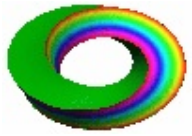
ATOMIC MOTION

in

APERIODIC SOLIDS

Sponsoring



CRC 701, Bielefeld

Jean BELLISSARD

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

Collaborations

J. Pearson, (*Gatech*, Atlanta, GA)

J. Savinien, (*U. Metz*, Metz, France)

A. Julien, (*U. Victoria*, Victoria, BC)

I. Palmer, (*NSA*, Washington DC)

R. Parada, (*Gatech*, Atlanta, GA)

Main References

C. Janot, *Quasicrystals: A Primer*, Oxford Univ. Press, New York, (1992).

H. Takakura, C. Pay Gómez, A. Yamamoto, M. de Boissieu, A. P.Tsai, Nature Mat., **6**, (2007), 58-63.

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

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.

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

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

Content

1. Aperiodic Materials
2. Structure
3. The Tiling Space
4. Atomic Motion

I - Aperiodic Materials

A List of Materials

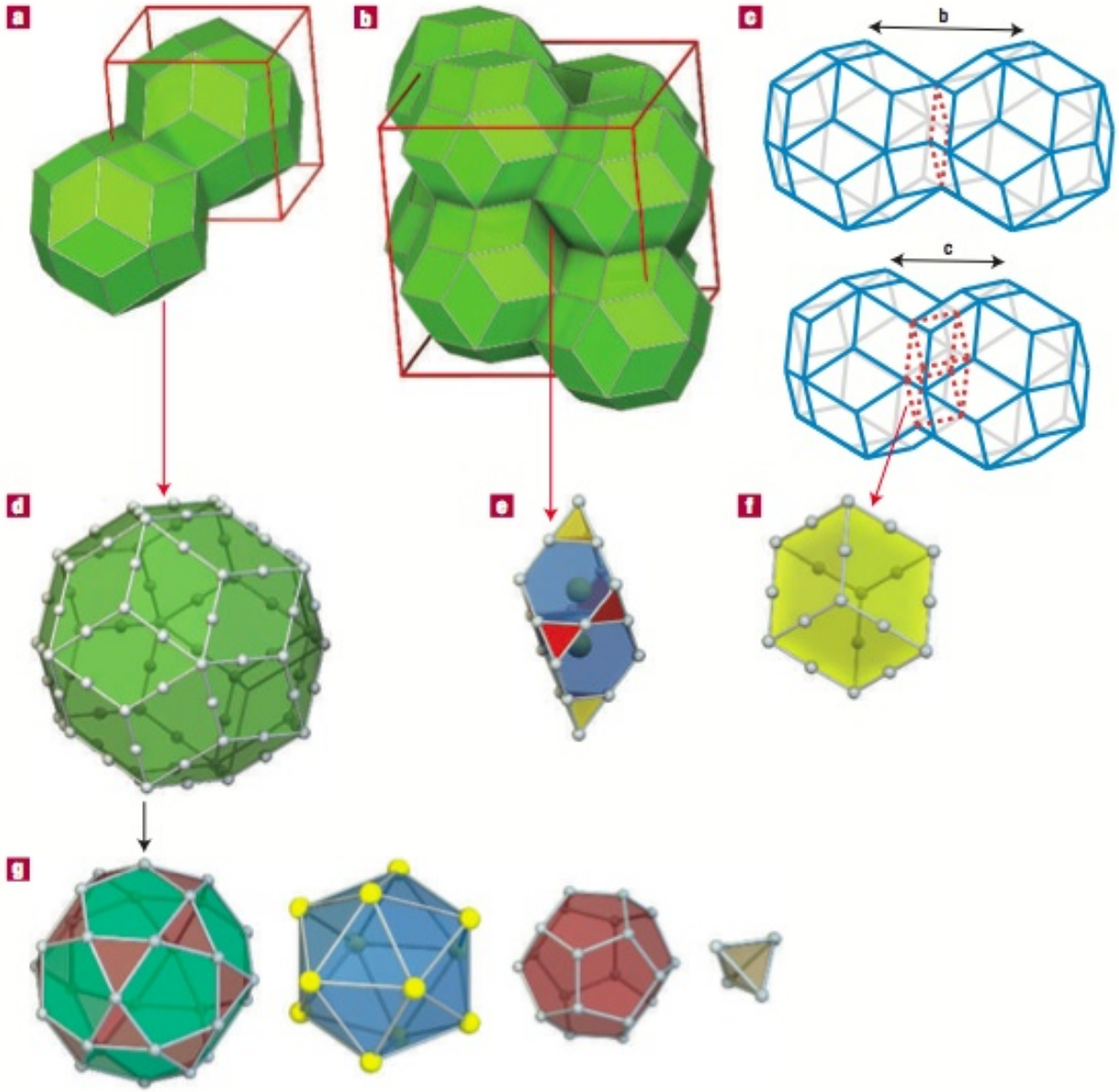
1. Aperiodicity for Electrons
   - Crystals in a Uniform Magnetic Field
   - Semiconductors at very low temperature

2. Atomic Aperiodicity
   - Quasicrystals
   - Glasses
   - Bulk Metallic Glasses

Quasicrystals

1. Stable Ternary Alloys *(icosahedral symmetry)*
   - High Quality: **AlCuFe** ($Al_{62.5}Cu_{25}Fe_{12.5}$)
   - Stable Perfect: **AlPdMn** ($Al_{70.}Pd_{22}Mn_{7.5}$)
     AlPdRe ($Al_{70.}Pd_{21}Re_{8.5}$)

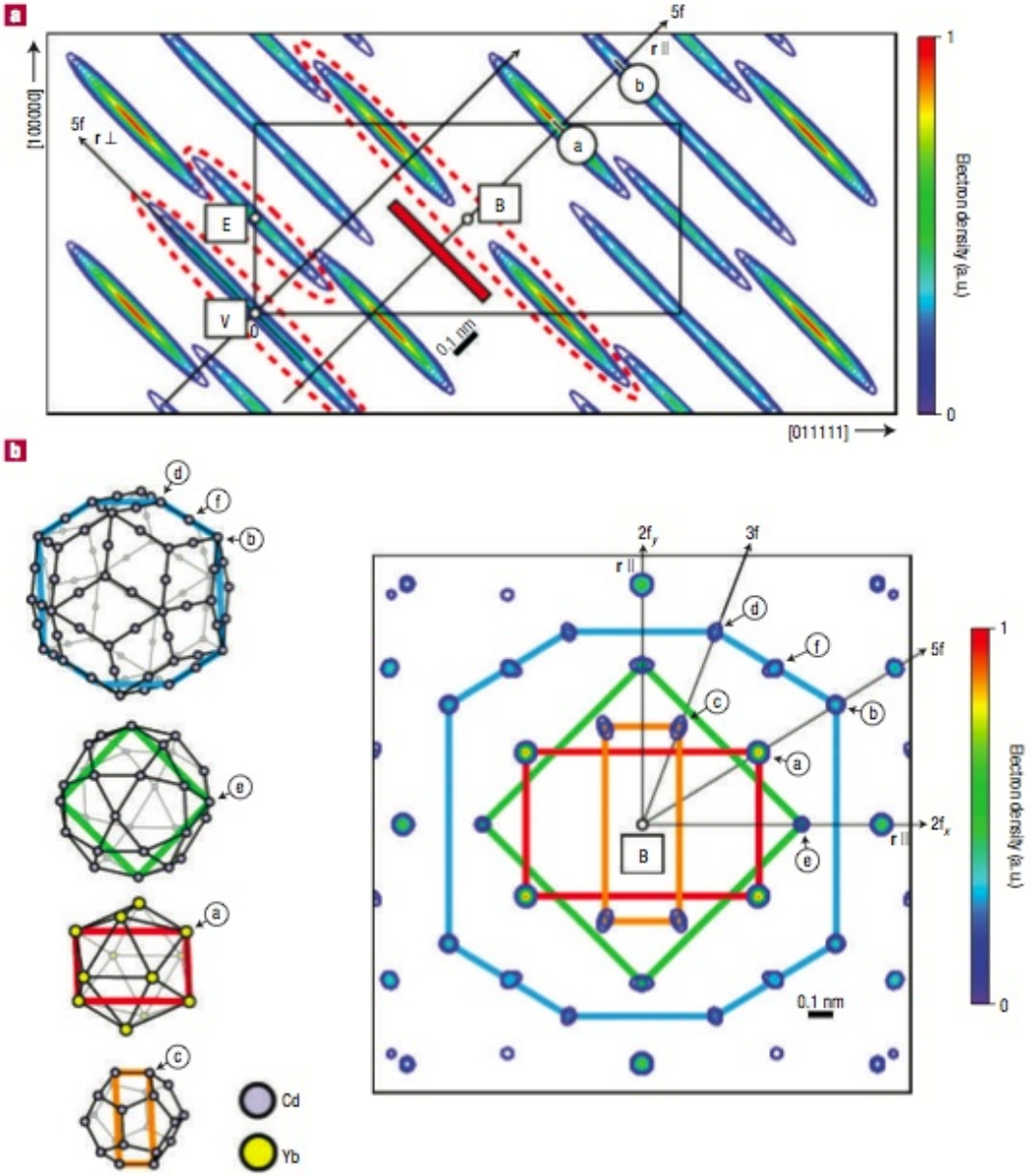
2. Stable Binary Alloys
   - Periodic Approximants: **$YbCd_6$, $YbCd_{5.8}$**
   - Icosahedral Phase **$YbCd_{5.7}$**



Clusters in *YbCd*-approximants.

(Cd in grey, Yb in yellow)

H. Takakura, et al., Nat. Mat. '04

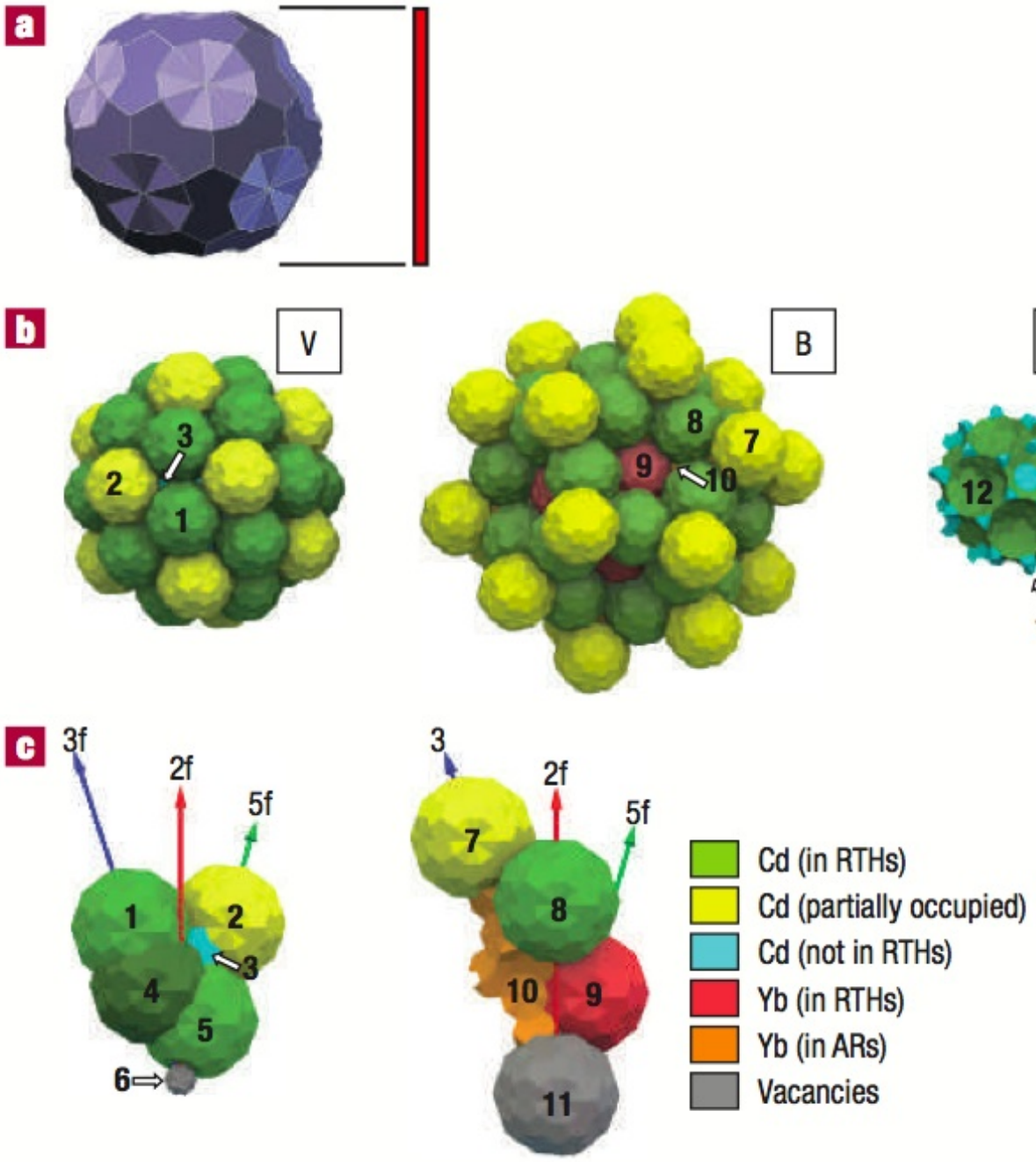


Clusters in

i-YbCd.

(Cd in grey, Yb in yellow)

H. Takakura, et al., Nat. Mat. '04



Acceptance domains in *Tiling Space*

H. Takakura, et al., Nat. Mat. '04

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, ...*

II - Structure

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 (ℓ_{e-e} = average $e-e$ distance, P=pressure)

$$P \sim \ell_{e-e}^{5}$$

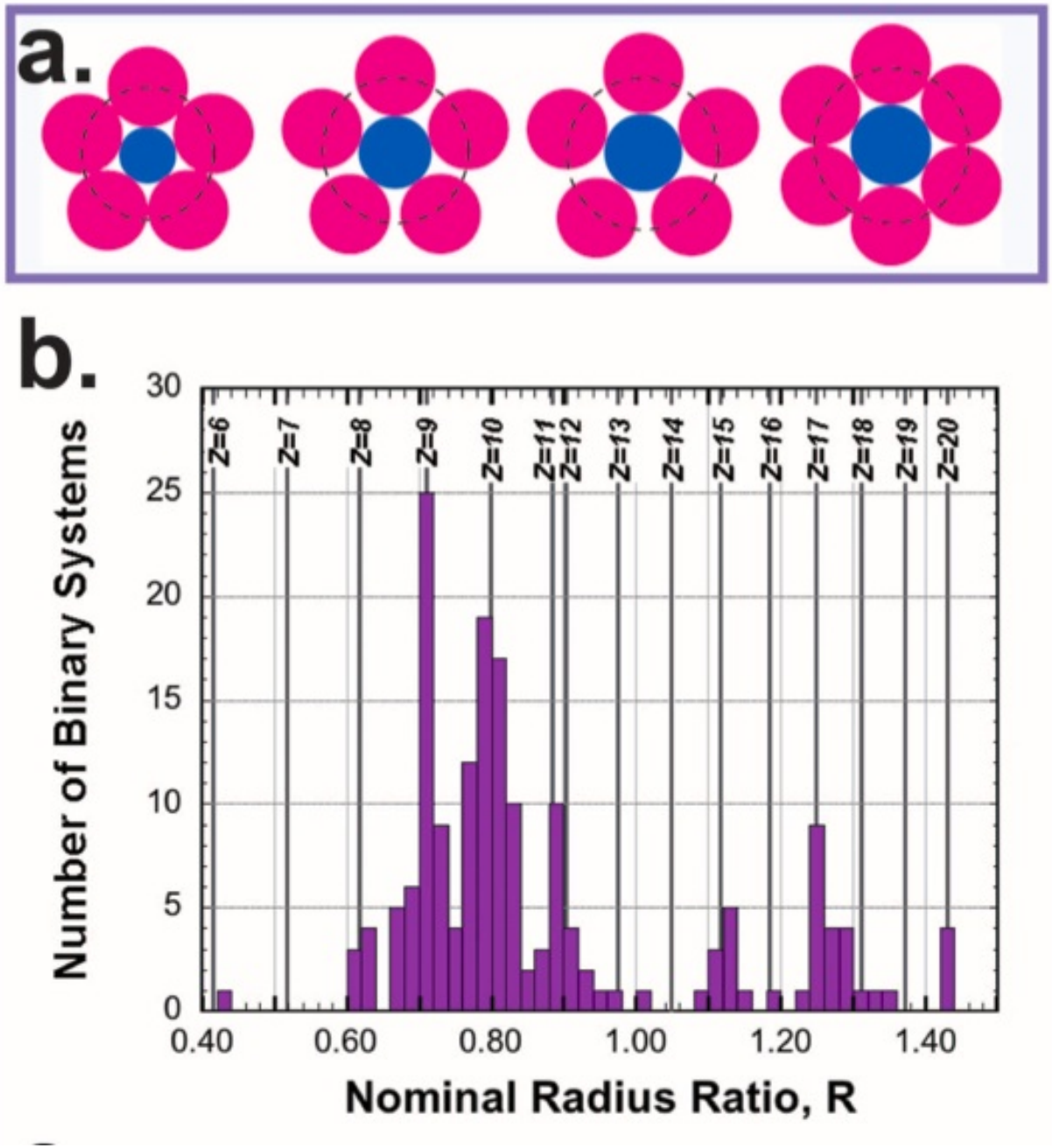
3. In metals, valence electrons are *delocalized*, approximately free. Atomic cores localize themselves to *minimize* the Fermi sea *energy* (*jellium*).
4. The atomic distribution can be seen as a distribution of *hard spheres* with various radii for various atomic species.

Cluster Models

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

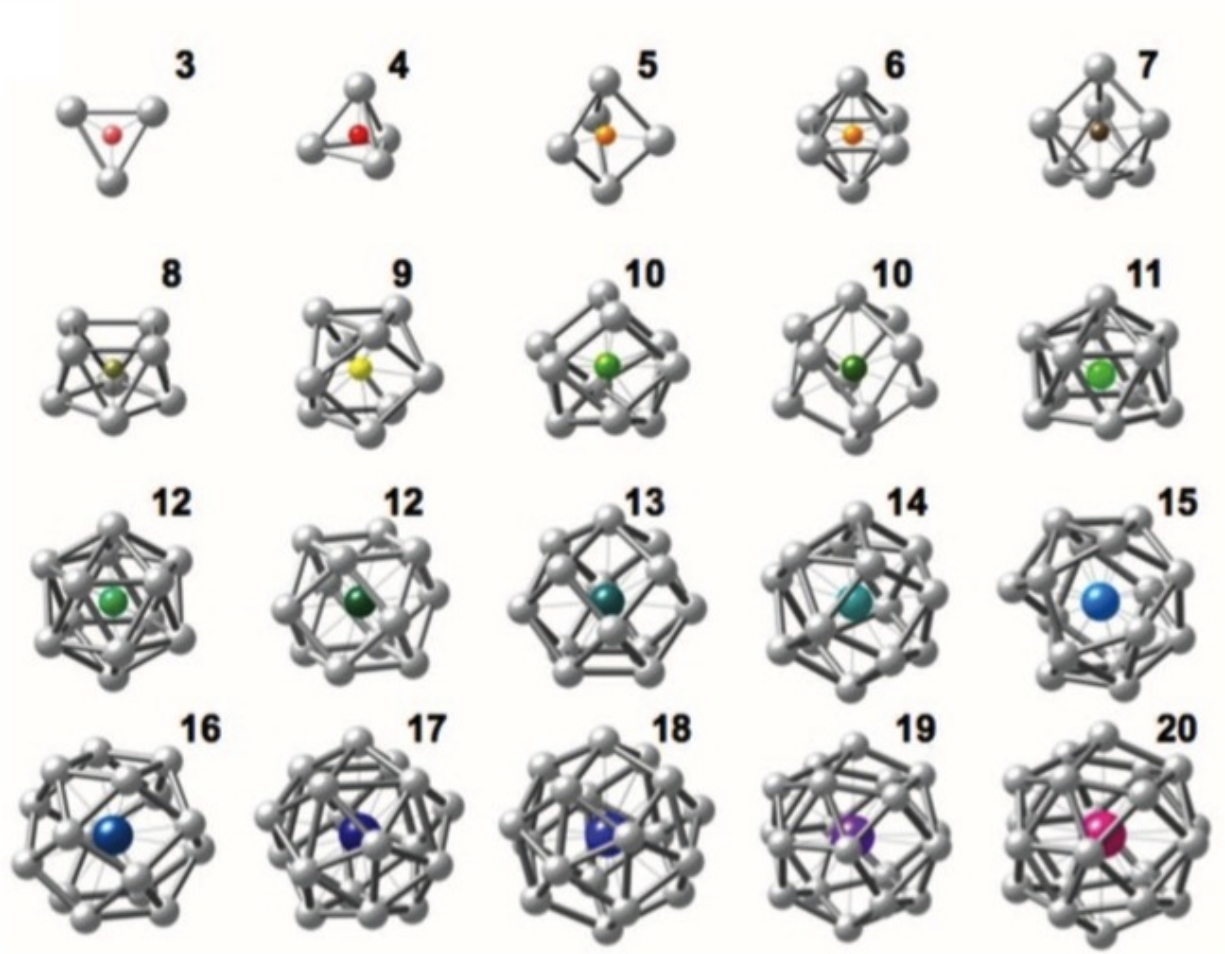
D. B. Miracle, *A structural model for metallic glasses*, Nature Mat., **3**, (2004), 697-702.

1. Cluster models are based on *densest packing* distributions of hard spheres.
2. A *cluster* is formed from one solute atom and a layer of solvent atoms.
3. At larger scales cluster behave like new particles with almost spherical shape.



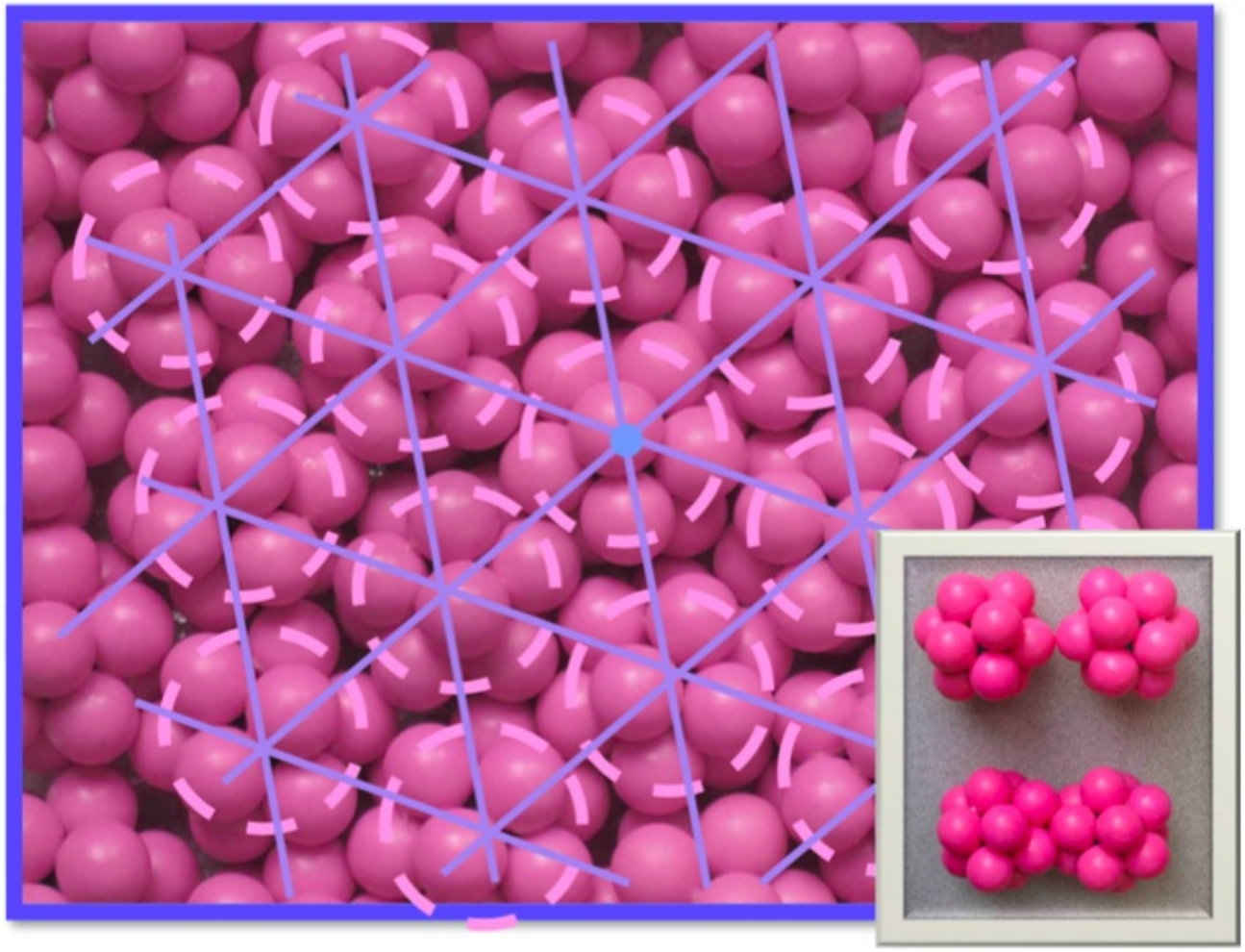
2*D*-clusters

(D. Miracle, et al. '04)



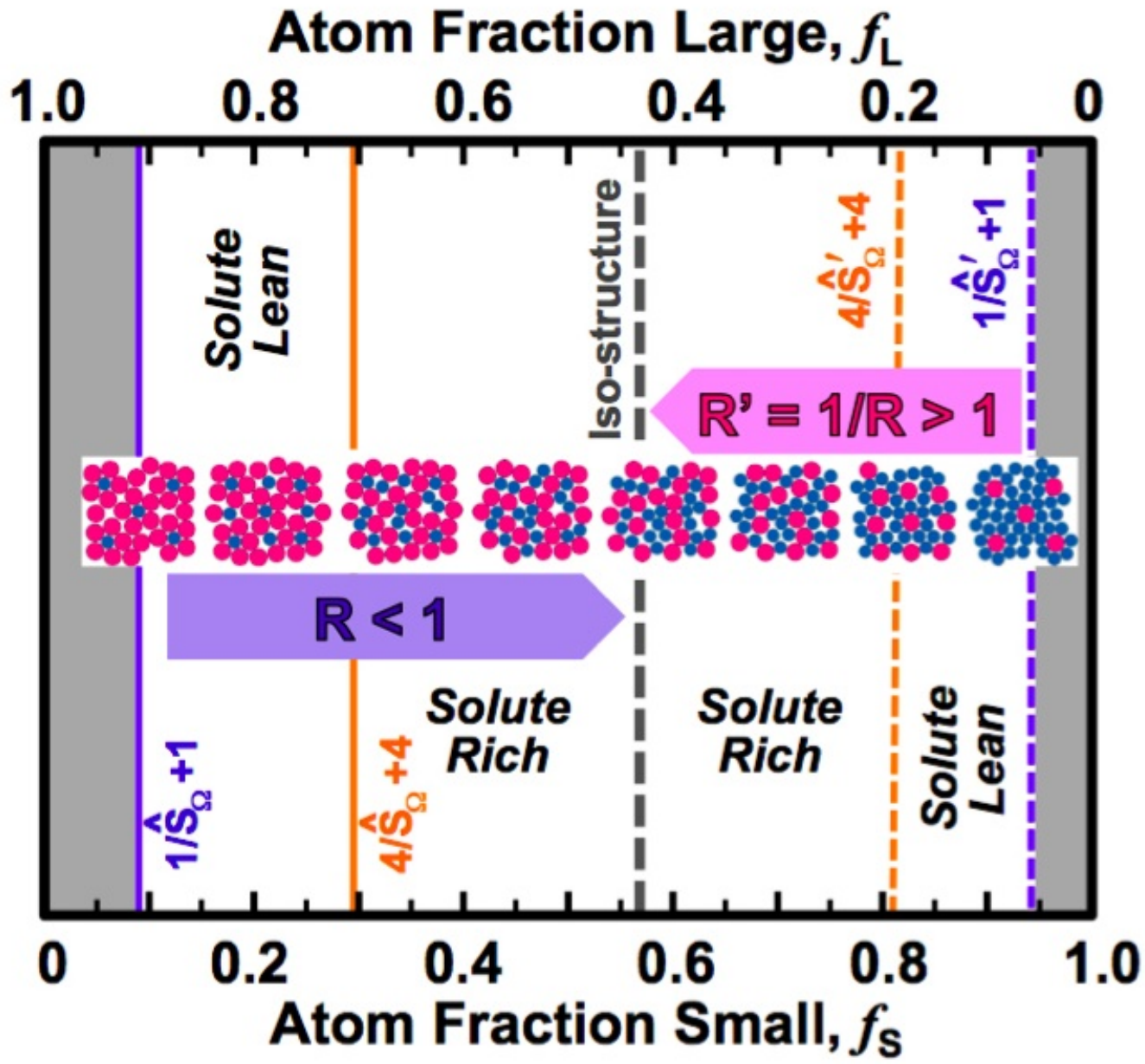
3*D*-clusters

(D. Miracle, et al. '04)



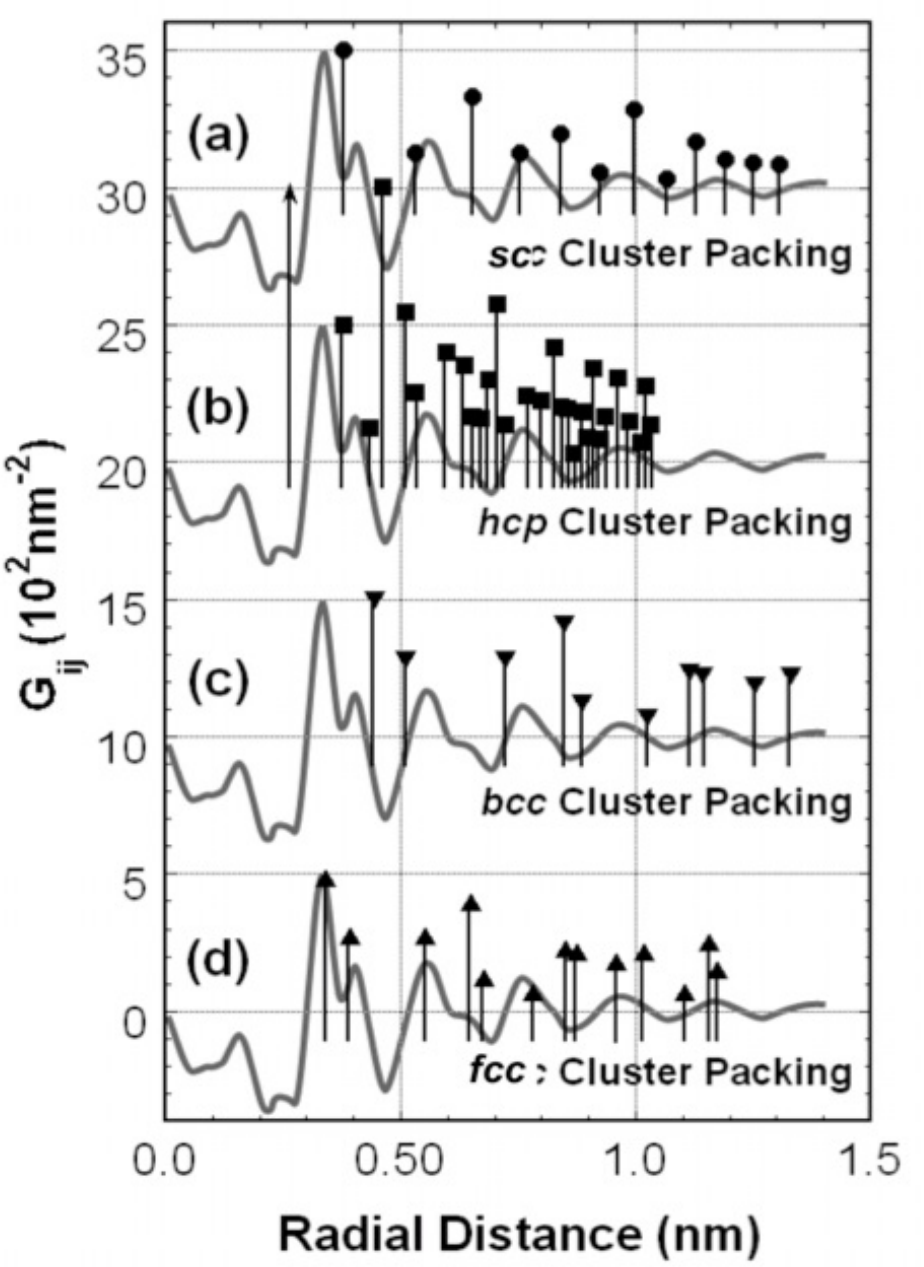
Packing Clusters

(D. Miracle, et al. '04)



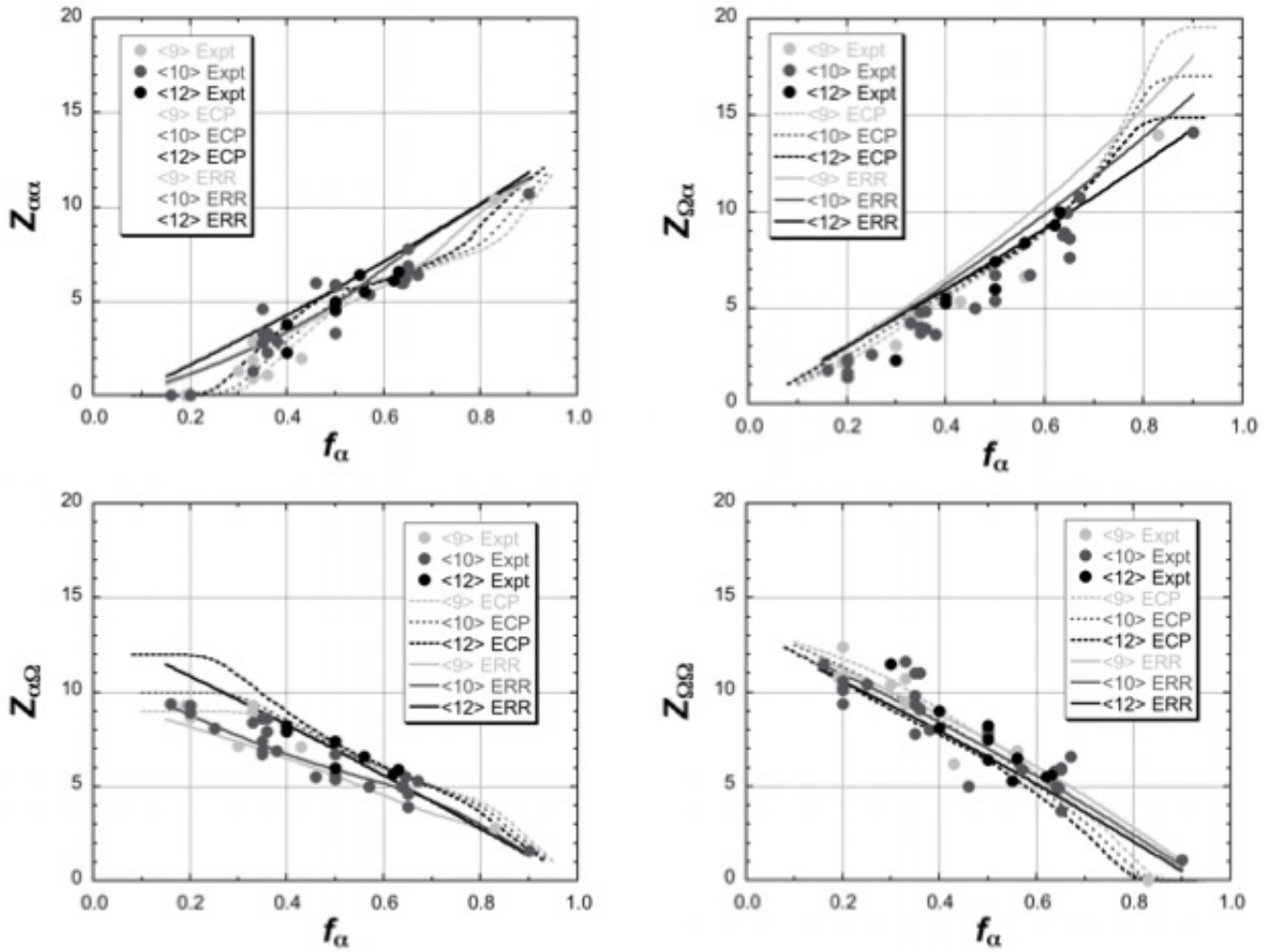
Clusters Evolution

(D. Miracle, et al. '04)



Comparison between cluster packing and Correlation for various crystals

(D. Miracle, et al. '04)



Measured (filled circles) and predicted (lines) partial coordination numbers.

(D. Miracle, et al. '04)

Medium Range Structure

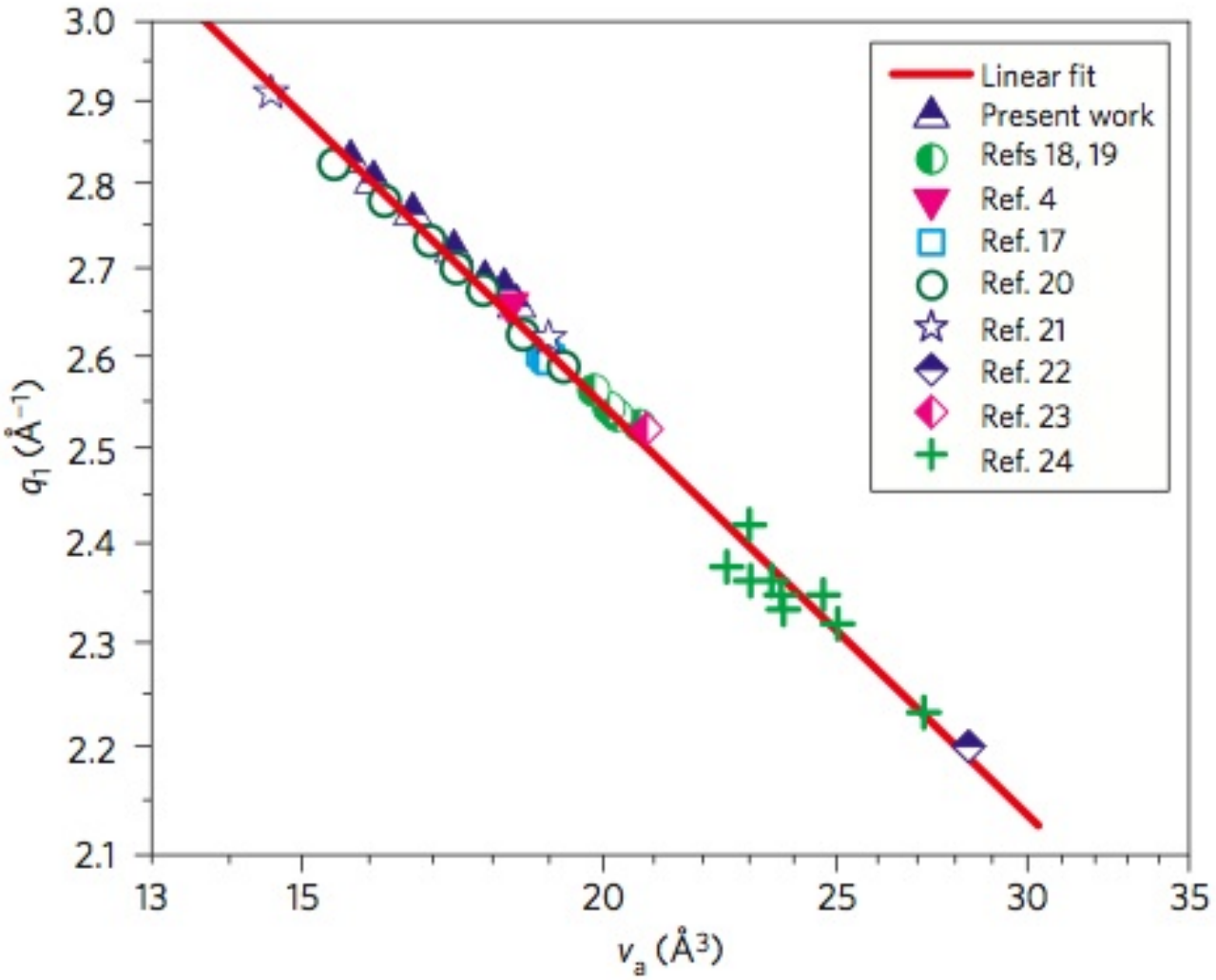
D. Ma, A. D. Stoica, X.-L. Wang, Nature Mat., **8**, (2009), 30-34.

- The *Medium Range* (MR) structure has been studied using neutron and X-ray diffractions techniques.
- If q_1 denotes the position of the *first sharp diffraction peak* and if v is the *atomic volume*, the Ehrenfest relation predicts

$$q_1 v^{1/3} = const. \qquad \textbf{(Ehrenfest)}$$

- In BMG's *measurements* show that, at distance of order 4-6$\mathring{A}$.

$$q_1 v^{\alpha} = \kappa \qquad \alpha = 0.433 \pm 0.007 \qquad \kappa = 9.3 \pm 0.2$$



Experimental fit with

$q_1 v_a^{\alpha} = \kappa$

(D.Ma et al. '09)

III - Tiling Space

Configurations

- Each atom is represented by a pair (x, a), where $x \in \mathbb{R}^3$ is the *position* of its nucleus, and $a \in \mathcal{A}$ labels the atomic *species*. Hence $\mathcal{A}$ is finite with $\#\mathcal{A} = (2, 3, 4, 5)$ in practice.

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- Let $r_a > 0$ be the radius of the hard sphere representing atoms of species a. Then

$$\operatorname{dist}\left((x, a), (y, b)\right) \geq r_a + r_b \tag{3}$$

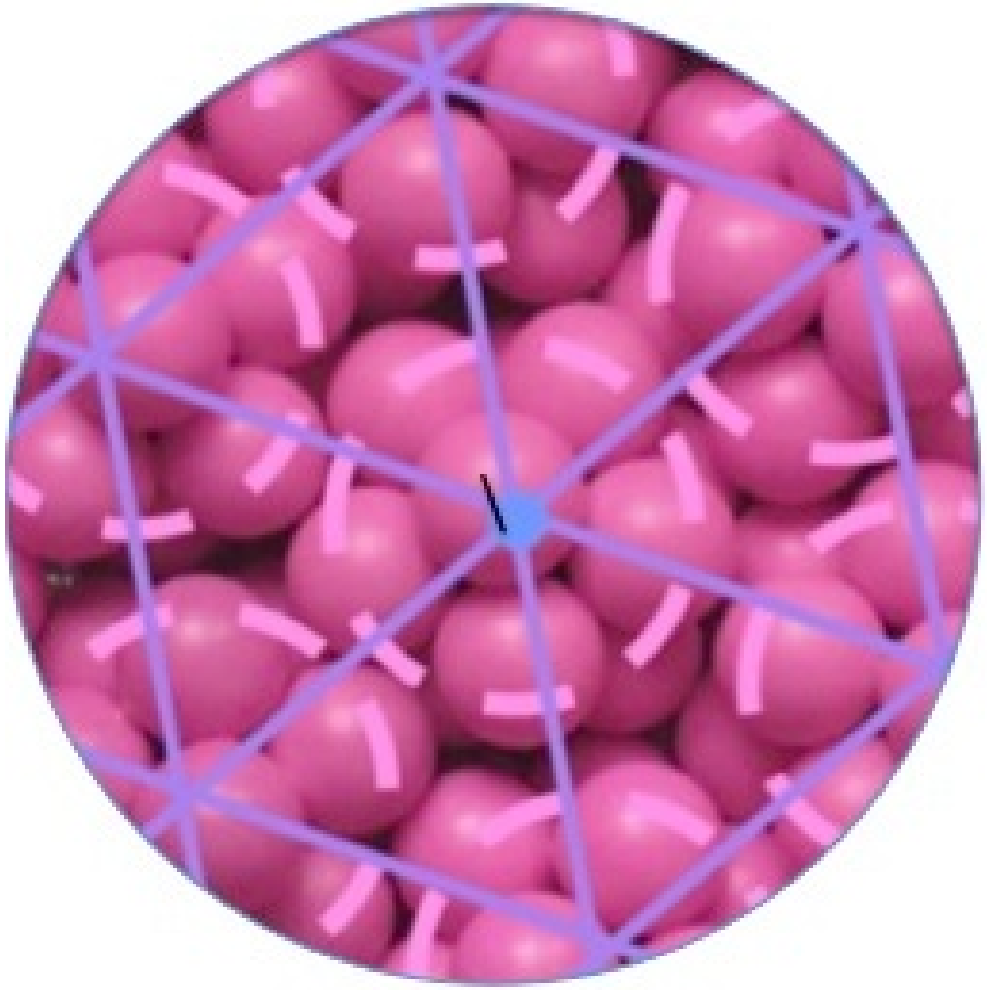
- ρ_a denotes the number of atoms of species a per unit volume.
- A *configuration* $\mathcal{L}$ is a family of all (x, a)'s in the solid, satisfying eq. (1) and with concentration $\rho = (\rho_a)_{a \in \mathcal{A}}$. The set of atomic positions is $\operatorname{supp}(\mathcal{L})$.

Local Patches

- A *patch* of *radius* $r > 0$ is a finite set of atoms in a ball of radius $r > 0$ centered at one atomic position and translated at the origin

$$p = \{(y - x, a)\,;\,(y, a) \in \mathcal{L}\,,\ \|y - x\| \leq r\}$$

Local Patches



A local patch

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- There is a way to measure the *distance* between two patches, using the so-called *Hausdorff metric*. Let $\mathcal{Q}_r$ denotes the *completion* of $\mathcal{Q}_r^{(0)}$. Then

$$\mathcal{Q}_r \textit{ is compact}$$

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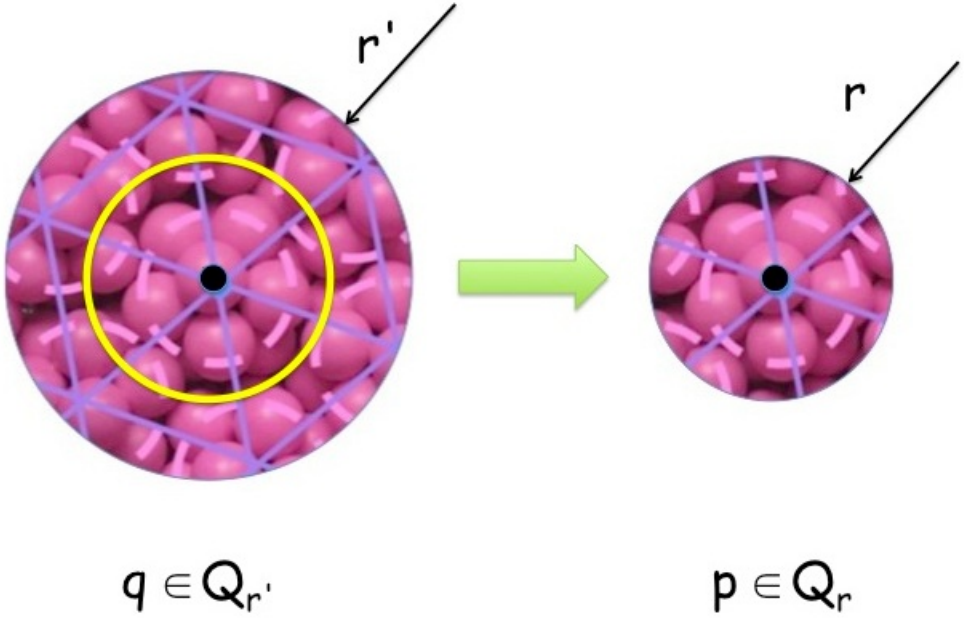
- A *point* in $\mathcal{Q}_r$is a limit of local patches, namely, a *configuration* of atoms in a ball of radius r with *one atom* at the *origin*.

Restriction Map



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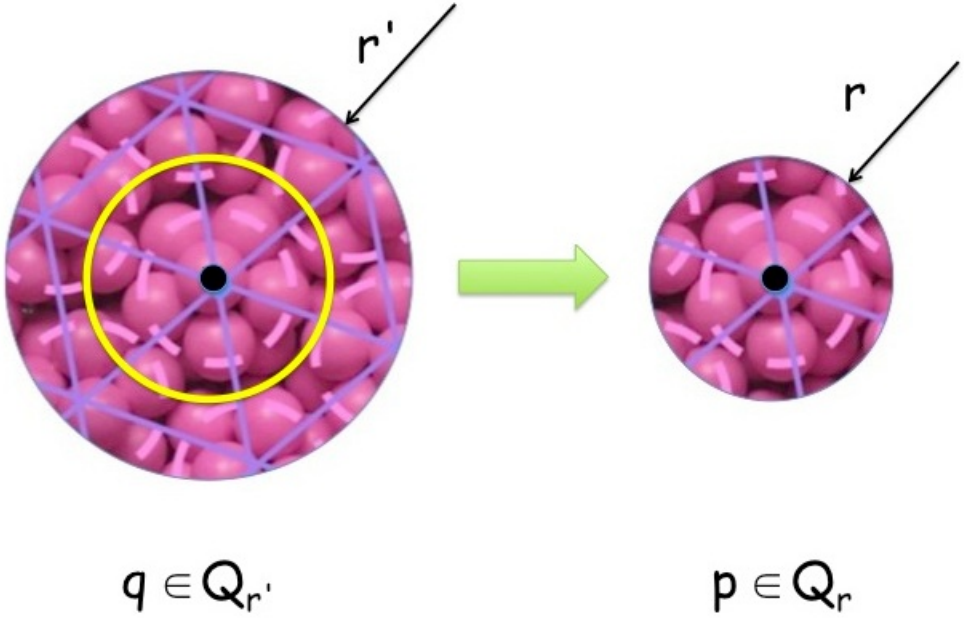
Restriction Map



If $r' > r$ there is a *restriction* map

$$\pi_{r \leftarrow r'}(q) = p$$

this map is continuous

Inverse Limit

- The *inverse limit* $\Xi = \lim_{\leftarrow}(\mathcal{Q}_r, \pi_{r \leftarrow r'})$ is the set of *increasing compatible* families of patches

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- Ξ is called the *tiling space*. Ξ *is a compact space*.

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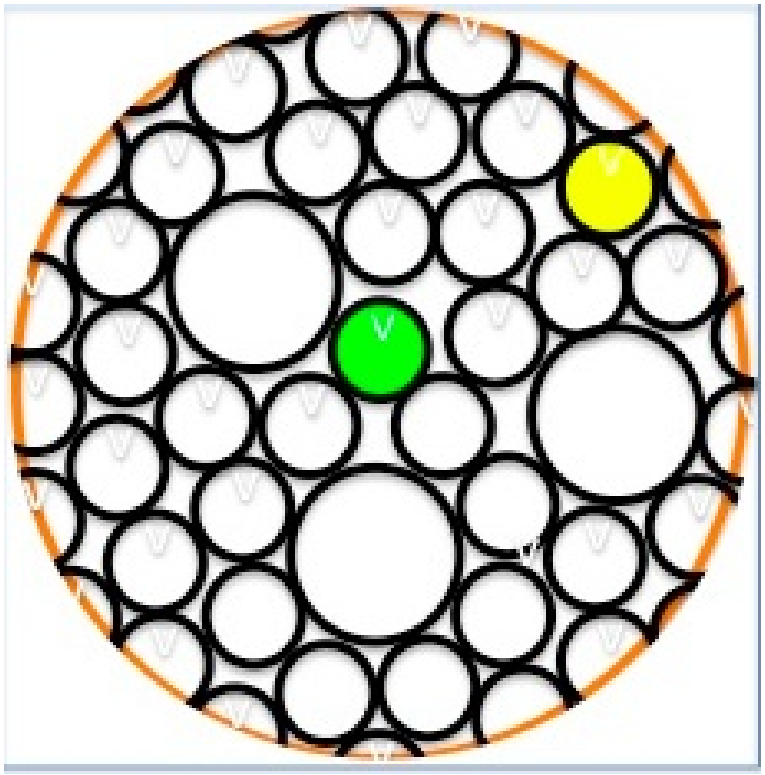
- Ξ is called the *tiling space*. Ξ *is a compact space*.

- A point $\xi \in \Xi$ represents a *possible configuration* of atoms for the solid

IV - Atomic Motion

A Model and some Speculations

Atoms Motion in Patches



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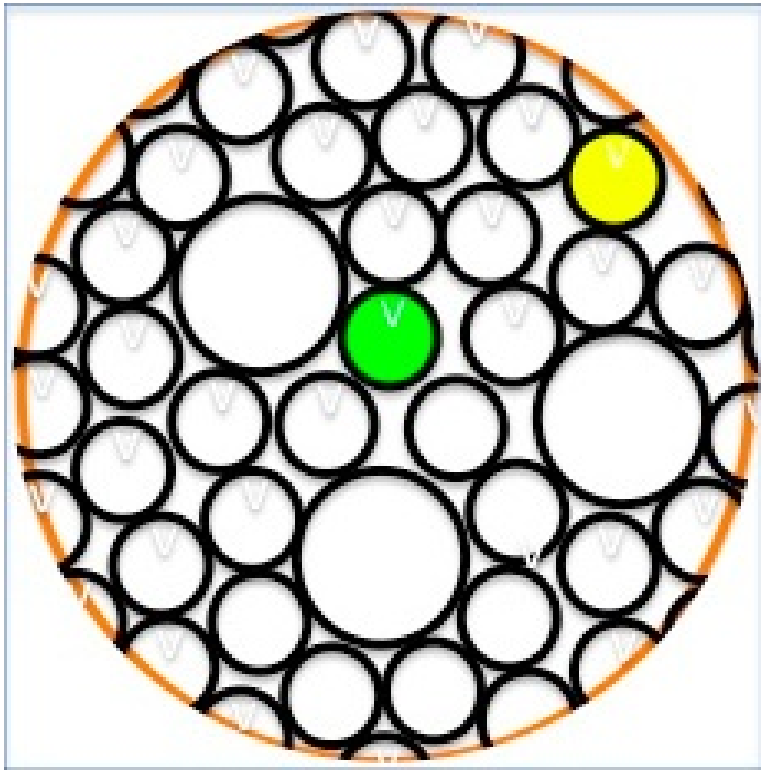

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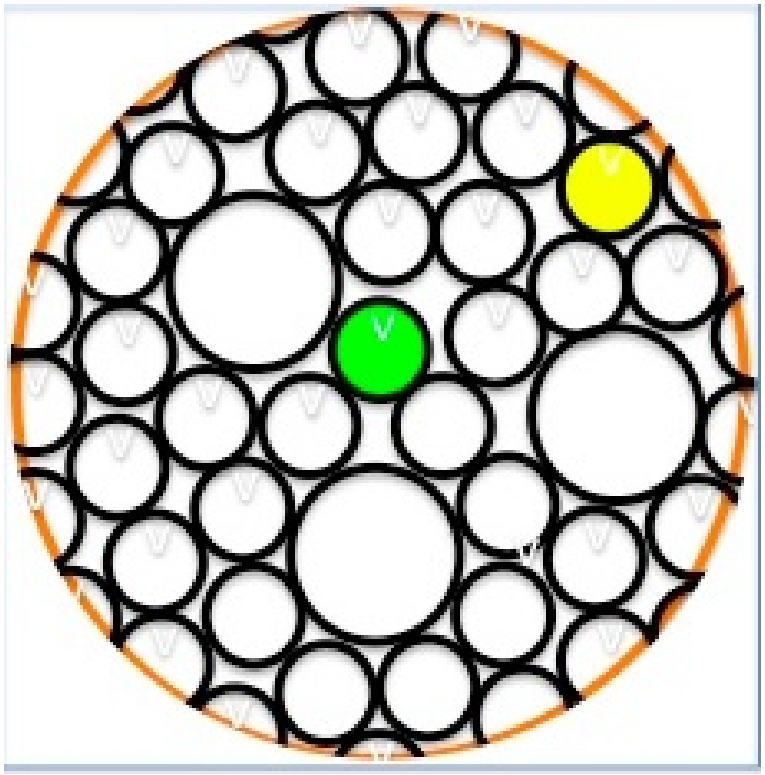

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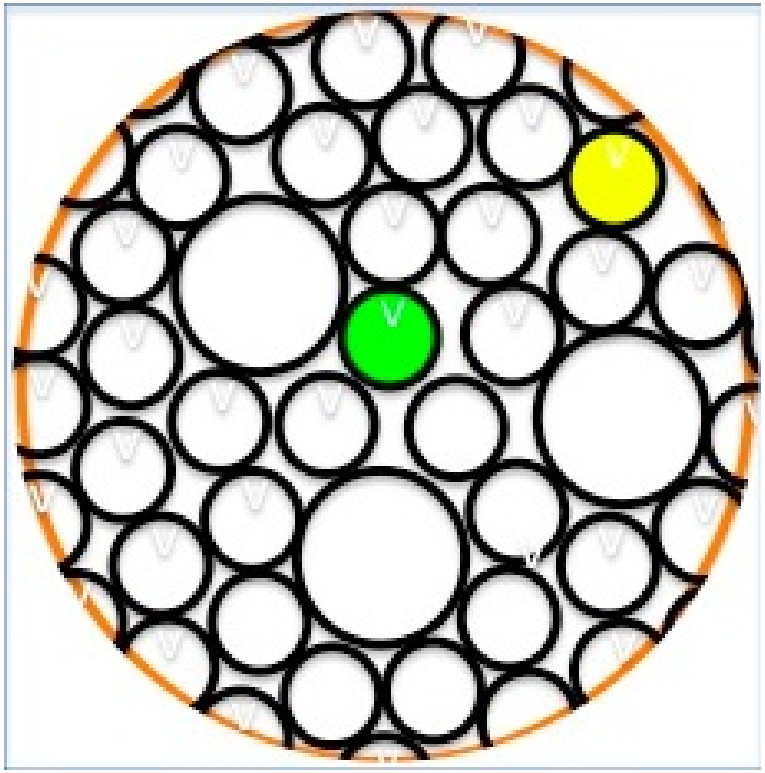

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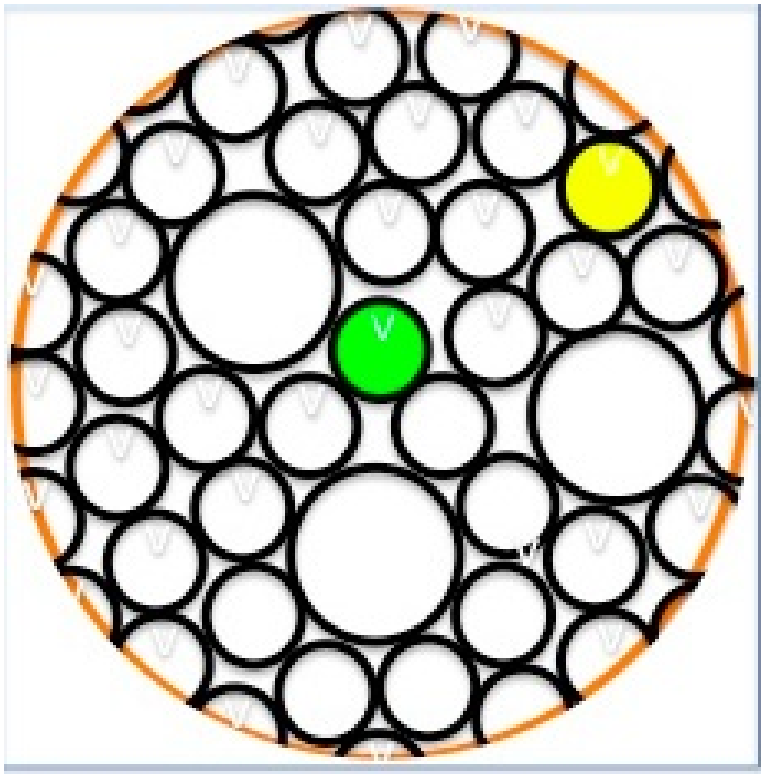

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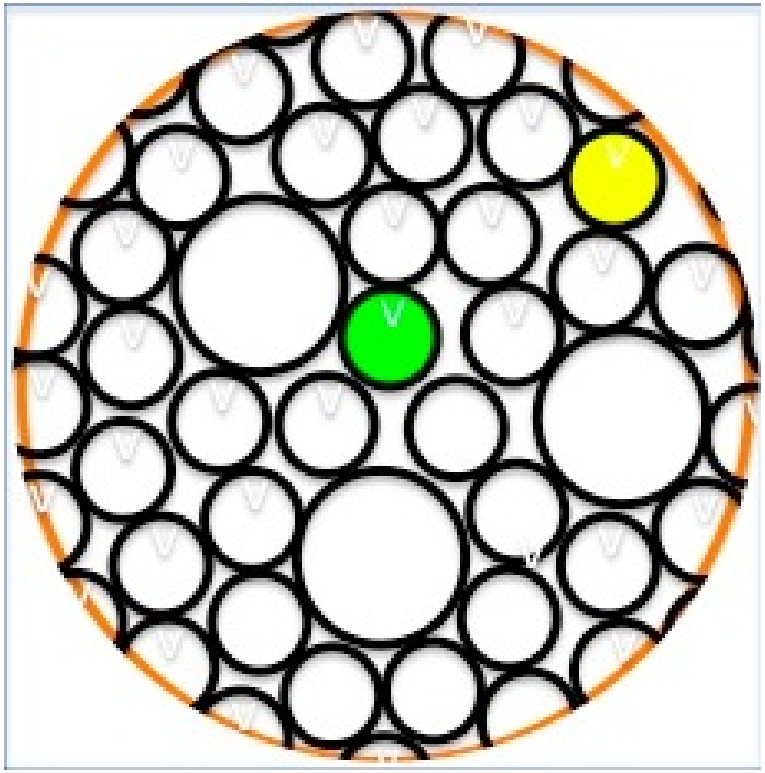

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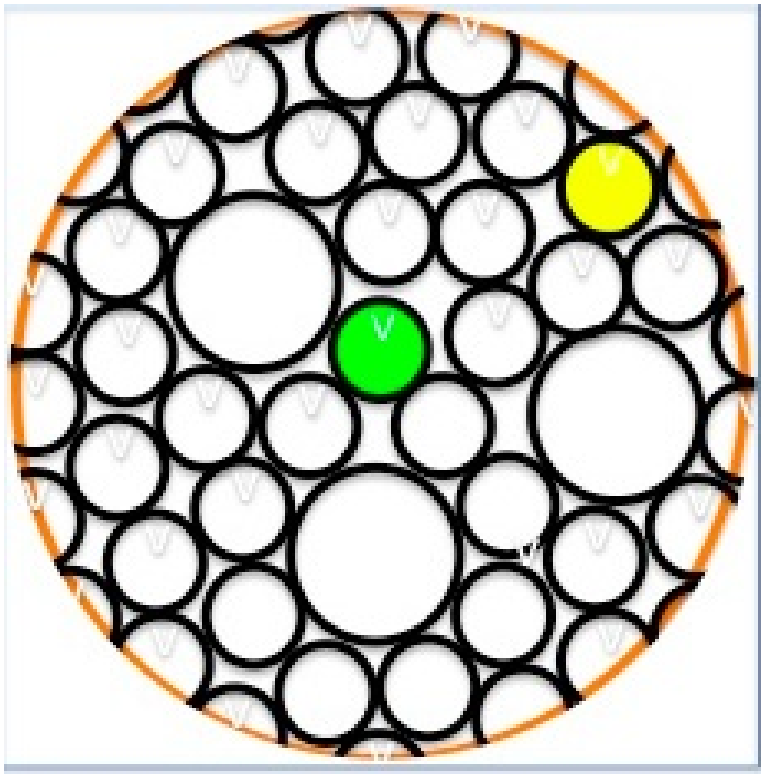

Random Jumps

- Atomic motion is due to *thermal noise* or *tunneling*.
  Both mechanisms are *random*.
- Local motion can be represented by a *jumps* from local patches to local patches.
- The *jump probability rate* $P(p \to q)$ between two patches p and q is proportional to
  - The *Gibbs* factor $\exp\{-\beta(F(q) - F(p))\}$, where $\beta = 1/k_B T$ and F is the *free energy* of the patch.
  - The inverse of the *jump time* $\tau_{p \to q}$ depending upon the height of the *energy barrier* between p and q

Random Jumps

The *free energy* of a patch p is given by

$$F(p) = U(p) - \sum_{a \in \mathcal{A}} \mu_a \, N_a + \mathrm{tr}\,\{\Pi \; \Sigma(p)\}$$

where

- U is the *mechanical* energy,
- N_a is the *number* of atoms of species a,
- μ_a is the corresponding *chemical potential*,
- Π is the *stress* tensor
- $\Sigma(p)$ is the *deformation* of p

Random Jumps

- The *tunneling time* is proportional to

$$\tau_{\text{tunn}} \sim \exp\left\{\frac{S_{p\to q}}{\hbar}\right\}$$

  where $S_{p\to q}$ is the tunneling action between the two patches

- The *noise transition time* is provided by Kramers law given, in the limit of high viscosity, by

$$\tau_{\text{noise}} \sim \exp\left\{\frac{W_{p\to q}}{\epsilon^2}\right\}$$

  where $W_{p\to q}$ is the height of the energy barrier measured from p and ϵ is the noise intensity. For thermal noise $\epsilon^2 = k_{\text{B}}T$.

A Markov Process

- The probability $\mathbb{P}_t(q)$ at time t of the patch $q \in \mathcal{Q}_r$ is given by

$$\frac{d\mathbb{P}_t(q)}{dt} = \sum_{p \in \mathcal{Q}_r} P(p \to q)\ \mathbb{P}_t(p)$$

- This equation is *not rigorous*, unless $\mathcal{Q}_r$ is finite (namely for tilings with *finite local complexity*, such as quasicrystals)

- Solving this equation gives a calculation of *transport coefficients*, such as the *elasticity tensor* or the response of the solid to stress.

Questions and Problems

- *Coarse graining* of each $\mathcal{Q}_r$ allows to replace it by a *finite* number of local patches.

  How is the Markov process behaving in the continuum limit ?

- Letting the radius $r \to \infty$ is equivalent to look at *small scale* in the tiling space Ξ.

  How can one control this infinite volume limit ?

Questions and Problems

- Experimental results at *Medium Range*, suggest that $\mathcal{Q}_r$ is fractal for $r \sim$ 4-6Å.

- At *small stress*, the *elasticity theory* applies and suggests that the large scale behavior, namely the *small scale* in Ξ is *universal*

  Can one approximate this dynamics by a smooth one ?

- Is such a model able to account for *discontinuities* at *large stress* ?

Merci de votre attention !

Thanks for listening !