MODELING LIQUID METALS

and

BULK METALLIC GLASSES

Jean BELLISSARD

Georgia Institute of Technology, Atlanta
School of Mathematics & School of Physics
e-mail: jeanbel@math.gatech.edu

Sponsoring

This material is based upon work supported by the National Science Foundation
Grant No. DMS-1160962

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Teaching, Counseling, Support, Thanks

Takeshi EGAMI, (*JINS*, Oak Ridge & U. Tennessee, Knoxville)

Plasticity

James S. LANGER, (*Physics Department*, UC Santa Barbara, California)

Main References

T. Egami, *Atomic Level Stress*, Prog. Mat. Sci., **56**, (2011), 637-653.

W. H. Wang, C. Dong, C. H. Shek, *Bulk Metallic Glasses*, Mater. Sci. Eng. Rep., **44**, (2004), 45-89.

M. Miller, P. Liaw, Eds., *Bulk Metallic Glasses: An Overview*, Springer, (2007).

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

Morrel H. Cohen & G. S. Grest, *Phys. Rev. B*, **20**, 1077-1098, (1979).

D. J. Plazek, J. H. Magill, *J. Chem. Phys.*, **45**, 3757, (1967); J. H. Magill, *ibid.* **47**, 2802, (1967).

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

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

J. D. Bernal, *the Structure of Liquids*, Proc. Roy. Soc., **A280**, (1964), 299-322.

D. B. Miracle, *A structural model for metallic glasses*, Nature Mat., **3**, (2004), 697-702.

D. B. Miracle, W. S. Sanders, N. Senkov, Phil. Mag., **83**, (2003), 2409-2428.

D. Ma, A. D. Stoica, X.-L. Wang, Nature Mat., **8**, (2009), 30-34.

T. Egami, D. Srolovitz, *J. Phys. F*, **12**, 2141-2163 (1982).

S.-P. Chen, T. Egami, V. Vitek, *Phys. Rev. B*, **37**, 2440-2449, (1988).

T. Egami, S. J. Poon, Z. Zhang, V. Keppens, *Phys. Rev. B*, **76**, 024203, (2007).

Content

1. Metal Liquids and Glasses
2. Elasticity and Plasticity
3. Delone Graphs
4. The Anankeon Theory
5. Towards a Dissipative Dynamics

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`*)*

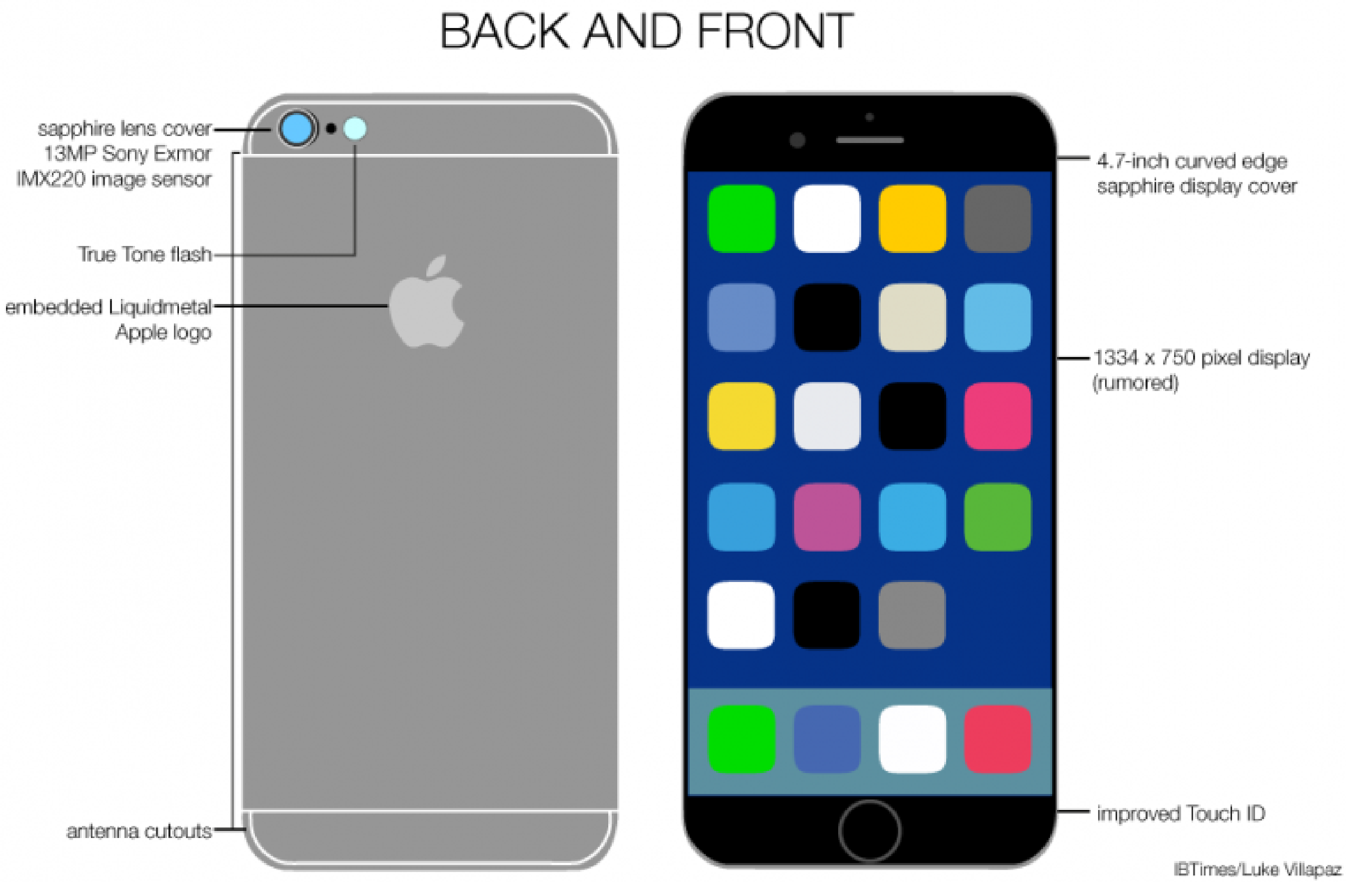
- *Orthopedic implants* and medical Instruments
- Material for *military components*
- Sport items, *golf clubs, tennis rackets, ski, snowboard, ...*

Pieces of Titanium-Based Structural Metallic-Glass Composites

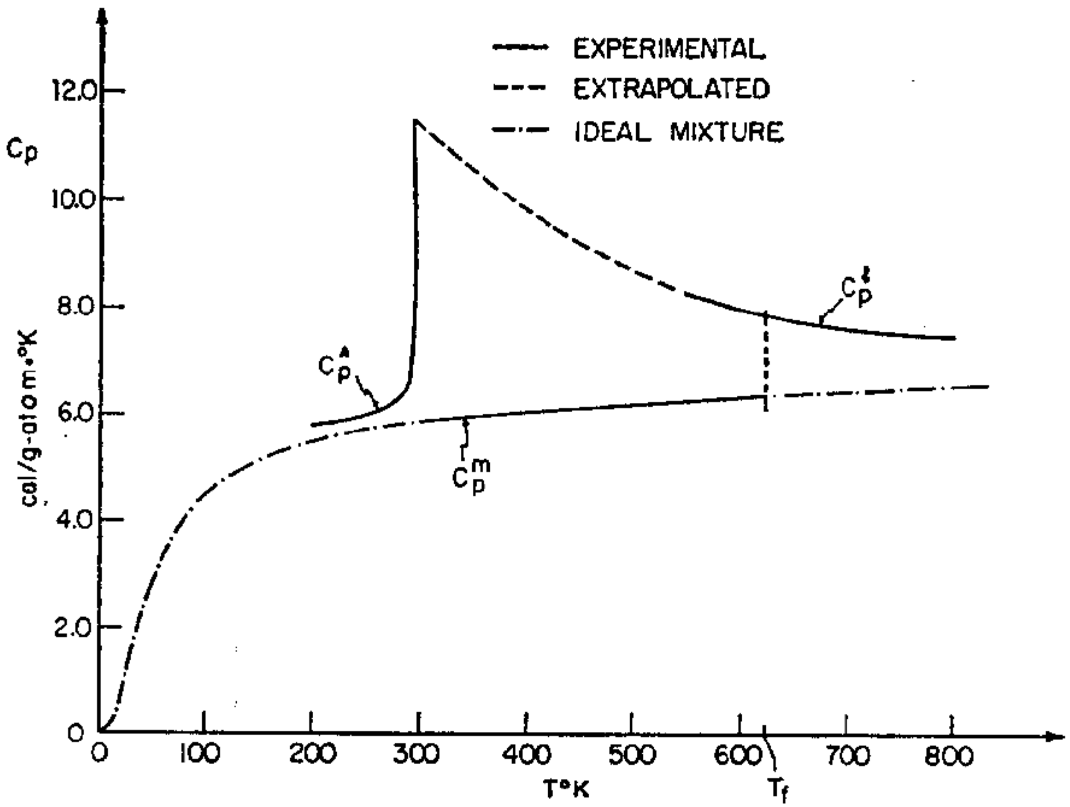
(Johnson's group, Caltech, 2008)

Bulk Metallic Glasses

- iPhone 6 *logo*



Bulk Metallic Glasses

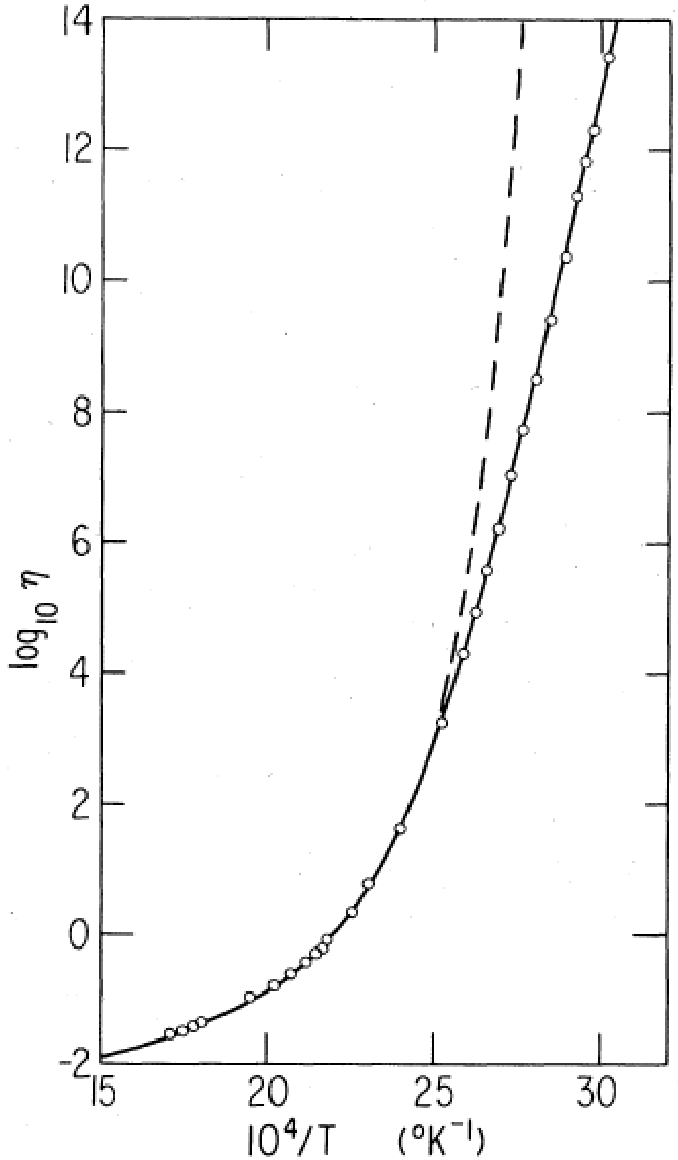


Smoothed values of specific heats of $Au_{.77}Ge_{.136}Si_{.094}$ signaling a glass-liquid transition

"*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

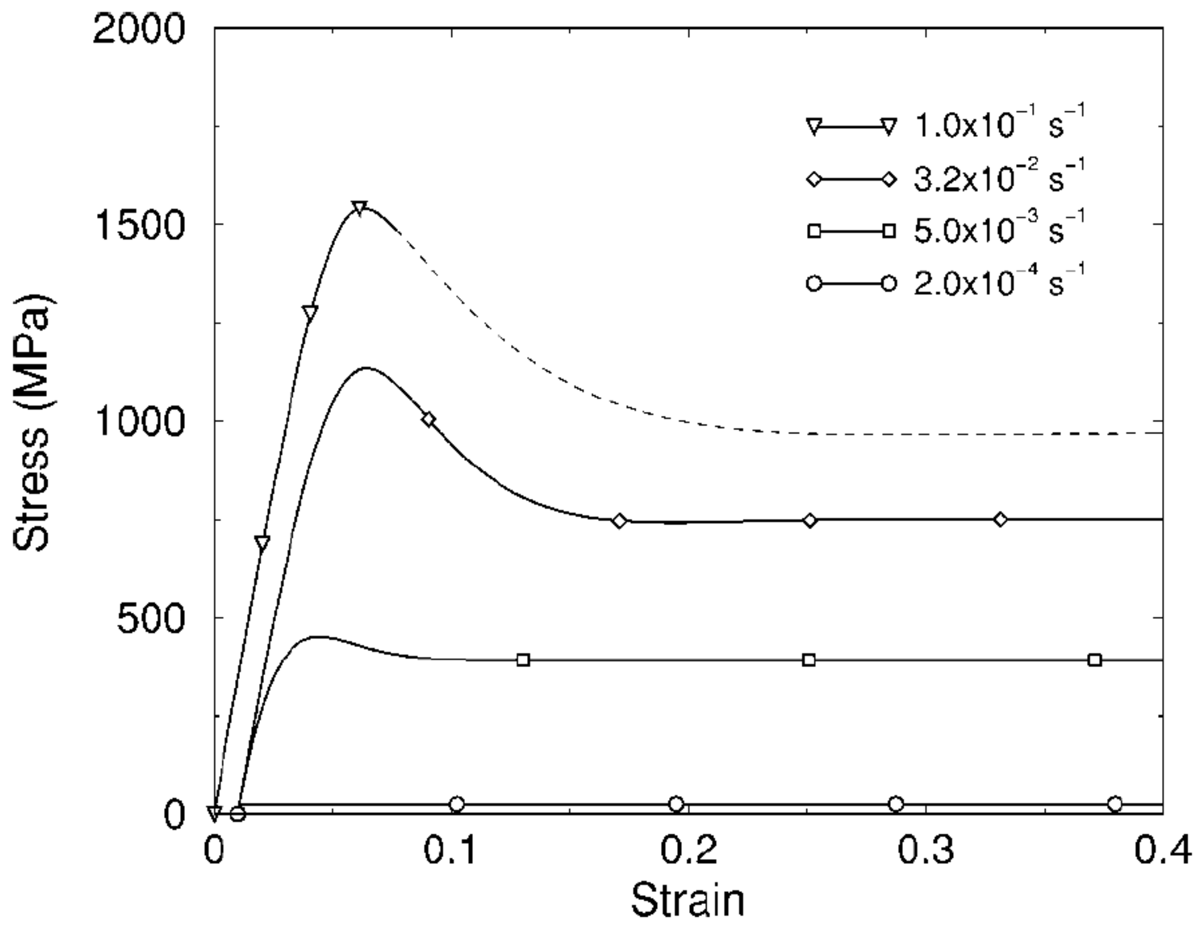


Viscosity vs temperature for tri-anaphthylbenzene, with fits coming from the *free volume theory*

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)

Bulk Metallic Glasses

1. No *structural difference* between liquid and glass. No sharp discontinuity of equilibrium variables

2. The *time scales change sharply* from liquid to glass. The glass transition temperature is defined by a conventional time scale beyond which the dynamics is hard to observe.

II - Elasticity and Plasticity

Strain

- A solid is treated as a *continuum*. Under any type of force an atom of the solid is moved from its location $x \in \mathbb{R}^d$ to $x' = x + u(x)$. u is called the *deformation vector*.
- This move is interpreted as a deformation of the *local metric*, namely $dx' = (1 + Du)dx$ implying

$$d\ell^2 = \langle dx|(1 + \widehat{\epsilon}(x))\, dx\rangle$$

where $\widehat{\epsilon}$ is the *strain tensor*

$$\widehat{\epsilon}_{ij} = \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \sum_{k=1}^{d} \frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}$$

Stress

- The *force* F applied to a region $V \subset \mathbb{R}^d$ is expressed as

$$F = \int_{\partial V} \widehat{\sigma}(s)\, \widehat{n}(s)\, ds$$

where $\widehat{n}(s)$ is the *outside unit normal* to V at the point $s \in \partial V$ and $\widehat{\sigma}(x)$ is the *stress tensor* at x.

- **Hooke's Law:** *the stress is a linear function of the strain*

$$\widehat{\sigma} = C\, \widehat{\epsilon}$$

Stress

- If the material is *homogeneous* and *isotropic*, Hooke's law becomes

$$\widehat{\sigma}(x) = \lambda \operatorname{tr}(\widehat{\epsilon}(x)) + 2\mu\, \widehat{\epsilon}(x)$$

(λ, μ are the Lamé coefficients)

- The local *pressure* p and the von Mises local *shear stress* τ are defined by

$$p = \frac{1}{3} \sum_{\alpha} \sigma^{\alpha\alpha} \qquad \tau = \sqrt{\sum_{\alpha<\beta} |\sigma^{\alpha\beta}|^2}$$

Elasticity Equations

- Applying *Newton's Law* on an infinitesimal volume of the material with density ρ gives

$$\rho\frac{\partial^2 u}{\partial t^2} = \mathrm{div}\,(\widehat{\sigma}\,) + F_e$$

where F_e *is the external force* per unit volume.

- In the limit of *small deformation*, for *homogeneous* and *isotropic* materials obeying *Hooke's Law*

$$\rho\frac{\partial^2 u}{\partial t^2} = \mu\Delta u + (\lambda + \mu)\nabla\mathrm{div}(u) + F_e$$

Mechanical Energy

- The *mechanical energy* stored in a region V can be computed to be

$$\mathcal{E}_V = \int_V \operatorname{tr}\left(\widehat{\epsilon}(x)\widehat{\sigma}(x)\right)\, dx$$

- In the limit of *small deformation*, for *homogeneous* and *isotropic* materials obeying *Hooke's Law* this gives

$$\mathcal{E}_V = \int_V \left(\frac{p^2}{2B} + \frac{\tau^2}{2G}\right) dx$$

where B is the *bulk moduus* and G is the *shear modulus*, expressible in terms of Lamé's coefficients.

Eshelby Effective Medium Theory

- If a small spherical cavity is *carved* inside the solid and if one tries to *insert* a deformed sphere (ellipsoid) in the cavity, the stress applied to the insertion from the outside can be computed as an *effective force* applied to the insertion.

- It leads to a modification of the mechanical energy in the form of

$$B \to \frac{B}{K_\alpha} \quad B \to \frac{G}{K_\gamma} \qquad K_\alpha = \frac{3(1-\nu)}{2(1-2\nu)} \quad K_\gamma = \frac{15(1-\nu)}{7-5\nu}$$

where ν is called *Poisson ratio* which expresses the ratio between the *longitudinal* and the *transverse* deformation when pulling or pushing on a sample.

Plasticity and STZ Theory

- *Plasticity* is what happens when the Hooke's Law is invalid: the *stress-strain* relationship becomes *nonlinear*.

- A group led by James S. Langler since 1998 proposed a theory based on the concept of *shear transformation zone* or *STZ*, which will be microscopically associated with the *anankeons*.

- The STZ theory reproduces the strain-stress experimental curves and describes quantitatively the creation of cracks in a material when one pulls on it.

- The *STZ* theory requires *more phenomenological parameters* than elasticity theory, addressing the question of an atomic scale theory.

III - 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.

Topology

- Let $U \subset \mathbb{R}^d$ be *open* and *bounded*.

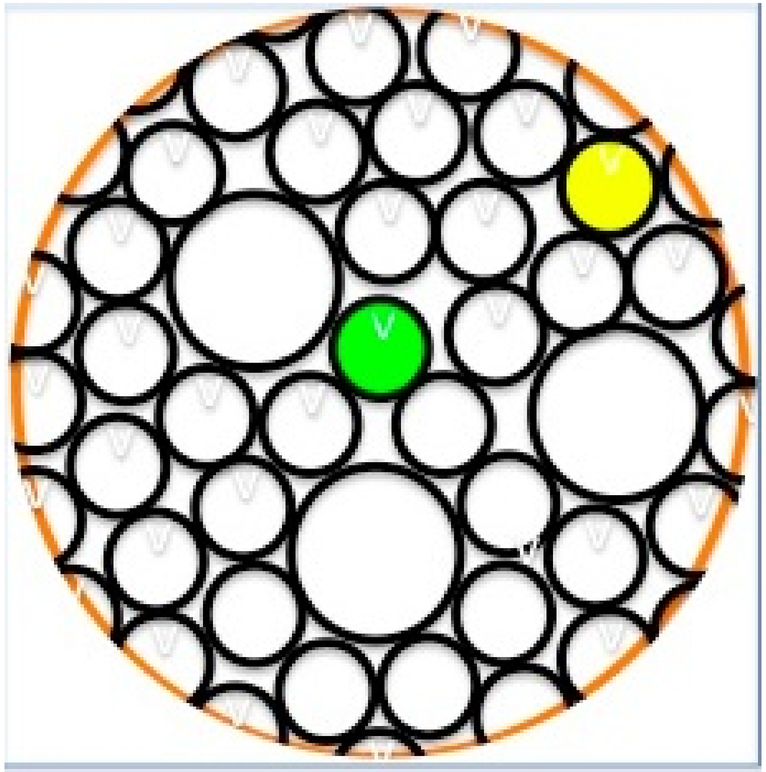
- If $\epsilon > 0$ and if $\mathcal{V} \in \mathrm{Del}_{b,h}$ let $\mathcal{U}(U, \epsilon, \mathcal{V})$ to be the set of Delone sets $\mathcal{W}$ such that the Hausdorff distance satisfies

$$d_H(\mathcal{V} \cap U, \mathcal{W} \cap U) < \epsilon \,.$$

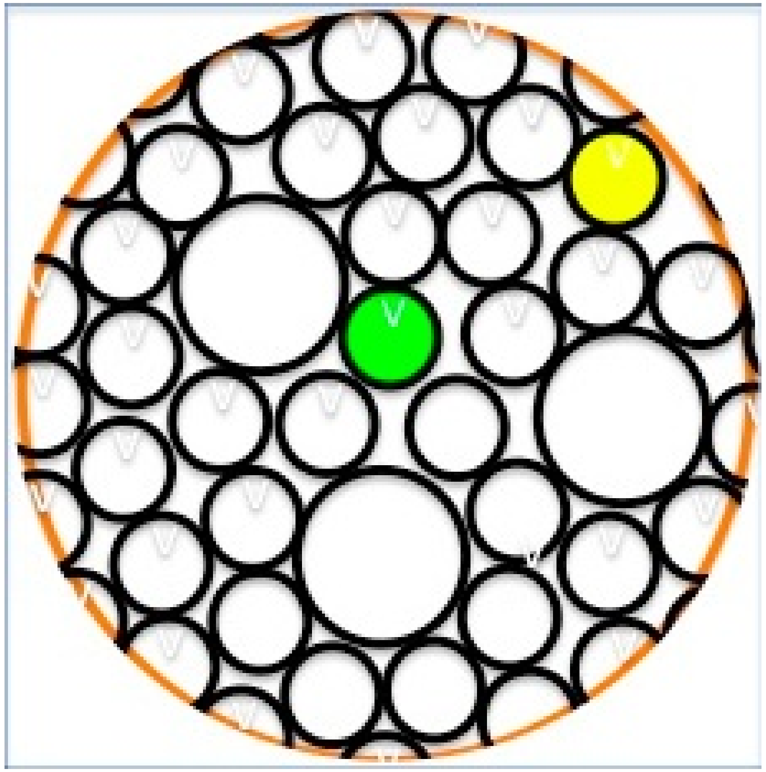
- The family $\mathcal{U}(U, \epsilon, \mathcal{V})$ is a *basis of open sets* for the topology on $\mathrm{Del}_{b,h}$

- **Theorem:** *The space* $\mathrm{Del}_{b,h}$ *is compact*

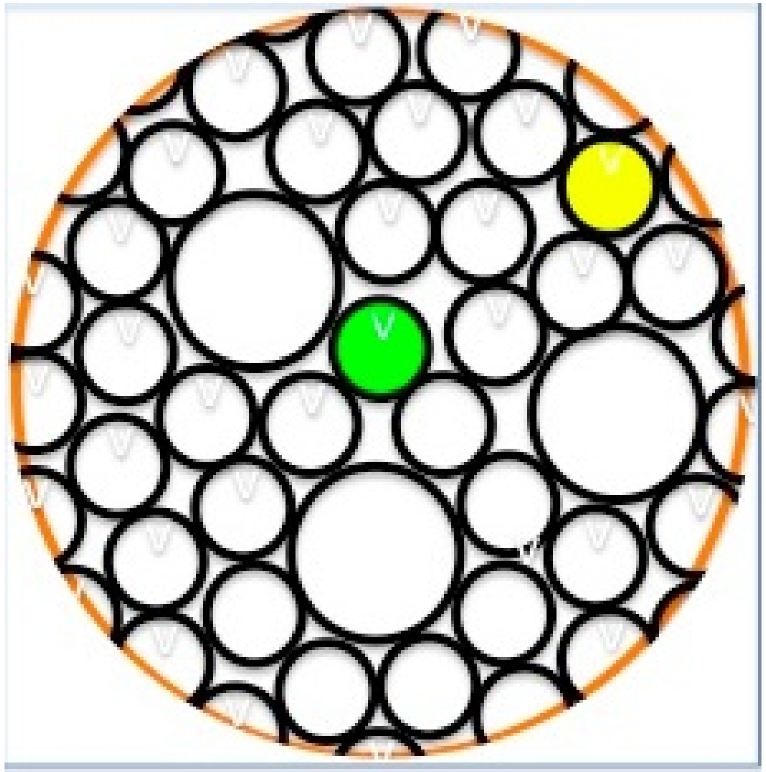
Delone Neighborhoods



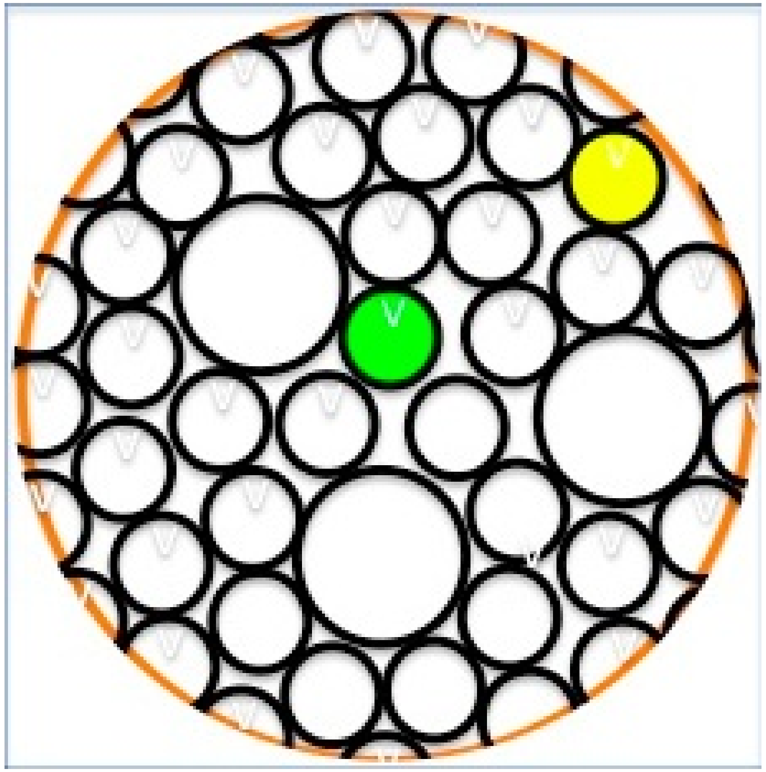
Delone Neighborhoods



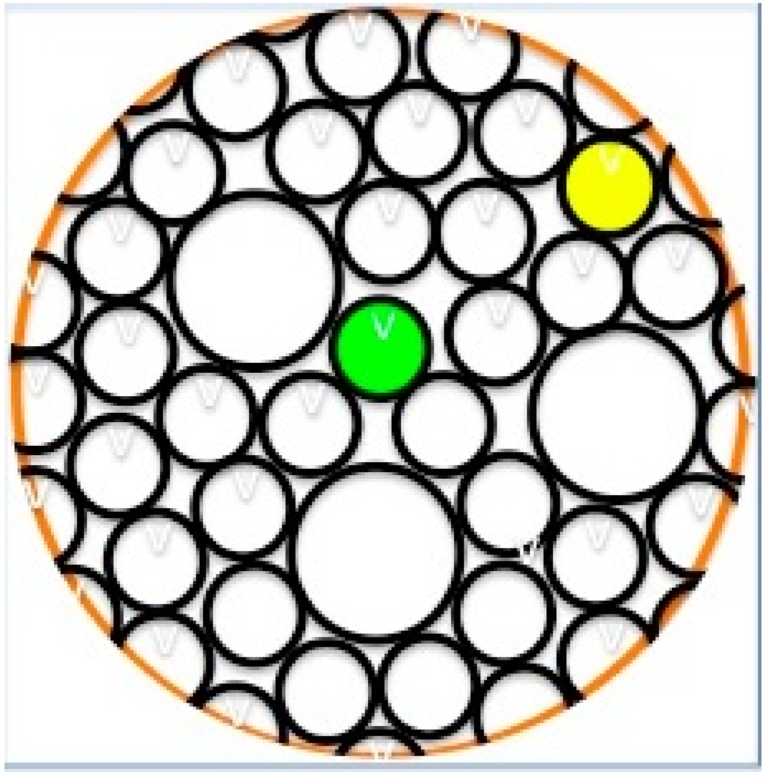
Delone Neighborhoods



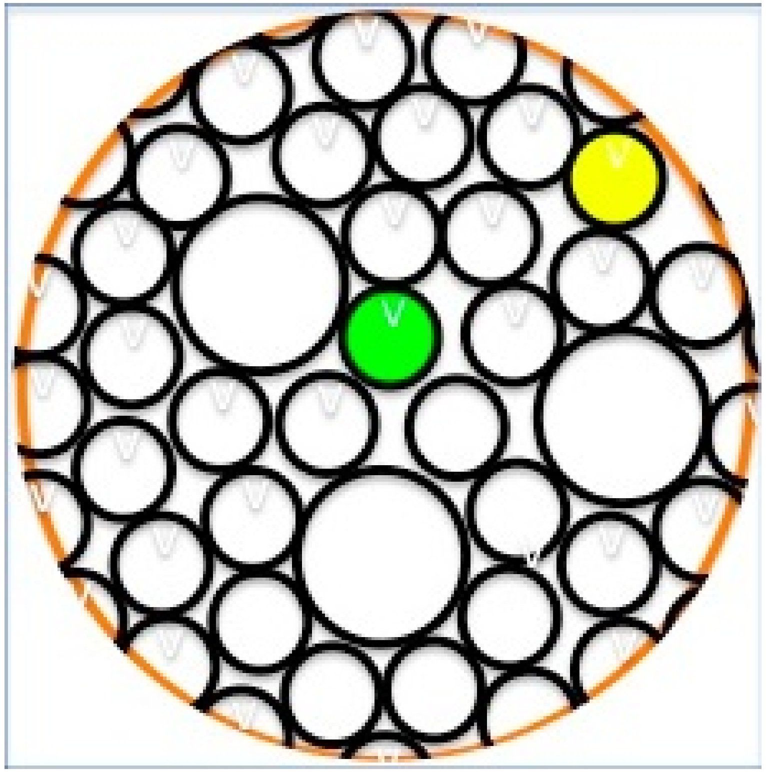
Delone Neighborhoods



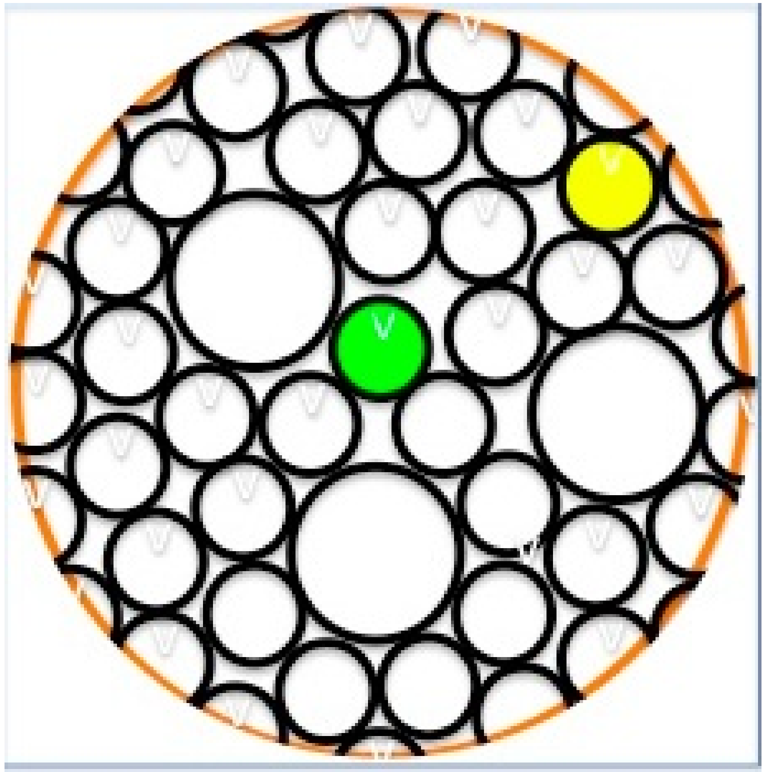
Delone Neighborhoods



Delone Neighborhoods



Delone Neighborhoods



Locally a.c. Measures

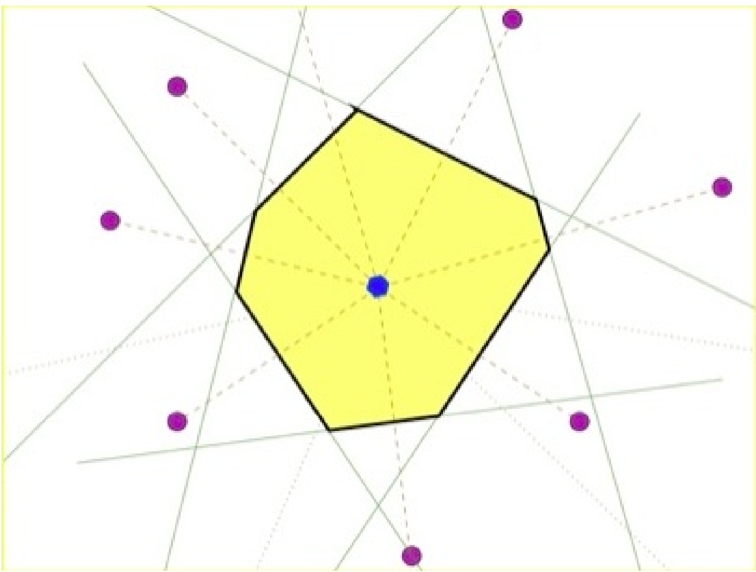
- Let $U \subset \mathbb{R}^d$ be *open* and *bounded*.
- A Delone set $\mathcal{V}$ can be described locally in $\mathbb{R}^d$ through a finite family of points inside U
- The set of all Delone sets with $|\mathcal{V} \cap U| = n$ is a Borel set homeomorphic to a Borel set in $\mathbb{R}^{dn}$
- Through this homeomorphism, the concept of *zero Lebesgue measure set* can be transported on to $\mathrm{Del}_{b,h}$.
- A probability measure on $\mathrm{Del}_{b,h}$ is *locally absolutely continuous* whenever any subset of zero Lebesgue measure has zero probability.

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 called the *Voronoi tile* of x



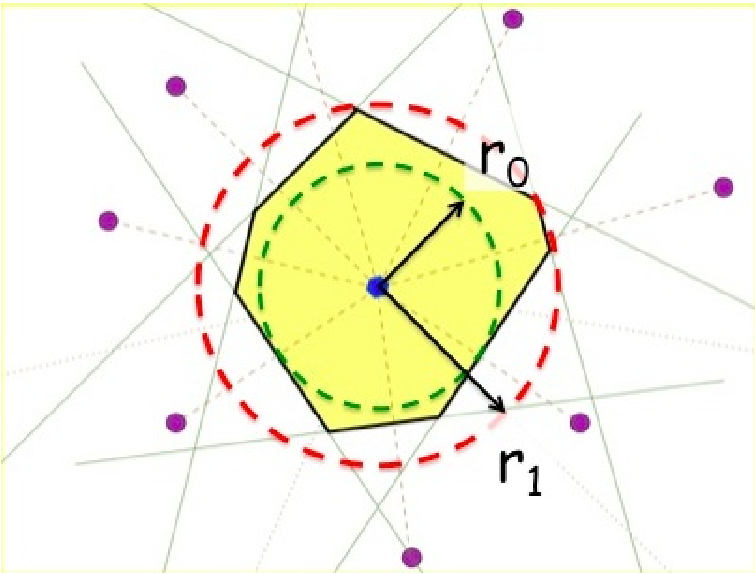
Proposition: *If $\mathcal{V} \in \mathrm{Del}_{r_0,r_1}$ the Voronoi tile of any $x \in \mathcal{V}$ is a convex polytope*

Voronoi Cells

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

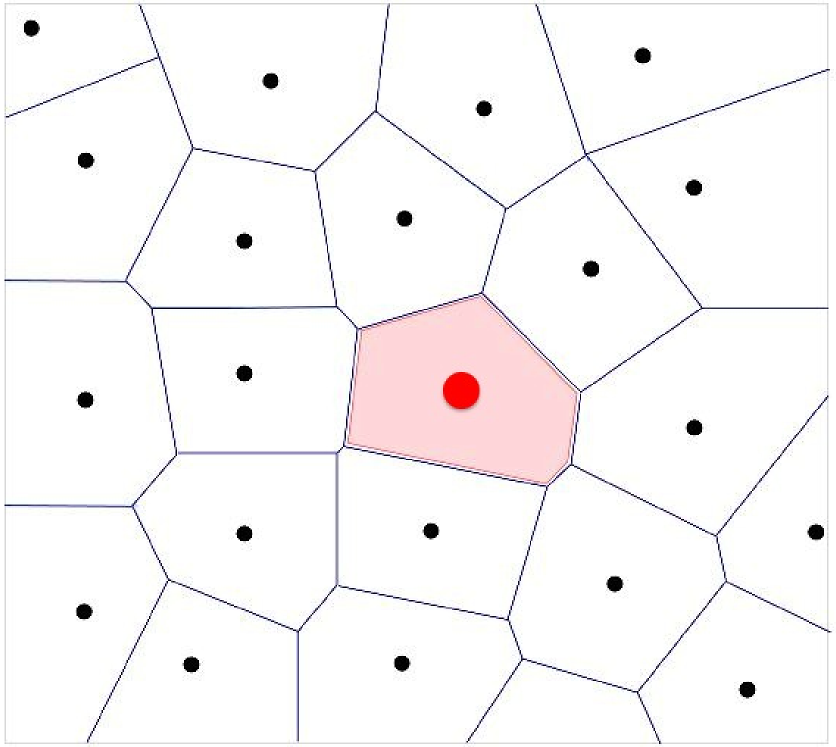
$$V(x) = \{y \in \mathbb{R}^d\,;\, |y - x| < |y - x'|\, \forall x' \in \mathcal{V}\,,\, x' \neq x\}$$

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



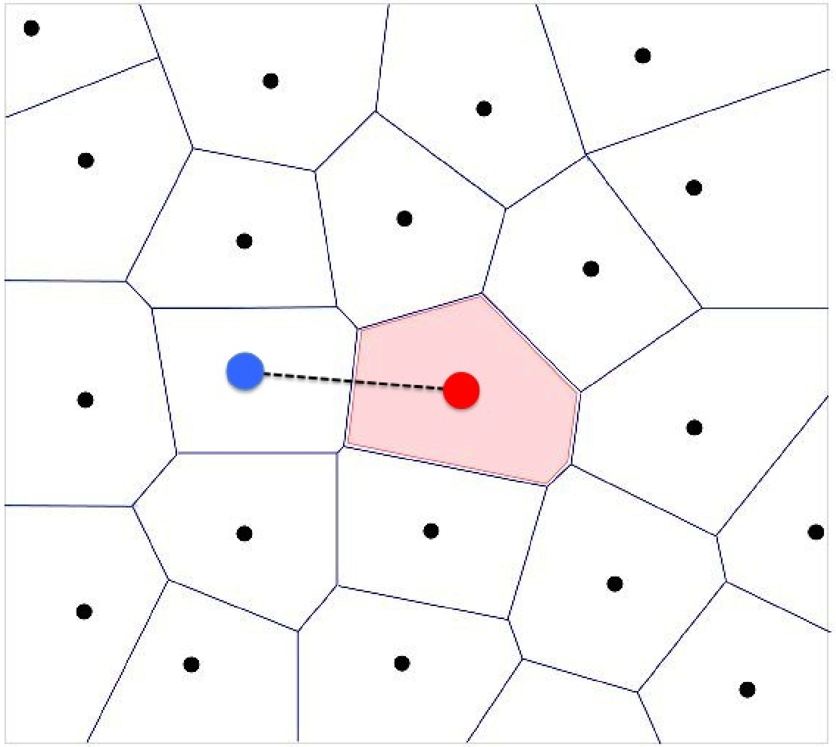
Proposition: *If $\mathcal{V} \in \mathrm{Del}_{r_0,r_1}$ the Voronoi tile of any $x \in \mathcal{V}$ is a convex polytope containing the ball $\overline{\mathrm{B}}(x; r_0)$ and contained in the ball $\overline{\mathrm{B}}(x; r_1)$*

The Delone Graph



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

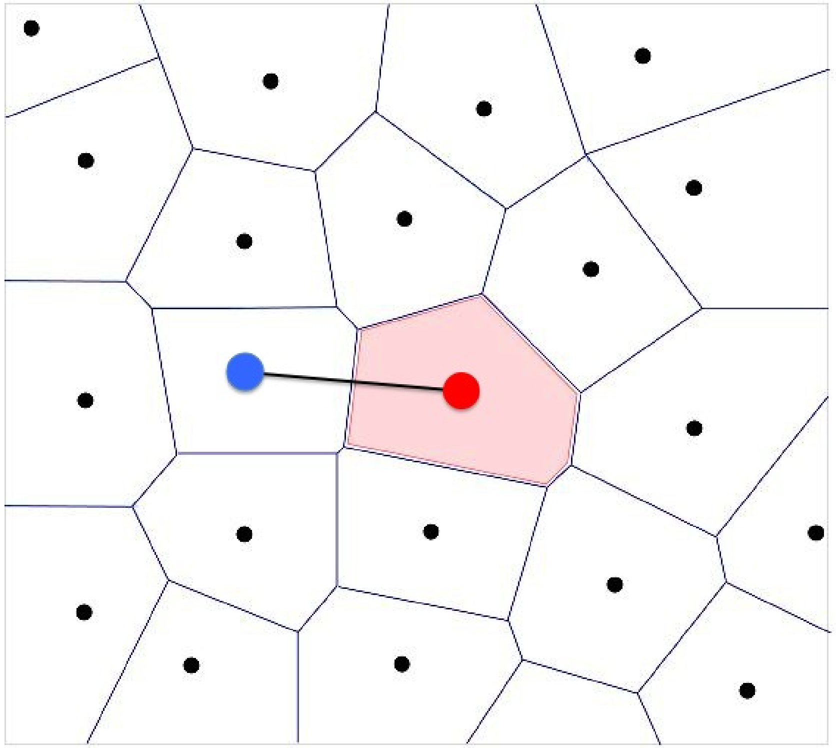
The Delone Graph



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

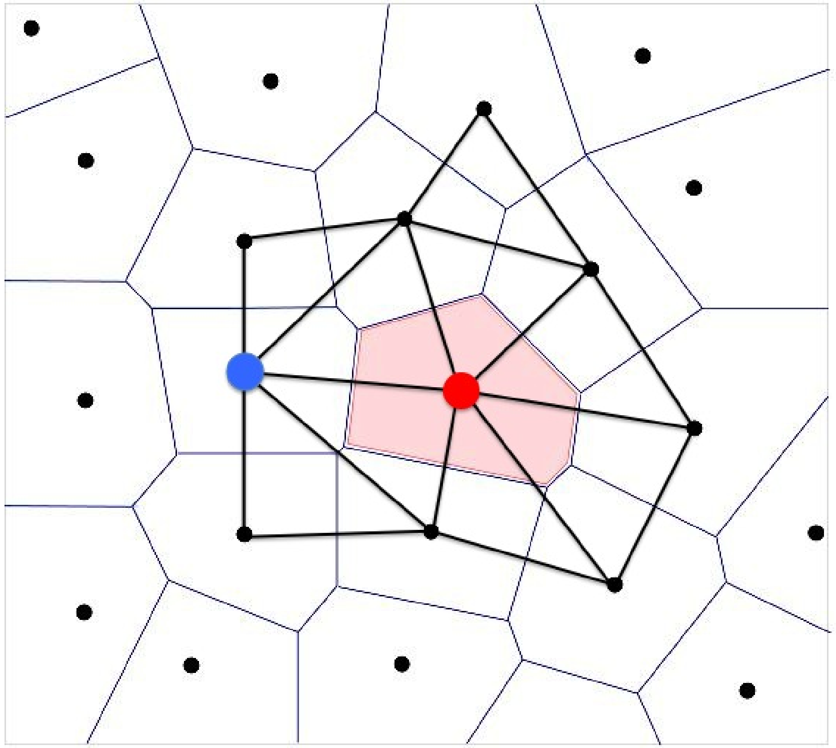


Proposition: *the Voronoi tiles of a Delone set touch face-to-face*

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

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

The Delone Graph



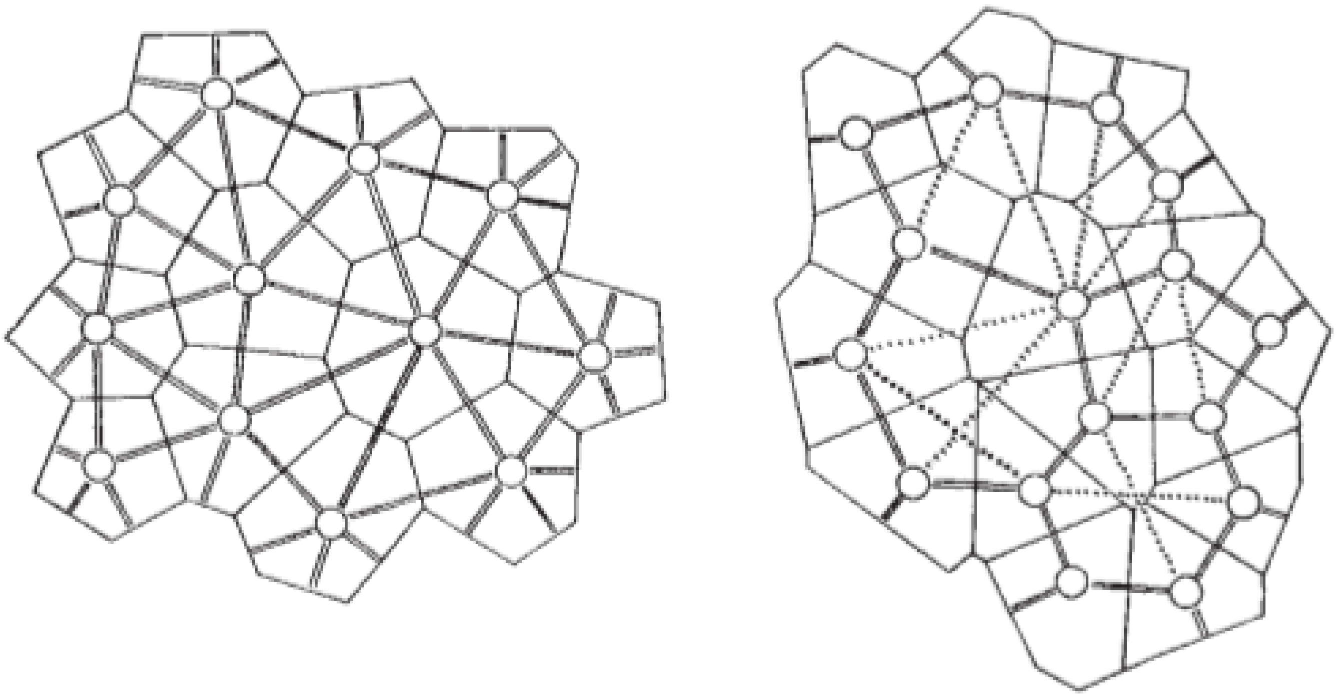
Proposition: *the Voronoi tiles of a Delone set touch face-to-face*

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

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

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

The Delone Graph



(a) (b)

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

- **Graphs:** a *simple non-oriented* graph $\mathcal{G} = (\mathcal{V}, \mathcal{E})$ is a pair of sets with a one-to-one map $\partial : \mathcal{E} \to \mathfrak{P}_2(\mathcal{V})$, called *boundary map*, ($\mathfrak{P}_2(\mathcal{V})$ = set of part of $\mathcal{V}$ with 2 points or less).
- **Graph maps:** $f : \mathcal{G} = (\mathcal{V}, \mathcal{E}) \to \mathcal{G}' = (\mathcal{V}', \mathcal{E}')$ is a pair of maps $f_v : \mathcal{V} \to \mathcal{V}'$, $f_e : \mathcal{E} \to \mathcal{E}'$ such that

$$\partial \, f_e(e) = f_v(\partial e)$$

- **Composition:** $f \circ g = (f_v \circ g_v, f_e \circ g_e,)$.
- **Isomorphism:** $f : \mathcal{G} = (\mathcal{V}, \mathcal{E}) \to \mathcal{G}' = (\mathcal{V}', \mathcal{E}')$ is an isomorphism if $\exists\, g : \mathcal{G}' = (\mathcal{V}', \mathcal{E}') \to \mathcal{G} = (\mathcal{V}, \mathcal{E})$ with $f \circ g = \mathbf{1}_{\mathcal{G}'}$, $g \circ f = \mathbf{1}_{\mathcal{G}}$.

Properties of the D-graph

Remark: *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: Genericity

Genericity is a topological concept.

- In a topological space X, a subset $A \subset X$ is *dense* if any nonempty open set intersects A.

- A *G_δ-set* is the intersection of a countable family of open sets.

- *Baire Category Theorem: if X is homeomorphic to a complete metric space, then a countable intersection of dense open sets is dense.*

- A property is called *generic* when it holds in a dense G_δ.

Likelyhood: Almost Surely

Almost Surely is a measure theoretic or probability concept concept.

- A *probability space* is a triple $(X, \Sigma, \mathbb{P})$, where X is a set, Σ a family of subsets of X containing X, that is closed under complementation and countable intersection (called the *σ-algebra of measurable sets*) and $\mathbb{P}$ is a *probability measure*, namely $\mathbb{P} : \Sigma \to [0, 1]$ satisfying standard assumptions.

- In a probability space $(X, \Sigma, \mathbb{P})$, a property is *almost sure* whenever it occurs in a measurable subset $A \in \Sigma$ having probability $\mathbb{P}(A) = 1$.

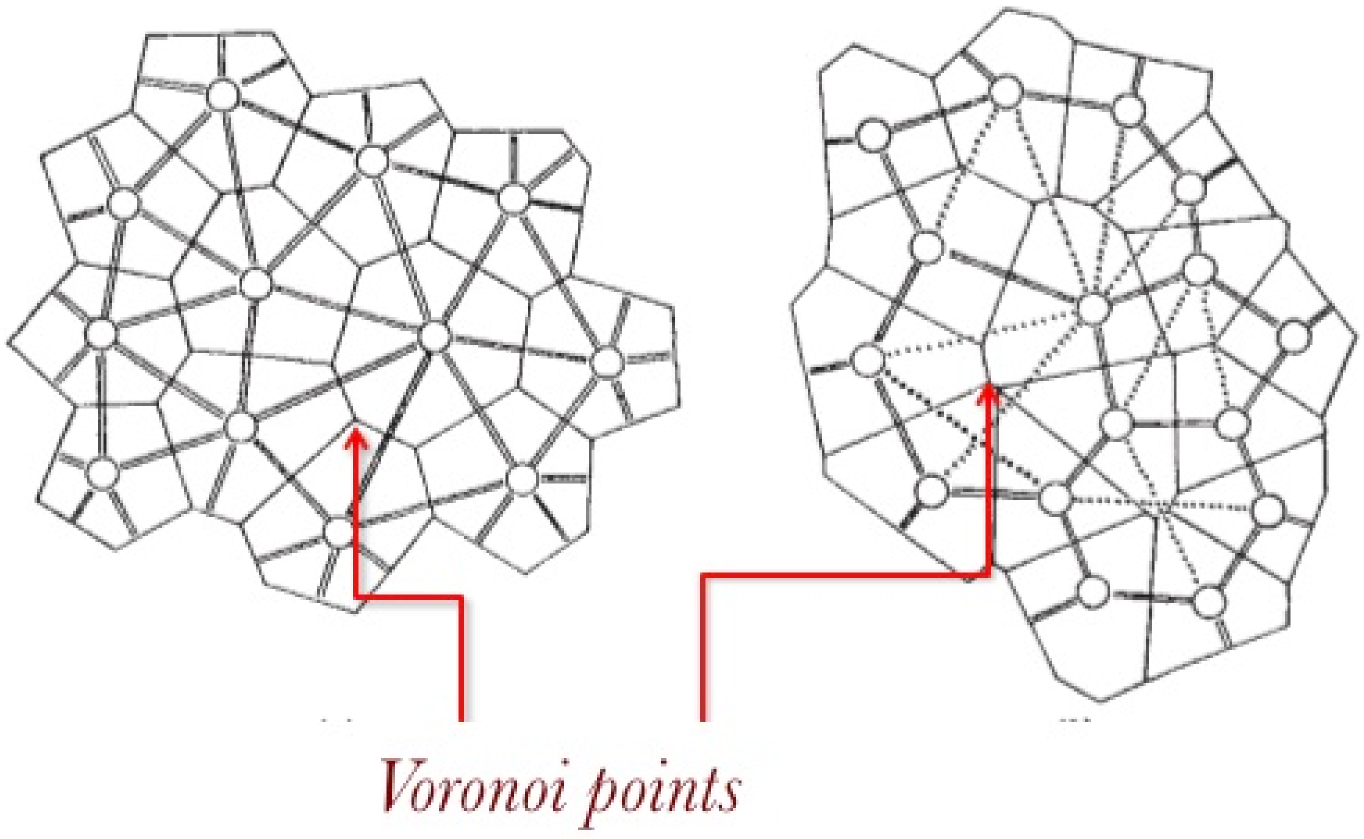
Likelyhood

- There are examples of *generic subsets* of $[0,1]$ with *zero probability* (*w.r.t* the Lebesgue measure), the complement of which is almost sure without being generic.

- *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.*

- **Definition:** A property will be called *almost sure* in the space $\mathrm{Del}_{b,h}$ whenever it occurs on the *complement of a set of locally Lebesgue measure zero*.

Voronoi Points



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

Voronoi Points

Let $\mathcal{V}$ be a Delone set and let y be one of its Voronoi points.

- Any point in the Delone set having a tiles touching y will be called an *atomic neighbor*.

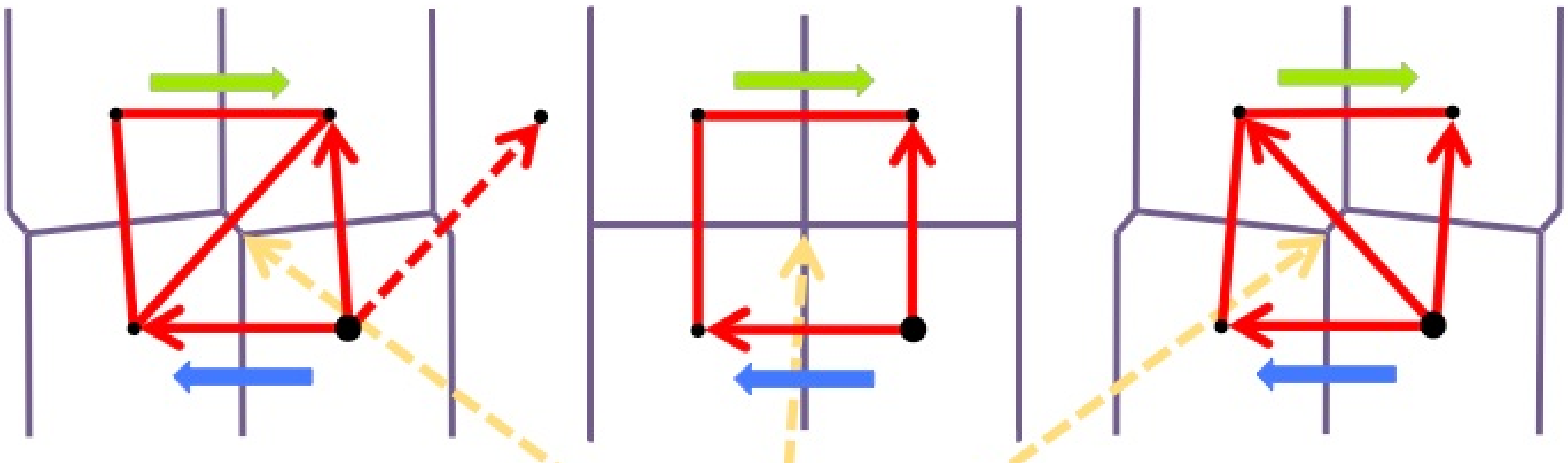
- *A Voronoi point admits at least* $d+1$ *atomic neighbors.*

- A Voronoi point will be called *simple* whenever it has exactly $d+1$ atomic neighbors.

- **Theorem:** *The atomic neighbors of a Voronoi point y belong to a common sphere centered at y and y is interior to the convex hull of its atomic neighbors.*

- **Theorem:** *Generically and (locally Lebesgue) almost surely a Voronoi point is simple.*

Generic Local Patches

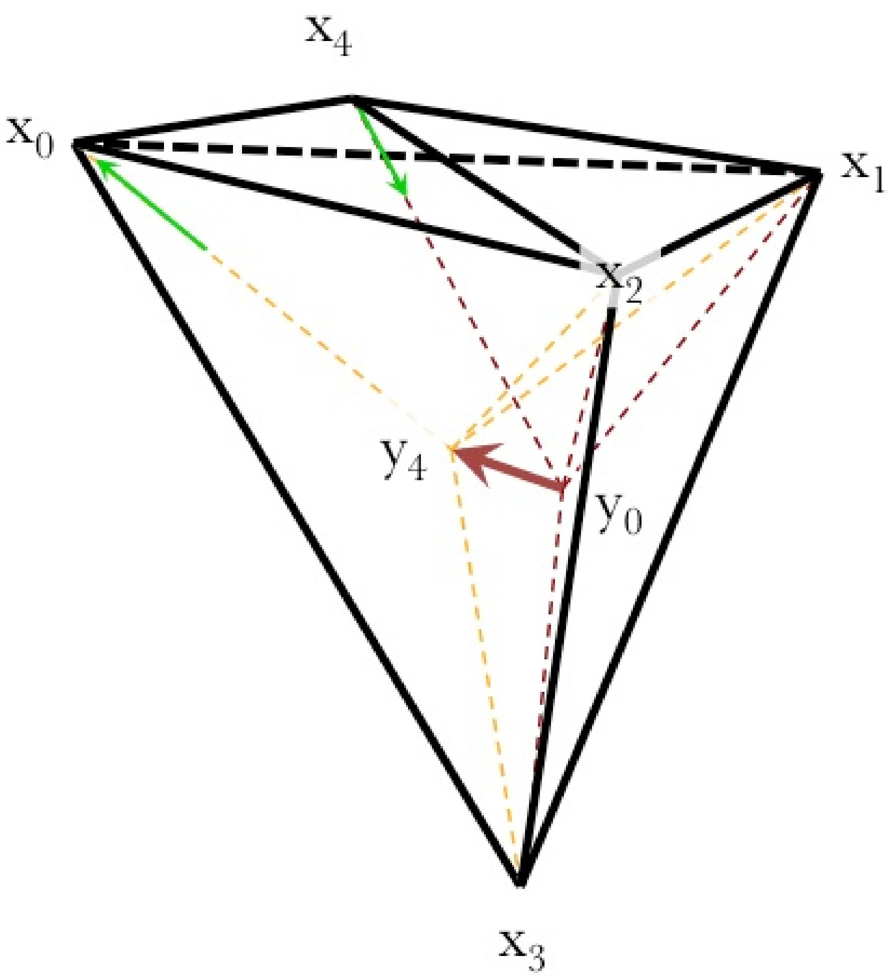


Shear modifies local patches. The middle one is *unstable*. The transition from left to right requires transiting through a *saddle point* of the potential energy.

The Voronoi cell boundaries are shown in blue.

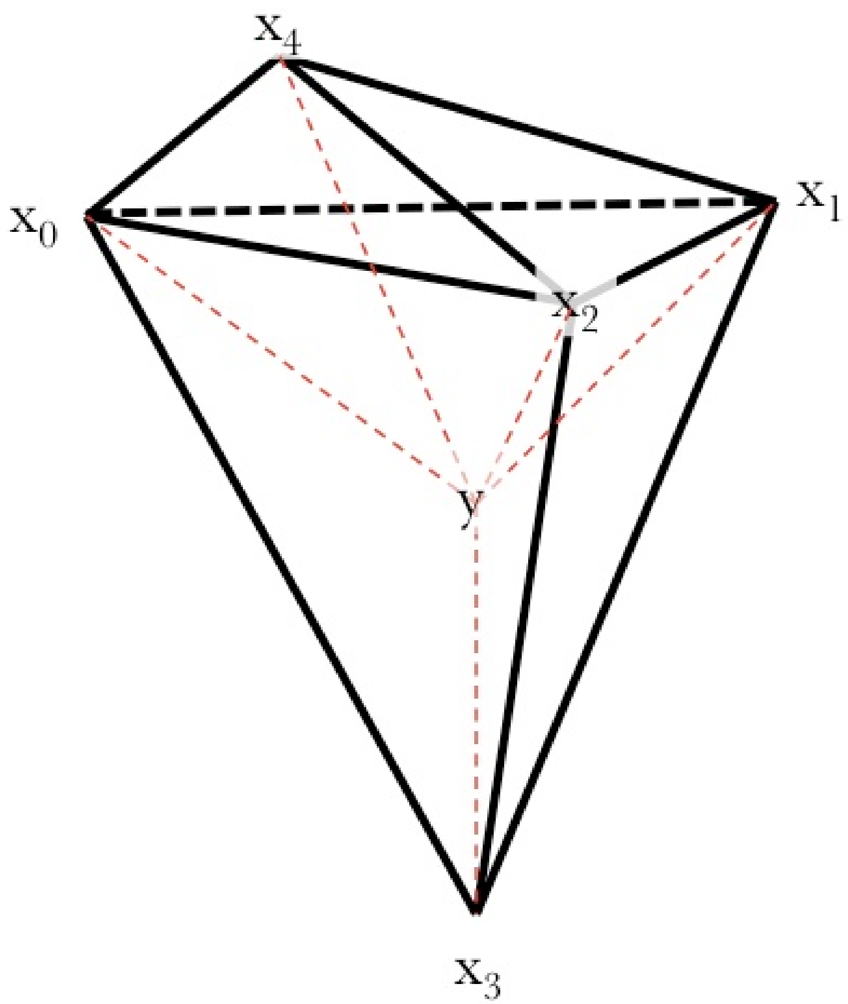
At the bifurcation a Voronoi vertex touches one more Voronoi cell than in the generic case

Generic Local Patches



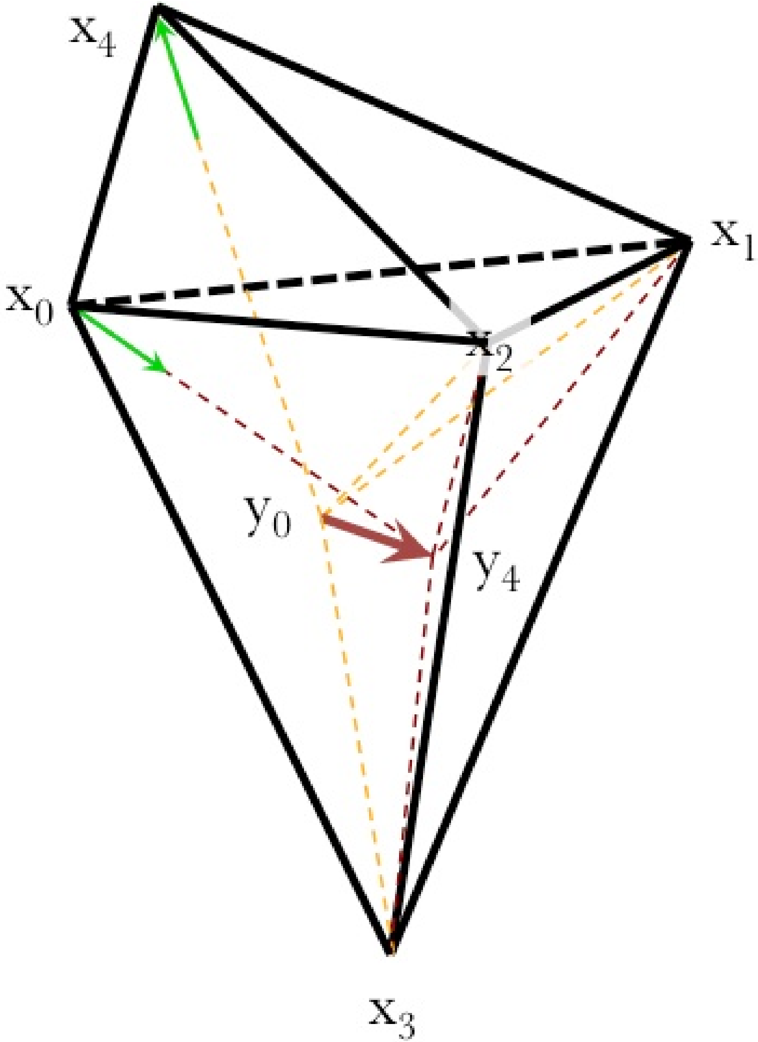
An example of a generic 3D bifurcation.

Generic Local Patches



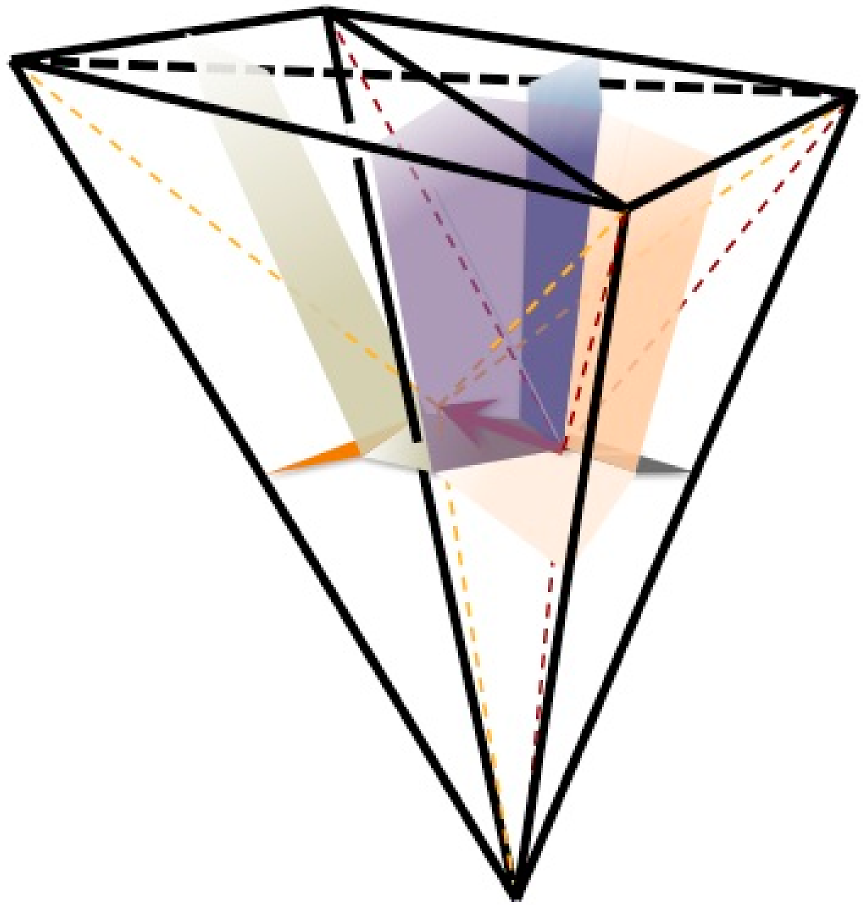
An example of a generic 3D bifurcation.

Generic Local Patches



An example of a generic 3D bifurcation.

Generic Local Patches

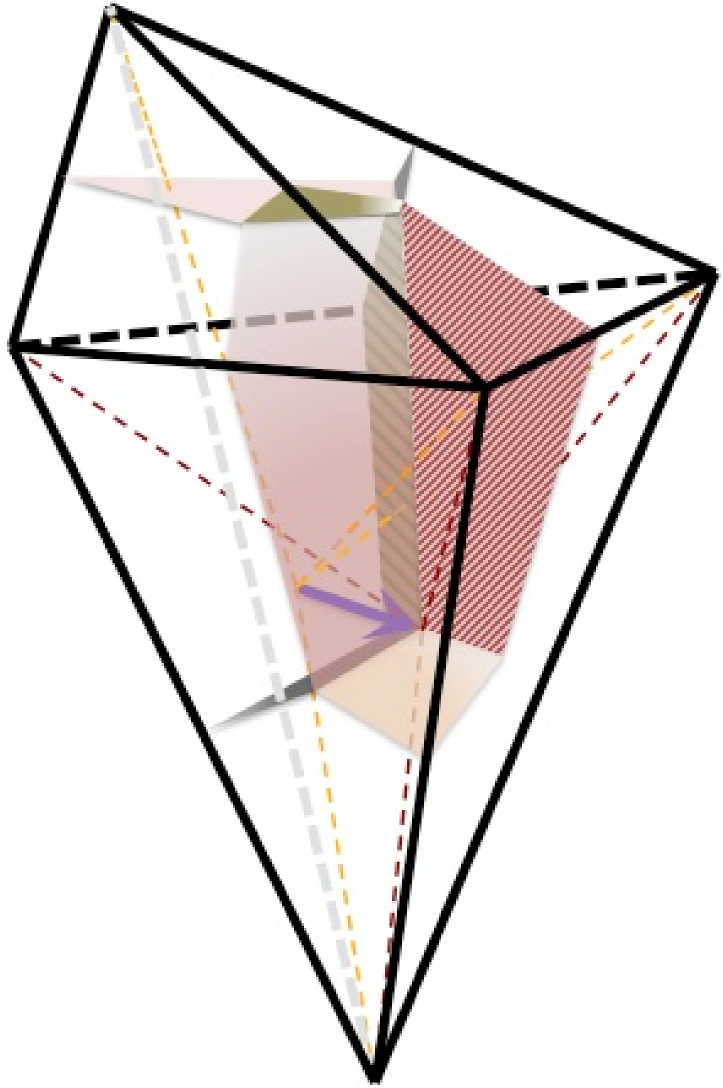


An example of a generic 3D bifurcation.

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



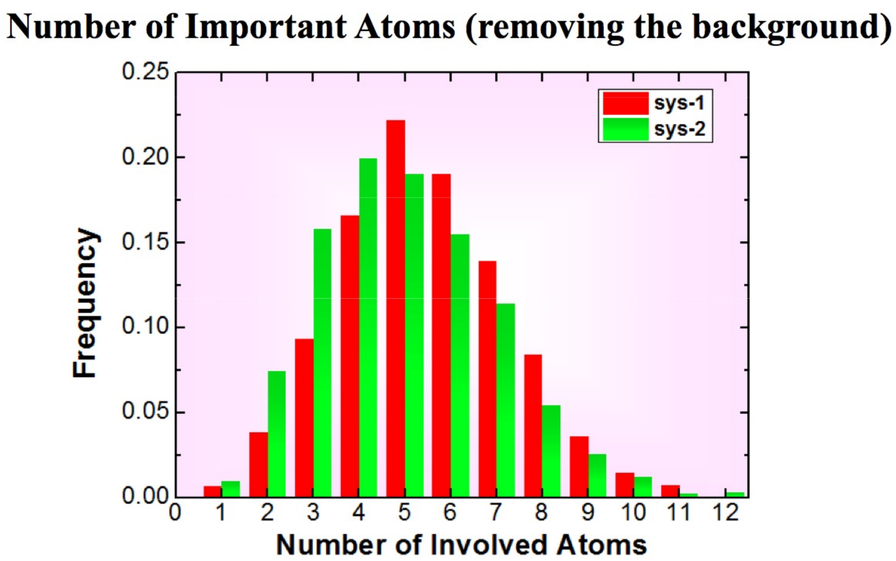
An example of a generic 3D bifurcation.

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

- A bifurcation involves 5 *atoms in dimension* 3.



Statistics of the number of atoms involved in a bifurcation

(Y. Fan, T. Iwashita, T. Egami, '14).

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.

- A *representative* of a local patch $\mathcal{G} \in \mathcal{P}_n$ is a *graph ball* of radius n contained in the Delone graph.

Acceptance Domains

- **Theorem:** *$\mathcal{G} \in \mathfrak{V}_n$ if and only if $\Sigma_{\mathcal{G}}$ is open and its boundary is piecewise smooth.*

- **Theorem:** *$\mathcal{G} \in \mathfrak{V}_n$ if and only if it admits a representative in the Voronoi tiling having only simple Voronoi points*

- **Theorem:** *The union of acceptance domains of the generic patches of size n is dense.*

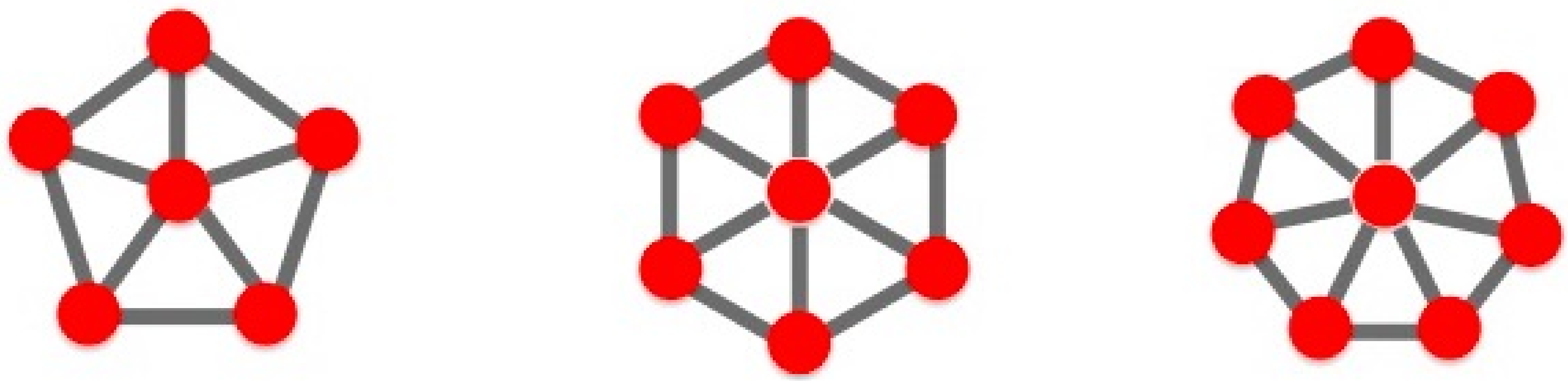
- **Theorem:** *In particular (locally Lebesgue) almost surely and generically an atomic configuration admits a generic local patch.*

Acceptance Domains

- **Empty Sphere Property:** The atomic neighbors of a Voronoi point y are lying on a *sphere* centered at y inside which there is *no other atoms*. In addition y is *interior* to the convex hull of its atomic neighbors.

- **Theorem:** A LOCAL PATCH IS GENERIC IF AND ONLY IF ITS ATOMS ARE THE VERTEX OF A TRIANGULATION, EACH ELEMENTARY SIMPLEX OF WHICH HAVE THE EMPTY SPHERE PROPERTY.

Acceptance Domains



List of graph balls of size 1 (*local cluster*) in 2D
for $h/b < \sqrt{2}$.

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*.

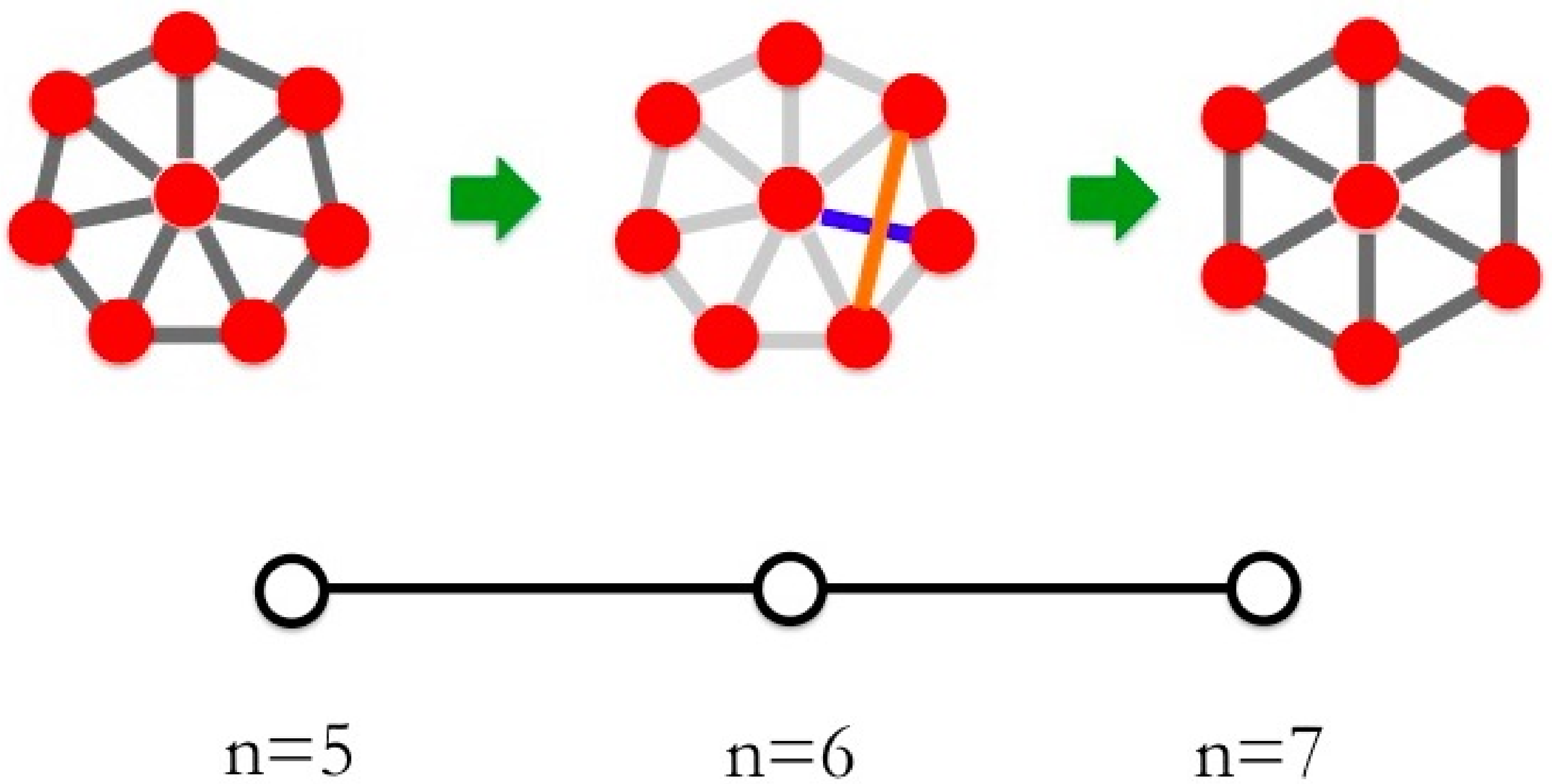
- The set $\mathfrak{V}_n$ itself can then be seen as the set of vertices of a graph

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

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*

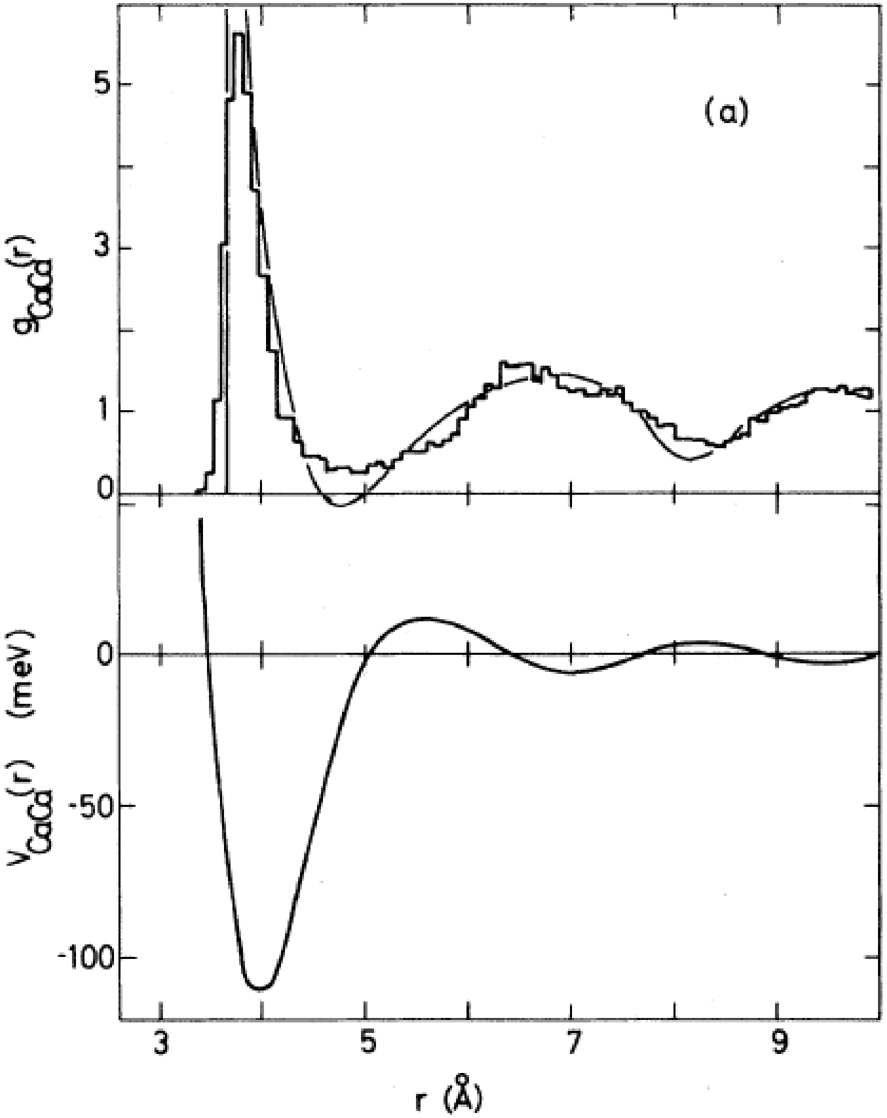


IV - The Anankeon Theory

Fundamental Laws

1. The *Coulomb forces* between atomic cores and valence electrons create *chemical bonding* and *cohesion* in solids
2. Electrons are *fermions*: they resist compression. For free Fermi gas ($\ell_{e-e} =$ average $e - e$ distance, P=pressure)
$$P \sim \ell_{e-e}^{5}$$
3. In metals, valence electrons are *delocalized*, approximately free. Atomic cores localize themselves to *minimize* the Fermi sea *energy* (*jellium*).
4. A good description of the effective atom-atom interactions is provided by *pair potential* with strong repulsion at short distances, Friedel's oscillations at medium range and exponentially decaying tail.

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 and the Ergodic Paradox

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, the principle of Statistical Mechanics and the *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

- *Persistence* theory gives an idea about why large vacancies have a short lifetime. On discrete subset $\mathcal{V} \subset \mathbb{R}^d$, let, $(n_x)_{x\in\mathcal{V}}$, be a family of *i.i.d random variables* with $n_x \in \{0,1\}$ and $\text{Prob}\{n_x = 0\} = p > 0$, $\text{Prob}\{n_x = 1\} = 1-p > 0$.
- Then, if $\Lambda \subset \mathcal{V}$ is a finite set, let $P_\Lambda(t)$ be the probability that $n_x = 0$ for $x \in \Lambda$ and times between 0 and t, given that $n_x = 0$ at $t = 0$ for $x \in \Lambda$. By independence

$$P_\Lambda(t) = \prod_{x\in\Lambda} P_{\{x\}}(t)$$

- Usually $P_{\{x\}}(t) \simeq e^{-t/\tau}$. Hence the life time of Λ as a vacancy is τ/N if Λ has N atoms.

Bonds and Phonons

T. Egami, *Atomic Level Stress*, Prog. Mat. Sci., **56**, (2011), 637-653.

1. Atoms can be related by *edges* using Voronoi cells construction. Long edges are *loose*. Short edges are *bonds*.
2. If r is the vector linking two atoms of a bond, there is a local 6D *stress tensor* defined by

$$\sigma^{\alpha\beta} = V'(|r|) \; \frac{r^{\alpha}\, r^{\beta}}{|r|}$$

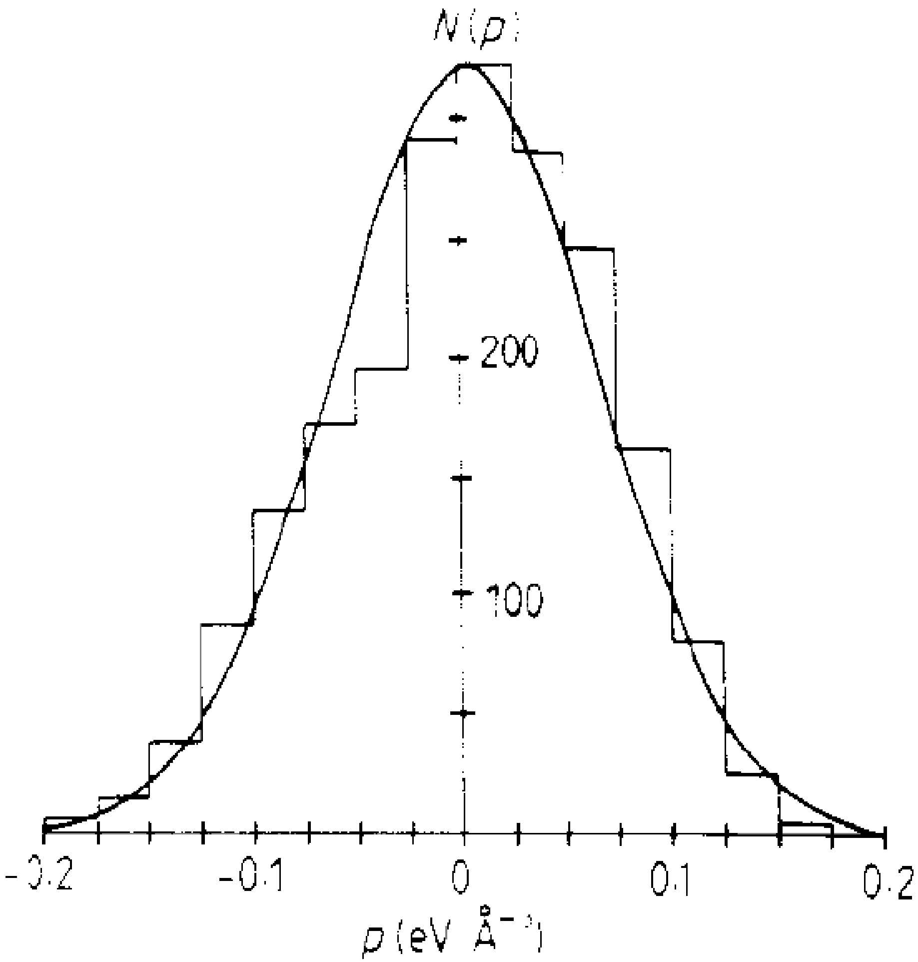
3. **Liquid Phase:** Bonds constitute the *dominant* degrees of freedom ! Phonons are *damped*.
4. **Glass Phase:** Phonons are the *dominant* degrees of freedom. Bonds are *blocked*.

Local Stress Distribution

1. In the liquid state atoms do not find a position minimizing the potential energy, due to *geometrical frustration*. Thermal agitation result in atomic *bond exchanges*, to help atoms minimize their potential energy.
2. The stress tensors associated with bonds behave like *independent random Gaussian variables* !
3. Thanks to *isotropy*, this can be seen on the local *pressure* p and the von Mises local *shear stress* τ

$$p = \frac{1}{3}\sum_{\alpha}\sigma^{\alpha\alpha} \qquad \tau = \sqrt{\sum_{\alpha<\beta}|\sigma^{\alpha\beta}|^2}$$

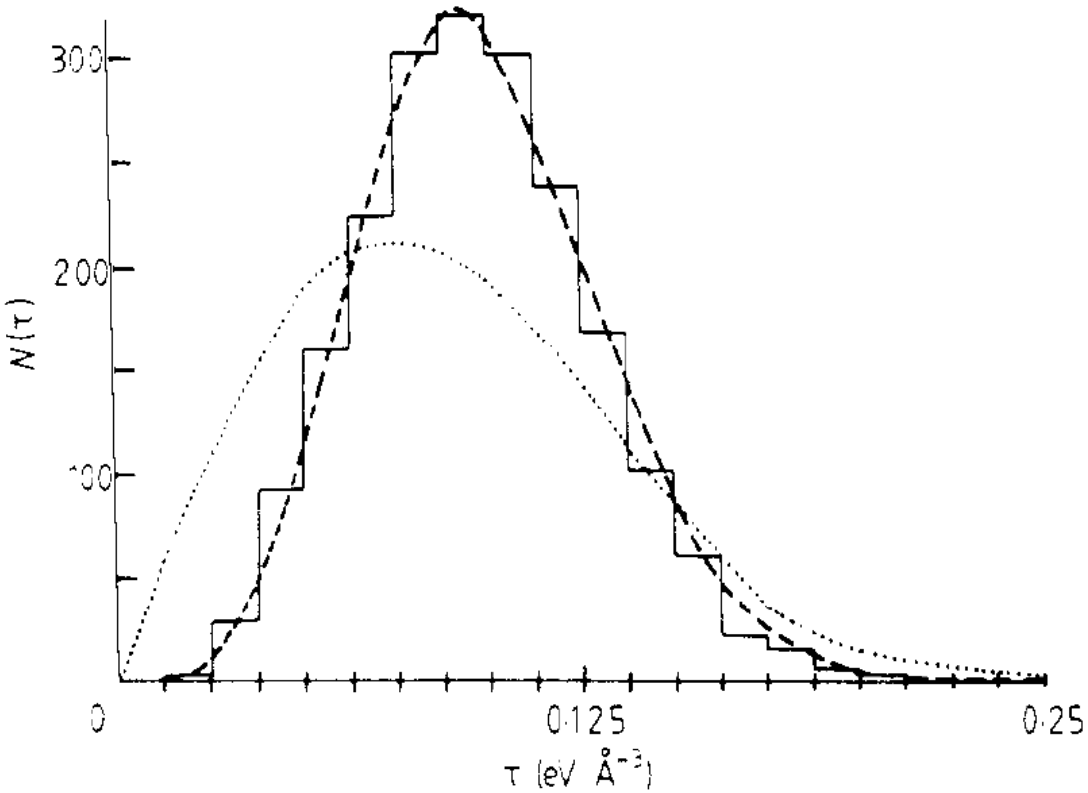
Local Stress Distribution



Pressure distribution in amorphous and liquid metals

taken from
T. Egami & D. Srolovitz, *J. Phys. F*, **12**, 2141-2163 (1982)

Local Stress Distribution



Shear stress distribution in amorphous and liquid metals

Dotted curve: 2*D*-Gaussian
Broken curve: 5*D*-Gaussian

taken from
T. Egami & D. Srolovitz, *J. Phys. F*, **12**, 2141-2163 (1982)

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.

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

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.

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

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.

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

The Anankeon Theory

- Edge partition function

$$Z(e) = (1-\pi)\int_{\mathbb{R}^6} e^{-(p^2/2B+\tau^2/2G)/k_\mathrm{B}T} dp\, d^5\tau \ + \pi$$

  - π is the probability for an edge to be *loose*
    (V_0 is the pair-potential *maximal depth*)

$$\pi \sim e^{-V_0/k_\mathrm{B}T}$$

  - B is the *bulk modulus*
  - G is the *shear modulus*
- Edge free energy $F(e) = -k_\mathrm{B}T \ln Z(e)$

The Anankeon Theory

As a consequence of the anankeon theory, at high temperature, the total potential energy per edge, $3/2\ k_{\mathrm{B}}T$, is equally distributed over the six elastic self-energy of the stress components (equipartition)

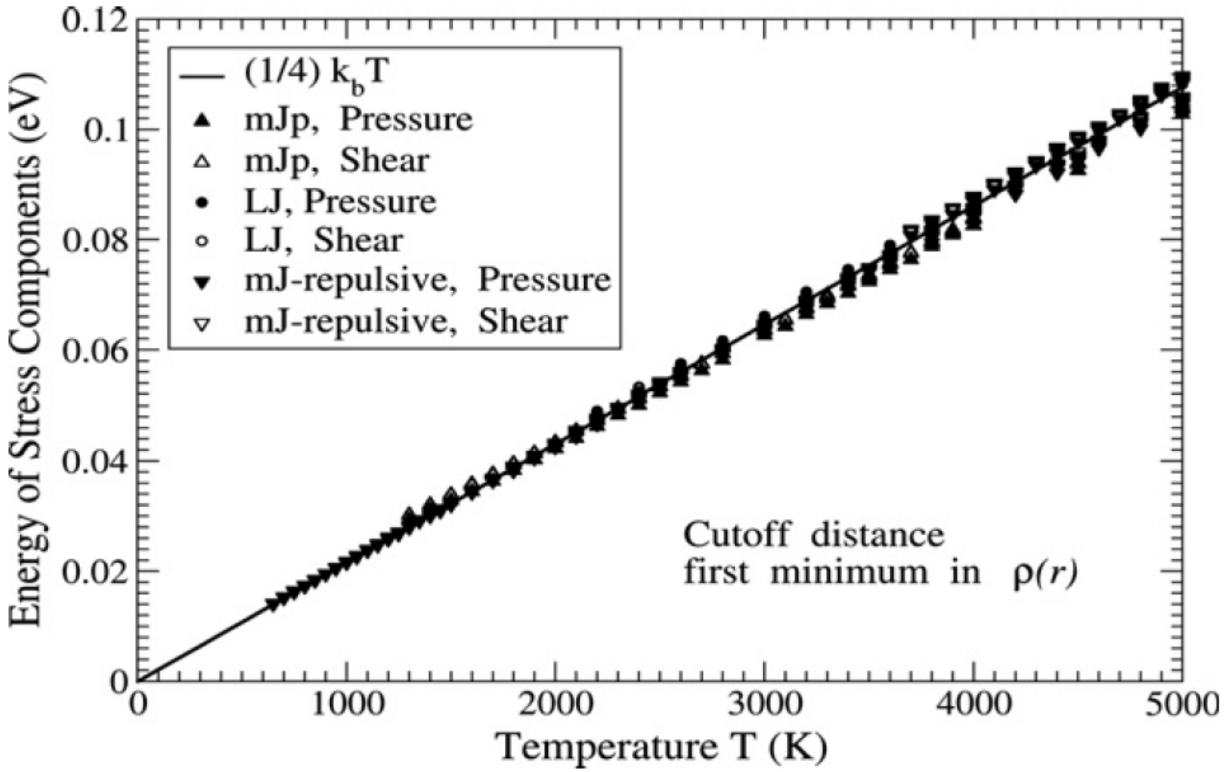
$$\frac{\langle p^2 \rangle}{2B} = \frac{\langle \tau^2 \rangle}{2G} = \frac{k_{\mathrm{B}}T}{4}$$

In particular, the specific heat follows a *law of Dulong-Petit*

$$C_p \overset{T\uparrow\infty}{\sim} \frac{3k_{\mathrm{B}}}{2}$$

The corresponding degrees of freedom are the 6 components of the *stress tensor* on each bond.

The Anankeon Theory



Elastic self-energy of atomic level stresses tested for various pair potentials

LJ: Lennard-Jones potential
mJ: Johnson potential including Friedel's oscillations.

taken from
S.-P. Chen, T. Egami & V. Vitek,
Phys. Rev. B, **37**, 2440-2449, (1988)

The Anankeon Theory

As the temperature decreases, the local edges feel a *long-range stress field* around them. This field can be described through a mean field theory using *continuum elasticity* *(Eshleby '57)*. The stress field is renormalized as

$$K_\alpha \frac{\langle p^2 \rangle}{2B} = K_\gamma \frac{\langle \tau^2 \rangle}{2G} = \frac{k_B T}{4} \qquad K_\alpha = \frac{3(1-\nu)}{2(1-2\nu)} \quad K_\gamma = \frac{15(1-\nu)}{7-5\nu}$$

with ν = *Poisson ratio*. This leads to a prediction of the *glass transition temperature* where $\epsilon_v^{T,crit} \simeq 0.095$ is the *critical strain* computed from percolation theory *(Egami T, Poon SJ, Zhang Z, Keppens V., '07)*

$$T_g = \frac{2BV}{k_B K_\alpha} (\epsilon_v^{T,crit})^2$$

V - Towards a Dissipative Dynamics

(Work in Progress)

Elasticity and Plasticity at Atomic Scale

- Given a fixed *D-patches (local topology, finite volume)*, the domain of validity of elasticity is provided by the acceptance domains, namely the *small atomic movements* which are not changing the *local topology*.

- Microscopically, elastic waves correspond to *phonons* *(Einstein 1907)*.

- *Inelasticity* occurs when the local topology changes, namely when there is a *jump* in the graph of *contiguity*. Such jumps are *unpredictable* in practice. They correspond to the *anankeon* degrees of freedom

Configuration Space

- Given $\mathcal{G} \in \mathfrak{B}_n$, each edge e of $\mathcal{G}$ is either *loose* or a *bond*. This can be represented by a random variable $N_e \in \{0, 1\}$ where
  - $N_e = 0$ if e is *loose*
  - $N_e = 1$ if e is a *bond*
  - $\text{Prob}\{N = 0\} = \pi, \ \text{Prob}\{N = 1\} = 1 - \pi$
  - if $e \neq e'$, then $N_e, N_{e'}$ are *independent*.
- Each edge $e \in \mathcal{G}$ with $N_e = 1$ supports the *six components* of a local stress tensor σ_e which is distributed according to *Maxwell-Boltzmann*

$$\text{Prob}\left\{\sigma_e \in \Delta \subset \mathbb{R}^6 | N_e = 1\right\} = \int_\Delta \exp\left\{-\left(\frac{p_e^2}{2Bk_\text{B}T} + \frac{\tau_e^2}{2Gk_\text{B}T}\right)\right\} d^6\sigma_e$$

Interactions

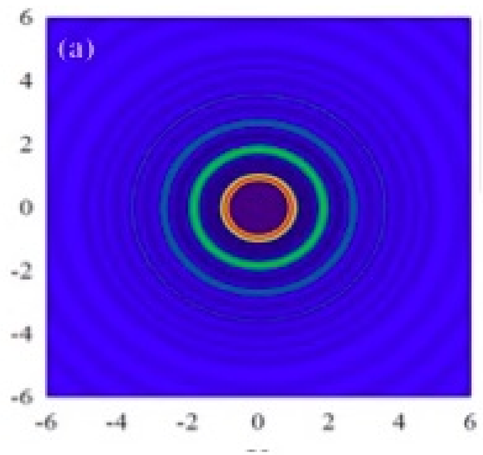
- $g_{\alpha,\beta}(r,\vec{u})$ denotes the 2-points correlation function between sites with *local shear stress* with sign $\alpha = \pm$ and $\beta = \pm$ respectively and located at distance $r > 0$ in the direction $\vec{u} = \vec{r}/|\vec{r}|$.
- For $d = 2$ the *isotropic* and *quadrupolar* parts are defined by

$$g_0 = \frac{1}{4}(g_{+,+} + g_{+,-} + g_{-,+} + g_{-,-}) \qquad G = \frac{1}{4}(g_{+,+} - g_{+,-} - g_{-,+} + g_{-,-})$$

- Numerical simulation (molecular dynamics) performed in the liquid phase *(Egami's group 2015)* have shown that $g_{\alpha,\beta}(r,\vec{u})$ exhibits *oscillations* and *exponential decay* in r and a 4-fold symmetry in $\vec{u}$.
- A similar results occurs for the *stress-stress* correlation function and also in dimension $d = 3$.

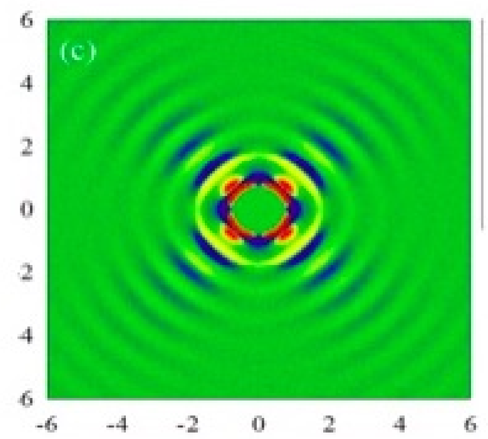
Interactions

isotropic component



Asymmetric Density Correlation Function

quadrupolar component



Interactions

- A comparison with the Eshelby theory suggests that the cavity method should apply at the atomic scale as well explaining the numerical results.

- This suggests an *Ising type model* for the interaction between local stress since *only the sign* of the shear stress seems to matter.

- The *frustration* created by the quadrupole and isotropic interaction should lead to a *spin-glass like transition* at lower temperature.

Markov Dynamics

- The contiguousness graph $\mathfrak{G}_n$ should leads to a *Markov process* represented by the rate probability of transition $\mathbb{P}^n_{\mathcal{G}\to\mathcal{G}'}$ between two generic *contiguous* local patches

$$\mathbb{P}^n_{\mathcal{G}\to\mathcal{G}'} = \Gamma(\mathcal{G} \to \mathcal{G}') \exp\left\{-\left(F_{\mathcal{G}'}(\sigma') - F_{\mathcal{G}}(\sigma)\right)/k_{\mathrm{B}}T\right\}$$

  where $F_{\mathcal{G}}(\sigma)$ represents the configuration dependent free energy associated with the local patch $\mathcal{G} \in \mathfrak{V}_n$.

- Here $\Gamma(\mathcal{G} \to \mathcal{G}') \sim e^{-W/k_{\mathrm{B}}T}$ is proportional to the inverse of the *typical transition time*. This time is controlled by the height W of the potential energy barrier between the two configurations, following an *Arrhenius law*.

Markov Dynamics

- Once the model established the *infinite volume limit*, corresponding to the limit $n \to \infty$ must be considered. Standard theorems exist in the literature on *Dirichlet forms* about the existence and the uniqueness of such limiting processes.

- Then it will be necessary to prove that, within this model, the main properties discovered by theoreticians are actually a consequence of the model.

- One critical data will be to look at the time scale involved in the liquid and the glassy state.

INSTITUT
MITTAG-LEFFLER
THE ROYAL SWEDISH ACADEMY OF SCIENCES

"bringing together the past and present for the future of mathematics"

Thanks for Listening !