

Matériaux Nanostructurés homogènes

- Nanocristaux
- Cristaux de nanocages: clathrates et fullerites.
- Assamblages de nanotubes

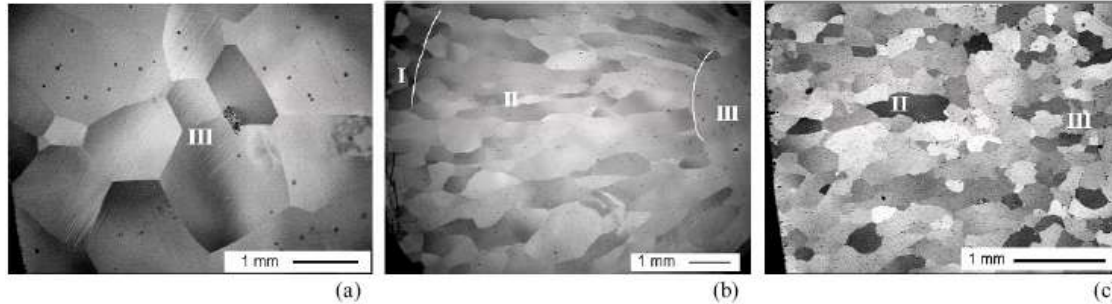
Nanocristaux

Nanocrystalline materials may exhibit increased strength/hardness, improved toughness, reduced elastic modulus and ductility, enhanced diffusivity, higher specific heat, enhanced thermal expansion coefficient (CTE), and superior soft magnetic properties in comparison with conventional polycrystalline materials.

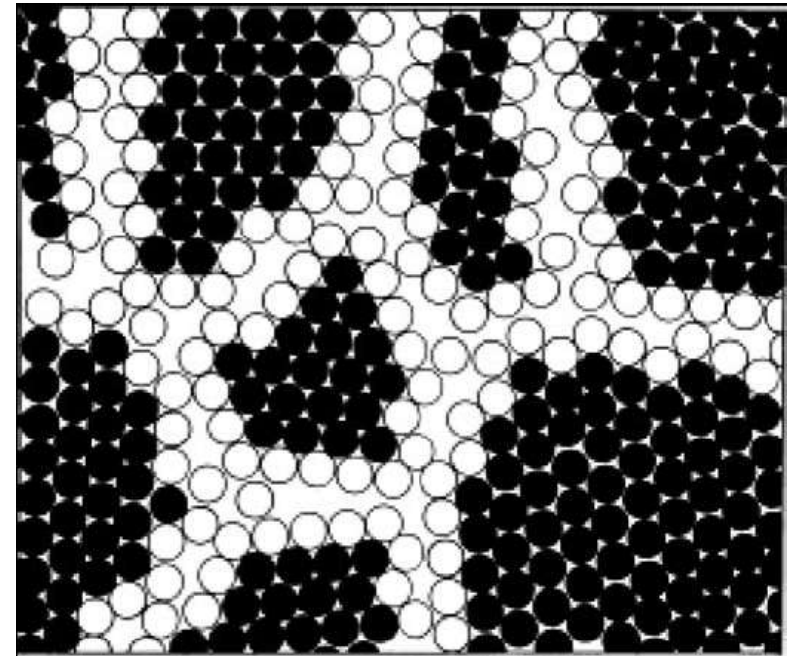
HISTORY : The synthesis and use of nanostructures are not new phenomena. In 1906, Wilm observed age hardening in an Al–Cu–Mg–Mn alloy. Merica et al. proposed in 1919 that the age hardening was caused by the precipitation of submicrometer-sized particles, which were later confirmed by X-ray and transmission electron microscopy (TEM). The precipitates are known as GP zones, GPII zones ($h00$) and metastable ($h0$) precipitates, and are typically 10 nm in thickness and 100 nm in diameter. In particular, the GP zones (named after Guinier and Preston, who suggested their existence through diffuse X-ray scattering) have thicknesses on the order of 1 nm. The accidental introduction of these precipitates into aluminum in the early 1900s revolutionized the aluminum industry, since it had a dramatic effect on its strength which enabled its widespread use in the burgeoning aircraft industry. Many important defects and phenomena in the mechanical behavior of materials take place at the nanoscale; thus, the realization that nanoscale is of utter importance has been a cornerstone of materials science for the past half century.

The quest for ultrafine grain sizes started in the 1960s by Embury and Fischer and Armstrong et al. . The driving force behind this effort was the possibility of synthesizing materials with strengths approaching the theoretical value ($G/10$) by reducing the grain size, a reasonable assumption from the Hall–Petch relationship.

Associations de nanocristaux



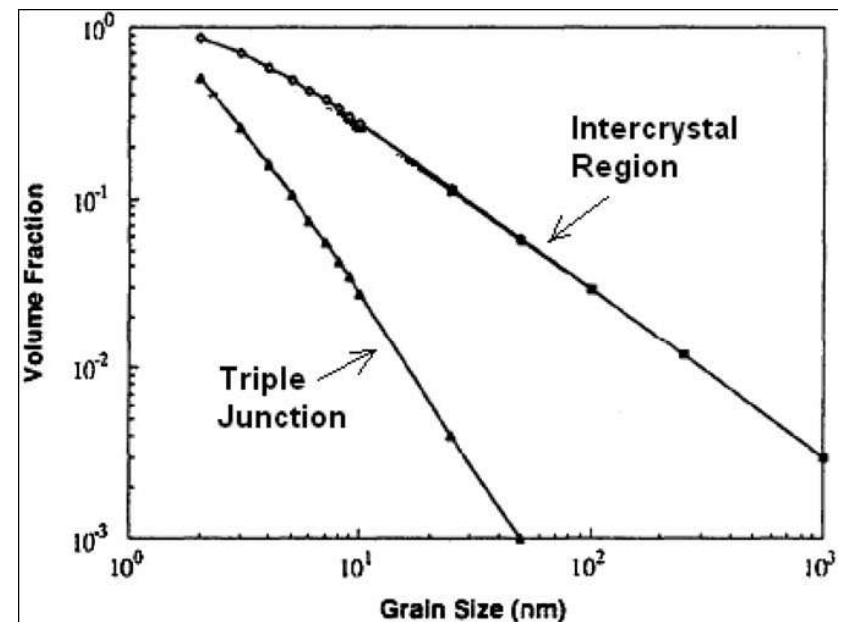
Exemples de microcristaux « traditionnels »



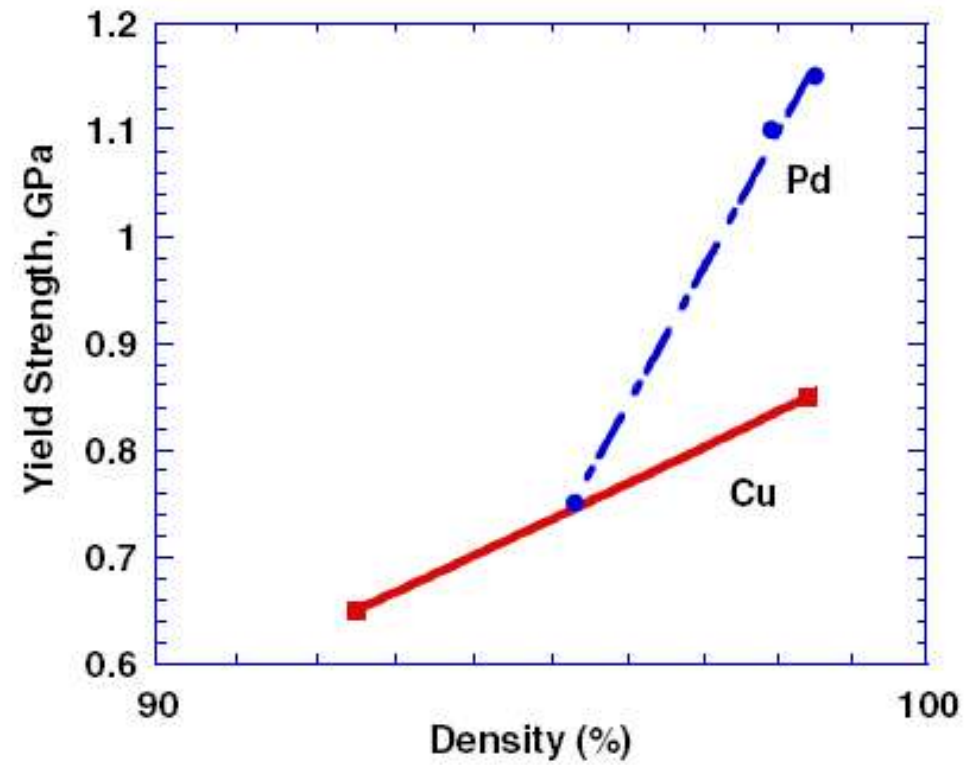
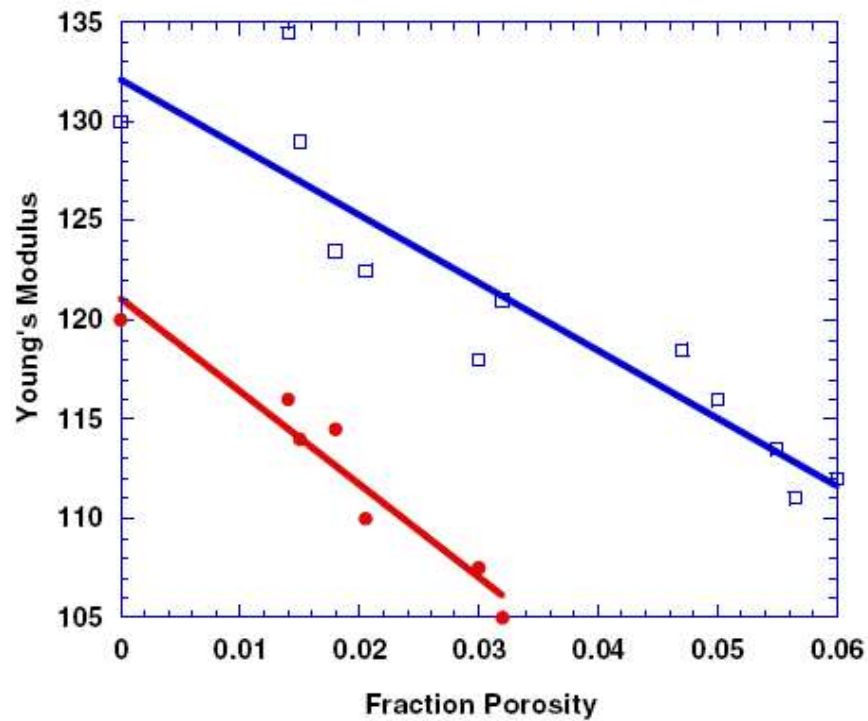
Nanocristaux : Importance des interfaces (« atomes blancs »)

the volume fraction of interfaces can be as much as

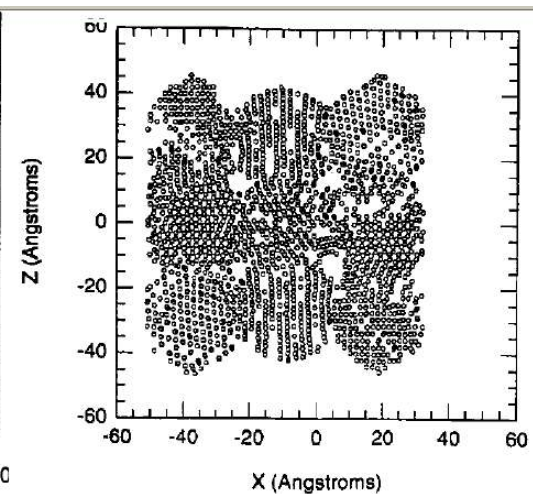
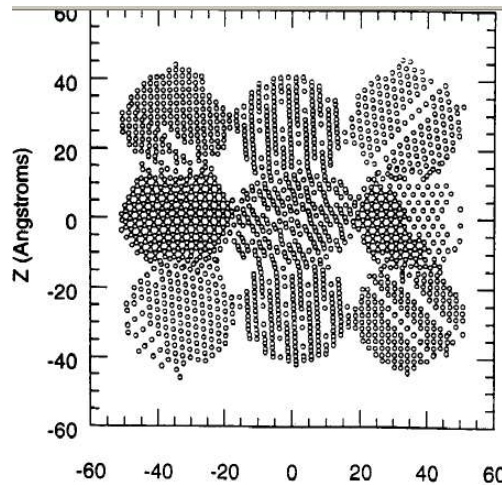
- * 50% for 5 nm grains
- * 30% for 10 nm grains
- * ~ 3% for 100 nm grains.



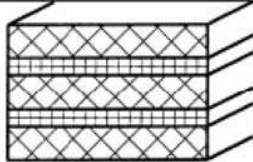
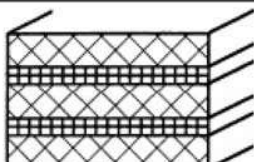
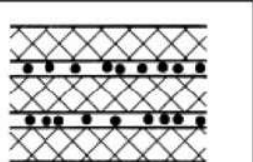
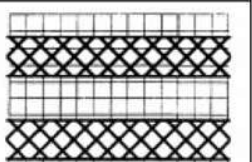
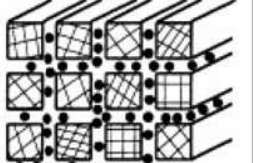
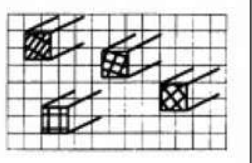
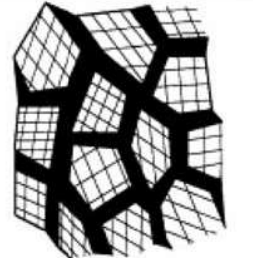
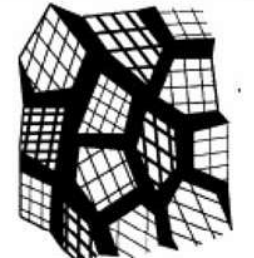
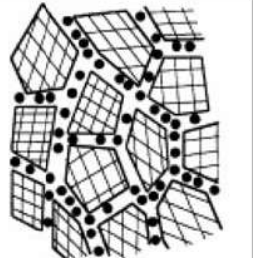
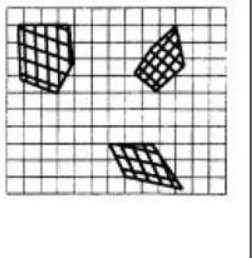
Importance de la porosité



Nécessité d'un consolidation sous pression



Types de nanocristaux

Chem. comp. of crystallites	Same	Different for different crystallites	Composition of boundaries and crystallites different	Crystallites dispersed in matrix of different composition
Shape of crystallites				
Layer- shaped				
Rod- shaped				
Equiaxed crystallized				

Relation de Hall-Petch

(loi empirique)

Dans un polycristal, la limite d'élasticité (*yield strength* en anglais), σ_y , dépend de la taille moyenne (d) des cristallites suivant la relation :

$$\sigma_y = \sigma_0 + \frac{K}{\sqrt{d}}$$

avec σ_0 la limite d'élasticité du monocristal

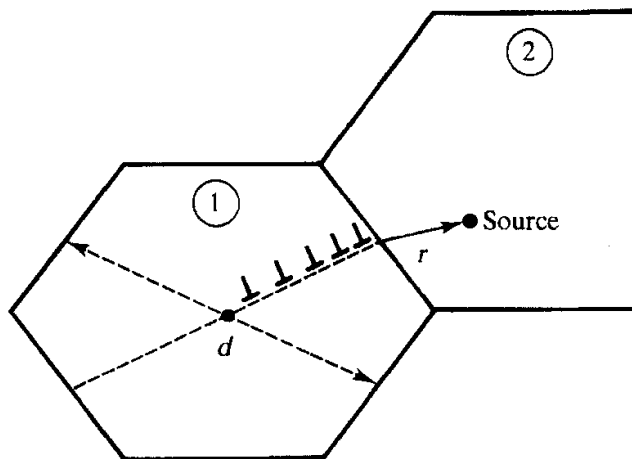
K dépend du type de matériau : K est grand pour les aciers (leurs propriétés mécaniques s'améliorent avec la diminution de la taille des grains) mais elle est plus faible pour les structures c.f.c ou h.c..

Hall-Petch Effect

- The Hall-Petch effect is remarkably simple to express but still difficult to explain in fundamental terms.
- At ambient conditions (no creep), yield strength rises as the grain size decreases.
- The Hall-Petch effect is named for E.O. Hall and N.J. Petch from their papers of the early 1950's, e.g. "The Cleavage Strength of Crystals" N.J. Petch, *J. Iron & Steel Inst.*, **174**, 25-28.

Dislocation Pile-ups

- Classical explanation for the Hall-Petch effect :
 - 1) Some stress concentration in a given grain is required to initiate slip in its neighboring grain.
 - 2) Stress concentration is most plausibly obtained through a dislocation pile-up, as stress is higher as the number of dislocations increases.
 - 3) Thus the larger the grain size, the more quickly (in terms of macroscopic strain) is the critical stress reached at which slip is initiated in the neighboring grain.



Grain boundary stress due to dislocation pile-ups may cause:

- dislocation emission from the boundary in grain 1
- activate a new dislocation source at point r (in grain 2)

Material Dependence

- The Hall-Petch constant, k in the equation, varies considerably amongst materials. This in itself raises some questions about the mechanism(s) underlying the effect. The explanation given is purely geometrical and although the material dependence could be explained through the ratio d/r , it is not clear why this should be so!
- Solutes tend to enhance the magnitude of the Hall-Petch effect.

Material	Crystal structure	k_y (MN/m ^{3/2})
Low-carbon steel	bcc	0.307
Armco iron	bcc	0.583
Molybdenum	bcc	1.768
Zinc	hcp	0.220
Magnesium	hcp	0.279
Titanium	hcp	0.403
Copper	fcc	0.112
Aluminum	fcc	0.068

Source: Adapted from J. D. Embury, *Strengthening Methods in Crystals*, ed. A. Kelly and R. B. Nicholson, Wiley, New York, 1971.
 Original data from: R. Armstrong et al., *Phil. Mag.*, **7**, 45, 1962;
 E. Anderson et al., *Trans TMS-AIME*, **242**, 115, 1968; A. A. Johnson,
Phil. Mag., **4**, 194, 1959; F. E. Hauser et al., *Trans TMS-AIME*, **206**,
 889, 1956; R. W. Guard, *WADC Tech. Report 55-RL-1339*, 1955;
 F. Feltham and J. E. Meakin, *Phil. Mag.*, **2**, 105, 1959; R. P. Carreker
 and W. R. Hibbard, *Trans. TMS-AIME*, **209**, 1157, 1957.

Table 5.1
 Values of k_y for several materials

Grain Size and Fracture

- Grain size also has a marked effect on fracture, which was, in fact, part of Petch's original contribution.

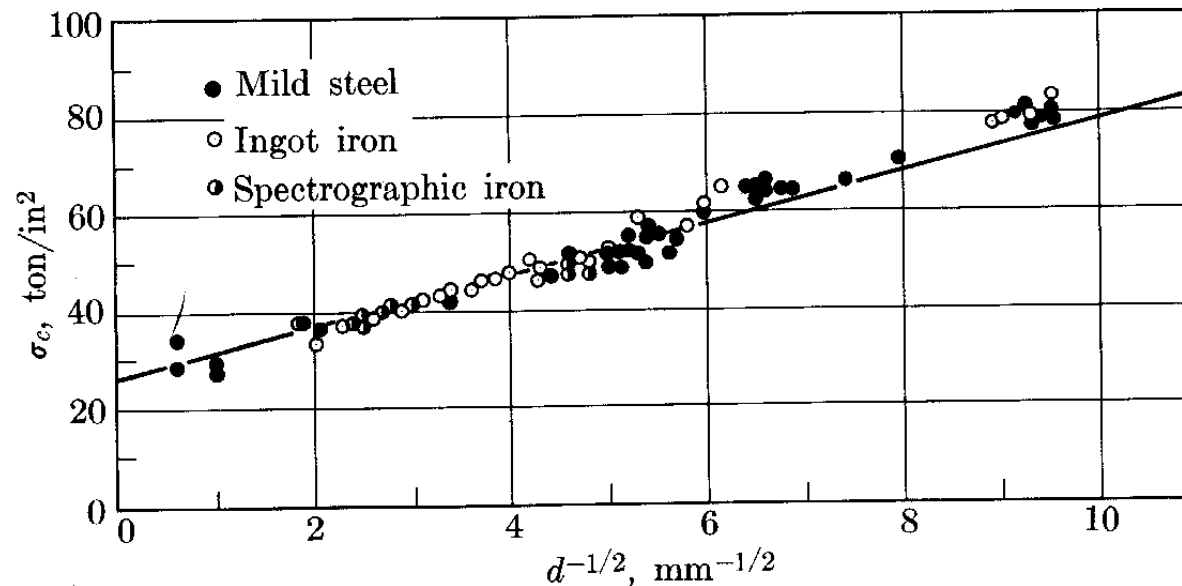


FIG. 17.14. Dependence of the brittle fracture stress on grain size at 77°K. (Petch, 1953. Courtesy of British Iron and Steel Institute.)

Is Hall-Petch valid in nanocrystalline materials ?

- The Hall-Petch relation suggests that remarkably strong materials can be generated for grain sizes in the nanometer scale.
- The processing (in metals) relies on either compaction of fine powders (which requires second phase particles in order to maintain the small grain sizes at sintering temperatures) or heavy deformations allied with recrystallization.
- This is an exciting area and is a lively area of research and development.

Possible limits to Hall-Petch : Creep

- An important property of materials is their resistance to *creep*.
- Creep is irreversible (plastic) flow at low rates under low stresses.
- Creep is highly sensitive to temperature because thermal activation makes the largest contribution to plastic flow when the stress is too small to overcome mechanical barriers to dislocation motion.
- Diffusion coefficients ($D = D_0 \exp\{-Q/RT\}$) are strongly (exponentially!) dependent on temperature.
- The activation energy (enthalpy, strictly speaking) is approximately proportional to the melting point of the material.
- At the same temperature, a higher melting point material will exhibit slower diffusion than a lower melting point material.

Possible limits to Hall-Petch : Creep

- Therefore it is common to use *homologous temperature* as a measure of relative temperature:

$$T' = T/T_{melt}$$

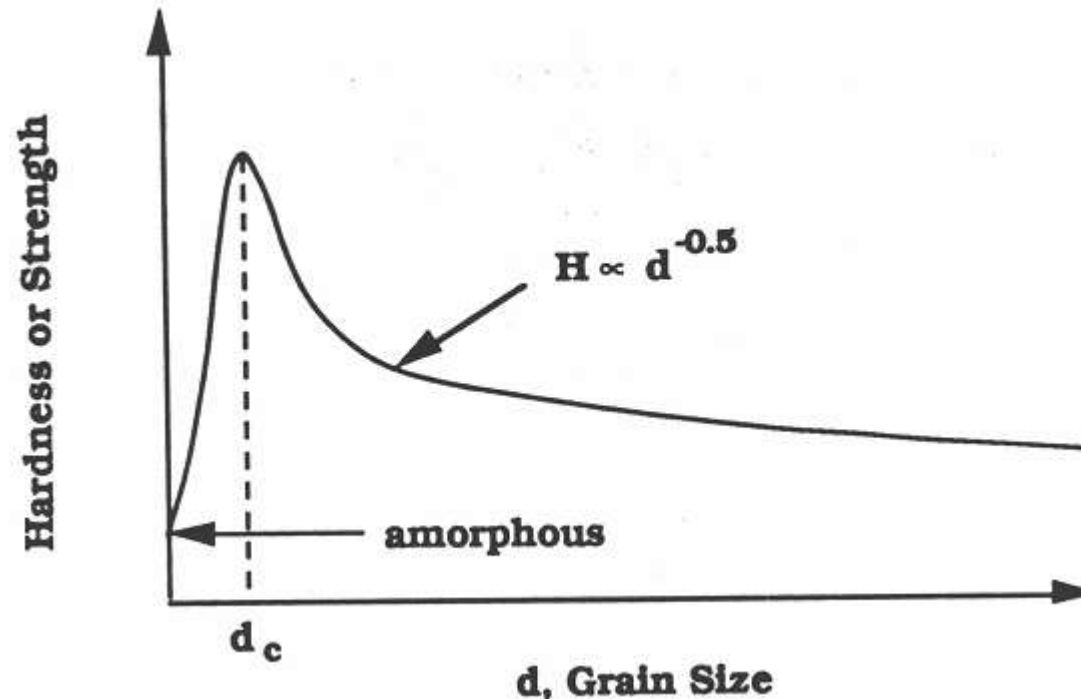
- Materials will tend to creep at high homologous temperatures because diffusion allows changes in shape. This is the *Nabarro-Herring creep* mechanism.
- In nanometer crystals, T_{melt} diminish considerably when reducing size, i.e., there is a possible limit to Hall-Petch through Nabarro-Herring creep.

Things can be more complex..

Creep Mechanisms

- *Dislocation Glide*. This is self-explanatory: dislocations move (conservatively) in response to shear stresses.
- *Nabarro-Herring Creep*. Creep can occur by mass transport, i.e. diffusion of atoms from regions of lower (algebraically) stress to regions of higher (more tensile) stress. This is equally effective in amorphous materials as in crystalline.
- *Coble Creep*. Mass transport can occur either in the bulk (leading to N-H Creep) or along interfaces such as grain boundaries. In the latter case it is known as Coble creep. Both of these mechanisms result in a significant grain size dependence.
- *Solute Drag Creep*. For dislocations gliding at high T, not only do the solute atoms interact with the dislocations but they can also move sufficiently rapidly for the drag effect to be significant.
- *Dislocation Climb-Glide Creep*. In between the (low) temperatures at which only dislocation glide is important, and the (high) temperatures at which diffusion dominates (at low stresses), a combination of glide and climb controls creep. That is to say, dislocation motion carries most of the strain but the dislocations circumvent obstacles by climb.
- *Grain Boundary Sliding* accommodated by diffusional flow. In superplasticity especially, sliding of one grain relative to another is very important.
- *Grain Boundary Sliding* accommodated by Dislocation Flow. This is the same mechanism of g.b. sliding but the accommodation is achieved by dislocation glide. Clearly one expects this to dominate over diffusion at lower temperatures.

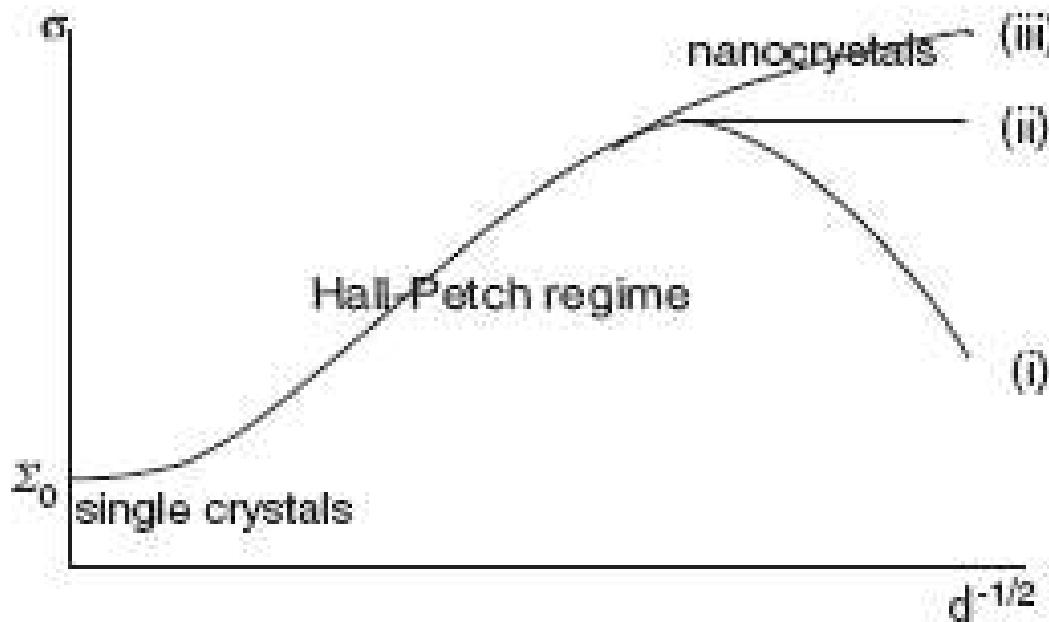
Crossover from 'normal' to 'inverse' Hall-Petch effect



- 'normal' Hall-Petch effect: $\sigma \sim d^{-0.5}$ (dislocation mechanism)
- 'inverse' Hall-Petch effect: $\sigma \sim d^{+1 \dots +3}$ (grain-boundary mechanism)
- Dislocation nucleation from the grain boundaries involves **length-scale competition** between dislocation splitting and grain size
- Transition from dislocation-slip to grain-boundary deformation mechanisms with decreasing grain size results in a **crossover in the mechanical properties**
- This transition is governed by the **length-scale competition** between dislocation splitting and grain size

Is « inverse » Hall-Petch unavoidable ?

Experimentally a variety of results have been observed



At nanoscales, the Hall-Petch breakdown leads to three possible behaviors according to whether dislocations are nucleated at vertices (i), at grain boundary (GB) triple junctions (ii), or at GBs (iii).

F. Louchet et al.
PRL **97**, 075504 (2006)

Theoretically different types of models are proposed

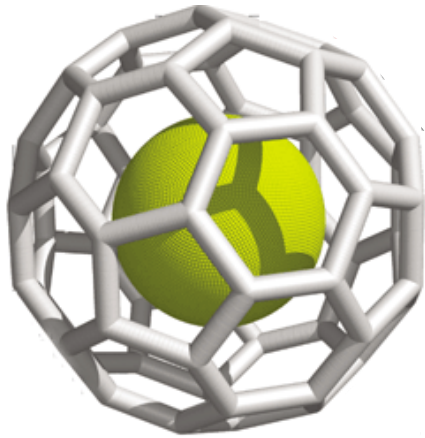
Answers to this are current research .

Matériaux à base de nanocages :

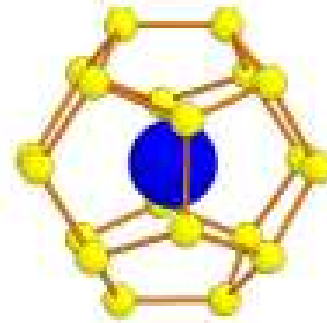
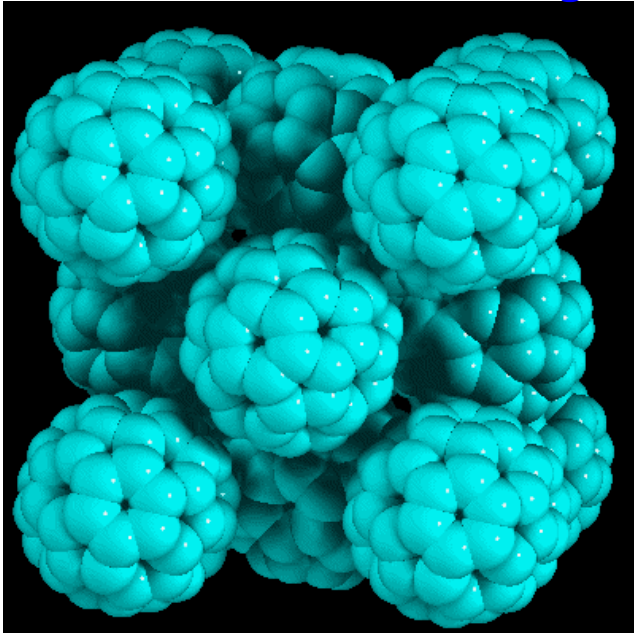
- Clathrates

- Fullerites

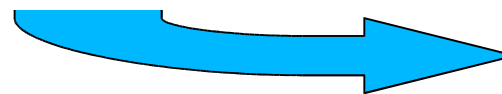
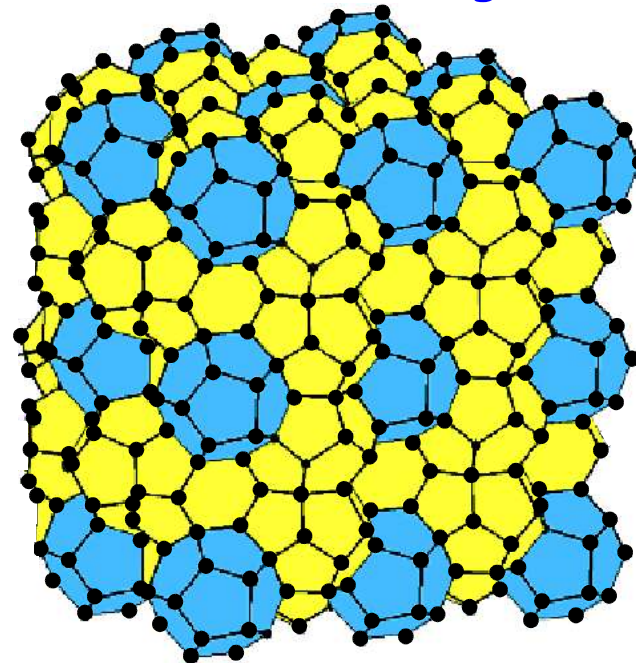
Clathrates and fullerites



Van der Waals bonding



Covalent bonding



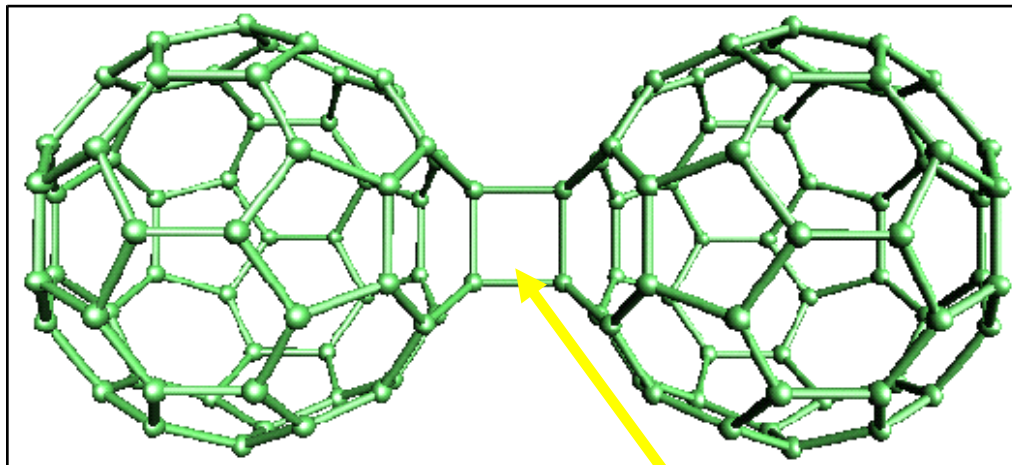
Tetrahedral bonds

Polymerized C₆₀

How to polymerize fullerenes :

- UV or visible light
- HTHP
- non hydrostaticity of pressure at room T
- intercalation

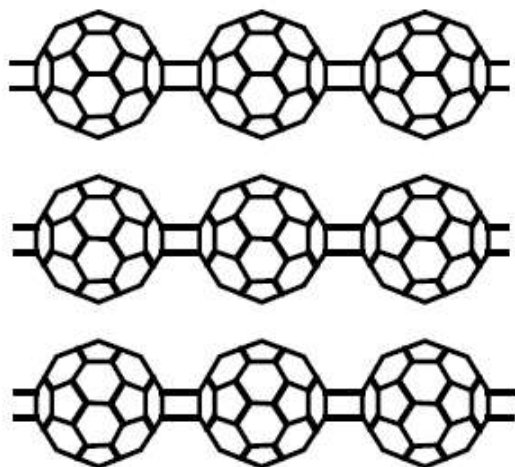
2+2 cycloaddition



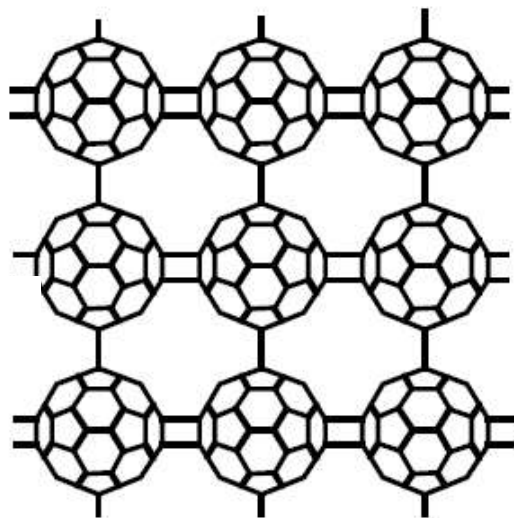
covalent **sp³** bonds

Some proposed C_{60} polymer geometries

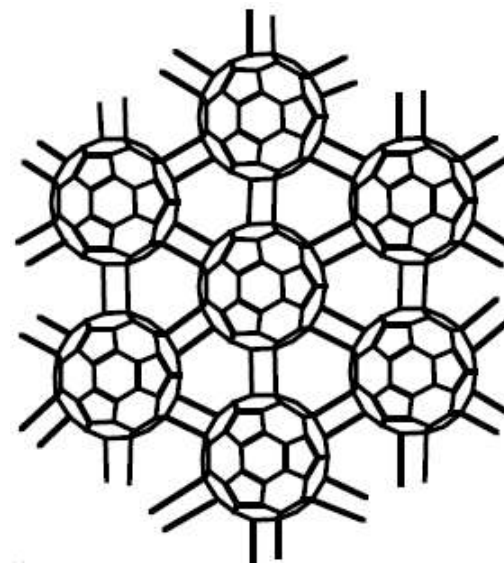
a)



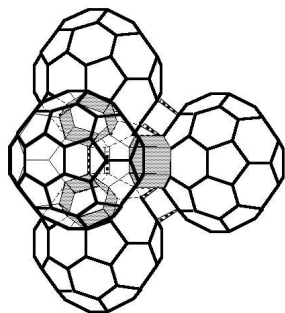
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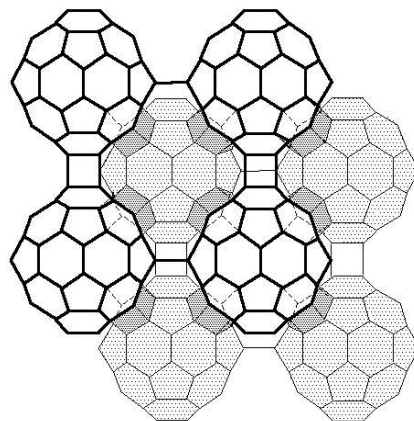
c)



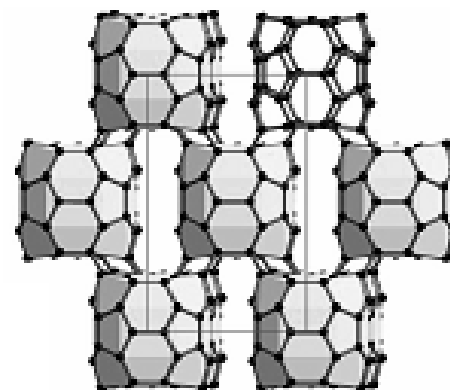
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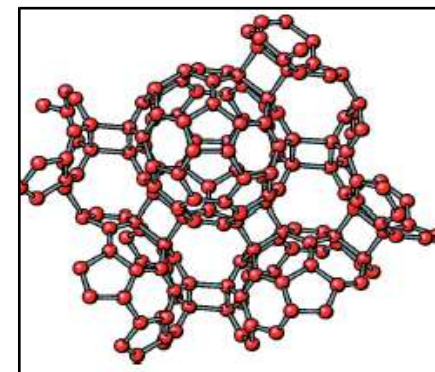
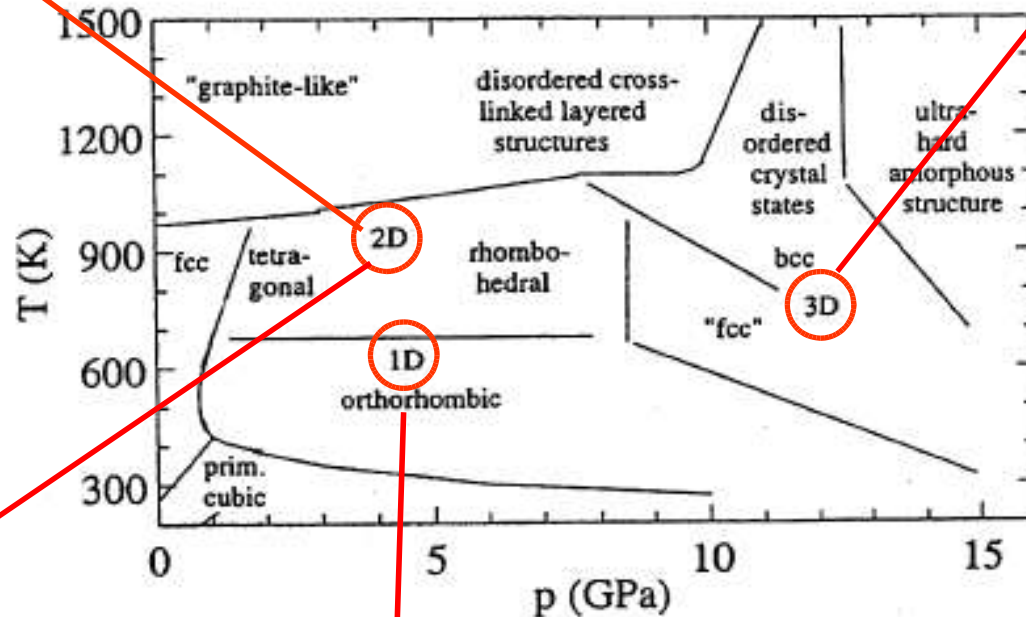
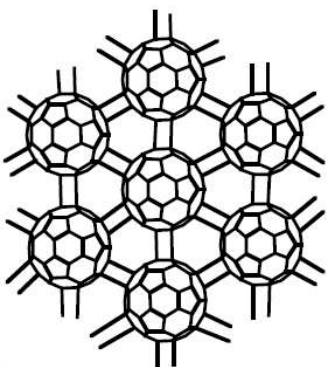
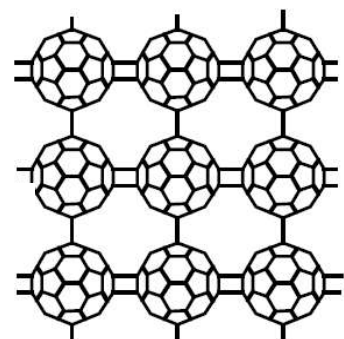
e)



f)



C_{60} P-T *ex situ* diagram or “reaction diagram”



Marques *et al.*, Science 283



C_{60} polymerization is not fully understood:

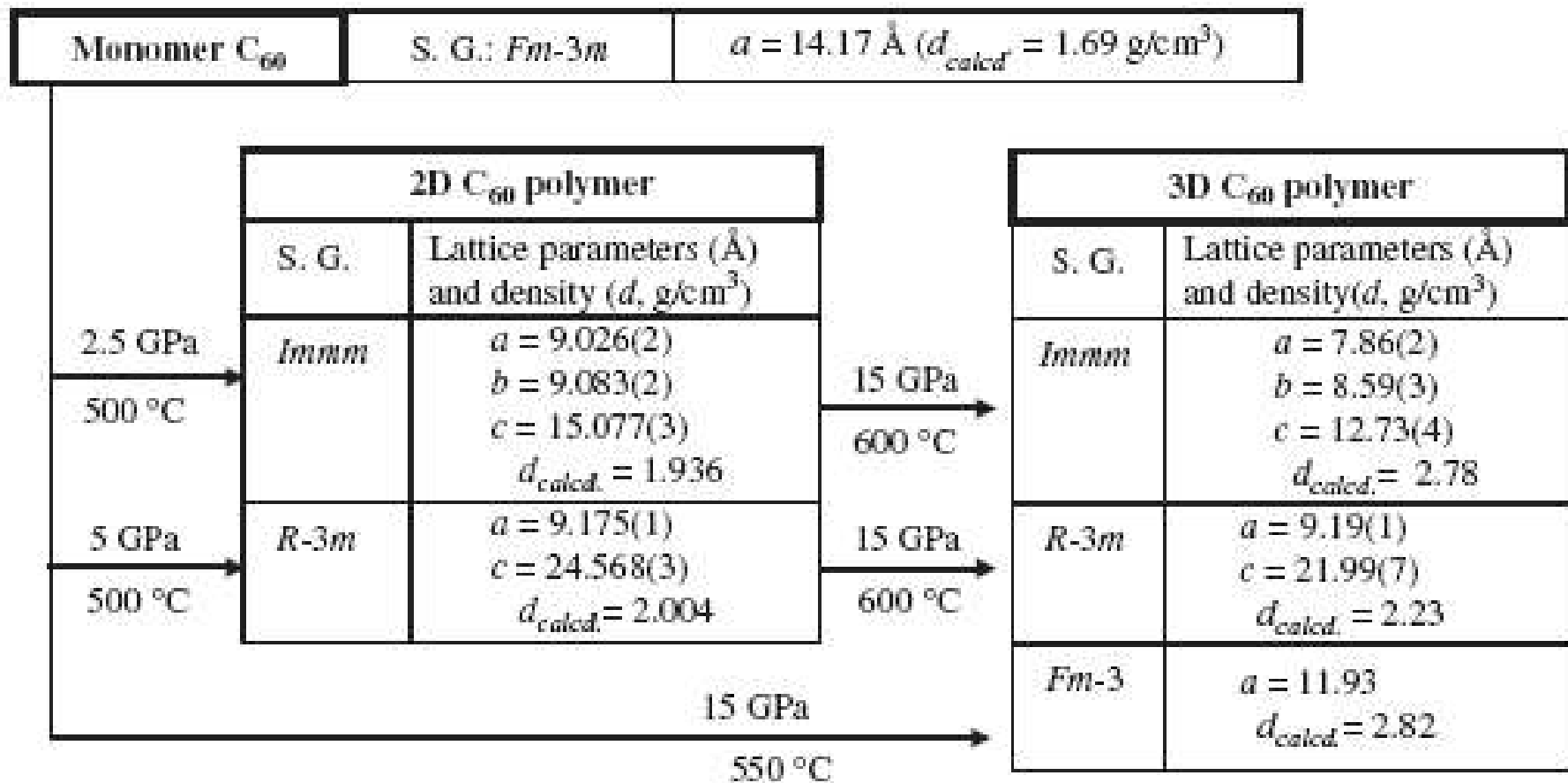
- *ex situ* measurements
- different results from different groups

Experiments show that:

- disordered phases
- uniaxial p favorize order
- reversible only up to low P-T (1 GPa- 400 K)

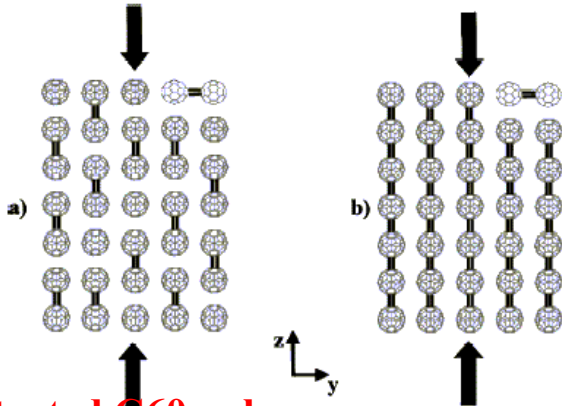
Núñez-Regueiro *et al.*, PRL 74

Some high pressure and high temperature pathes for C_{60} polymerisation

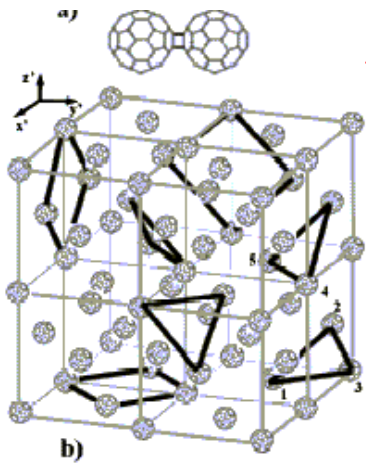


Geometric frustration upon polymerization

Avoiding frustration



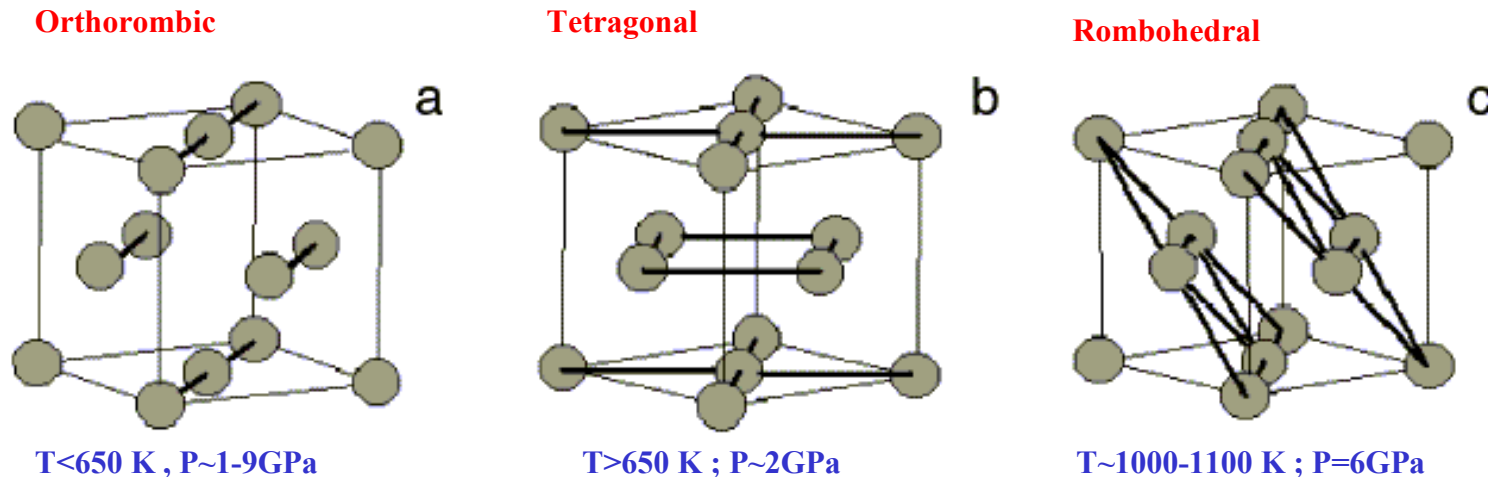
Frustrated C60 polymer



- Avoid geometrical frustration by stress-driven bond selection
- Applied anisotropic stress selects the directions of bonding

[L.Marques et al, PR B68, 193408 (2003)]

Polymeric fullerenes



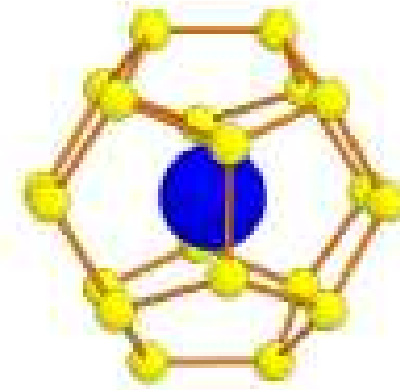
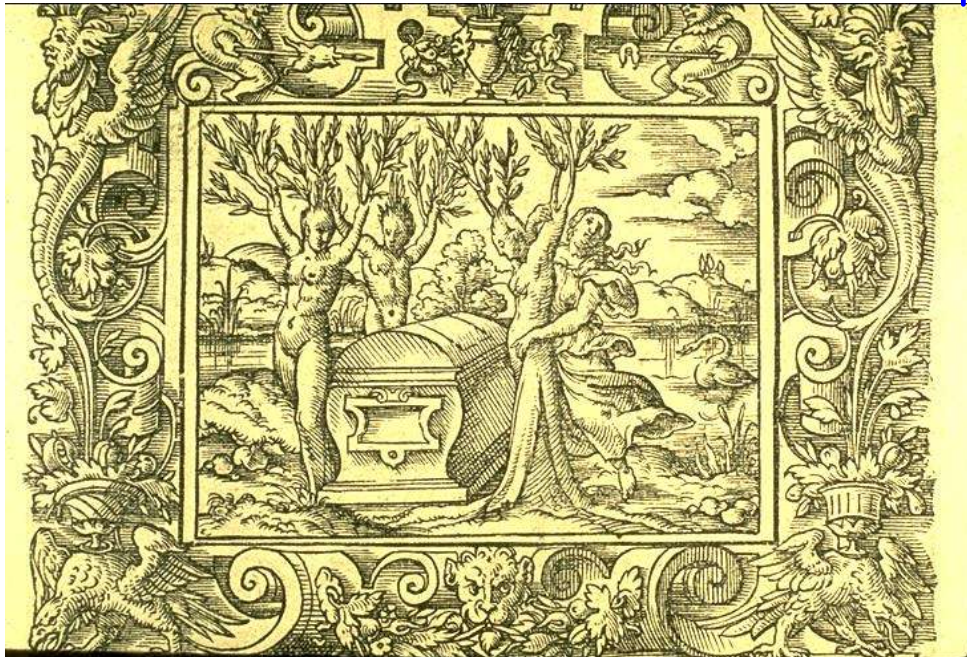
- Tetragonal and Rhombohedral polymers are 2D (along $\langle 110 \rangle$ and $\langle 111 \rangle$ directions respectively) ; interlayer coupling of van der Waals type as in graphite. The orthorhombic phase is 3D.
- In C_{60} -polymers the distance between the C_{60} molecules is $\sim 9.1\text{-}9.2 \text{ \AA}$. In non polymerized systems the distance is $\sim 10 \text{ \AA}$.
- **Polymerized C_{60} is a geometrically frustrated system.**

Virgile's recipe for a clathrate ("klethra") [1]



Alder tree = « klethra »

Phaëthon end at the Oracular island

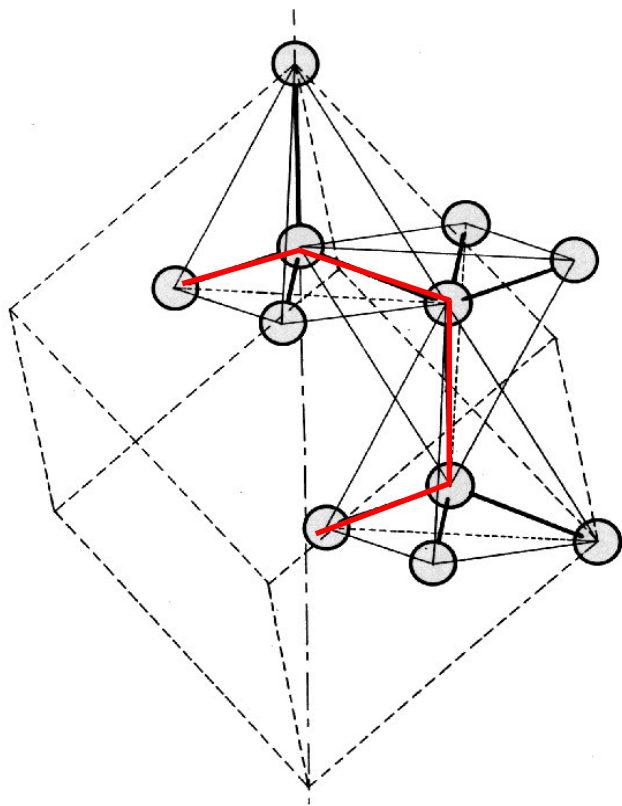


[1] Virgil's Aeneid version of the metamorphosis of the Heliades

How to Make cages with tetrahedra ?

Diamond

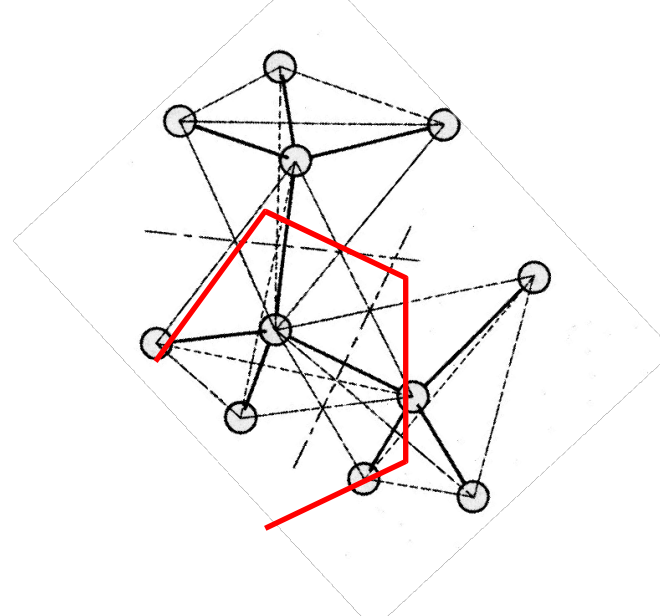
Hexagonal cycles



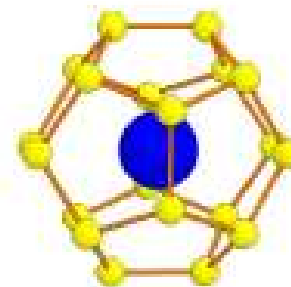
Staggered tetrahedra

Clathrates

Pentagonal cycles

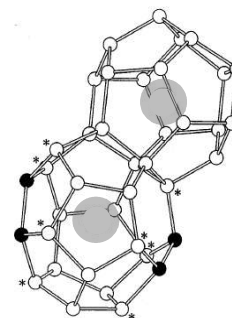
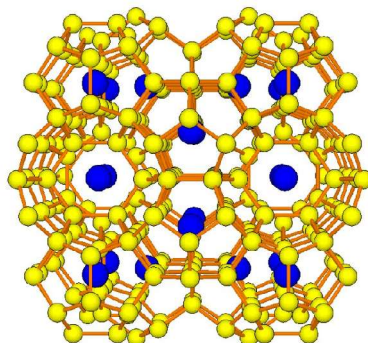
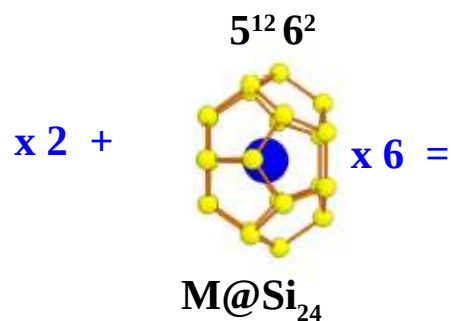


Eclipsed tetrahedra

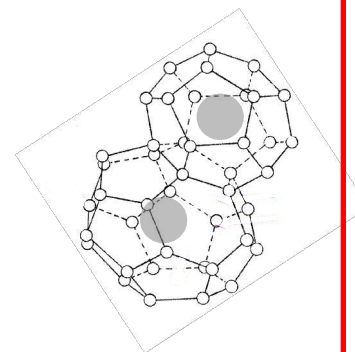
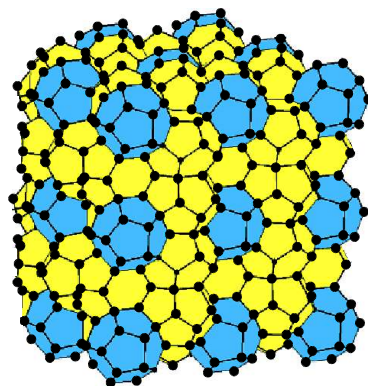
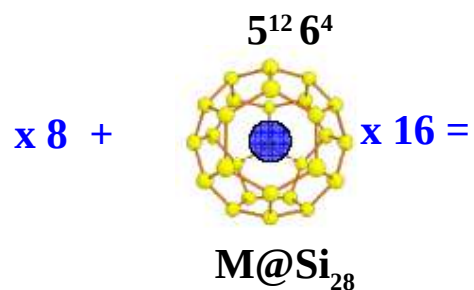


Main clathrate structures

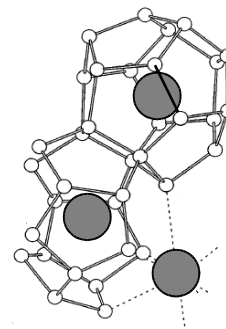
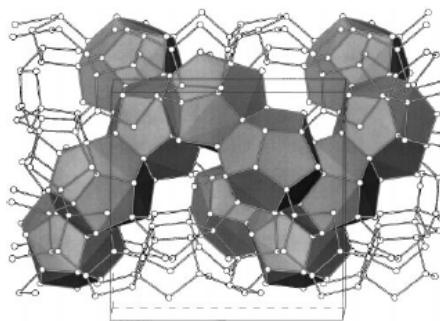
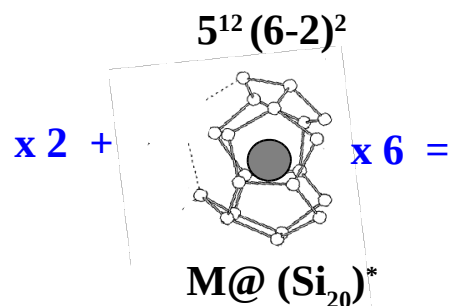
Type-I M_8Si_{46}



Type-II $M_{24}Si_{136}$



Type-III $M_{24}Si_{100}$



sp^3
framework

sp^2 / sp^3
framework

