2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

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Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

- **Free volume and the glass transition**
- **Glass transition**

  - Classification of phase transition
- **Glass: Solid? or liquid?**
- **Amorphous vs Nanocrystalline**

  1) Microstructural observation

  2) Thermal analysis

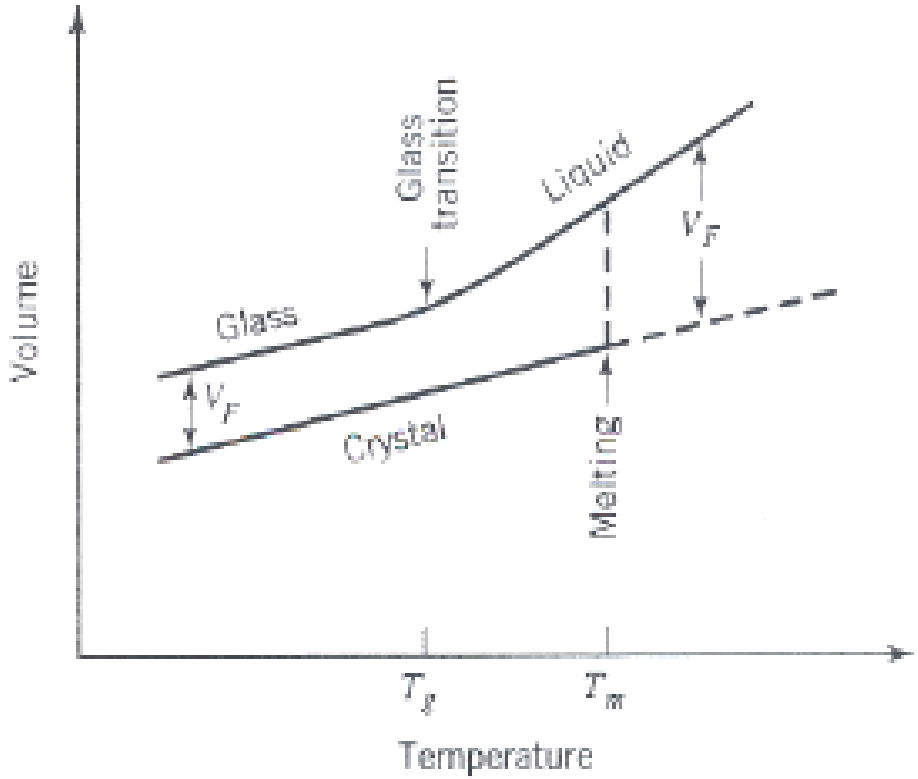
  - DSC (Differential Scanning Calorimetry)

→ **local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.**

: *Characterization of structure by pair distribution function*

Free volume and the glass transition

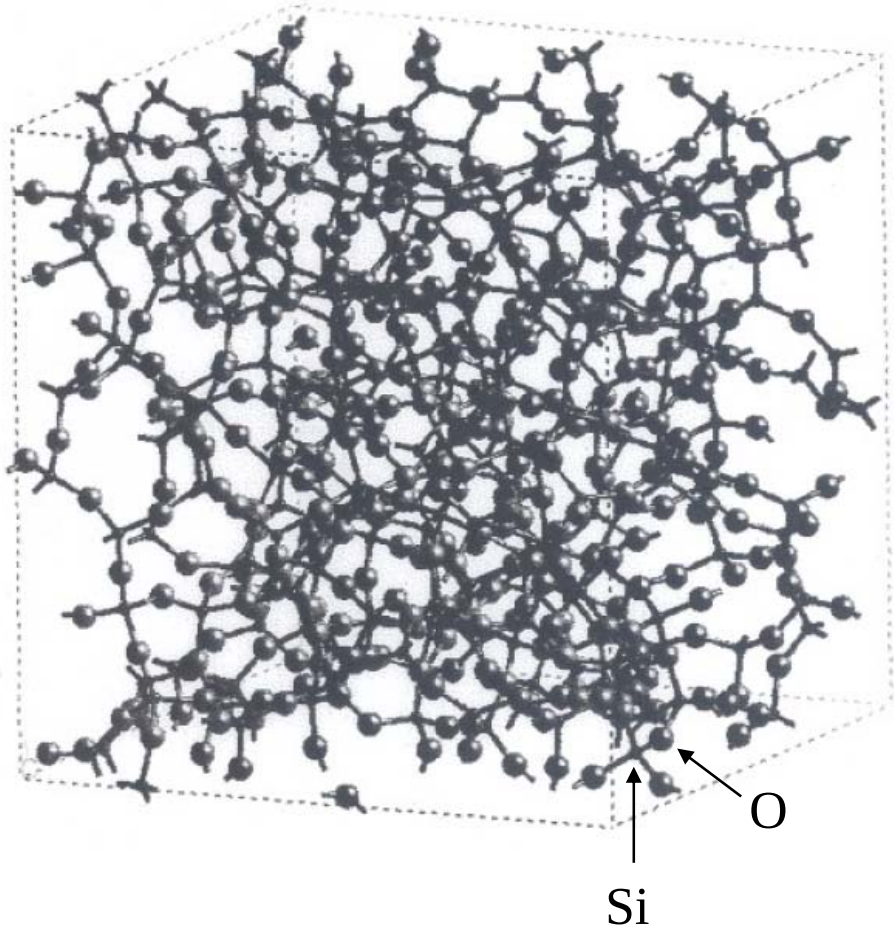
Free volume = specific volume (volume per unit mass) of glass - specific volume of the corresponding crystal



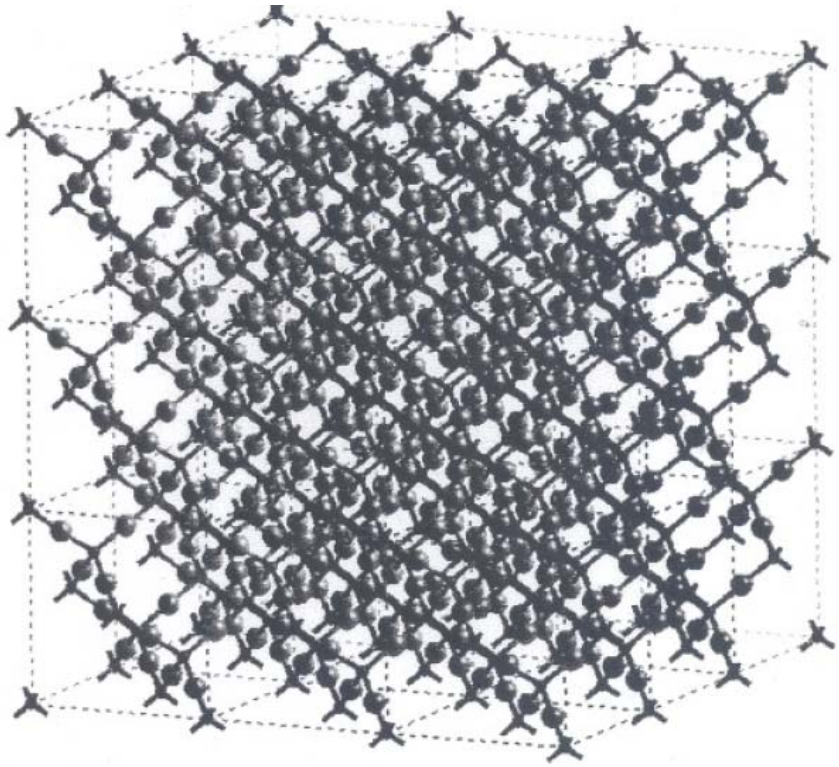
At the glass transition temperature, T_g, the free volume increases leading to atomic mobility and liquid-like behavior. Below the glass transition temperature atoms (ions) are not mobile and the material behaves like solid

Silica - SiO_2

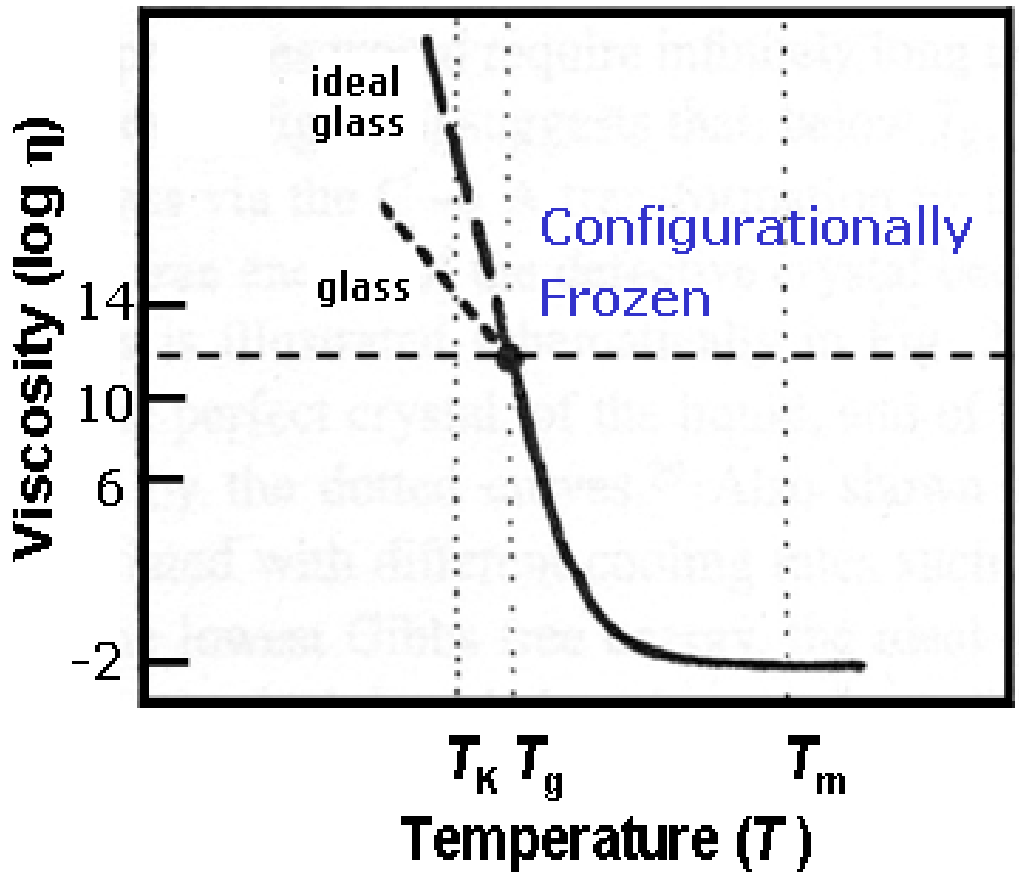
Amorphous silica



Crystalline SiO_2



Glass : *undercooled liquid with high viscosity*



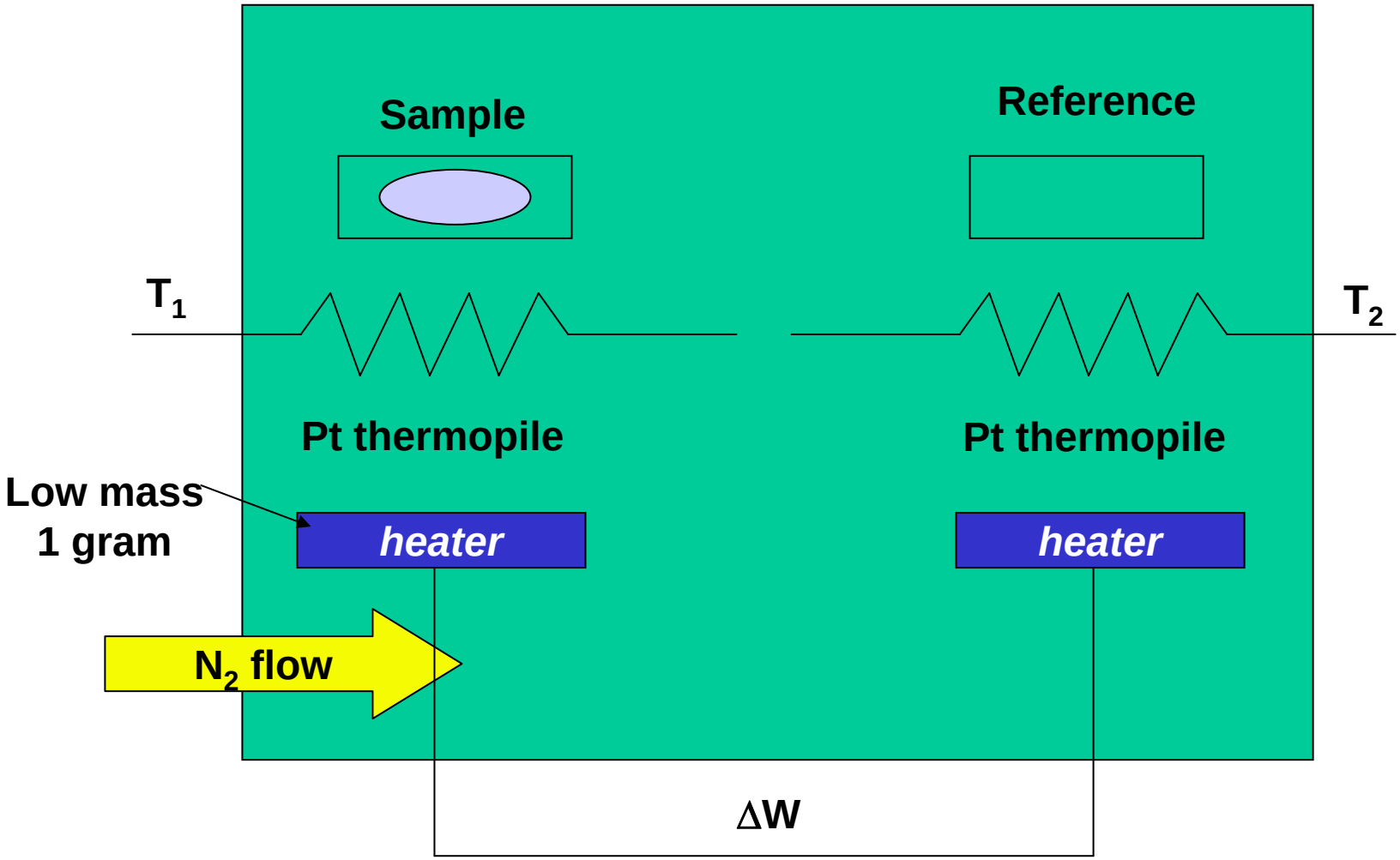
A solid is a materials whose viscosity exceeds $10^{14.6}$ poise

cf) liquid ~*10^{-2} poise*

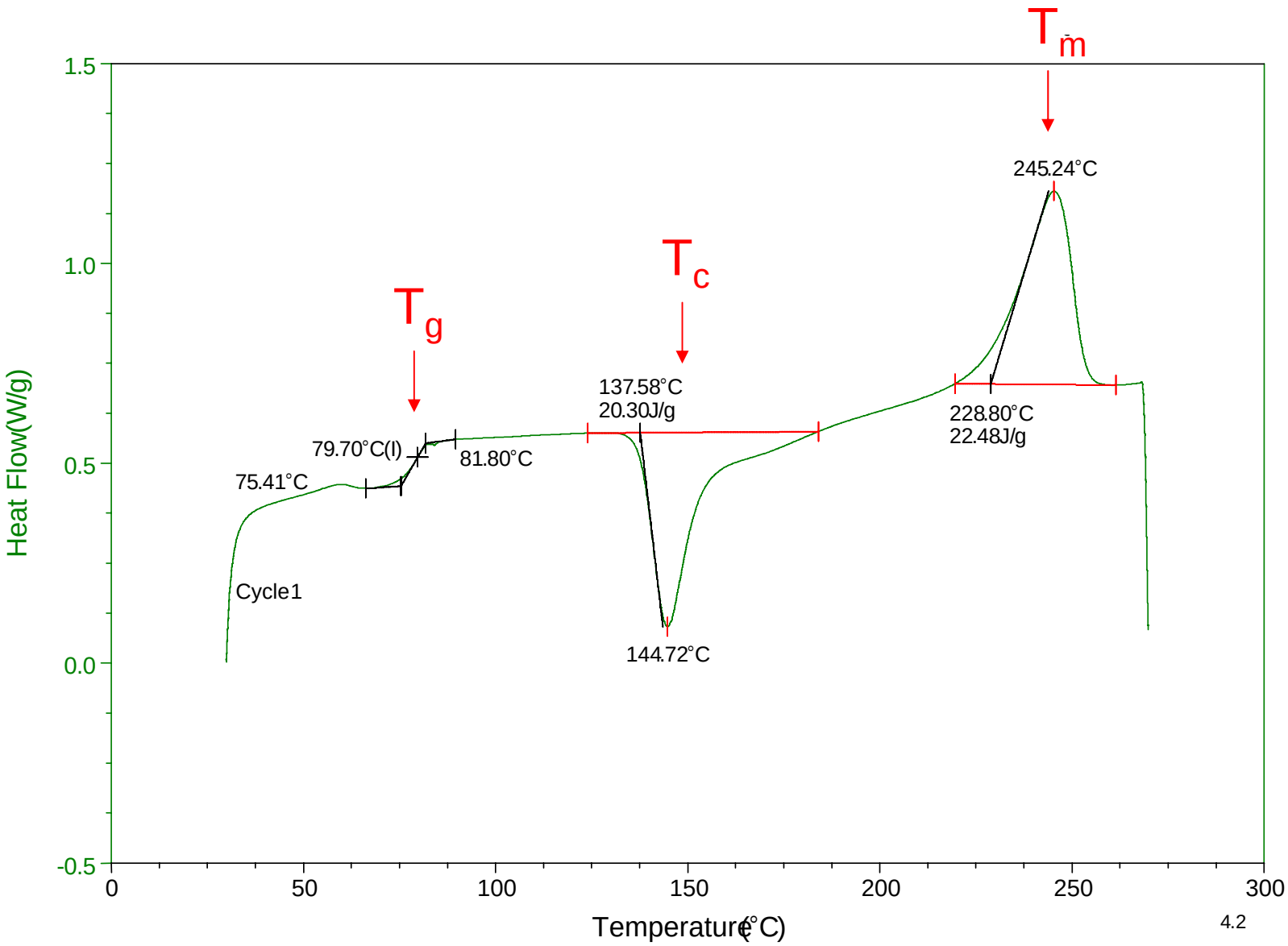
Definitions

- A ***calorimeter*** measures the heat into or out of a sample.
- A ***differential calorimeter*** measures the heat of a sample relative to a reference.
- A ***differential scanning calorimeter*** does all of the above and heats the sample with a linear temperature ramp.
- Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere.

Schematic of DSC Instrument



Example DSC – PET (polyethylene terephthalate)



What Can You Measure with DSC?

- **Glass transitions**
- **Melting and boiling points**
- **Crystallization time and temperature**
- Percent crystallinity
- **Heats of fusion and reactions**
- Specific heat capacity
- Oxidative/thermal stability
- **Rate and degree of cure**
- Reaction kinetics
- Purity

Contents for today's class

- **Amorphous vs Nanocrystalline**

  1) Microstructural observation

  2) Thermal analysis

  - DSC (Differential Scanning Calorimetry)

→ **local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.**

: Characterization of structure by pair distribution function

3) Intensive Structural Analysis*: *radial distribution function

- ***Amorphous vs Nanocrystalline***

  1) Microstructural observation

  XRD, (HR)TEM, EXAFS …

  2) Thermal analysis

  DSC (Differential Scanning Calorimetry)

  : Measure heat absorbed or liberated during heating or cooling

  cf) - glass → nucleation & growth

  (perfect random)

  - ***local clustering*: quenched-in nuclei → *only growth***
  - ***Nanocrystalline → growth***

  → **local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.**

  : *Characterization of structure by pair distribution function*

  3) Intensive Structural Analysis*: *radial distribution function

- ***Chen & Sapepen*** **(Harvard,1988)**

glass → ***nucleation & growth***

(perfect random)

→ **Isothermal annealing**

: rapid heating + maintain the temp.

- ***Glass :***

$$x = 1 - \exp(-bt^n)$$ **(*n: 2~4, nucleation mechanism*)**

crystallized volume fraction after time t

→ ***Corresponding heat release***

$$-\frac{dH}{dt} = \Delta H(1-x)n \cdot bt^{n-1}$$

(*ΔH: total transformation enthalpy*)

Glass

: exothermic peak at non-zero time

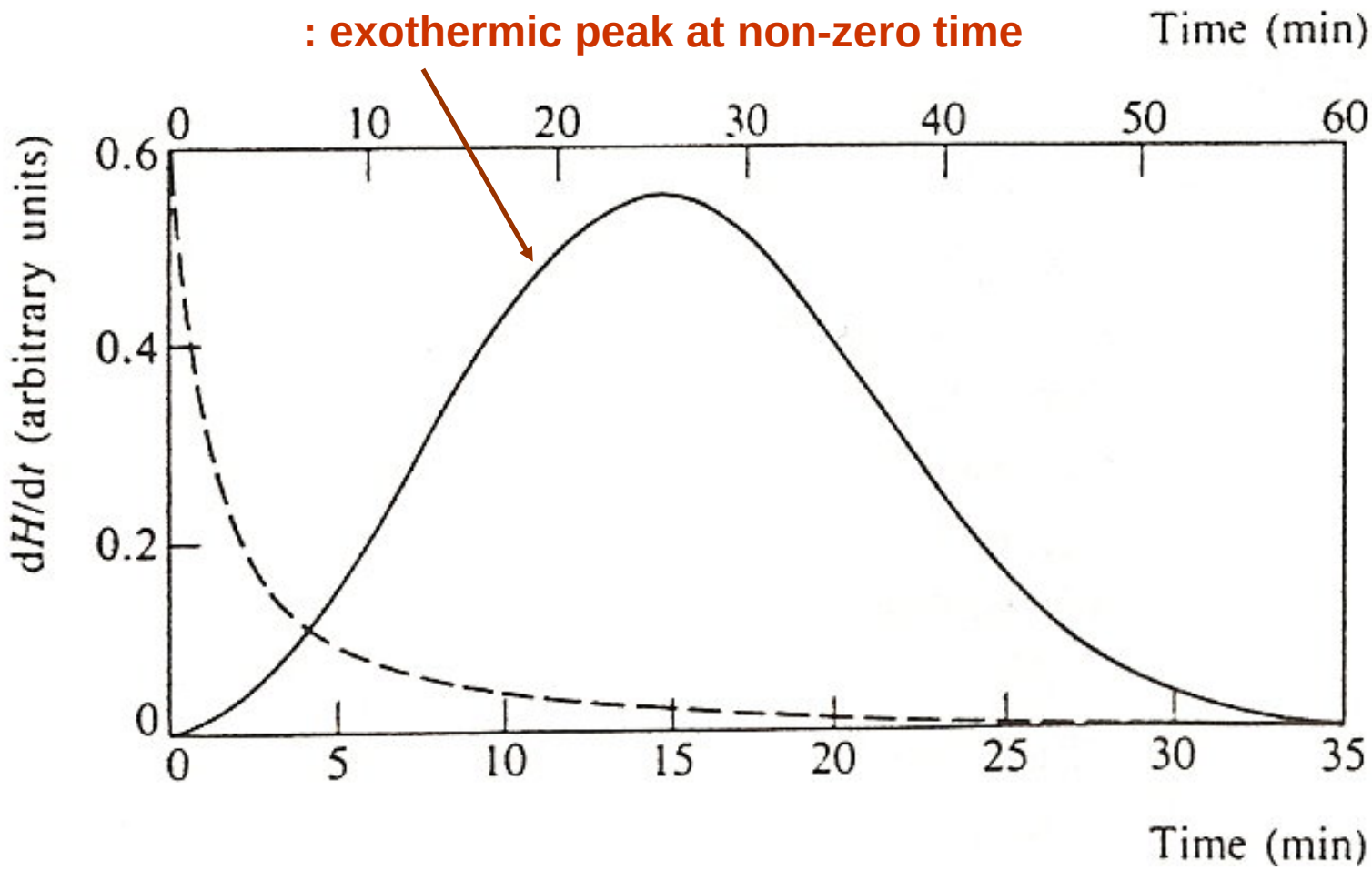


Fig. 1.4 Isothermal enthalpy release rates for crystallite nucleation and growth (solid line) and crystallite grain-coarsening mechanisms (dashed line)

- ***Nanocrystalline → grain growth***

$$\rightarrow \quad \frac{dr}{dt} = M \cdot \frac{\gamma}{r^{m}}$$

(***M*: *atomic mobility*, *γ*: *interficial surface tension***)

→ ***corresponding heat release***

$$-\frac{dH}{dt} = H(0) \cdot r(0) \cdot M\gamma / r^{m+2}$$

(***H(0)*: *zerotime enthalpy of a grain size of r (0)***)

→ ***Monotonically decreasing curve***

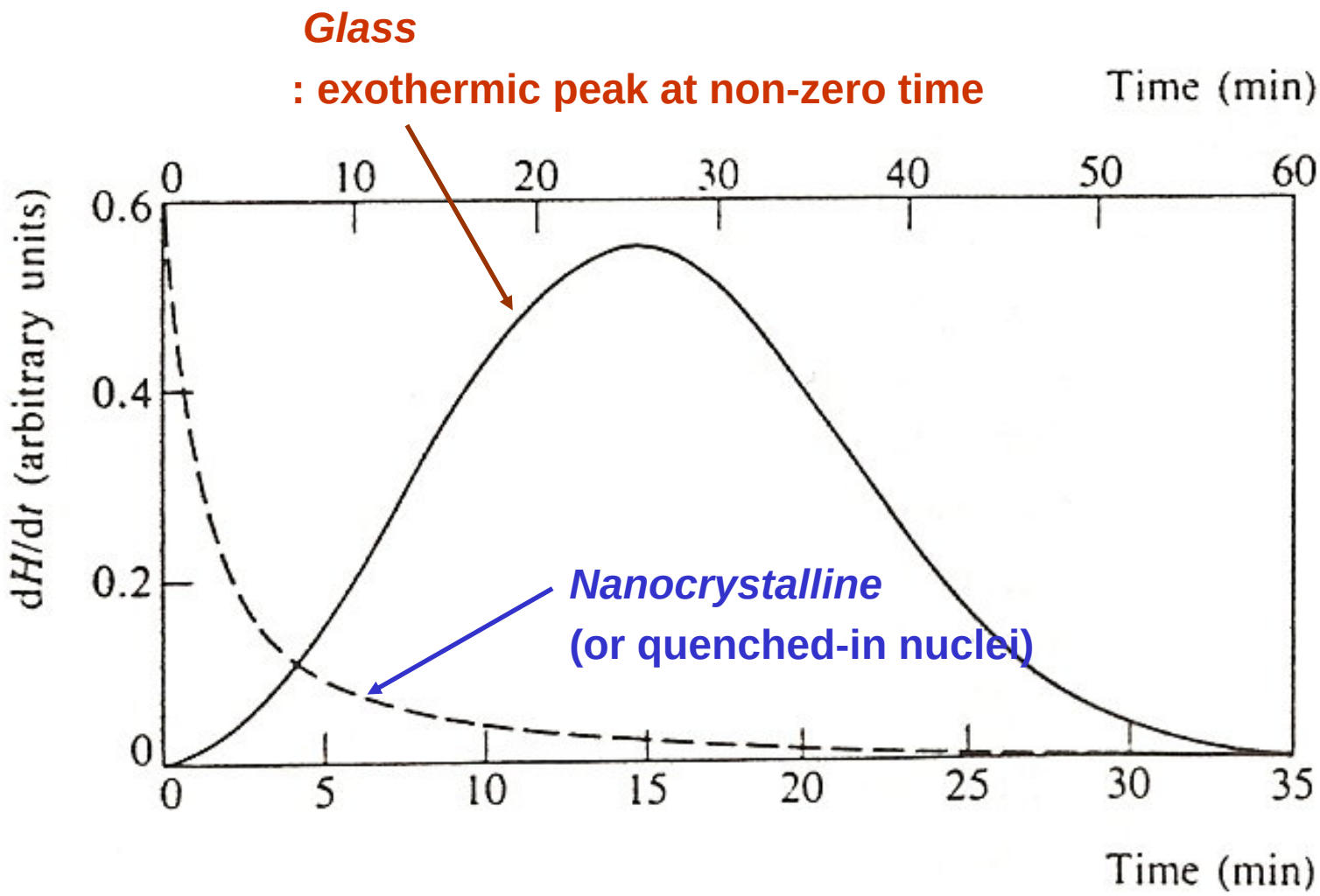


Fig. 1.4 Isothermal enthalpy release rates for crystallite nucleation and growth (solid line) and crystallite grain-coarsening mechanisms (dashed line)

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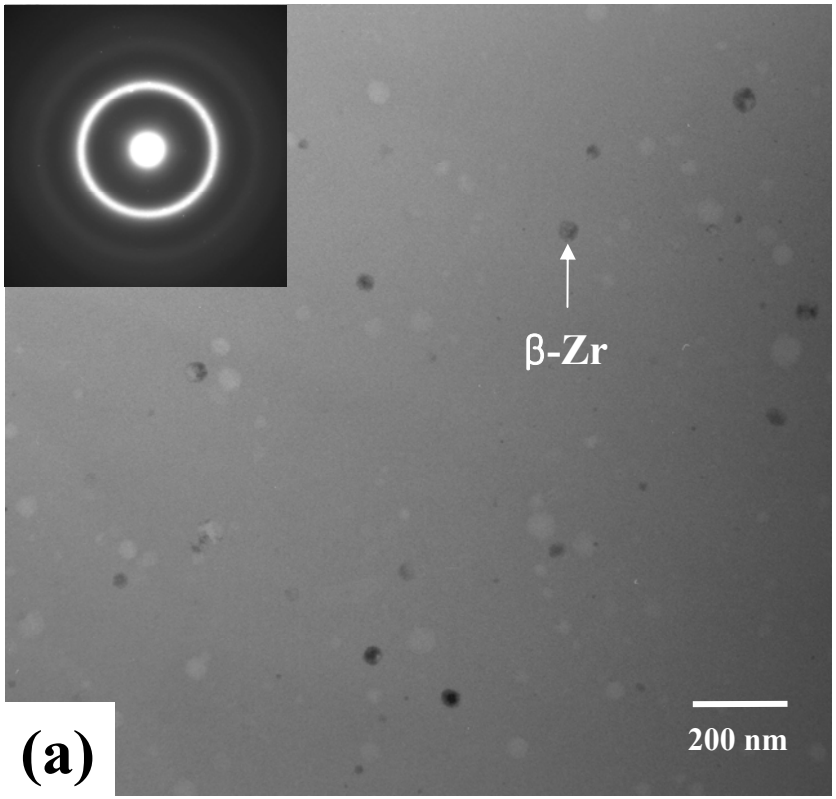
  : *Characterization of structure by pair distribution function*

  3) Intensive Structural Analysis*: *radial distribution function

Effect of quenched-in quasicrystal nuclei

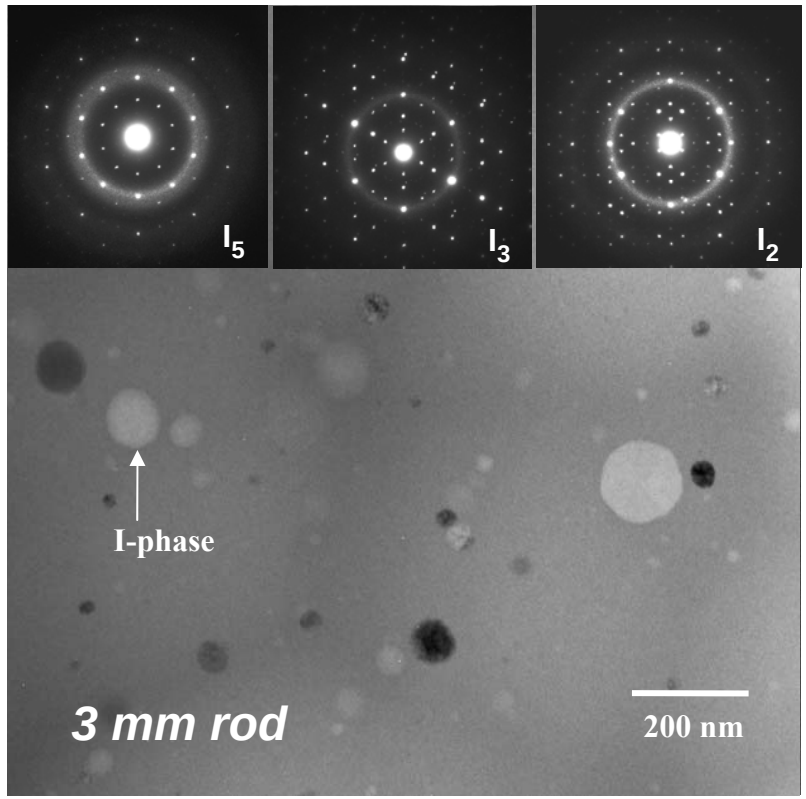
2 mm rod

(a) $Zr_{63}Ti_5Nb_2Cu_{15.8}Ni_{6.3}Al_{7.9}$



β-Zr particle(~70 nm) in amorphous matrix

(b) $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$

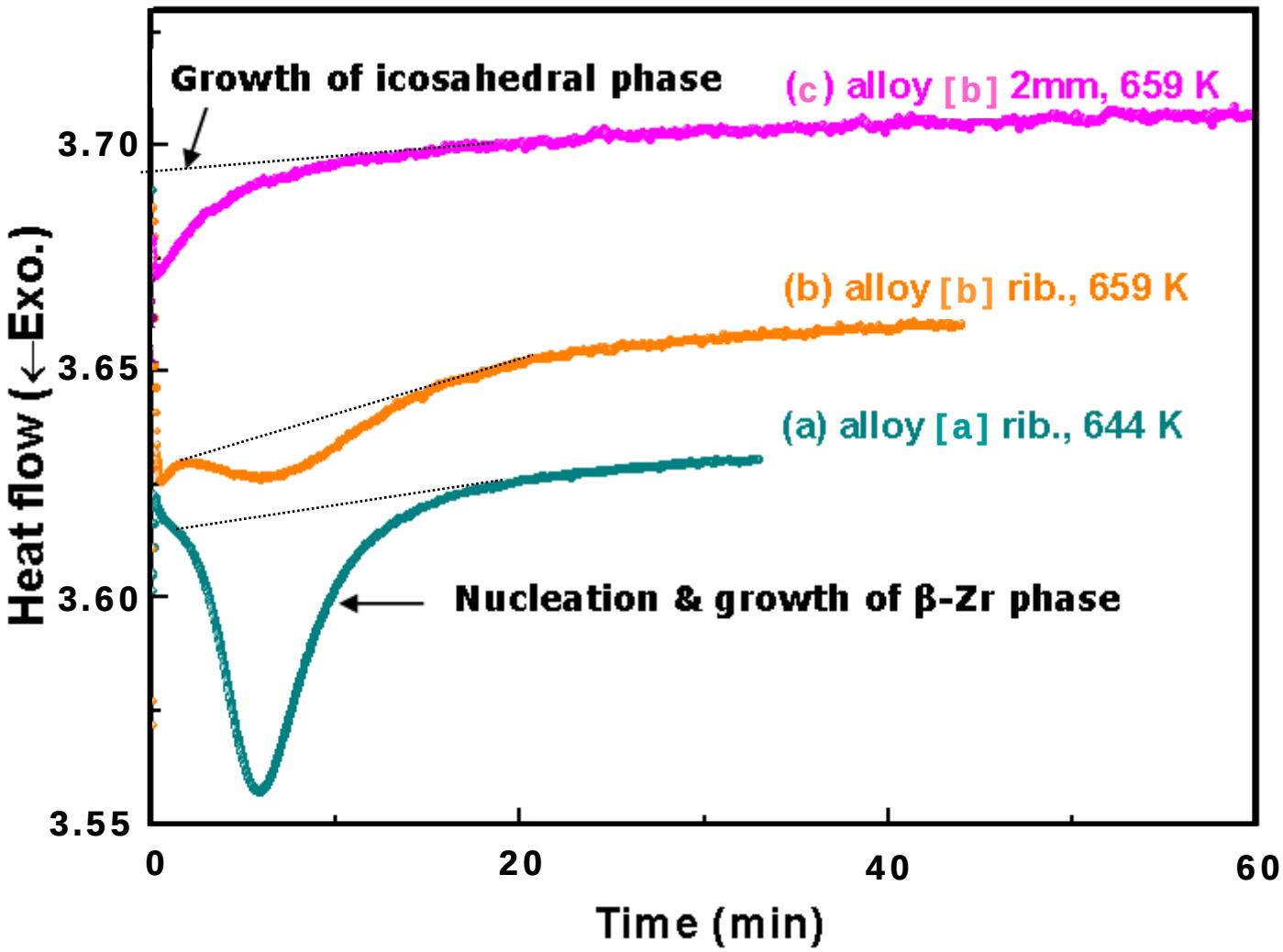


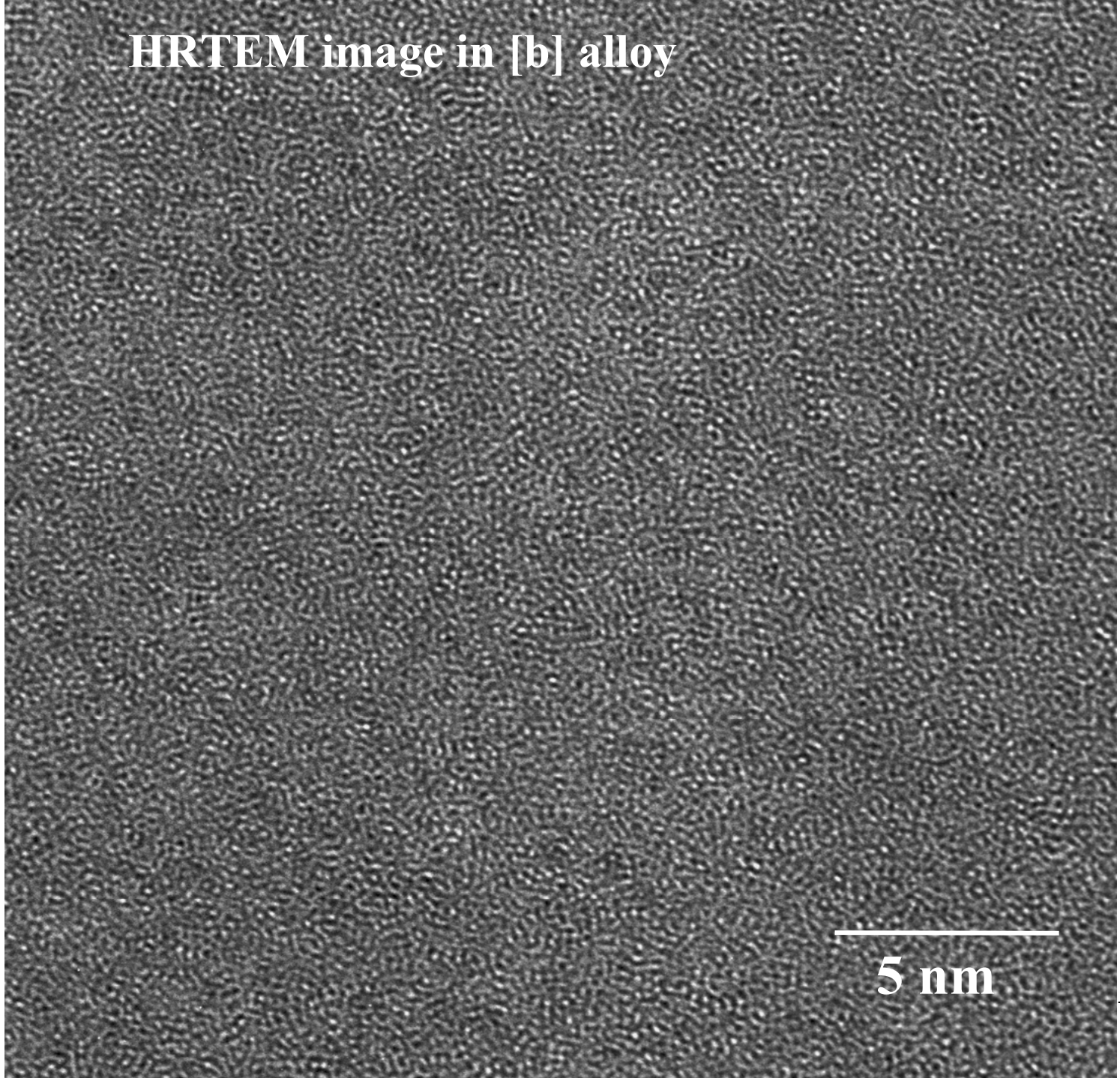
Fully amorphous structure

Effect of quenched-in quasicrystal nuclei

- Isotherm in DSC

Isothermal annealing

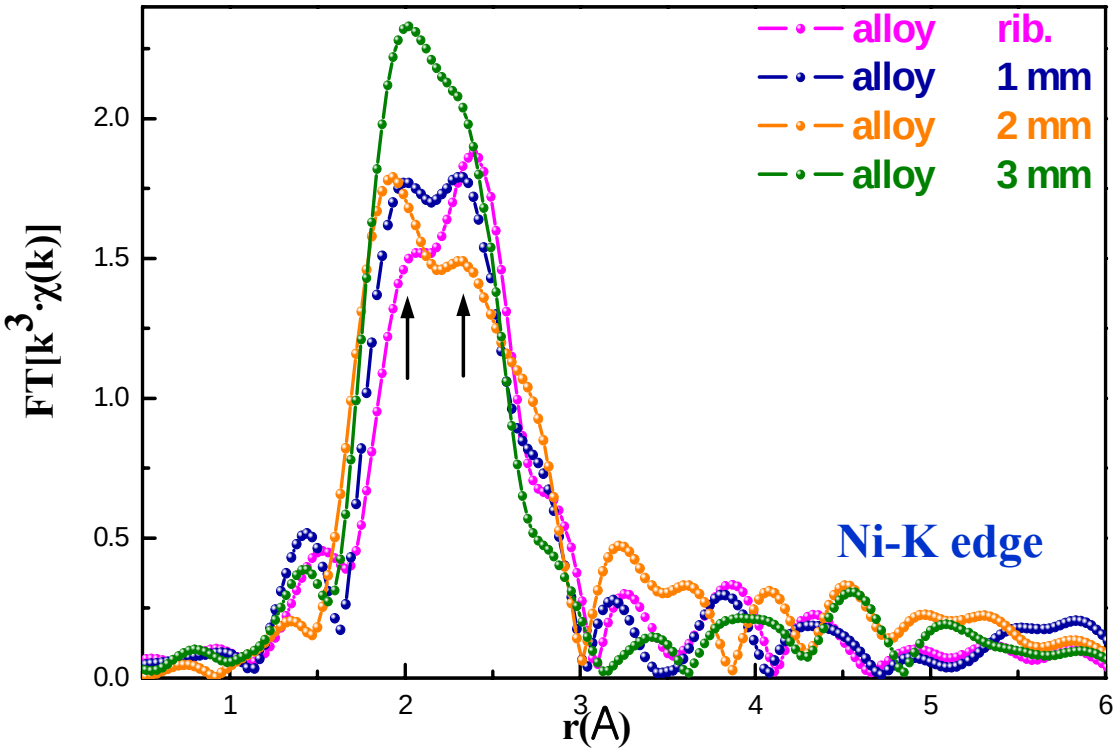


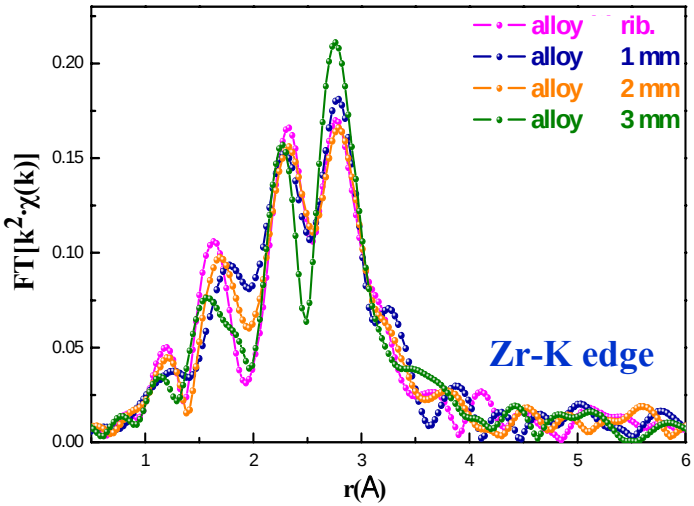

HRTEM image in [b] alloy
5 nm

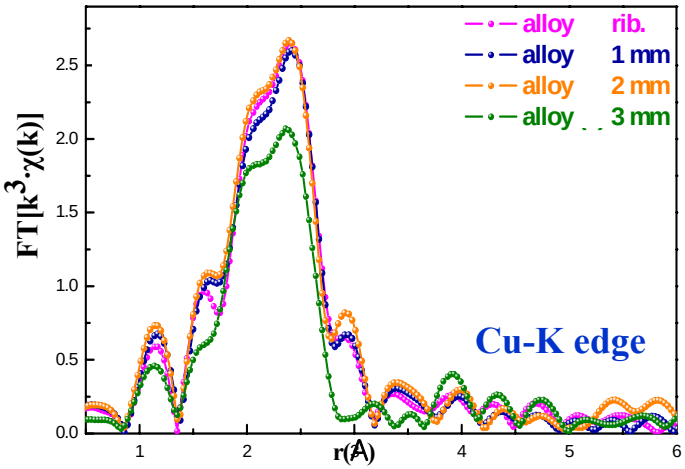
Effect of quenched-in quasicrystal nuclei

- **EXAFS analysis**

(b) $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$







Distinctive structural change around Ni atom

Intensity change due to microstructural change

- ***Amorphous vs Nanocrystalline***

1) Microstructural observation

XRD, (HR)TEM, EXAFS …

2) Thermal analysis

DSC (Differential Scanning Calorimetry)

: Measure heat absorbed or liberated during heating or cooling

cf) - glass → nucleation & growth

(perfect random)

- *local clustering*: quenched-in nuclei → *only growth*

- *Nanocrystalline* → *growth*

→ local clusters with atomic scale are difficult to identify by conventional observation tools of microstructure.

: Characterization of structure by pair distribution function

3) Intensive Structural Analysis*: *radial distribution function

Characterizing the structure - radial distribution function,

also called pair distribution function

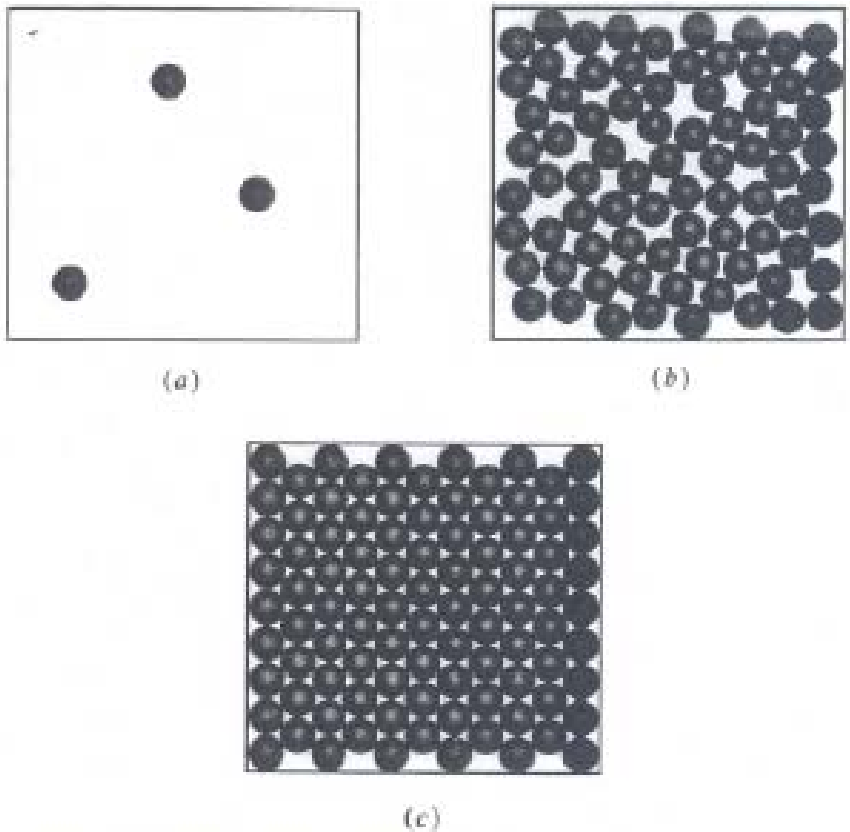


Figure 2.4 Hard-sphere model of (*a*) gas, (*b*) liquid/glass, and (*c*) crystalline solid.

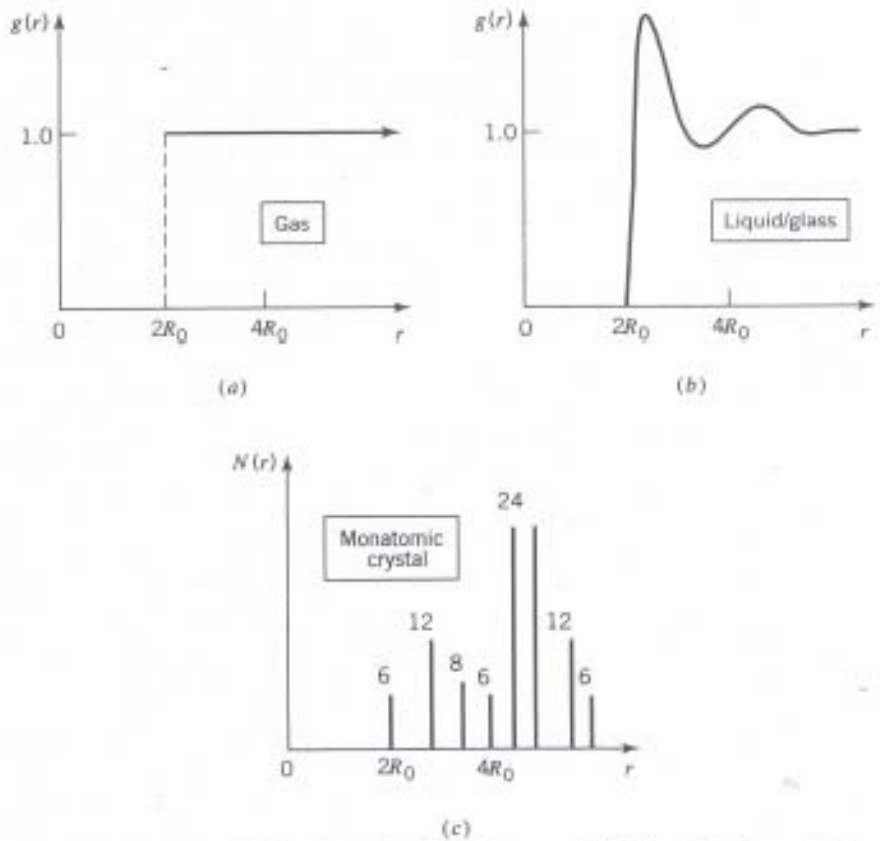
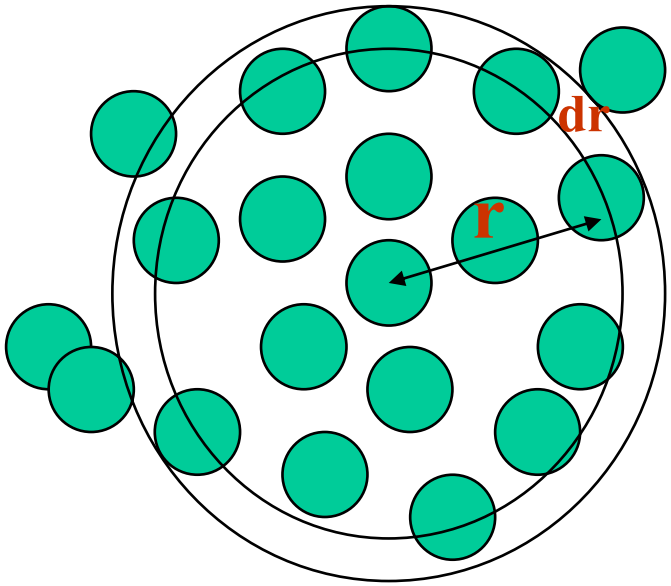


Figure 2.5 Pair-distribution functions for (*a*) a gas and (*b*) liquid or glass. (*c*) The radial dependence of the number of neighbors $N(r)$ for a primitive cubic crystal with one atom per lattice site.

Gas, amorphous/liquid and crystal structures have very different radial distribution function

Radial distribution function - definition



1. Carve a shell of size r and r + dr around a center of an atom. The volume of the shell is $dv=4\pi r^2 dr$
2. Count number of atoms with centers within the shell (dn)
3. Average over all atoms in the system
4. Divide by the average atomic density $\langle\rho\rangle$

$$g(r) = \frac{1}{\langle\rho\rangle}\frac{dn(r, r+dr)}{dv(r, r+dr)}$$

Count thy neighbours

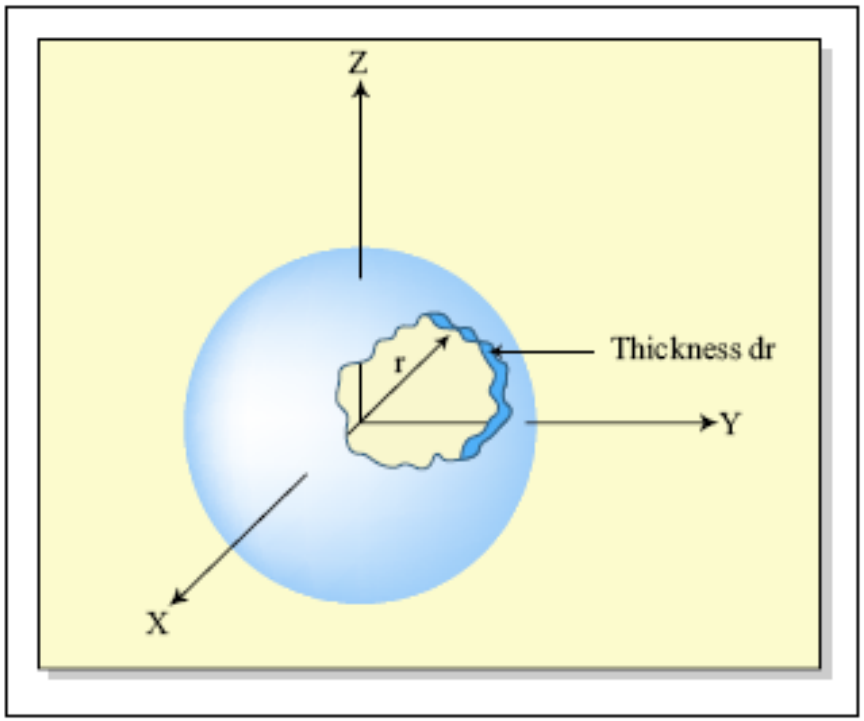
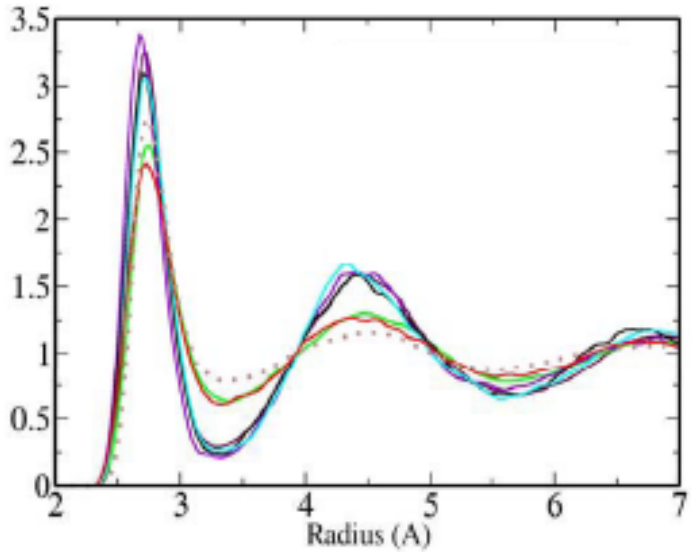


Figure by MIT OCW.



Properties of the radial distribution function

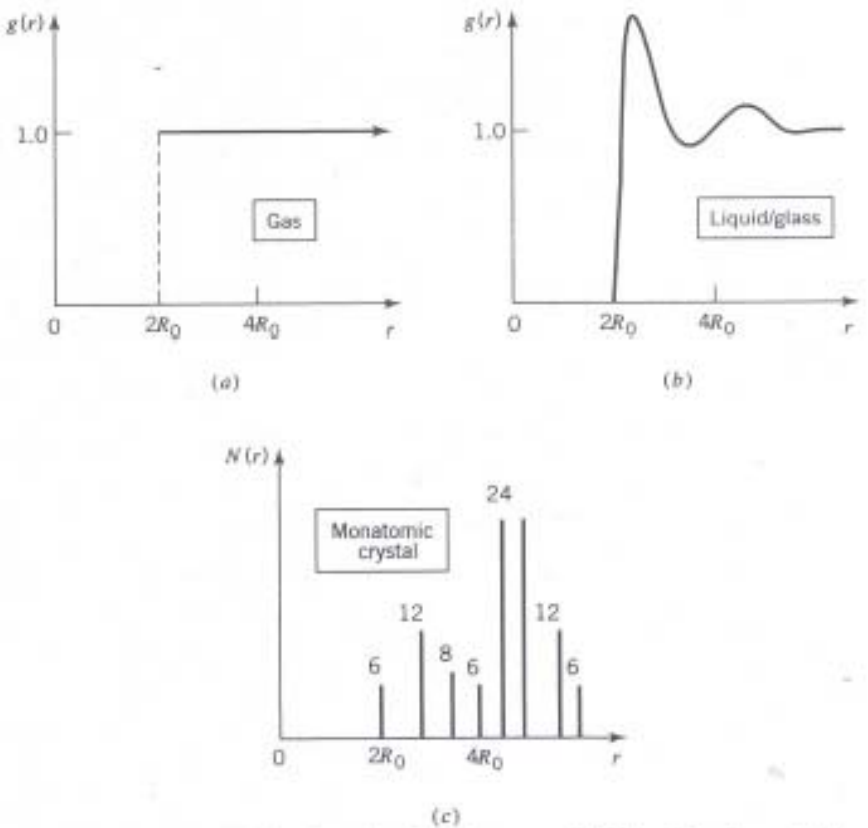


Figure 2.5 Pair-distribution functions for (*a*) a gas and (*b*) liquid or glass. (*c*) The radial dependence of the number of neighbors $N(r)$ for a primitive cubic crystal with one atom per lattice site.

For gases, liquids and amorphous solids g(r) becomes unity for large enough r.

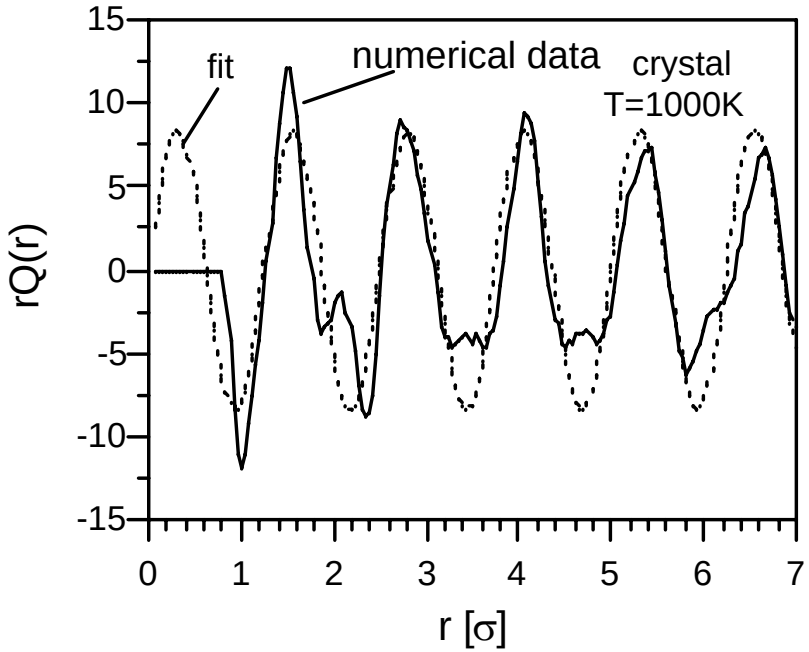
The distance over which g(r) becomes unity is called the correlation distance which is a measure of the extent of so-called short range order (SRO)

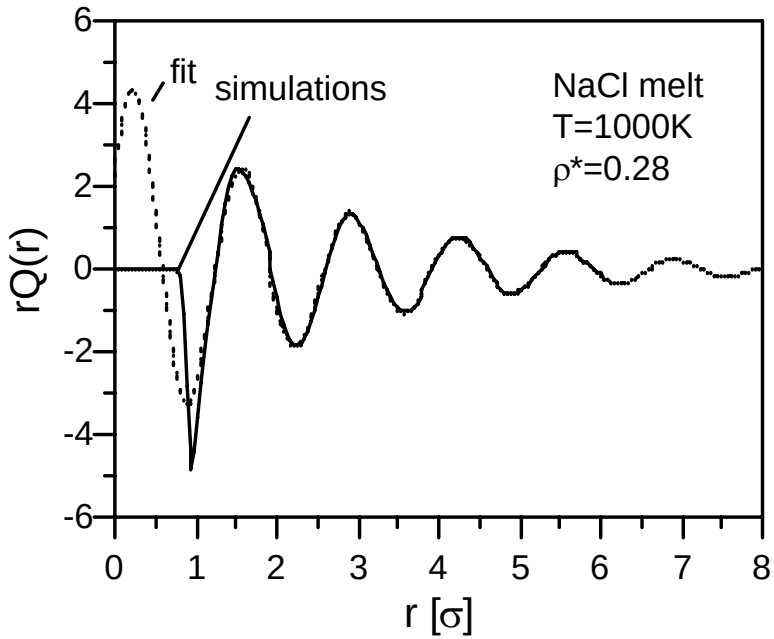
The first peak corresponds to an average nearest neighbor distance

Features in g(r) for liquids and amorphous solids are due to packing (exclude volume) and possibly bonding characteristics

Radial Distribution Function - Crystal and Liquid

$$Q(r) = g(r) - 1 \sim \frac{1}{r}\sin(r/d + \varphi)\exp(r/\lambda)$$





Liquid/amorphous g(r), for large r exhibit oscillatory exponential decay
Crystal g(r) does not exhibit an exponential decay ($\lambda \to \infty$)

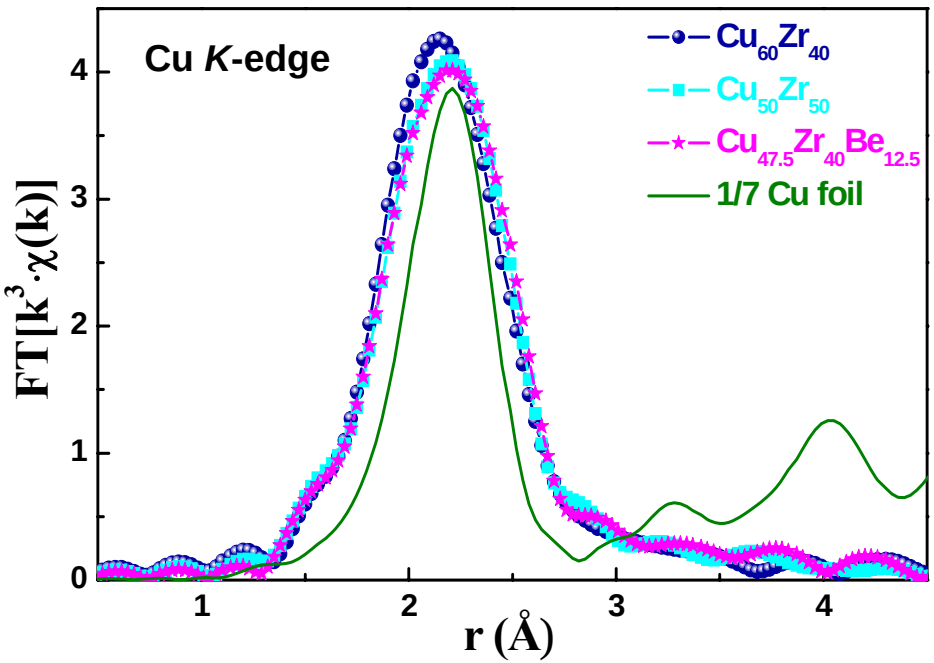
Radial distribution functions and the structure factor

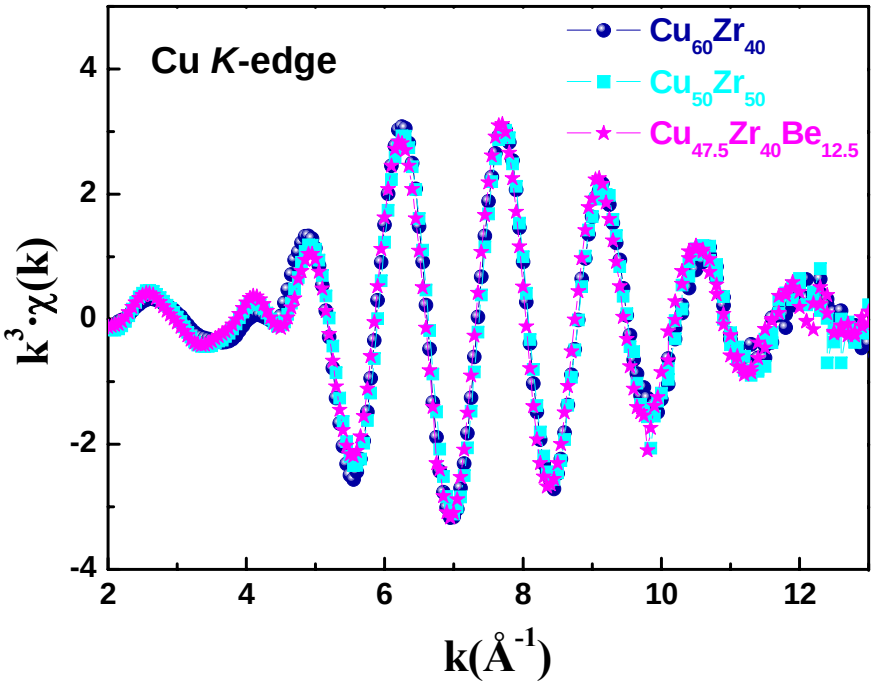
- The structure factor, S(k), which can be measured experimentally (e.g. by X-rays such as EXAFS) is given by the Fourier transform of the radial distribution function and vice versa

$$S(k) = 1 + \frac{4\pi\langle\rho\rangle}{k}\int_0^\infty r[g(r)-1]\sin(kr)dr$$

Radial distribution functions can be obtained from experiment and compared with that from the structural model

Radial distribution functions ⟺ ***Structure factor***





More detailed structural characterization - Voronoi Polyhedra

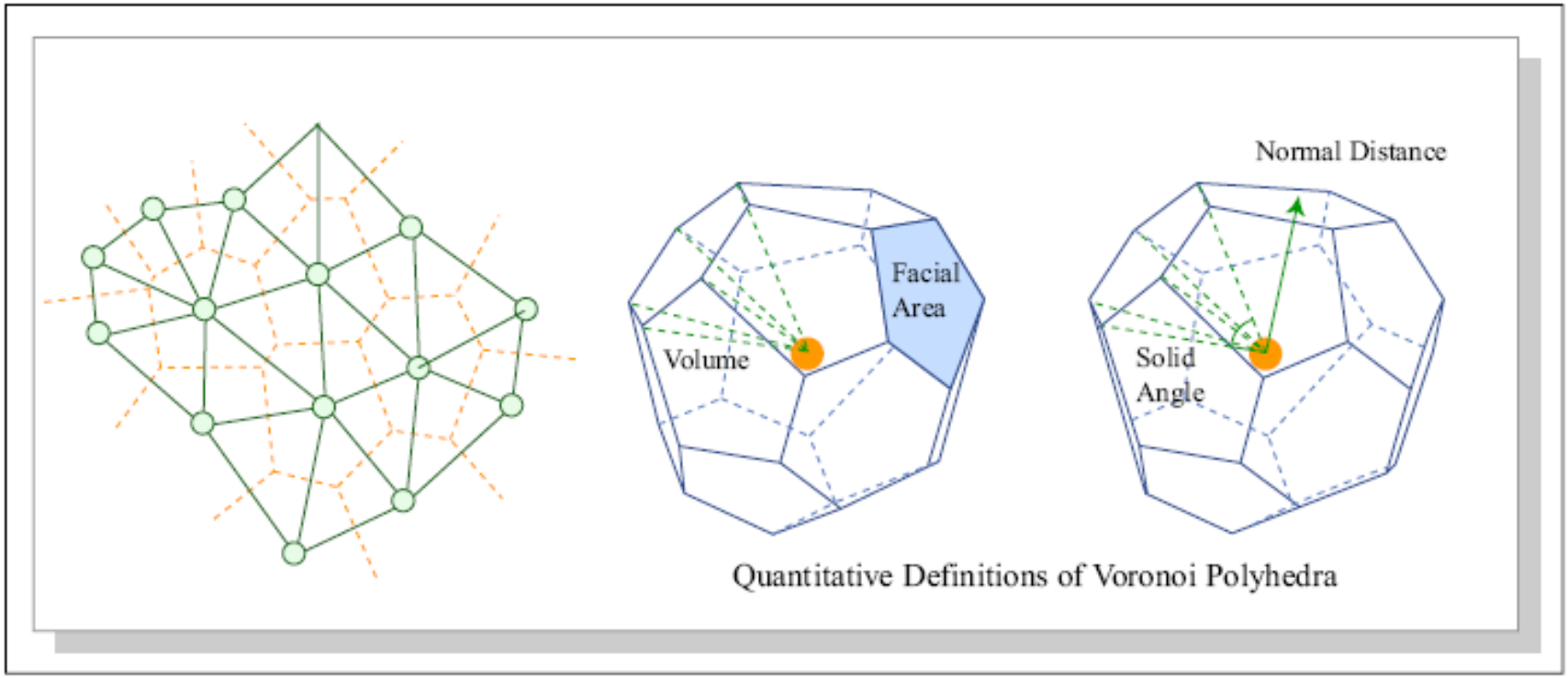
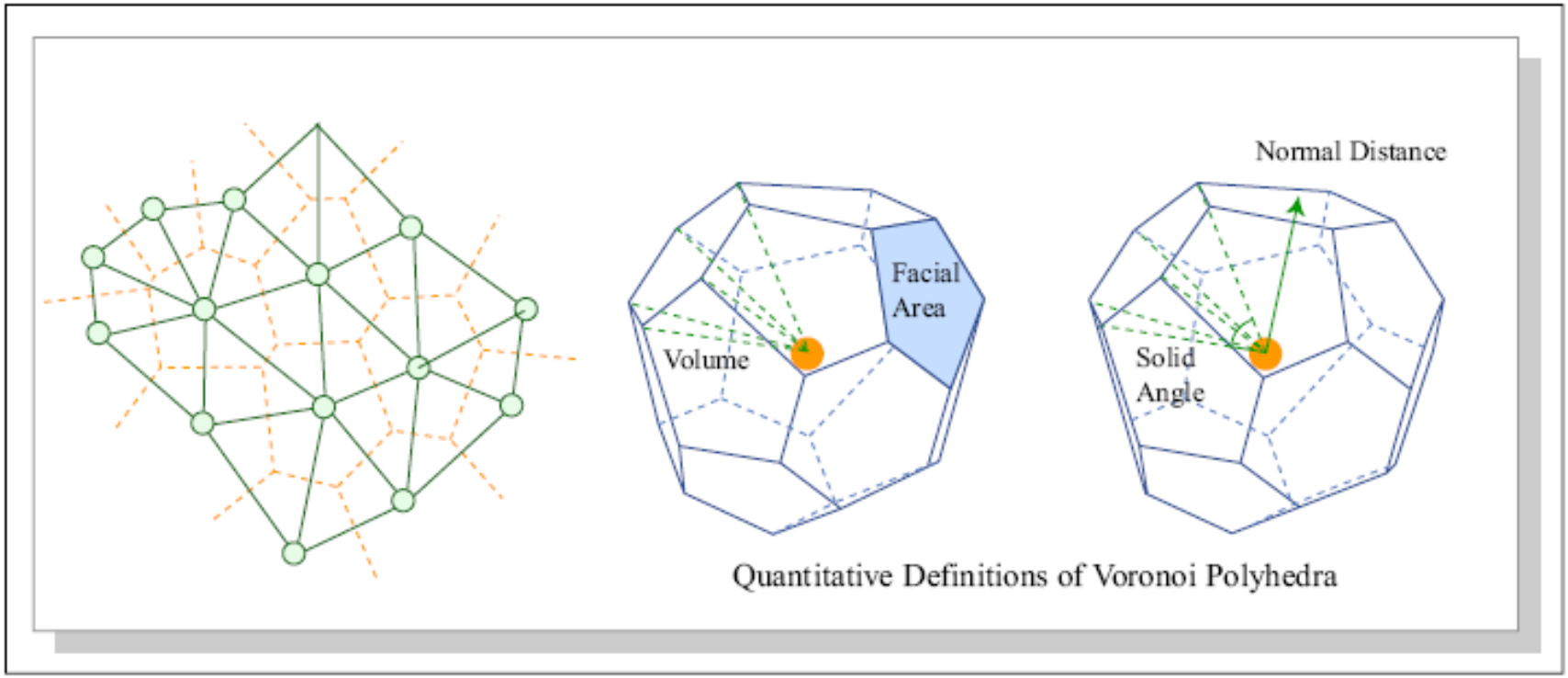


Figure by MIT OCW.

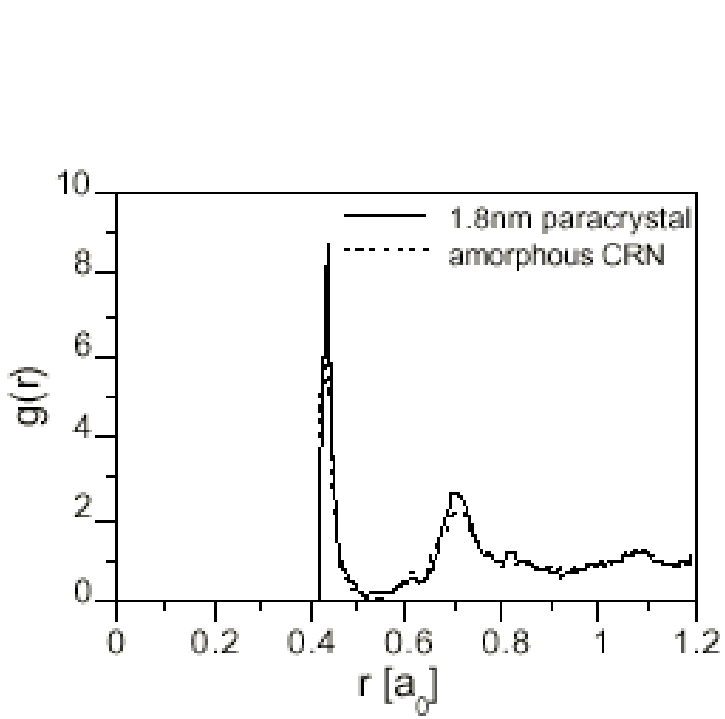
- **Draw lines between a center of an atom and nearby atoms.**
- **Construct planes bisecting the lines perpendicularly**
- **The sets of planes the closest to the central atom forms a convex polyhedron**
- **Perform the statistical analysis of such constructed polyhedrons, most notably evaluate an average number of faces**

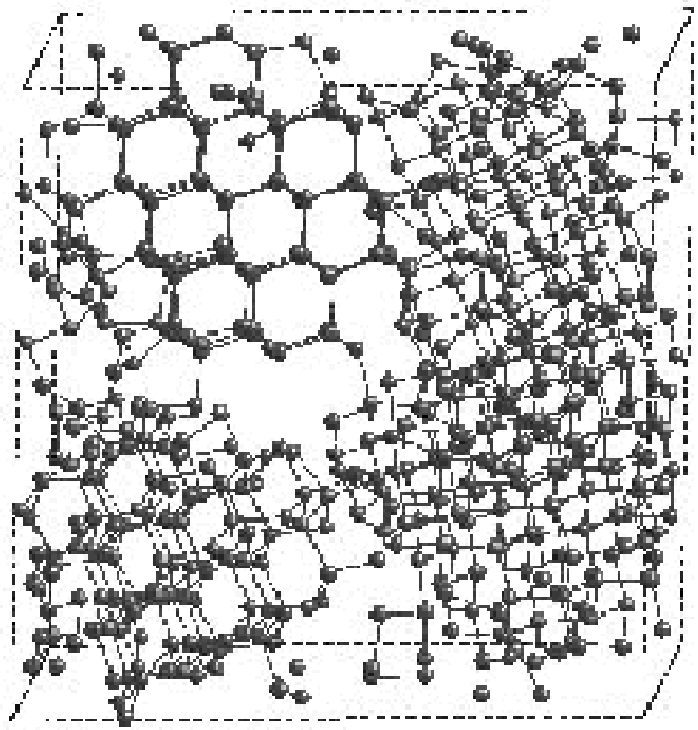
More detailed structural characterization - Voronoi Polyhedra



- **For no-directional bonding promoting packing number of faces is large ~ 13-14 (metallic glasses)**
- **For directional bonding (covalent glasses) number of faces is small**
- **Ionic glasses - intermediate**
- **In all cases the number of faces is closely related to the number of nearest neighbors (the coordination number)**

Medium range order and radial distribution function

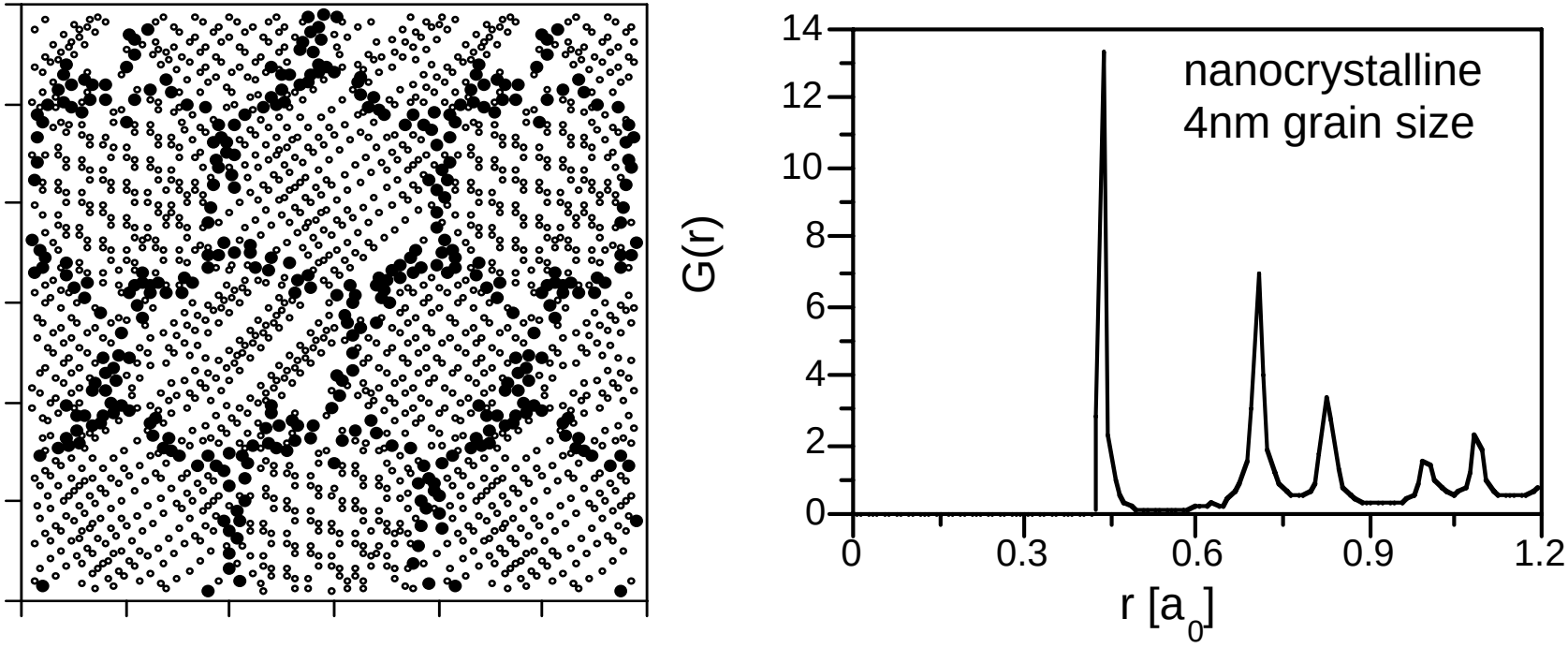




Radial distribution functions (and also X-ray) of amorphous silicon and model Si with ~ 2 nm crystalline grains are essentially the same - medium range order difficult to see by standard characterization tools. Such structure is called a paracrystal.

Radial Distribution Function

Nanocrystalline material



Nanocrystalline materials shows clear crystalline peaks with some background coming from the grain boundary