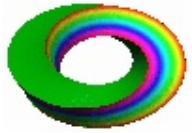
HULL & TILING SPACE
of
APERIODIC SOLIDS

Sponsoring



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Some References

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

J. Bellissard, D. Hermmann, M. Zarrouati, in *Directions in Mathematical Quasicrystals*, CRM Monograph Series, **13**, 207-259, M.B. Baake & R.V. Moody Eds., AMS Providence, (2000).

J. Bellissard, C. Radin, S. Shlosman, *J. Phys. A: Math. Theor.*, **43**, (2010), 305001.

Content

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3. Thermal Equilibrium
4. Atomic Motion

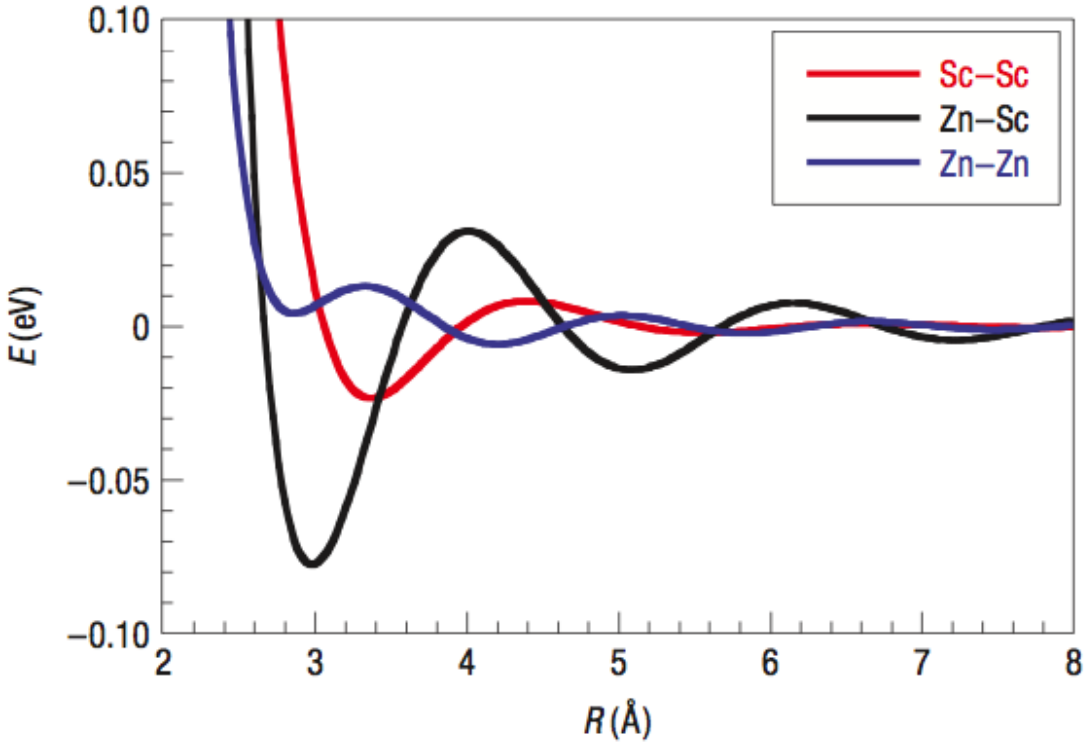
I - Representing Aperiodic Solids

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. A *pair potential* with strong repulsion at short distances, Friedel's oscillations at medium range and exponentially decaying tail, gives a good description of the effective atom-atom interactions.



An example of atom-atom pair potential in *ZnMgSc* icosahedral quasicrystal (de Boissieu *et al.*, *Nat. Mat.*, **6**, 977-984 (2007))

Figure 6 Fitted pair potential used in the simulation. The blue, red and black lines stand for Zn–Zn, Sc–Sc and Zn–Sc pair potentials. The potential energy, in eV, is given as a function of the interatomic distance *R*. Note the oscillating part, reminiscent of Friedel-like oscillations. As expected from the large atomic size differences, the Zn–Zn potential has a first (shallow) minimum located at 2.85 Å whereas the Sc–Sc potential's is located at 3.34 Å.

A Conjecture

J. Bellissard, D. Hermmann, M. Zarrouati, in *Directions in Mathematical Quasicrystals*,

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- Representing atoms by a point located at its nucleus position, in the infinite volume limit, gives a *discrete set* $\mathcal{L} \subset \mathbb{R}^d$ $(d = 1, 2, 3)$ in space.
- Such a set is *uniformly discrete* if the minimum distance between atom is *positive* (nonzero).

Conjecture: *For an assembly of atoms with an isotropic pair potential interaction decaying fast enough at infinity and with a strong enough repulsion at short distance, the equilibrium configurations are almost surely uniformly discrete in the zero temperature limit.*

Delone Sets

- A uniformly discrete set $\mathcal{L}$ is *Delone* is the size of its *holes* (vacancies) is bounded from above.
- A Delone sets has *finite local complexity (FLC)* is for each $r > 0$ it has only a *finite* number of local patches of radius r *modulo translation*.
- A Delone sets is *repetitive* if for any $r > 0,\ \epsilon > 0$ and any local patch p of radius r, there is $R > 0$ such that a translated copy of p occurs in any ball of radius R modulo an error ϵ.
- A Delone sets is a *Meyer* if the set of vectors joining any pair of its points is itself Delone.

Examples

- *Periodic* solids or *quasicrystals* are represented, in the zero temperature limit, by *repetitive, FLC, Meyer* set.
- As soon as the temperature is nonzero, *vacancies* in a solid have *unbounded size*: a Delone set representation can only be an approximation.
- Hence the best that can be expected is to represent a solid by a *uniformly discrete set*. However

Theorem: *The groundstate configurations of a system of attracting hard balls are Delone with probability one.* *(JB, Radin Shlosman, '10)*

II - Tiling Space

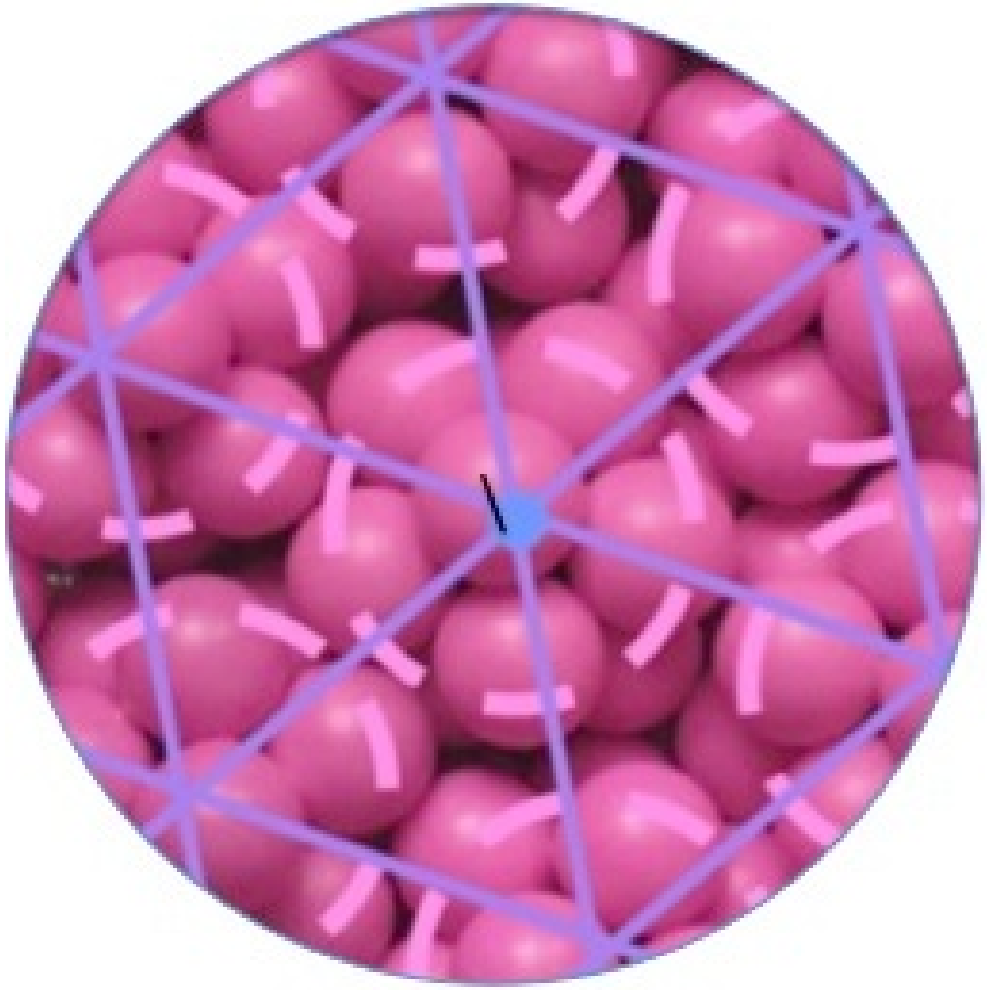
Local Patches

- 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

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

- The set of patches of radius r in $\mathcal{L}$ is called $\mathcal{Q}_r^{(0)}$.
- 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 $\mathcal{Q}_r^{(0)}$.
- 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*.

Local Patches



A local patch

Compactness

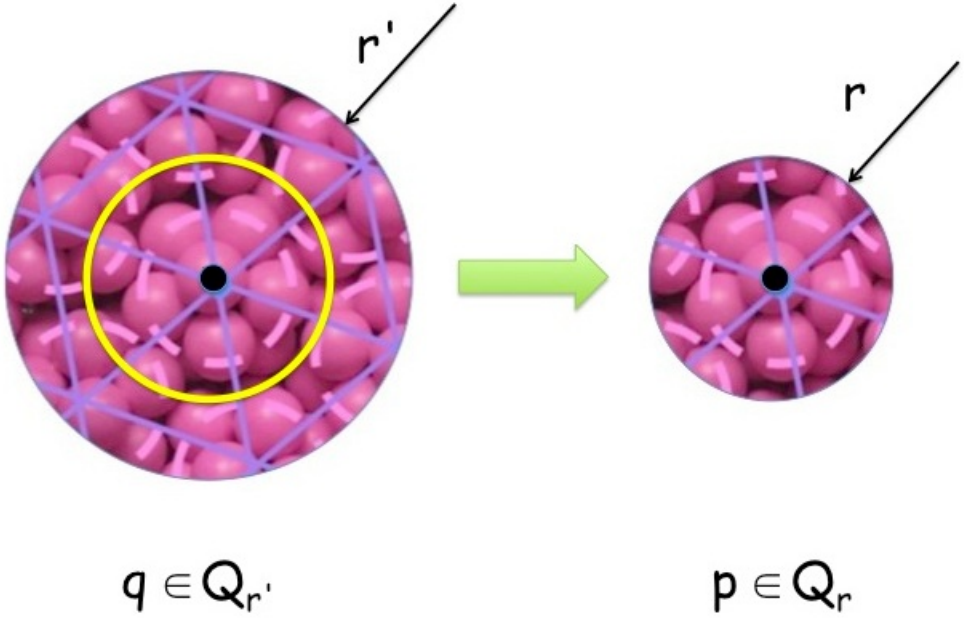
- **Theorem:** $\mathcal{Q}_r$ *is compact.*

- Compactness means

  1. $\mathcal{Q}_r$ is *totally bounded*: given any $\epsilon > 0$ there is a finite cover of $\mathcal{Q}_r$ by balls of radius ϵ. Hence $\mathcal{Q}_r$ can be *approximate by a finite number* of points.

  2. $\mathcal{Q}_r$ is *closed*, meaning that the limit points of any sequence of local patch still belongs to $\mathcal{Q}_r$.

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* $\Xi = \lim_{\leftarrow}(\Omega_r, \pi_{r \leftarrow r'})$ is the set of *increasing compatible* families of patches

  1. $\xi \in \Xi \Rightarrow \xi = (p_r)_{r>0}$
  2. $p_r \in \Omega_r$ for all $r > 0$
  3. $\pi_{r \leftarrow r'}(p'_r) = p_r$ for $r' > r$

- 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

Known Results

- **Result 1:** the patch space $\mathcal{Q}_r$ of an FLC uniformly discrete set is finite.

- **Result 2:** *(J. Kellendonk '97)* the tiling space of an FLC uniformly discrete set is *completely discontinuous* (each connected subset is a point). If the set is FLC, repetitive and if no element of the tiling space is periodic, then the tiling space is a *Cantor set*.

- **Example:** the tiling space of a quasicrystal is a *Cantor set*

- **Guess:** the patch space $\mathcal{Q}_r$ of a BMG is invariant by rotation. Modulo rotation it is finite for r small (SRO) *(Egami et al '84, Miracle '04)*, it contains continuous paths for r large enough (MRO and LRO) *(see e.g. Langer et al. STZ theory)*.

The Hull

- Given $\mathcal{L}$ uniformly discrete, its *Hull* is the set of limit points of the family $\{\mathcal{L} - a\,;\, a \in \mathbb{R}^d\}$ of translate of $\mathcal{L}$.

- *The limit is understood in the following sense: a sequence $(\mathcal{L}_n)_{n>0}$ of uniformly discrete set converges to $\mathcal{L}$ whenever given $\epsilon > 0$ (small) and $R > 0$ (large) there is N integer such that for $n > N$, each point of the patch of radius R around the origin in $\mathcal{L}_n$ is within a distance at most ϵ from a point of the corresponding patch for $\mathcal{L}$.*

- Elements of the Hull are *atomic configurations*.

- **The Hull is compact**.

The Hull

The *canonical transversal* is the set of elements of the Hull with one atom at the origin.

Theorem: *The canonical transversal coincides with the Tiling Space*

III - Thermal Equilibrium

Gibbs States

- For N_a-atoms of the species a labelled by (i,a) and located in a region Λ of volume $V = |\Lambda|$ with a *pair potential* interaction $\mathcal{V}_{ab}$, the total potential energy is

$$U_\Lambda = \sum_{a,b} \sum_{i,j} \mathcal{V}_{ab}(|r_{i,a} - r_{j,b}|)$$

- If μ_a represents the chemical potential for the species a, the *partition function* at temperature T, $\beta = 1/k_B T$ is given by

$$Z_\Lambda = \sum_{N_a \geq 0} \frac{e^{\beta \sum_a N_a \mu_a}}{\prod_a N_a!} \prod_{i,a} \int_\Lambda d^d r_{i,a}\, e^{-\beta U_\Lambda}$$

Gibbs States

- Average of observables

$$\langle A \rangle_\Lambda = \frac{1}{Z_\Lambda} \sum_{N_a \geq 0} \frac{e^{\beta \sum_a N_a \mu_a}}{\prod_a N_a!} \prod_{i,a} \int_\Lambda d^d r_{i,a} \, e^{-\beta U_\Lambda} A(\underline{r})$$

- It defines a *probability* measure that will be denoted by $\mathbb{P}_\Lambda$, depending upon the temperature and chemical potentials.

  General results *(O. Lanford III, '69)* show that there are limit probabilities for the family $\{\mathbb{P}_\Lambda\}_\Lambda$ as $V = |\Lambda| \to \infty$.

  Any such limits is called a *Gibbs state*

- **Results:** the set of translation invariant Gibbs states is not empty

Gibbs States

- **Result 1:** the set of Gibbs states is *compact, convex*.
- **Result 2:** the set of translation invariant Gibbs states is *not empty*, also compact and convex. Extremal points are *ergodic w.r.t.* translation.
- **Result 3:** if $\mathbb{P}$ is a *limit points* of translation invariant Gibbs states at $T \to 0$ which is ergodic, then the *Hull* of almost all configuration is the same *(JB, Hermmann, Zarrouati '00)*.

  If the set of uniformly discrete configurations of atoms has $\mathbb{P}$-probability one, there is a non random $r_0 > 0$ such almost all configurations have minimum interatomic distance r_0.

Groundstates

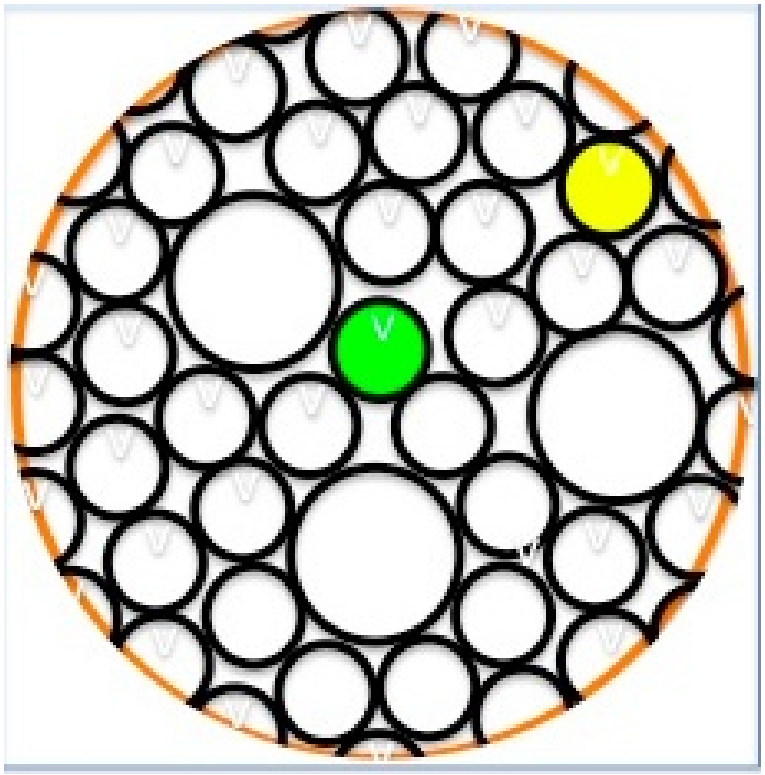
- Points of the Hull are expected to represent the *groundstates*, namely the pure phases at zero temperature.

- At nonzero but *low temperature*, various degrees of freedom, like *phonons* or *vacancies*, can be described by a statistical mechanic model with background lattice provided by configurations of the Hull.

IV - Atomic Motion

A Model and some Speculations

Atoms Motion in Patches



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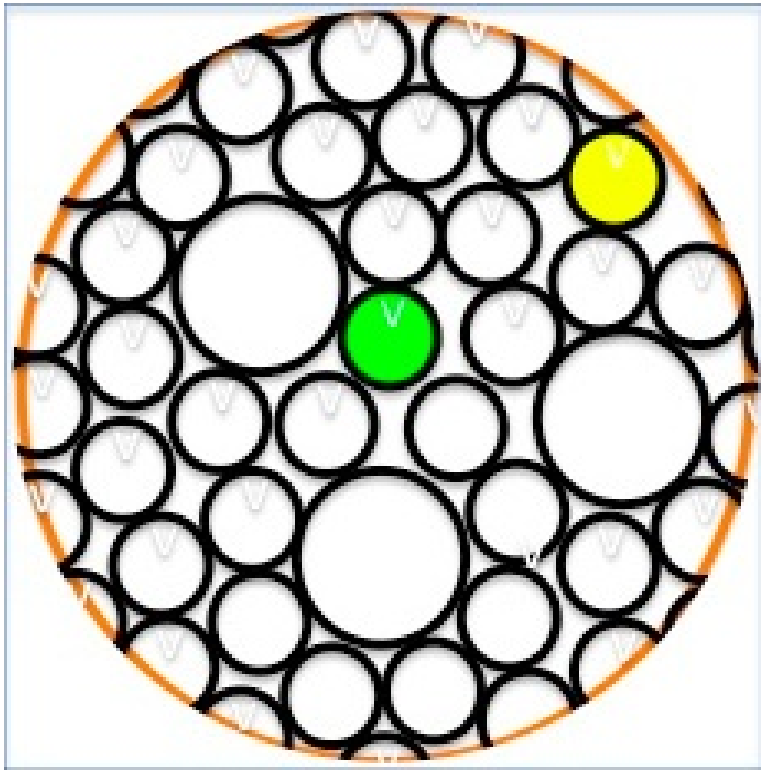

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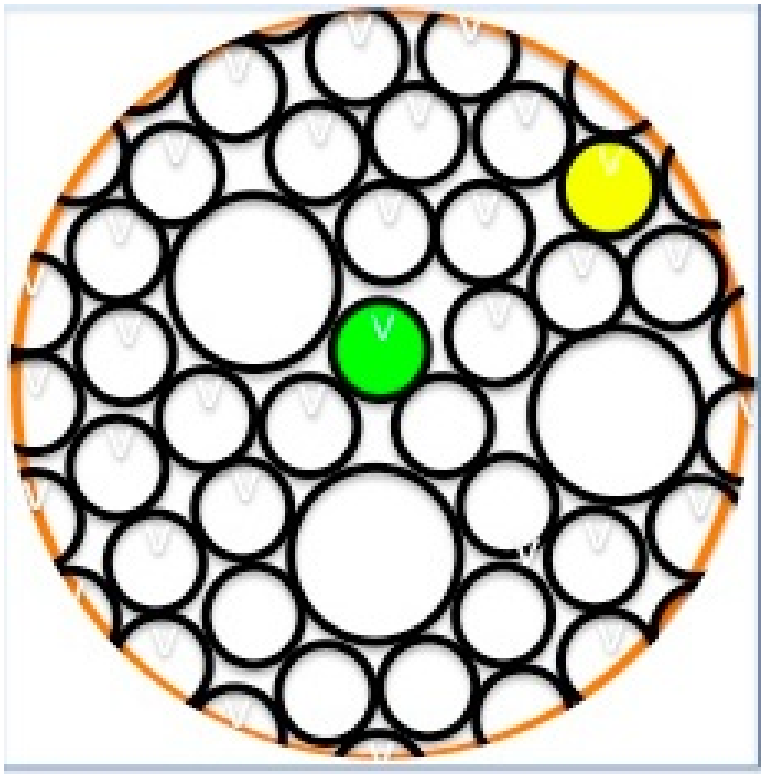

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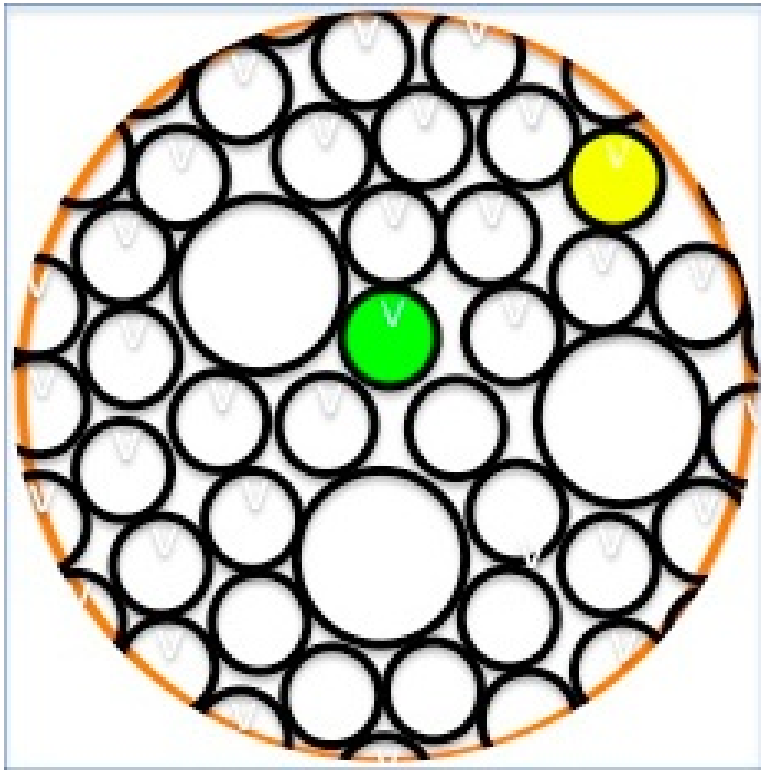

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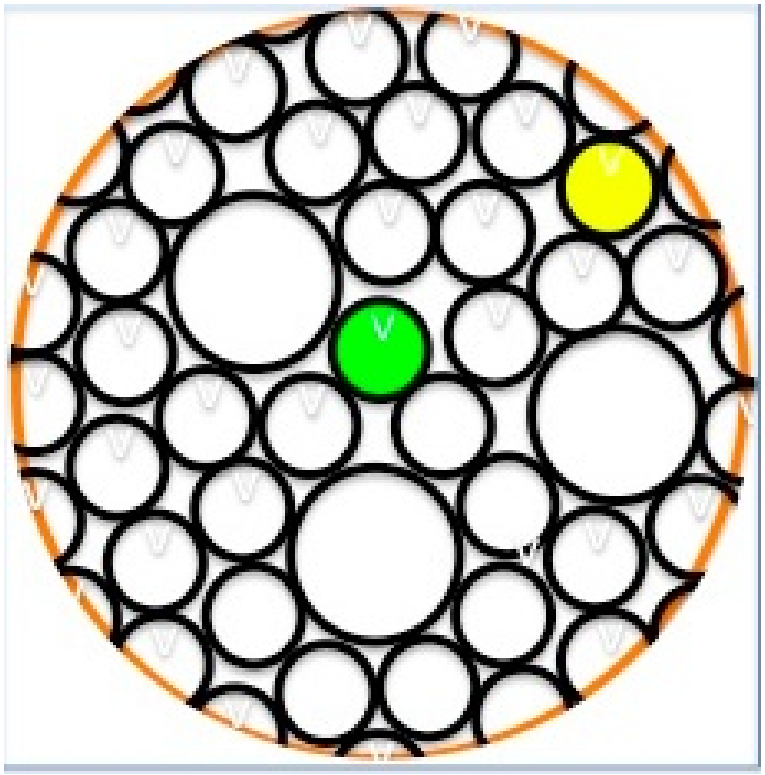

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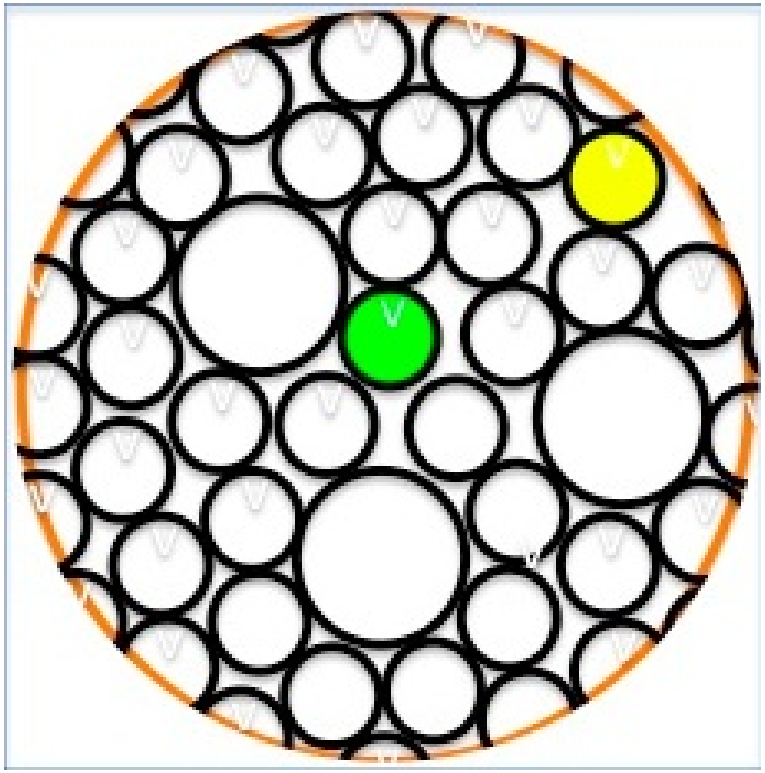

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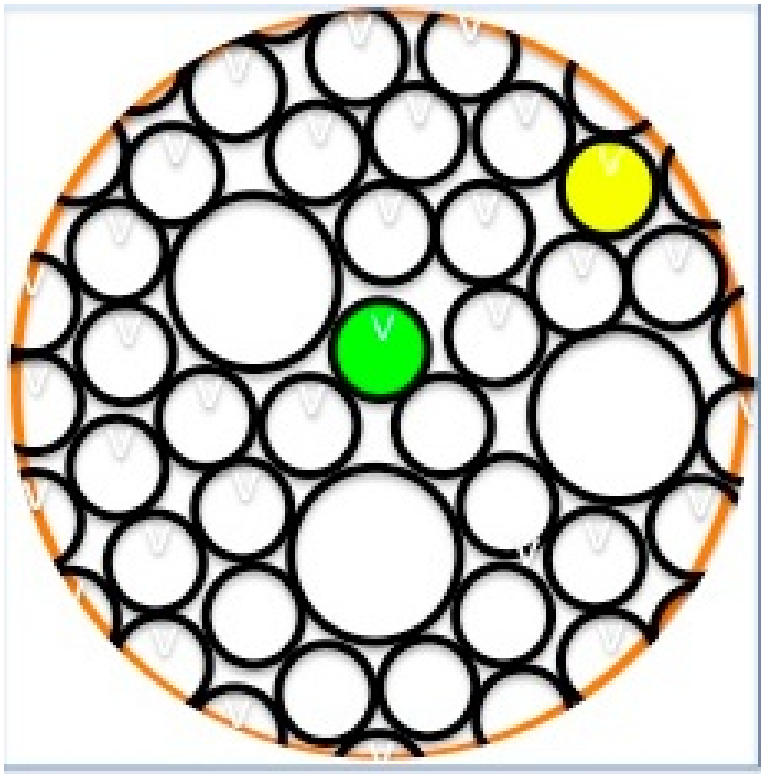

Random Jumps

- 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 !