

Non crystalline state

Crystalline solids & liquids represent

two extremes:

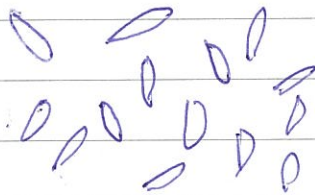
liquid: invariant under arbitrary translations & rotations, no long-range order

crystalline solids: invariant under discrete translation & point group operations

Remarkably, there exist states with intermediate orders.

Liquid crystals are one of examples.

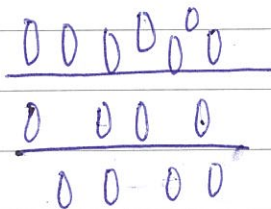
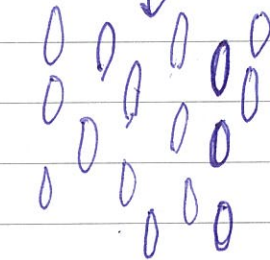
(example of molecule $C_5H_{11}O$ -- $C_{10}H_7$)



isotropic & homogeneous
(liquid) - $C_{10}H_7$
6503L

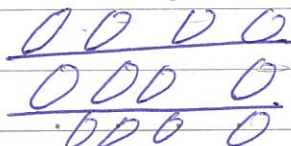


nematic: orientation order
position X



smectic-A: position (partial order)

orientational order

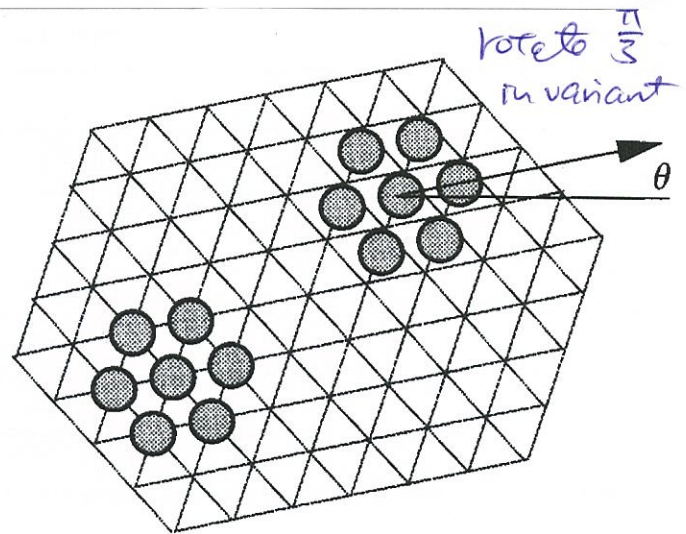
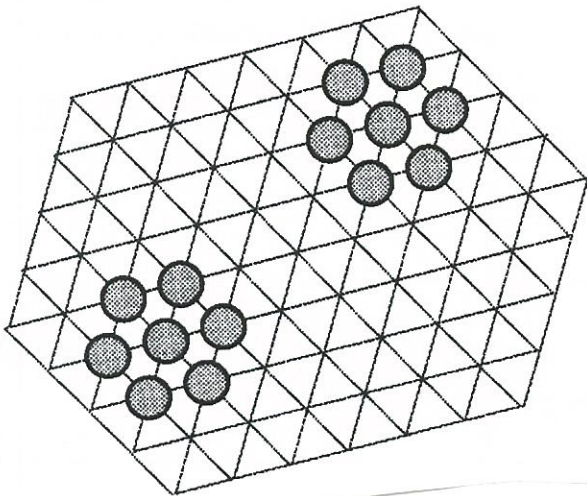


smectic-C

"

Hexatic phase

Between smectic-A & smectic-C, there exists so-called hexatic phase. In

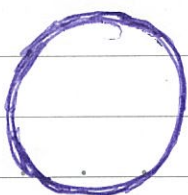


the hexatic phase, local orientation order is kept but position order is lost (see above). The order parameter

$$\equiv \psi_6 = e^{6i\theta} \quad (\text{invariant} = \theta \rightarrow \theta + \pi/3)$$

$$\text{Since } R(\pi/3) \vec{r}_i = \vec{r}_i, \therefore |e^{i\vec{s} \cdot \vec{r}_i}|^2 = |e^{i\vec{s} \cdot R(\pi/3) \vec{r}_i}|^2 \\ = |e^{iR(\pi/3) \vec{s} \cdot \vec{r}_i}|^2$$

\therefore In the structure factor, it is periodic in the angle of \vec{s} with 6-fold symmetry.

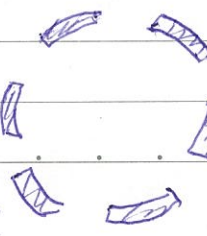


nematic



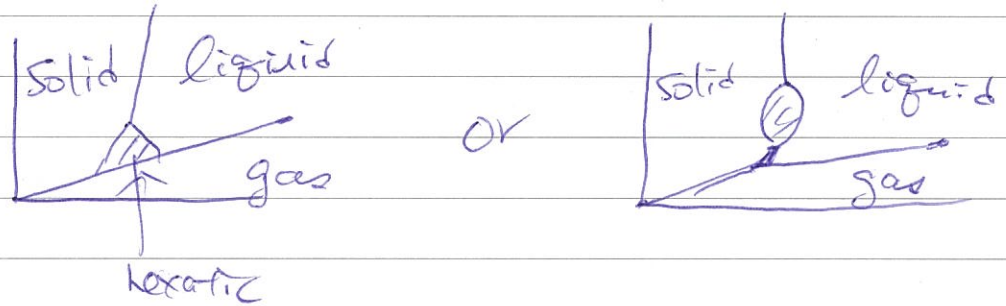
hexatic

Turbid



Smectic-C

The Hexatic phase is an intermediate phase between liquid & solid with orientational order.

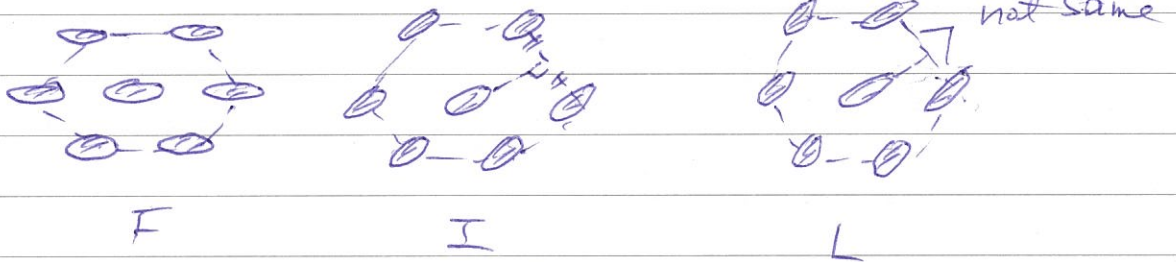


Due to its existence, the transition from liquid to solid is two-step and is continuous transition in this region.

For liquid crystals, there are three possible

hexatic phases: smectic-F, -I & -L:

viewed from c-axis



Lyotropic liquid crystals & microemulsions (≡乳液)

Phase transitions induced by temperatures ⇒ Thermotropic liquid crystals.

Phase transitions induced by change of concentration ⇒ Lyotropic liquid crystals.

Lyotropic liquid crystals are usually formed

by amphiphilic molecules consisting of two

parts that repel each other and are

soluble in different solution.

The most widely studied are those called lipids

and surfactant molecules (such as soaps).

These molecules usually consists of hydrophilic (water "liking") and hydrophobic (water "hating")

parts. Hydrophobic parts usually consists of hydrocarbon chains 8-20 carbon atoms.

Hydrophilic part has a charge or a dipole moment

Example: surfactant molecules



When these molecules are in contact with water,

lipids will self-organize into structures in

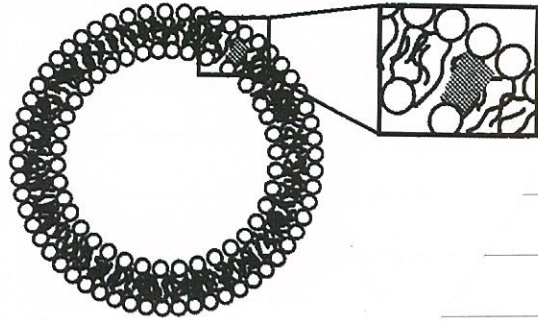
which hydrophobic tails are shielded from water.

(see the following figures)

By doing this way, they are soluble in oil &

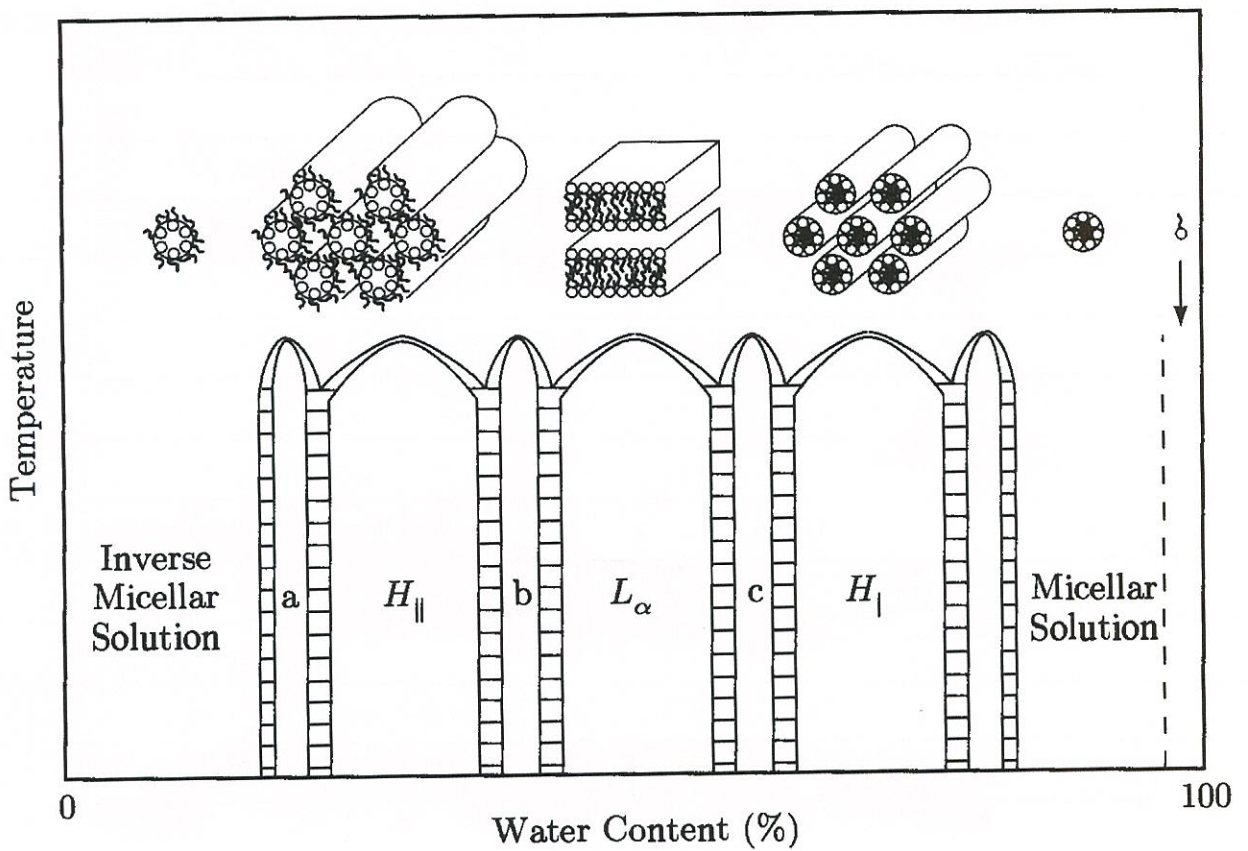
water. The equilibrium mixtures of water, oil &

surfactant (amphiphiles) are called microemulsions.



bilayer vesicle

a typical lipid



Phase diagram.

Incommensurate structure

Another intermediate structure between crystals & liquid (random) is the modulations (periodic)

with two or more relative irrational periods.

Such structures are also called quasi-periodic and the system is still long-range ordered!

A one-dimensional example:

$$n(x) = \sum_{n, m} \delta(x - na) + \delta(x - \alpha ma)$$

$\alpha = \text{rational} \Rightarrow$ two sets $\{ \pm a, \pm 2a, \pm 3a, \dots \}$
 $\{ 0, \pm \alpha a, \pm 2\alpha a, \pm 3\alpha a, \dots \}$

are commensurate

$\alpha = \text{irrational} \Rightarrow$ incommensurate

In this case, X-ray scattering observes

$$I_{\alpha} \quad |\vec{S}_{\vec{g}}|^2 \quad \vec{S}_{\vec{g}} = \sum_{n, n'} \delta \left(\vec{g} - \left(\frac{2\pi n}{a} + \frac{2\pi n'}{\alpha a} \right) \right)$$

$$\text{if } \alpha = \frac{q}{p} \text{ (rational), } \quad \frac{n}{a} + \frac{n'}{\alpha a} = \frac{n}{a} + \frac{pn'}{qa} = \frac{1}{qa}$$

$$(p, q) = 1$$

$$\times \underbrace{(gn + pn')}_{N}$$

$$\text{hence } \vec{S}_{\vec{g}} = \sum_{\substack{\text{Negative } n, n' \\ n, n'}} \delta \left(\vec{g} - \frac{2\pi N}{qa} \right) \dots \dots \dots \text{is periodic}$$

$a' = qa.$

However, not ^{cell} Bragg's peak have the

same intensity as it is clear from

$$n(x) = \sum_{n,m} f(x-na) + f(x - \frac{g}{p} ma) \quad \text{Some lattice}$$

point ^{such as}

$$n=g, m=p, x=ga, \text{ density} = 2f(x-ga)$$

is larger! This is the same effect as that due to superstructure!

As an example, one set $\alpha=2$.

In this case, one has so-called superlattice

with $a'=2a$, basis $0, a$, so that

$$F_g = 1 + 2e^{i\theta a}$$

$$I \propto \left| \left(\sum_n e^{i\theta \cdot n(2a)} \right) (1 + 2e^{i\theta a}) \right|^2$$

$$f\left(\theta - \frac{2\pi m}{2a}\right)$$

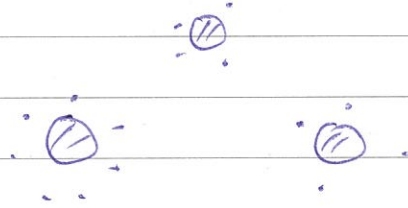
$$F\left(\theta = \frac{\pi m}{a}\right) = 1 + 2e^{i m \pi} = \begin{cases} 3 & m = \text{even} \\ -1 & m = \text{odd} \end{cases}$$

\Rightarrow

if $\alpha = \text{irrational}$, one needs two integers to describe peaks in reciprocal lattice. furthermore, vectors formed are dense in reciprocal lattice.

Since $g = G \pm \underbrace{\left(\frac{1}{a} \pm i\right)}_{\frac{2\pi}{a}n} \underbrace{\frac{2\pi}{b}m}_{b}$, one usually

finds satellite peaks in x-ray for incommensurate structures.



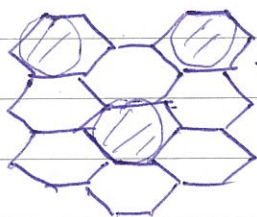
Incommensurate structures result from competition between two scales. Hence this often

happens when the crystal develops additional order such as magnetic structures, electric dipoles, incommensurate

Heterostructures such as depositing atoms onto substrate also provides another possibility.

Example: atoms (Kr, Xenon) adsorbs on

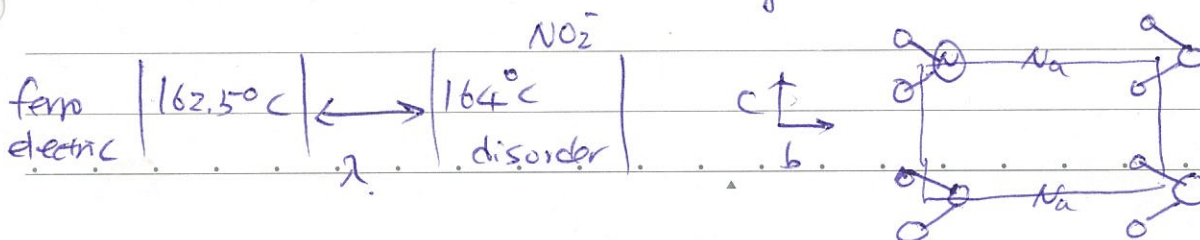
graphite surface \uparrow larger \Rightarrow incommensurate
Commensurate



$$\sqrt{3} \times \sqrt{3} R 30^\circ$$

Tanigaki

NaNO2 (1st material exhibiting incommensurate structure, 1961)



Satellites due to incommensurate modulation.

Example: $X_n = a(n + \epsilon \sin gna)$

ZFD: $\sum_n e^{i\theta na} = \frac{2\pi}{a} \sum_{k=-\infty}^{\infty} \delta(\theta - \frac{2\pi}{a}k)$

Using $e^{z \sin \theta z} = \sum_{m=-\infty}^{\infty} e^{im\theta} J_m(z)$

$$e^{i\theta \epsilon \sin gna} = \sum_{m=-\infty}^{\infty} e^{im(gna)} J_m\left(\frac{\theta \epsilon \epsilon}{2}\right),$$

One has $S(\theta) = \sum_n e^{i\theta na} e^{i\theta \epsilon \sin gna}$

$$= \sum_m \left[\sum_n e^{in(\theta + m g)a} \right] J_m\left(\frac{\theta \epsilon \epsilon}{2}\right)$$

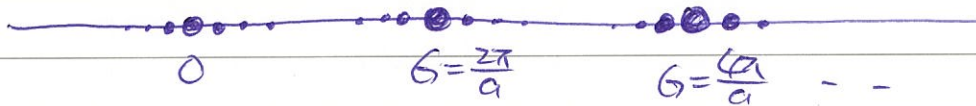
$$= \frac{2\pi}{a} \sum_m J_m\left(\frac{\theta \epsilon \epsilon}{2}\right) \sum_{k=-\infty}^{\infty} \delta(\theta + m g - \frac{2\pi k}{a})$$

∴ if g is commensurate with $\frac{2\pi}{a}$, peaks

at $-m g + \frac{2\pi k}{a}$ form infinite set with amplitudes

$\propto J_m\left(\frac{\theta \epsilon \epsilon}{2}\right)$ which decays with m . ∴

only small # of satellites are observed.



Fibonacci sequence & higher dimension projection

A very useful example of 1D quasi-crystal

is the Fibonacci chain. It's devised in 1202:

pairs of large and small rabbits: L and S

After a generation, a pair of large rabbits \Rightarrow a pair ^{give birth to} of small rabbits

a pair of small rabbits grow up to two large ones.

$\therefore L \rightarrow LS$ (including original pair)

$S \rightarrow L$

$\therefore S \rightarrow L \rightarrow LS \rightarrow LSL \rightarrow LSLLS \rightarrow LSLLSLSL$

$\rightarrow \dots$

Fibonacci #s: 1, 1, 2, 3, 5, 8, ...

recursion $u_{n+1} = u_n + u_{n-1}$, $u_1 = 1, u_2 = 1$

$$\frac{u_{n+1}}{u_n} = 1 + \frac{u_{n-1}}{u_n} = 1 + \frac{1}{\frac{u_n}{u_{n-1}}} = 1 + \frac{1}{1 + \frac{1}{1 + \dots}}$$

$$z = \lim_{n \rightarrow \infty} \frac{u_{n+1}}{u_n} = 1 + \frac{1}{1+z}, \quad z^2 - z - 1 = 0$$

$$z = \frac{1+\sqrt{5}}{2} = 1.618, \dots \text{ (Golden ratio)}$$

One can construct a lattice so that the nearest neighbor distances show the same pattern.

$$X_n = n + (z-1) \left[\frac{n}{z} \right] \quad [x] = \text{integer part of } x$$

$$\therefore X_1 = 1, \quad X_2 = z+1, \quad X_3 = z+2, \quad X_4 = 2z+2,$$

$$X_5 = 3z+2, \dots$$

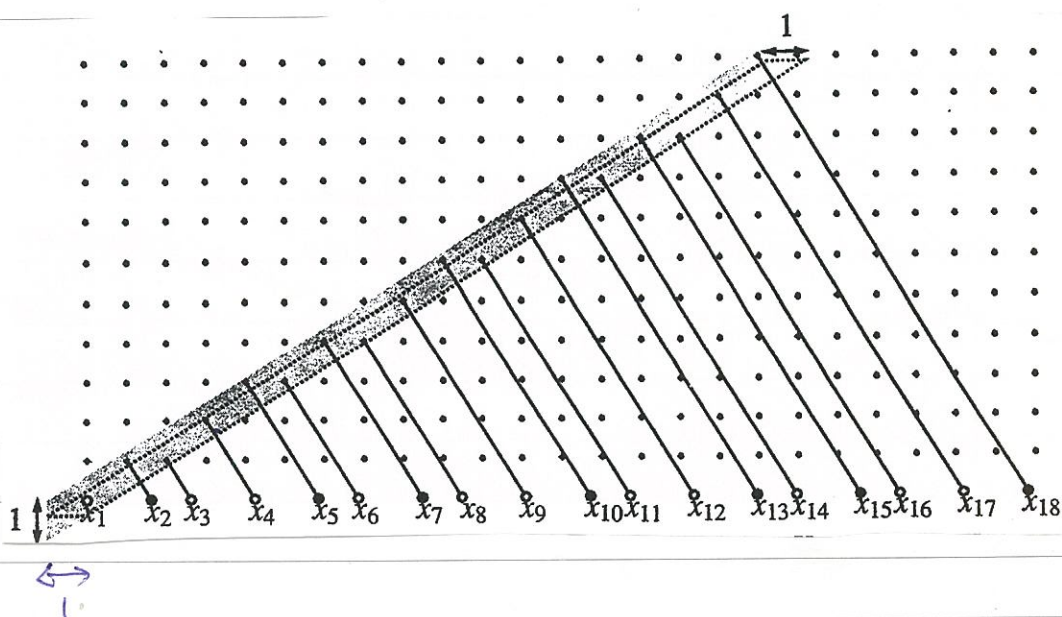
$$\Delta X = X_n - X_{n-1}, \text{ one sees that } \Delta X = 1 \text{ if } \left[\frac{n+1}{z} \right] - \left[\frac{n}{z} \right] = 0$$

$$\Delta X = z \text{ if } \left[\frac{n+1}{z} \right] - \left[\frac{n}{z} \right] = 1$$

$$\therefore L \leftrightarrow z, \quad S \leftrightarrow 1$$

x_1	x_2	x_3	x_4	x_5	...
┌───┬───┬───┬───┬───┐					
z	1	z	z	1	
L	S	L	L	S	...

X_n can be viewed as projection of 2D Square Lattice to one-dimensional stripe:



$$\text{Slope} = \frac{1}{z} = z-1, \quad x_2 = 2 + \frac{1}{z} = z+1, \quad x_3 = x_2 + 1 = z+2$$

$$x_4 = 4 + \frac{2}{z} = 4 + 2(z-1) = z+2z$$

Quasi-periodicity

Fibonacci sequence is quasi-periodic. This can be best seen by its Fourier transformation.

We first note that

$$X_n = n + \underbrace{\sum_m m \theta(m - \frac{n}{2} + 1) \theta(\frac{n}{2} - m)}_{\substack{\parallel \\ \frac{n}{2} - 1 \leq \text{integer} \leq \frac{n}{2}}} \underbrace{\frac{1}{2}}_{\substack{\parallel \\ \frac{n}{2} - 1}}$$

$$S(\vec{g}) = \sum_n e^{i\vec{g} \cdot X_n} = \sum_{n,m} e^{i\vec{g} \cdot (n + \frac{m}{2})} \theta(m - \frac{n}{2} + 1) \theta(\frac{n}{2} - m)$$

$$= \int dx \int dy e^{i\vec{g} \cdot (x, y)} \underbrace{\left(\sum_{n,m} \delta(x-n) \delta(y-m) \right)}_{f(x, y)} \underbrace{\theta(y - \frac{x}{2} + 1) \theta(\frac{x}{2} - y)}_{g(x, y)}$$

= Convolution of $f(x, y)$ & $g(x, y)$

$$f(\vec{g}) = \int dx \int dy \sum_{n,m} \delta(x-n) \delta(y-m) e^{i\vec{g} \cdot x} e^{i\vec{g} \cdot y}$$

$$= N \frac{(2\pi)^2}{V} \sum_{n', m'} \delta(\vec{g} \cdot x - 2\pi n') \delta(\vec{g} \cdot y - 2\pi m')$$

$$\left(\sum_{\vec{R}} e^{i\vec{R} \cdot \vec{g}} = \sum_{\vec{G}} N \frac{(2\pi)^3}{V} \delta(\vec{g} - \vec{G}) \right)$$

$$g(\vec{g}) = \int dx \int dy g(x, y) e^{i(\vec{g} \cdot x + \vec{g} \cdot y)} = \int dx \int_{\frac{x}{2}}^{\frac{x}{2}} dy e^{i(\vec{g} \cdot x + \vec{g} \cdot y)}$$

$$= \int dx e^{i\mathbf{q} \cdot \mathbf{x}} \frac{e^{i\mathbf{q}_0 \cdot (\mathbf{x}/2)} - e^{i\mathbf{q}_0 \cdot (\mathbf{x}/2 - \mathbf{1})}}{i\mathbf{q}_0}$$

$$S(\mathbf{q}) = \int d\mathbf{q}_x' \int d\mathbf{q}_y' f(\mathbf{q} - \mathbf{q}') g(\mathbf{q}')$$

$$= N \frac{(\Delta x)^3}{V} \int dx \int d\mathbf{q}_x' \int d\mathbf{q}_y' \sum_{h'm'} f(\mathbf{q} - \mathbf{q}_x' - 2\pi h') g(\mathbf{q}/2 - \mathbf{q}_y' - 2\pi m')$$

$$\times \frac{e^{i\mathbf{q}_y' \cdot (\mathbf{x}/2)} - e^{i\mathbf{q}_y' \cdot (\mathbf{x}/2 - \mathbf{1})}}{i\mathbf{q}_y'} e^{i\mathbf{q}_x' \cdot \mathbf{x}}$$

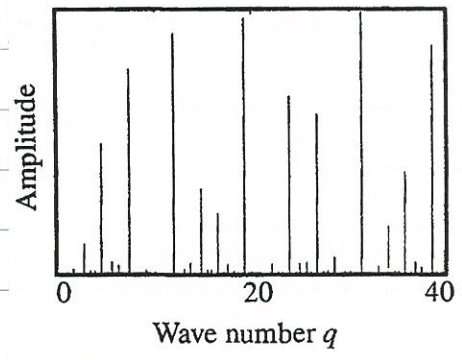
$$= N \frac{(\Delta x)^3}{V} \int dx \sum_{h'm'} \frac{e^{i(\mathbf{q}/2 - 2\pi m') \cdot (\mathbf{x}/2)} - e^{i(\mathbf{q}/2 - 2\pi m') \cdot (\mathbf{x}/2 - \mathbf{1})}}{i\mathbf{q}/2 - 2\pi m'} e^{i(\mathbf{q} - 2\pi h') \cdot \mathbf{x}}$$

$$= N \frac{(\Delta x)^3}{V} \times 2\pi \sum_{h'm'} \frac{(1 - e^{-i(\mathbf{q}/2 - 2\pi m')})}{i\mathbf{q}/2 - 2\pi m'} f\left(\frac{2\pi m' - \mathbf{q}/2}{2} + 2\pi h' \cdot \mathbf{g}\right)$$

$\therefore S(\mathbf{q})$ peaks at $\mathbf{q} = \frac{2\pi(m'/2 + h')}{1 + 2z}$ (containing two incommensurate periods)

$$I(\mathbf{q}) \propto |S(\mathbf{q})|^2 \propto \frac{\sin^2\left(\pi \frac{(h'z + m')}{2 + 2z}\right)}{(\mathbf{q}/2 - 2\pi m')^2}$$

\Rightarrow Plot



Quasicrystals

Quasiperiodic is not the only ingredient to quasicrystals. It must also incorporate orientational order. By doing so, one can escape the forbidden rules imposed by periodicity.

Schechtman et al. (PRL 53, 1951, 1984) discovered

that $\text{Al}_{76}\text{Mn}_{14}$, when cooled at rates of 10^6 K s^{-1} ,
 the alloy
 (originally they were set to find metallic glass),

has 5-fold symmetry! This discovery is completely unexpected. By close examination of the sample at different angles, it exhibits different symmetries. The overall symmetry pattern

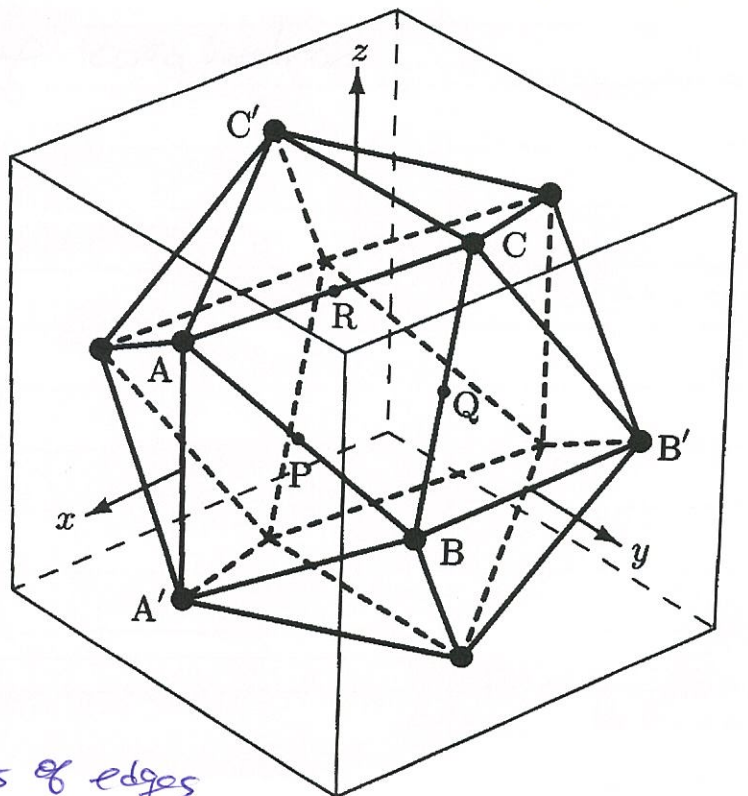
is the same as that of a icosahedron.

(20面体)

(12 vertices, 20
 triangular faces &
 30 edges)

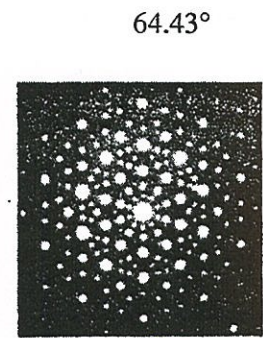
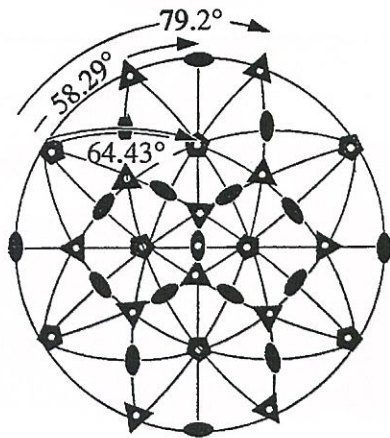
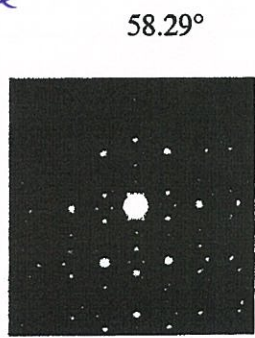
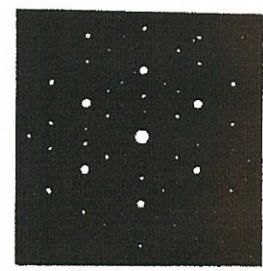
5-fold axes passes through
 vertices.

3-fold axes " " centers
 of faces, 2-fold " " centers of edges



$$G = \sum_n A_n C_n$$

presence of negative vectors turns
($A_n = \pm 1, 0, \pm 2$)
5-fold into 10-fold.



Therefore, the alloy is not just a collection of 5 crystals bond together. (Pauling 1985)!

Levine & Steinhardt (1984) termed this type of lattice as a quasicrystal. (later, decagonal and octagonal quasicrystals are also found)

It is now realized that basic ingredients for generation of a quasicrystal are

- (i) quasi-periodic translational order
- (ii) Minimal separation of atoms: therefore quasicrystals are not just set obtained by superimposing two periodic lattices with incommensurate ratios! (In this case, then, there is no min. separation)

(iii) long-ranged orientational order.

Penrose constructed a 2D quasicrystal that turns out to be consistent with the plane that exhibit 5-fold symmetry.

The construction is to tile 2D space using

Penrose tiles: one is fat rhombus

$$(\theta = 2\pi/5)$$

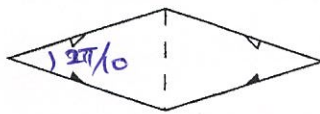
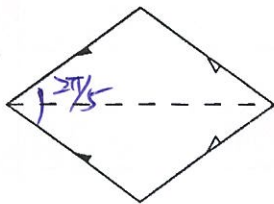
the other is skinny rhombus

$$(\theta = 2\pi/10)$$

lengths of all sides = 1

long diagonal of fat rhombus = $\frac{\sqrt{5}+1}{2} = \tau$

short " skinny " = $\frac{1}{\tau}$

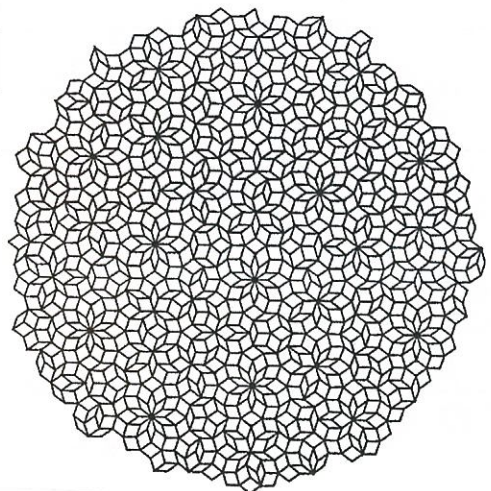


matching rules of tiling is shown by half triangles one has to match them when put them in adjacent.

The resulting Penrose tiling

is shown in the right

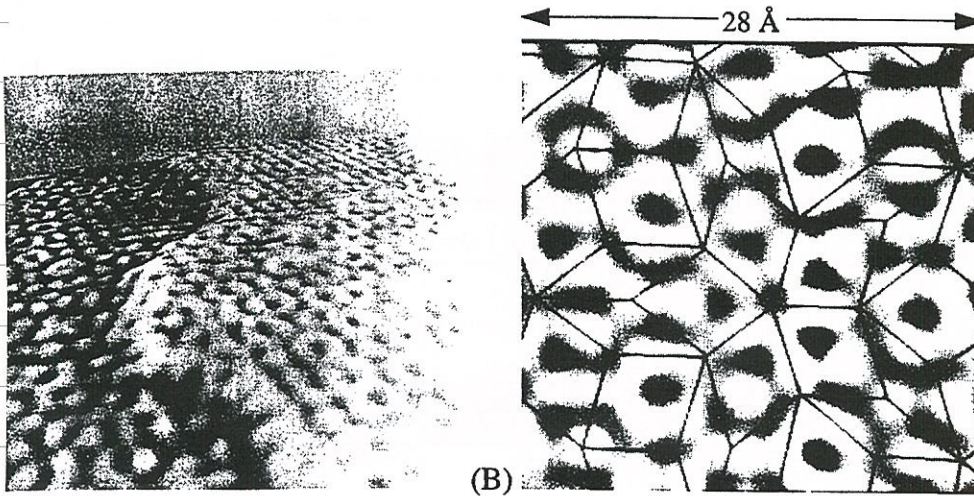
figure.



With Penrose tiling, one can then decorate

it with atoms. It agrees with STM image

well in alloy Al_{0.5}Cr_{0.5}Co_{2.0}. (F.T. also agrees with x-ray!)



A. R. Kertan (1996), in

Encyclopedia of Applied Physics

Ammann grid:

It is not easy to see 5-fold symmetry & quasi-periodicity in the tiling. It turns out

that there is an equivalent way to generate

Penrose tiling. This is known as Ammann grid,

(i) One first specify point group symmetry

& corresponding "star vectors". For 5-fold

symmetry, star vectors are

$$e_1, e_2, e_3, e_4, e_5 \quad \theta = \frac{2\pi}{5}$$

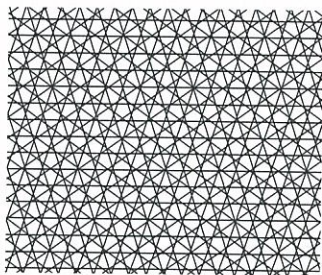
(ii) form parallel lines $\perp \hat{e}_0$

these parallel lines will intersect
with each other and form a grid!

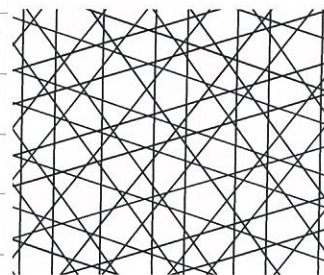
Obviously, as shown in below, if parallel
lines are equally spaced, they are periodic
and at the same are 5-fold symmetric.

cells created by their intersections have
infinitely many shapes and furthermore, cells
can be very small so that there is no
minimum separation between vertices surrounding
each cell.

\Rightarrow This is consistent with the ^{result of} forbidden symmetry
obtained by requiring periodicity.



equally spaced



spacing is quasi-periodic

However, if spacing between parallel lines

are quasi-periodic, one sees that cells generated have finite #s of shapes. (see the above figure)

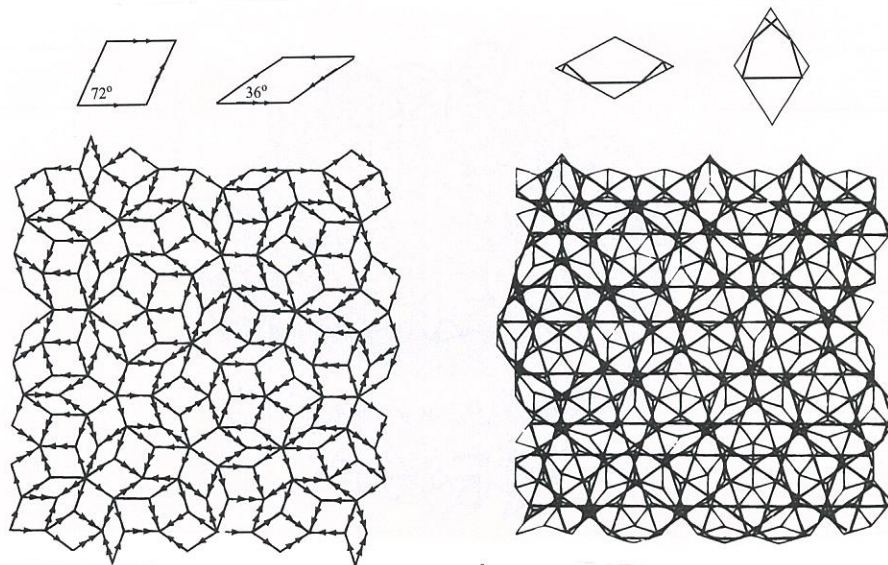
Dual lattice to a grid (Ammann lattice)

= Penrose tiling with decoration

If we put a lattice point to the center of each cell and take Fibonacci sequence

in the spacing of parallel lines, one obtains

the Penrose tiling. 5-fold symmetry & quasi-periodicity is then clear.



Fullerenes

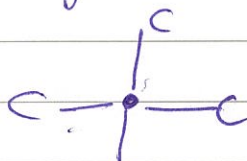
Another structure that is related to the forbidden point-group symmetry is the fullerenes.

A fullerene is any molecule composed of entirely by carbon.

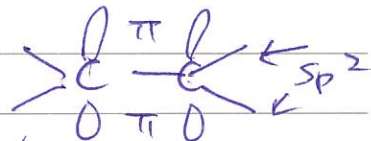
The name comes from the architect, Buckminster Fuller, as one of fullerenes, C_{60} , discovered in 1985 by R. Smalley's group at Rice Univ. is named

buckminsterfullerene due to its resemblance to one of structures designed by him.

For 3D materials such as diamond, each carbon can connect to 4 neighbours by mixing 2s & 2p into 4 sp^3 orbitals.



For fullerenes, however, it is more interesting to another possibility in which each carbon connects to 3 carbon atoms by 3 sp^2 orbitals.



In this case, carbon atoms can form polyhedrons.

According to Euler's theorem,

$$F = E - V + 2$$

$F = \#$ of faces

$V = \#$ of vertices

Since each carbon has 3 neighbours, $\therefore \frac{3V}{2} = E$.

; we find $F = E - V + 2 = \frac{V}{2} + 2$

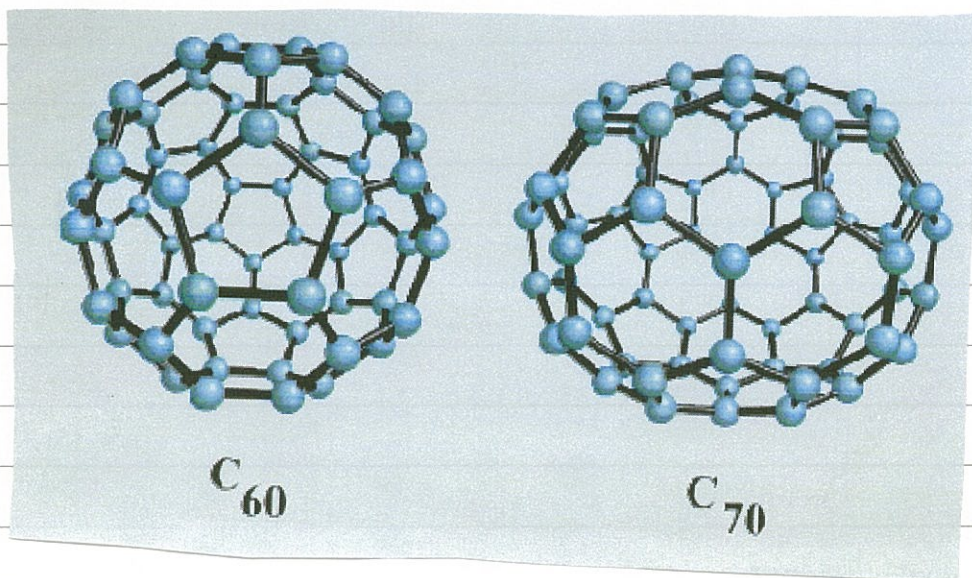
if $F_s = \#$ of s -sided polygons, we have

$$\left. \begin{aligned} F &= \sum_s F_s \\ E &= \frac{1}{2} \sum_s s F_s \\ V &= \frac{1}{3} \sum_s s F_s \end{aligned} \right\} \begin{aligned} \sum_s F_s &= \frac{1}{6} \sum_s s F_s + 2 \\ \text{i.e. } \sum_s (6-s) F_s &= 12 \end{aligned}$$

\therefore One sees that if $s=6$, F_s is arbitrary.

Using this fact, one can form C_{60} & C_{70} ...

with 12 pentagons. Hence these molecules are 5-fold symmetric!



C_{60}

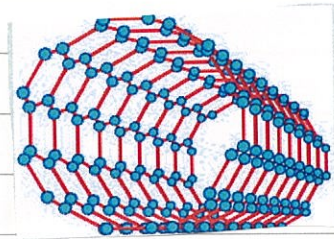
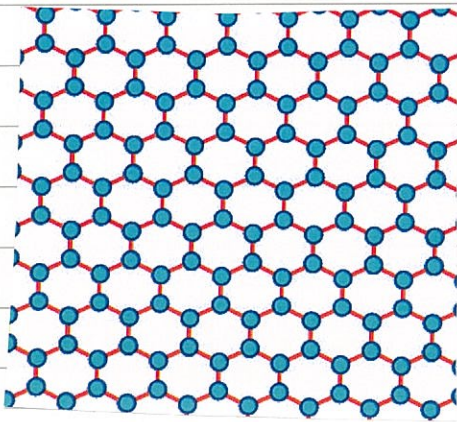
C_{70}

$F_5 = 12$

$F_5 = 12$

In addition to closed molecules, sp^2 orbitals also allow carbons to form graphene, carbon nanotubes.

Here graphene is discovered in 2004 by Geim's group.
nanotube is " in 1993 by Sumio Iijima.



Crystals of C_{60}

Since C_{60} has 5-fold symmetric axes, it would be interesting to see how this symmetry does with the crystal of C_{60} .

It turns out C_{60} molecules interact with Van-der Waals interaction in high temperature ($T > T_c = 250^\circ C$).

The crystal is FCC but C_{60} is freely rotating ^{each} so that 5-fold symmetry is smeared into isotropy!

$T < T_c$,



4 C_{60} at $(0, 0, 0)$ $(\frac{1}{2}, \frac{1}{2}, 0)$
 $(\frac{1}{2}, 0, \frac{1}{2})$ $(0, \frac{1}{2}, \frac{1}{2})$.

3-fold axis of each C_{60} points to

4 $\langle 111 \rangle$ directions respectively. Rotations

w.r.t. this axis show 4-fold symmetry!

(P.A. Heiney et al, PRL 63, 2911, (1991))

Polymers & Random isotropic fractals

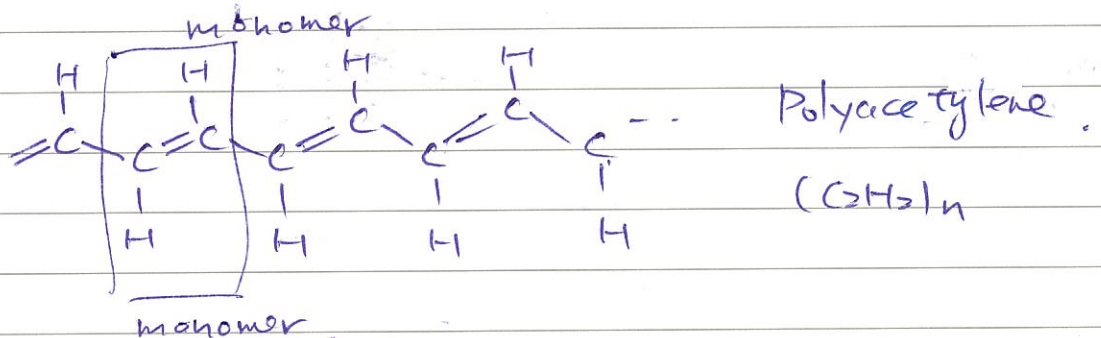
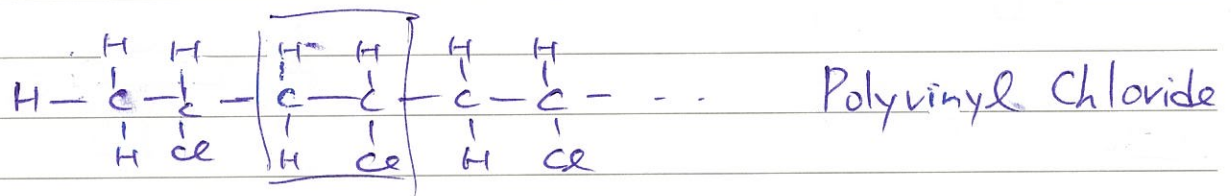
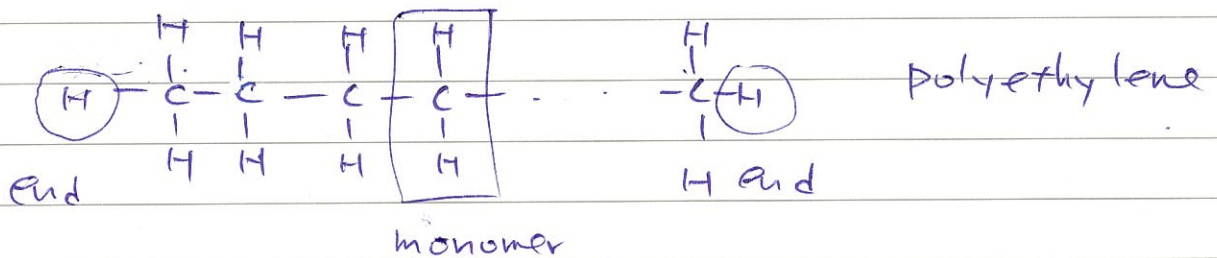
Polymers consist of long chain molecules.

These molecules are huge and are called macromolecules. They are usually composed by units (monomer) that can be repeated connected.

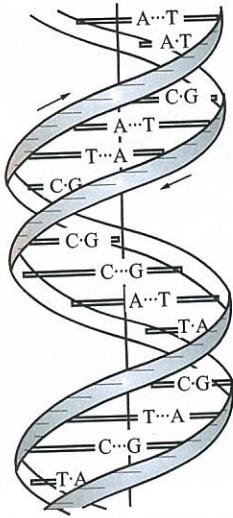
Typical macromolecules contain $10^2 - 10^5$ monomers.

If two or more different monomers are used, this is called copolymer.

Examples:

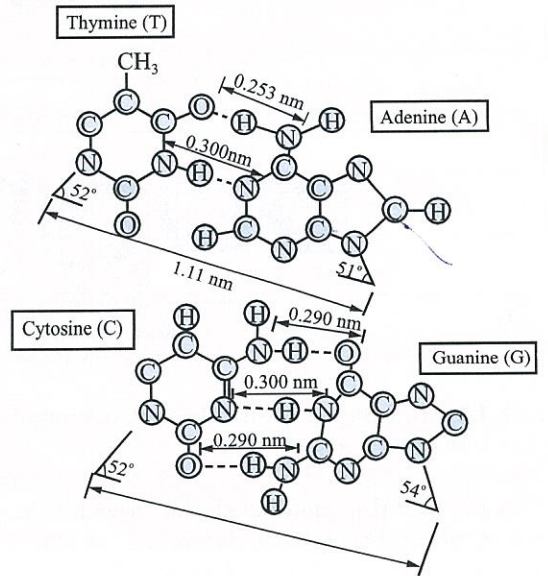


Biopolymers : DNA (deoxyribonucleic acid)
& protein

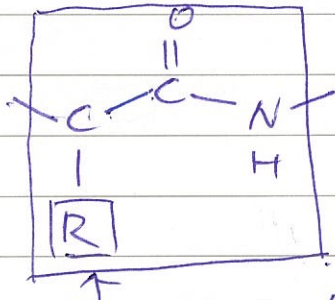


double-helix structure
(Watson & Crick, 1951)

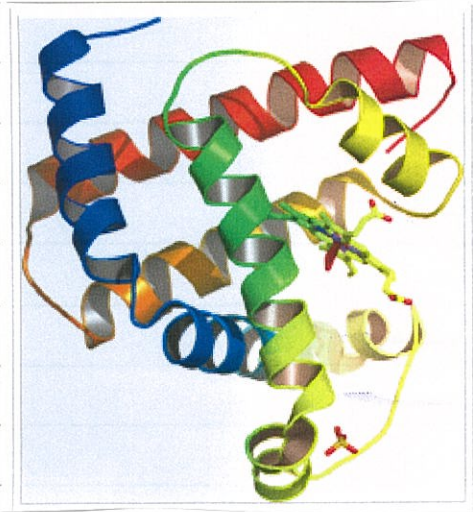
A = adenine
T = thymine
G = guanine
C = cytosine



Protein (polypeptide)



amino acids (20 for Human)



Typical cartoon picture of proteins (myoglobin) showing α -helices.

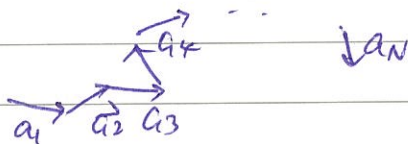
Macromolecules are of two types: rigid chain & flexible chain. Macromolecules with benzene rings or heterocyclic rings are usually rigid. Others such as polyethylene in the main chain are quite flexible. In addition, there are also interactions

between different parts of molecules so that some particular conformations are formed. This is particularly true for DNA & α -helix (β -sheet) of proteins.

We shall not discuss those with special conformation but focus on flexible chains. These are disordered polymers and can be modeled by random walk as first proposed by P. T. Flory in 1949.

Suppose an ideal polymer chain composed of N monomers of length a . If we ignore volume of monomer and treat the end of the polymer as a random walker, characterized by \vec{R} , one has

$$\langle \vec{R} \rangle = 0 \quad (\text{The origin is set to the 1st monomer.})$$



$$\begin{aligned} \text{Since } \vec{R} &= \vec{a}_1 + \vec{a}_2 + \dots + \vec{a}_N, & \langle R^2 \rangle &= \left\langle \sum_{i \neq j} \vec{a}_i \cdot \vec{a}_j + \sum_i a_i^2 \right\rangle \\ & & &= Na^2. \end{aligned}$$

Similar dependence also applies the average radius

of gyration R_G (measured from center of mass).

$$R_G \sim \langle R^2 \rangle^{1/2} = a N^{1/2}$$

In fact, for any large distance $r \gg a$, polymers look self-similar. Hence, if $n(r)$ = # of monomer inside the sphere of radius r , $r \sim n^{1/2} \therefore n(r) \sim r^2/a^2$

then, one can deduce $g(r)$ = pair distribution function at r

$$4\pi r^2 g(r) dr \sim n(r+dr) - n(r) = dn(r)$$

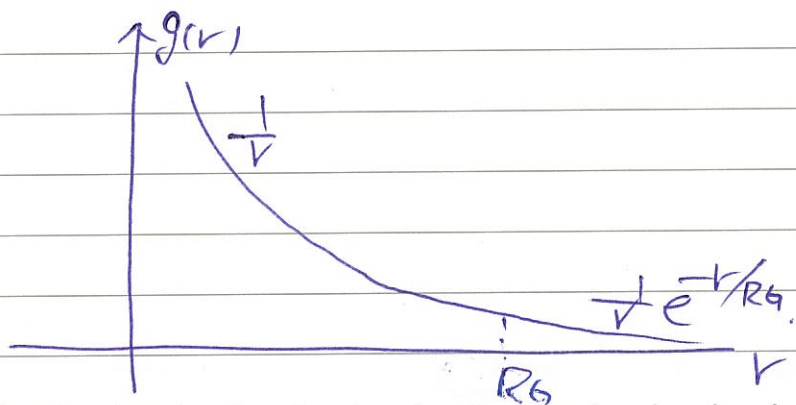
$$g(r) \sim \frac{1}{4\pi r^2} \frac{dn(r)}{dr} \sim \frac{n(r)}{r^3} \sim \frac{1}{a^2 r} \quad \text{for } a \ll r < R_G$$

$$(\text{for } d\text{-dim, } g(r) \sim \frac{1}{r^{d-1}} \frac{dn}{dr} \sim \frac{1}{r^{d/2}})$$

For $r > R_G$, $n(r)$ is expected to fall off exponentially: $n(r) \sim r^2/a^2 e^{-r/R_G}$

$$\therefore g(r) \sim \frac{1}{a^2 r} e^{-r/R_G} \quad \text{for } r > R_G$$

Therefore one expects



This will reflect in neutron scattering intensity:

$$I \propto |S(q)|^2, \quad S(q) \propto \int g(r) e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

$$r \ll R_G, \quad g(r) \sim r^{-\alpha} \quad (\alpha=1, \text{ for } d=3)$$

$$\vec{q}\cdot\vec{r} \equiv \vec{x}$$

$$\int g(r) e^{i\vec{q}\cdot\vec{r}} d\vec{r} \sim \int \frac{1}{r^\alpha} e^{i\vec{q}\cdot\vec{r}} d^d\vec{r}$$

$$\sim \frac{q^\alpha}{q^d} \int e^{i\vec{x}\cdot\vec{q}} d^d\vec{x} \propto q^{\alpha-d}$$

$$\therefore S(q) \propto \frac{1}{q^{2-\alpha}} \quad q R_G \gg 1 \quad (\text{power law!})$$

For real polymers in a solution, there exists repulsive interactions among monomers, so that monomers can't occupy the same space. As a result,

polymers tend to expand, so that $R_G = a N^\nu$ $\nu > \frac{1}{2}$.

The effects that monomers can't occupy the same space are often modelled by self-avoiding random walk (SAW).

Numerically, one finds $\nu = \frac{3}{d+2}$ (consistent

with mean-field results obtained by Flory.

Whether self-avoiding interactions are important or

depends on solutions. If the interaction between monomers and solvent is attractive, the solvent is poor. Features of self-avoiding are reduced; otherwise, the solvent is good, one needs to include self-avoiding interactions. This can be quantitatively defined via the correction to the ideal gas law:

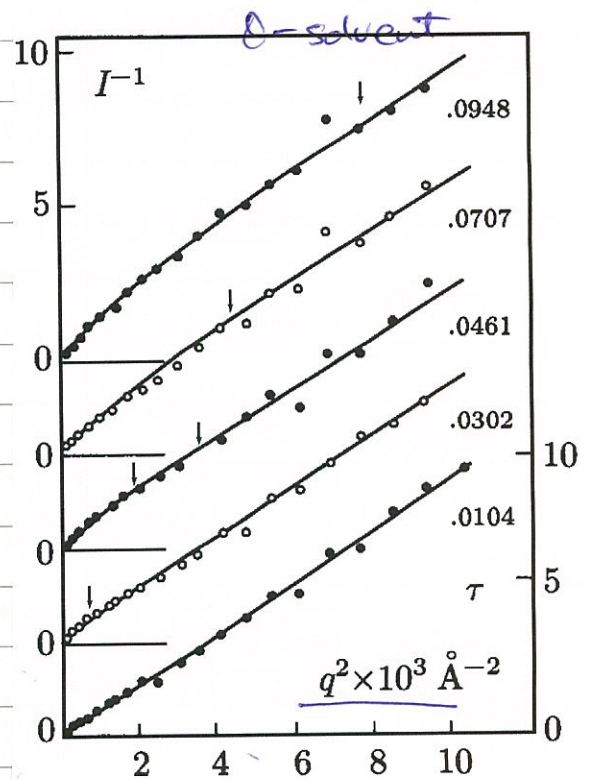
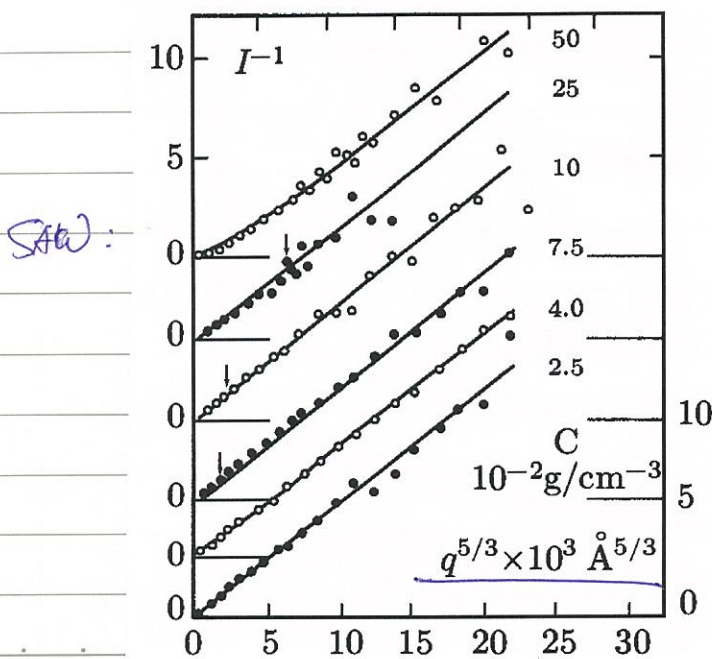
$$\rightarrow \frac{\Pi}{RT} = \frac{c}{M} + BC^2 + \dots \quad B=0 \Rightarrow \theta \text{ solvent}$$

Osmotic pressure due to polymers in solvent (ideal random walk)

In the SAW, one has $n(r) \sim \left(\frac{r}{a}\right)^{-d} \sim \left(\frac{r}{a}\right)^{-5/3}$ ($d=3$)

$$g(r) \sim \frac{n(r)}{r^3} \sim \frac{1}{r^{4/3} a^{5/3}}$$

$$S(0) \sim \frac{1}{(8a)^{5/3}} \sim (8a)^{-5/3}$$



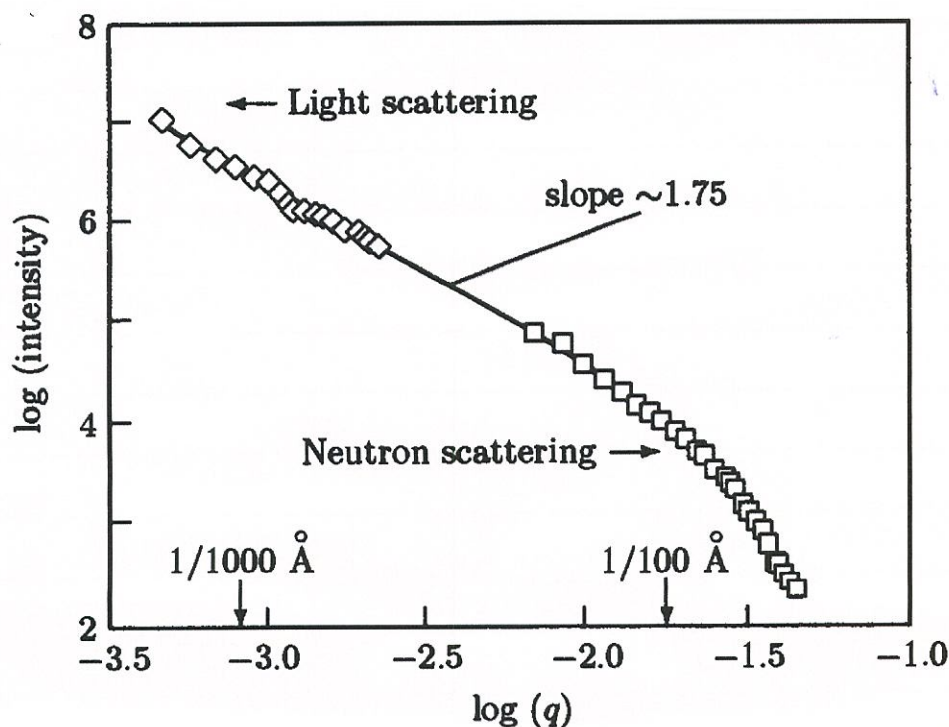
(Farnoux, J. de physique 39, 27, 1978)

The behavior of polymer is an example of fractal. In general, in the case of aggregation of atoms (or some other object), the aggregate may look like a fractal in the sense that the covering of the aggregate $N(r) \sim (r/a)^{d_f}$

$d_f < d$, d_f is the so-called Hausdorff dimension or fractal dimension.

An example is the diffusion limited aggregation (DLA) in which particles diffuse around and stick to the aggregate once they hit the aggregate.

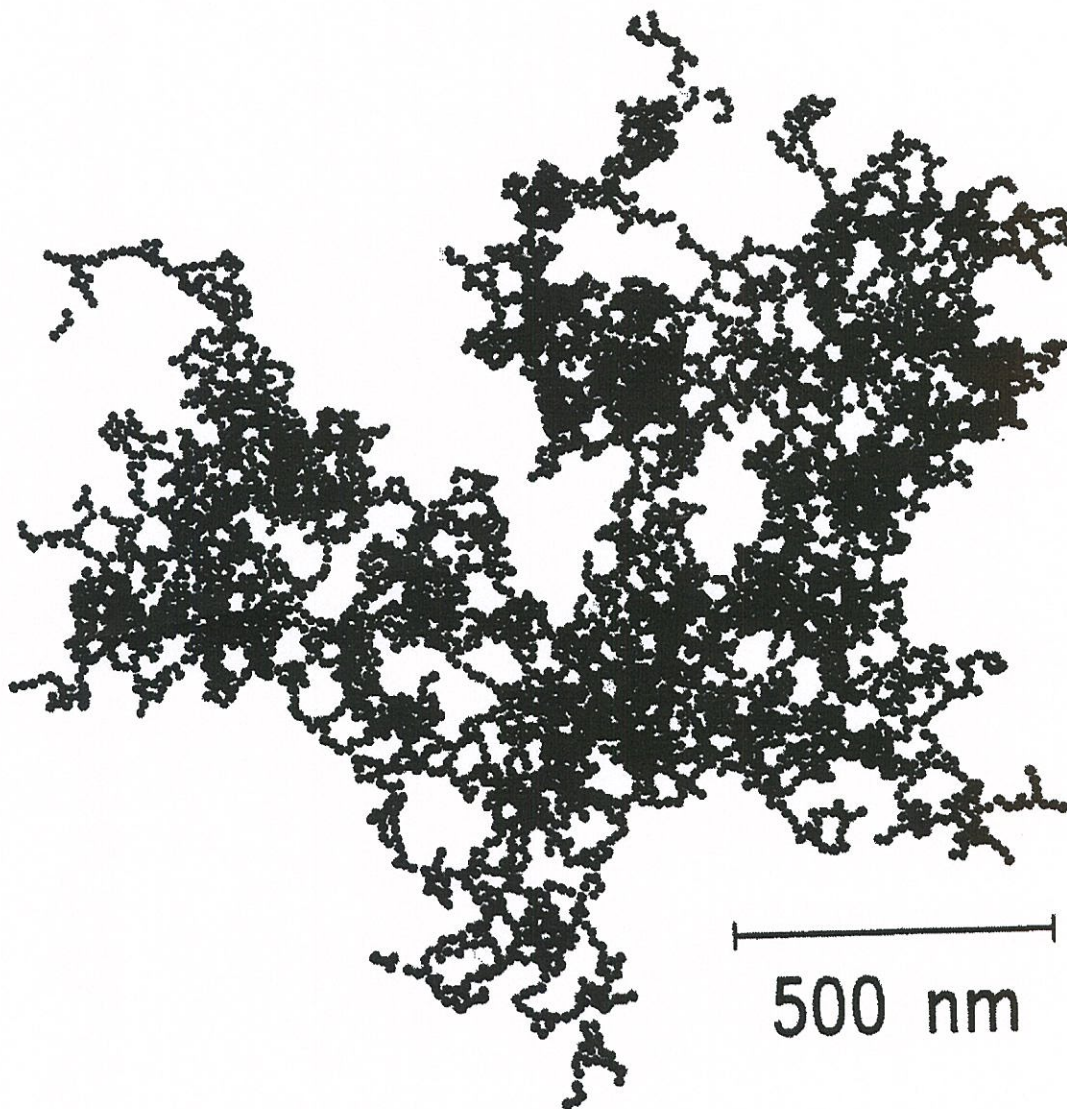
In this case, $N(r) \sim \frac{1}{a^{d-d_f} r^{d-d_f}}$, $S(r) \sim \frac{1}{(ra)^{d_f}}$



(PRL 57, 515, 1986)

S(1) of
fractals
(see the
next page)

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A fractal aggregate of gold particles.

(D. A. Weitz in Kinetics of aggregation
& gelation)