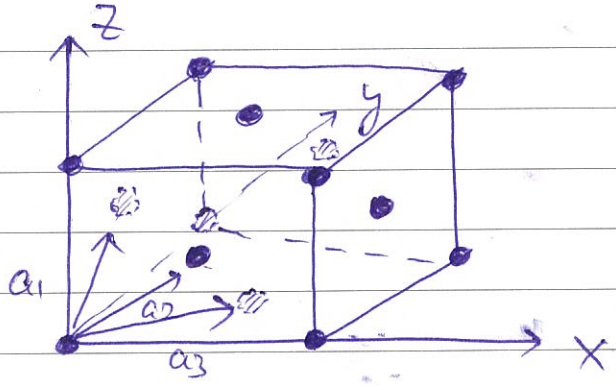
$= 2\vec{a}_3 - \vec{a}_1 - \vec{a}_2$

more symmetric one : $\vec{a}_1' = (\frac{-1}{2}, \frac{1}{2}, \frac{1}{2})$

$\vec{a}_2' = (\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$

$\vec{a}_3' = (\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$

face-centered cubic (fcc)



$\vec{a}_1 = (0, \frac{1}{2}, \frac{1}{2})$

$\vec{a}_2 = (\frac{1}{2}, 0, \frac{1}{2})$

$\vec{a}_3 = (\frac{1}{2}, \frac{1}{2}, 0)$

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

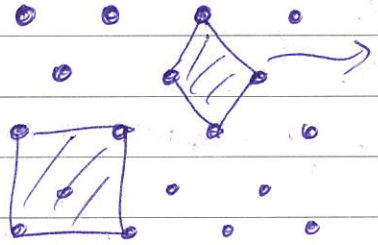
$\vec{a}_1 + \vec{a}_3 - \vec{a}_2 = (0, 1, 0)$

Coordination # = # of nearest neighbours

Unit cell : fills all space without overlap or voids when translated through some subset of vectors of a Bravais lattice

In 2D, One says that they (cells) form a tiling.

example



primitive unit cell (containing one lattice point)

↓

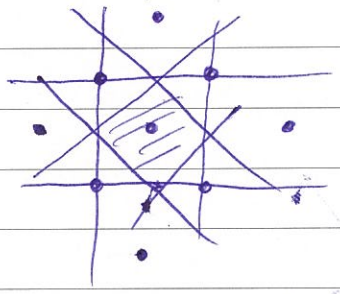
unit cell (containg two lattice points)

n = density of points, V = volume of the primitive cell

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

$nV = 1$, $V = 1/n$

Wigner - Seitz cell : regions that is closest (volume), respect symmetry of Bravais lattice to any lattice point



(i) any point in space must be closest to a unique lattice point

(ii) translational invariant

∴ Wigner - Seitz cell fill all space without overlapping & voids

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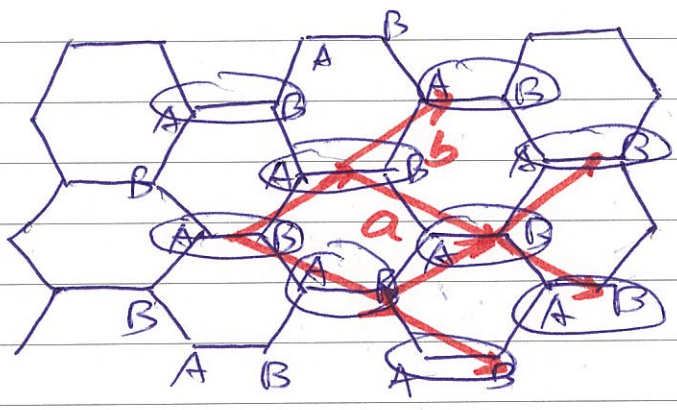
* Crystal structure = lattice with bases

When one put atoms or molecules (bases) on to the idealized mathematical points in a Bravais lattice, one forms a crystal.

Therefore, crystal structure

= lattice with bases

special example : graphene is not a Bravais lattice, but if one includes basis it's a lattice. A & B form triangular lattice individually.



In general, it is a molecule (or motif) that is the bais putting on each lattice point.

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* Classification & enumeration of lattices

Lattices are classified according to their symmetries. These symmetries are summarized as a collection of operations that act on lattices and leave lattices invariant. The collection is known as a group.

For crystals, this group is known as space group. and operations acting on lattice points include translation by lattice vectors $\vec{a}$, rotations, reflections, inversions and their combinations. The operations that act on a fixed lattice point is known as point group. For 3D, there are 230 space, whose correct enumeration was done in early 1890s by Fedorov and Schönflies.

We shall not go into detailed enumeration but illustrate key points by considering 2D lattices and crystals.

2D lattices Point group includes N-fold rotational operation (in Schönflies's notion, C_N) & reflections.

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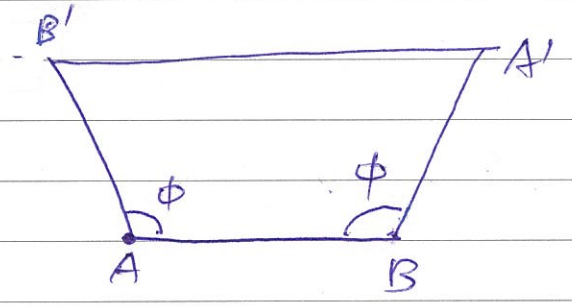
The N-fold operation C_N brings the lattice back to itself after N rotations

identical rigid

$\therefore$ The angle of rotation $\phi = \frac{2\pi}{N} \times n$, $n = 0, 1, 2, \ldots$

The combination of lattice translation & rotation will fix N

First, it is clear, if A, B are nearest-neighbour lattices (see below), B' must be a lattice point.



Now, if we shift the origin of rotation to B, rotation $-\phi$ $\left(= \frac{(N-1)}{N} 2\pi n = 2\pi n - \frac{2\pi}{N} n\right)$ brings A to A'.

Since $-\phi$ must be a part of N-fold operation,

$\therefore$, A' must be a lattice point too.

Both A' & B' are lattice points, so

$$\overline{A'B'} = m\overline{AB}$$

But $\overline{A'B'} = \overline{AB} + 2\overline{AB}\sin(\phi - \pi/2) = \overline{AB}(1 - 2\cos\phi)$

$\therefore$ $1 - 2\cos\phi = m$, $\cos\phi = \frac{1}{2}(1-m)$

only, $m = 0, 1, 2, 3$ are possible.

$\therefore \phi = \frac{2\pi}{N}$ $N = 2, 3, 4, 6$ ($\phi = 2\pi$ is a trivial rotation)

i.e. $\phi = \pi$ 2-fold symmetry

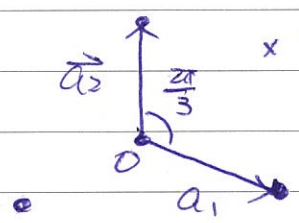
$\frac{2\pi}{3}$ 3-fold "

$\frac{\pi}{2}$ 4-fold "

$\frac{\pi}{3}$ 6-fold "

$\therefore$ One can't have 5-fold symmetry (as observed in quasi-crystal, to be discussed latter.)

Now, pure $\phi = \frac{2\pi}{3}$ is not possible:

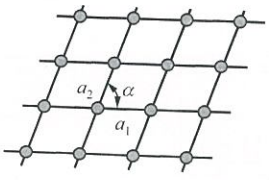


$\therefore \vec{a_1} + \vec{a_2} = \vec{OA}$

$\therefore \frac{2\pi}{3}$ must be the same as $\pi/3$.

Hence, one can only have 4 kinds of symmetries: (5 lattices)

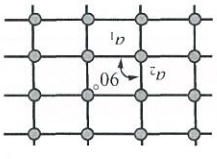
(a) Oblique



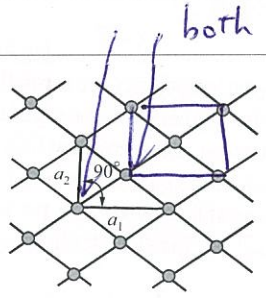
π 2-fold

2π

(b) rectangular



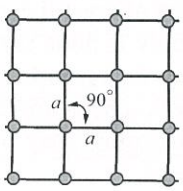
(c)



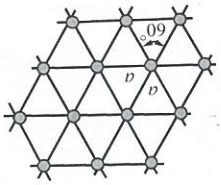
both can be centers for π mirror

(rhombic)

(d) Square



$\frac{\pi}{2}$ mirror. (centered square | — = square)



(e) hexagonal

$\frac{\pi}{3}$, mirror ✗

(4 crystal systems in 2D)

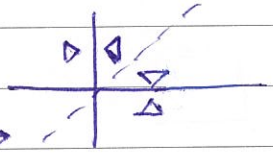
Point-Group nomenclature & notations:

there are two systems: Schönflies & international

Schoenflies	International
(i) C_n: n-fold rational axis	n
(ii) C_{nv}: n-fold axis + mirror planes containing axis of rotations	nmm (n=even) / nm (n=odd) — one m for each type of mirror plane

note that n-rotations bring a mirror plane into n mirror planes ⇒ same type ⇒ one m.

two mirror planes automatically generate → another mirror plane



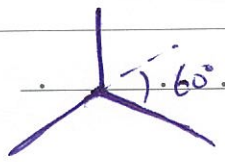
another type: one m!

∴ 2n mm

(iii) C_{nh}: n-fold axis + a single mirror plane ⊥ axes	n/m
	$\bar{n}$

C_{6h}, C_{4h}, C_{2h} ⇒ n/m (6/m, 4/m, 2/m)

C_{3h} = 6-fold inversion axis ⇒ $\bar{6}$



I $R_{60°}$ = mirror. R $\frac{2\pi}{3}$

$C_{1h} = m$ (not $\frac{1}{m}$)

(iv) S_n n-fold rotation-reflection axis. $\bar{n}$ n-fold rotation-inversion axis

$S_4 \Rightarrow \bar{4}$, $S_6 \Rightarrow \bar{3}$, $S_2 \Rightarrow \bar{1}$

(v) D_n n-fold rotation axis

+ 2-fold axis $\perp$ n-fold axis $n \geq 2$ (n even)

+ generated by n-fold rotation $n \geq 3$ (n odd)

(vi) D_{nh} D_n + a mirror plane $\perp$ n-fold axis n/m $3/m$ $2/m$ (or n/mmm)

D_{3h} (just as C_{3h}) $\Rightarrow$ $\bar{6} \geq m$

$\bar{6}$

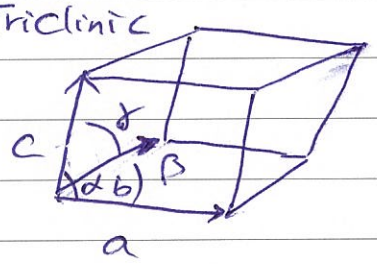
$\bar{n} \geq m$ (n even)

(vii) D_{nd} D_n + mirror planes containing n-fold axis which bisect angles between the 2-fold axes $\bar{n}\frac{2}{m}$ (n odd)

For 3D, one has 14 Bravais lattices (using the above notations)
(7 crystal systems)

Starting from the most general unit cell (primitive)

(1) Triclinic

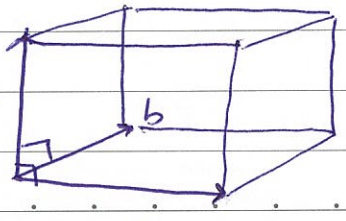


$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma$

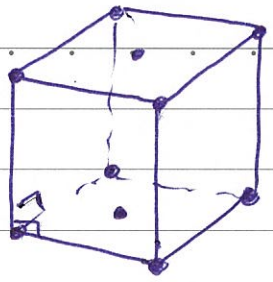
↓ path 1, increasing symmetry

(2) Monoclinic



$a \neq b \neq c$

$(a,c) = (b,c) = 90°$

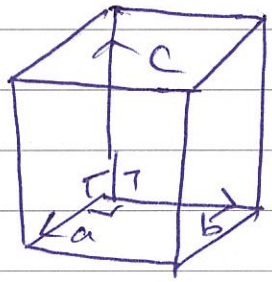


reflection symmetry w.r.t. (a c) & (b.c) plane

Remark: The unit cell with only one 90° angle has the same symmetry as triclinic

↓

(3) Orthorhombic



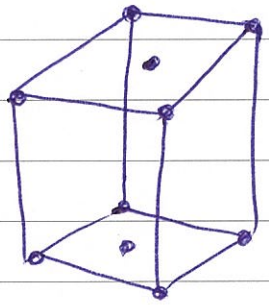
$a \neq b \neq c$

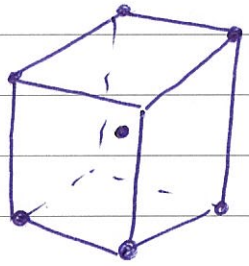
$(a,b) = (b,c) = (c,a) = 90°$

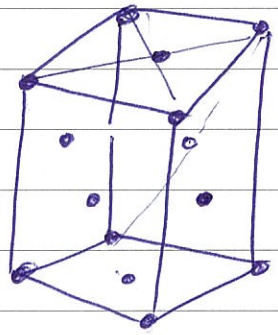
e.g. HTc materials

$YBa_2Cu_3O_7$

La_2CuO_{4-y}

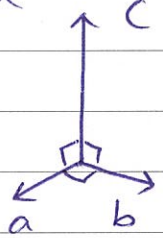






↓

(4) Tetragonal



$a = b \neq |c|$

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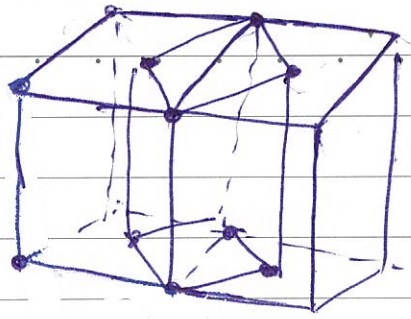
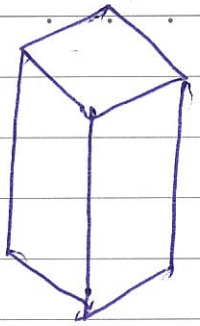
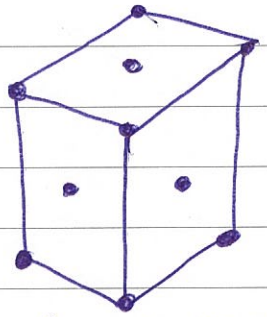
note that



=

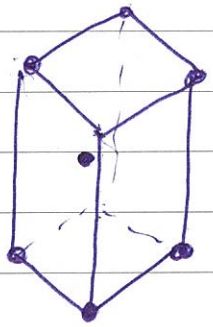


(simple tetragonal)



face-centered

=

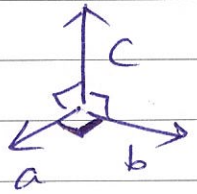


(centered tetragonal)

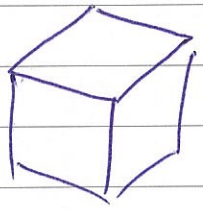
∴ only

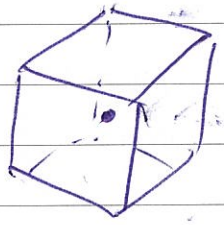
↓

(5) Cubic

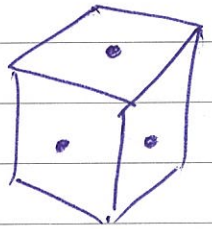


$a=b=c$





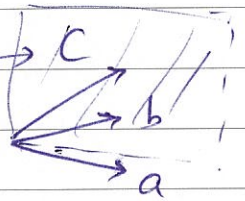
BCC



FCC

(6)
Path 2 Trigonal (Rhombohedral)

(stretch cube along body diagonal)



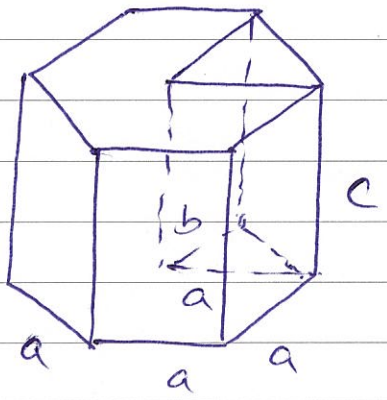
$a=b=c$ $(a,b)=(b,c)=(c,a)\neq 90°$

Symmetry: reflection about planes bisect angles (a,b) (b,c) or (c,a) → (e.g. E)

(7)

path 3.

Hexagonal



$a = b \neq c$

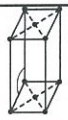
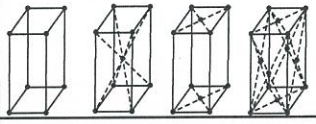
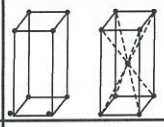
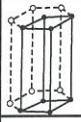
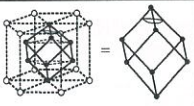
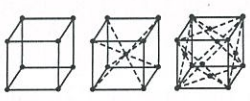
$(a,b) = 60°$

$(a,c) = (b,c) = 90°$

Symmetries:

rotational symmetry ($60°$)

reflection symmetry

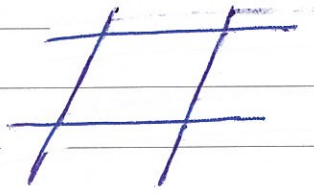
Crystal System	Type of Lattices					Related Point Group
	P	I	C	F	R	
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90$						$1, \bar{1}$
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90$ $\beta \neq 90$						$2, m, \frac{2}{m}$
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90$						$222, 2mm,$ $\frac{2}{m}\frac{2}{m}\frac{2}{m}(mmm)$
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90$						$4, \bar{4}, \frac{4}{m}$ 422, $4mm, \bar{4}2m,$ $\frac{4}{m}\frac{2}{m}\frac{2}{m}(4/mmm)$
Hexagonal $a = b \neq c$ $\alpha = \beta = 90$ $\gamma = 120$						$6, \frac{3}{m}, \frac{6}{m}$,622, $6mm, \bar{6}2m,$ $\frac{6}{m}\frac{2}{m}\frac{2}{m}(6/mmm)$
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90$						$3, \bar{3}, 32, 3m,$ $\bar{3}\frac{2}{m}$ $(\bar{3}m)$
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90$						$23, \frac{2}{m}\bar{3}(\bar{3}m),$ $432, \bar{4}3m,$ $\frac{4}{m}\bar{3}\frac{2}{m}(m\bar{3}m)$

P (Primitive) , I (Body Center) , C (Bottom Center), F (Face Center), R (Rhombohedron)

Crystal structures = lattice + basis

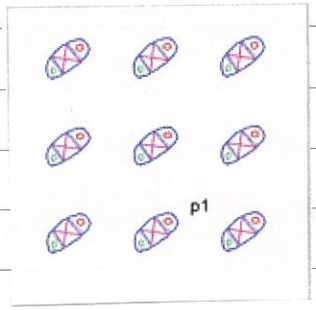
- mathematical points in lattices are isotropic. In reality, basis has its own symmetry, therefore, the combination of basis & lattice further increases the possibilities.

It turns out that for 2D, there are 17 crystal structures (17 plane groups), in 3D, there are 230 space groups. (32 point groups in 3D). We shall not list all of them but illustrate some of them in 2D.

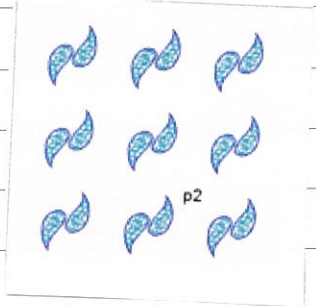


+ basis

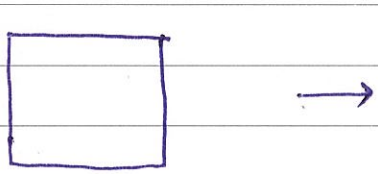
=

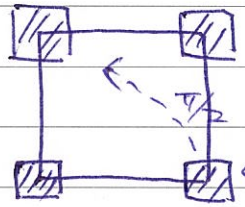


or

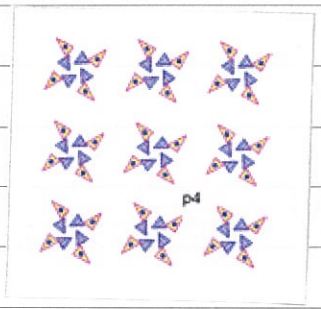


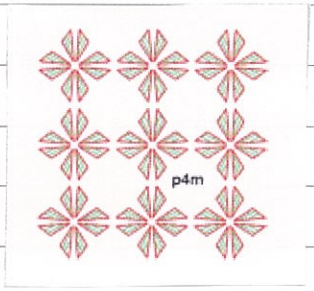
In general, basis's symmetries has to be compatible with those of lattices. (In the above example, Symmetries of oblique $= \pi$ or 2π, $\therefore$ Symmetries of basis $= \pi$ or 2π, which are the two examples given!)





← basis is also rotated by $\pi/2$





Complete list is in 2-20

<u>New Symmetries</u>: the combination of point group and translation yields new symmetries.

Those are invariant under point group and translation separately ⇒ Symmorphic (73 out of 230)

The remainings, however, are invariant only when point group & translation are combined (not in Bravais lattice vector)

⇒ non symmorphic

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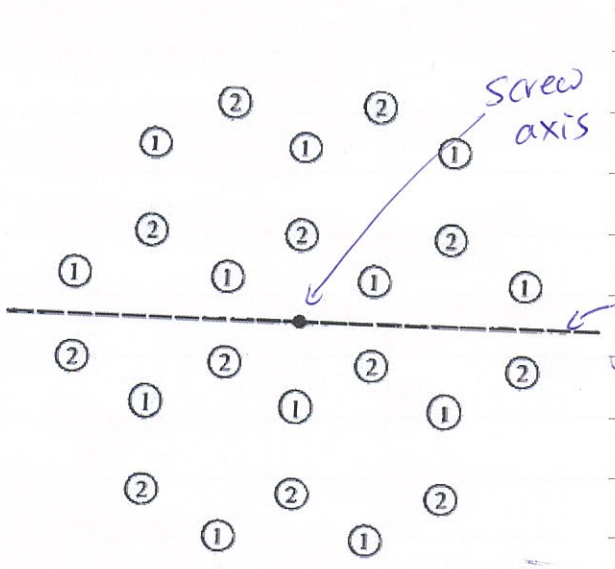
Screw Axes & Glide planes

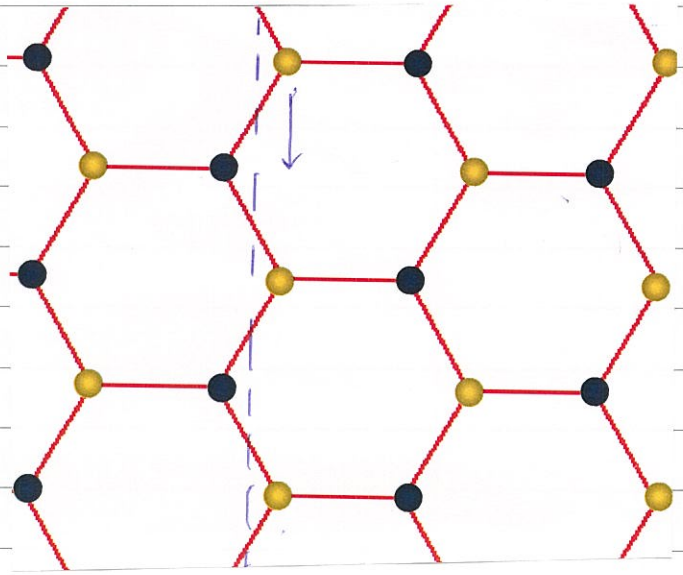
Screw & gliding are two new operations that are invariant.



Take hexagonal close-packed (hcp) as an example (see left)

① are in the same plane differing by $c/2$ to the plane of ②

screw: translate by $c/2$, then rotate 60°
⇒ is invariant



gliding: translate $c/2$ then mirror imaging with to the dash plane
⇒ invariant

in 2D, glide planes become lines.

For example, for graphene, the dash line is a gliding line

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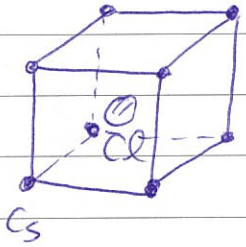
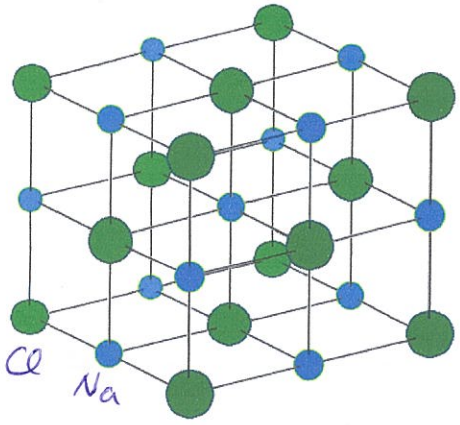
Important examples of crystal structures

(1) Cesium Chloride — Simple cubic with basis : CsCl



AgCd CsBr
AgMg
AgZn

(2) Sodium Chbride (NaCl) — Rocksalt
AgCl, AgBr, MgO, ... NaF, NaI, ..



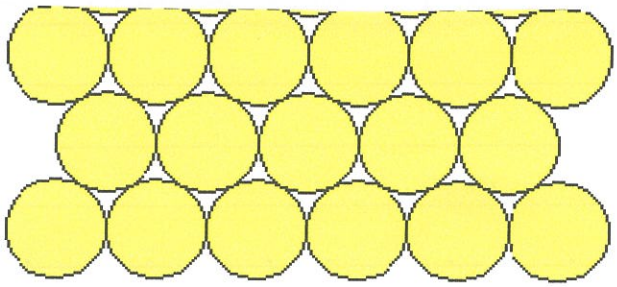
Can be viewed as

FCC with $\begin{cases} Cl\,(0,0,0) \\ Na\,(\frac{a}{2},0,0) \end{cases}$

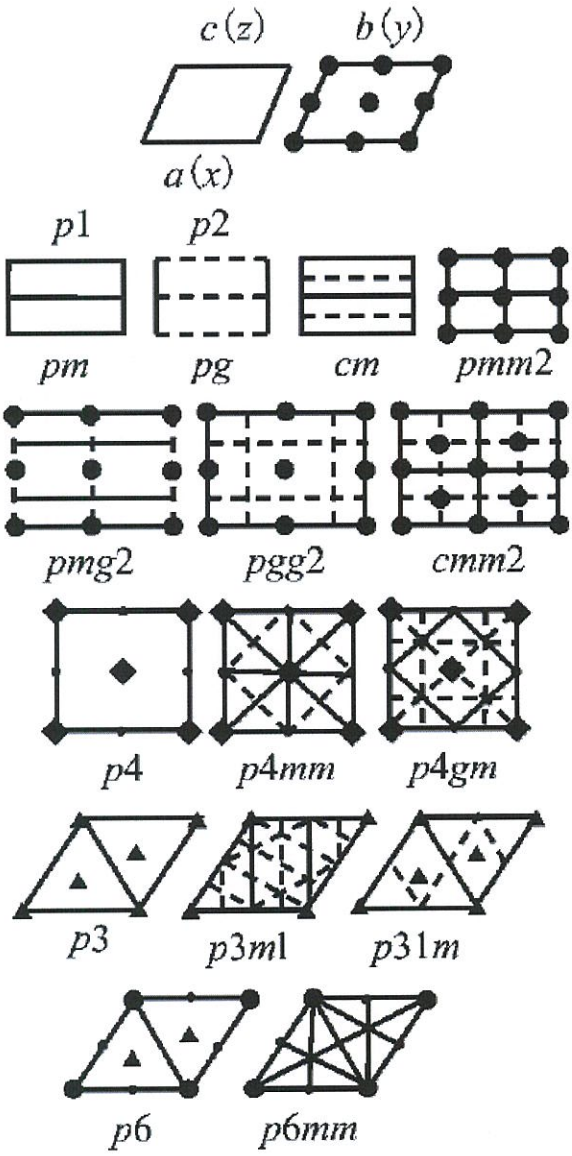
as a basis

(3) Close-packed structure.

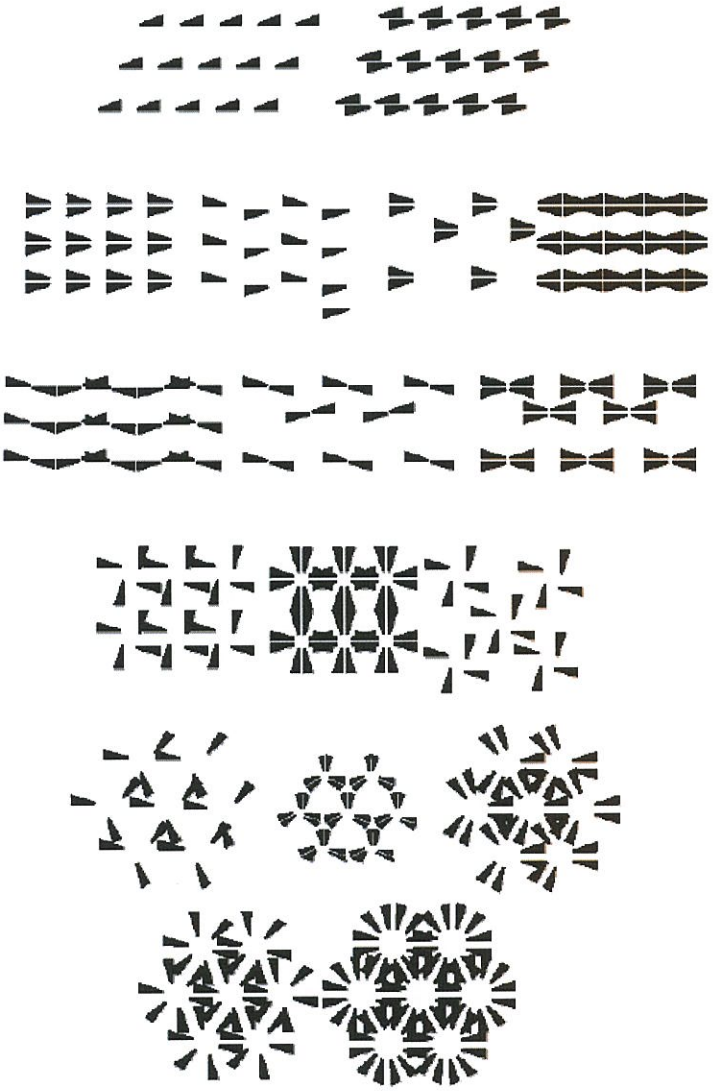
Close-packed can lower down the total energy, ideally, one can treat atoms as spheres and ask for close-packed structures. It's clear that in 2D, it is hexagonal lattice which is closed-packed!



17 plane groups (reference)



(a)



(b)

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Date.

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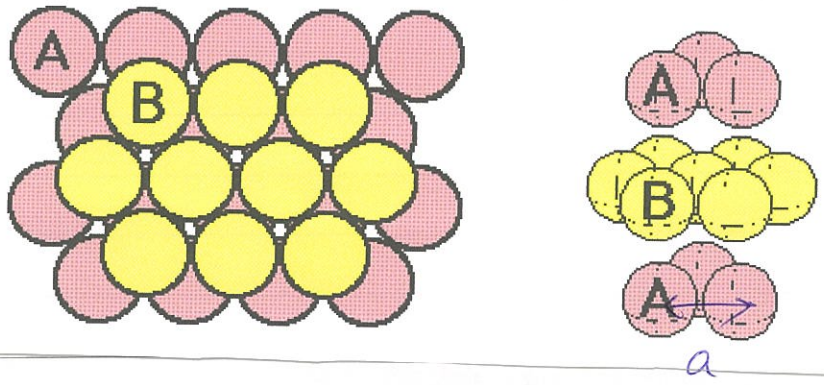
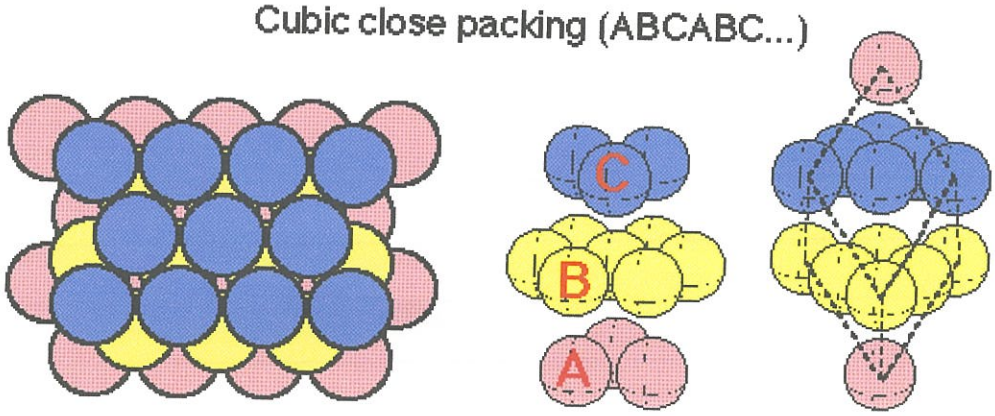
For 3D, obviously, one has two ways to close-pack spheres:



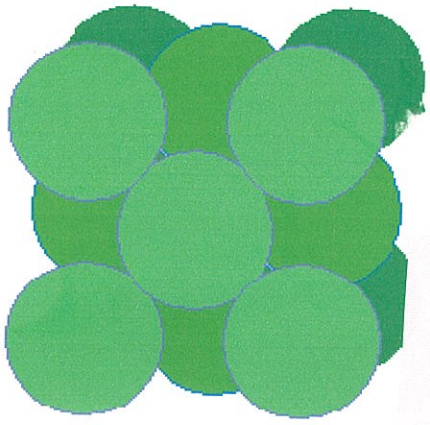
graphite, ..

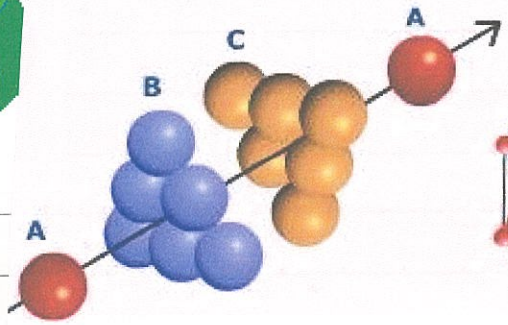
c/a ratio can be varied but the symmetry is the same.

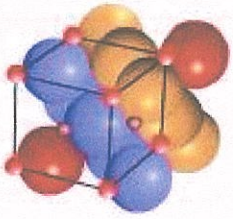
When $c/a = \sqrt{\frac{8}{3}}$, it's truly close-packed

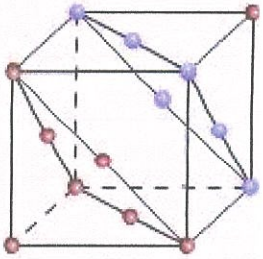


ABAB.. stacking is known as hexagonal closed-packed (hcp) structure, while ABCABC.. stacking turns out to be the same as FCC (see below)









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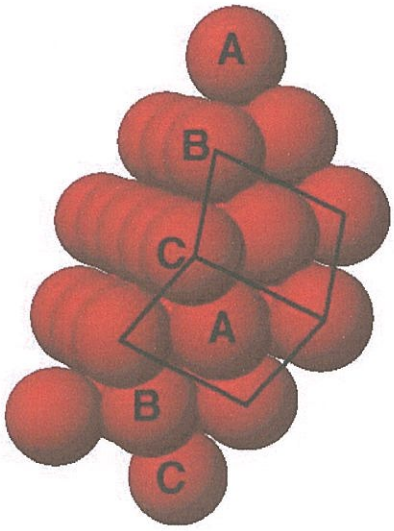
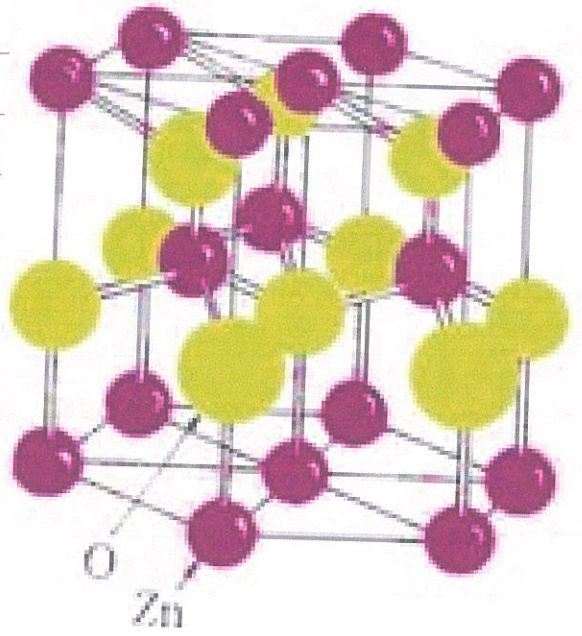


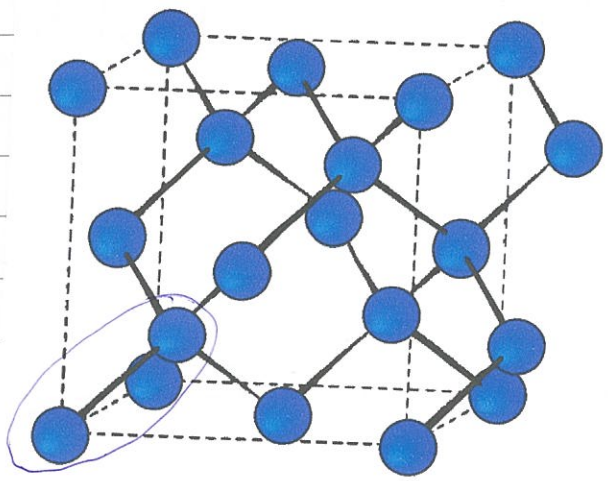
← FCC as ABCABC··· Stacking

(4) Wurtzite (ZnO, Zinc Oxide)



(5) Diamond structure : FCC.

basis : C-C (0,0,0), $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$



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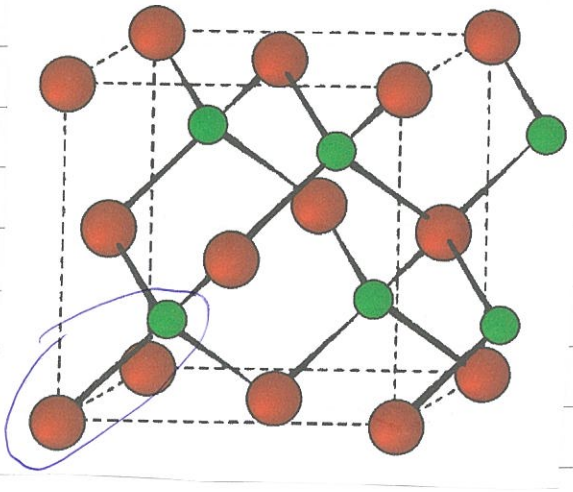
(6) Zinc blend structure Zinc - Sulfur

(0,0,0) $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$



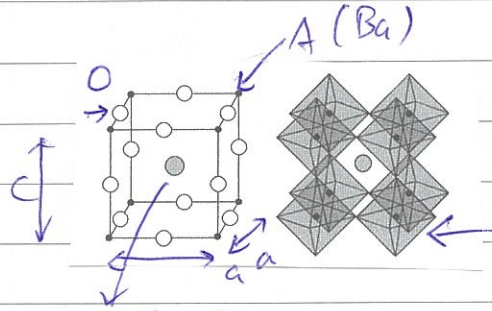
(7) Perovskite structure (ABX_3)

$CaTiO_3$, $BaTiO_3$, ...

$LaMnO_3$ (orthorhombic perovskite, $a \neq b \neq c$)

Tilted MnO_6 octahedra

colossal magnetoresistance (CMR) in doped $LaMnO_3$



$T > T_c$ $C = a$ (Cubic)

$T < T_c$ $C > a = b$ ($BaTiO_3$) (tetragonal)

Ba^+, Ti^+ moves ↑

O^{--} ↙ produces dipoles

⇒ Ferroelectric crystals

ABX_3 is enlarged to include K_2NiF_4 (layered perovskite) & parent compound of high T_c

La_2CuO_4 3 unit cells of ABX_3 stack one by one, in the middle, A & B exchanged.

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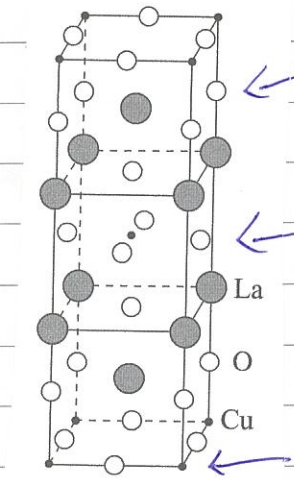


A=Cu
B=La

A=La
B=Cu

A=Cu
B=La

discovered by Bednorz & Müller

$La_{2-x}Ba_xCuO_4$

(Sr)

Mathematical description of ideal lattices
3D Fourier series & Reciprocal lattices

For ideal lattices, positions of atoms/ions are fixed. Therefore, physical quantities such as $n(\vec{r})$ (density of electrons) are periodic functions:

$$f(\vec{r}+l\vec{a}_1+m\vec{a}_2+n\vec{a}_3) = f(\vec{r}).$$

For 1D, periodic functions satisfy

$$f(x+a) = f(x)$$

therefore $f(x+2a) = f(x+a) = f(x)$

$$\Rightarrow f(x+na) = f(x)$$

Such functions are expressible as combinations of $\sin\frac{2\pi}{a}x$, $\cos\frac{2\pi}{a}x$, $\sin 2x\frac{2\pi}{a}x$, $\cos 2x\frac{2\pi}{a}x$, ...

i.e. only $K = \frac{2\pi}{a} x n$ survive in ....

$n = 1, 2 ..$

the Fourier transformation:

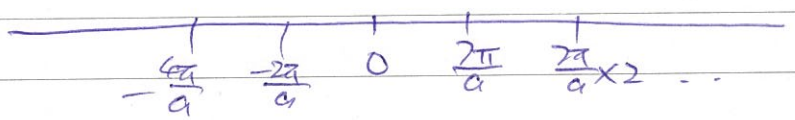
$$f(x) = \sum_n f_n \, e^{i \frac{2\pi i x}{a} x n}$$

This is known as <u>Fourier series</u>!

One can set $g = \frac{2\pi}{a} x n$, then

$$f(x) = \sum_g f_g \, e^{igx}$$

$g = n \frac{2\pi}{a}$ form another lattice in K space



Known as reciprocal lattice

$\frac{2\pi}{a}$ = reciprocal lattice constant.

Here f_n could be complex.

$$f_n = \frac{1}{a} \int_0^a f(x) \, e^{-i \frac{2\pi n x}{a}} \, dx$$

$$= \frac{1}{a} \int_{\text{primitive cell}} f(x) \, e^{-igx} \, dx$$

$\Uparrow$

$0 < x \leq a$ ....

How do we generalize the Fourier series to 2D or 3D?

Clearly, we try to write by generalizing g to

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

$\because f(\vec{r} + l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3) = f(\vec{r})$ for any l, m, n

$\therefore$ One requires $e^{i(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3)\cdot\vec{g}} = 1$

for any integers l, m & n.

$\therefore (l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3)\cdot\vec{g} = 2\pi N$ $\quad N =$ some integer

$\longleftarrow$ ①

Consider special cases:

$l=1,\ m=n=0.$ $\quad \vec{a}_1\cdot\vec{g}_1 = 2\pi$

$l=0=n=0,\ m=1.$ $\quad \vec{a}_2\cdot\vec{g}_2 = 2\pi$

$l=m=0,\ n=1$ $\quad \vec{a}_3\cdot\vec{g}_3 = 2\pi$

These don't determine $\vec{g}_1, \vec{g}_2$, & $\vec{g}_3$ uniquely.

If we further define $\vec{a}_i\cdot\vec{g}_j = 0$ for $i \neq j$,

Since $\vec{g}_j$ has 3 components and there are

3 equations for each $\vec{g}_j$, $\vec{g}_j$ are determined

uniquely.

Furthermore, $\vec{g}_1$, $\vec{g}_2$ & $\vec{g}_3$ are linearly independent.

$\therefore$ Any $\vec{g} = \alpha \vec{g}_1 + \beta \vec{g}_2 + \gamma \vec{g}_3$

① implies $l\alpha + m\beta + n\gamma = N$ for any $(l, m, n) \in \mathbb{Z}$ ← ②

Since $(l+1, m, n)$ is a solution to ②,

$\therefore$ α must be an integer

Similarly, β, γ must be integers.

$\therefore$ $\vec{g} = n_1 \vec{g}_1 + n_2 \vec{g}_2 + n_3 \vec{g}_3$ $\quad n_i \in \mathbb{Z}$

describe a lattice formed by $\vec{g}_1$, $\vec{g}_2$, & $\vec{g}_3$.

This is 3D reciprocal lattice.

We can further express $\vec{g}_i$ in terms of $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$.

$\because$ $\vec{g}_1 \cdot \vec{a}_2 = 0$, $\vec{g}_1 \cdot \vec{a}_3 = 0$

$\therefore$ $\vec{g}_1 \propto \vec{a}_2 \times \vec{a}_3$, $\quad \vec{g}_1 \equiv \alpha_1 \vec{a}_2 \times \vec{a}_3$

$\vec{a}_1 \cdot \vec{g}_1 = 2\pi = \alpha_1 \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

$\therefore$ $\alpha_1 = \dfrac{2\pi}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$ $\quad \vec{g}_1 = 2\pi \dfrac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

Similarly, $\vec{g}_2 = 2\pi \dfrac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}$, $\vec{g}_3 = 2\pi \dfrac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$

Now from $f(\vec{r}) = \sum_{\vec{g}} A_{\vec{g}}\, e^{i\vec{g}\cdot\vec{r}}$

One gets

$$\int e^{-i\vec{g}\cdot\vec{r}} f(\vec{r}) = \sum_{\vec{g}'} A_{\vec{g}'} \int e^{i(\vec{g}'-\vec{g})\cdot\vec{r}}\, d\vec{r} \quad \text{--- (2)}$$

For $\Delta\vec{g} \neq 0$

$$\int_{\text{unit cell}} e^{i\Delta\vec{g}\cdot\vec{r}}\, d\vec{r}, \quad \begin{cases} \vec{r} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3 \\ \Delta\vec{g} = \Delta n_1\vec{g}_1 + \Delta n_2\vec{g}_2 + \Delta n_3\vec{g}_3 \end{cases}$$

$$= \int_0^1\int_0^1\int_0^1 e^{i2\pi(x\Delta n_1 + y\Delta n_2 + z\Delta n_3)}\, dx\, dy\, dz$$

$\neq 0$ only when $\Delta n_1 = \Delta n_2 = \Delta n_3 = 0$

$$\therefore \int_{\text{unit cell}} e^{i\Delta\vec{g}\cdot\vec{r}}\, d\vec{r} = \delta_{\vec{g},\vec{g}'}\, v_{\text{cell}}$$

$\therefore$ Eq. (2) implies $A_{\vec{g}} = \frac{1}{v_{\text{cell}}} \int_{\text{unit cell}} f(\vec{r})\, e^{-i\vec{g}\cdot\vec{r}}\, d\vec{r}$

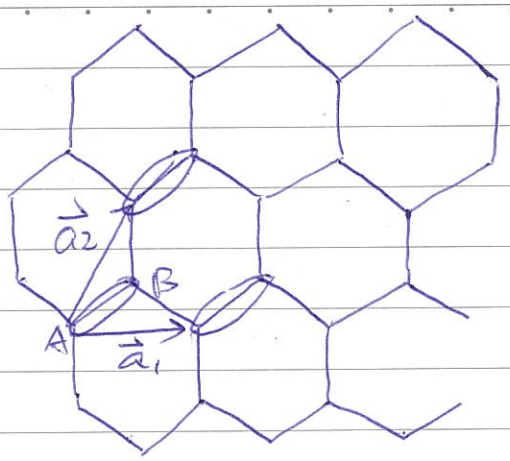
Examples : reciprocal lattices of simple cubic

= simple cubic $\left(\frac{2\pi}{a}\right)$

fcc → bcc (exercise)

bcc → fcc

graphene :



$\vec{a}_1 = (a, 0, 0)$ $\quad \vec{a}_2 = (\frac{a}{2}, \frac{\sqrt{3}}{2}a, 0)$

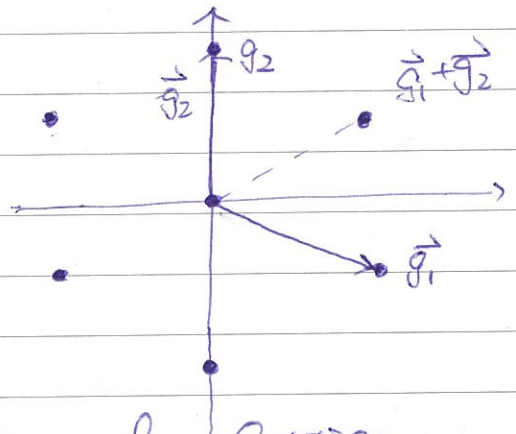
$\vec{a}_3 = (0, 0, 1)$

$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{\sqrt{3}}{2}a \cdot 2 = v_{cell}$

$\vec{g}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{v} = 2\pi (\frac{1}{a}, -\frac{1}{\sqrt{3}a}, 0) = \frac{4\pi}{\sqrt{3}a} (\frac{\sqrt{3}}{2}, \frac{-1}{2}, 0)$

$\vec{g}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{v} = \frac{4\pi}{\sqrt{3}a} (0, 1, 0)$, $|\vec{g}_1| = |\vec{g}_2| = \frac{4\pi}{\sqrt{3}a}$

$\vec{g}_3 = 2\pi (0, 0, 1)$



$n\vec{g}_1 + m\vec{g}_2$ = hexagonal lattice

$\frac{1}{v} n(\vec{r})$ = density of atoms $= \sum_i f(\vec{r} - \vec{r}_{Ai}) + f(\vec{r} - \vec{r}_{Bi})$

$\therefore A_g = \frac{1}{\frac{\sqrt{3}}{2}a^2} [1 + e^{-i\vec{g}\cdot\vec{r}_B}]$ $\quad \vec{r}_B = \frac{a}{\sqrt{3}} (\frac{\sqrt{3}}{2}, \frac{1}{2})$

$A_{n,m} = \frac{2}{\sqrt{3}a^2} [1 + e^{-i\frac{2\pi}{3}(n+m)}]$ $\quad = (\frac{a}{2}, \frac{a}{2\sqrt{3}})$

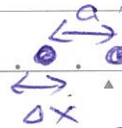
$= \frac{1}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2$

Experimental determination : Scattering

Scattering is one of the oldest ways to probe the structure of materials. The way we look at this world is just one example.

There are many experimental techniques in condensed matter physics that are based on scatterings. Two most important examples are X-rays scattering & neutron scatterings. (other expts may include ARPES, Raman scattering expt. etc.).

Using X-rays to probe crystal dates back to M. von Laue in 1912. In early days, researchers (such as Sommerfeld, Wen) do not believe that one can use X-rays scattering off crystals as ordinary light scatters off a diffraction grating to "observe" crystals (atoms in a crystal).

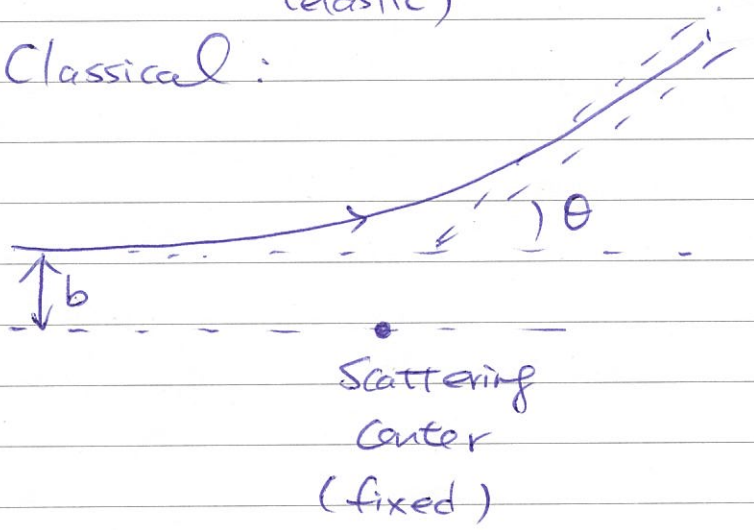
The main argument is that the thermal fluctuations may destroy the diffraction effects!  $\sqrt{\langle \delta x \rangle} \lesssim a$. As we shall see, this turns out not to be crucial.

Theory of Scattering in (elastic)

Collimated Matter $dN(\Omega)$/per sec

$d\Omega$.

Classical:



b = impact parameter

θ = scattering angle

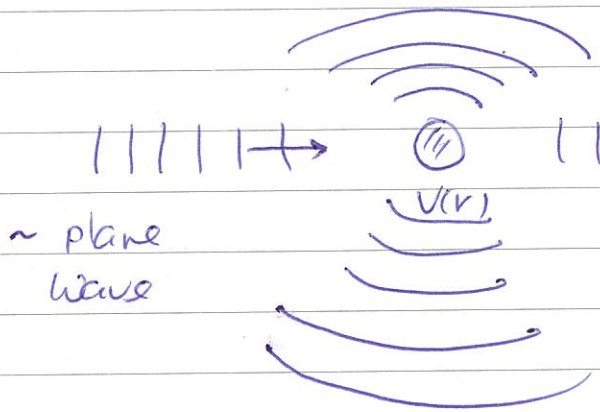
Scattering Center (fixed)

$$\sigma(\Omega) = \frac{d\sigma}{d\Omega} \qquad d\sigma = \frac{dN(\Omega)}{I}$$

= differential cross-section

I = flux = $\frac{\#\text{ of particle}}{\text{area sec}}$

Quantum scattering : Single scattering center



incident : $e^{i\vec{k}_0\cdot\vec{r}}\, e^{-i\frac{E\omega}{\hbar}t}$ for particles (e.g. neutrons.)

$e^{i\vec{k}\cdot\vec{r}}\, e^{-i\omega t}$ for X-ray, light.

Surviving Scattering wave $\psi_s = \frac{e^{ikr}}{r} f(\Omega)$, $k = k_0$ other power $\frac{1}{r^\alpha}$.

$\uparrow \theta, \phi$

$\alpha > 1$ will not go out

Far away current $\vec{J}_{sc} = \frac{\hbar k}{m} \left|\frac{f(\Omega)}{r}\right|^2 \hat{r}$

$$\therefore dN(\Omega) = \vec{J}_{sc} \cdot \hat{r}\, r^2 d\Omega$$

$$= |f(\Omega)|^2 \frac{\hbar k}{m} d\Omega, \quad k = k_0$$

$$J_{incident} = \frac{\hbar k_0}{m}$$

$$\therefore d\sigma = \frac{dN}{J_{in}} = |f(\Omega)|^2 d\Omega$$

$$\frac{d\sigma(\Omega)}{d\Omega} = |f(\Omega)|^2 \equiv I \text{ (Scattering intensity)}$$

&

$$\psi = e^{i\vec{k}_0 \cdot \vec{r}} + \frac{e^{ikr}}{r} f(\theta, \phi) \quad \left(\text{assumption } rV(r) \to 0 \text{ as } r \to \infty\right)$$

$\hat{r}$

Many scattering centers (cases encountered in condensed matter) $\because e^{ik\vec{r}} = e^{ik_0 \cdot \vec{r}_i} e^{i\vec{k}_0 \cdot (\vec{r} - \vec{r}_i)}$

$$\psi_s(\vec{r}) = \sum_i \psi_s(\vec{r} - \vec{r}_i)$$

$$\psi_s(\vec{r} - \vec{r}_i) = f(\vec{r}) \frac{e^{ik_0|\vec{r} - \vec{r}_i|}}{|\vec{r} - \vec{r}_i|} \underbrace{e^{i\vec{k}_0 \cdot \vec{r}_i}}_{\text{accounting for}}$$

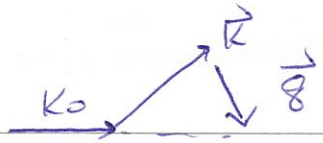
→ plane wave phase difference at different centers.

for large r

$$\because k_0|\vec{r} - \vec{r}_i| \simeq k_0 r - k_0 \frac{\vec{r}}{r} \cdot \vec{r}_i \equiv k_0 - \vec{k} \cdot \vec{r}_i \quad \vec{k} = k_0 \hat{r}$$

$$\therefore \psi_s(\vec{r} - \vec{r}_i) \simeq f(\vec{r})\, e^{i\vec{q} \cdot \vec{r}_i} \frac{e^{ikr}}{r}$$

$\hbar\vec{q} = \hbar(\vec{k}_0 - \vec{k})$ is the momentum change



$$\therefore \psi_s \approx \left(\sum_i e^{i\vec{q}\cdot\vec{r}_i}\right) f(\vec{r}) \frac{e^{ikr}}{r}$$

$$I \propto \left|\sum_i e^{i\vec{q}\cdot\vec{r}_i}\right|^2$$

$$= \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} \underbrace{\sum_i \delta(\vec{r}-\vec{r}_i)}_{n(\vec{r})\ \text{density of scatters}} \cdot \int d\vec{r}'\, e^{-i\vec{q}\cdot\vec{r}'} \sum_i \delta(\vec{r}'-\vec{r}_i)$$

$$= |n(\vec{q})|^2 \qquad (n(-\vec{q}) = n^*(\vec{q}))$$

$$= \int d\vec{r}_1 \int d\vec{r}_2\, e^{i\vec{q}\cdot\vec{r}_1} e^{-i\vec{q}\cdot\vec{r}_2}\, n(\vec{r}_1)\, n(\vec{r}_2)$$

Here $n(\vec{r})$ = density of scatters. In real experiments, positions of scatters are not fixed. Therefore, the measured I is the average of I over the measuring period Δt.

$$\therefore I \sim \int d\vec{r}_1 \int d\vec{r}_2\, e^{i\vec{q}(\vec{r}_1-\vec{r}_2)} \frac{1}{\Delta t} \int n(\vec{r}_1,t)\, n(\vec{r}_2,t)\, dt$$

If Δt is sufficiently large, one can replace $\frac{1}{\Delta t}\int n(r_1,t)\, n(r_2,t)\, dt$ by thermal averaging

$$\langle n(\vec{r}_1)\, n(\vec{r}_2)\rangle$$

Therefore,

$$I = I_0 \left| \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2$$

scattering intensity from single atom $\propto |f(\hat{r})|^2$

$$= I_0 \int dr_1 \int dr_2 \; e^{i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} \langle n(r_1)\, n(r_2) \rangle$$

$$= I_0 \langle n(q)\, n(-q) \rangle$$

Hence, scattering expts. measure $\langle A_q A_{-q} \rangle$ which is known as correlation functions. or $\langle n(r_1)\, n(r_2) \rangle$

example: x-rays : electron density correlation

neutron : spin-spin correlation (because neutron does not carry charge, it is sensitive to spin of electron)

& atom's density density correlation

Correlation functions : (相干散射)

$$G_{nn}(r, r') = \langle n(r)\, n(r') \rangle - \langle n(r) \rangle \langle n(r') \rangle$$

is a quantity that measure the correlation of n at r & r', more precisely, two-point correlation function. It can be generalized to n-point correlation functions.

Note that for general two point correlation function, if A & B are independent, $\langle AB \rangle = \langle A \rangle \langle B \rangle$, Hence, one has to substract $\langle A \rangle \langle B \rangle$ so that $G_{AB} = \langle AB \rangle - \langle A \rangle \langle B \rangle$ vanishes for A & B being independent!

For translational invariant systems (such as liquids), one has $G_{nn}(r,r') = G_{nn}(r-r')$

Hence $$\frac{I}{N I_0} = \frac{1}{N} \int dr \int dr' e^{-i\vec{q}\cdot(\vec{r}-\vec{r}')} [G_{nn}(r-r') + n_0^2]$$

N → total # of scatters

$$= \frac{V}{N} G(q) + \frac{V^2}{N} n_0^2 \delta(q)$$

with $G(q) = \int dR\, e^{i\vec{q}\cdot\vec{R}} G(\vec{R})$ being the Fourier transformation of $G(\vec{R})$.

Since $\delta(q)$ contributes only when $q=0$, the 2nd term is know as forward scattering and can be omitted as one often concerns scattering away from the original k_0 direction.

In general, $G_{nn}(r,r') \neq G_{nn}(r-r')$, one defines $\frac{I}{N I_0} = S(\vec{q})$ as the structure factor.

$$\therefore S(\vec{q}) = \frac{1}{N} \sum_{i,j} \langle e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} \rangle$$

$$= \frac{1}{N} \left\langle \int d^3\vec{r} \sum_{i,j} e^{i\vec{q}\cdot\vec{r}} \, \delta(\vec{r} + \vec{r}_j - \vec{r}_i) \right\rangle$$

$$\left\langle \sum_{i,j} \delta(\vec{r} + \vec{r}_j - \vec{r}_i) \right\rangle = \underbrace{\left\langle \sum_{i \neq j} \delta(\vec{r} + \vec{r}_j - \vec{r}_i) \right\rangle}_{\| \; N \cdot \rho \, g(r)} + N \delta(\vec{r}) \quad (i = j), \qquad \rho = N/V$$

$$\therefore S(\vec{q}) = 1 + \rho \int d^3\vec{r} \, g(r) \, e^{i\vec{q}\cdot\vec{r}}$$

Here $g(r) = \frac{1}{N\rho} \left\langle \sum_{i \neq j} \delta(\vec{r} + \vec{r}_j - \vec{r}_i) \right\rangle$ is termed as pair distribution function or radial distribution function, whose meanig is as follows:

$$N\rho \int g(\vec{r}) \, d\vec{r} = \left\langle \sum_{i \neq j} \right\rangle = N(N-1) \; (N(N-1) \simeq N^2)$$

$$\therefore \int \rho g(\vec{r}) \, d\vec{r} = N - 1$$

$\rho g(\vec{r})$ is normalized to $N-1$!

$\rho g(\vec{r})$ = probability dasity of (Simultaneously) finding two atoms separated by $\vec{r}$.

or $\propto$ probability of finding another atom at $\vec{r}$ when there is one at $\vec{r}=0$

... by using $P(A \cap B) = \frac{P(A/B)}{P(B)}$ ← conditional probability

i.e. $\rho g(\vec{r}) = \dfrac{\langle \rho(0)\,\rho(r)\rangle}{\rho(0)}$

Since $\int e^{i\vec{q}\cdot\vec{r}}\, d^3r \propto \delta(\vec{q})$ is omitted in expt.,

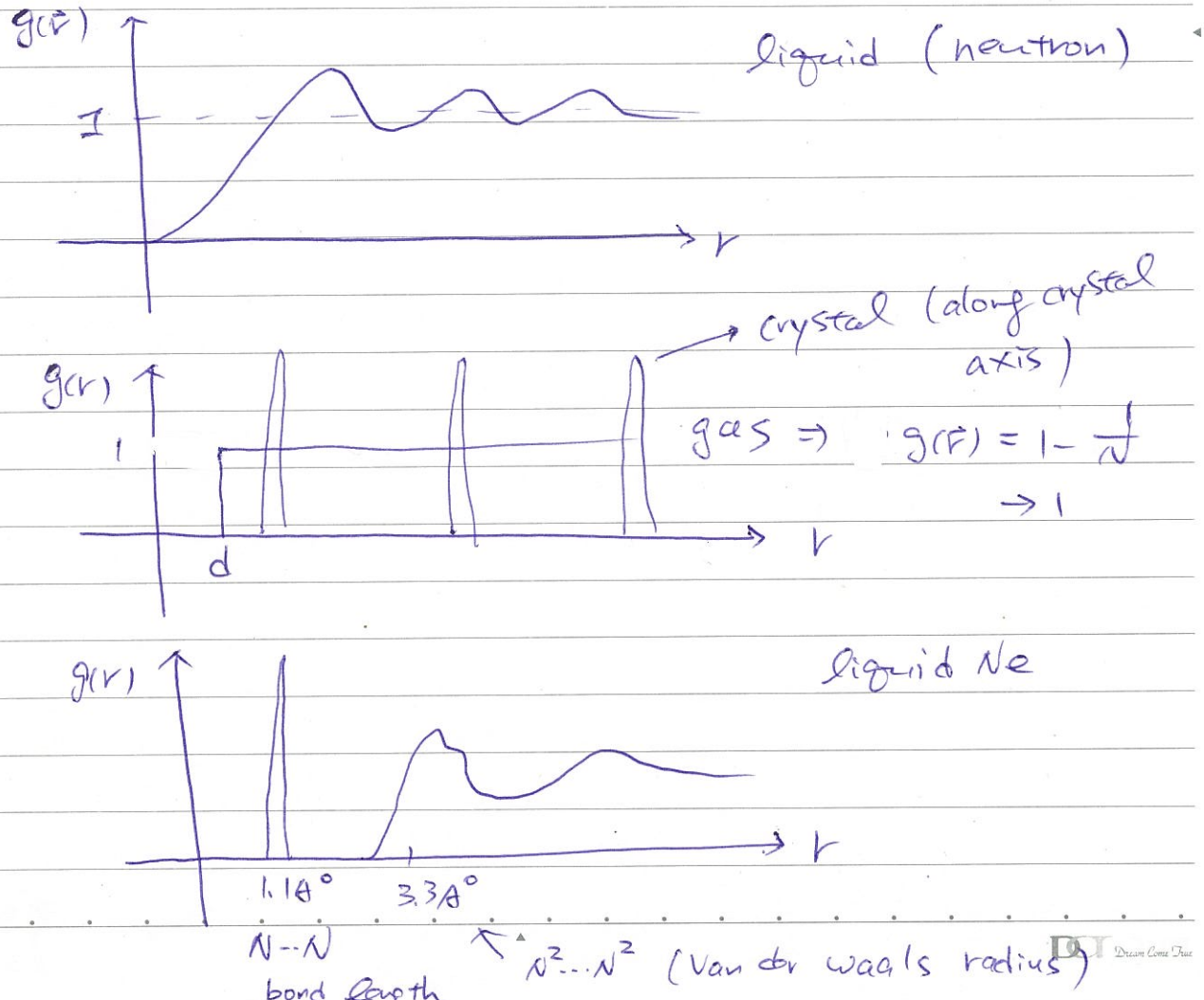
One often writes

$$S(\vec{q}) = 1 + \rho \int d^3r\ (g(r)-1)\, e^{i\vec{q}\cdot\vec{r}}$$

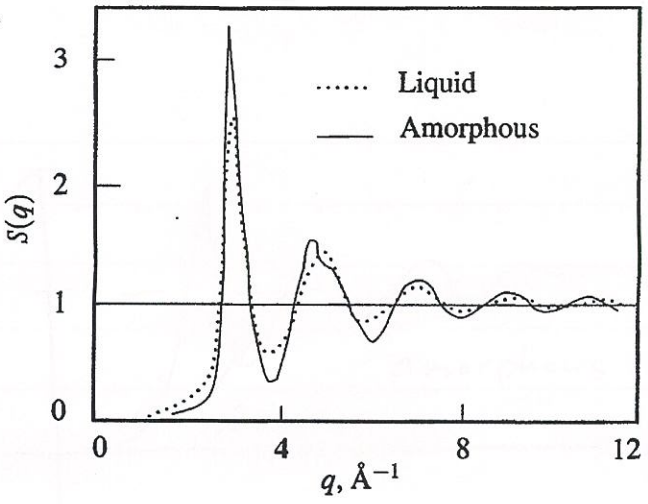
$g(r)-1 = \dfrac{\langle \rho(0)\,\rho(r)\rangle - \rho^2}{\rho^2}$ is clearly dimensionless

correlation function of density.

Some examples of $g(r)$



S(q)



Waseda (1980)

Near critical point

$S(q) \sim \frac{1}{q^2 + \kappa^2}$: Lorentzian form

in 3D

$S(r) \sim \frac{1}{r} e^{-\kappa r}$ → i.e. $\langle n(r)\, n(0) \rangle \sim \frac{1}{r} e^{-r/\xi}$

$\kappa \equiv 1/\xi$

$\xi \equiv$ correlation length. (相関長)

$\kappa = 1/\xi$ determines the width of peak of $S(q)$ at $q=0$ around T_c.

At $T = T_c$, peak $\to \infty$, $\therefore \kappa \to 0$, $\xi \to \infty$

This is known as the critical state (no particular length scale exists, $S(q)$ has a power law.)

"Here the system is long range correlated".

Many ordered phases, phase transitions have similar behavior