

# Lecture 23

## Materials and their structure

### Textbooks:

- Introduction to materials science and Engineering: V. Raghavan
- Materials Science and Engineering: Callister and Rethwisch

Prof. Divya Nayar

Department of Materials Science and Engineering

[divyanayar@mse.iitd.ac.in](mailto:divyanayar@mse.iitd.ac.in)

# Recap

- Types of chemical bonding (Primary bonding)
  1. Ionic bonding: ion-ion (Coulombic attraction and repulsion)
  2. Covalent bonding (polar covalent and non-polar covalent bond)
  3. Metallic bonding
- Non-bonding intermolecular forces (Secondary bonding):
  1. Electrostatic interactions (multipoles): ion-dipole, dipole-dipole
  2. Induction interactions
  3. Dispersion interactions
  4. Hydrogen bonding
  5. Hydrophobic interactions

# Non-bonding Intermolecular forces

- **Electrostatic interactions:** originate from interactions between molecular multipoles. The strength depends on  $1/r^n$   
e.g. ion-ion, ion-dipole, dipole-dipole, dipole-quadrupole etc.
- **Induction interactions:** that arise from interaction between a static multipole moment of one molecule and polarizability of the other molecule. *Arise from distortion in charge distribution.*  
E.g. ion-induced dipole, dipole-induced dipole
- **London or dispersion forces:** originates from correlations between instantaneous dipoles of neighboring atoms. *Arise from fluctuations in charge distribution.*

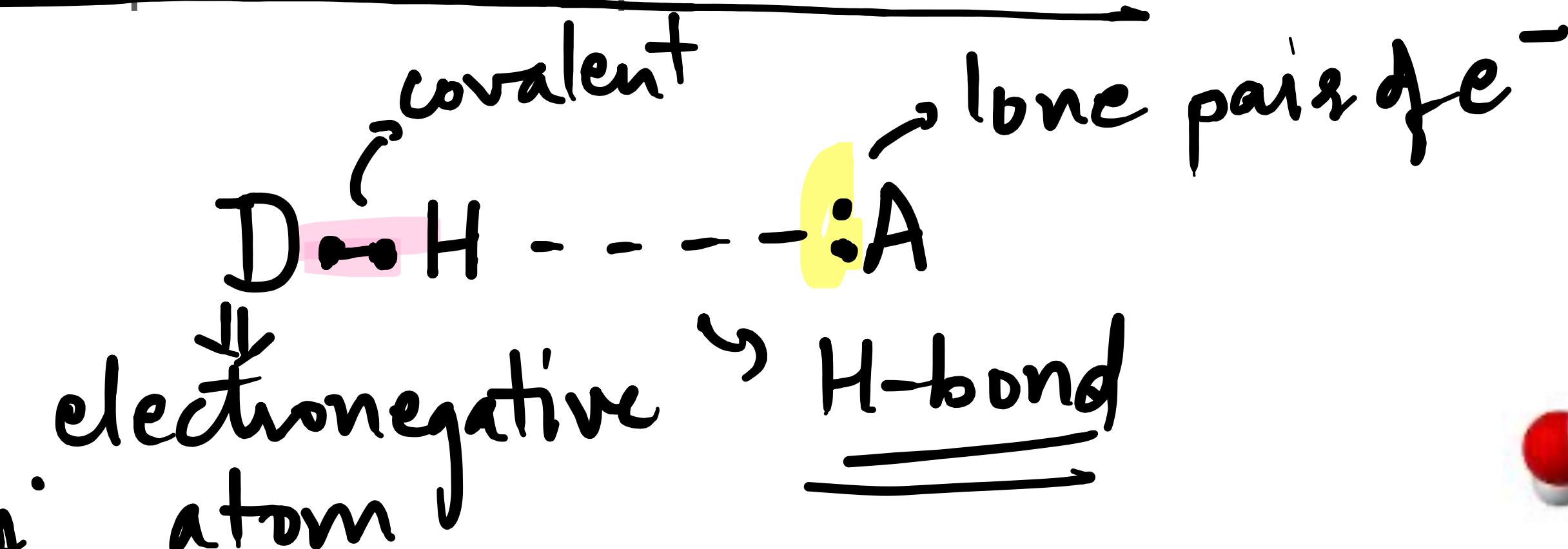
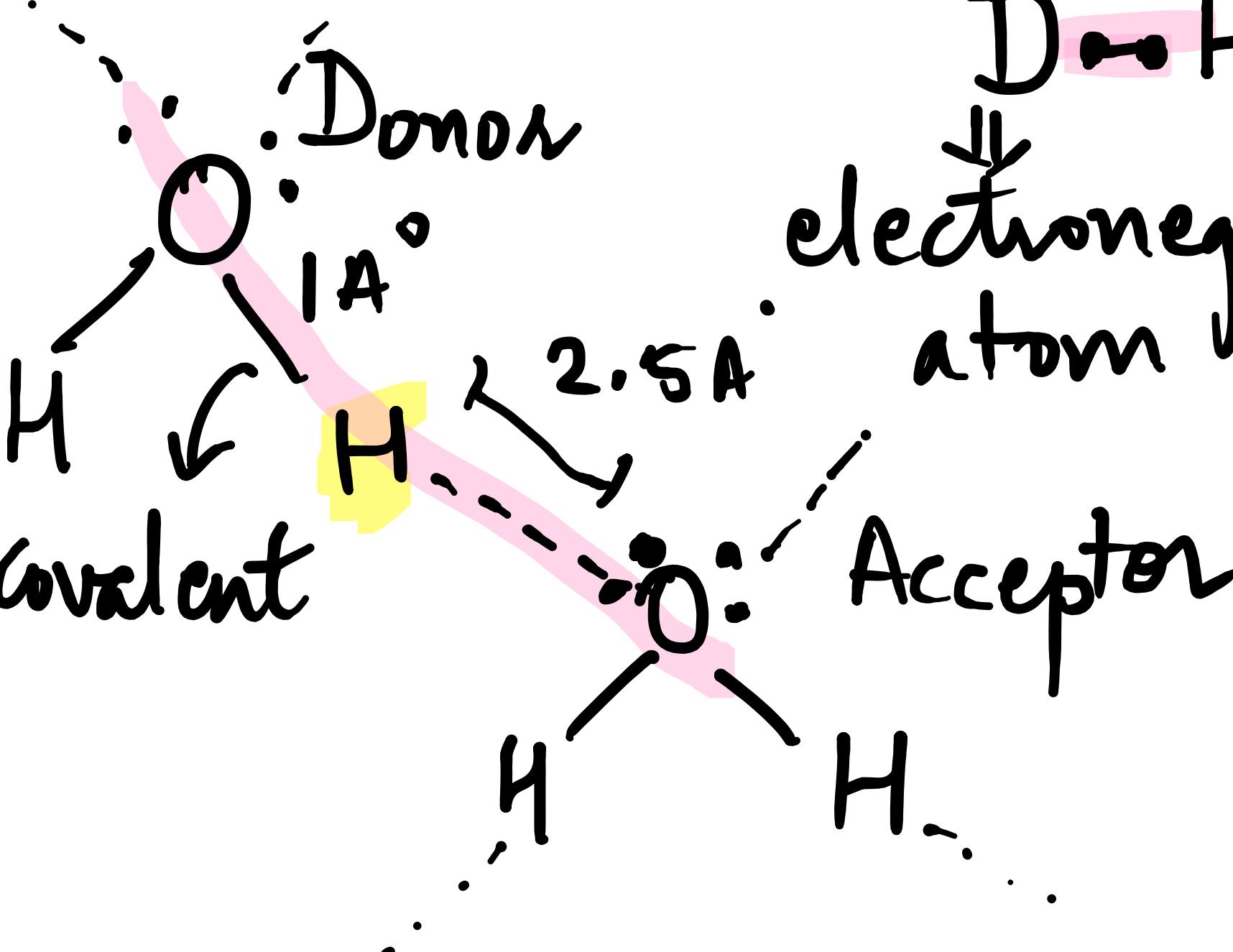
$$\downarrow E_{vdw} = \frac{4\epsilon}{r^6} \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

$\mu$  = dipole moment  
 $\alpha$  = polarizability

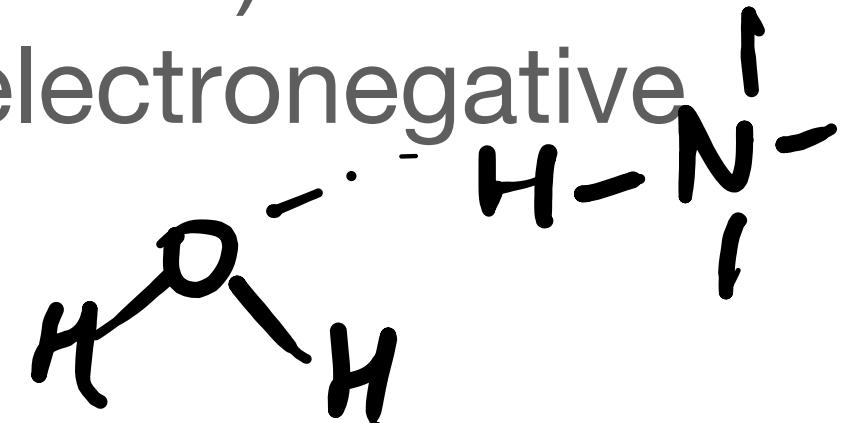
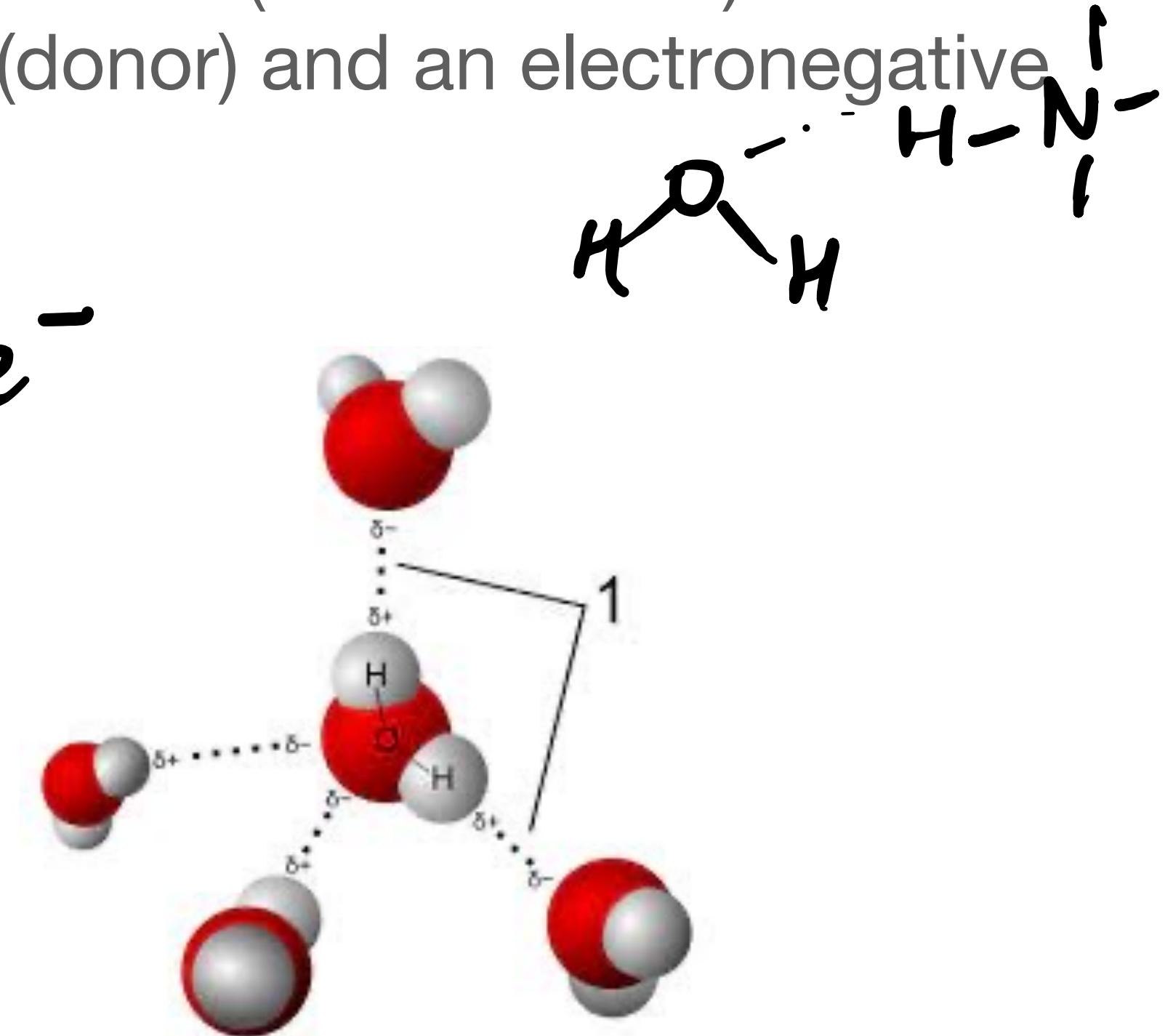
$$E_{ind} = - \frac{2\mu^2 \alpha}{4\pi \epsilon_0 r^6}$$

# Hydrogen bonding

- It is intermediate between electrostatic interactions and a true chemical bond
- The energy of interaction lies between that of a covalent and an ionic bond (20-30 kJ/mol).
- Formed between a H covalently bonded to an electronegative atom (donor) and an electronegative atom (acceptor)
- Interaction of a bonded pair with a lone pair of electrons.
- Directional bonding

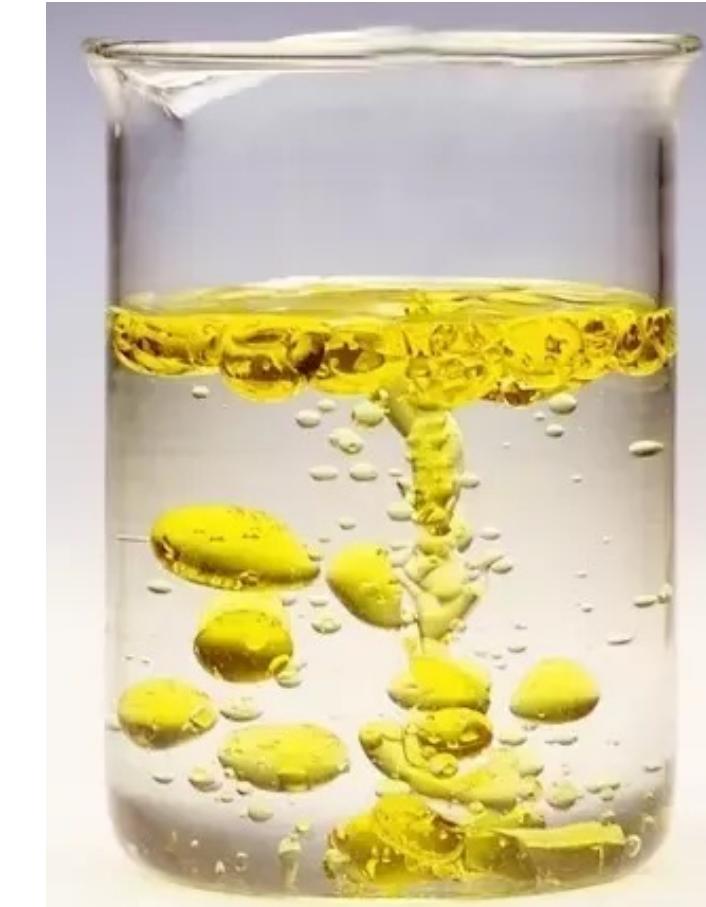


Distance :  $H - A \approx 2.5 \text{ \AA}$   
 Orientation :  $\angle AHD > 150^\circ$



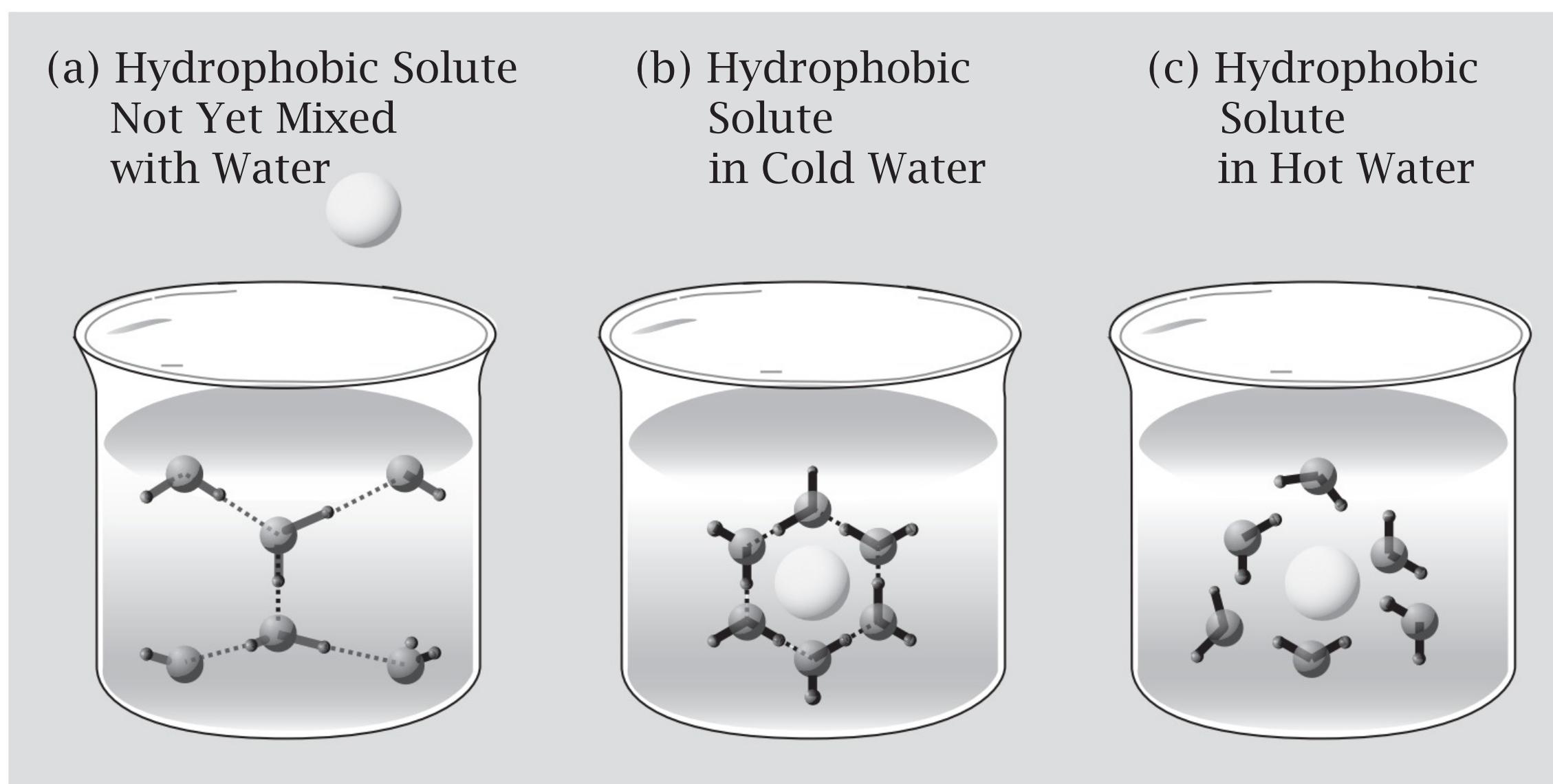
# Hydrophobic interactions

- Interactions between non-polar solutes (hydrophobes) in water.
- Water molecules reorganize around the hydrophobe in an ordered manner that is entropically favourable.
- At high temperatures, the ordering of water is broken and enthalpically it is favourable to solvate the hydrophobe.
- Often found in biomaterials.



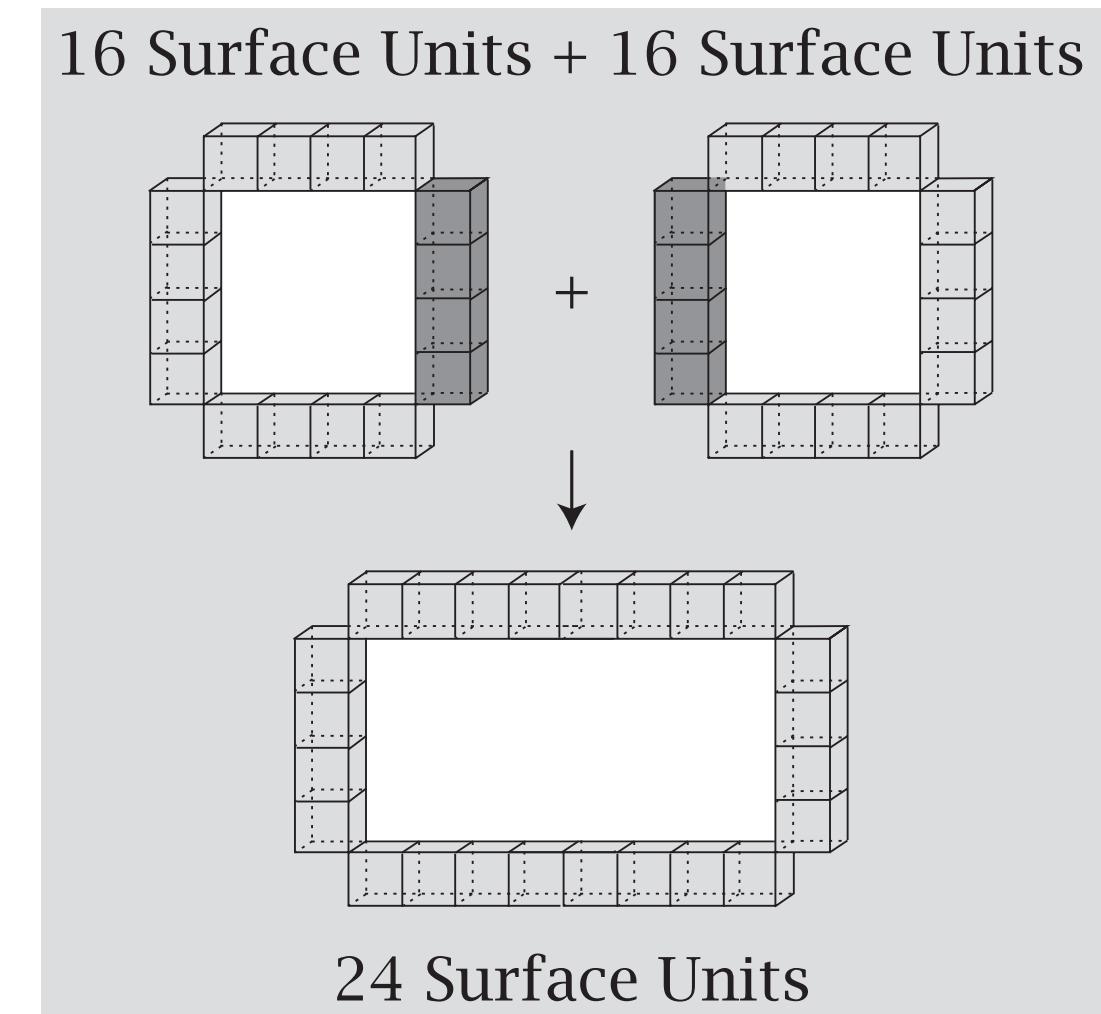
Oil in water

## Hydrophobic solvation

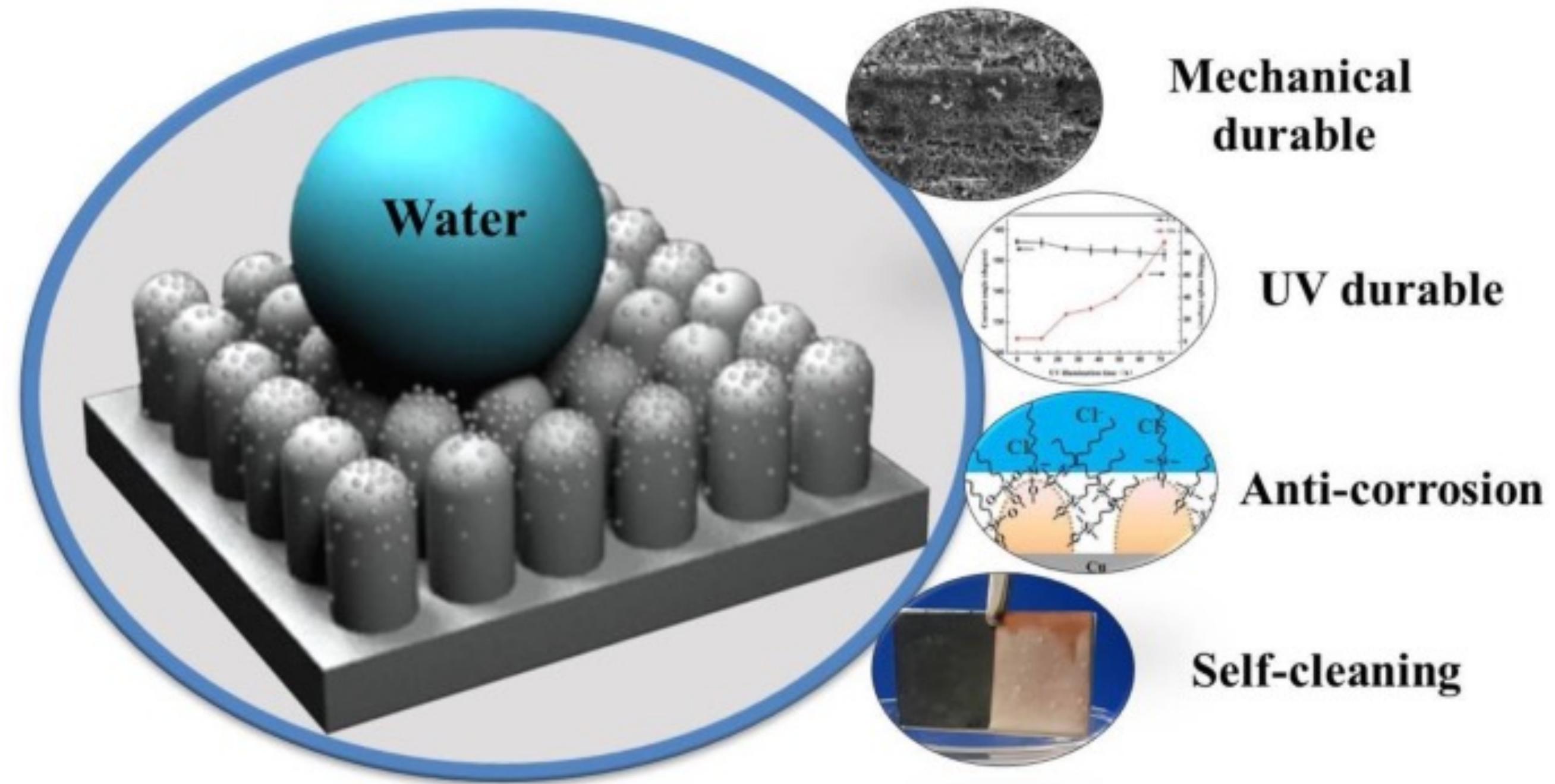


## Hydrophobic association

**Figure 31.8** Why do nonpolar solutes associate in water? Association reduces the total surface area of contact between solute molecules and the surrounding water. When the two solutes are separated, they have, in total, 32 units of surface contact with the solvent. But when the solutes contact each other, they have only 24 units of surface contact with water.

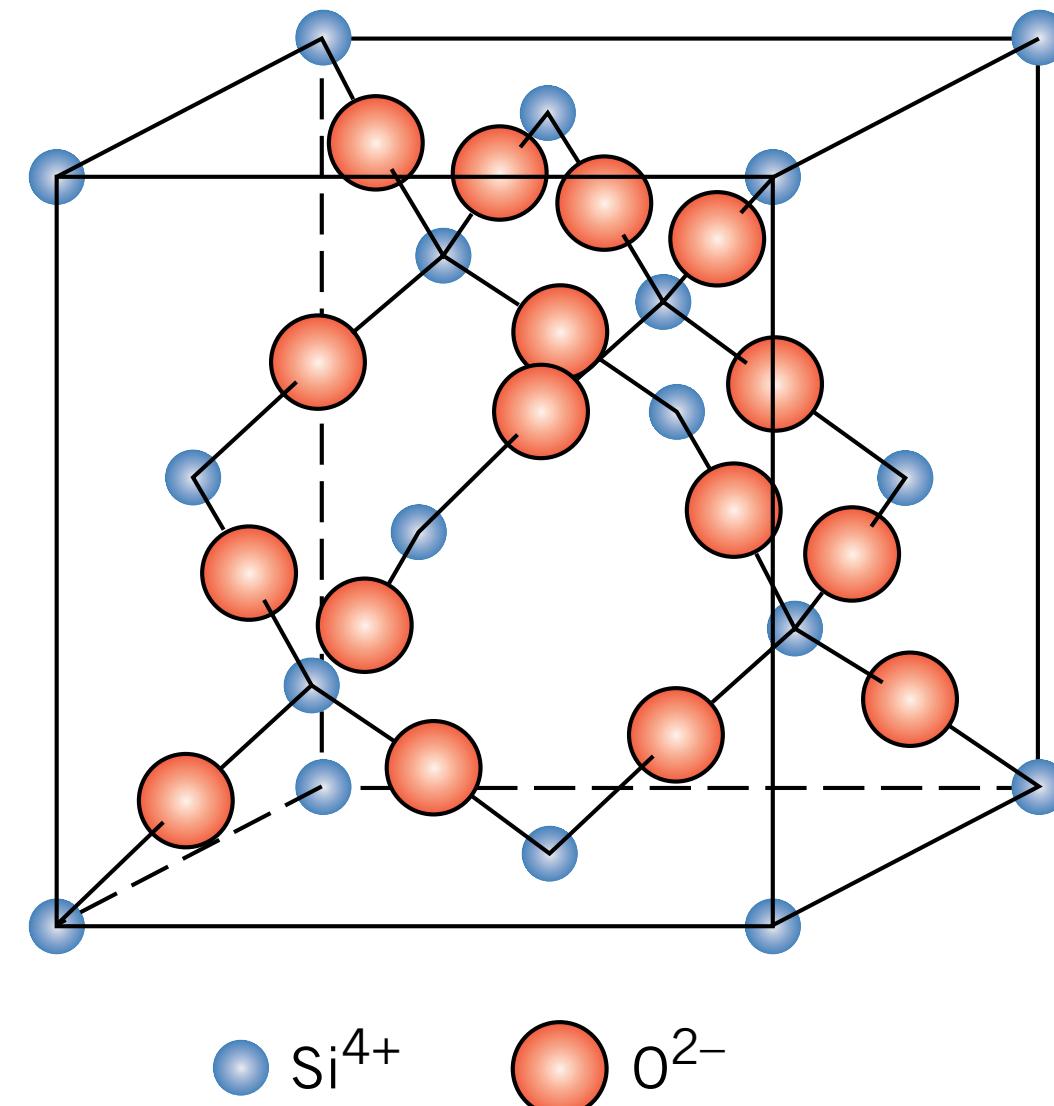


# Superhydrophobic surface

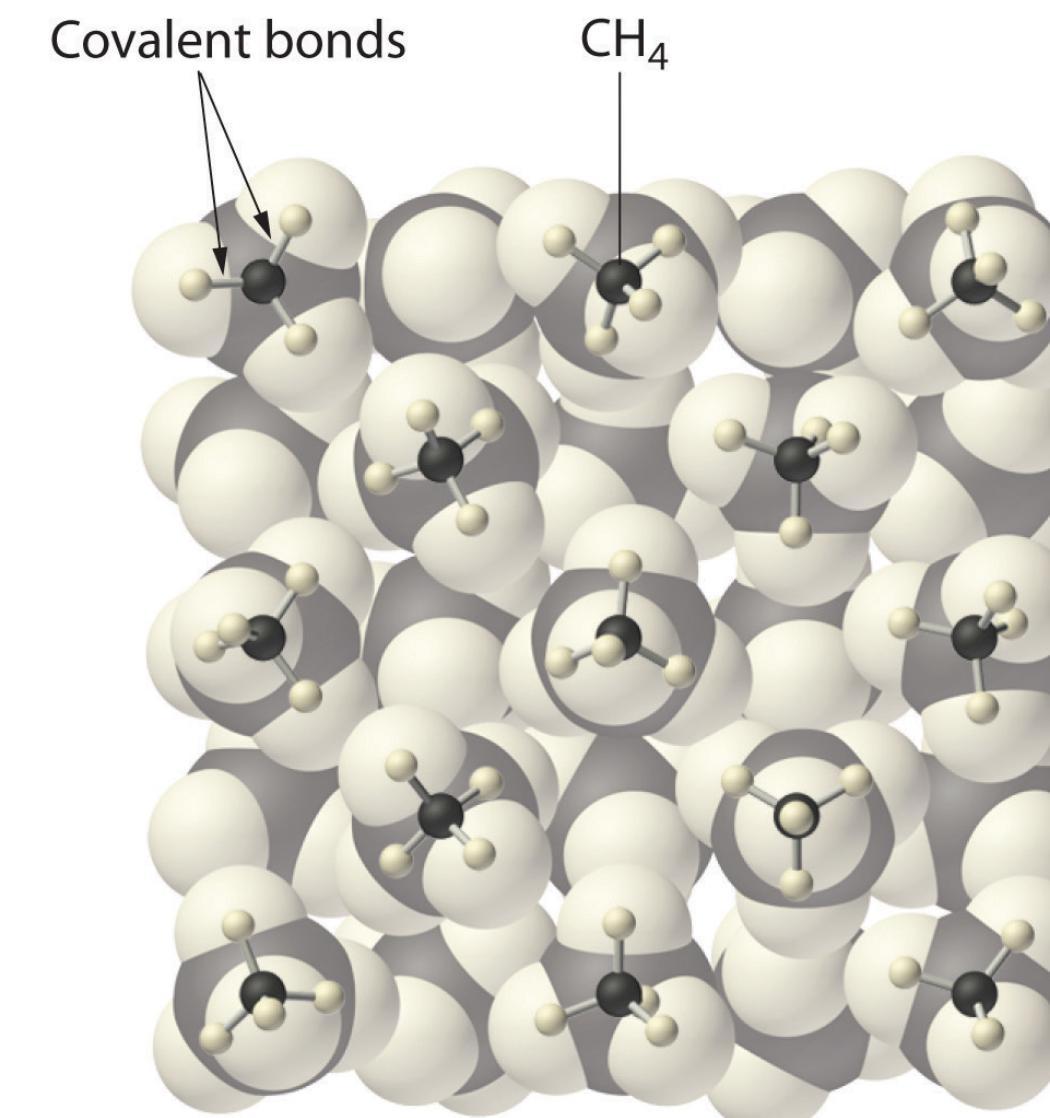


# Bonding character and properties

- **Melting and boiling temperatures:** covalent and ionic solids have higher melting and boiling points.
- When a solid consists of molecules held together by secondary bonds, the melting and boiling points of the solid reflect only the strength of the secondary bonds between the molecules, and not the strength of the primary bonds within the molecule.



- 3-D network of Si-O bonds
- No secondary bonding
- Melting point of 1723 °C
- During melting Si-O bonds are broken



- Secondary bonding: van der Waals forces between CH<sub>4</sub> molecules (strength 1.36 kJ/mol)
  - Melting point of -182 °C
  - C-H bond strength is 413 kJ/mol > Si-O strength of 375 kJ/mol
  - During melting van der Waals forces are weakened

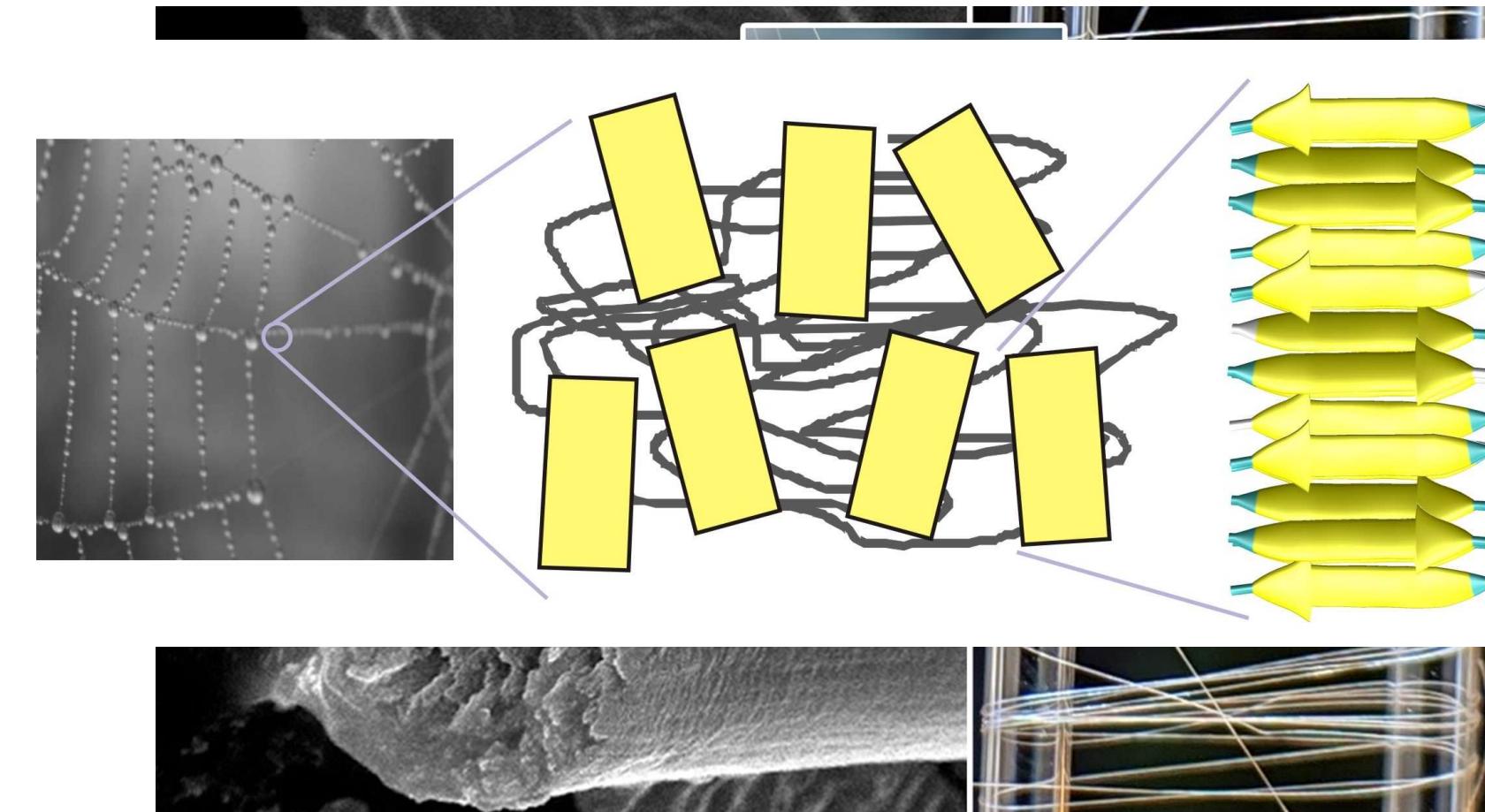
- ***Thermal expansion:*** asymmetry of the potential energy versus distance curve
  - Thermal expansion at a given temperature tends to be less for strongly bonded materials than for weakly bonded materials.
  - Deep potential wells are more symmetrical about the equilibrium position  $r_0$  than shallow potential wells.
- 
- ***Mechanical Properties*** of solids are dependent on the strength of the bonds as well as the directional nature of bonding.
  - Solids with strong and directional bonds tend to be brittle
  - Diamond: *covalently bonded* → hard and brittle
  - *Metallic bonds* are relatively weak and nondirectional, metals are soft, ductile and malleable.
  - *Ionic solids* fall in between covalent and metallic solids in that they may exhibit a very limited amount of ductility.

# Why do we need to understand the intermolecular forces?



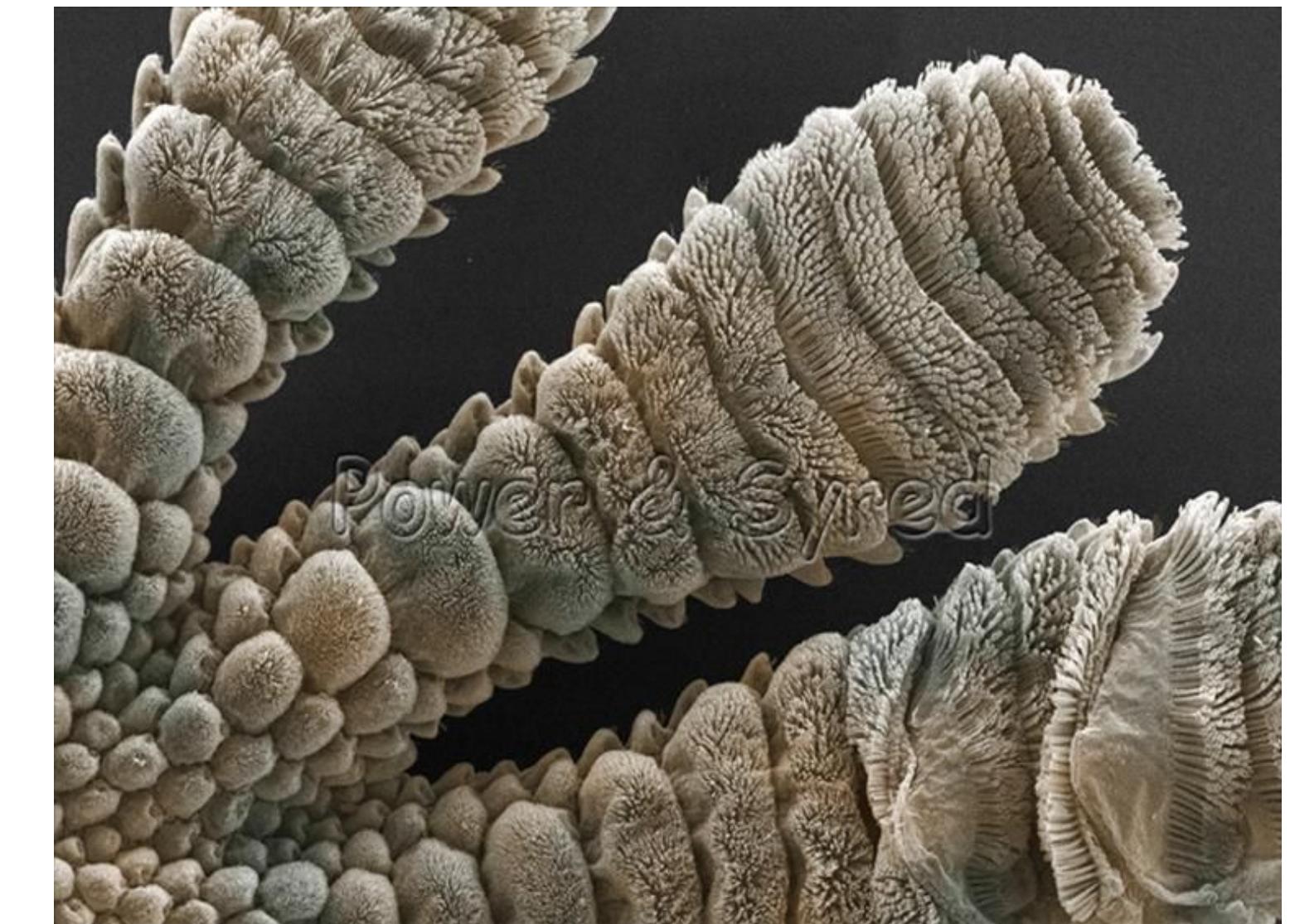
Designing superhydrophobic surfaces, self-cleaning applications

***Hydrophobic interactions***



Designing materials stronger than Kevlar  
**SEM image of spider silk fiber**

***Hydrogen bonding***



Designing materials with adhesive properties  
**SEM image of Gecko feet**

***Van der Waals forces***

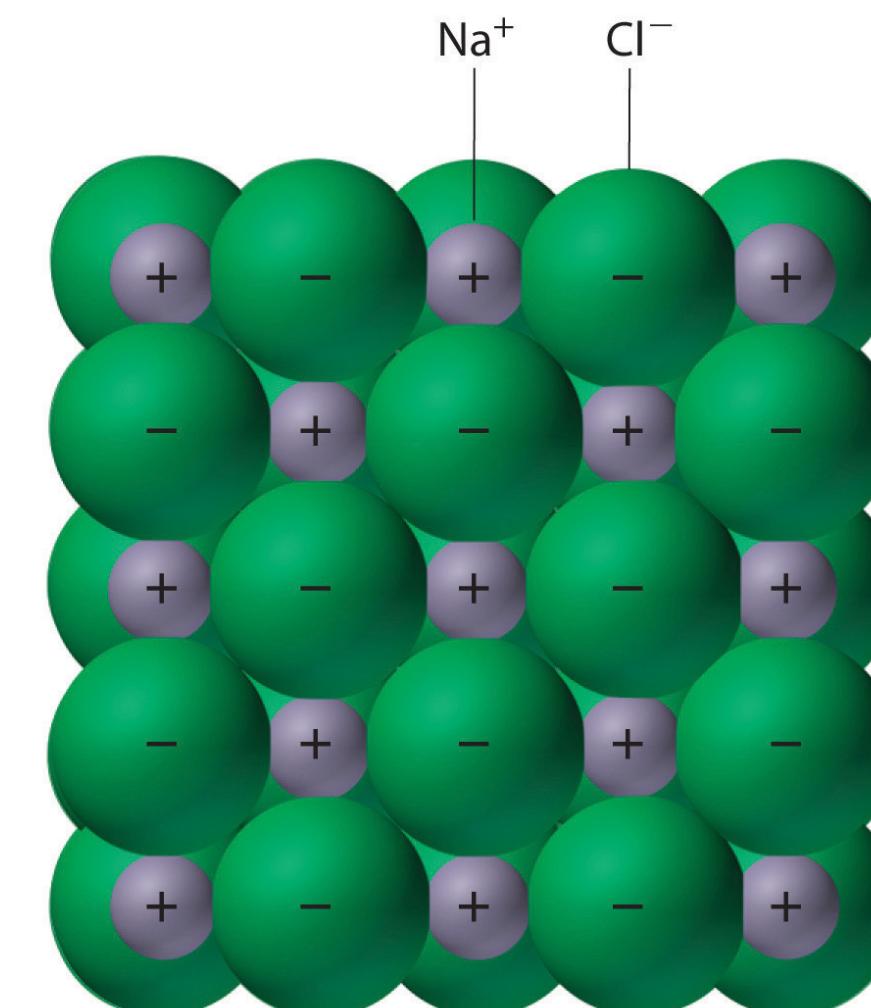
# Structure of solids

*Food for thought... (partially answered)*

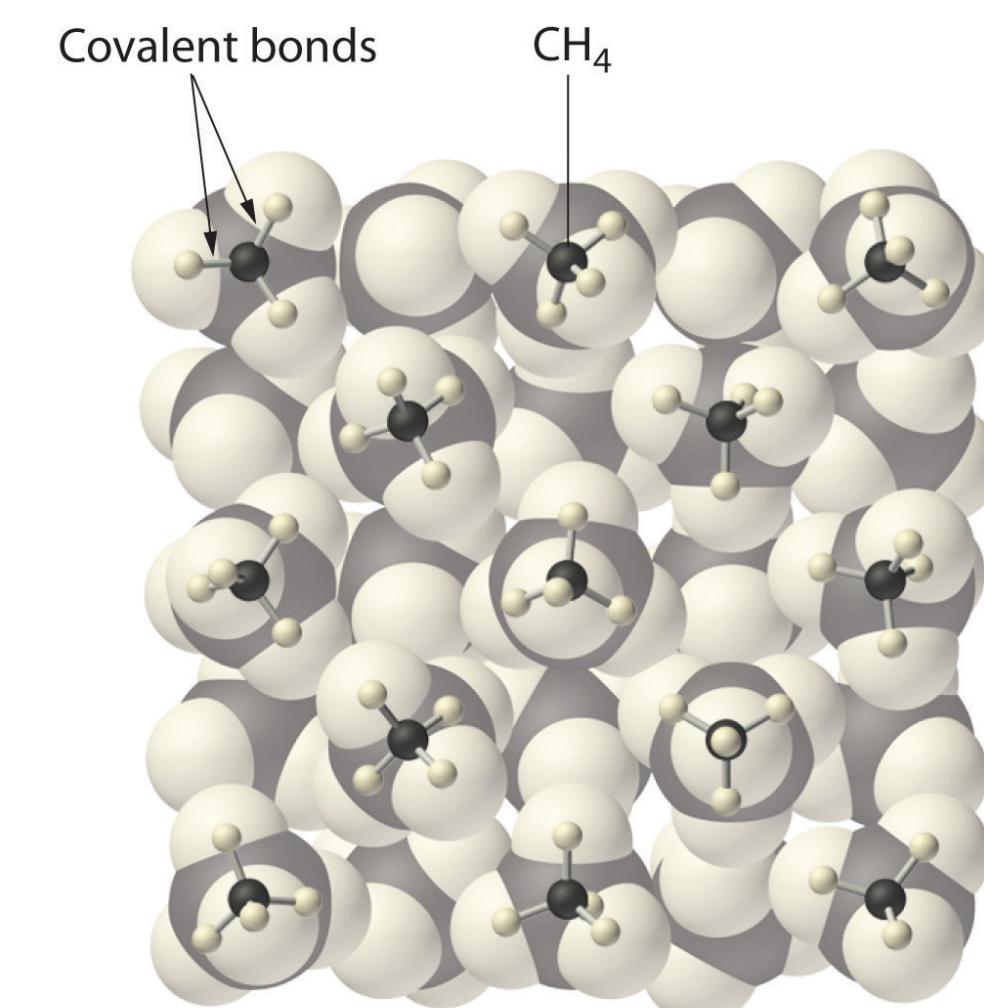
- *Why don't all solids have same strength?*
- *Why do they have any strength at all?*
- *Why aren't they much stronger?*
- *When do we call them strong?*

# Classification of solids

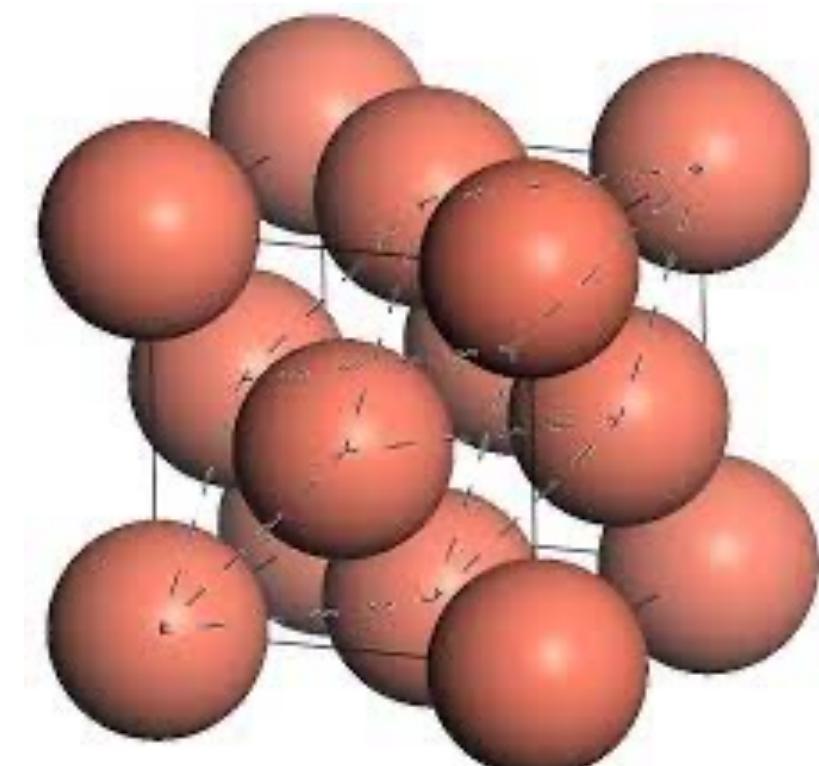
- Ionic solids
- Metallic solids
- Covalent network solids
- Molecular solids



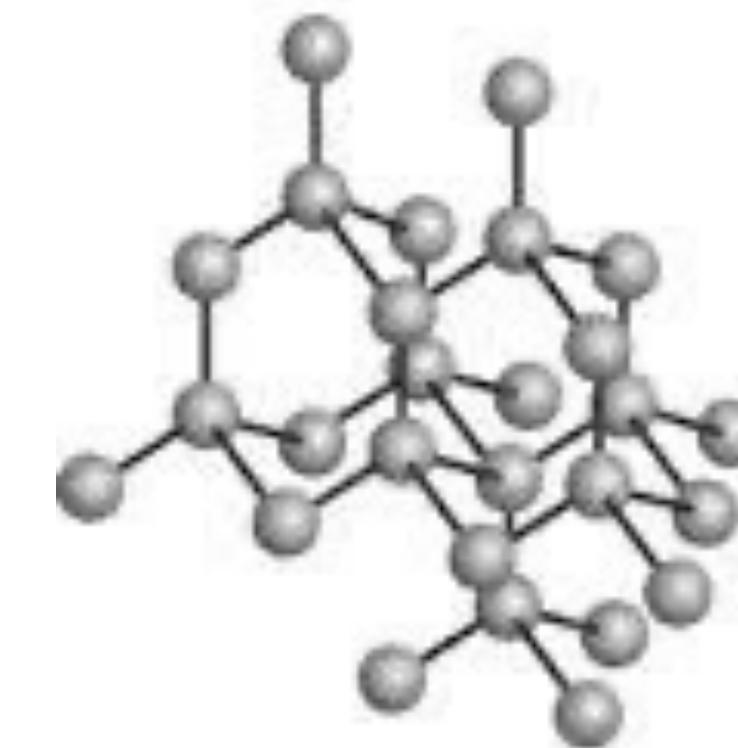
(a) Ionic solid: strong electrostatic interactions



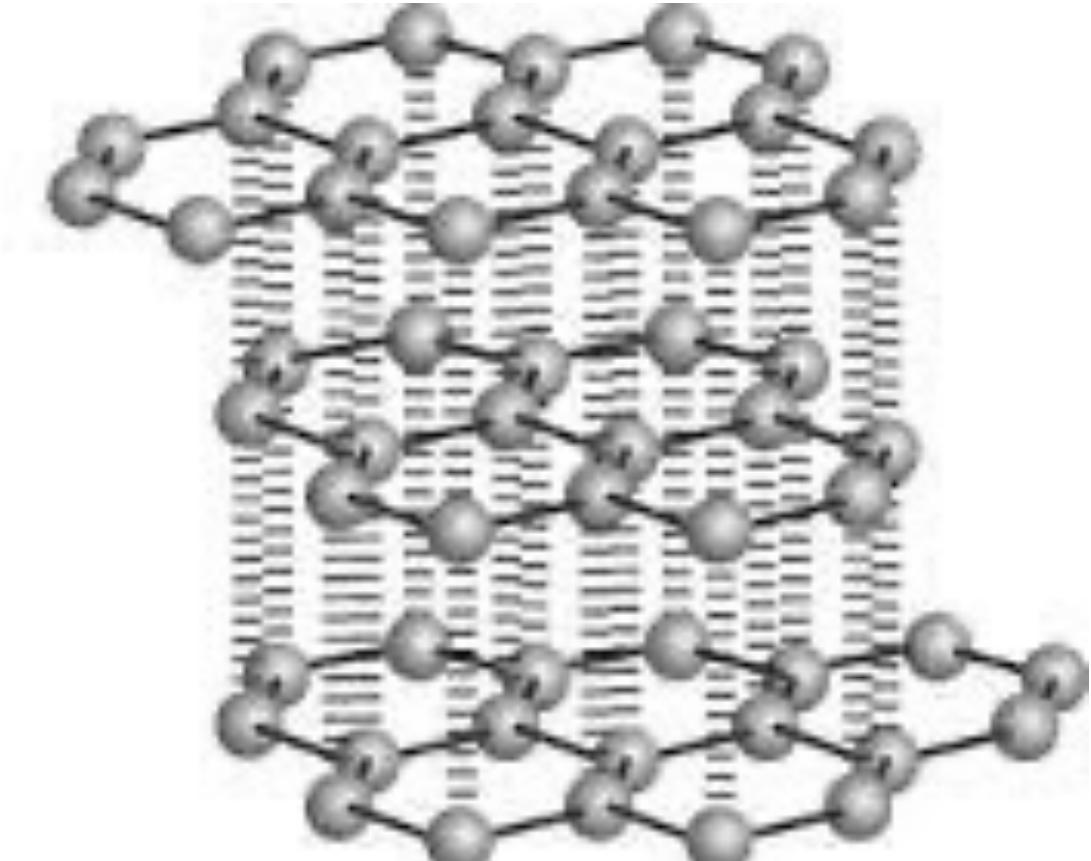
(b) Molecular solid: weak intermolecular forces



Metallic solids like Cu, Fe



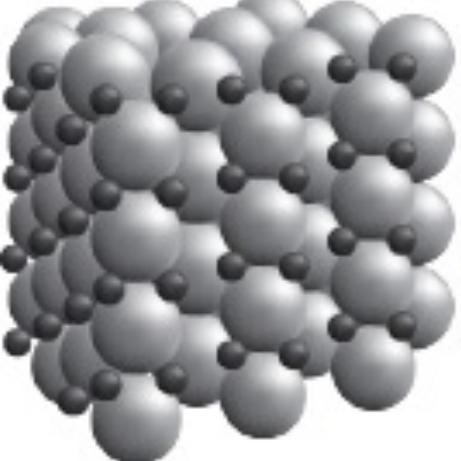
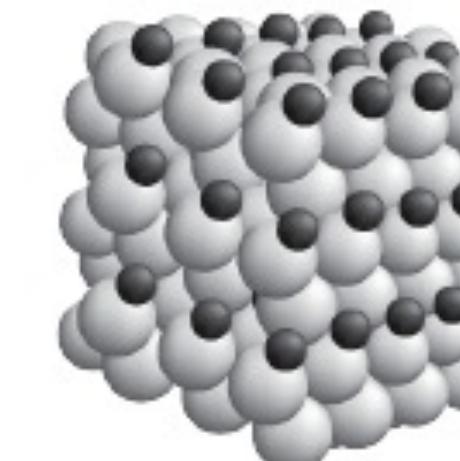
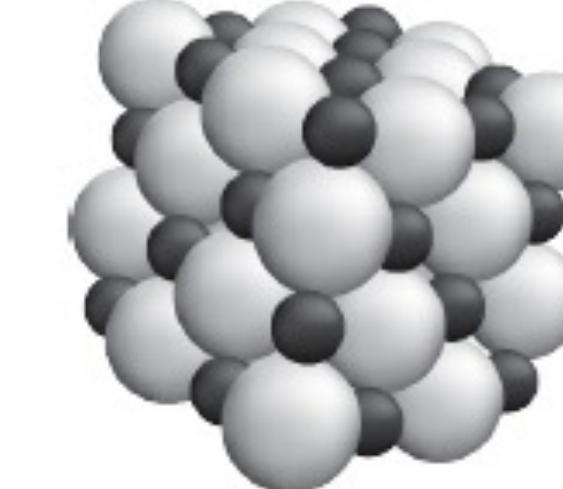
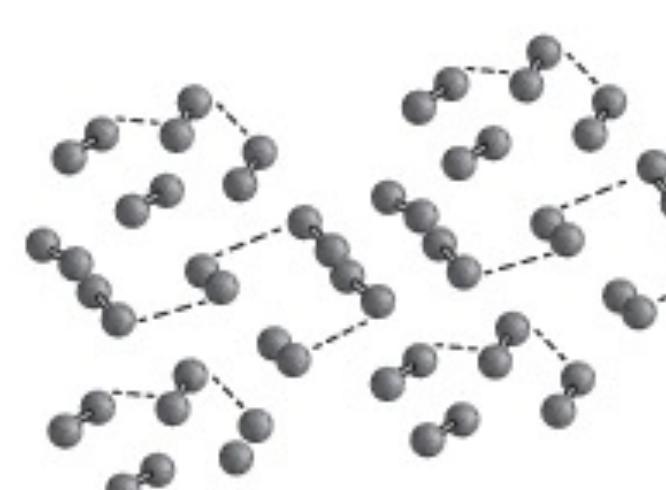
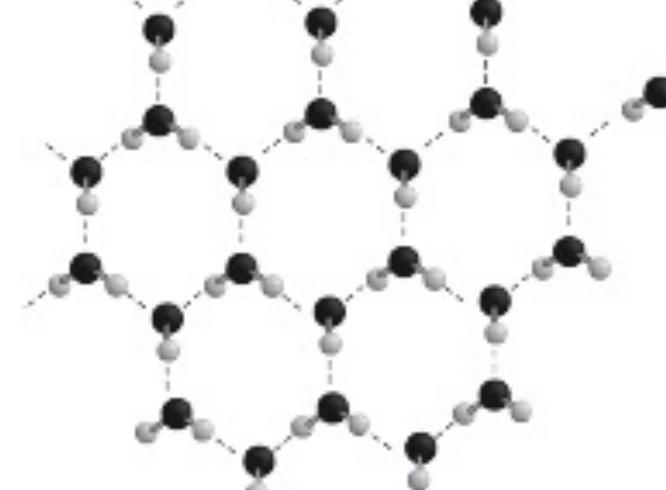
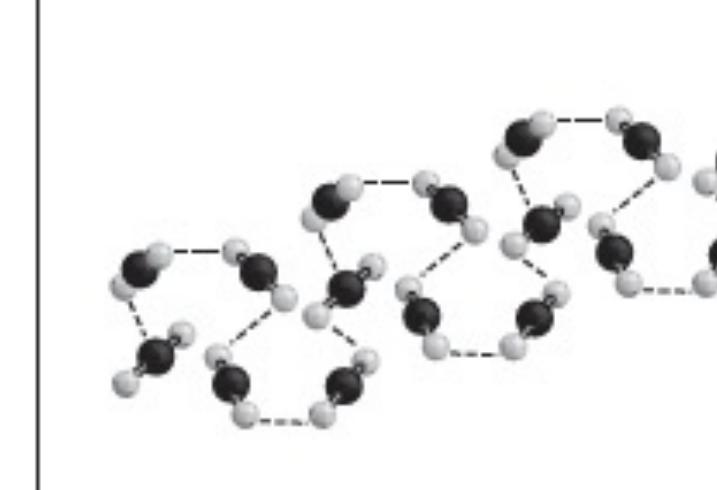
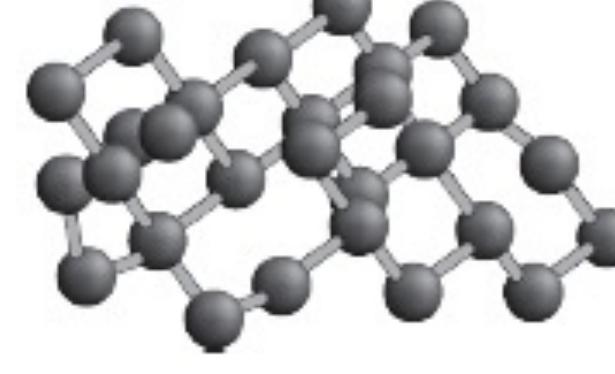
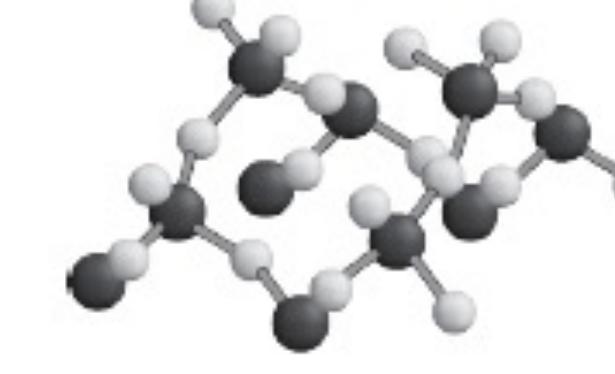
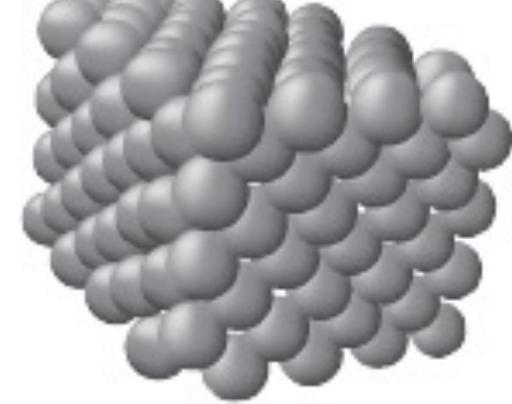
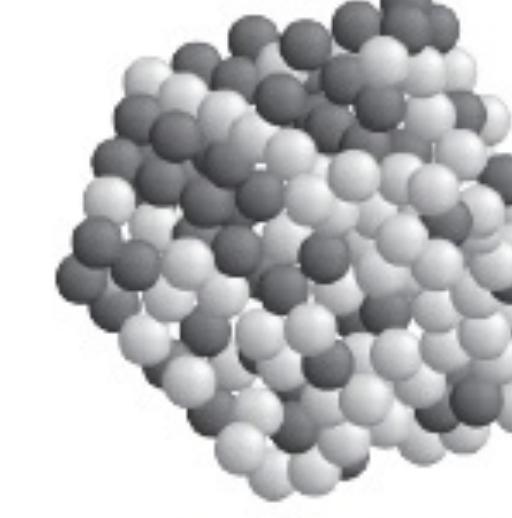
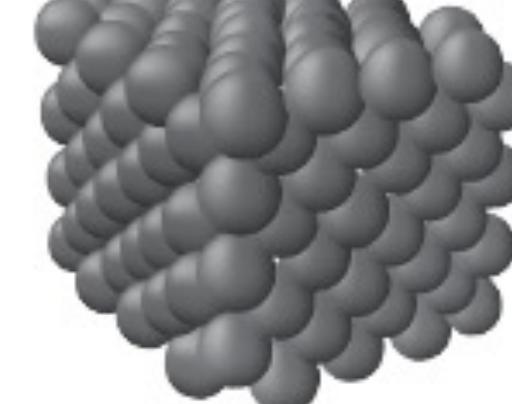
Diamond



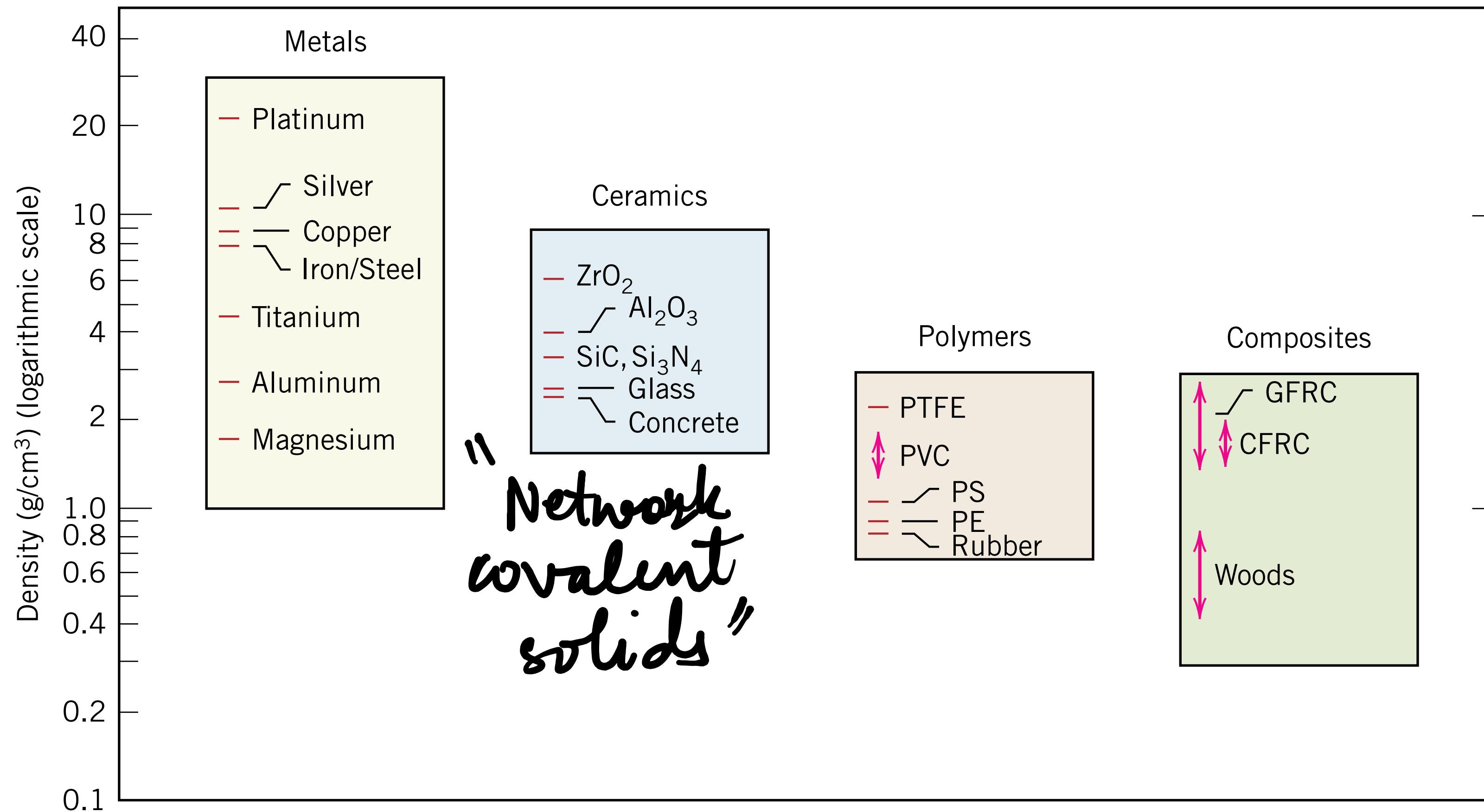
Graphite

Extended networks of atoms held by covalent bonds eg.  $\text{SiO}_2$ , C allotropes

# Some examples

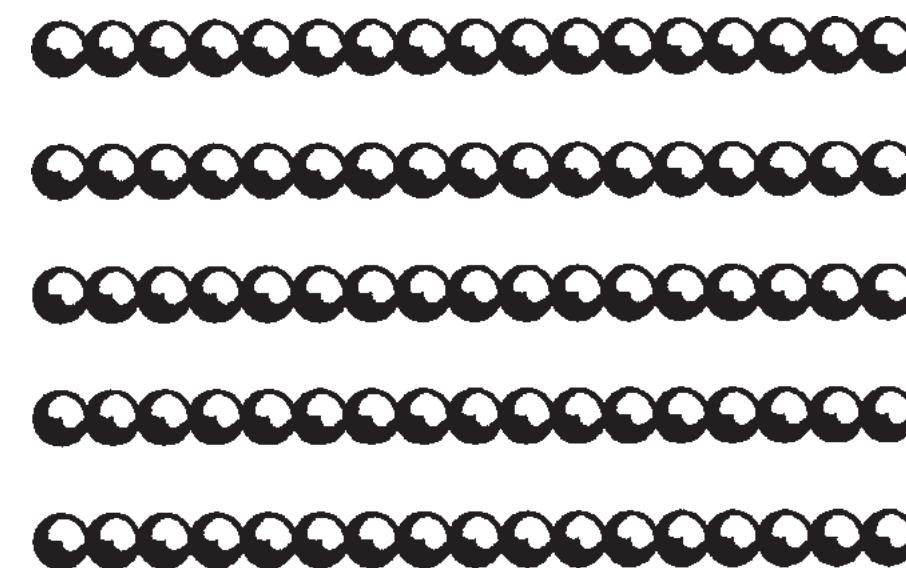
Ionic Solids			
Molecular Solids			
Network Covalent Solids			
Metallic Solids			

# Classification of materials

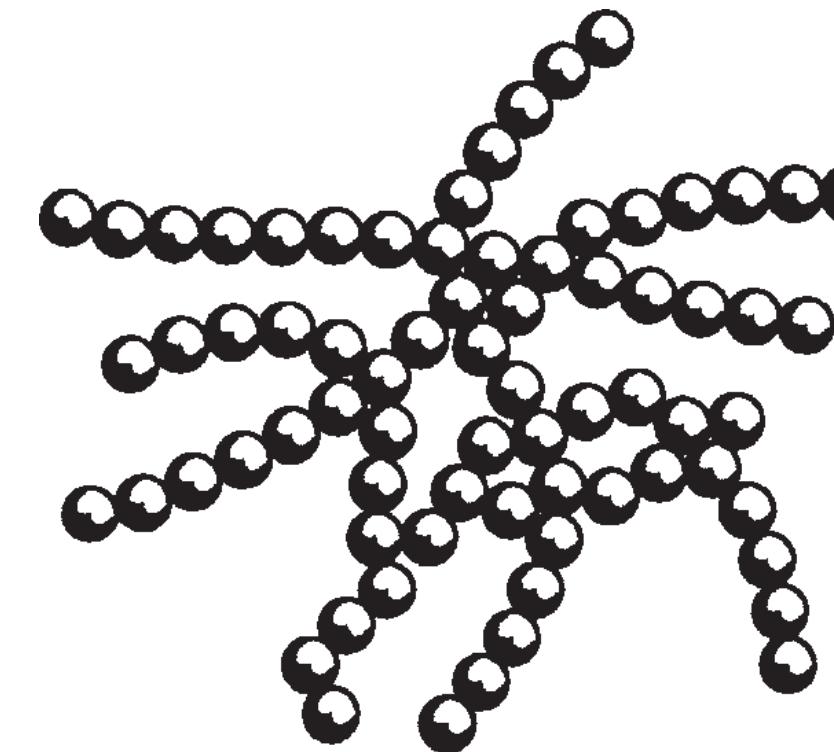


# Crystalline and non-crystalline states

Crystalline state



Molten or glassy state



When primary bonds do not extend in all directions, one-dimensional chain molecules or two-dimensional sheet molecules are formed. Such units have to be aided by secondary bonding forces to form a three-dimensional crystal.



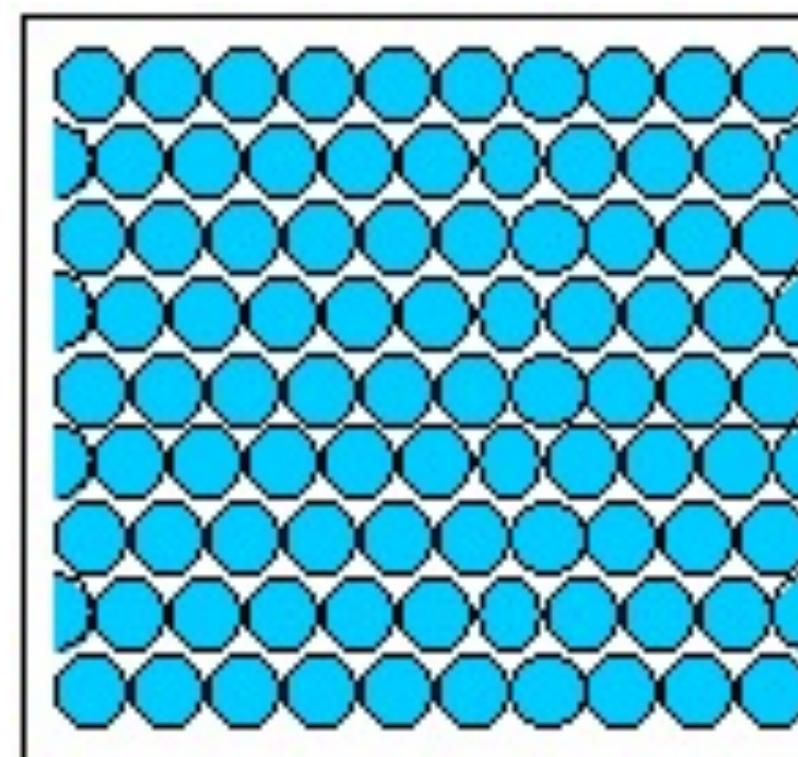
# Crystalline and non-crystalline states

## Crystalline solids

- Long-range order (translational periodicity)
- Defects (vacancy, dislocations etc)
- Atomic arrangement is ordered
- Sharp melting point
- Need slow cooling rates
- Free energy is lowest
- Grain boundaries
- Example: metallic Cu, NaCl

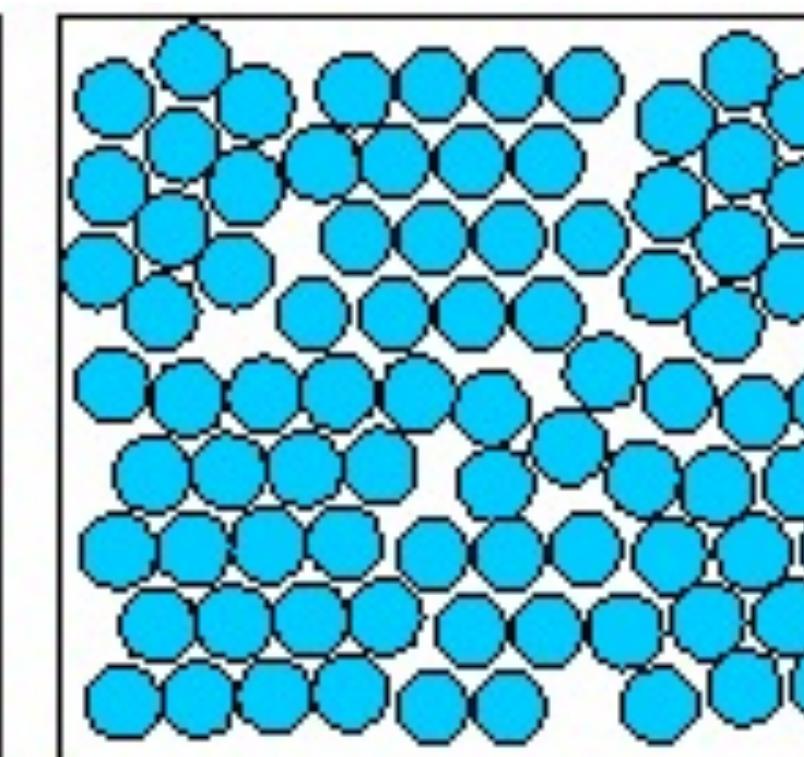
## Amorphous solids

- No long-range translational order i.e. short-range order (not totally random)
- Disordered or random arrangements of atoms
- Gradually softens over a range of temperature.
- Fast cooling rates.
- Free energy is high
- No grain boundaries
- Example: glassy solids (silicates)



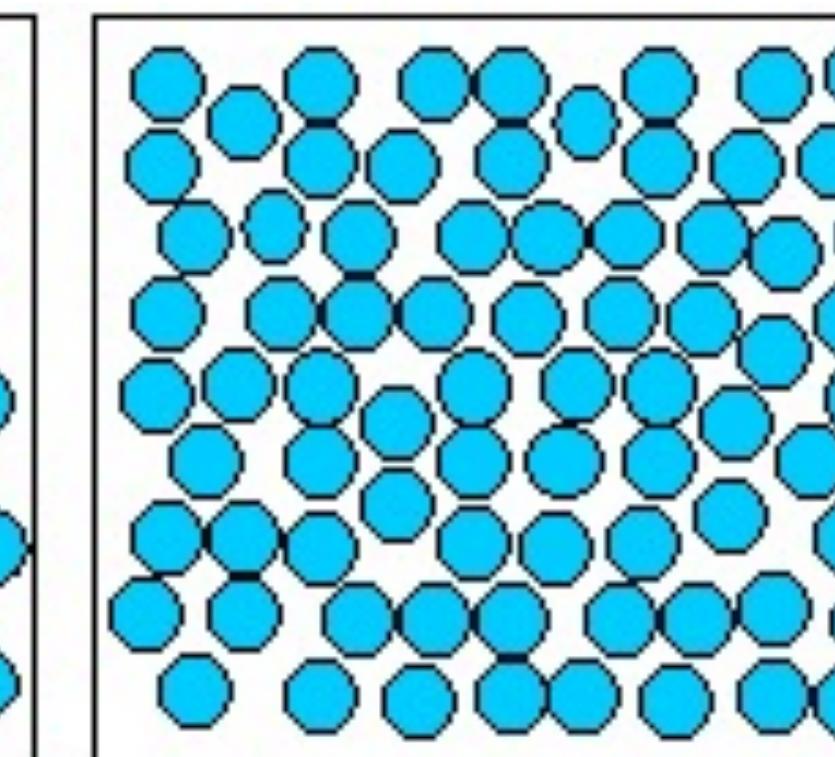
Single crystal

Periodic across the  
whole volume.



Polycrystal

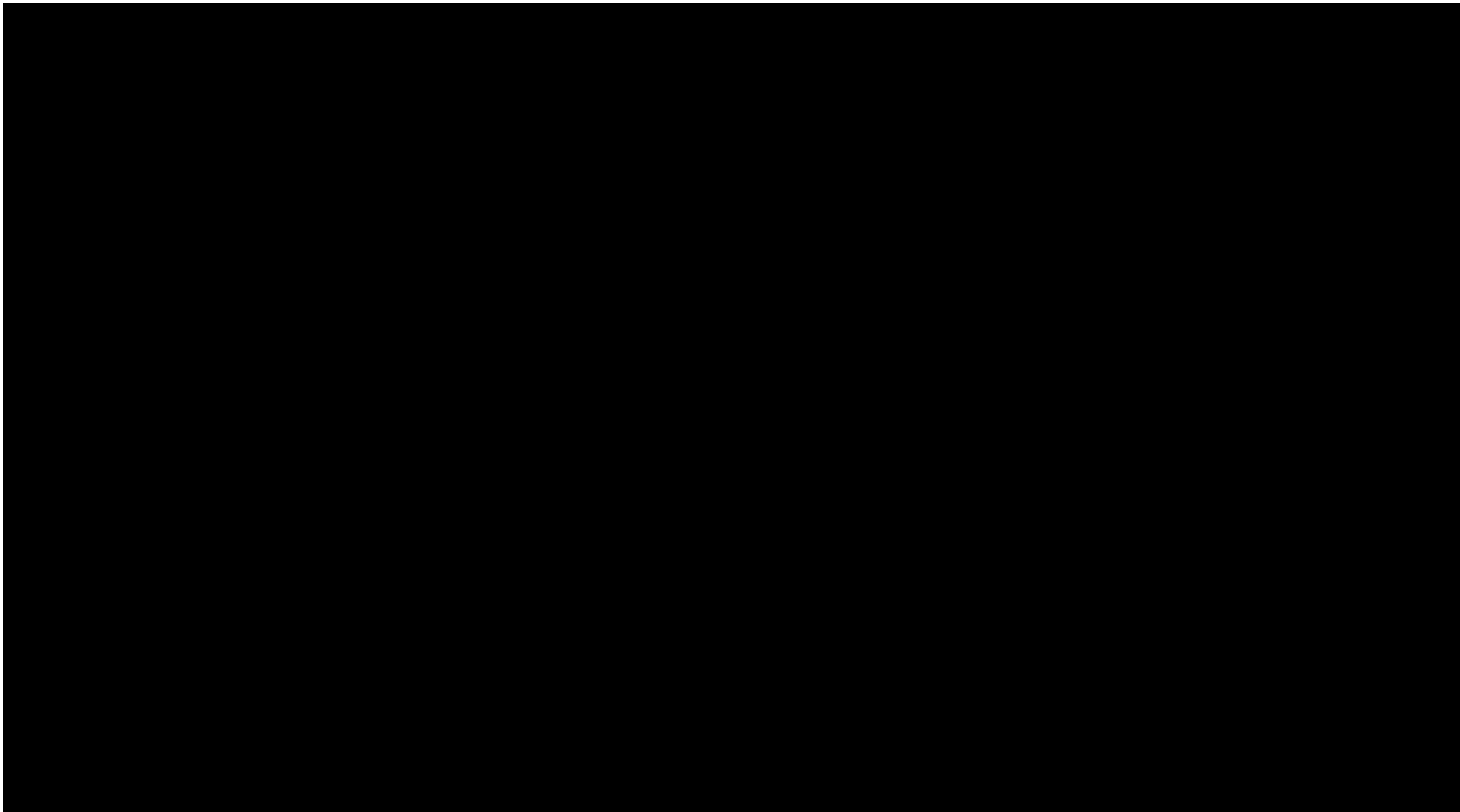
Periodic across  
each grain.



Amorphous solid

Not periodic.

# Is glass a solid or a liquid?



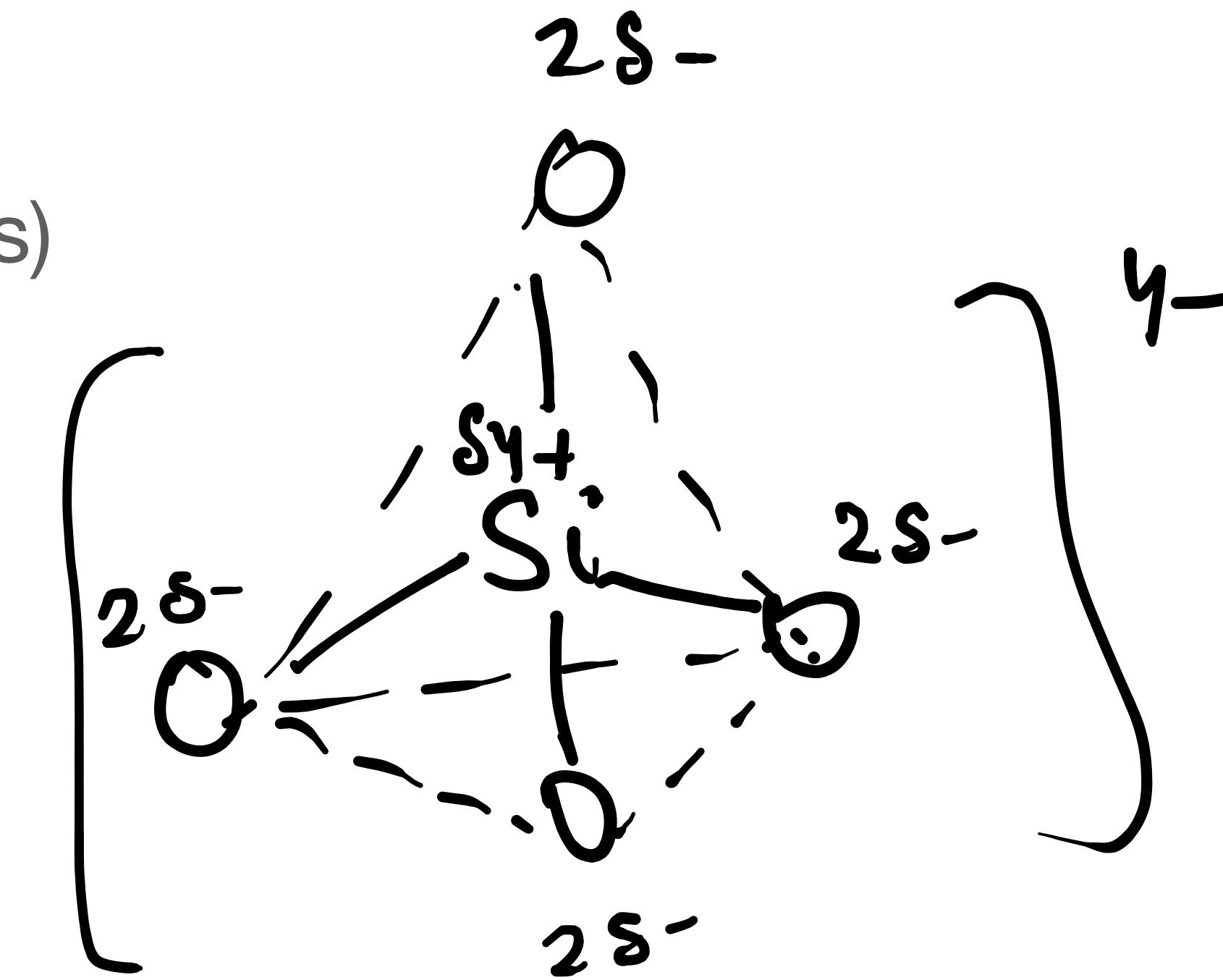
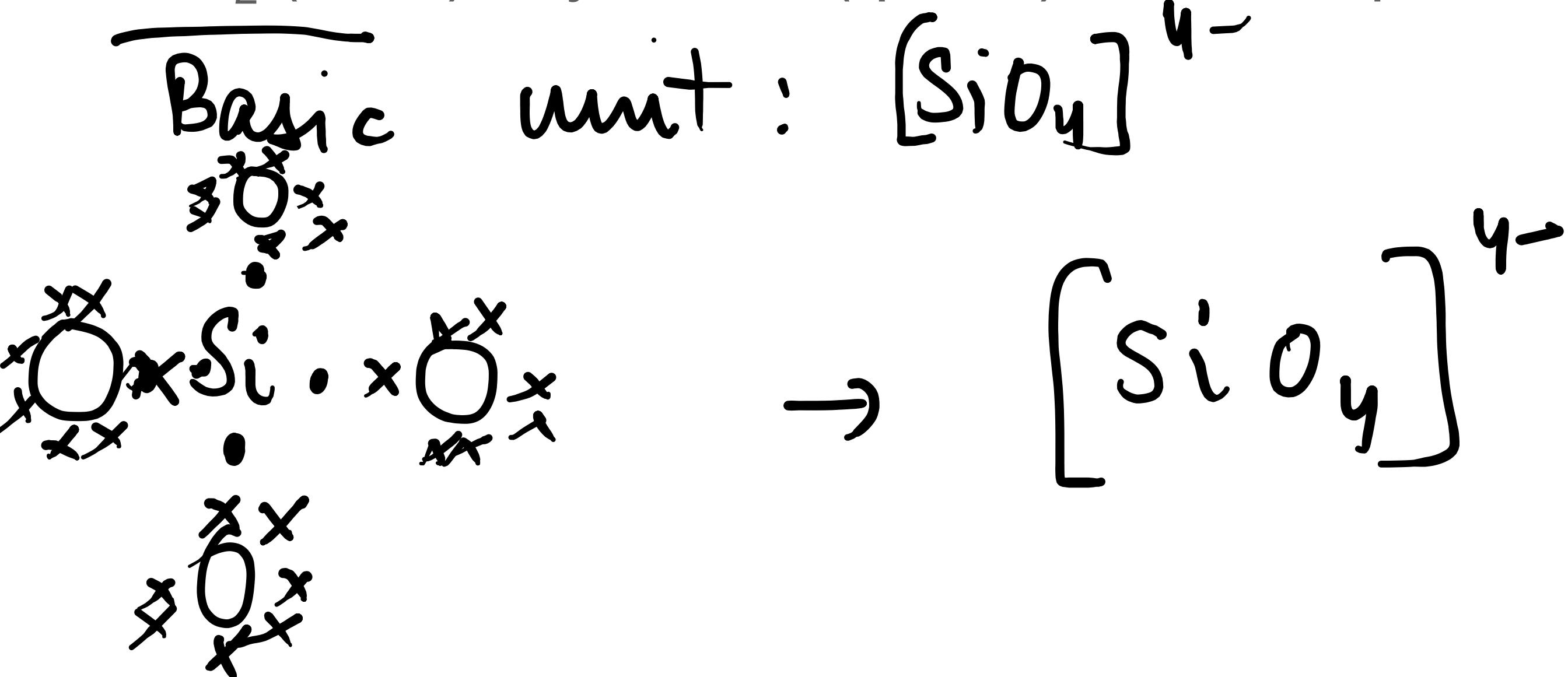
# Amorphous solids (Ceramics: glass)

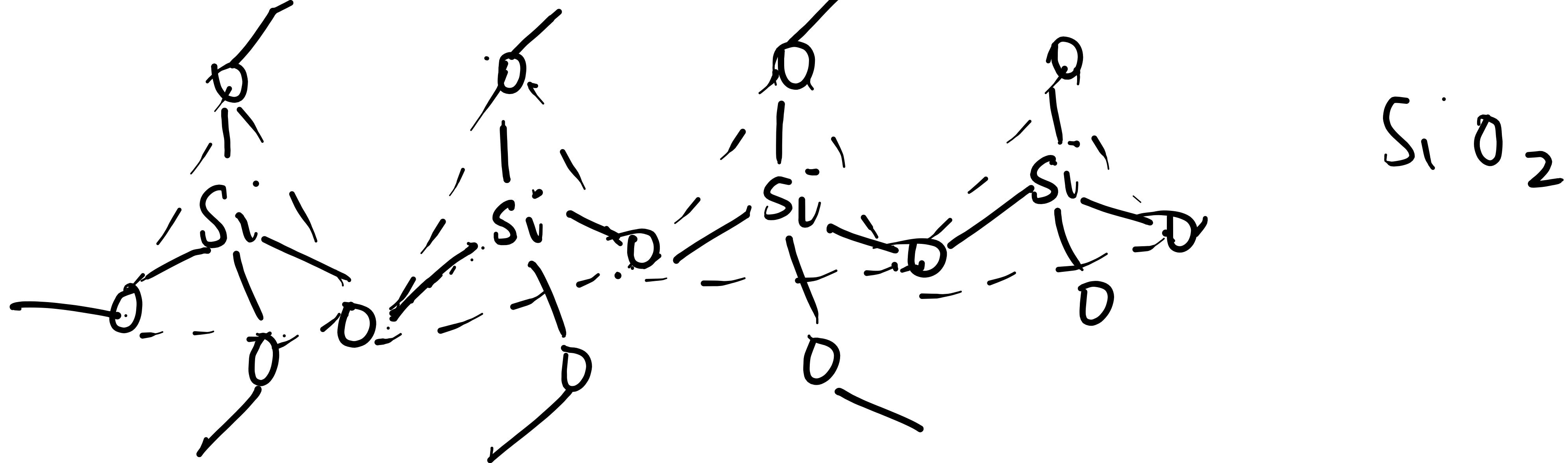
## Silicates: Glassy solids

Ceramics: composed of clay minerals (i.e., porcelain), as well as cement, and glass e.g. aluminum oxide (or alumina,  $\text{Al}_2\text{O}_3$ ), silicon dioxide (or *silica*,  $\text{SiO}_2$ ), silicon carbide ( $\text{SiC}$ ), silicon nitride ( $\text{Si}_3\text{N}_4$ )

- stiff and strong
- Brittle (less ductile)
- Susceptible to fracture
- Low heat and electrical conductivities

$\text{SiO}_2$  (silica): crystalline (quartz) and amorphous (glass)



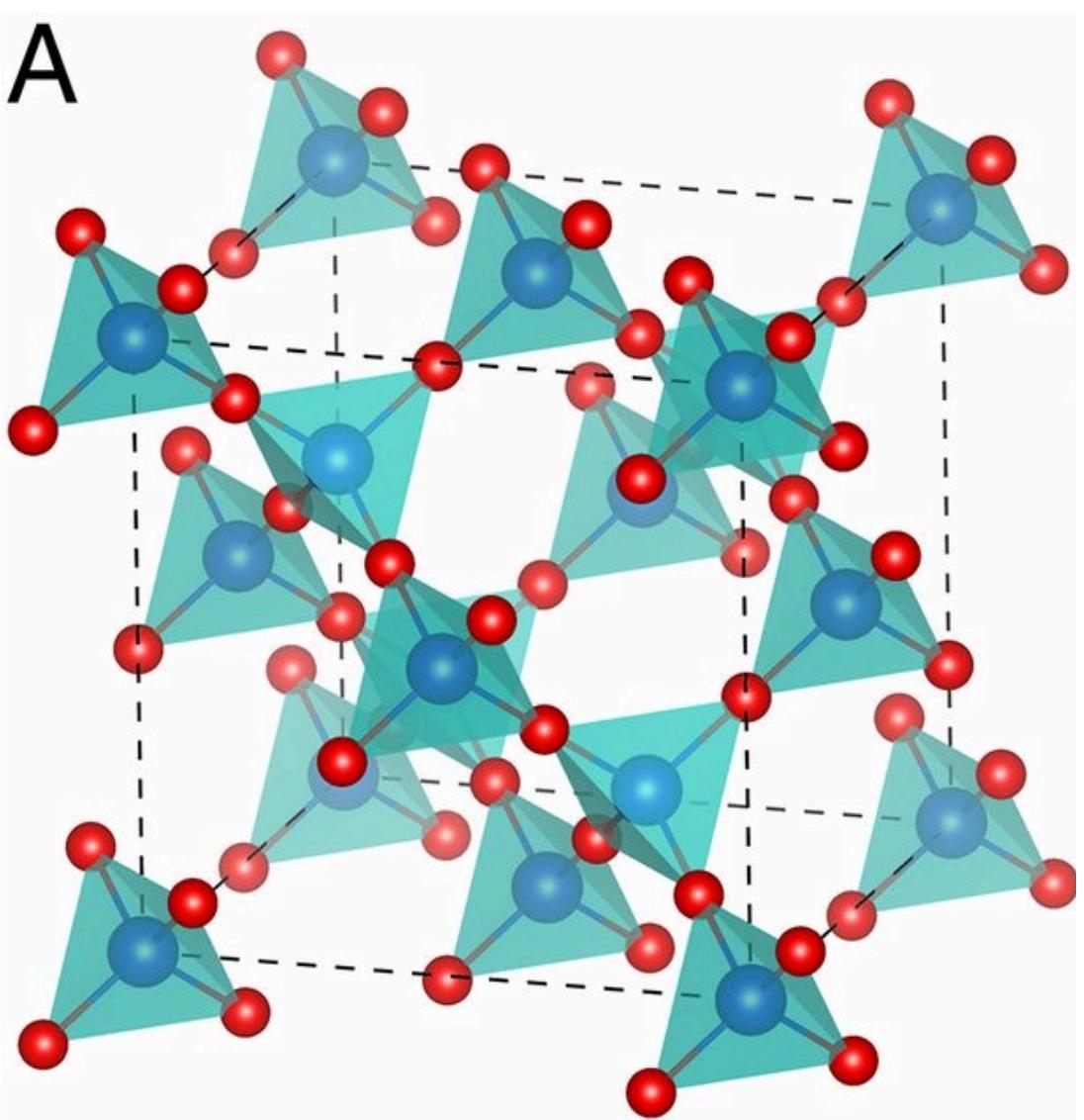


$\frac{1}{2} \times 40$  per tetrahedron  $\rightarrow$  1 Si per TH }  $\text{SiO}_2$   
 $\frac{1}{2} \times 40$  per tetrahedron  $\rightarrow$  20 per TH

- Composition is maintained
- Electro neutrality is "

# Three-dimensional network of silicate

*Tetrahedra can rotate*



**Crystalline**  
Slow cooling

**Amorphous**  
Fast cooling

