ATOMIC MOTION
in
APERIODIC SOLIDS

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Collaborations

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Main References


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: \(\text{AlCuFe} (\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5})\)
   - Stable Perfect: \(\text{AlPdMn} (\text{Al}_{70.9}\text{Pd}_{22}\text{Mn}_{7.5})\)
     \(\text{AlPdRe} (\text{Al}_{70.9}\text{Pd}_{21}\text{Re}_{8.5})\)

2. Stable Binary Alloys
   - Periodic Approximants: \(\text{YbCd}_6, \text{YbCd}_{5.8}\)
   - Icosahedral Phase \(\text{YbCd}_{5.7}\)
Clusters in $YbCd$-approximants.

(Cd in grey, Yb in yellow)

H. Takakura, et al., Nat. Mat. ’04
Clusters in $i$-$\text{YbCd}$.

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

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
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 ($\ell_{e-e} = \text{average } e - e \text{ distance, } P=\text{pressure}$)

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

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


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.
2D-clusters

(D. Miracle, et al. ‘04)
3D-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

- 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
  \[ q_1 v^{1/3} = \text{const}. \]  
  \[ (Ehrenfest) \]
- In BMG’s measurements show that, at distance of order 4-6Å.
  \[ q_1 v^\alpha = \kappa \quad \alpha = 0.433 \pm 0.007 \quad \kappa = 9.3 \pm 0.2 \]
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

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\text{dist}((x, a), (y, b)) \geq r_a + r_b
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(3)

• \(\rho_a\) 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 \(\rho = (\rho_a)_{a \in A}\). The set of atomic positions is \(\text{supp}(\mathcal{L})\).
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
Local Patches

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

- The set of patches of radius $r$ in $\mathcal{L}$ is called $Q_r^{(0)}$. 
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• There is a way to measure the *distance* between two patches, using the so-called *Hausdorff metric*. Let $Q_r$ denotes the *completion* of $Q_r^{(0)}$. Then

$$Q_r \text{ is compact}$$
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• A *point* in $Q_r$ is a limit of local patches, namely, a *configuration* of atoms in a ball of radius $r$ with *one atom* at the *origin*. 
If $r' > r$ there is a restriction map

$$\pi_{r \leftarrow r'}(q) = p$$
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this map is continuous
Inverse Limit

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- $\Xi$ is called the *tiling space*. $\Xi$ is a compact space.
Inverse Limit

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• $\Xi$ is called the tiling space. $\Xi$ 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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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* $P(p \rightarrow q)$ 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* $\tau_{p \rightarrow q}$ depending upon the height of the *energy barrier* between $p$ and $q$. 
Random Jumps

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

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

where

- $U$ is the mechanical energy,
- $N_a$ is the number of atoms of species $a$,
- $\mu_a$ is the corresponding chemical potential,
- $\Pi$ is the stress tensor
- $\Sigma(p)$ is the deformation of $p$
Random Jumps

• The *tunneling time* is proportional to

\[ \tau_{\text{tunn}} \sim \exp \left\{ \frac{S_{p\rightarrow q}}{\hbar} \right\} \]

where \( S_{p\rightarrow q} \) 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

\[ \tau_{\text{noise}} \sim \exp \left\{ \frac{W_{p\rightarrow q}}{\epsilon^2} \right\} \]

where \( W_{p\rightarrow q} \) is the height of the energy barrier measured from \( p \) and \( \epsilon \) is the noise intensity. For thermal noise \( \epsilon^2 = k_B T \).
A Markov Process

- The probability $P_t(q)$ at time $t$ of the patch $q \in Q_r$ is given by
  \[
  \frac{dP_t(q)}{dt} = \sum_{p \in Q_r} P(p \rightarrow q) P_t(p)
  \]

- This equation is *not* rigorous, unless $Q_r$ 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 $Q_r$ 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 $\Xi$.

  *How can one control this infinite volume limit?*
Questions and Problems

• Experimental results at Medium Range, suggest that $Q_r$ is fractal for $r \sim 4-6\text{Å}$.

• At small stress, the elasticity theory applies and suggests that the large scale behavior, namely the small scale in $\Xi$ 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 !