

**Zeitschrift:** Helvetica Physica Acta  
**Band:** 56 (1983)  
**Heft:** 1-3  
  
**Artikel:** Small aggregates  
**Autor:** Friedel, J.  
**DOI:** <https://doi.org/10.5169/seals-115395>

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## SMALL AGGREGATES

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### Introduction.

Small aggregates, from a few to a about 1000 atoms constitute a specific domain, which differs both from the simple atomic or molecular gases and from macroscopic condensed matter.

It is fairly new, except for the (macro)molecules of organic chemistry, the photographic reaction, the GP zones in duralumin ... In metals, it can be dated from Kubo's theoretical predictions on metals (1962) and Ino's first observations of the atomic structure of metals (1966).

In Europe, general conferences have been held in Lyon (1976) and Lausanne (1980), and the next one will be in Berlin (1984).

Besides its general interest, I have chosen this topic in recognition of the work done in it in Lausanne by Borel's group, and also because Orsay has been early active in the field: Jean Farges' group on the atomic structure of rare gases ; C. Taupin and Charvolin's early work on Li platelets ; Slodzian and then Joyes' group work on polyions in secondary ionic emission.

### a - A 'simple' case : rare gases.

#### 1 - Electronic structure.

The interatomic potentials - due to short range overlap and long range dispersion - are well known for two atoms and can

be treated as additive, although this point should be looked more carefully, especially in aggregates (fig. 1).

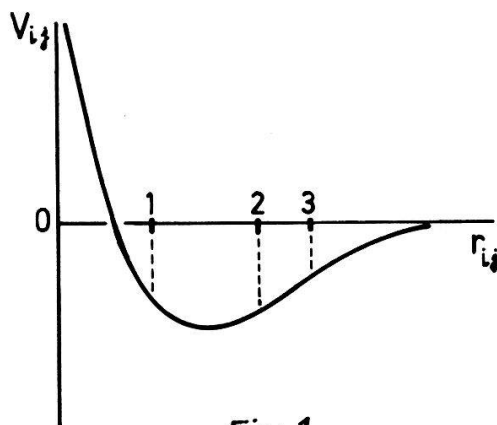


Fig: 1

1 - Interatomic potential for rare gases.

## 2 - Atomic structure.

Simple predictions have then been made, already before the war, for equilibrium forms of very small clusters (fig. 2):

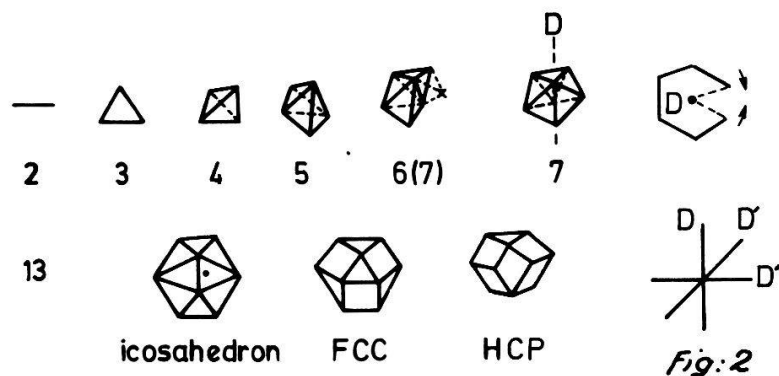


Fig: 2

2 - Configuration of very small rare gas clusters.

atomic pair, equilateral triangle, regular tetrahedron, bitetrahedron. A sixth atom can be added to any of the equivalent faces. And the seventh atom must then be added in the reentrant angle, thus formed, because when building one regular tetrahedron with 3 atoms, it is not far from a fourth and profits from its long range attraction (fig. 1). In fact a more stable configuration is obtained by distorting the bonds so as to form a regular double pentagonal pyramid. A full new bond has been formed at the

expense of a small elastic distortion, which is that of a 'disclination' line D along the axis of the pyramid and of positive sign (matter removed, empty angle closed).

For 13 atoms, one can similarly build an icosahedron, where each surface atom has 5 surface neighbours, against four for the nuclei of the FCC or HCP phases. The larger number of bonds is obtained at the expense of a small elastic distortion equivalent to that of ~~some~~ interpenetrating positive disclinations D, D', D".

Computer studies have been made for larger aggregates. The configurations obtained by quenching small liquid droplets were compared in their internal energies. Both kinetics and equilibrium studies lead to the following succession :

- 15 to 50 atoms : a quasiamorphous structure built with interpenetrating icosahedra.

- 50 to 1000 atoms : 'multilayer icosahedra' where on one icosahedron FCC sectors are built, in spinelle twinning relations to each other, so as to preserve the five fold symmetries of the icosahedron ; the configuration leads to very close packed surfaces at the expense of a small elastic distortion.

- more than 1000 atoms : FCC crystals with irregular twins.

Electron scattering on vapour jets have lead simultaneously to the same conclusions.

Thus even in such an apparently simple case, the nucleation process is complex and dominated by the drive for smooth surfaces.

### 3 - Remarks.

The pentagonal symmetries observed here are typical of aggregates and impossible in the long range crystalline order.

Pentagonal symmetries related to icosahedra were early invoked in the short range order of complex structures : Bernal and Frank for liquids and amorphous phases, Frank and Kasper for complex crystalline phases with large atomic cells.

These thoughts were recently systematized under the drive of Sadoc and Kleman. Thus the surface atoms of an icosahedron

dron (fig. 2) build a regular network with five fold symmetry on a sphere. We can project such a network on a plane only at the expense of elastic distortions, which become prohibitive if the projection is not local. In the same way, the icosahedron itself can be thought of as the local projection on a flat three dimensional space of part of a regular lattice inscribed on a space of positive curvature. Again the projection must be local to avoid too large distortions.

A continuous macroscopic piece of matter can be built by fitting a number of such local projections. The best fitting leaves singular lines which are negative disclinations. Such lines were early described by Rivier. With regularly spaced lines one builds crystals with large unit cells which describe the structure of many transition or actinide metals. With irregularly spaced lines, one can hope to describe amorphous or liquid structures of rare gases or metals.

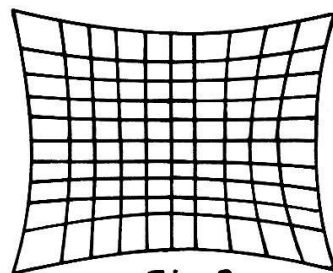
As pointed out above, the state of elastic stresses in such structures are the same as that of two interpenetrating networks of disclinations, with opposite signs ; the positive disclinations are stabilized by the fact that they have a continuous core of negative energy.

It would be topologically equivalent to start from local projections from negatively curved space, fitted together with positive disclination lines. This would be a better description in structures where the negative disclinations can have a continuous core. Some amorphous covalent systems might possibly be better described that way.

- The static distortions just described are related to the long range attractions of the interatomic potentials  $V_{ij}$  (Fig. 1). They are general in aggregates. In crystals, the fact that  $V_{ij}$  reaches to more than first neighbours leads to

- a surface dilatation (between planes and in plane).
- thus a general dilatation, decreasing as  $1/D$ .
- a sharpening of edges and summits.

These effects, schematised figure 3, have been computed and, for the second one, observed in small rare gas crystals.

*Fig: 3*

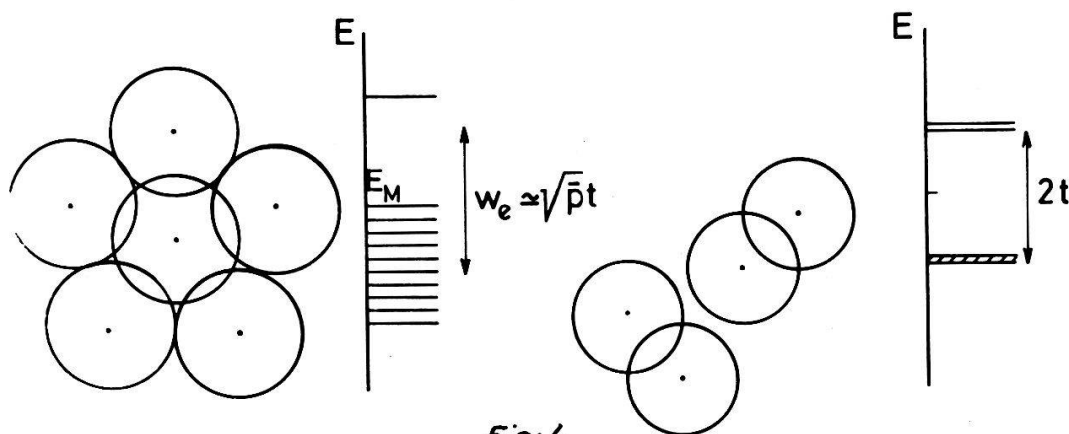
3 - Relaxations in a small rare gas crystal (schematic).

- Finite temperatures produce surface vibrations and diffusion, together with thermal expansion. They help the kinetics of conformation changes in a way that has not been studied at all. Finally for such small finite systems, the melting point is only an approximate concept. Thermal fluctuations play however a larger role in problems such as superparamagnetism or superconductivity where the coherence length is usually much larger than the interatomic distance.

b - Metals.

1 - Atomic structure.

Close packing is expected : the delocalized valence electrons broaden their atomic level into a band with an effective width which increases roughly as the average number of neighbours  $\bar{p}$ , a result which can be deduced from the second moment of the band or from a random walk argument. The cohesive energy, proportional to the lowering of the average one electrons energies, thus to this width, favours the maximum possible nearest neighbours (figure 4).

*Fig: 4*

4 - Band structure of close packed structures, compared with the two levels systems of dimers (monovalent metals).

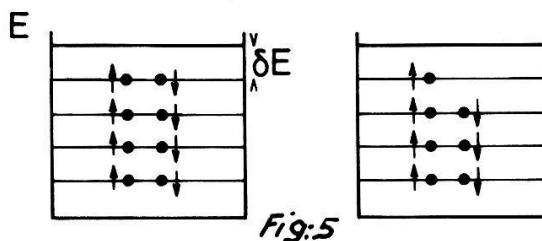
It is therefore no surprise that Au aggregates formed in vapour jets present exactly the same succession of conformations, with the same limiting numbers, as a rare gas such as Argon.

However,

- for other metals (e.g. Pt), the crystals seem more stable for small clusters.
- even for Au, vapour deposition on substrate can give other clusters, often half of the previous ones.
- interatomic forces are more complex : they are not additive, as shown in the fact that cohesion is not proportional to  $\bar{p}$ , and they oscillate at long range. Correlatively, in most crystals, one observes a surface contraction and a volume contraction of small grains, contrary to rare gases.
- non additivity could lead to dimerisation in small clusters ( $\bar{p} < 4$ ), for which, as shown figure 4, dimers should have a larger cohesion. However in trimers of alkalis, computations and resonance agree with only a very small dimerisation, leading to a nearly equilateral triangle where the three atoms exchange their role by alternative stretching of bonds, in a way similar to a Jahn-Teller effect.

## 2 - Electronic structure.

Kubo first pointed out that, in a small enough aggregate and at low enough temperature  $T$ , the energy difference  $\delta E$  between successive delocalized valence states near the Fermi level should become larger than the thermal energy  $k_B T$  (figure 5).



- 5 - Quantization effect for delocalized electrons in small metallic clusters.

Aggregates with an even number of electrons should then have a temperature independent susceptibility (dia or para according to the strength of the spin orbit couplings) ; those with an odd number of electrons should have a Curie susceptibility in  $T^{-1}$ , with one Bohr magneton per aggregate.

These two types of behaviour were first observed in Orsay by resonance (NMR and EPR) techniques in small Li platelets developed in LiF by neutron irradiation. More recently, Knight has shown that in very small alkali clusters in vapours, only clusters with an odd number of atoms hence of electrons are magnetic, with a maximum moment of one Bohr magneton. Some complications arise from the rotation and Jahn Teller effects.

More systematic if less direct evidence come from a systematic study of neutral vapours in equilibrium and of ionized clusters produced by secondary ionic emission or in sparks sources. One expects of course the probability of observing a cluster to decrease with increasing size. But if for metals with an even valency such as Mg the decrease is continuous, for metals with an odd valency, the decrease exhibits systematic zigzags (figure 6). All these observations can be systematized by assuming

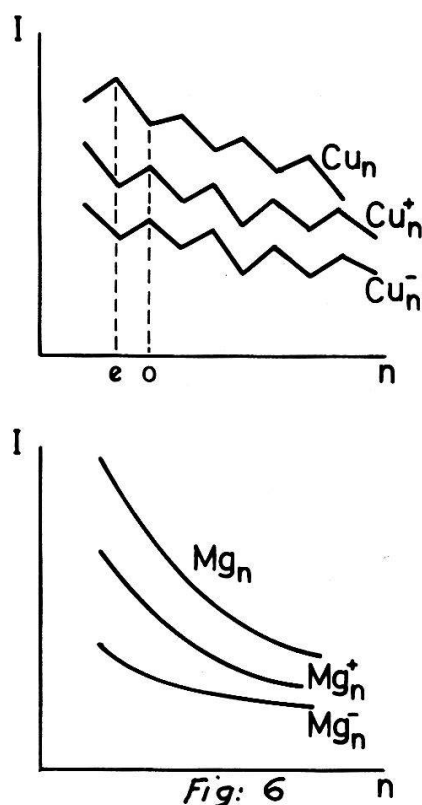


Fig: 6

6 - Probability of measuring neutral and ionized clusters  $X_n$ .



that in all those experiences the most stable aggregates are by far prevalent, and that aggregates with an even number of electrons are systematically a little more stable than those with an odd number of electrons. This can indeed be shown for independent electrons in a small box, and comes from the obviously smaller average kinetic energy for an even number of electrons.

These results are valid for many metals and alloys, and for polyions of various sizes. These follow roughly the macroscopic stability rule that the charge should be less than  $8 \pi \sqrt{\epsilon_0} \gamma r^{3/2}$  ( $\gamma$  surface tension,  $\epsilon_0$  dielectric constant,  $r$  radius).

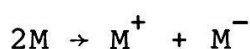
Finally electronic ionizations show up similar zig zags that can be explained in the same way.

### 3 - Problems.

- Statistics. The most stable form seems generally preferred for an aggregate of a given size. But many observations are made on a distribution of sizes or purities. A physical quantity is then the two levels distribution function of states near the Fermi level. A prediction by Wigner and Dyson has been proved by Efetov, using supersymmetry techniques, that the scattering by normal potentials, magnetic scatterers or spin orbit coupling scatterers lead to different distributions, associated with the orthogonal, unitary and symplectic groups. The same distinctions occur in localization by disorder. As in that last case, the corrections due to electron correlations or electron phonon couplings should be considered.

#### c - Electron correlations.

Interatomic correlations come from the changes of energy induced by the atomic charge fluctuations produced by the motion of the delocalized valence electrons. The typical energy involved in such a reaction producing ions out of neutral atoms



is an energy

$$U_e = I - A \approx I$$

( $I$  first potential of ionization,  $A$  affinity).

Intraatomic correlations lower the average Coulomb energy  $U$  of two uncorrelated electrons, so that

$$U_e = U - \frac{|\langle \quad \rangle|}{\Delta E} \ll U^2.$$

Figure 7 shows that  $U_e$  increases with valency, while the band width  $w_e$  decreases (both because p bonding leads to fewer possible neighbours than s bonding and because atomic orbits decrease with increasing valency). Hence, in metals

$$U_e < w_e \quad (1)$$

If  $U_e > w_e$ , one expects

- Kubo zig zags to vanish (because the electron repulsion kills the spin pairing on the same atom).

- magnetism to appear.

- dimerisation. This shows up already when  $U_e$  is treated as a perturbation. The cohesive energy then reads

$$E_{\text{coh}} \cong \alpha w_e - \beta U_e + \gamma \frac{U_e^2}{w_e} \quad (\alpha, \beta, \gamma \text{ positive constants}) \quad (2)$$

The correlation correction  $U_e^2/w_e$  does not favour broad band or close packing. And dimerisation is expected if we also add the supplementary dispersion attraction between dimers.

None of such effects are observed in metals, a rather conclusive evidence for condition (1) to hold.

$U_e^{\text{ev}}$	5	10	15	20
	Li	Be B C	ON	F
	Na	Cl		
	K	⊙ Br		
	Rb	⊙ I		
	Cs	⊙ ⊙		

Fig. 7

7 - Variation of  $U_e$  in the periodic table.

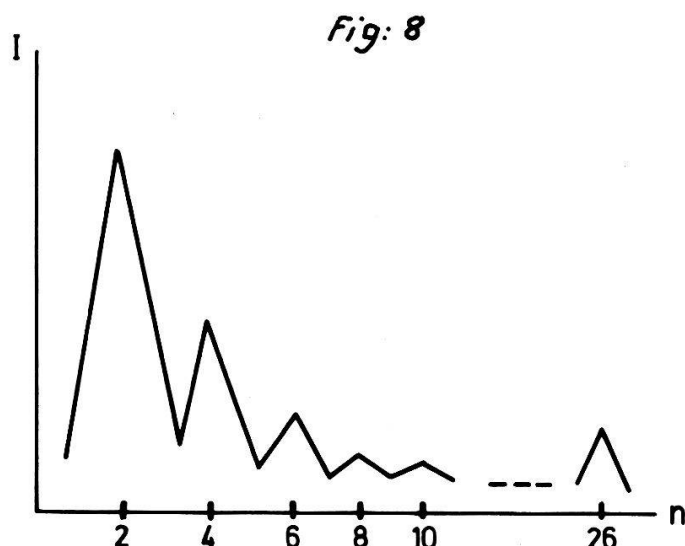
d - Covalents.

1 - Monovalents etc ....

As figure 7 suggests, elements on the right of the sp series are such that  $U_e > w_e$ . It is indeed well known that under

normal conditions macroscopic crystals are made up of close packed dimers in H, the halogens, N, O ...

It is thus no surprise that small aggregates  $X_n$  of halogens show a strong zig zag of intensity versus size  $n$ , with a strong preference for  $n$  even, thus an exact number of dimers (Fig. 8). A definite peak is observed in halogens for  $n = 26$ ,



8 - Concentration of neutral aggregates  $X_n$  of halogens.

suggesting an icosahedron of dimers. And multilayer icosahedra of molecules are observed in aggregates produced in jets of nitrogen (for  $n > 2 \times 55$ ) and for methane, but not for  $\text{Co}_2$  (where crystals are observed for  $n > 2 \times 20$ ).

In conclusion, correlations stabilize dimers on the right of the sp series; aggregates are close packed arrangements of such dimers; these concepts seem to extend to aggregates of other molecules with nearly 'spherical' form.

## 2 - Tetravalents.

Three fundamental types of bonding can a priori occur (fig. 9) :

- linear with  $\sigma \times \pi \times \pi$  bonding.
- planar with  $\sigma \times \pi$  bonding.
- three dimensional with  $\sigma$  bonding.

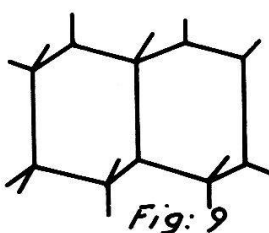
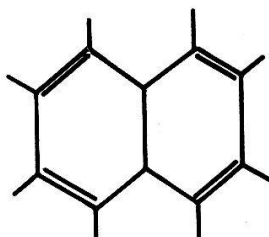
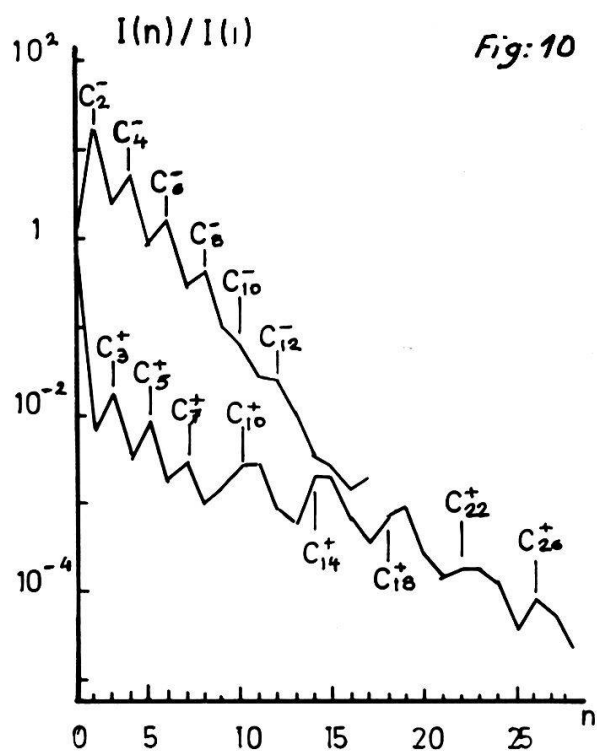


Fig: 9

9 - 3 types of bonding for tetra-valent aggregates.

Increasing size of aggregates should favour increasing dimensionality of bonding, because the ratio of surface broken bonds to volume bonds increases, and the stability of volume bonds increases, at least for small aggregates.

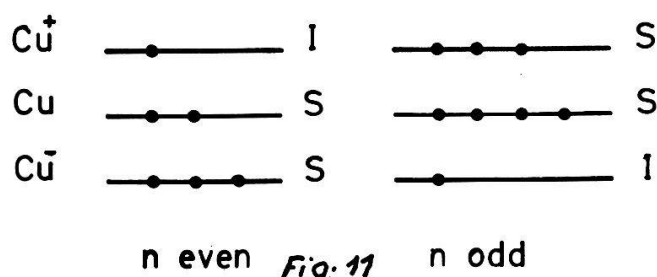
Experiments on C vapours and on ionic secondary emissions show typical zig zags (figure 10) with a period of  $n = 2$



10 - Probability of emission of  $C_n^+$  and  $C_n^-$  polyions in secondary ionic emission (The behaviour of  $C_n$  in vapours is analogous to that of  $C_n^+$ ).

for  $n \leq 8$  and  $n = 4$  for  $8 < n < 24$ . This can be explained by

- A linear chain for  $n \leq 8$ , with a greater stability of aggregates with a last occupied state with 4 electrons than 2 and with 3 electrons than 1, as indeed expected for independent electrons, owing to the double degeneracy of the  $\pi$  bands and assuming the 2 broken  $\sigma$  bonds saturated (fig. 11).



11 - Relative stability for aggregates  $C_n^+$ ,  $C_n$ ,  $C_n^-$ , as related to the population of the last occupied degenerate  $\pi$  state, with maximum energy.

- A planar arrangement for  $8 < d < 24$  where full successive benzene rings (for  $n = 10, 14, 18, 20, 24$ ) are especially stables.

It is worth pointing out that an independent electron picture would predict the linear and planar arrangements to be stable only for much smaller values for  $n$ . It is probably the electron correlations which stabilize these configurations, owing to the smaller  $\pi$  band width, compared with the energy difference between the bonding and antibonding  $\sigma$  bands which would appear for pure  $\sigma$  three dimensional bonding in the corrective term due to correlations in equation (2). It is the same effect which stabilizes (macroscopic) graphite compared with diamond.

Aggregates with pure  $\sigma$  three dimensional bonds have nevertheless been studied. Indeed slight distortions of the bonds can produce aggregates with few broken bonds, and thus fairly large stability. It is no surprise that the two smallest ones are the centred icosahedron (with 17 atoms) and the dodecahedron (with 20 atoms), which is the conjugate of the icosahedron (fig. 12). Both show the same typical pentagonal symmetries, and can be

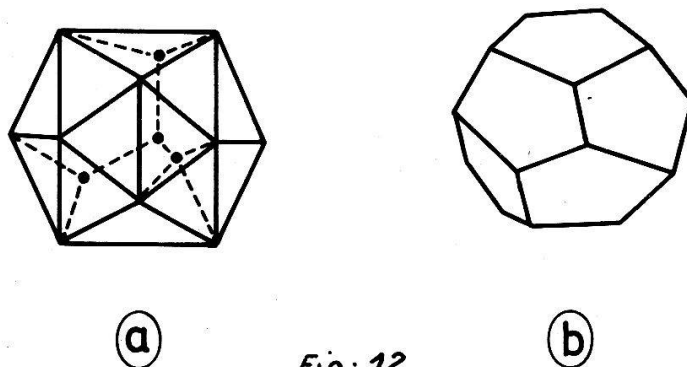


Fig: 12

12 - a - centred icosahedron ; b - dedecahedron.

the centres of multilayer figures when surrounded by twinned crystal sectors of the diamond lattice. They are possibly involved in precipitation from supersaturated solutions, as nuclei for amorphous or crystalline forms. They are also involved in the description of local order in amorphous structures. But systematic studies in vapour jets are sadly lacking, owing to experimental difficulties.

It is fairly clear that similar discussions hold for aggregates built with Si, Ge,  $\text{SiO}_2$ ,  $\text{H}_2\text{O}$  ... and for their amorphous forms.

### Conclusions.

This brief review has not emphasized the potential applications.

A main conclusion is that all nucleation processes must be very carefully studied, on an atomic and electronic scale, and that each specific case must be analyzed for itself. This refers to first order transitions, either condensation from vapours or liquids-the case of ice is of interest to meteorologists and astrophysicists - or in condensed matter, where the early example of GP zones shows the importance of the elastic stresses developed. It also refers to kinetics of reactions, especially radiolysis or recovery of radiation damages in solids.

A connected field is that of catalysis, especially that produced by very divided solids.

Two fields where somewhat similar properties emerge are those of nuclei in nuclear physics and of icosahedral virus packing in biology.

Also important phenomena on a somewhat larger scale have been skipped. They refer to varied fields: sintering of powders, optical properties of metal aggregates, magnetism (superparamagnetism, ferrofluids), superconductivity ....