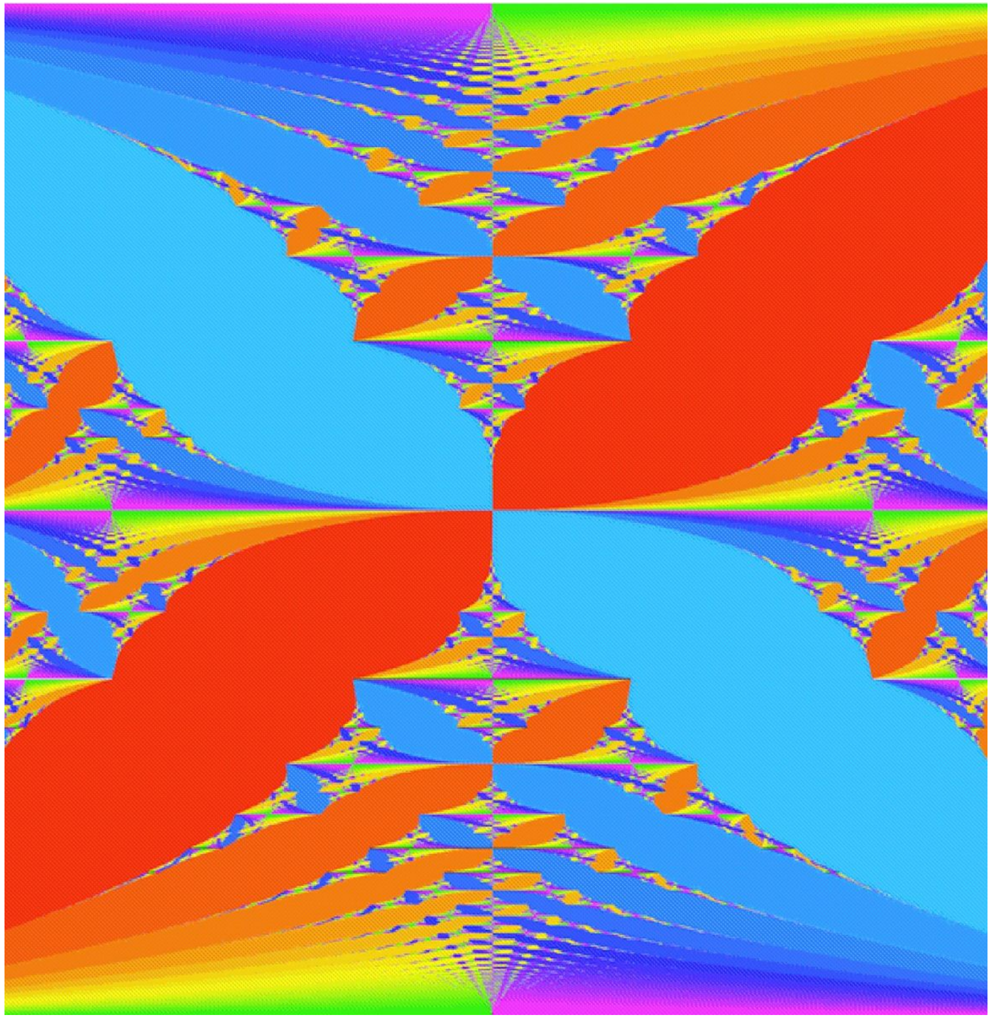

Happy Birthday

Yosi !

MODELING LIQUID METALS

and

BULK METALLIC GLASSES

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Content

1. Metal Liquids and Glasses
2. Delone Graphs
3. Conclusion

I - Metal Liquids and Glasses

Bulk Metallic Glasses

1. Examples *(Ma, Stoica, Wang, Nat. Mat. '08)*

- $\mathbf{Zr}_x\mathbf{Cu}_{1-x}$ $\mathbf{Zr}_x\mathbf{Fe}_{1-x}$ $\mathbf{Zr}_x\mathbf{Ni}_{1-x}$
- $\mathbf{Cu}_{46}\mathbf{Zr}_{47-x}\mathbf{Al}_7\mathbf{Y}_x$ $\mathbf{Mg}_{60}\mathbf{Cu}_{30}\mathbf{Y}_{10}$

2. Properties *(Hufnagel web page, John Hopkins)*

- High *Glass Forming Ability* (GFA)
- High *Strength*, comparable or larger than steel
- Superior *Elastic limit*
- High *Wear* and *Corrosion* resistance
- *Brittleness* and *Fatigue* failure

Bulk Metallic Glasses

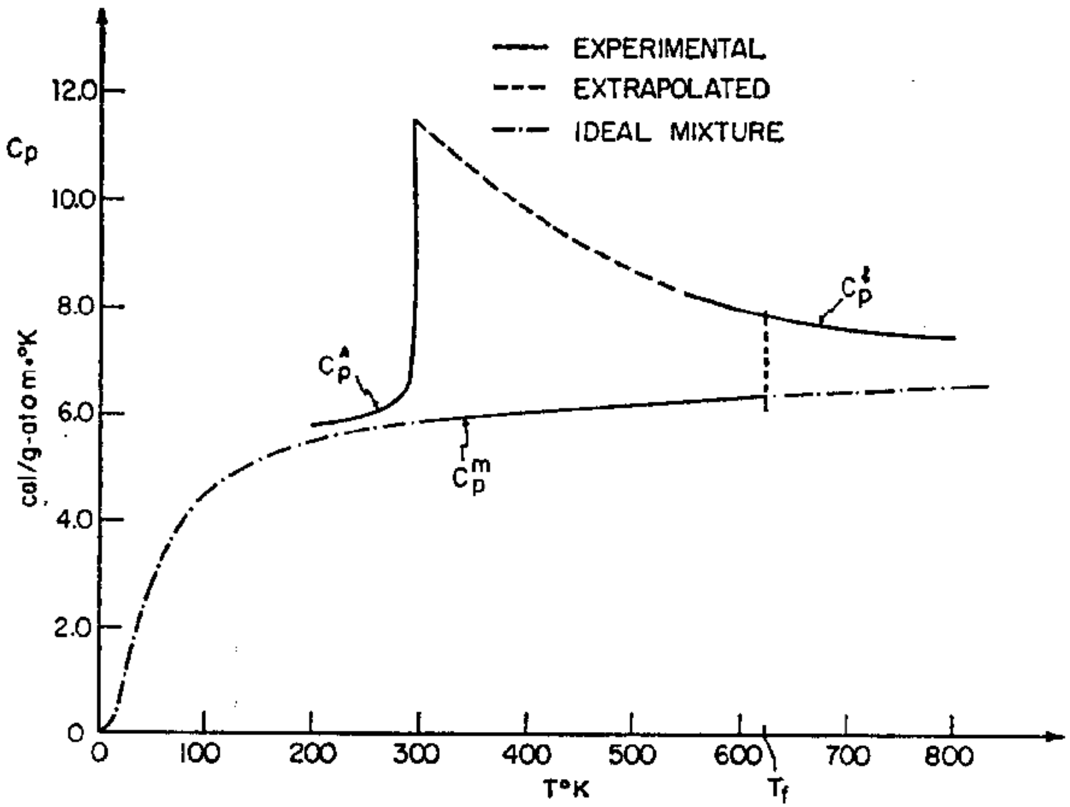
Applications *(Liquidemetal Technology* `www.liquidmetal.com`*)*

- *Orthopedic implants* and medical Instruments
- Material for *military components*
- Sport items, *golf clubs, tennis rackets, ski, snowboard, ...*

Pieces of Titanium-Based Structural Metallic-Glass Composites

(Johnson's group, Caltech, 2008)

Bulk Metallic Glasses

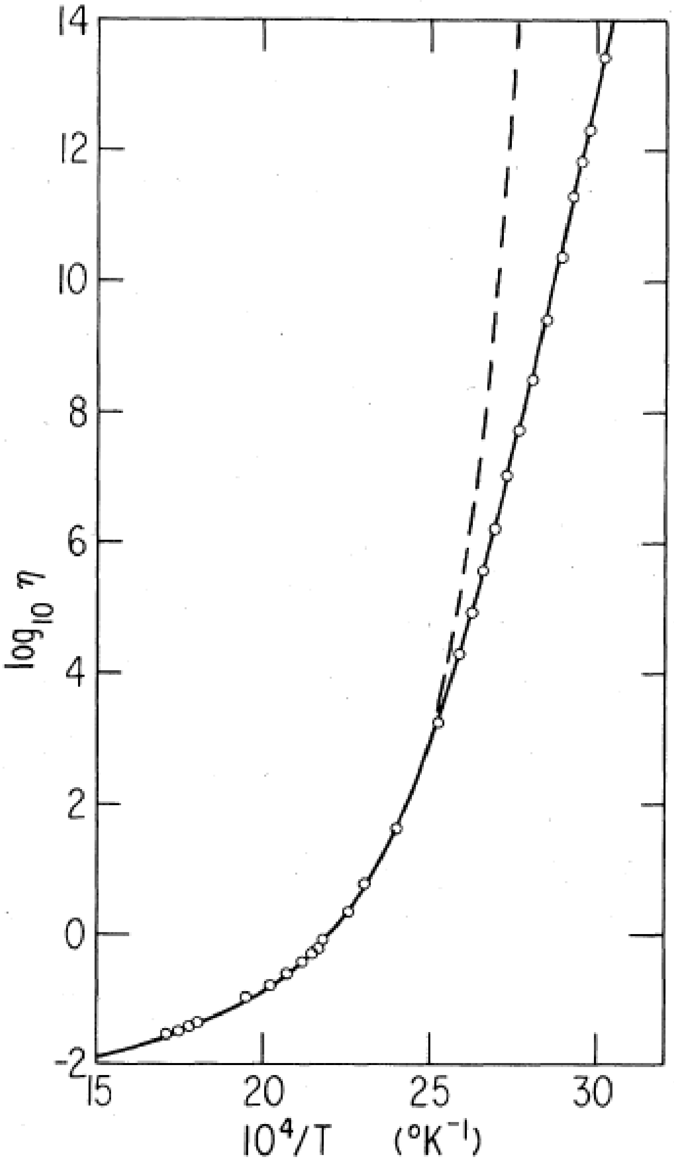


Smoothed values of specific heats of $Au_{.77}Ge_{.136}Si_{.094}$ signaling a glass-liquid transition

"*A*" designates the amorphous state
"*m*" designates the mixture
"*l*" designates the liquid

taken from
H. S. Chen and D. Turnbull, *J. Chem. Phys.*, **48**, 2560-2571, (1968)

Bulk Metallic Glasses



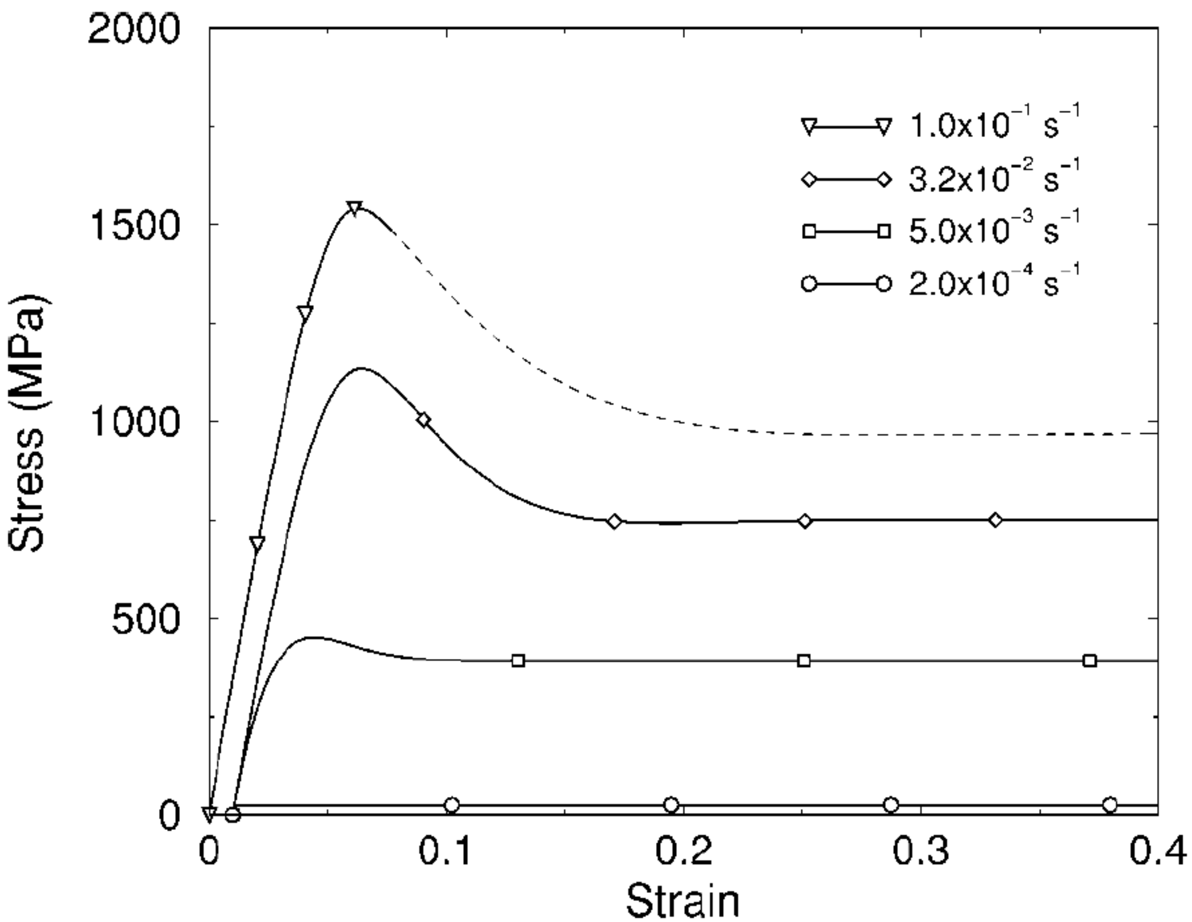
Viscosity vs temperature for tri-anaphthylbenzene, with fits coming from the *free volume theory*

Solid curve fit from [1] below
Dashed curve: fit from [1] with a simplified theory
Circles: data from [2] below

taken from

[1] Morrel H. Cohen & G. S. Grest, *Phys. Rev. B*, **20**, 1077-1098, (1979)
[2] D. J. Plazek and J. H. Magill, *J. Chem. Phys.*, **45**, 3757, (1967); J. H. Magill, *ibid.* **47**, 2802, (1967)

Bulk Metallic Glasses



Theoretical curves of tensile stress versus strain for the bulk metallic glass using the *STZ theory*

$$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$$

at several different strain rates as shown. The temperature is T=643 K.

For clarity, all but the first of these curves have been displaced by the same amount along the strain axis.

taken from

[1] M. L. Falk, J. S. Langer & L. Pechenik, *Phys. Rev. E*, **70**, 011507, (2004)

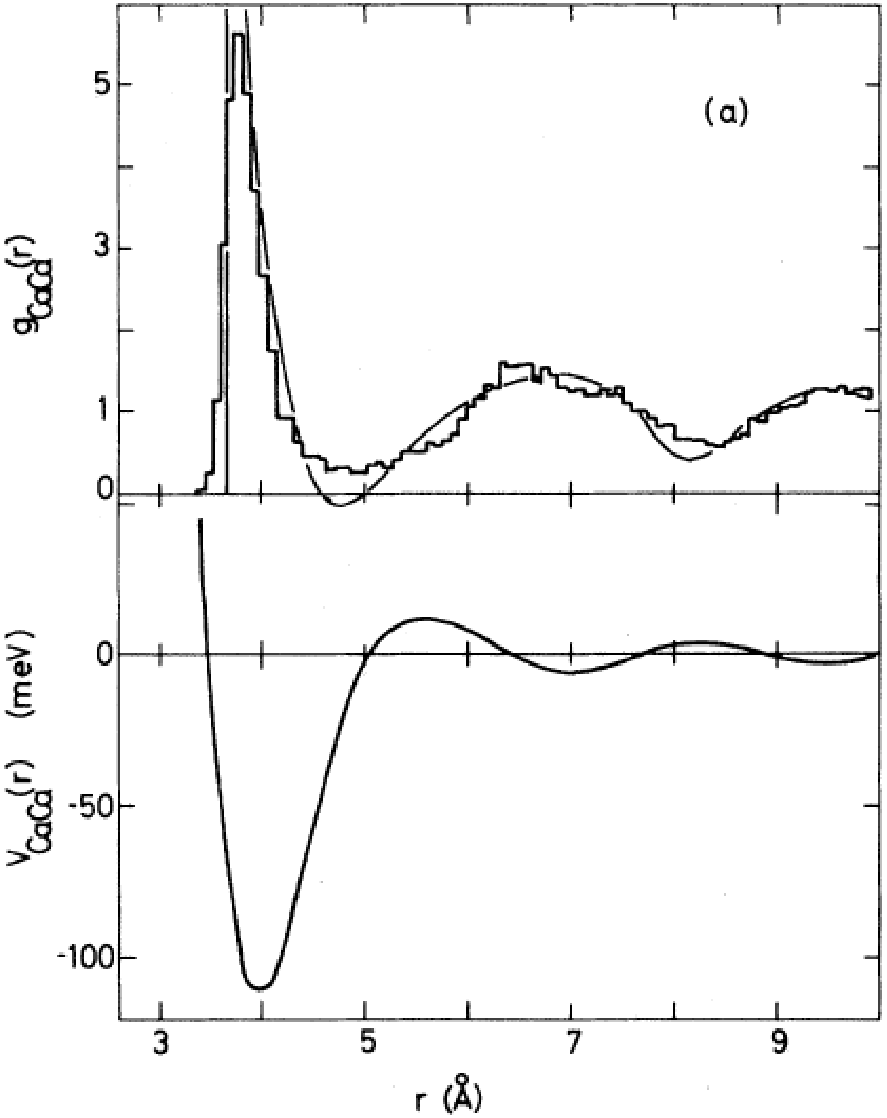
Available Theories

1. **Cluster Model:** *(T. Egami et al., '80's, D. Miracle '04)* gives a guide line to how to produce glassy state, explains the diffraction spectrum and the pair-distribution function. It introduces *frustration*

2. **Free Volume Theory:** *(Morell H. Cohen, G.S. Grest '79)* gives a good account for the viscosity

3. **Shear Transformation Zone (STZ):** *(J. Langer et al. '98-06)* gives effective continuum equation valid beyond the elasticity limit. Numerical simulations give a convincing description of the dynamics of cracks *(C.H. Rycroft, E. Bouchbinder '12)*

Pair Potentials



An example of atom-atom pair potential in the metallic glass $Ca_{70}Mg_{30}$

Top: the pair creation function
Bottom: the graph of the pair potential

taken from
J. Hafner, *Phys. Rev. B*, **27**, 678-695 (1983)

Dense Packing

1. The shape of the pair potential suggests that there is a *minimal distance* between two atoms.
2. Liquid and solids are *densely packed*. This suggests that there is a *maximal size for vacancies*.
3. However, Mathematics *(ergodic theory)* implies that, given an $\epsilon > 0$, with probability one
   - there are pairs of atoms with distance less than ϵ
   - there are vacancies with radius larger than $1/\epsilon$
4. But these rare events are not seen in practice because their *lifetime is negligibly small* (*Bennett et al. '79*). Persistence theory give an argument in this direction.

II - Delone Graphs

Delone Sets

- The set $\mathcal{V}$ of atomic positions is *uniformly discrete* if there is $b > 0$ such that in any ball of radius b there is at *most* one atomic nucleus.

  (Then minimum distance between atoms is $\geq 2b$*)*

- The set $\mathcal{V}$ is *relatively dense* if there is $h > 0$ such that in any ball of radius h there is at *least* one atomic nucleus.

  (Then maximal vacancy diameter is $\leq 2h$*)*

- If $\mathcal{V}$ is both uniformly discrete and relatively dense, it is called a *Delone set*.

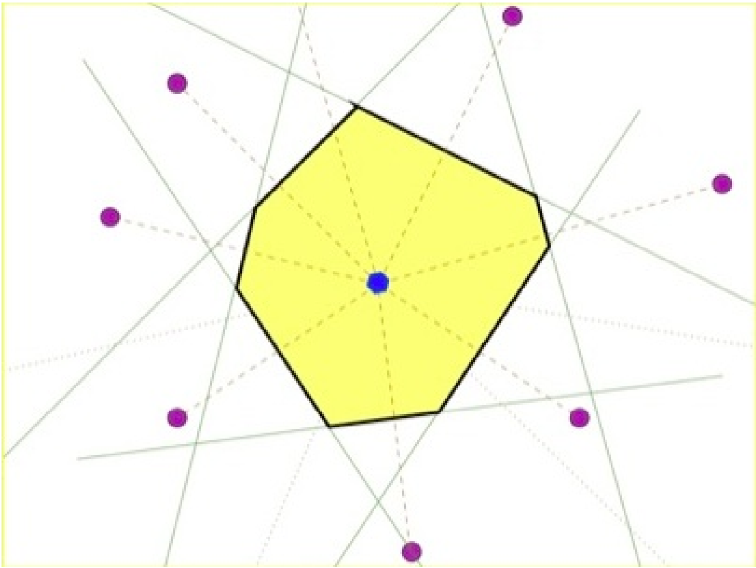
- $\mathrm{Del}_{b,h}$ denotes the set of *Delone sets* with parameters b, h.

Voronoi Cells

- Let $\mathcal{V} \in \mathrm{Del}_{b,h}$. If $x \in \mathcal{V}$ its *Voronoi cell* is defined by

$$V(x) = \{y \in \mathbb{R}^d\,;\ |y - x| < |y - x'|\ \forall x' \in \mathcal{V}\,,\ x' \neq x\}$$

$V(x)$ is open. Its closure $T(x) = \overline{V(x)}$ is the *Voronoi tile* of x



Proposition: *If $\mathcal{V} \in \mathrm{Del}_{r_0,r_1}$ the Voronoi tile of any $x \in \mathcal{V}$ is a convex polytope*

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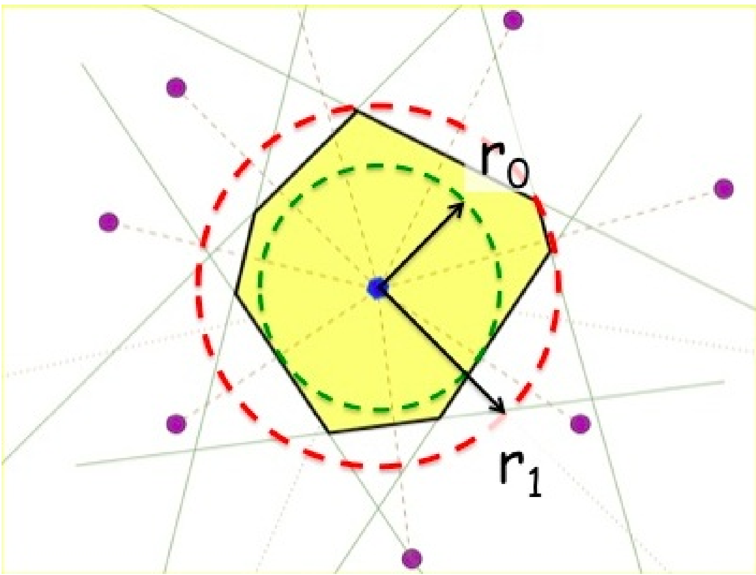
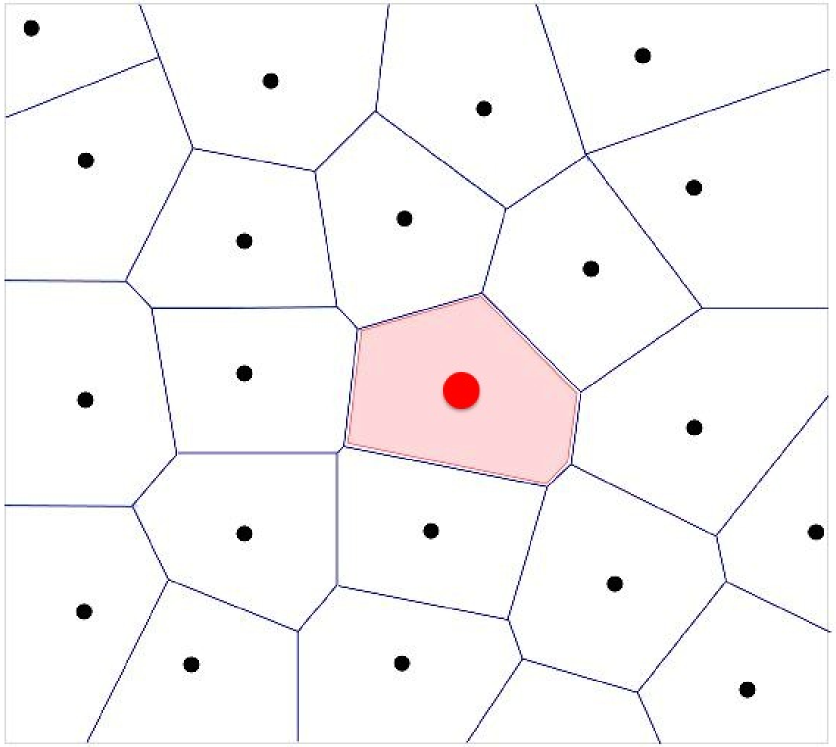


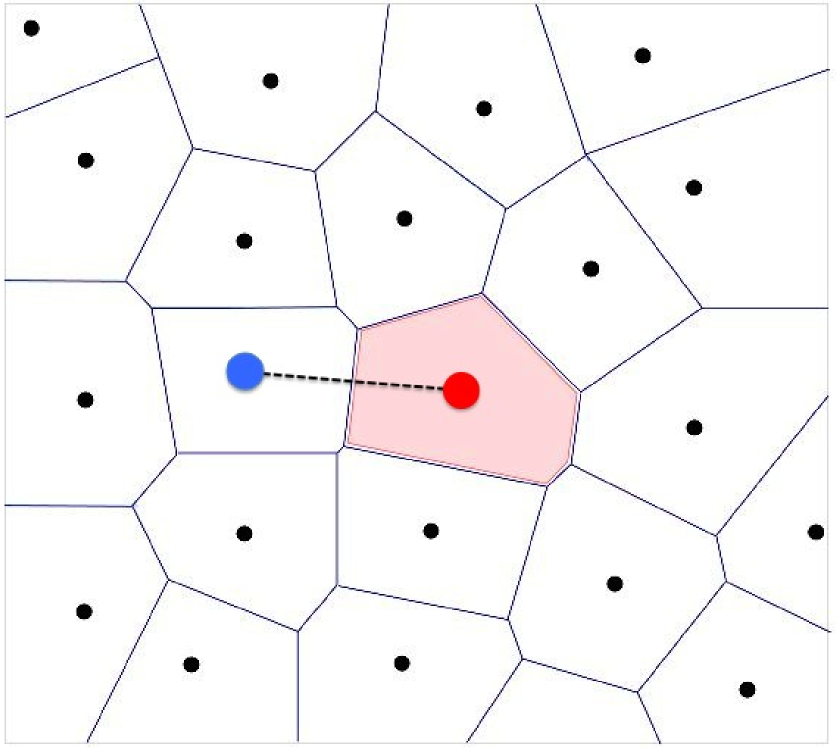
Proposition: *If $\mathcal{V} \in \mathrm{Del}_{r_0,r_1}$ the Voronoi tile of any $x \in \mathcal{V}$ is a convex polytope containing the ball $\overline{\mathrm{B}}(x; r_0)$ and contained in the ball $\overline{\mathrm{B}}(x; r_1)$*

The Delone Graph



Proposition: *the Voronoi tiles of a Delone set touch face-to-face*

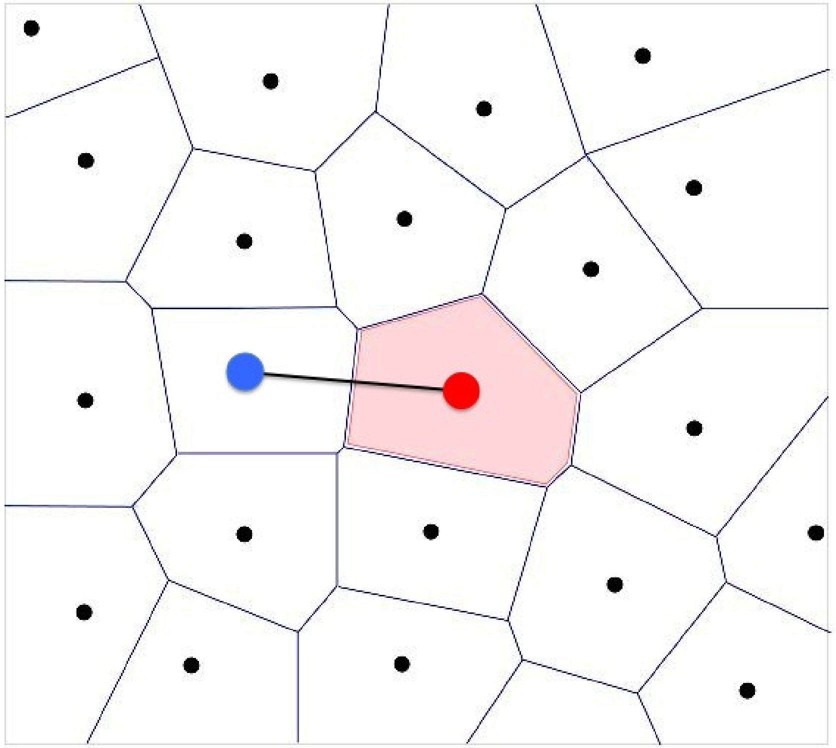
The Delone Graph



Proposition: *the Voronoi tiles of a Delone set touch face-to-face*

Two atoms are *nearest neighbors* if their Voronoi tiles touch along a face of *maximal dimension*.

The Delone Graph



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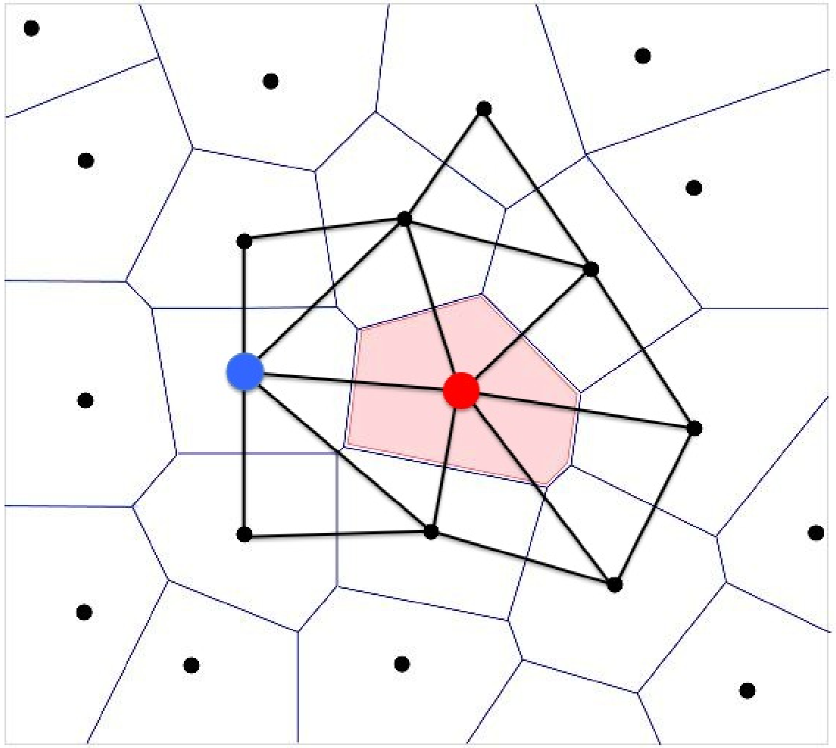
An *edge* is a pair of nearest neighbors. $\mathcal{E}$ denotes the set of edges.

The Delone Graph



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The family $\mathcal{G} = (\mathcal{V}, \mathcal{E})$ is the Delone graph.

The Delone Graph

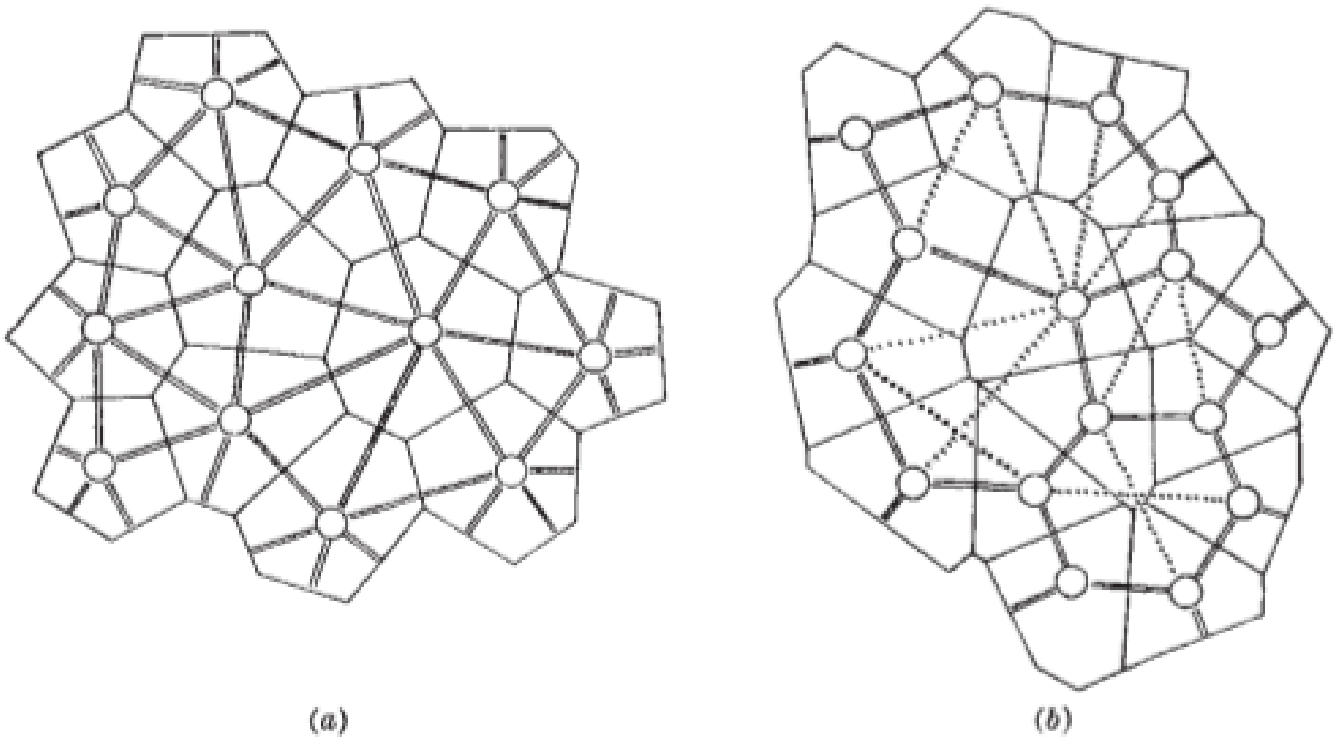


Fig. 1. Diagram of neighbourhood polyhedra, geometrical and physical, for two-dimensional arrays of points. (*a*) High co-ordinated; =, physical neighbours; (*b*) low co-ordinated; ...., geometrical neighbours

taken from J. D. Bernal, Nature, **183**, *141-147, (1959)*

Properties of the D-graph

- A Delone graph is *simple*: one edge at most between two vertices, no edge with one end point (tadpole).
- A *graph map* sends vertices to vertices, edge to edges and is compatible with the edge boundaries
- Graphs are identified modulo *graph isomoprhisms*
- *Given an integer N, the number of simple graphs modulo isomorphism with less than N vertices is finite*
- **Consequence:** There are only finitely many D-Graphs representing a configuration of the glass in a ball of finite radius. D-graphs *discretize* the information.

Properties of the D-graph

- The incidence number n_x of a vertex $x \in \mathcal{V}$ is bounded by

$$d + 1 \leq n_x \leq \frac{\sqrt{\pi}\, \Gamma\{(d-1)/2\}}{\Gamma(d/2)\, \int_0^{\theta_m} \sin^{d-1}(\theta)\, d\theta}, \qquad \sin\theta_m = b/2h\,.$$

- A *local patch* of radius $n \in \mathbb{N}$ is an *isomorphism class* of subgraphs $(x, \mathcal{V}_x, \mathcal{E}_x)$ of the Delone graph, such that $x \in \mathcal{V}$, $\mathcal{V}_x$ is the set of vertices at graph-distance at most n from x.
- If $\mathcal{P}_n$ denote the *set of local patches* of radius n then there is $C = C(b, h) > 0$ such that

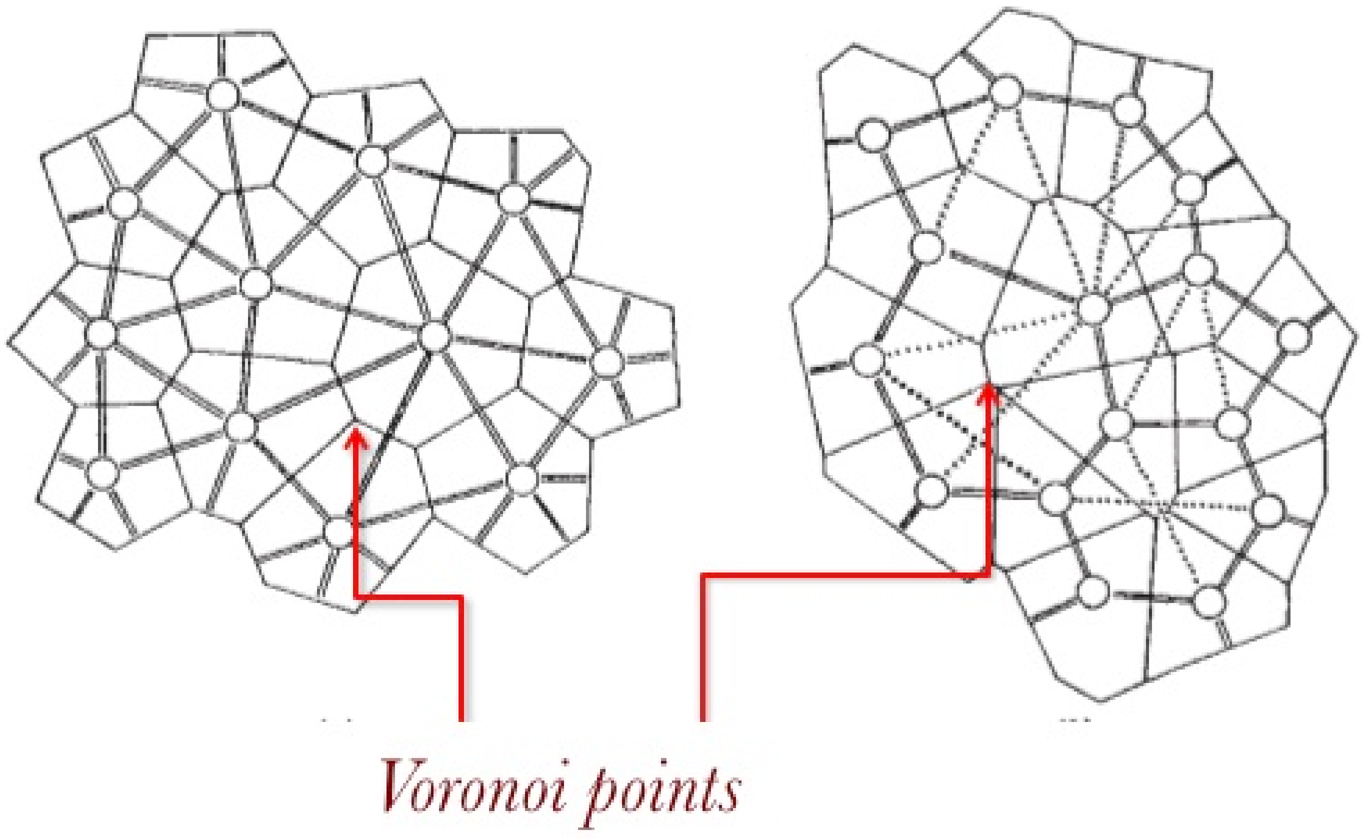
$$\#\mathcal{P}_n \leq e^{C(2n+1)^d}$$

Likelyhood

- Likelyhood can be expressed in various ways such as *topological genericity* or *full measure* (say *w.r.t* the Lebesgue measure)

- *If $X \subset \mathbb{R}^n$ is closed and if $\mathbb{P} = F(x)\, d^n x$ is "absolutely continuous", then a property valid of a dense open set $U \subset X$, with piecewise smooth boundary, is both generic and almost sure.*

Voronoi Points



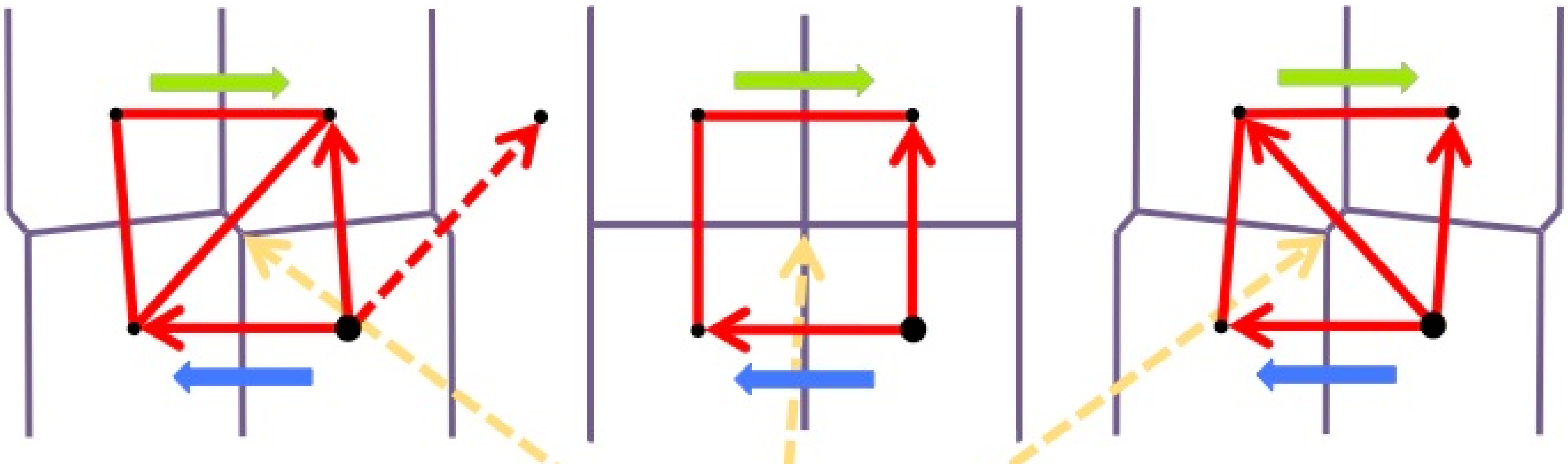
The vertices of the Voronoi cells are called *Voronoi Points*.

Voronoi Points

- **Theorem:** *A Voronoi point is at equal distance from every atom the Voronoi tile of which it belongs to.*

- **Theorem:** *Generically and almost surely a Voronoi point belongs to exactly* $d+1$ *Voronoi tiles in dimension* d.

Generic Local Patches

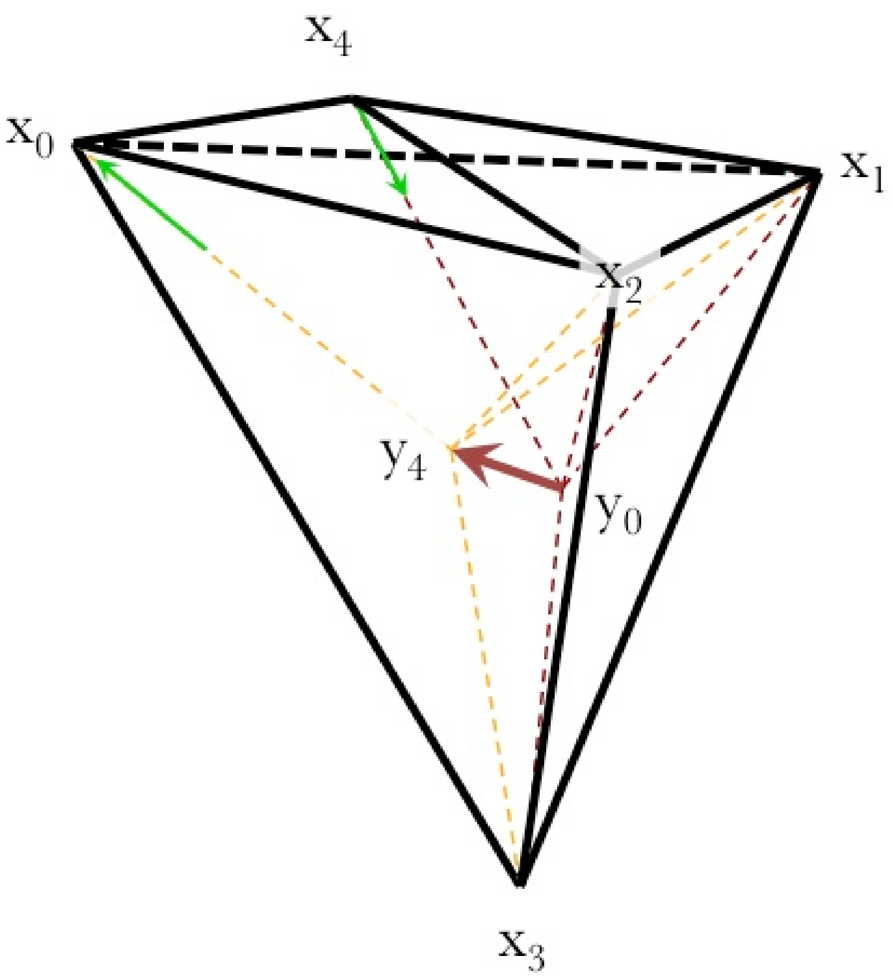


Shear modifies local patches. The middle one is *unstable*. The transition from left to right requires transiting through a *saddle point* of the potential energy.

The Voronoi cell boundaries are shown in blue.

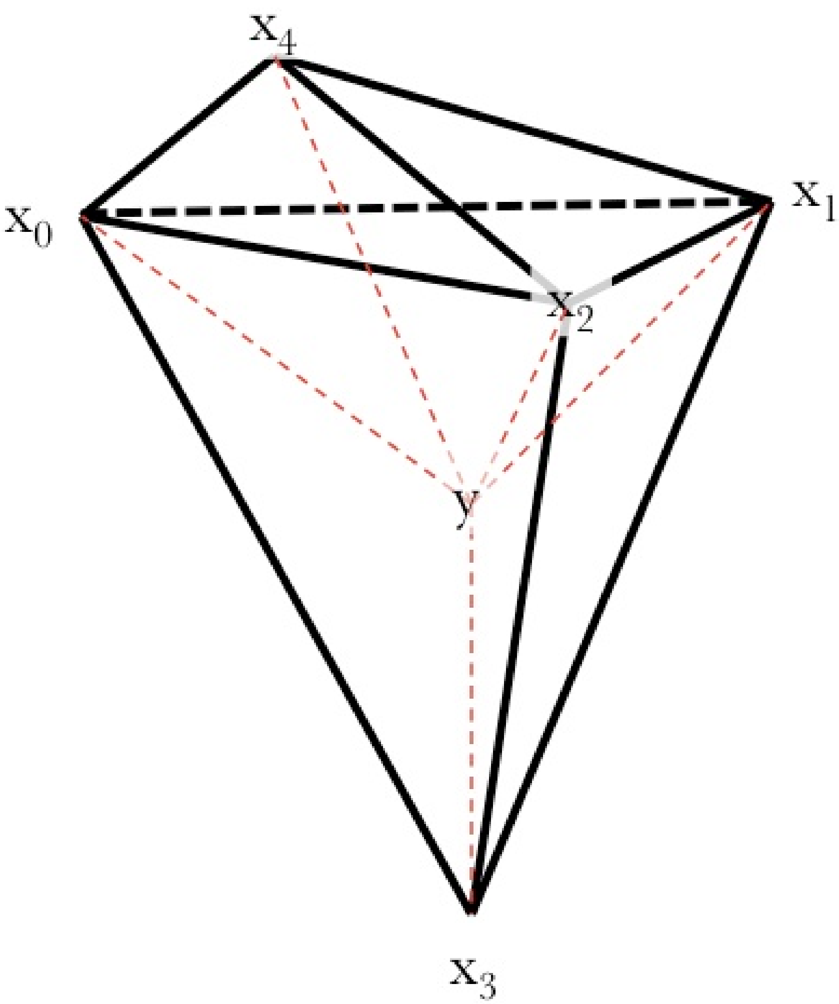
At the bifurcation a Voronoi vertex touches one more Voronoi cell than in the generic case

Generic Local Patches



An example of a generic 3D bifurcation.

Generic Local Patches



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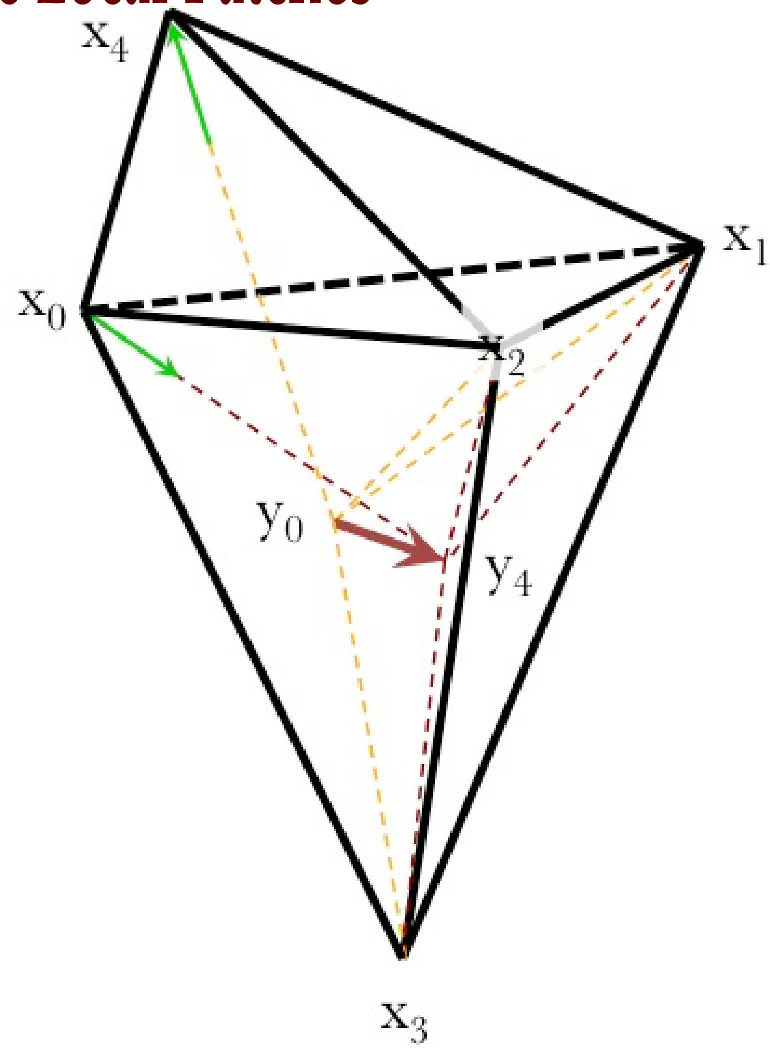

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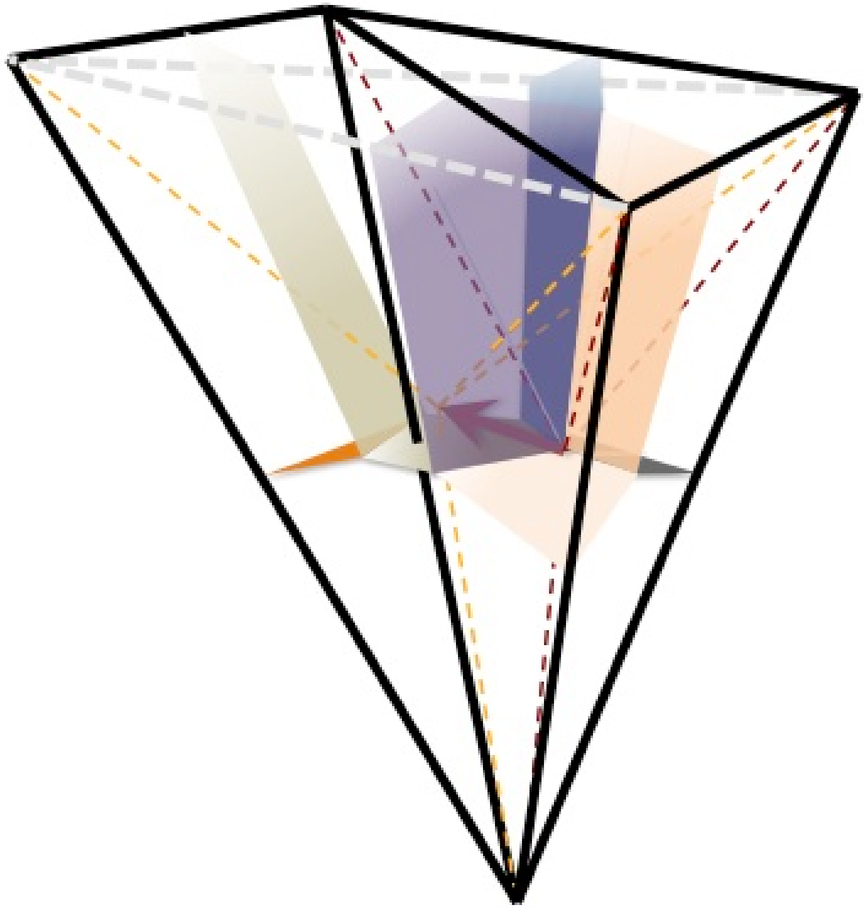
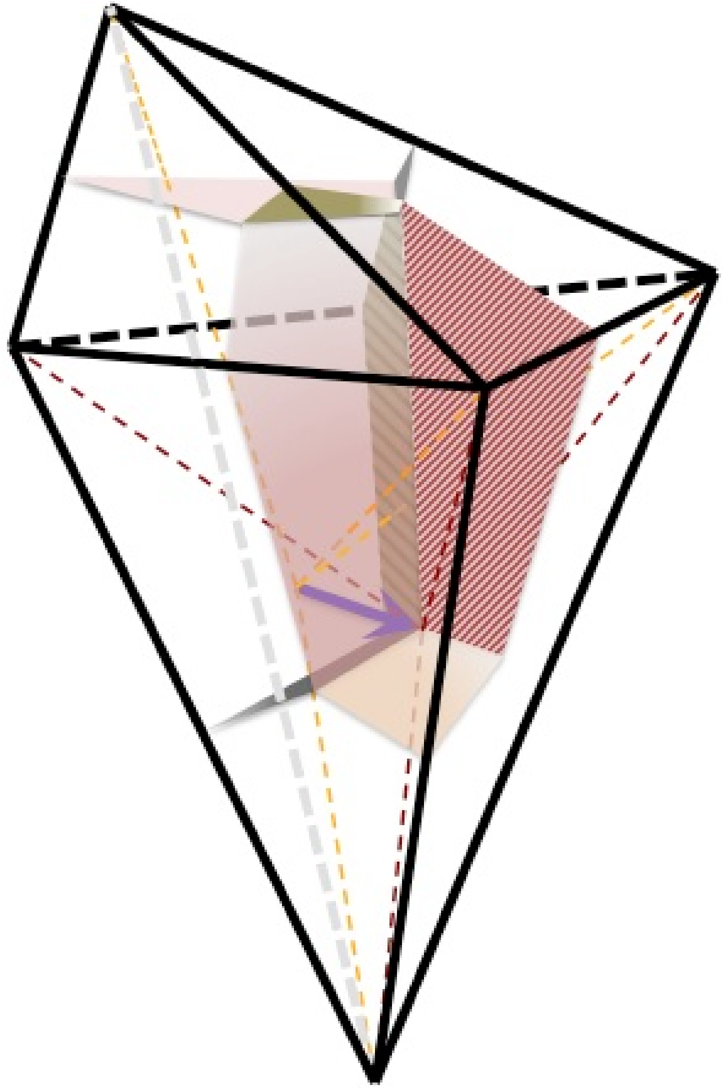


An example of a generic 3D bifurcation.

Graph changes

- The graph edges are indicated in black.
- The grey dotted edges have disappeared during the bifurcation.
- The colored plates are the boundaries of the Voronoi cells.

Generic Local Patches



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Acceptance Domains

- Given a local patch $\mathcal{G} \in \mathcal{P}_n$ its acceptance domain $\Sigma_{\mathcal{G}}$ is the set of all atomic configurations $\mathcal{V} \in \mathrm{Del}_{b,h}$ having $\mathcal{G}$ as their *local patch around the origin*.

- A local patch is *generic* whenever a small local deformation of the atomic configuration does not change the corresponding graph. Let $\mathfrak{B}_n \subset \mathcal{P}_n$ be the set of *generic local patches* of radius n.

- **Theorem:** *$\mathcal{G} \in \mathfrak{B}_n$ if and only if $\Sigma_{\mathcal{G}}$ is open and its boundary is piecewise smooth.*
  The union of acceptance domains of the generic patches of size n is dense.
  In particular almost surely and generically an atomic configuration admits a generic local patch.

Contiguousness

- The *boundary* of the acceptance domain of a generic graph contains a relatively open dense subset of codimension 1.

- **Definition:** *two generic graphs $\mathcal{G}, \mathcal{G}' \in \mathcal{Q}_n$ are contiguous whenever their boundary share a piece of codimension one*.

- The set $\mathfrak{V}_n$ itself can then be seen as the set of vertices of a graph

$$\mathfrak{G}_n = (\mathfrak{V}_n, \mathfrak{E}_n)$$

called the *graph of contiguousness* where *an edge $E \in \mathfrak{E}_n$ is a pair of contiguous generic local patches.*

Contiguousness

Theorem *two contiguous generic graphs differ only by one edge*

III - Conclusion

Degrees of Freedom

1. In the liquid phase, the short wave phonons are *short lived*. They do not contribute to the heat capacity.
2. The only relevant degree of freedom is the *bond motion*. The contiguousness relation expresses the combinatoric part of this degree of freedom
3. Each bond comes with a local *stress tensor*. In the liquid phase this stress tensor is *Gaussian distributed* (free Maxwell gas) $\Rightarrow$ *law of Dulong and Petit for the heat capacity*.
4. The bond degrees of freedom are called *anankeon*.

The Anankeon Theory

The bond degrees of freedom are the response of atoms to the stressful situation in which they are trying to find a better comfortable position, in vain.

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Behind the previous concept of bond degrees of freedom, there is the notion of stress, constraint, necessity, unrest and even torture.

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There is a a character of the Greek mythology that could fit with this concept:

the goddess Ananke

whose name comes from the greek word anagkeia *meaning the* stress of circumstances.

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whose name comes from the greek word anagkeia *meaning the* stress of circumstances. *Ananke was representing a power above all including the Gods of the Olympe "even gods don't fight against Ananke" claims a scholar. This character presided to the* creation of the world*, in various versions of the Greek mythology. It expresses the concepts of* "force, constraint, necessity" *and from there it also means* "fate, destiny" *to lead to the concepts of compulsion, torture.(from Wikipedia)*

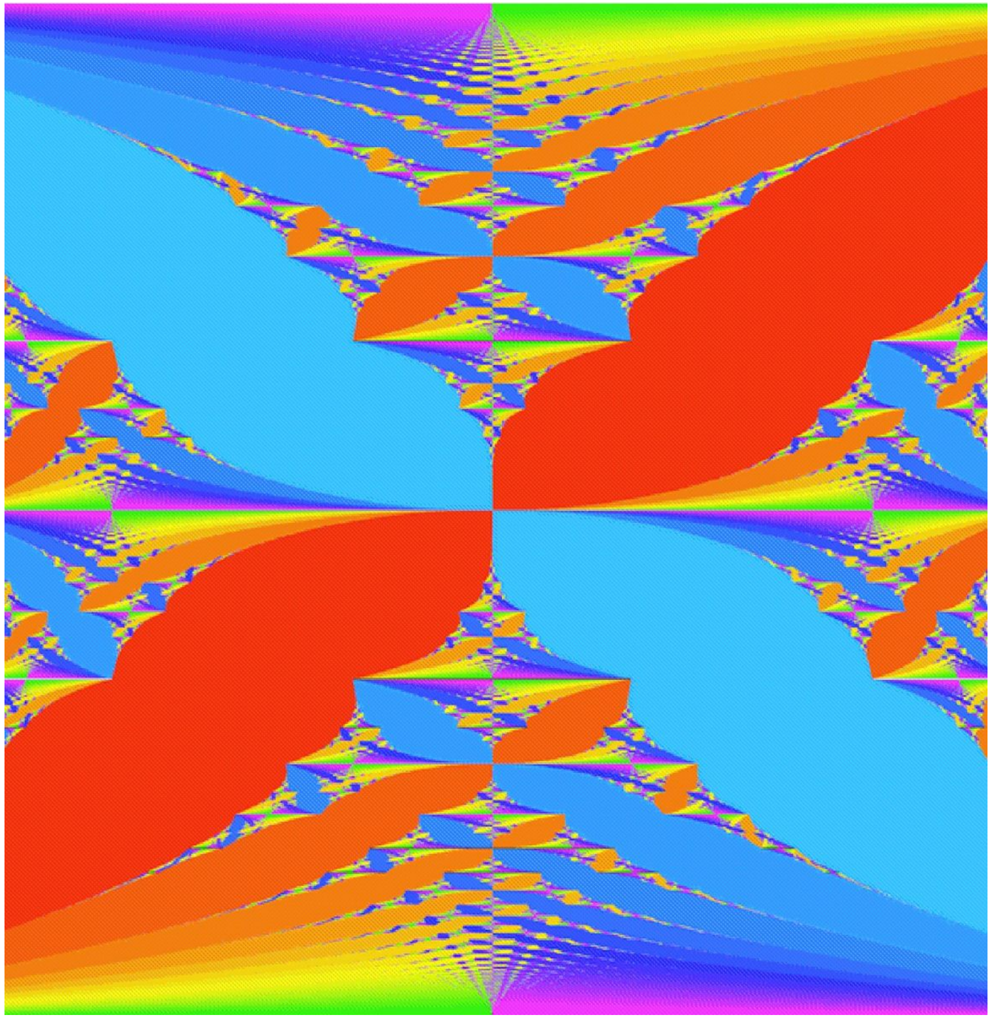
The Anankeon Theory

For this reason the configurational degrees of freedom associated with the stress tensor on each bond will be called

ANANKEONS

Modeling the Dynamics

1. A *Markov dynamics* can be built on the graph of *contiguousness*, describing the time evolution of the D-graph of both liquid and glasses, or the dynamics of the local bonds *(anankeons)*
2. Each D-graph is decorated by local degrees of freedom: local stress *(anankeon)*, local vibration *(phonons)*.
3. In the *liquid phase* the anankeon are free, phonons are suppressed, the theory gives a perfect gas solvable model.
4. The interaction *phonon-anankeon* is still ununderstood.



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