2010 Spring

"Amorphous Materials"

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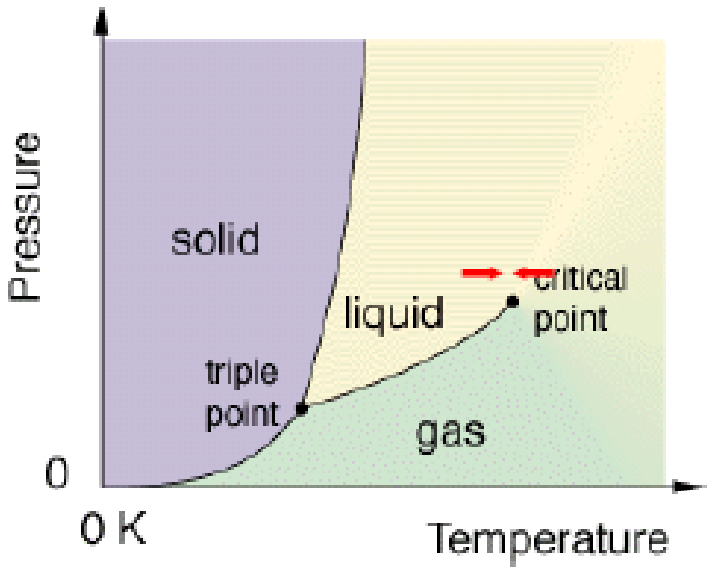
Contents for previous class

Glass transition

❖ The glass transition is **not first order transition** (such as melting), meaning there is no discontinuity in the thermodynamic functions (energy, entropy, density).

❖ The glass transition is **'pseudo' second-order phase transition**. And the transition depends on kinetic factors (cooling rate).



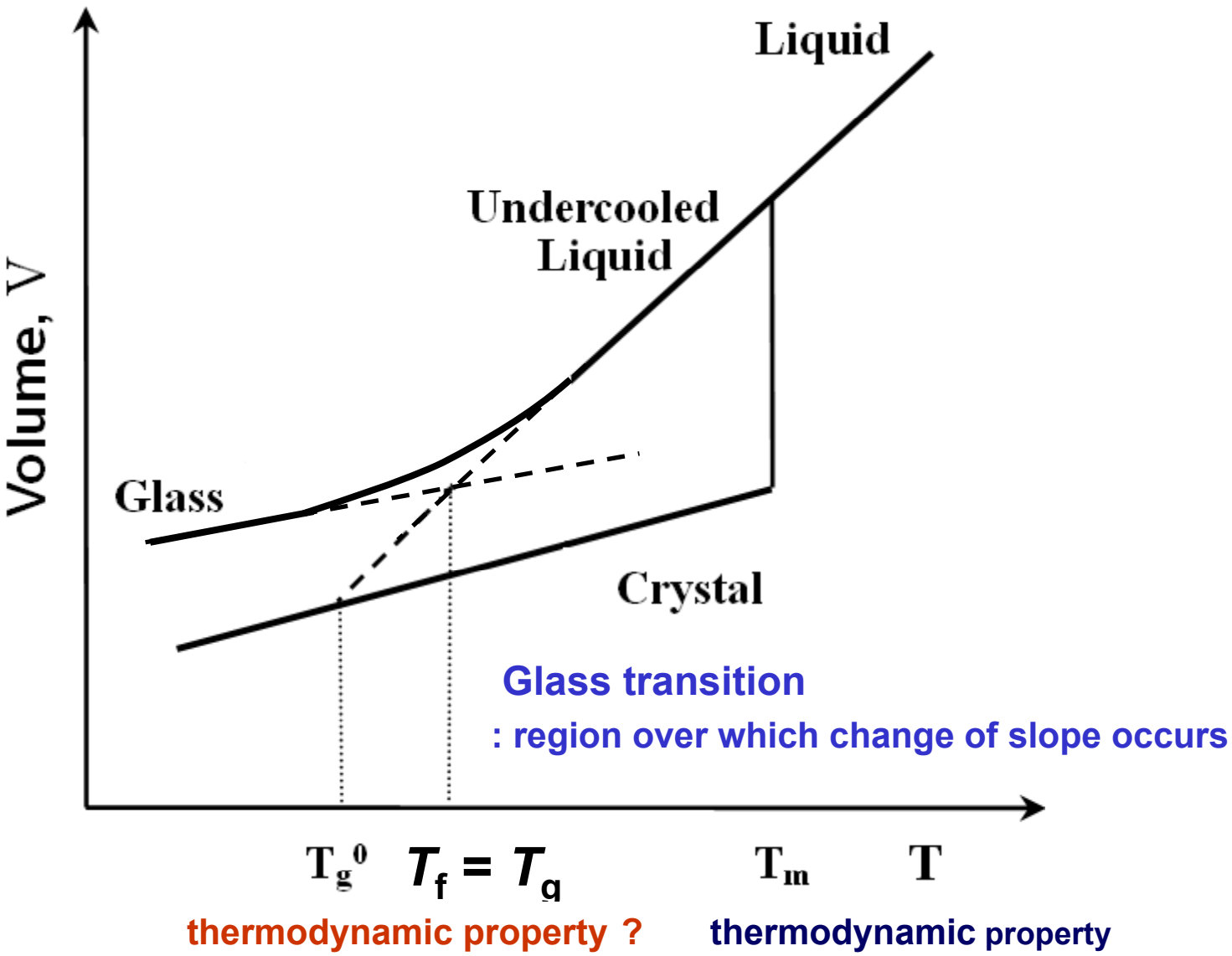
❖ No Latent heat

❖ Continuous Gibbs free energy

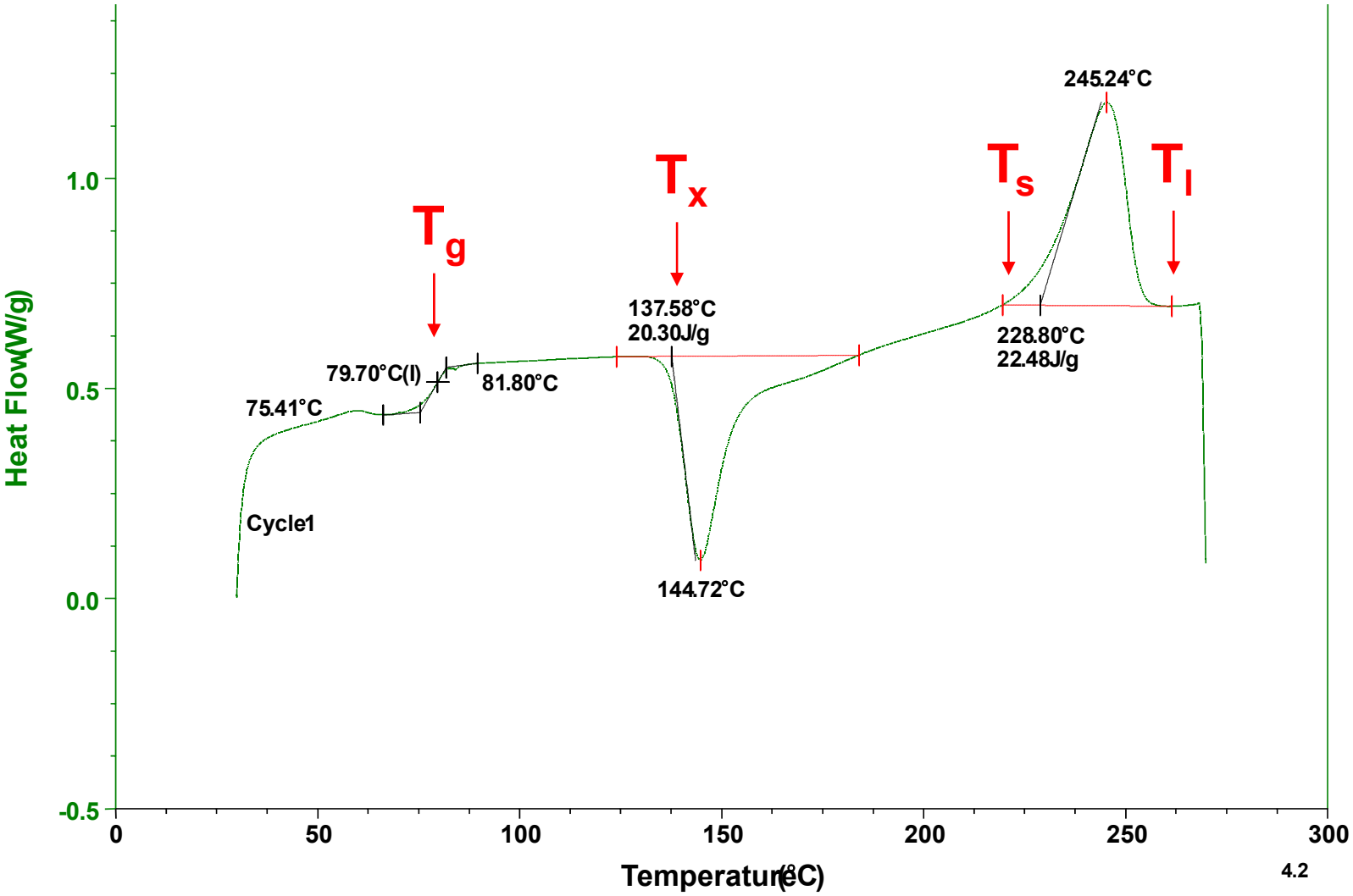
❖ Continuous entropy

❖ Discontinuous heat capacity

T_g = *fictive temperature*, T_f



- **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.**



• 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*)

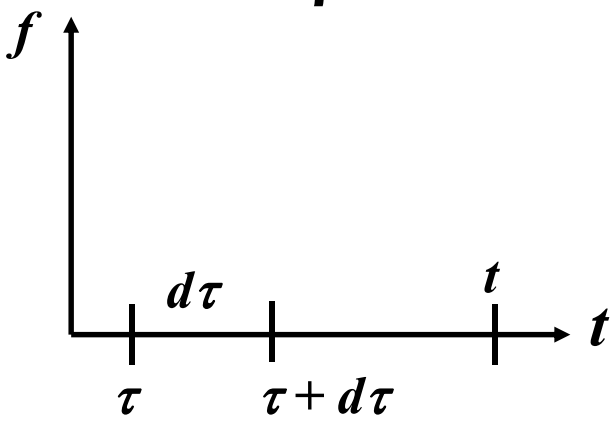
Johnson-Mehl-Avrami Equation : 변태속도 비교

Assumption:

- reaction produces by N + G
- nucleation occurs randomly throughout specimen
- reaction product grows radially until impingement

define volume fraction transformed $f = \dfrac{Vol\ .\ of\ \ new\ \ \ phase}{Vol\ .\ of\ \ specimen}$

α→β



v : cell growth rate (assumed const.)

N : nucleation rate (const.)

How much transformation occurred on time interval $d\tau$

$$df = \frac{\begin{pmatrix} vol.\ of\ one\ \ particle\ nucleated \\ during\ \ d\tau\ \ measured\ \ at\ time\ t \end{pmatrix} \times \begin{pmatrix} number\ of\ nuclei \\ formed\ \ during\ \ d\tau \end{pmatrix}}{volume\ of\ specimen}$$

$$\boxed{df = \frac{\frac{4}{3}\pi[v(t-\tau)]^3 \times (NV_0 d\tau)}{V_0}}$$

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\ (vt)^3$$

$$V' = \frac{4}{3}\ \pi v^3 (t-\tau)^3$$

$$f = \int_0^x d\hat{f} = \frac{4}{3}\pi N v^3 \int_0^t (t-\tau)^3 \, d\tau$$

$$f = \frac{\pi}{3} N v^3 t^4$$

→ do not consider impingement & repeated nucleation

→ only true for $f \ll 1$ ∵ 시간이 지날수록 충돌에 의한 변태속도 감소 증가

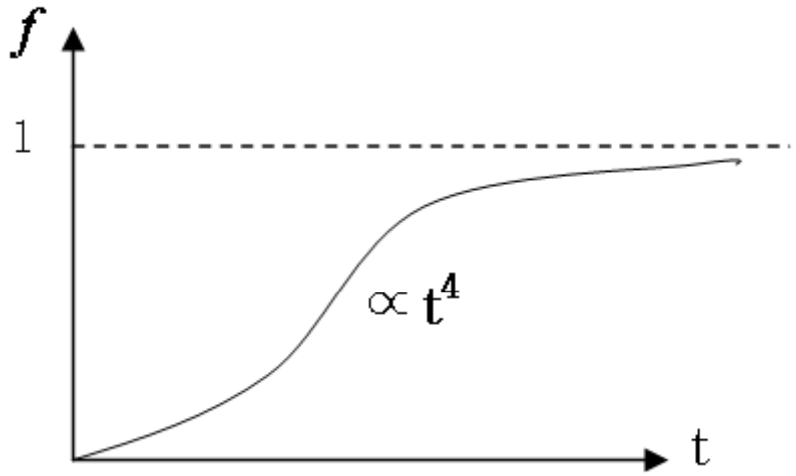
임의로 배열된 생성상의 충돌효과를 고려하면,

J-M-A Eq.

$$f = 1 - \exp\left(-\frac{\pi}{3} N v^3 t^4\right)$$

$$1 - \exp(z) \approx Z \qquad (z << 1)$$

$$f = 1 - \exp(-k t^n)$$



Example above.

k : sensitive to temp. (N, v)

n : 1 ~ 4

Growth controlled. **Nucleation-controlled.**

i.e. 50% transform

Exp (-0.7) = 0.5

$$k t_{0.5}^n = 0.7 \qquad t_{0.5} = \frac{0.7}{k^{1/n}} \qquad t_{0.5} = \frac{0.9}{N^{1/4} v^{3/4}}$$

*K*가 클때, 즉 핵생성 속도와 성장 속도가 클때 변태 속도가 빠름

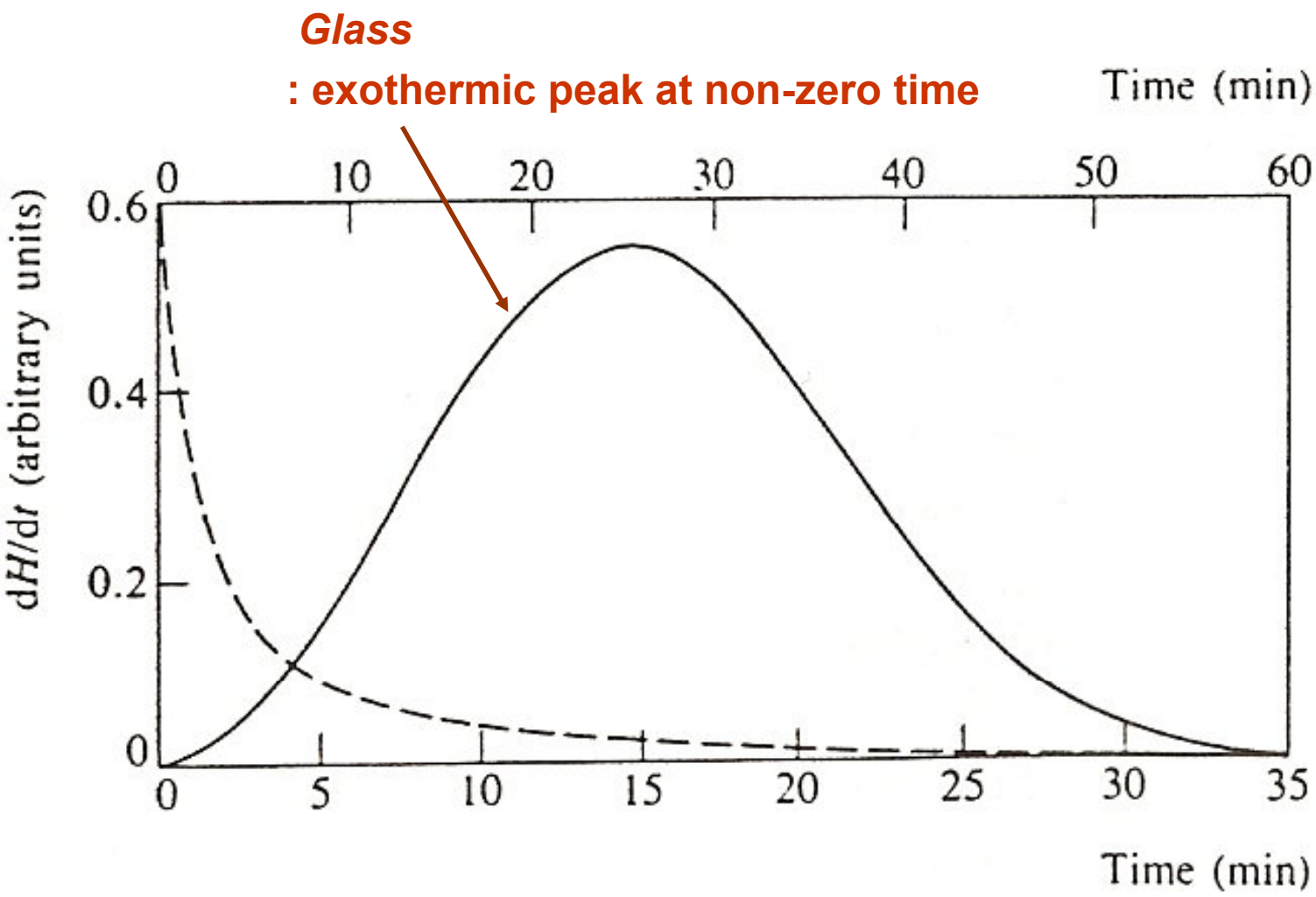


Fig. 1.4 **Isothermal enthalpy release rates for crystallite nucleation and growth (solid line) and crystallite grain-coarsening mechanisms (dashed line)**

- ***Nanocrystalline*** → ***grain growth***

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

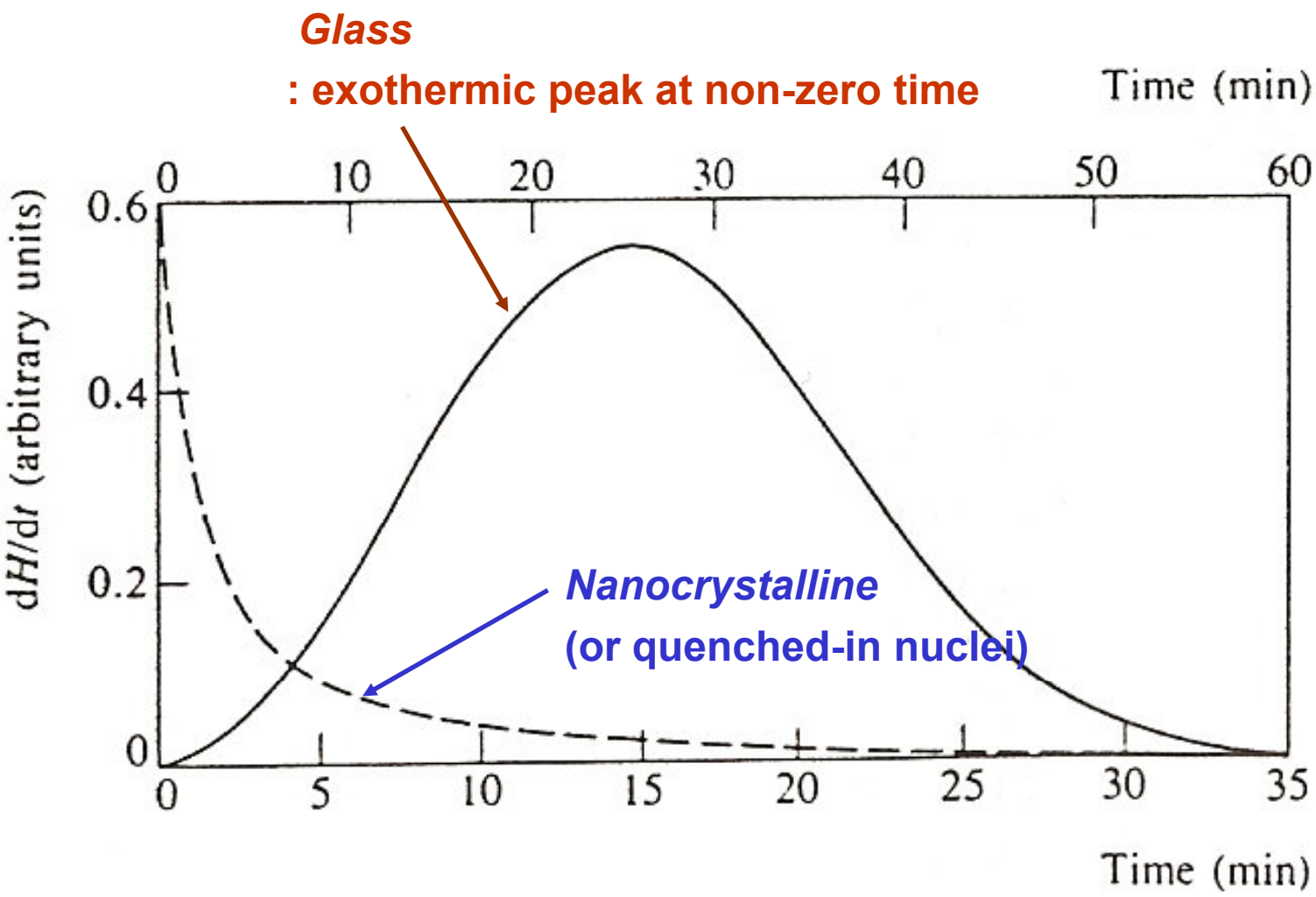
(***M***: ***atomic mobility,*** γ : ***interficial surface tension***)

→ ***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***



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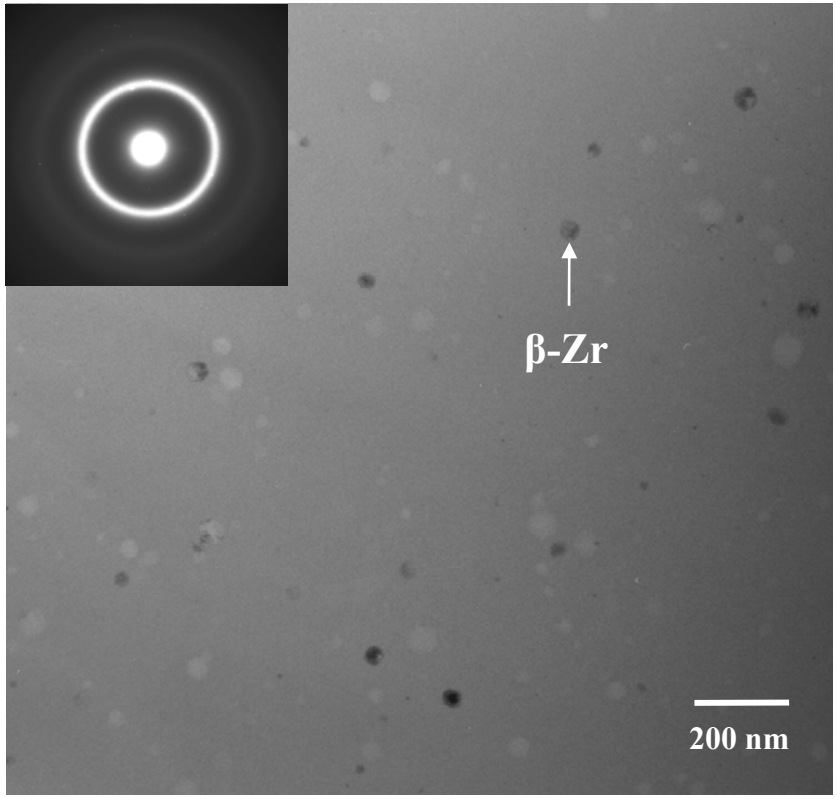
: Characterization of structure by pair distribution function

3) Intensive Structural Analysis: radial distribution function

Effect of quenched-in quasicrystal nuclei

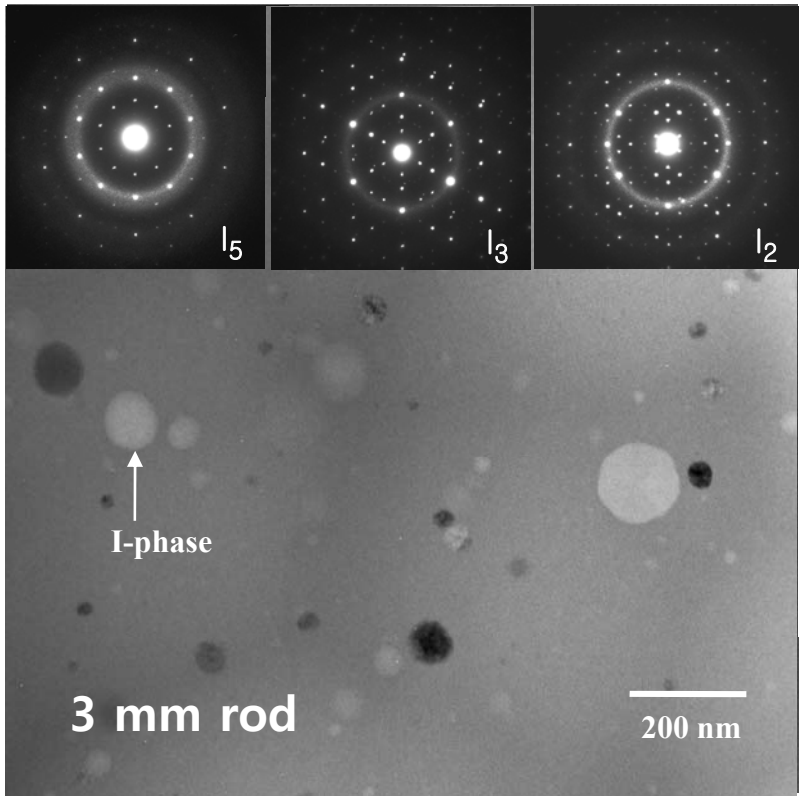
2 mm rod

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



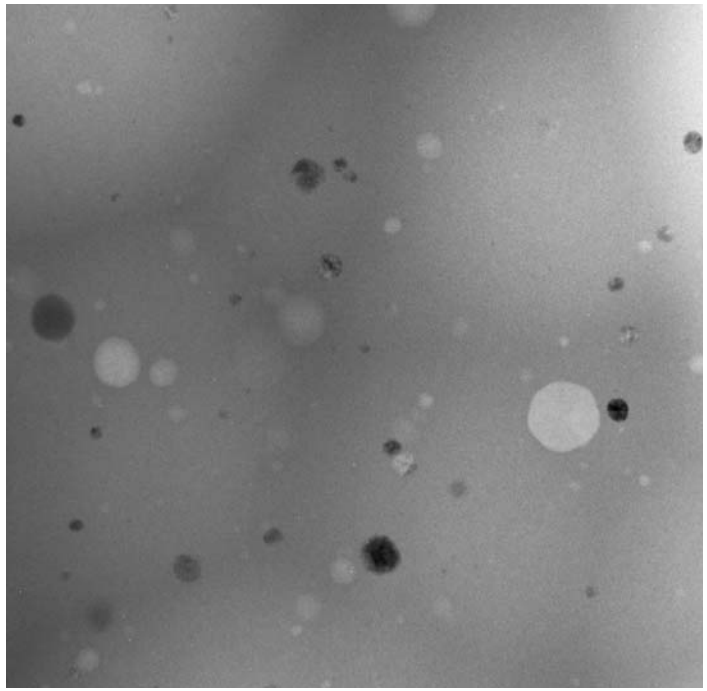
β-Zr particle (~70 nm) in amorphous matrix

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

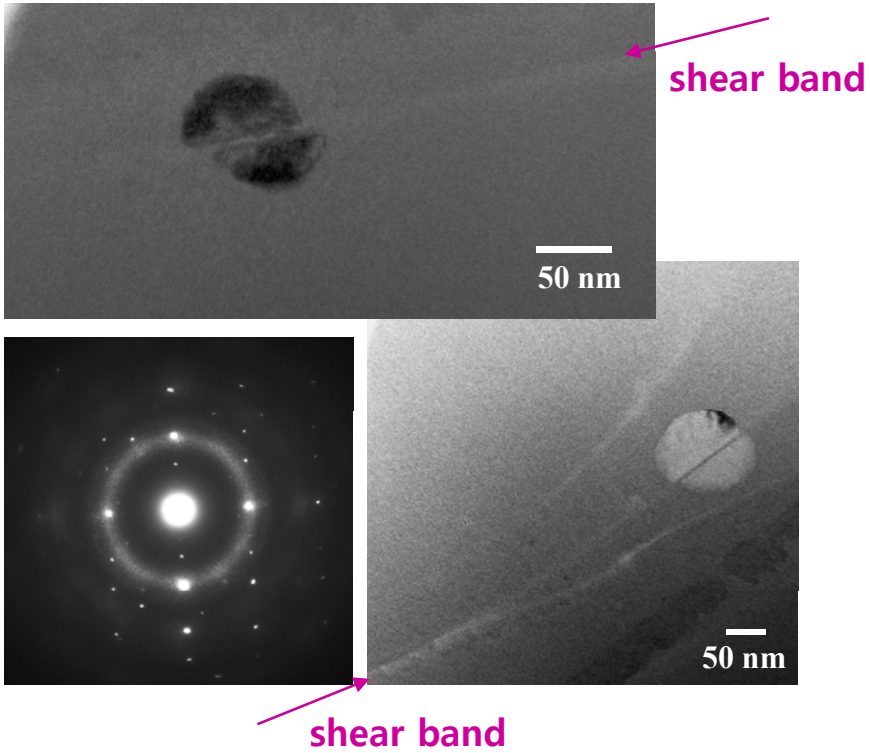


I-phase particle in amorphous matrix

Before deformation



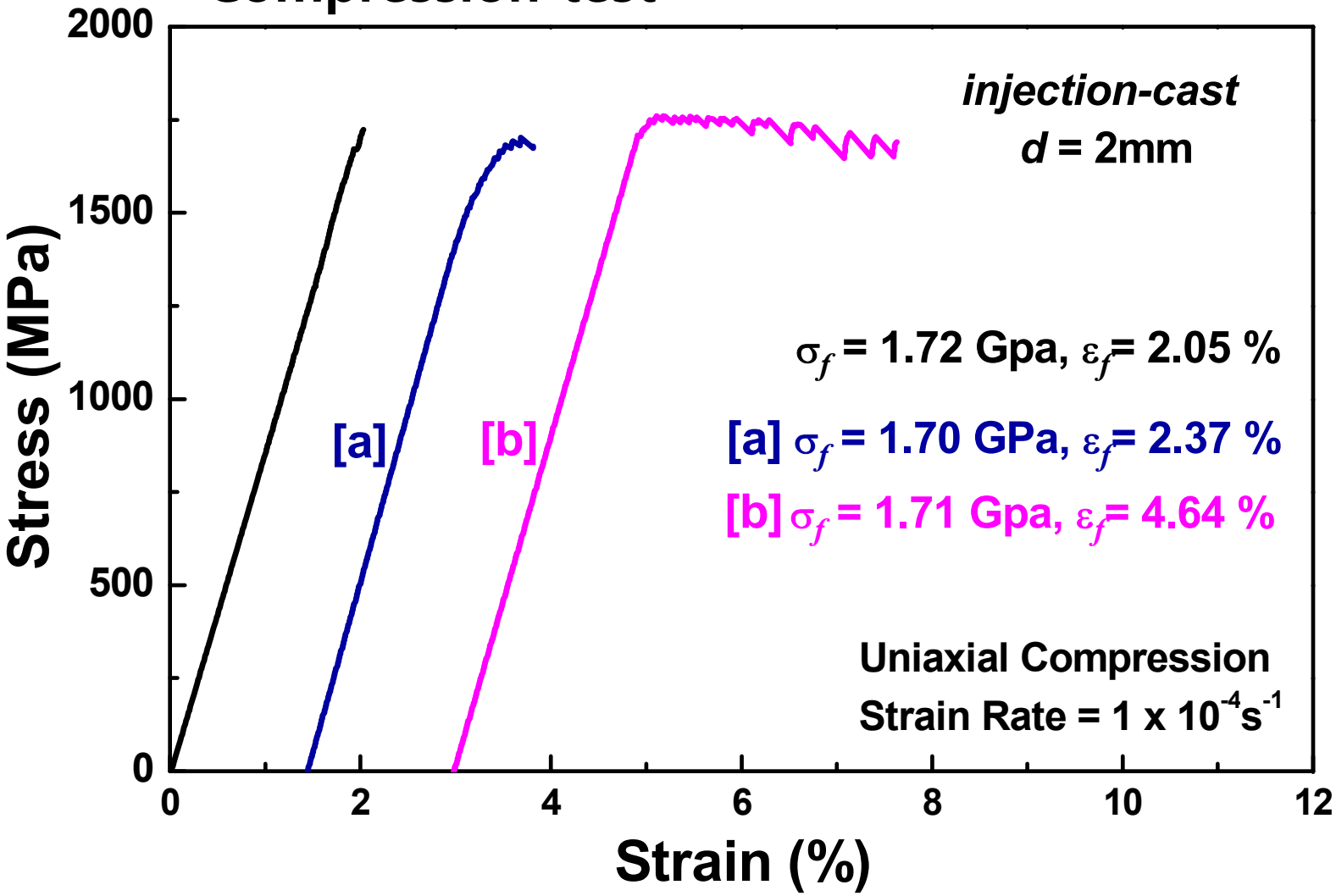
After deformation

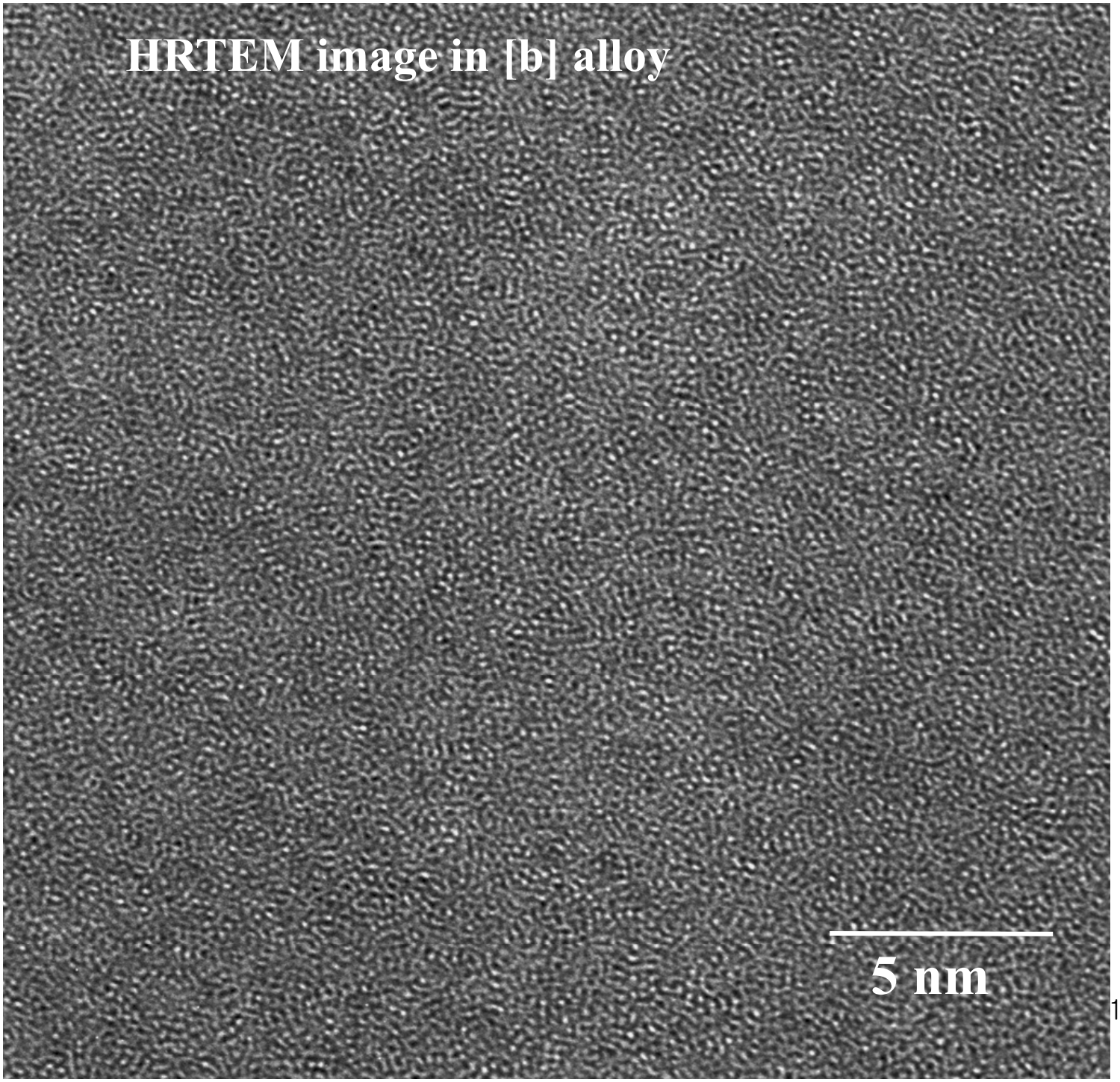


- No distribution of icosahedral particle to blocking the propagation of shear band.
- No enhancement of plasticity in MGMC with icosahedral particle

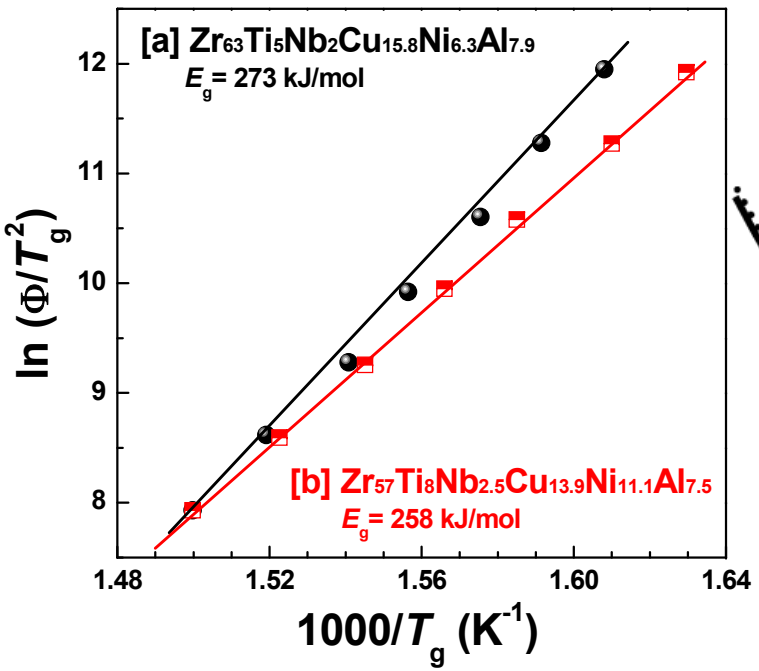
Compression test

* unpublished (2009)



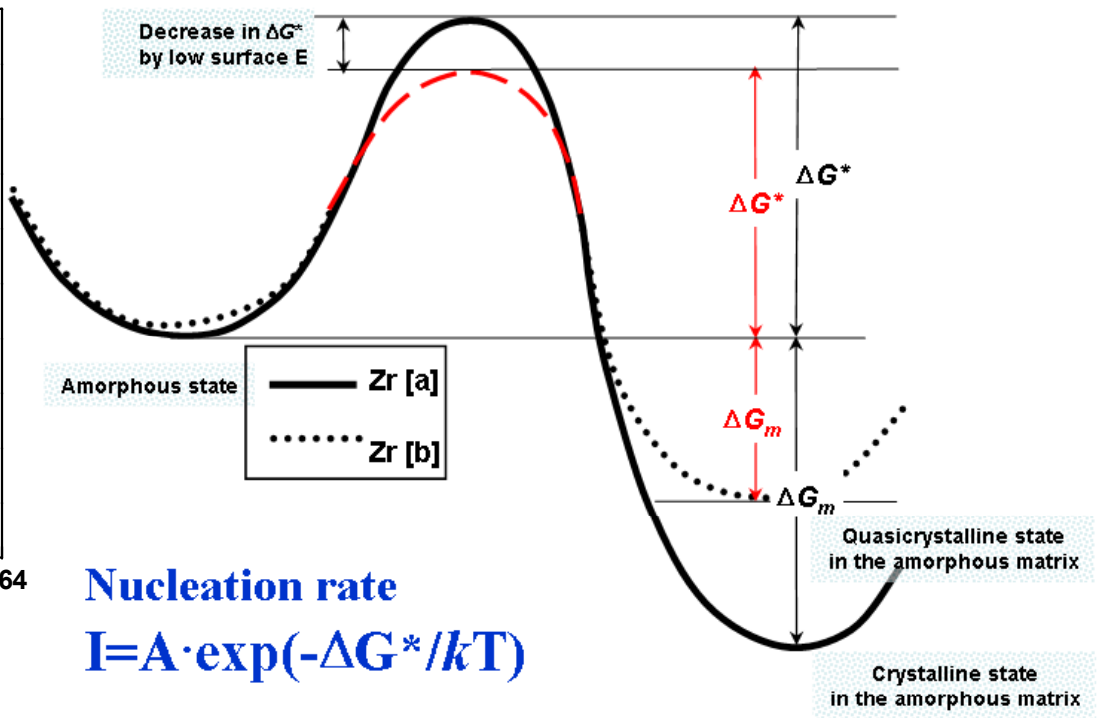

HRTEM image in [b] alloy
5 nm

Activation E : driving force for nucleation



Kissinger's equation

$$\ln(\Phi / T_g^2) = -Q / RT_g + const.$$



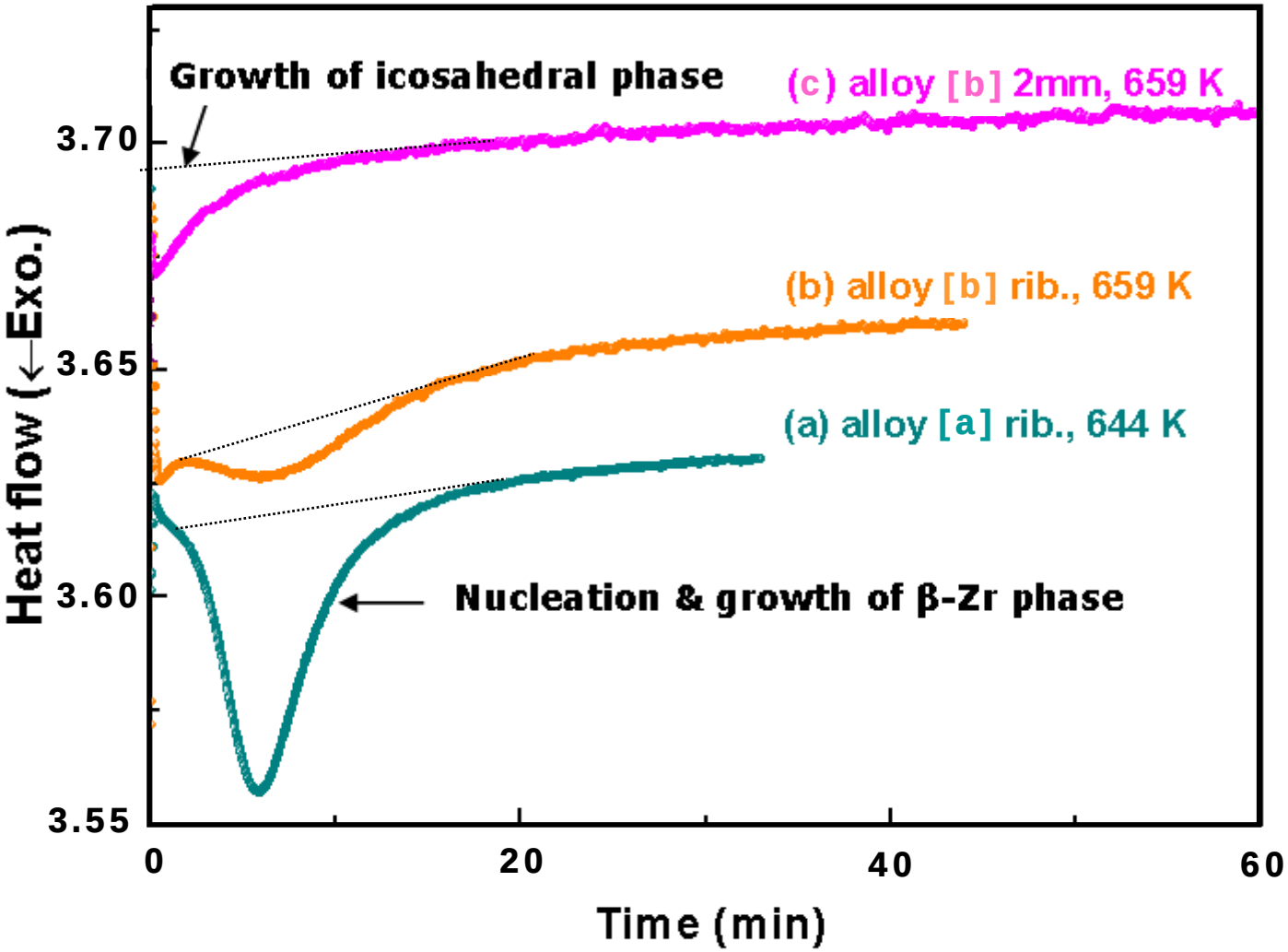
Nucleation rate

$$I = A \cdot \exp(-\Delta G^* / kT)$$

Effect of quenched-in quasicrystal nuclei

- Isotherm in DSC

Isothermal annealing



Effect of quenched-in quasicrystal nuclei

- **EXAFS analysis**

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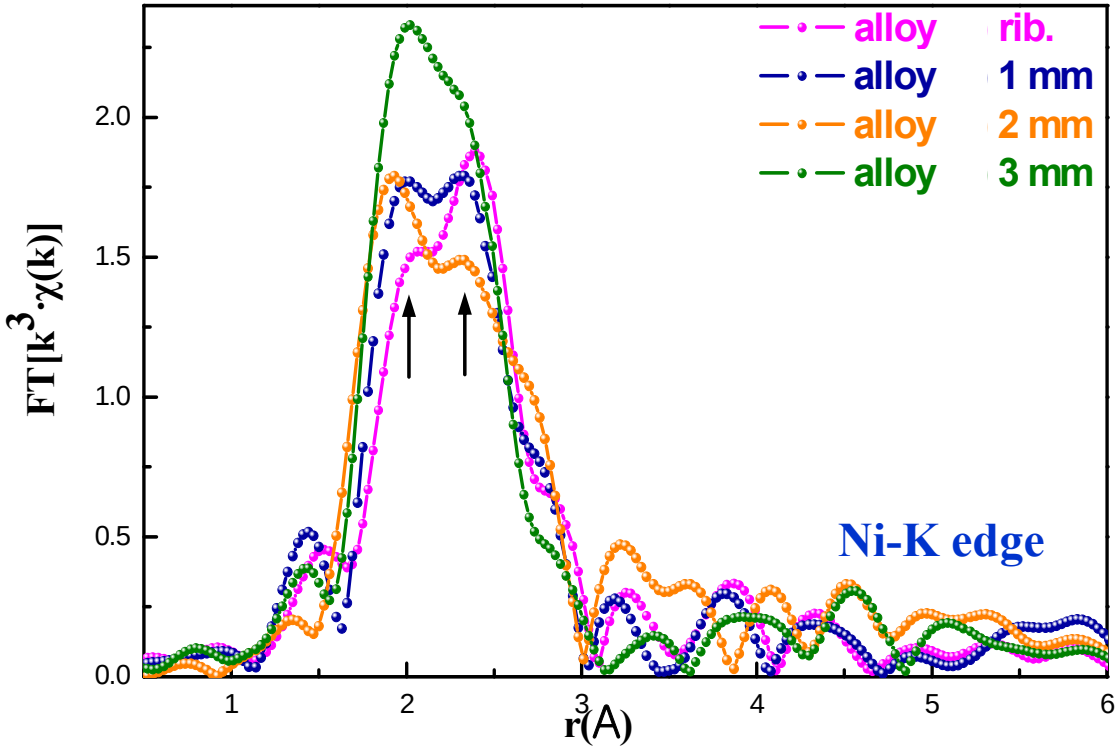

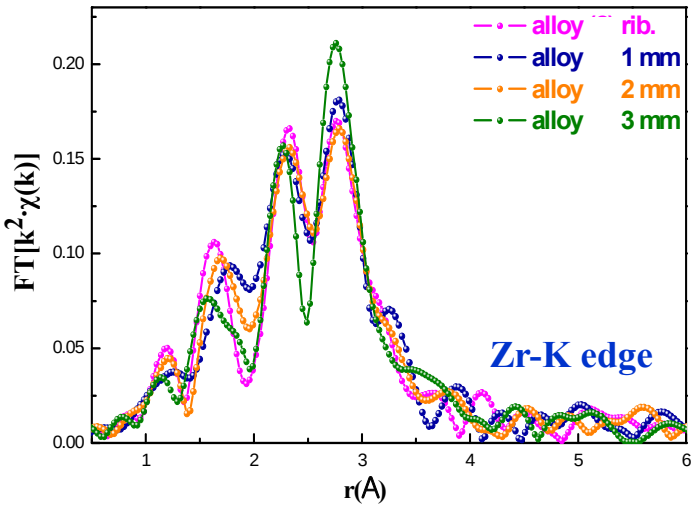

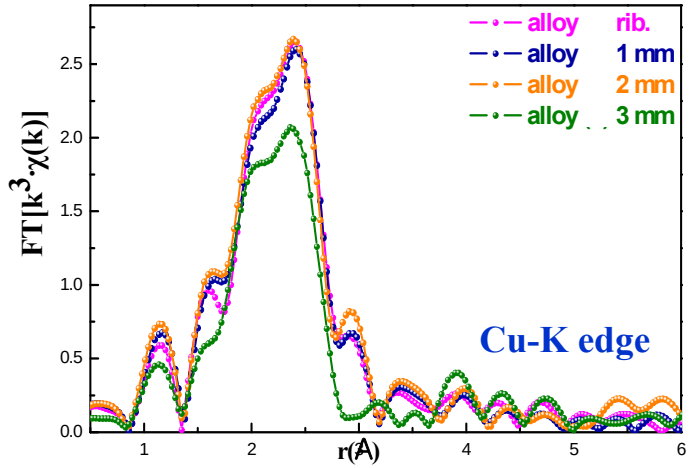

Distinctive structural change around Ni atom

Intensity change due to microstructural change

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: *Characterization of structure by pair distribution function*

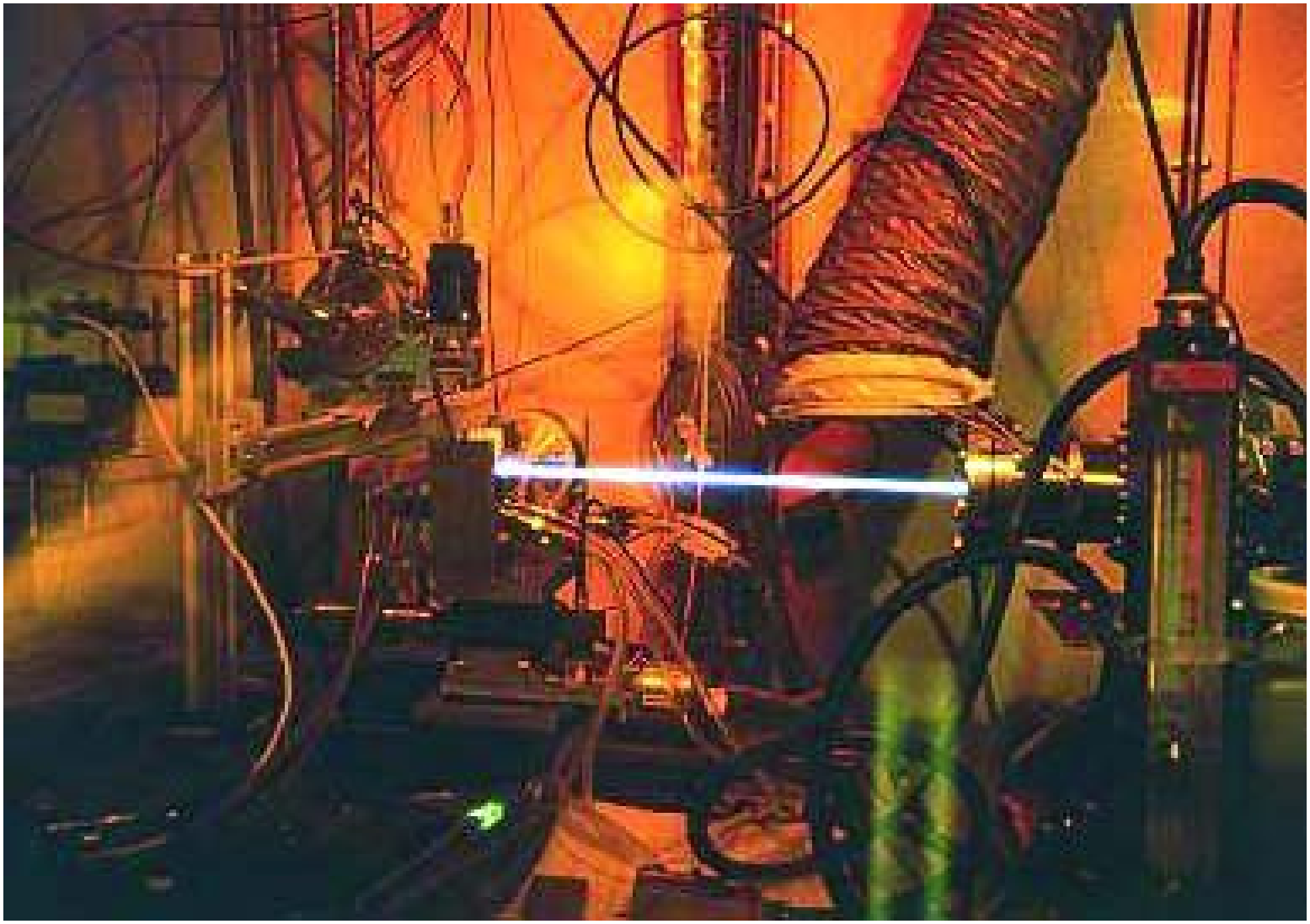
3) Intensive Structural Analysis*: *radial distribution function

Pohang accelerators

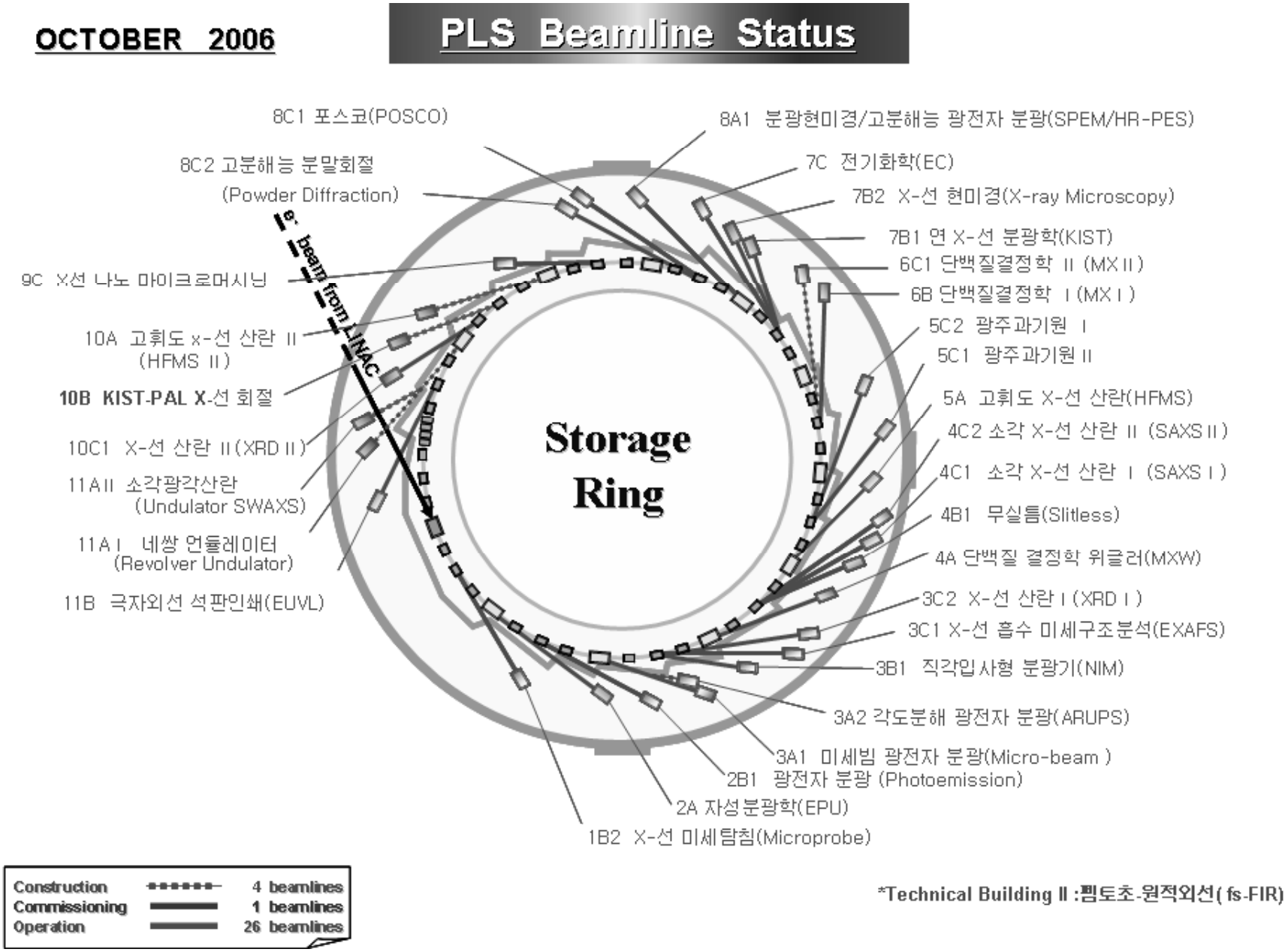
방사광이란?

- 광속으로 달리는 전자가 자기장 속을 지나면서 방향을 틀 때 접선방향으로 방출되는 아주 강력한 빛(high energy photons)을 말한다.
- 포항방사광 가속기는 태양보다 10억 배 이상 밝다.
- 방출되는 빛은 가시광선은 물론 자외선에서 X선에 이르는 모든 파장을 망라한다.

방사광의 실제 모습



포항가속기 연구소 빔라인 실험장치들



Characterizing the structure - radial distribution function,

also called pair distribution function

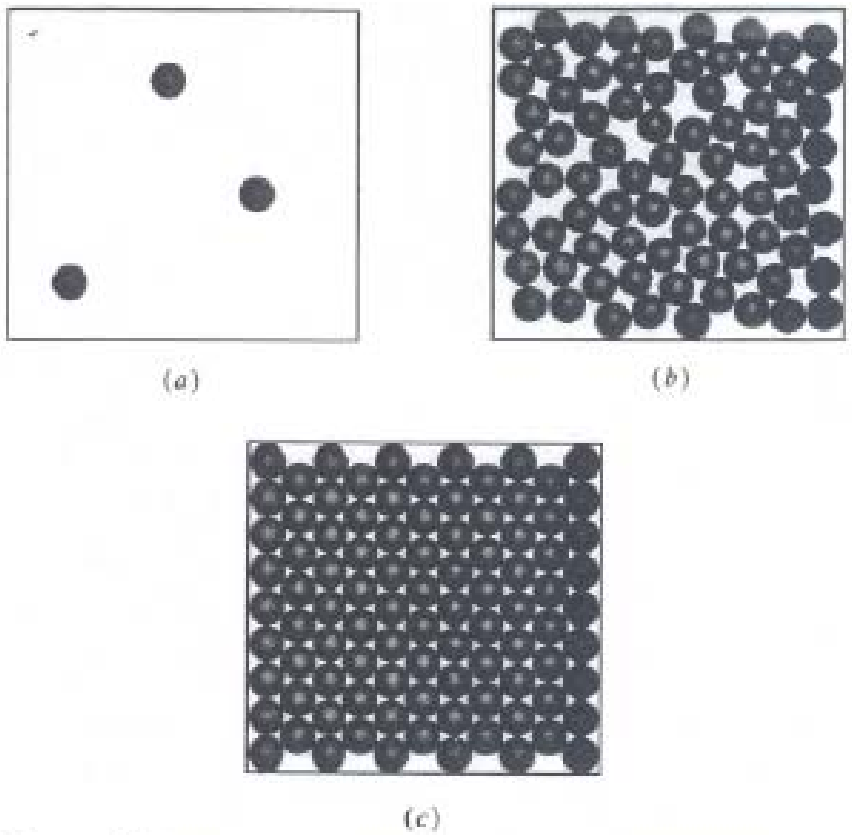


Figure 2.4 Hard-sphere model of (*a*) gas, (*b*) liquid/glass, and (*c*) crystalline solid.

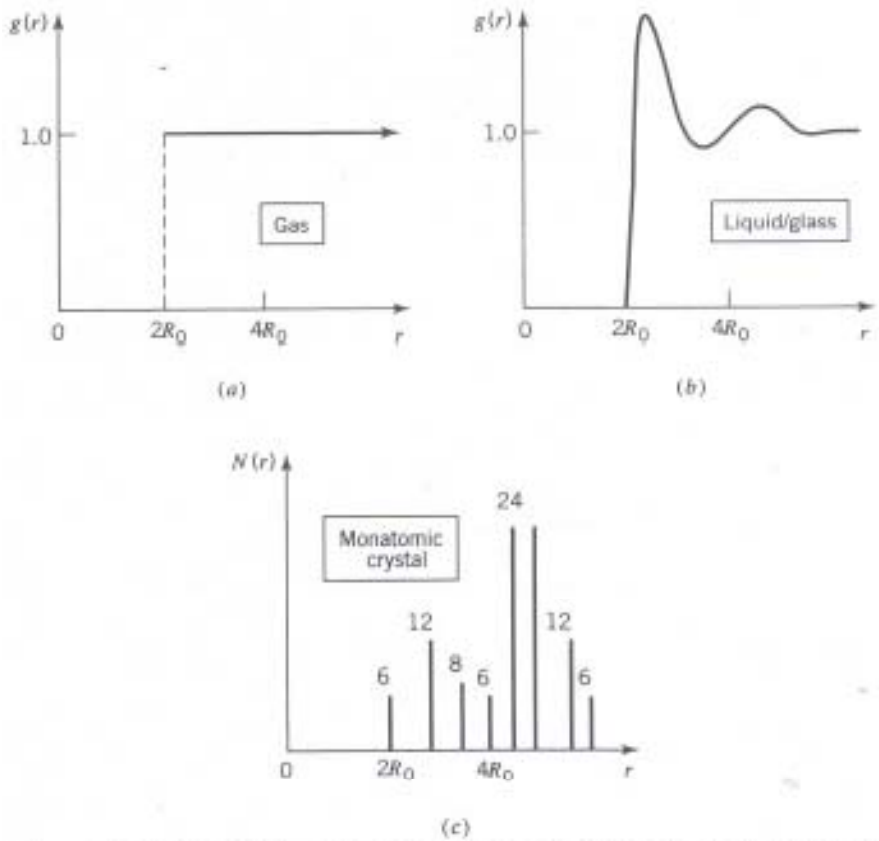
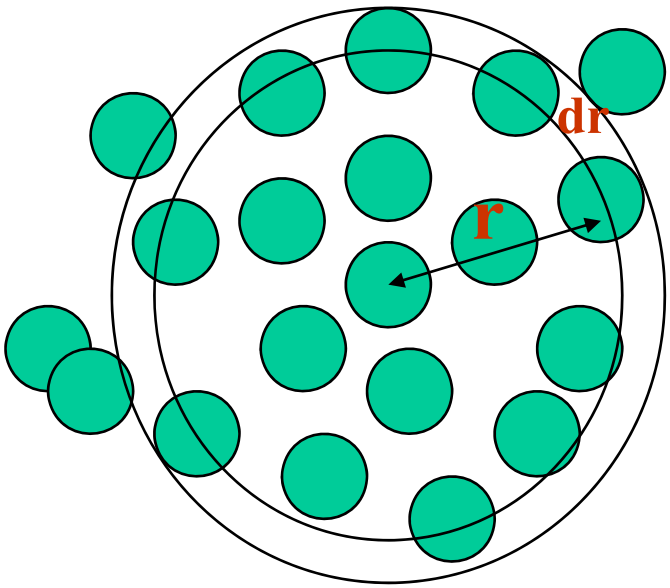


Figure 2.5 Pair-distribution functions for (*a*) a gas and (*b*) liquid or glass. (*c*) The radial dependence of the number of neighbors $N(r)$ for a primitive cubic crystal with one atom per lattice site.

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 <ρ>**

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

Count the neighbors

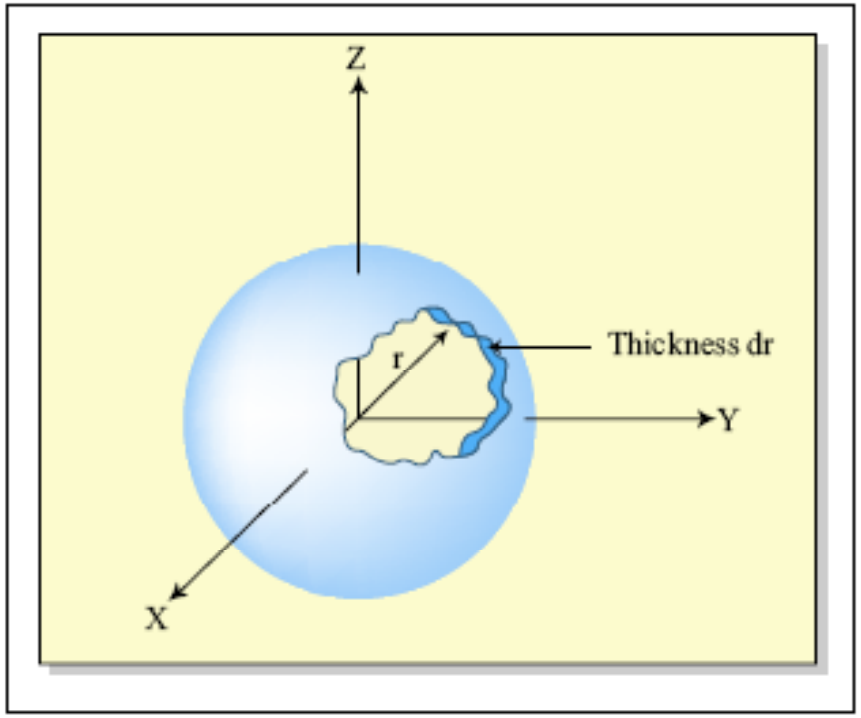
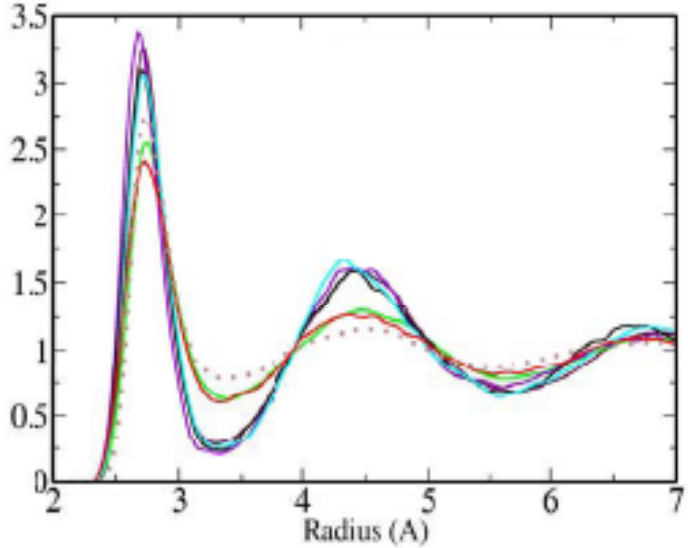


Figure by MIT OCW.



Properties of the radial distribution function

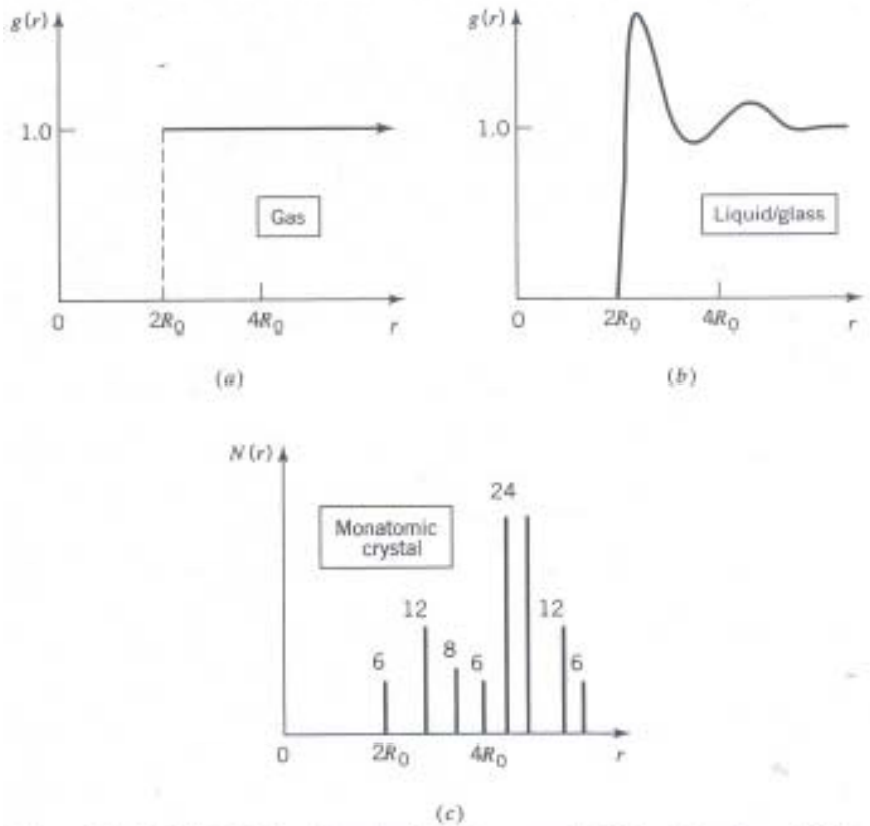


Figure 2.5 Pair-distribution functions for (*a*) a gas and (*b*) liquid or glass. (*c*) The radial dependence of the number of neighbors $N(r)$ for a primitive cubic crystal with one atom per lattice site.

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

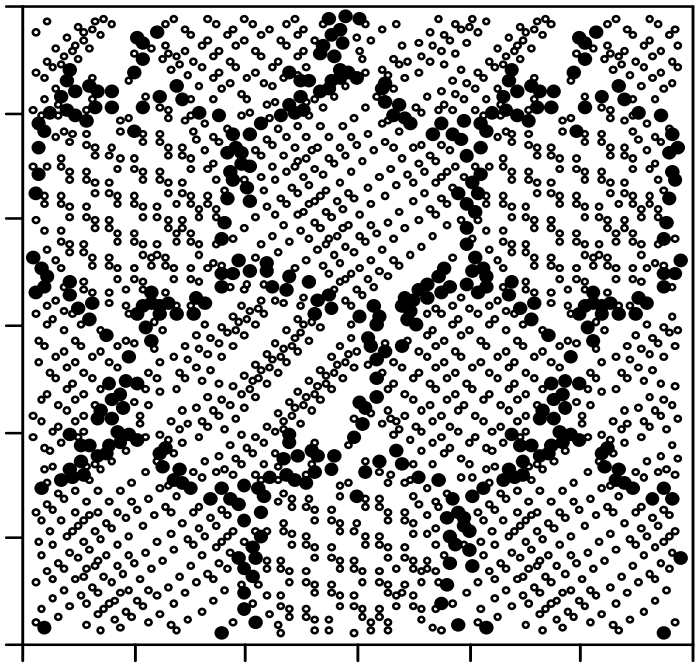
The distance over which g(r) becomes unity is called the correlation distance which is a measure of the extent of so-called short range order (SRO)

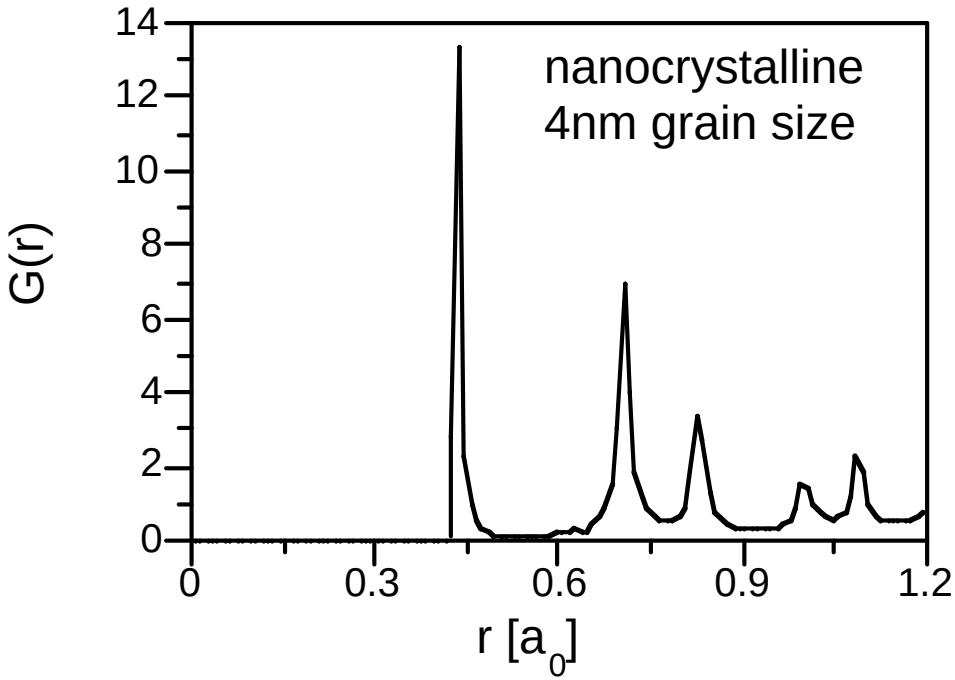
The first peak corresponds to an average nearest neighbor distance

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

Radial Distribution Function

Nanocrystalline material





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

- **Preparation of amorphous materials**

Sputtering	Surface coating
Thermal evaporation	
Glow-discharge decomposition	
Chemical vapor deposition	
electrolytic deposition	

Injection casting	Bulk type : sphere, rod, plate
Suction casting	
Squeeze casting	
Droplet quenching	

Gas atomization	powder

Melt-spinning	thin film
Splat quenching	thin plate

Irradiation

Pressure-induced amorphization

Solid-state diffusional amorphization