Disordered Materials: An Introduction

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OUTLINE

- Basic concepts:

  - Order and disorder

  - Types of disorder

  - Non-crystalline materials – amorphous solids and polymers

  - Computational modeling of amorphous solids

- Characterization of order/disorder in solids

  - Pair-correlation function

  - Bond-angle distribution

  - Other higher-order correlation

Order vs. Disorder

- Order – often difficult to define

- Can be defined in many ways

- depends on the length scale

- May depend on dimension of the (embedding) space

- Disorder – lack of ordering

Examples from real world

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Examples from real world

Calcutta, India

Yangon, Myanmar

Los Angeles, USA

Crystalline and non-crystalline solids
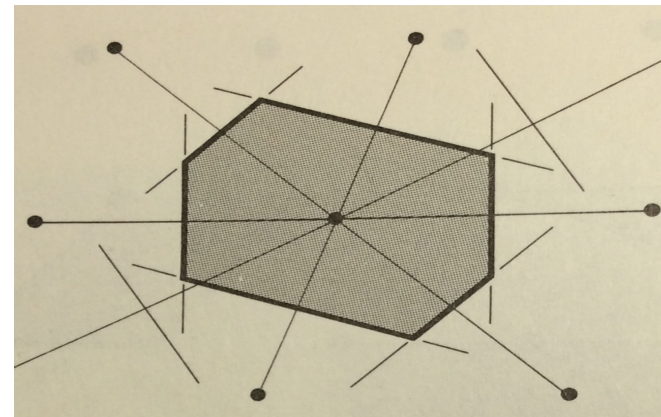
Crystals

In a perfect crystal, a group of atoms (or motif) are arranged in a pattern that repeats to an infinite extent.

$$\text{Crystal} \equiv \text{Lattice} + \text{Basis}$$

- Must have translational symmetry, $V(x) = V(x + a)$
- $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\Psi(x) = E\Psi(x)$
- Floquet's theorem leads to Blöch states: $\Psi(x + a) = \Psi(x)\exp(ik\,a)$
- $|\Psi(x)|^2 = |\Psi(x + a)|^2 \rightarrow$ Identical environment
- Symmetry $\rightarrow$ Primitive cell $\rightarrow$ Reciprocal space $\rightarrow$ Band theory
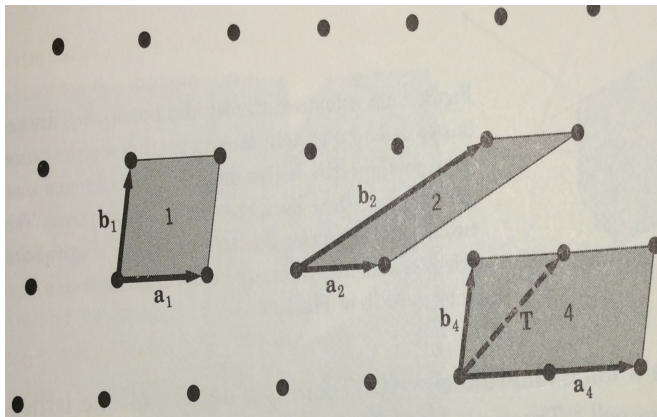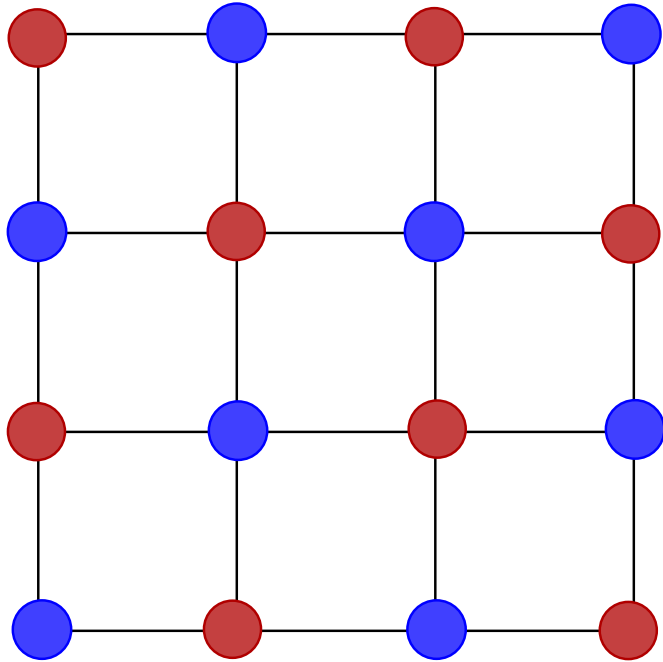

Unit cells

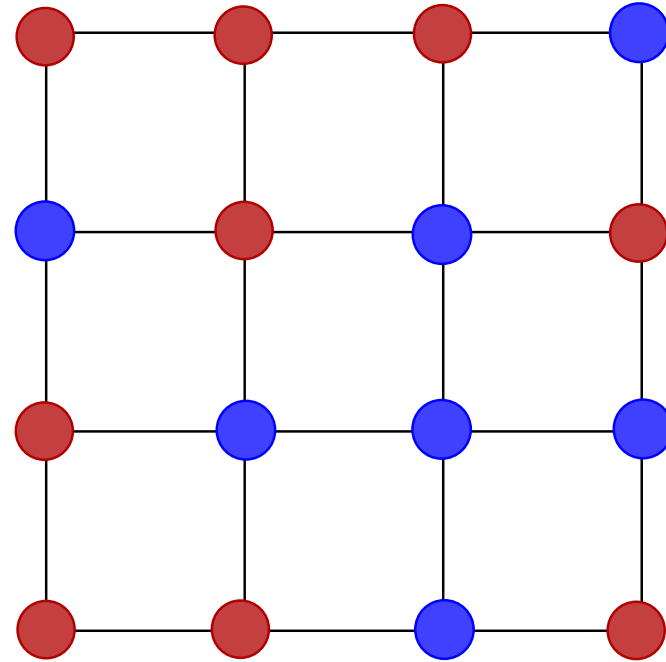Wigner-Seitz (primitive) cell

Binary alloys

Non-crystalline materials

No periodicity in atomic position; lattice may or may not exist

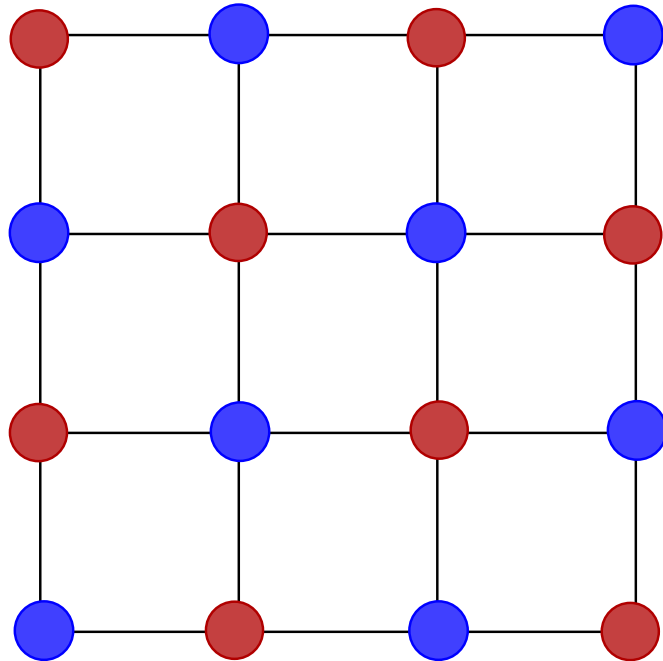Ordered   Disordered (solid solution)
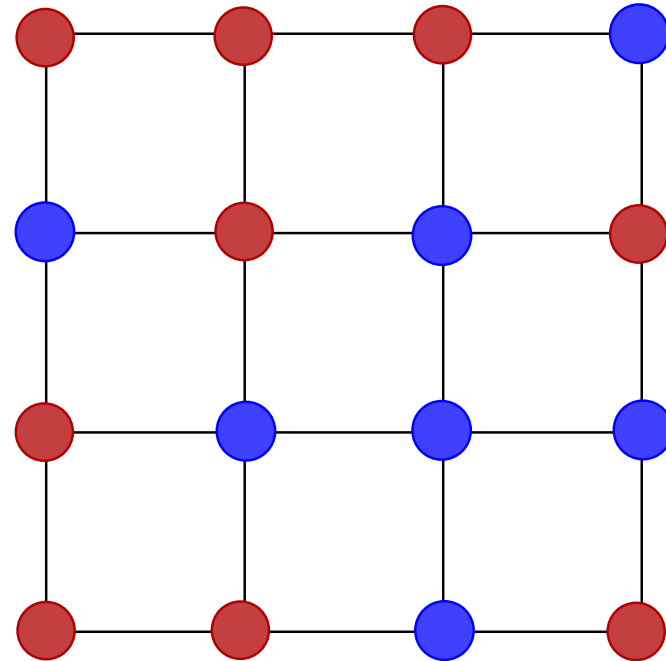
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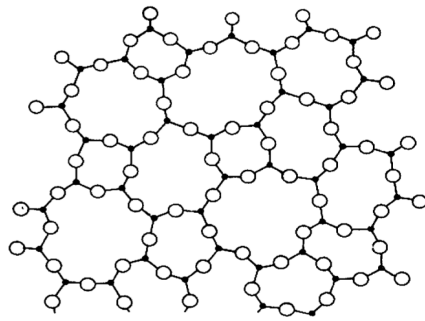
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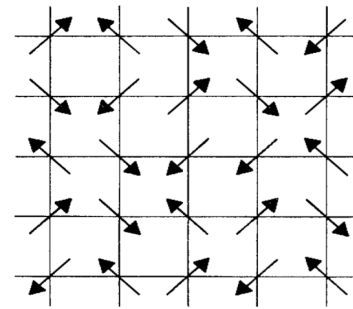
Lattice exists; a hypothetical 'crystal' can be (re)constructed using Coherent potential approximation (CPA)

Types of Disorder: A few examples

(a) Topological

(b) Spin

(c) Substitutional or cellular

(d) Vibrational
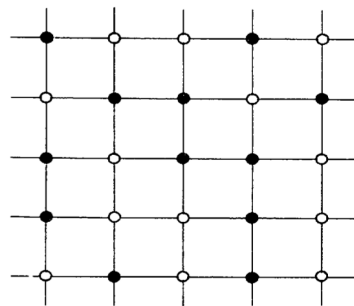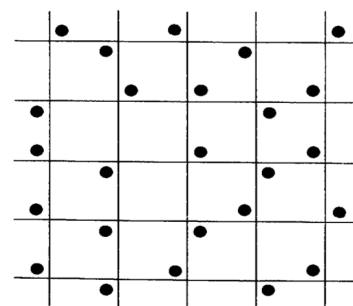
Figure courtesy: Prof. Stephen Elliott (Cambridge, UK)

Amorphous/glassy solids

Definition

- Solid: A material whose shear viscocity exceeds $10^{13.6}$ Nsm^{-2}
- Non-crystalline solids: No long-range translational order
- Amorphous: No lattice and no long-range order
- Glass: An amorphous solid that exhibits *glass* transition

How to prepare amorphous solids

Methods

- Thermal evaporation

- Sputtering

- Glow-discharge (GD) decomposition

- Chemical vapor deposition (CVD)

- Gel desiccation

- Irradiation

- Melt quenching

Melt-quenching plays an important role in computer simulation of glasses

The glass transition

Factors affecting glass formation

- Theromodynamic phase transition, entropy
- Structure and topology
- Compositions and free volume
- Relaxation
- Electronic structure
- Additional factors
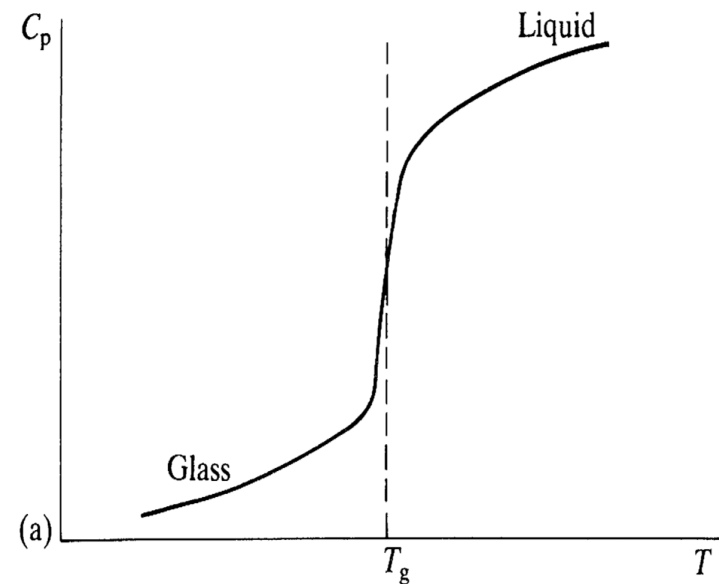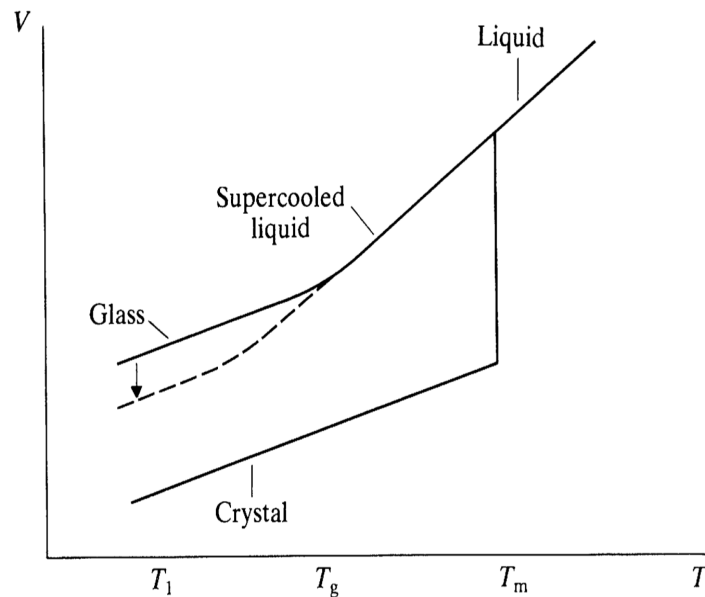
Disorderd solids: homogeneity and isotropy

- Homogeneity refers to the fact that local properties (e.g., density) at $\mathbf{r_1}$ and $\mathbf{r_2}$ are statistcally identical, i.e.,

$$\langle f(\mathbf{r_1}) \rangle = \langle f(\mathbf{r_2}) \rangle$$

- Isotropy suggests that local properties are independent of the direction of the position vector, i.e.,

$$f(\mathbf{r}) = f(r)$$

- Ergodicity implies that the time average of a physical observable (of a many-body system) is essentially identical to its ensemble average

$$\int f(x) P_{Boltz}(x)\, dx = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(x(t))\, dt$$

Note: A rigorous proof in $D \geq 2$ is still missing but a less stringent *mixing* hypothesis generally suffices for Statistical Mechanics

- Amorphous solids are non-ergodic in general

(Caution: Be mindful when applying the rules of statistical mechanics)

Atomic correlations

Two-body correlations : Real-space affairs

1

$$n_1(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{R_i}) \; ; \; n_2(\mathbf{r_1}, \mathbf{r_2}) = \sum_{i,j i =/j}^N \delta(\mathbf{r_1} - \mathbf{R_i}) \, \delta(\mathbf{r_2} - \mathbf{R_j})$$

$$n_2(\mathbf{r_1}, \mathbf{r_2}) = n_1(\mathbf{r_1}) \, n_1(\mathbf{r_2}) \, \boxed{g_2(\mathbf{r_1}, \mathbf{r_2})}$$

2 For a homogeneous system, $n_1(\mathbf{r_1}) = n_1(\mathbf{r_2}) = n_0 = N/V$, and writing $\mathbf{r_1} - \mathbf{r_2} = \mathbf{r}$,

$$n_2(\mathbf{r_1}, \mathbf{r_2}) = n_0^2 \, g_2(\mathbf{r})$$

3 Note that,

$$\int n_2(\mathbf{r_1}, \mathbf{r_2}) \, d\mathbf{r} = n_0 \int g_2(\mathbf{r}) d\mathbf{r} = N - 1$$

4 $n_0^2 g(\mathbf{r})$ gives the probability of finding a particle between $\mathbf{r}$ and $\mathbf{r} + \mathbf{dr}$.

5 Invoking isotropic of nature of disordered materials,

$$g_2(\mathbf{r}) = g_2(r), \qquad \lim_{r \to \infty} g_2(r) \to 1$$
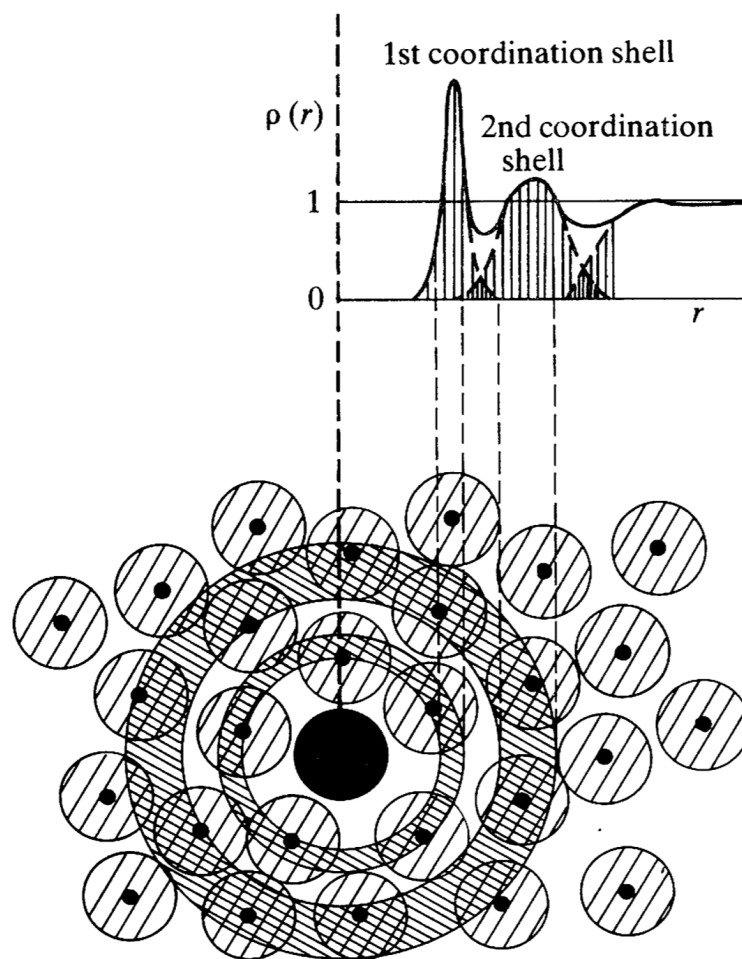
Figure courtsey: Stephen Elliott (Cambridge, UK)

Pair-correlation function

Algorithm PCF

1. Start at r_i; find the number of particles, $N_i(R, R + dR)$, between R and $R + dR$.

2. Repeat this for all i and compute the average

$$P(R) = \frac{1}{N} \sum_i N_i(R, R + dR).$$

3. Normalize $P(R)$ by the corresponding value of the uniform system, $P_h(R) = 4\pi R^2 dR\, \rho$, where $\rho = N/V$.

$$g(R) = \frac{P(R)}{P_h(R)}$$

4. Repeat this for different R.

5. Plot $g(R)$ against R – this is your PCF.

Disorderd solids: pair-correlation function

Periodic boundary condition

- Finite-size effects

- Boundary effects can play important roles in simulations

- Surface-to-volume ratio determines 'bulk' vs. 'surface' atoms ($\sim 3dr/R$ for a sphere with surface width dr)

- PBC is an ansatz to minimize boundry effects
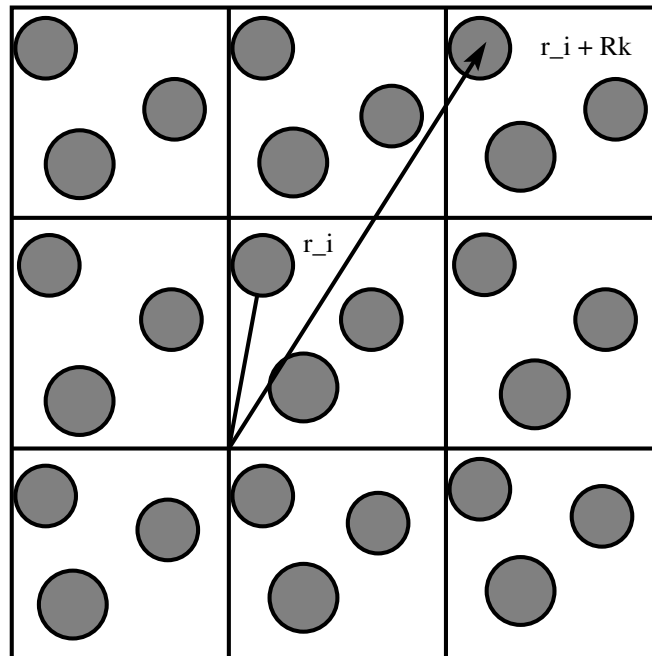
- Given $\mathbf{r_0}$, what is the probability of finding $\mathbf{r_1}$ and $\mathbf{r_2}$ at a given distance. Note $\mathbf{r} = (r, \theta)$.

- Bond-angle distributions provide a reduced form of three-body correlations.

- Similarly, dihedral angles provides some idea of reduced 4-body correlations.
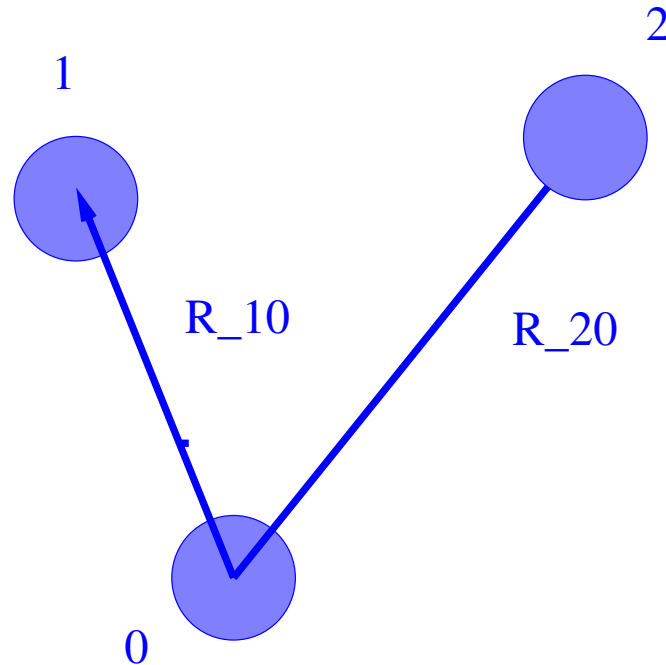
Bond-angle distribution (BAD)

Algorithm BAD

1. Angles are computed between nearest neigbors; define a rule to obtain such neighbors of the particle at site i.

2. Let $A(i,j)$ stores the jth neighbor of i ($j = 1 \cdots n$) and $iList(i)$ the maximum no. of neighbors (n_i) of i

3.
$$iList(i) = n_i \quad A(i,j) \leftarrow k_j \qquad k_j \text{ is the site index}$$

4. Choose a distinct triplet (i, j_1, j_2) from the neighbor list and compute the angle $\widehat{j_1 - i - j_2}$ at i.

5. Repeat the steps for each site

Include a figure to illustrate the idea

Scattering experiments

Scattering intensity from experiments

$$I_{eu} = \sum_\alpha \sum_\beta f_\alpha f_\beta \exp\left[\frac{2\pi i}{\lambda}(\mathbf{s} - \mathbf{s_0}).\mathbf{r}_{\alpha\beta}\right] \qquad \text{(For an assembly of atoms)}$$

Invoking isotropy, the Debye equation results:

$$I_{eu} = \sum_\alpha \sum_\beta f_\alpha f_\beta \frac{\sin kr_{\alpha\beta}}{kr_{\alpha\beta}} \qquad k = \frac{4\pi \sin\theta}{\lambda}, \text{ and } (\mathbf{s} - \mathbf{s_0}).\mathbf{r} = 2r\sin\theta\cos\phi$$

(a)

(b)

Information from wavevector space
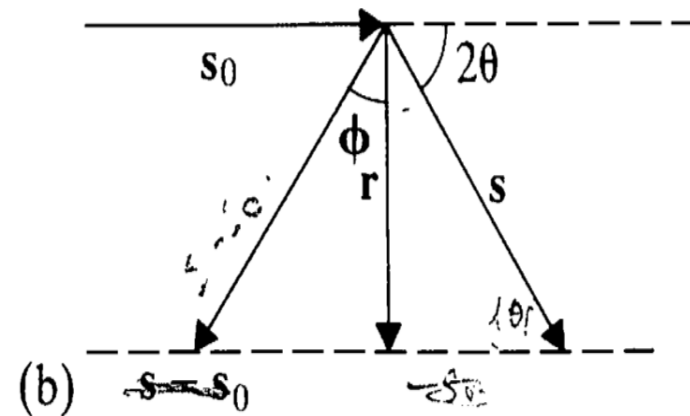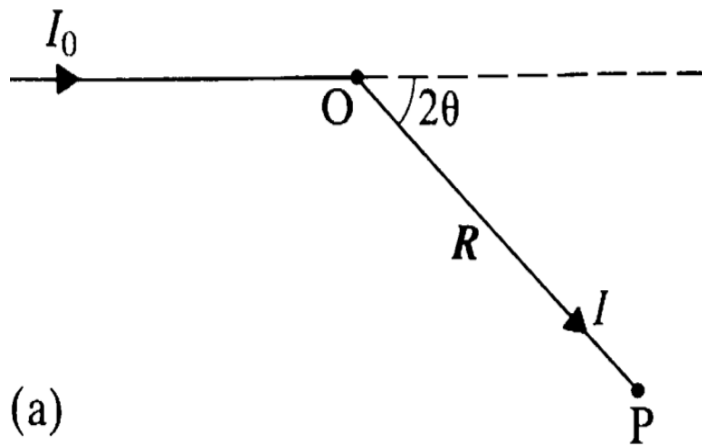
Structure factor

① Scattering experiments generally provide information in the reciprocal (k) space. (Think of 'Android' vs. 'iOS', each has their strength and weakness)

② In amorphous solids, the k-space collapses onto a single point (the so-called Γ-point). (In simulation, this may not be true – small models)

③ "Throw out the k-space" – the Cavendish motto (Heine 1968)

④ $Q = |\mathbf{k_f} - \mathbf{k_i}|$, the wavevector transfer during scattering, plays a crucial rule in measurements.

**⑤** For homogeneous and isotropic disordered systems, the SF is

$$S(k) = 1 + \frac{1}{Q} \int_0^\infty G(r) \sin Qr \, dr, \qquad G(r) = 4\pi\rho_0 r[g(r) - 1]$$

Structure factor $\rightleftharpoons$ pair-correlation function

Electronic structure: The tight-binding approximation

Solids sans k-space

1. No tanslational symmetry $\rightarrow$ No k-space $\rightarrow$ Breakdown of band theory

2. Schrödinger's equation must be solved in *real* space (Difficult!)

3. Use local bonding information – know your basis functions (Feynman)

4. Centers on the *principle of nearsightedness* of an equilibrium quantum system (Kohn 1996)

5. Forms a loose hierarchy in terms of the level of approximation (Cyrot-Lackmann 1969, Heine 1970)

t

C3
C2
C1
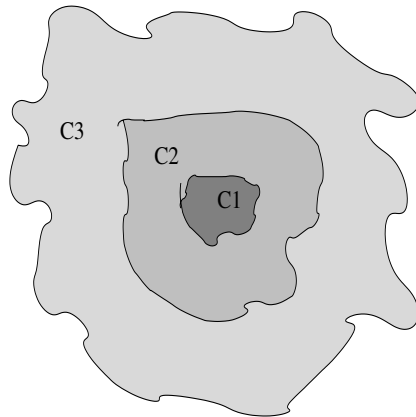
Morals: Know and Love Thy Neighbor

Figure: Local approach to electronic structure; progressively distant regions contribute less and lesser in the absence of long-range interactions

The nearsightedness principle of Kohn

Key ideas

- Description of the *bulk* is independent of the boundary (Friedel 1964)

- Most of the static properties of many-electron systems depend on local environment (Heine 1970)

- Local physical properties (static) of a part of a system are not generally affected by perturbation at a distant region (Kohn 1996, Thouless 1980)

- Beware of long-range intearctions (polarization, etc.) and treat them separately

Outcomes or Observations

- Existence of localized Wannier-like functions (Gödecker 1998, Marzari and Vanderbilt 1998)

- Fast decay of the density matrix at large distances (Baer and Head-Gordon 1996)

- Order-N calculations are possible (Martin and Drabold 1996)

- Generalized Wannier functions (GWF) can be localized in reduced dimensions (Blount 1980) (a general proof in 3D is still missing)

These ideas are particularly useful in disordered solids

Actung! Actung!

Equations ahead; Don't fall into sleep

Electronic structure: Effective medium theories

The tight-binding model

1

$$H = \sum_i \frac{p^2}{2m} + \sum_i V(x_i) \qquad \text{Note: one-electron effective medium Hamiltonian}$$

$$\hat{p} = i\hbar \frac{d}{dx}, \quad H\Psi(x_i) = E\Psi(x_i), \quad \rightarrow \quad \sum_i \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Psi(x) = E\Psi(x)$$

2

$$\Psi(x) = \sum_n a_n W_n(x - x_i)$$

3 $W_n(x)$s' are basis functions – can be local or global

4 Examples:
Local – Gaussian, Pseudoatomic orbitals, Wannier-like functions, etc.

Global – Plane waves or Blöch states

The TB model

1. Retain the nearest-neighbor integrals (the TB philosophy):

$$\epsilon_{i,\alpha} = \int W_\alpha^*(x - x_i)\, H\, W_\alpha(x - x_i)\, dx \qquad \text{(Diagonal contribution)}$$

2.

$$V_{i\alpha;j\beta} = \int W_\alpha^*(x - x_i) \sum_{k \neq i} V(x_k)\, W_\beta(x - x_j)\, dx \qquad \text{(Off-diagonal contribution)}$$

3. $\alpha \rightarrow$ electronic state (band) index ; $i \rightarrow$ site index

4.
$$H = \sum_{i\alpha} \epsilon_{i\alpha} a_{i\alpha}^+ a_{i\alpha} + \sum_{i\alpha} \sum_{j\beta} V_{i\alpha,j\beta} a_{i\alpha}^+ a_{j\beta}$$

5. In single-band approximation, this simplifies to:

$$H = \sum_i \epsilon_i a_i^+ a_i + \sum_i \sum_j V_{i,j} a_i^+ a_j \qquad \text{(The TB Hamiltonian)}$$

$a_i^+ \rightarrow$ Creation operator at site i

$a_i^- \rightarrow$ Annihilation operator at site j

The Resolvent operator and a magical formula

Density of electronic states

1 Hurrah! We have a tight-binding Hamiltonian matrix ...

$$(z\mathbf{I} - \mathbf{H})\Psi = \mathbf{0}; \qquad z = E + i\epsilon, \epsilon \to 0^+$$

$$\langle i|H|i \rangle = H_{ii} = \epsilon_i; \quad \langle i|H|j \rangle = V_{ij}$$

2 The Green's operator is given by:

$$(zI - H)G(z) = I \quad \to \quad G(z) = (zI - H)^{-1}$$

$$
\begin{aligned}
Tr\, G(z) \quad &= \quad \sum_s G_{ss}(z) = \sum_s \frac{1}{z - E_s} = \sum_s \frac{1}{(E + i\epsilon) - E_s} = \sum_s \frac{1}{(E + i\epsilon) - E_s} \\
&= \quad \sum_s \left[P\left(\frac{1}{E - E_s} \right) - i\pi\delta(E - E_s) \right]
\end{aligned}
\tag{1}
$$

3 The electronic density of states, $D(E)$, is:

$$D(E) = \sum_s \delta(E - E_s) = -\frac{1}{\pi}[\Im\, Tr\, G(z)]_{z \to E^+}$$

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No Green's function please!

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No Green's function please! Agreed!

"Come, my friend. 'T is not too late to seek a newer world" Lord Tennyson

Let us explore the beautiful world of disordered materials

Acknowledgments

- Dr. Daryl Hess (CMMT, NSF)

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