The Abdus Salam
International Centre for Theoretical Physics

United Nations
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1936-25

**Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications**

*7 - 25 April 2008*

# Small angle x-ray scattering (Application to structure transformations)

Aldo Craievich
*University de Sao Paulo*
*Brazil*

# A SAXS/WAXS application: Mechanisms of formation, melting and crystalization of metallic nanoclusters

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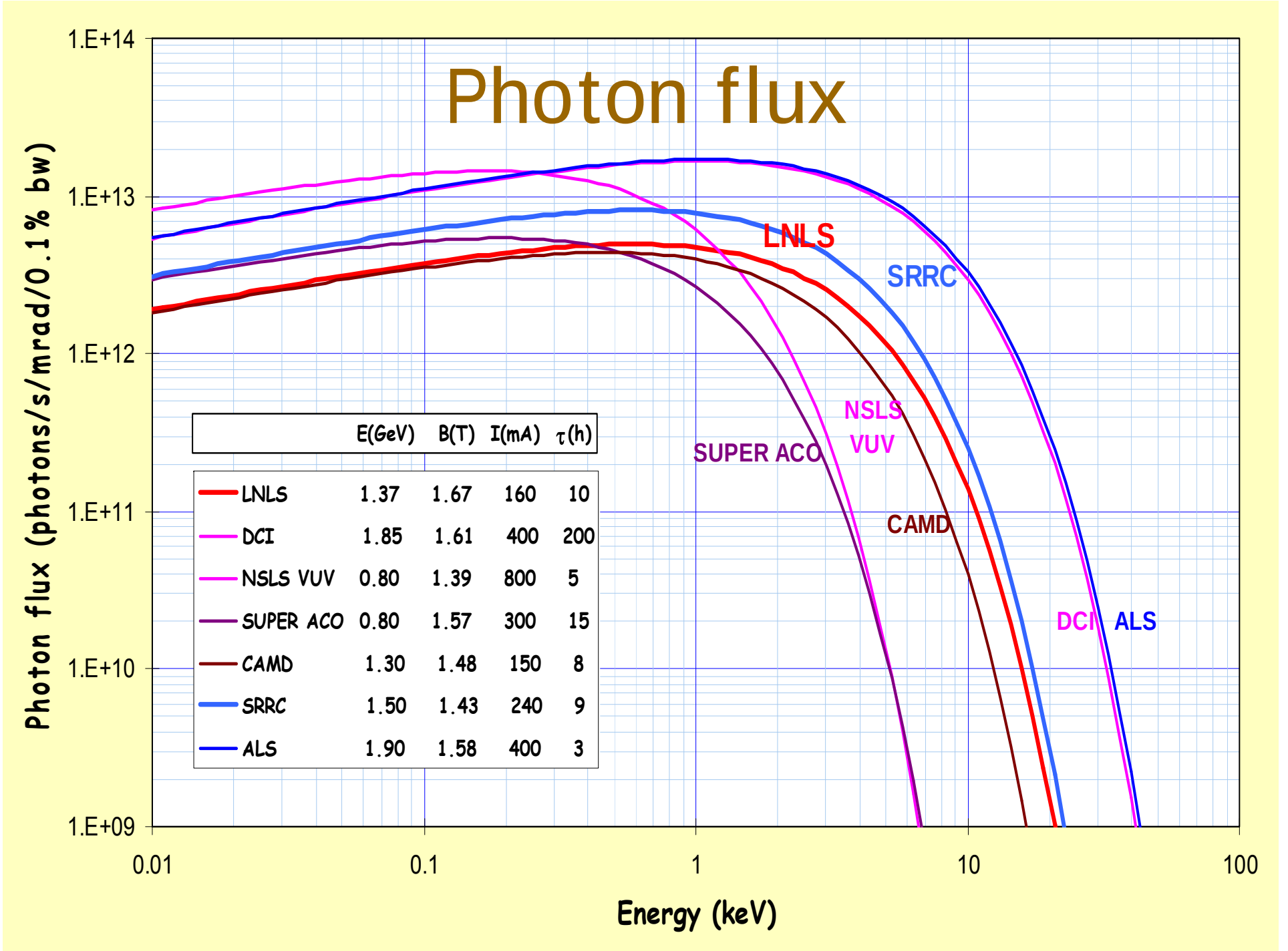
**Institute of Physics**

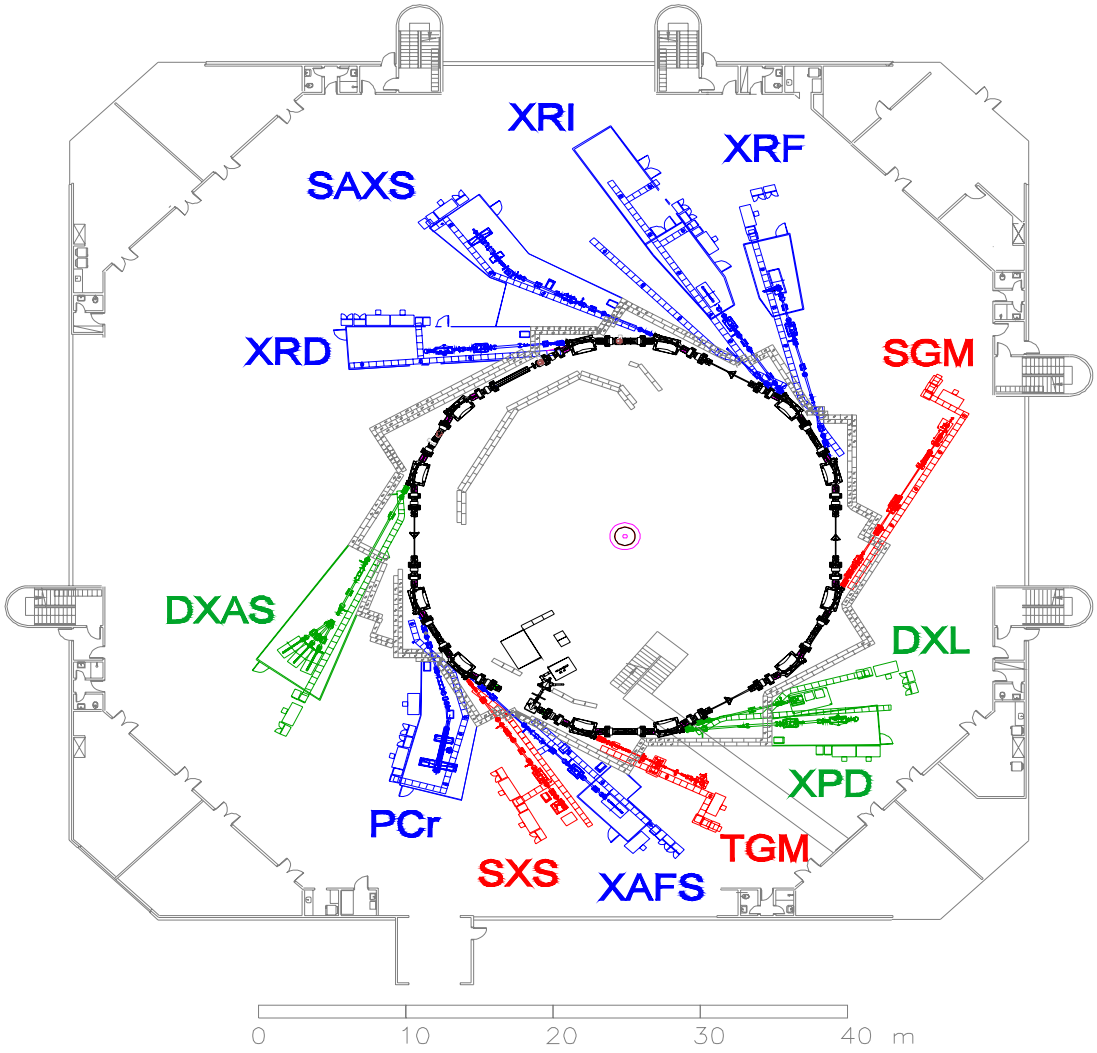
**University of São Paulo**

**Brazil**

**(craievich@if.usp.br)**

# 1.37 GeV electron storage ring – LNLS – Campinas - Brazil


Photon flux
Photon flux (photons/s/mrad/0.1% bw)
1.E+14
1.E+13
1.E+12
1.E+11
1.E+10
1.E+09
0.01
0.1
1
10
100
Energy (keV)
LNLS
SRRC
NSLS VUV
SUPER ACO
CAMD
DCI
ALS
E(GeV) B(T) I(mA) τ(h)
LNLS 1.37 1.67 160 10
DCI 1.85 1.61 400 200
NSLS VUV 0.80 1.39 800 5
SUPER ACO 0.80 1.57 300 15
CAMD 1.30 1.48 150 8
SRRC 1.50 1.43 240 9
ALS 1.90 1.58 400 3




- 8 hard x-rays
- 4 soft x-rays and VUV beamlines in operation

- 600MeV booster in operation
- 1 wiggler in operation
- 1 undulator planned

**LNLS 2006: 12 beam lines in operation**

**3 beam lines under construction**

# Nanostructured materials

*- Self-organized systems*

*- Mechanisms of formation and phase transitions*

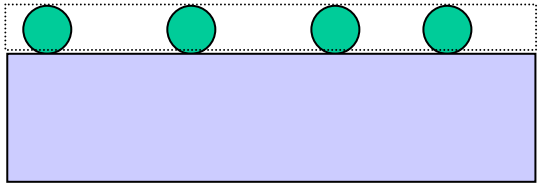
*- Structure characterization*

*- Structure and properties*

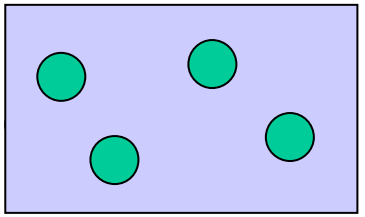
- Nanostructured materials:
  macroscopic objects composed of nanometric building blocks

*1 nm*

- Supported thin films

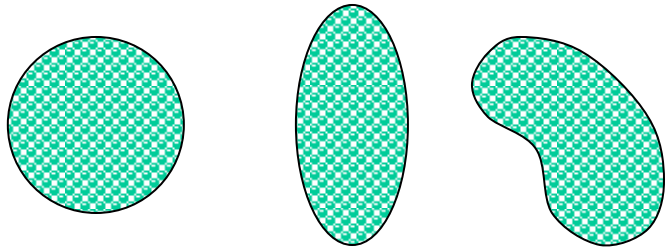


- Volume nanostructured materials



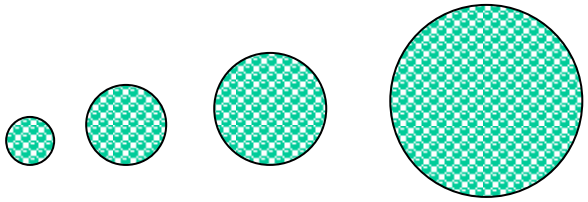
-Properties of nanostructured materials: They strongly depend on the shape and size of the nanometric building blocks.

**SHAPE**



**and**

**SIZE**

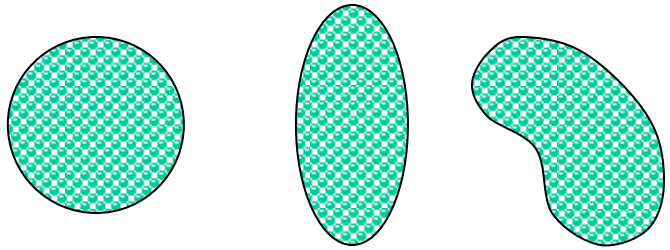


1 nm

*... are relevant structural characteristics.*

*-Properties of nanostructured materials: They strongly depend on the shape and size of the nanometric building blocks.*

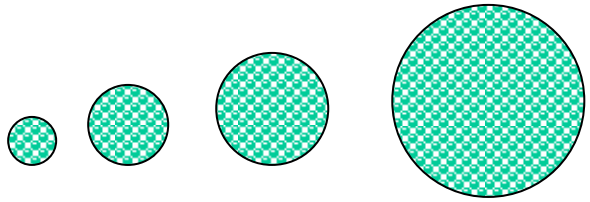
**SHAPE**

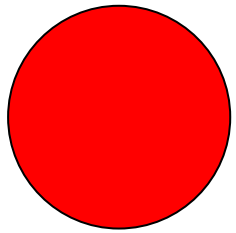


**Folding-unfolding of proteins**

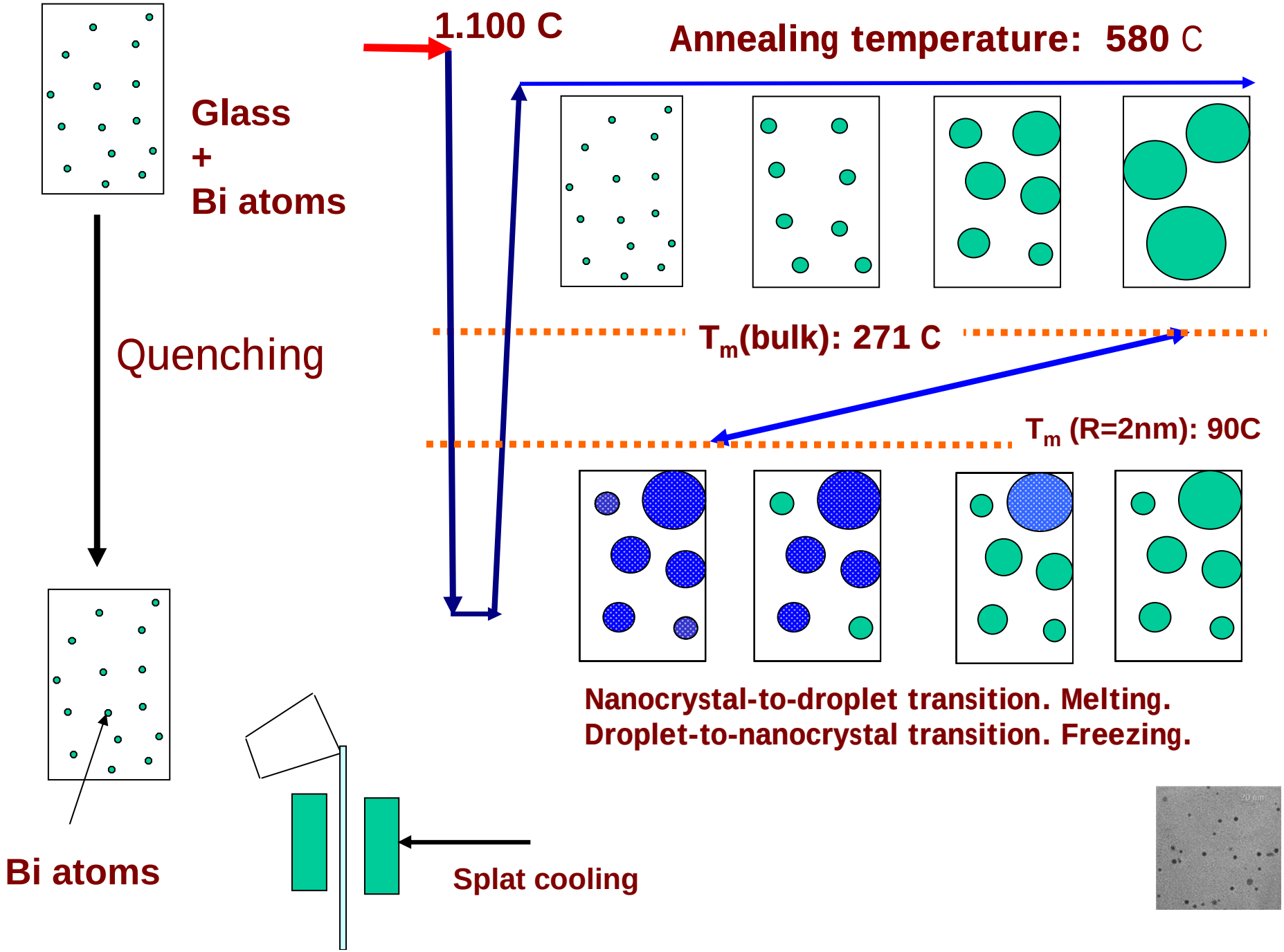
**and**

**SIZE**

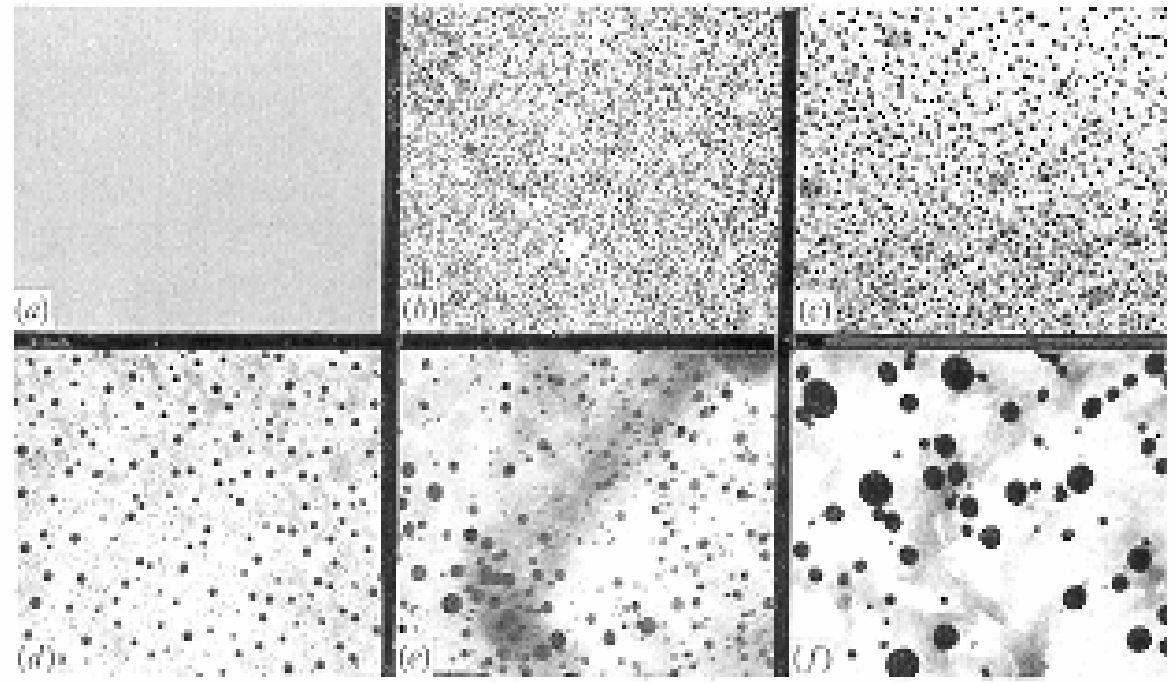


*... are relevant structural characteristics.*

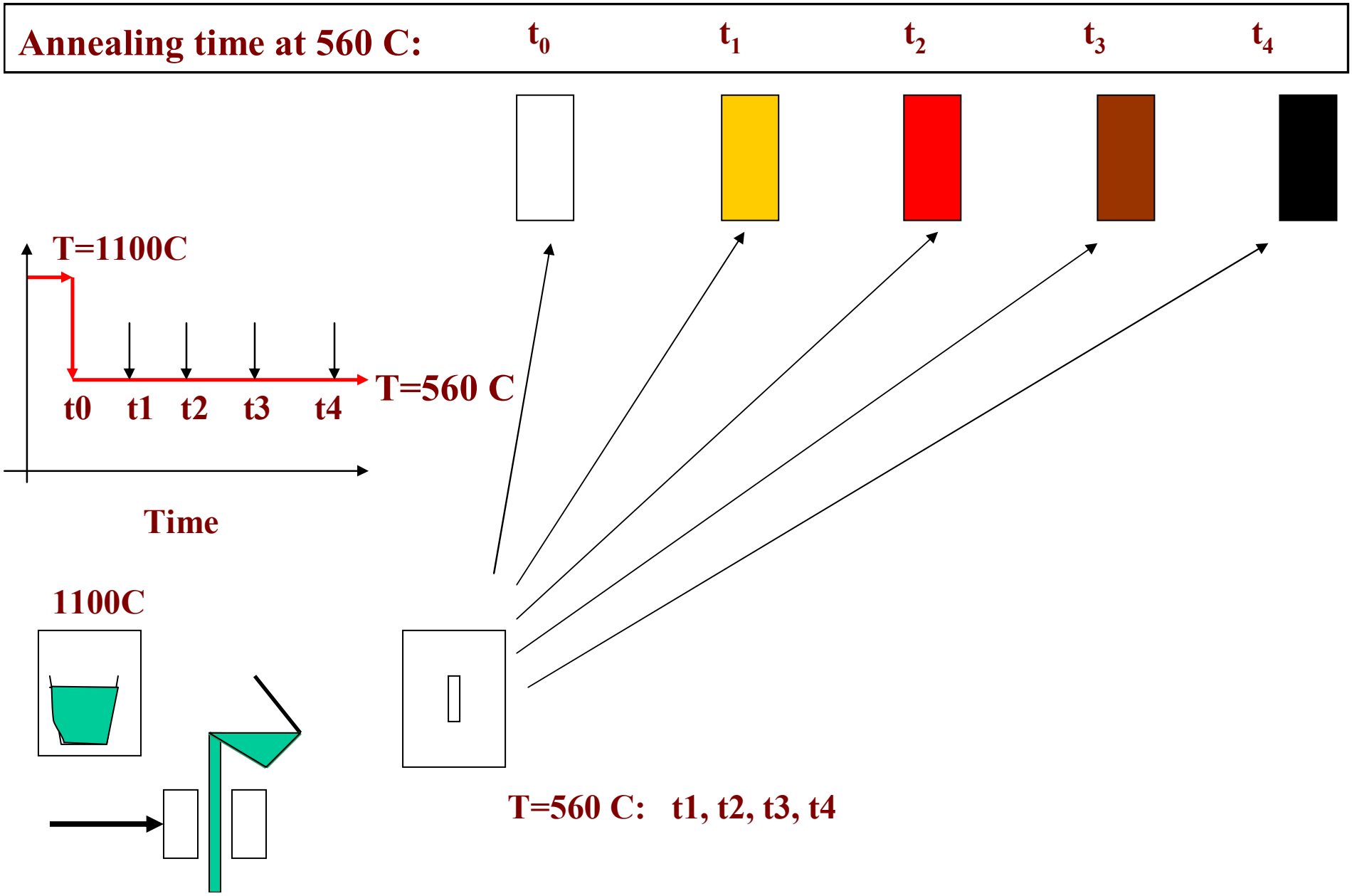

1.100 C
Annealing temperature: 580 C
Glass
+
Bi atoms
Quenching
$T_m$(bulk): 271 C
$T_m$ (R=2nm): 90C
Nanocrystal-to-droplet transition. Melting.
Droplet-to-nanocrystal transition. Freezing.
Bi atoms
Splat cooling

# Metallic clusters through different stages of growth: a TEM study

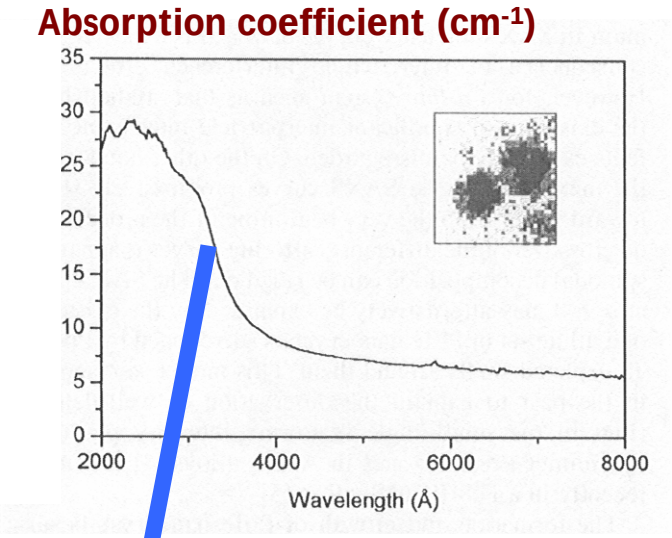


Nanoclusters (CdTeS, Bi) embedded in a glass matrix

# Preparation and optical properties

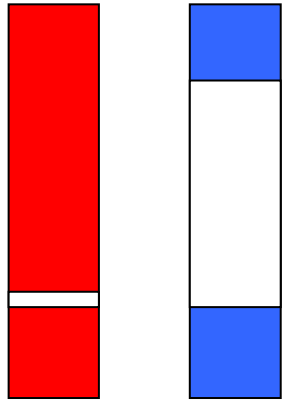


# PbTe nanocrystals
# Optical properties




**Band gap**

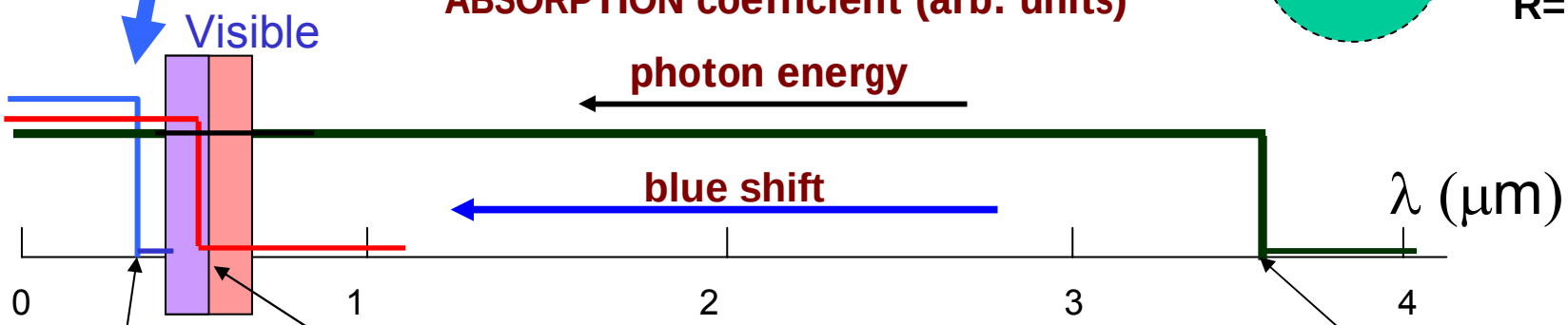
**$E_g$(Bulk)=0.34 eV**



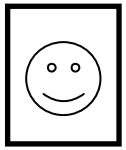
**$E_g$= 3.8 eV**


**R=14 A**

**ABSORPTION coefficient (arb. units)**




**3300 A - 3.8 eV (R=14 A)**



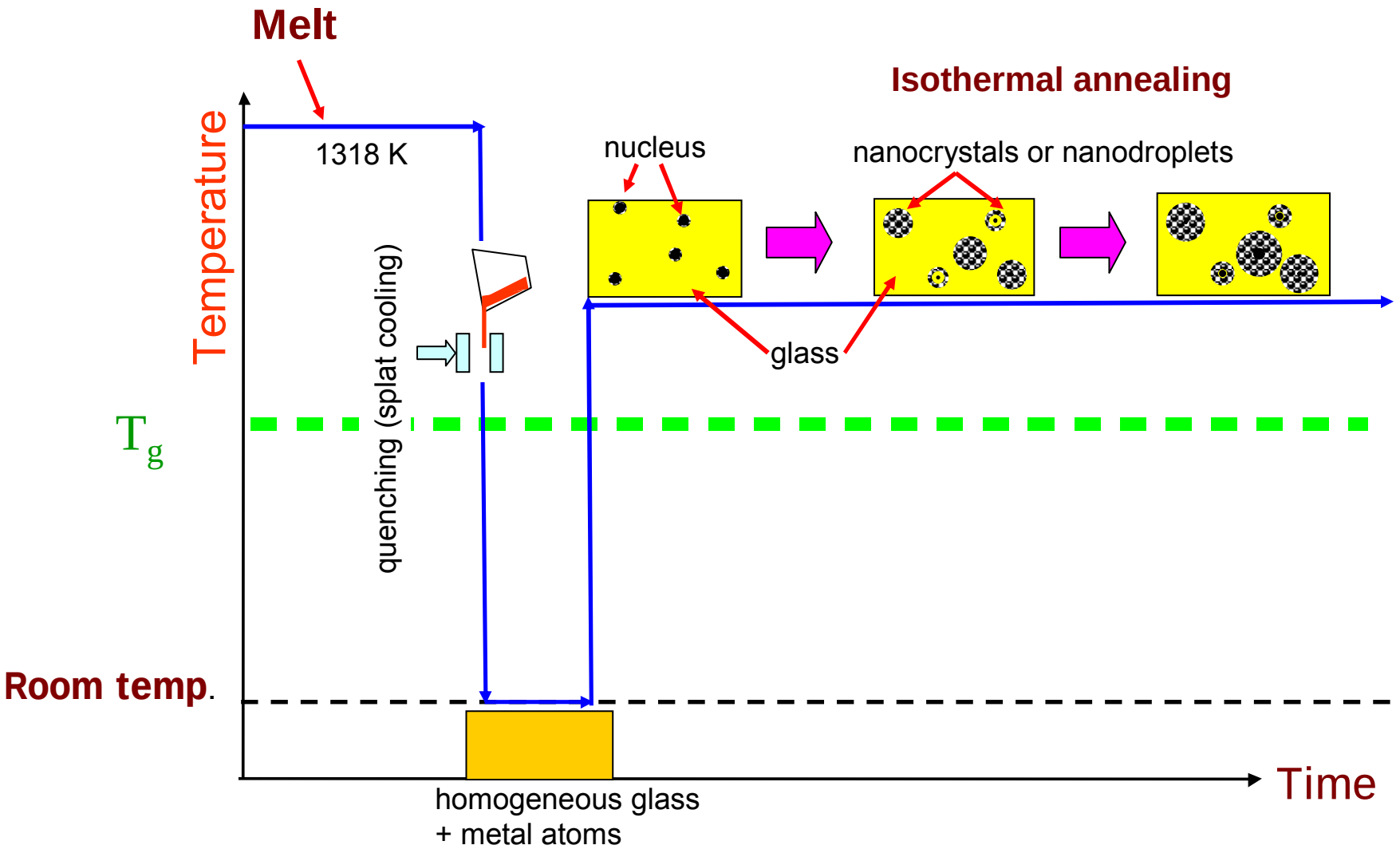
**14000 A, 0.8 eV (R= 33 A)**

$$E_g(R) = E_G(Bulk) + \frac{h^2}{8\mu}\left(\frac{1}{R^2}\right)$$

**(Efros and Efros)**

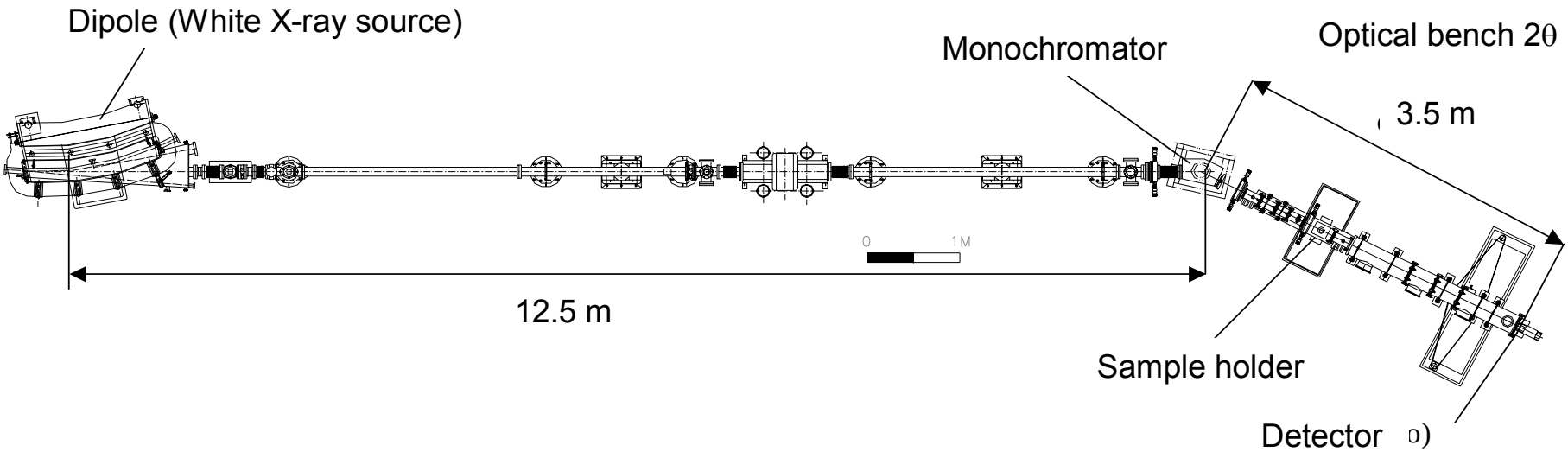
**36500A, 0.34eV (Bulk)**

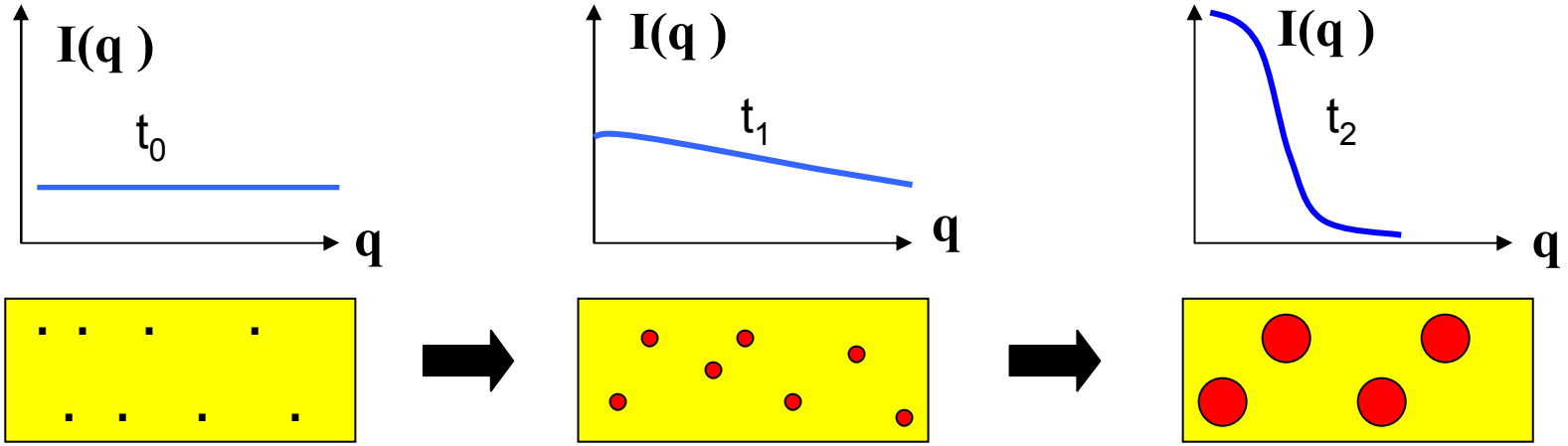
# Thermal history



# LNLS SAXS beamline

## Kellermann et al. J. Appl. Cryst. (1997) 30, 880-883



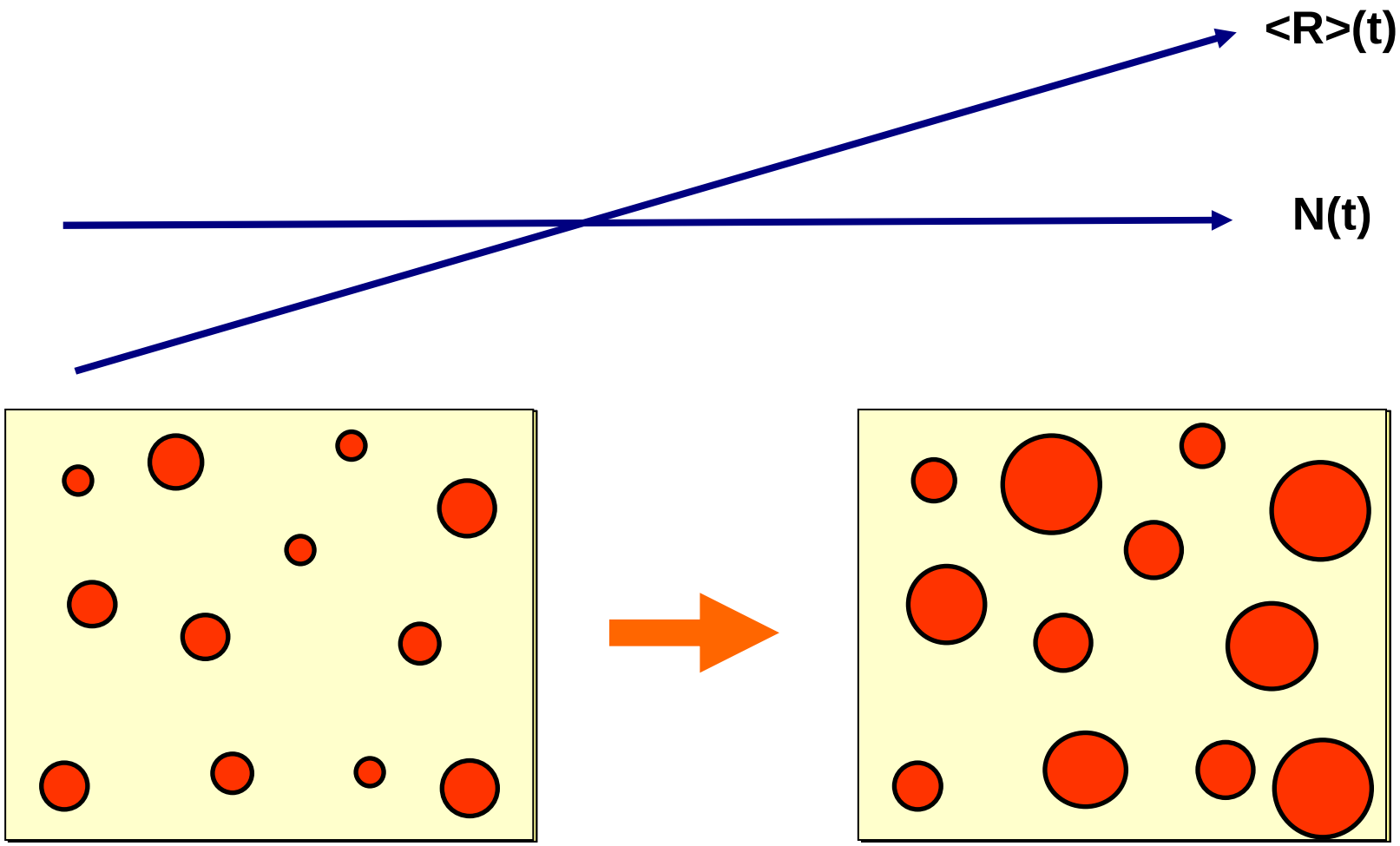




**Isothermal transformation** →

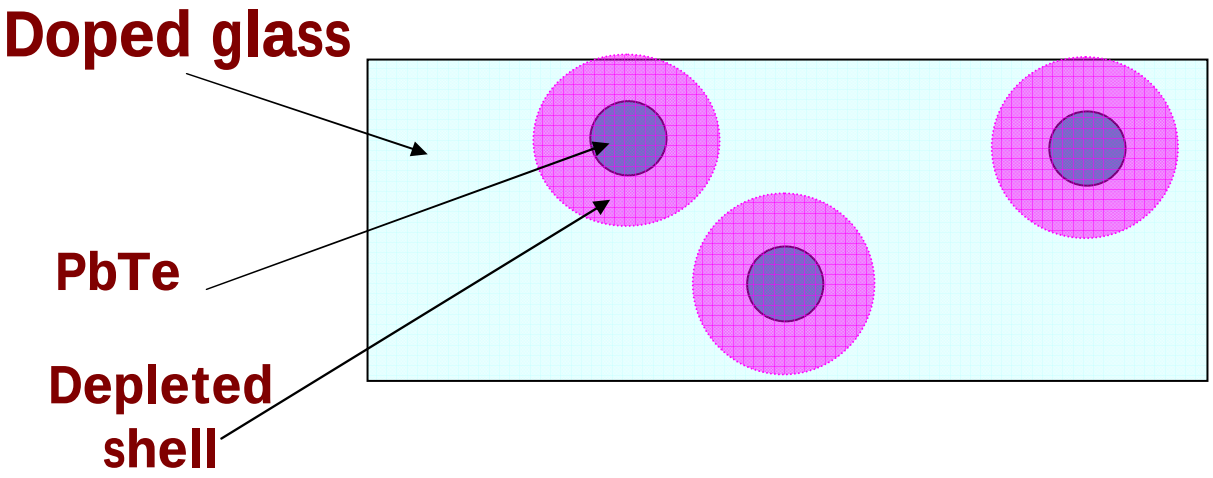

SAXS beam line

# Nucleation and growth of PbTe nanocrystals in a silicate glass

*- A. F.C., G. Kellermann, O.L. Alves and L.C. Barbosa. Phys. Rev. Lett. 89, 235503 (2002)*

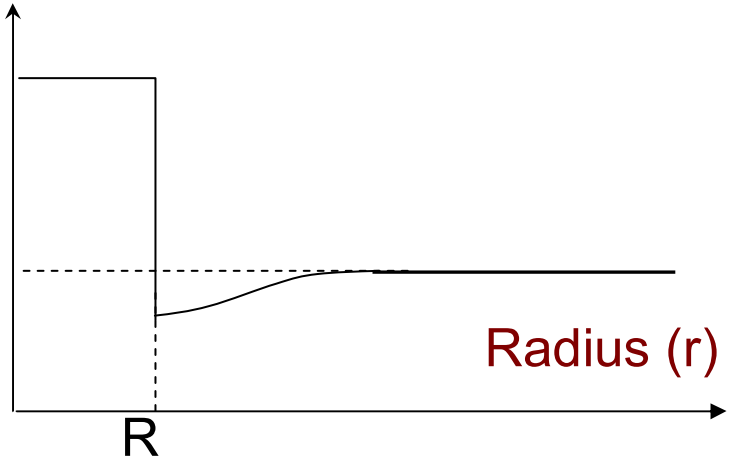


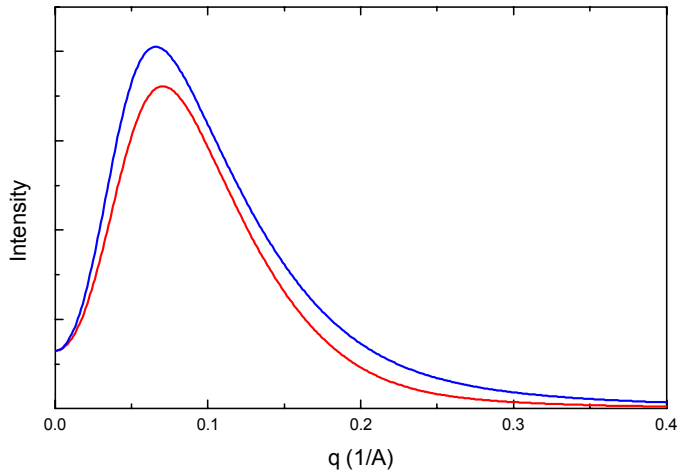
# Model



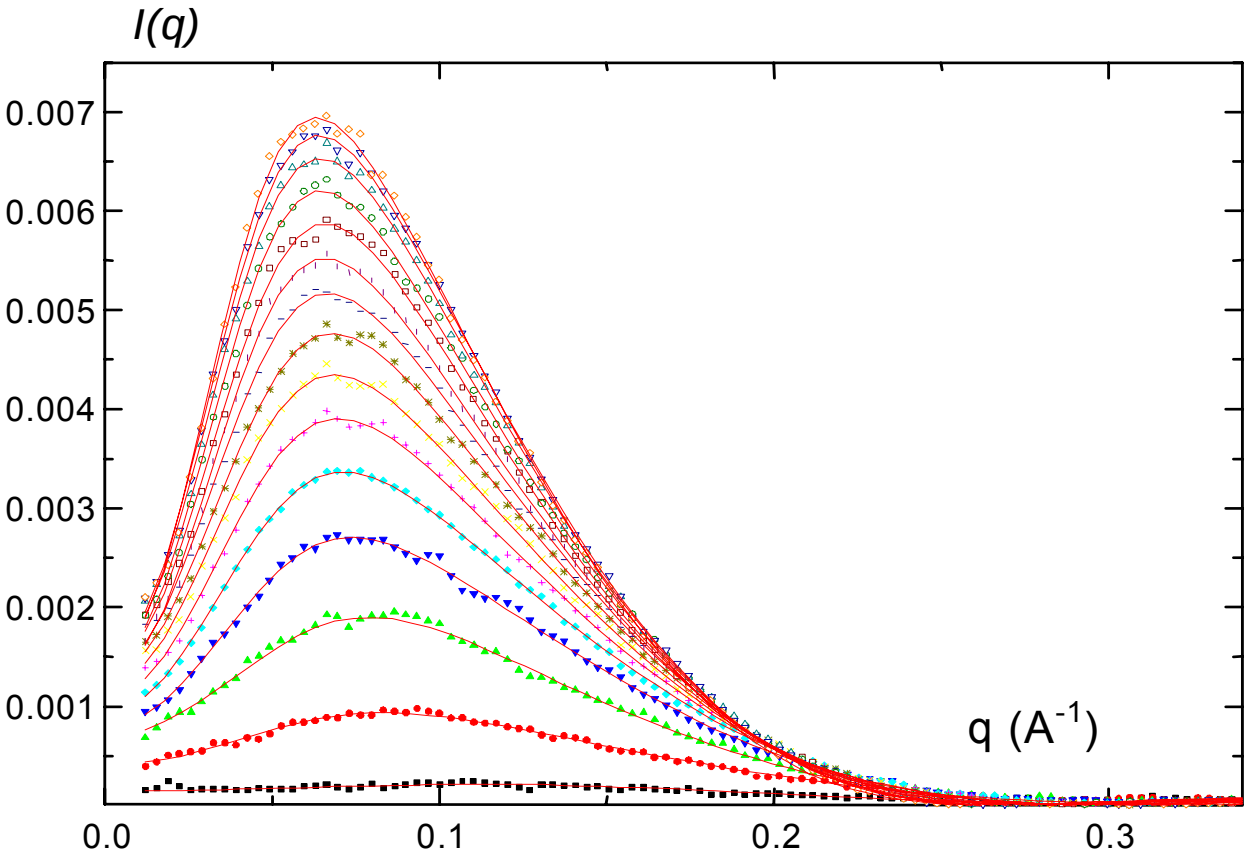

$$I(q) = A(\Delta n)^2 \left[ 3(1+a)\frac{\sin(qR) - (qR)\cos(qR)}{(qR)^3} - e^{-\frac{1}{6}R'^2 q^2} \right]^2$$

**Electron density**



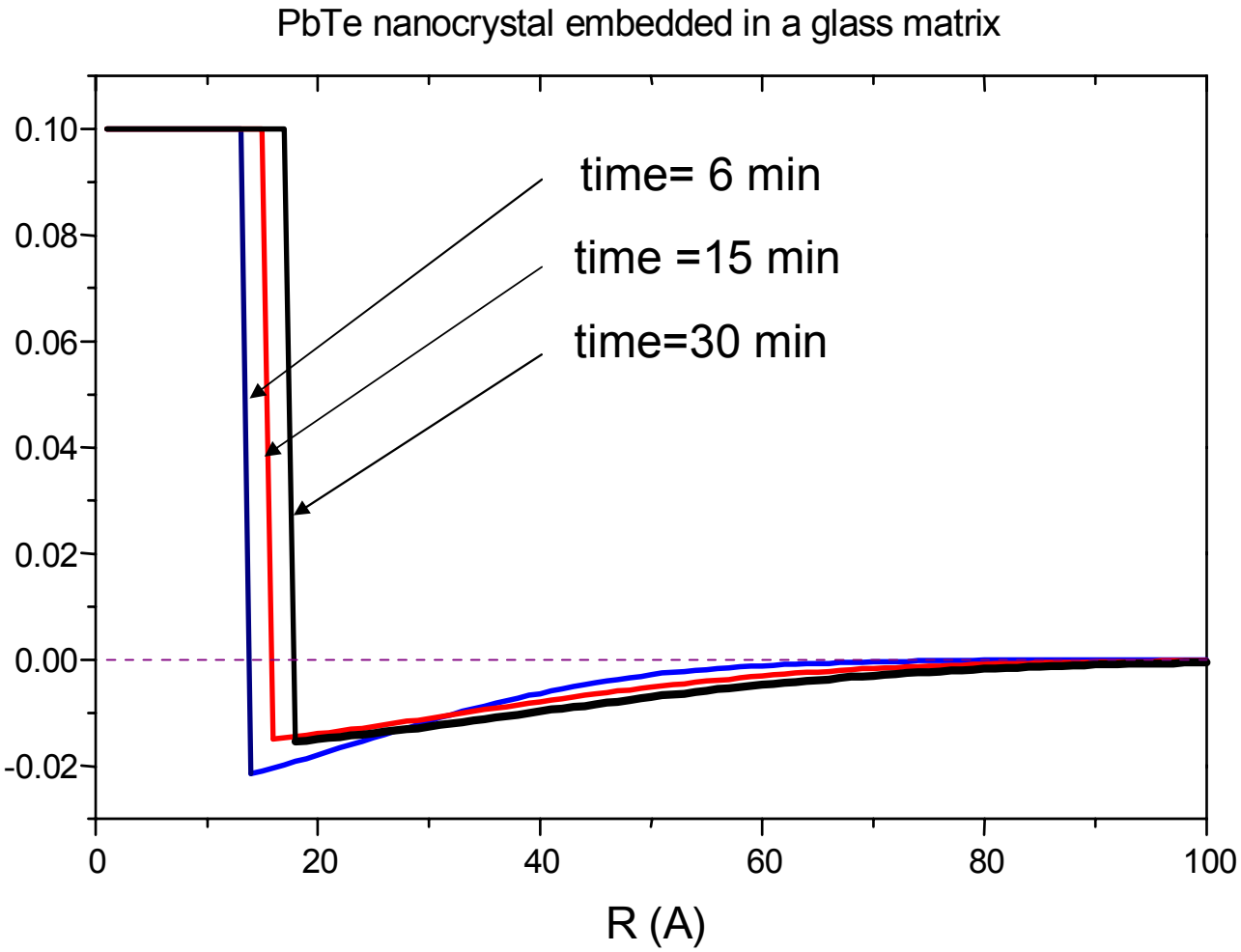



# SAXS results and modelling



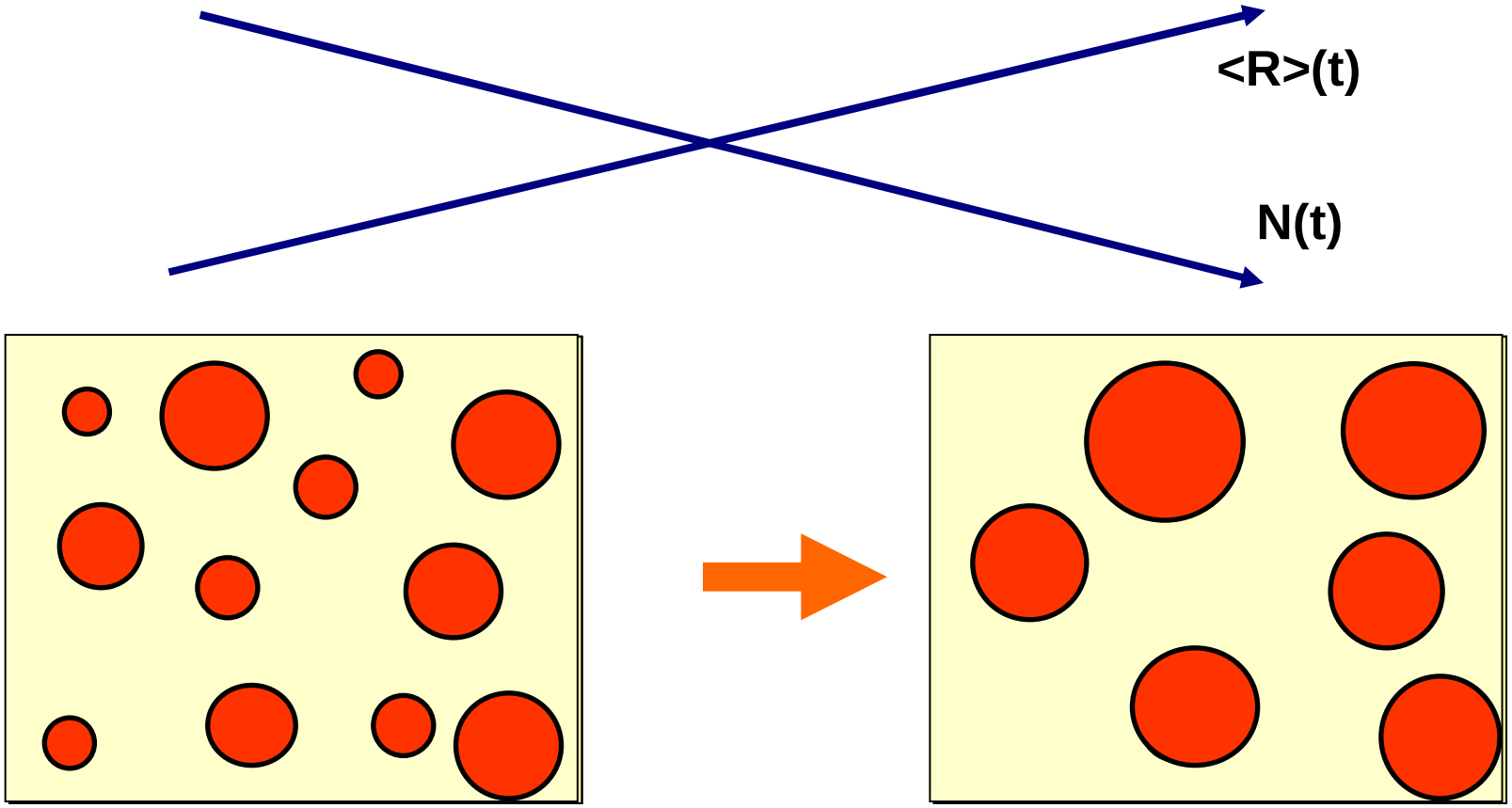

$$I(q) = A(\Delta n)^2 \left[ 3(1+a) \frac{\sin(qR) - (qR)\cos(qR)}{(qR)^3} - e^{-\frac{1}{6}R'^2 q^2} \right]^2$$

# *Time variation of the electron concentration function*

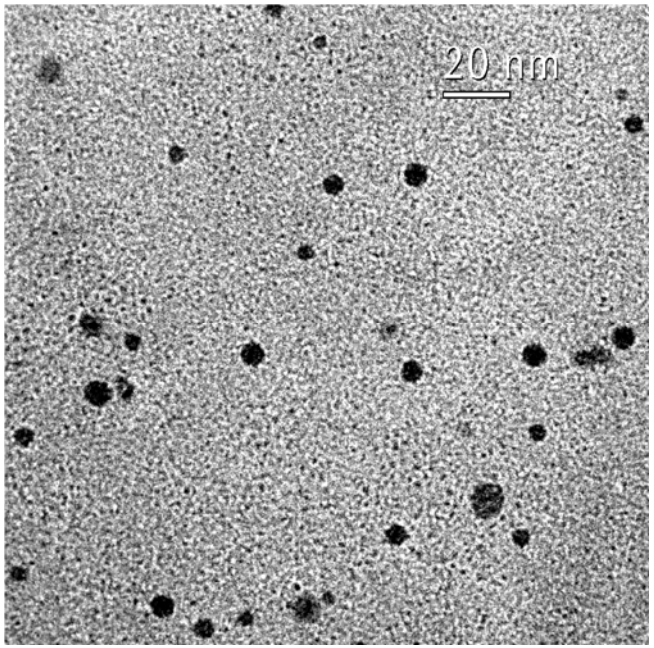


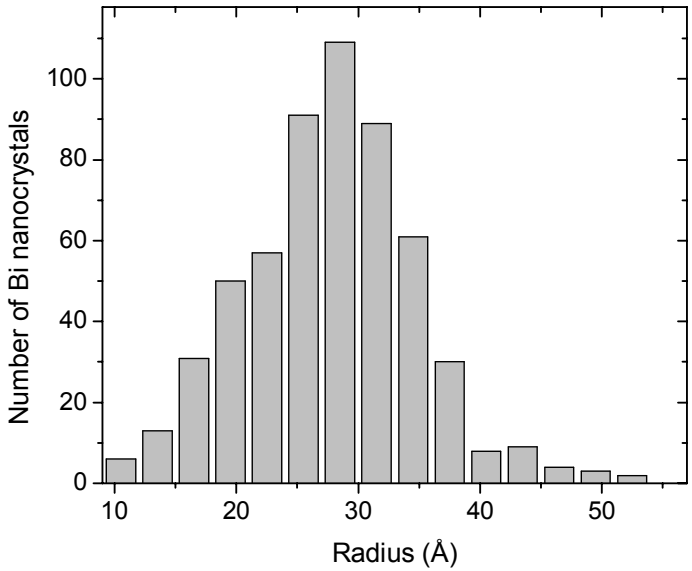
## Coarsening of liquid Bi nanodroplets

*G. Kellermann and A. F. C Phys. Rev. B, 67, 085405 (2003)*



# Bi in borate glass (TEM image)



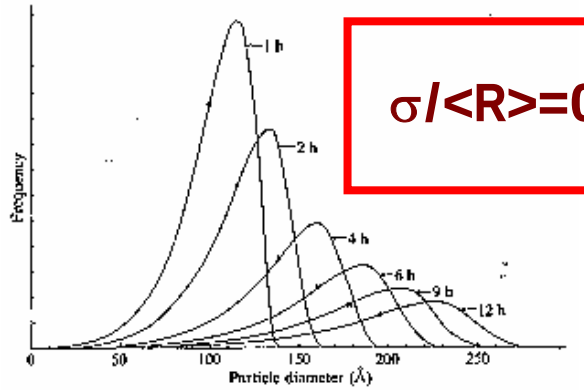
## 3. CLASSICAL THEORY OF DROPLET COARSENING

- According to the model proposed by Lifshitz-Slyosov (1961) [6] and Wagner (1961) [7] (LSW), when the supersaturation of the doping element in the matrix become small, *spherical clusters* with a radius $R$ smaller than a critical radius $R_c$ start to dissolve while those with radii larger that $R_c$ still grow.

$$N(R,t) = f(t)\frac{4(R/R_c)^2}{9}\left(\frac{3}{3+R/R_c}\right)^{7/3} \times \left(\frac{3/2}{3/2-R/R_c}\right)^{11/3} e^{\left(\frac{R/R_C}{-3/2+R/R_C}\right)}$$

where $f(t)$ is a function of the annealing time. During the coarsening stage $R_c$ coincides with $\langle R \rangle$. The concentration of solute atoms in the matrix c(t) and number density of clusters n(t) are time dependent functions.

**Absence of elastic strain**
(T>> $T_g$ temperature)




**σ/<R>=0.21 (time independent)**

Lifshitz-Slyosov (1961) and Wagner (1961)

# Theoretical predictions: Time dependence of structure parameters

**According to Lifshits-Slyosov (1961) and Wagner (1961) – LSW model:**

$$[< R >^3 (t)] =< R_0 >^3 + \kappa(t - t_0)$$

**<R>: average nanodroplet radius**

$$n^{-1}(t) = n_0^{-1} + \beta(t - t_0)$$

**n: droplet number density**

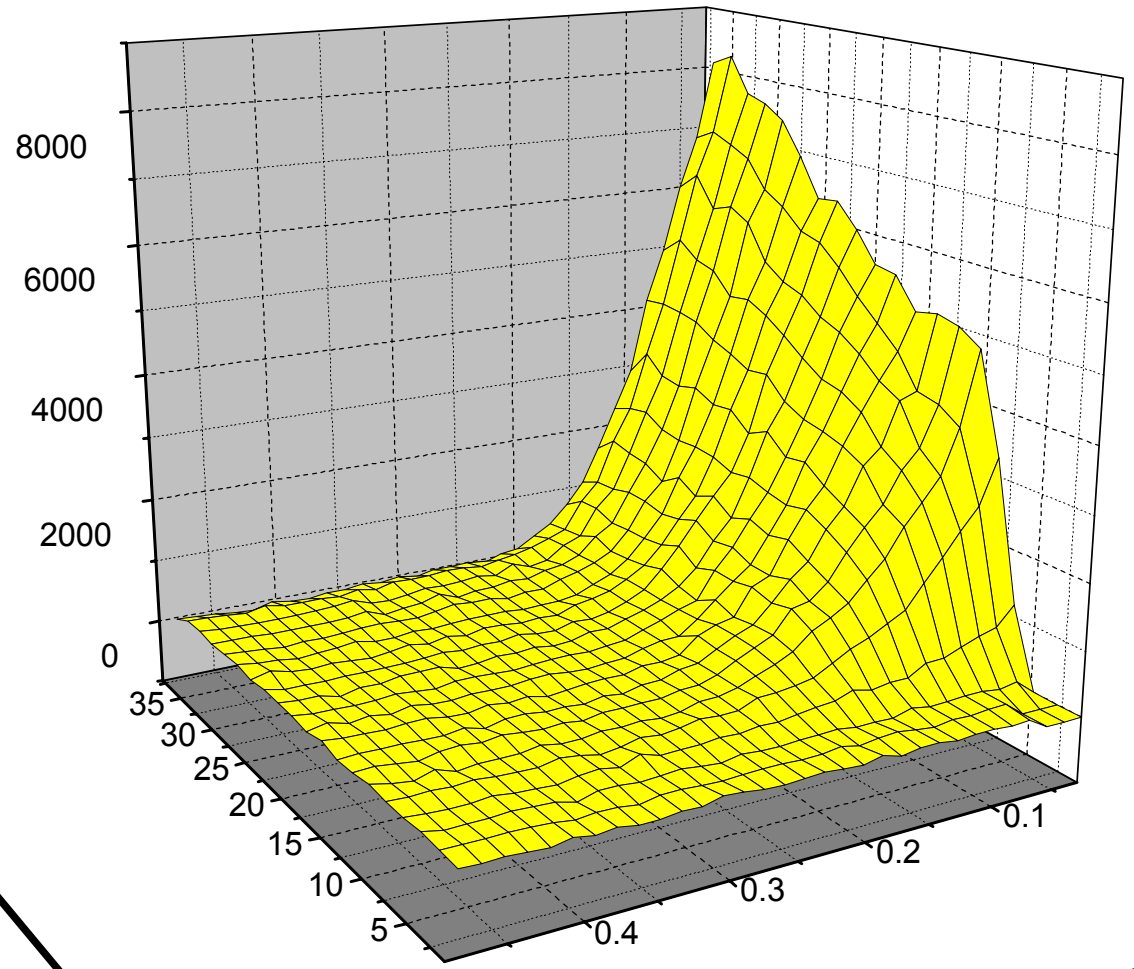
$$\varphi(t) = \varphi_e - [\chi'(t - t_0)]^{-1/3}$$

**φ: droplet total volume fraction**

**t: isothermal annealing time**
**$t_0$: intial time for "coarsening"**

# Liquid Bi nanodroplets embedded in a soda-borate glass .
# SAXS results

T = 843 K




Time (min)

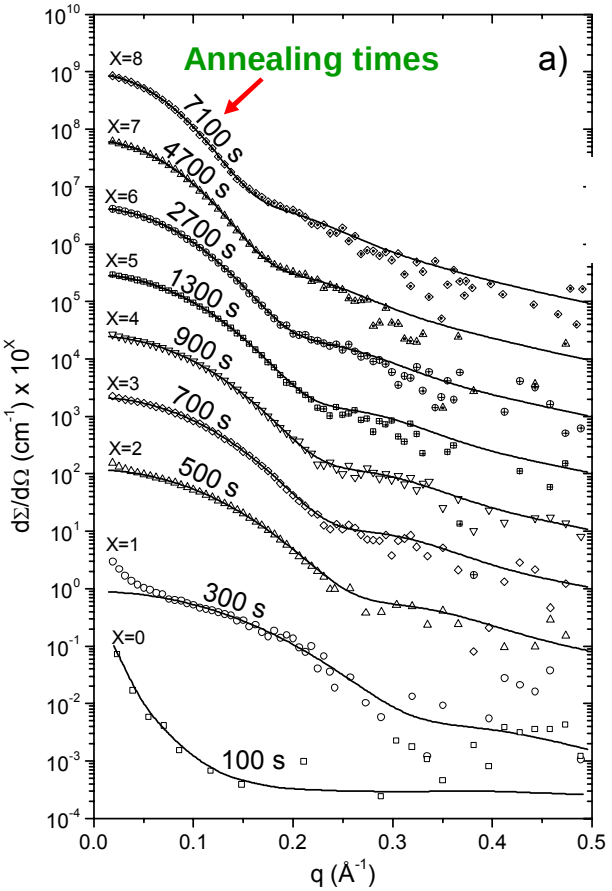
q ($A^{-1}$)

# SAXS curves corresponding to the nanocomposite during its coarsening under isothermal condition. High temperture in situ study

***Phys. Rev. B, 67, 085405 (2003)***

$$\frac{d\Sigma}{d\Omega}(q) = r_0^{\,2} \cdot \left(\rho_p - \langle\rho\rangle\right)^2 \left(\frac{4\pi}{3}\right)^2 \cdot \int_0^{\infty} N(R) \cdot \left[3\frac{sen(qR) - qR\cdot\cos(qR)}{(qR)^3}\right]^2 \cdot R^6 \cdot dR$$

**843 K :**

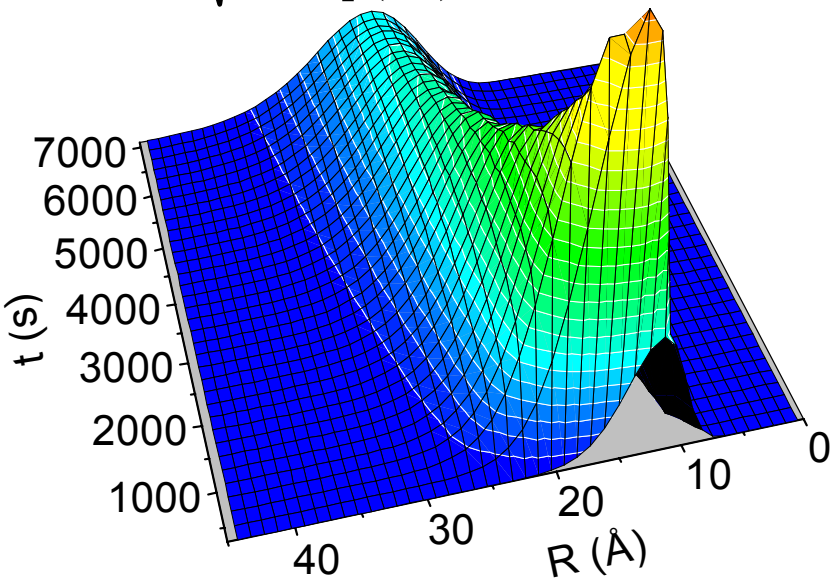



**Intensidad de SAXS**

**q (Å-1)**

## N(R)

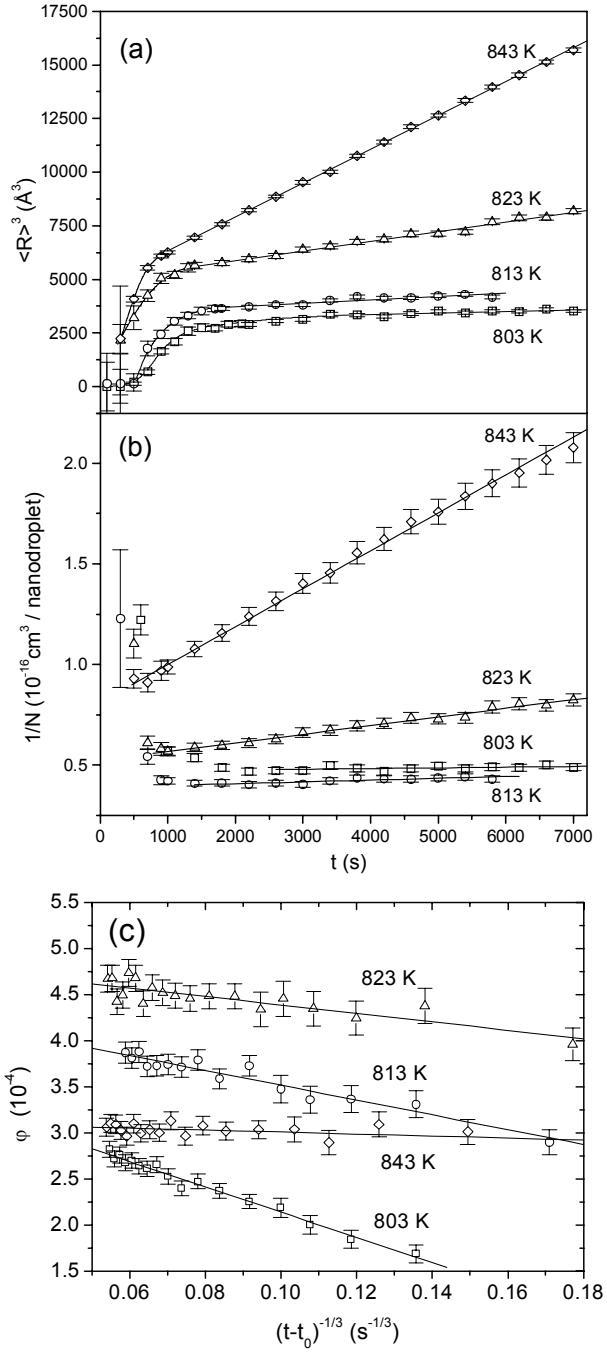
$$N(R) = \frac{n}{\sqrt{2\pi\exp(w^2)}\cdot wr}\, e^{-(\ln(R/r)/w)^2/2}$$



**<R>$^3$ versus t**

**$n^{-1}$ versus t**

**$\varphi$ versus $(t-t_0)^{-1/3}$**




Theory

$$[< R >^3 (t)] =< R_0 >^3 + \kappa(t - t_0)$$

$$n^{-1}(t) = n_0^{-1} + \beta(t - t_0)$$

$$\varphi(t) = \varphi_e - [\chi'(t - t_0)]^{-1/3}$$

# Determination of the coefficient of atomic diffusion from SAXS results

The parameters κ, β e χ' are related to the coefficient of atomic diffusion of the solute D by:

$$\kappa = \frac{8\sigma v^2 c_e D}{9kT} \qquad \beta = \frac{4\sigma c_e v D}{(c_0 - c_e)kT} \qquad \chi' = \left(\frac{1/v - c_e}{1 - \varphi_e}\right)^3 \chi$$

σ: free surface energy per unit nanodroplet-matrix interface area,
*v*: atomic solute volume; $c_e$: solute equilibrium concentration.

Since the parameters σ e $c_e$ are often unknown, these equations cannot be directly applied for the determination of D.

Assuming that $[1/v\text{-}c_e] \approx [1/v]$, we obtain:

$$D = \frac{9}{4}(\kappa^2 \chi')^{1/3}$$

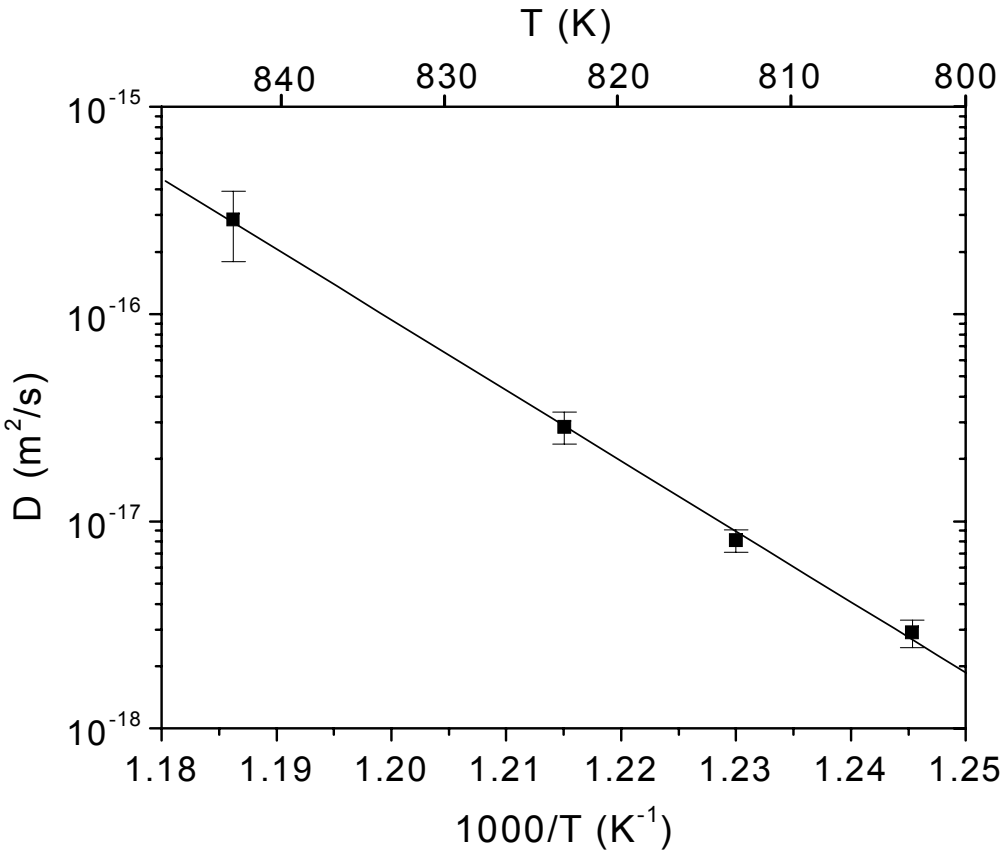
$$[< R >^3 (t)] = < R_0 >^3 + \kappa(t - t_0) \qquad \varphi(t) = \varphi_e - [\chi'(t - t_0)]^{-1/3}$$

Average radius

Volume fraction of nanodroplets

# Arrhenius plot

**Coefficient of Bi of atomic diffusion**




$$D(T) \propto e^{-E/\Re T}$$

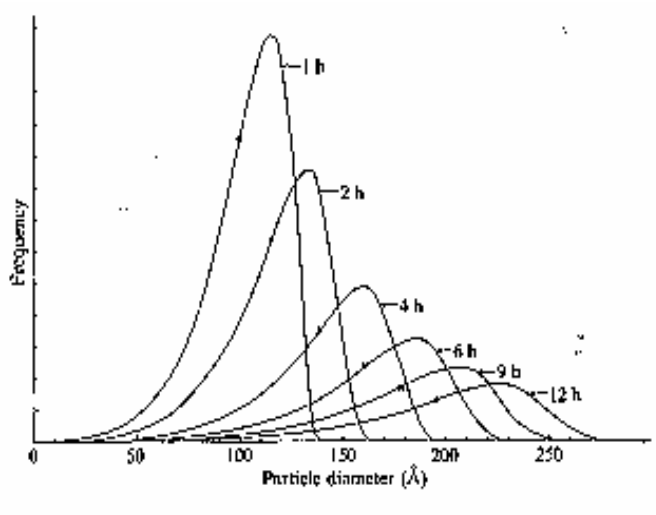
D: coefficient of Bi diffusion
E: activation energy
$\Re$ : Constant of gases
T: Absolute temperature

Slope: $E = (64 \pm 3) \times 10^4$ J/mol

**The relative width of the radius distribution, $s_R$=s/<R>=0.21, is invariant along the whole coarsening process for any system.**

**Remaining question: How to reduce the relative width of the size distribution ??**

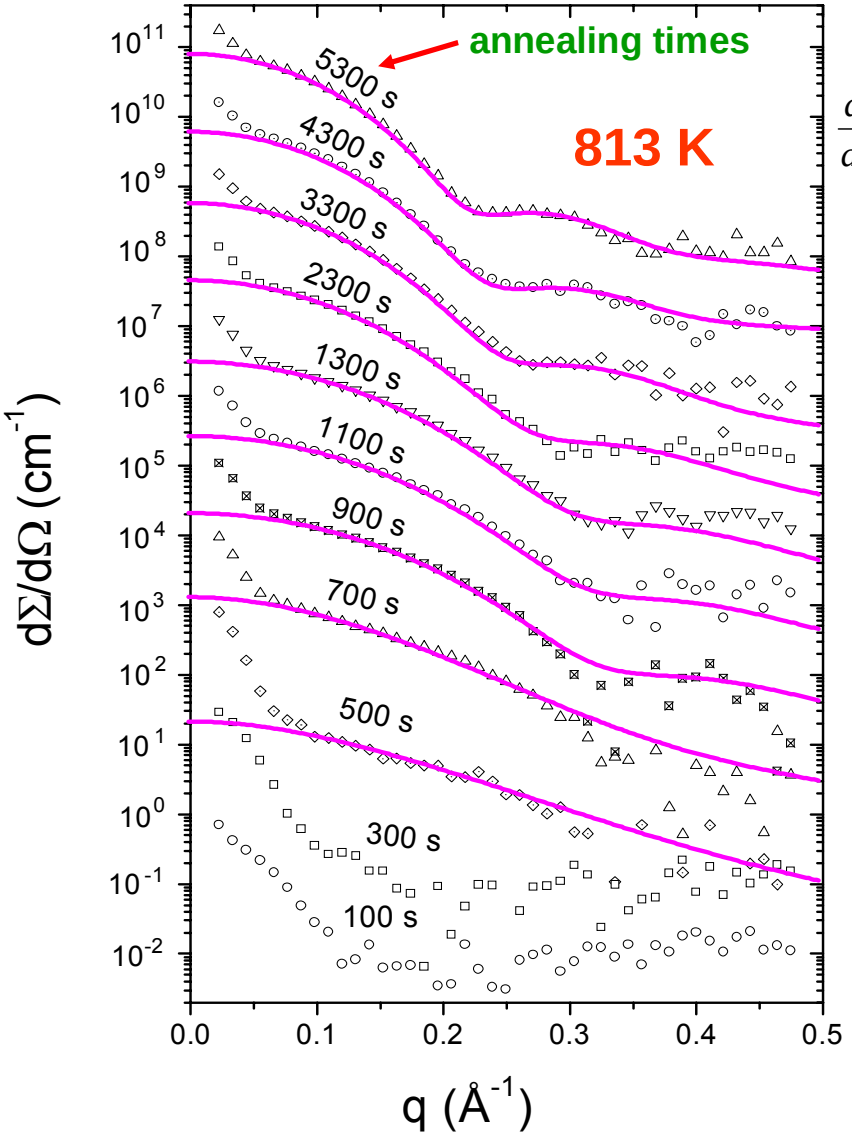
$\sigma_R$=σ/<R>=0.21 (time independent)



# Isothermal aggregation of Ag atoms in sodium-borate glass

G. Kellermann and A. F.C.
Phys. Rev. B70, 054106 (2004) and Phys. Rev. B 70, 099902 (2004).

# SAXS intensity



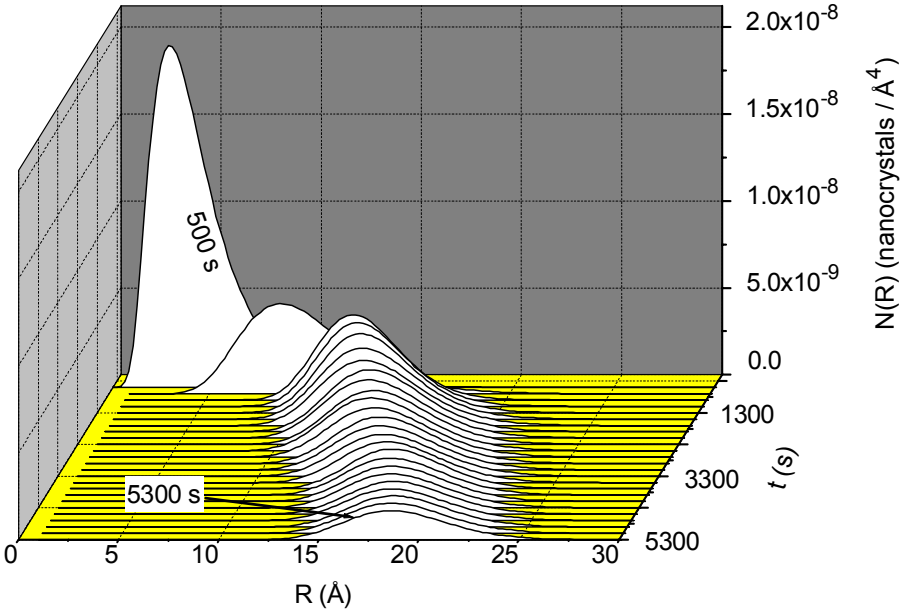

## SAXS intensity for a diluted set of spherical particles is given by:

$$\frac{d\Sigma}{d\Omega}(q) = r_0^{\,2} \cdot \left(\rho_p - \langle\rho\rangle\right)^2 \left(\frac{4\pi}{3}\right)^2 \cdot \int_0^{\infty} N(R) \cdot \left[3\frac{\mathrm{sen}(qR) - qR\cdot\cos(qR)}{(qR)^3}\right]^2 \cdot R^6 \cdot dR$$

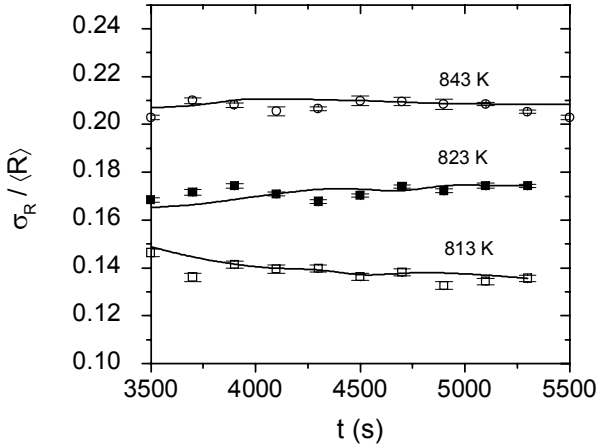
## Log-normal function

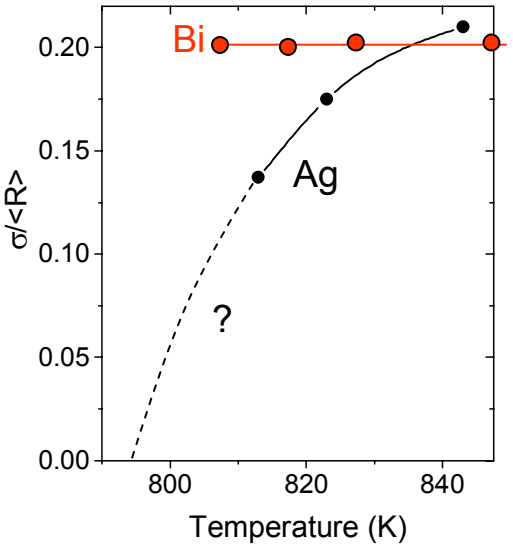
$$N(R) = \frac{n}{\sqrt{2\pi\exp(w^2)}\cdot wr}\, e^{-(\ln(R/r)/w)^2/2}$$

## Nanocrystals size distribution at different annealing times: N(R,t)

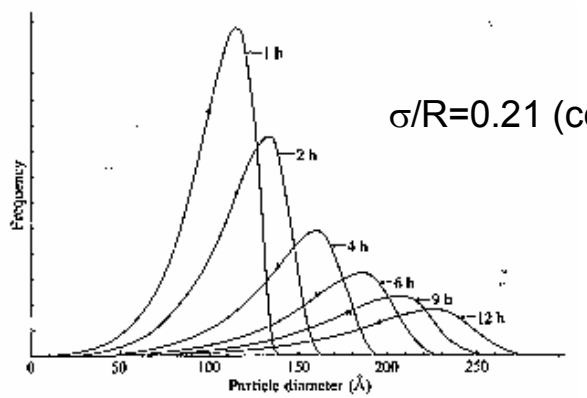


## Relative size dispersion



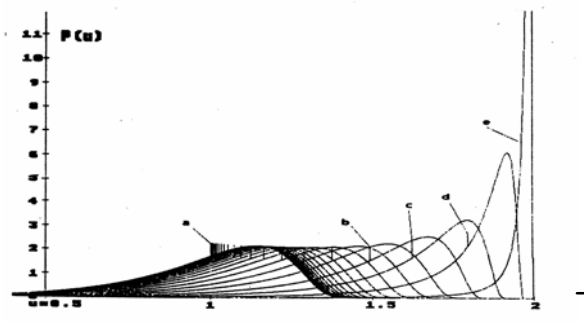

## Absence of elastic strain
(T>> $T_g$ temperature)



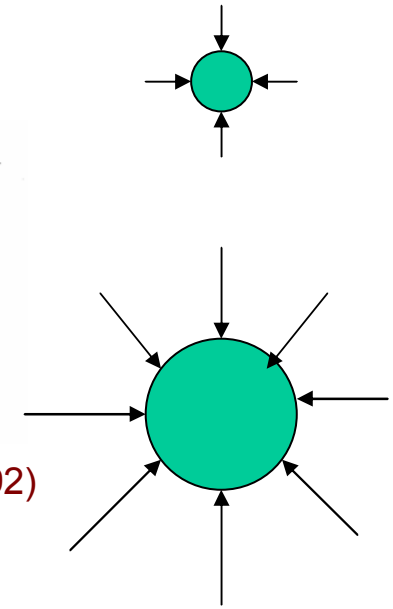

σ/R=0.21 (constant)

Lifshitz-Slyosov (1961) and Wagner (1961)

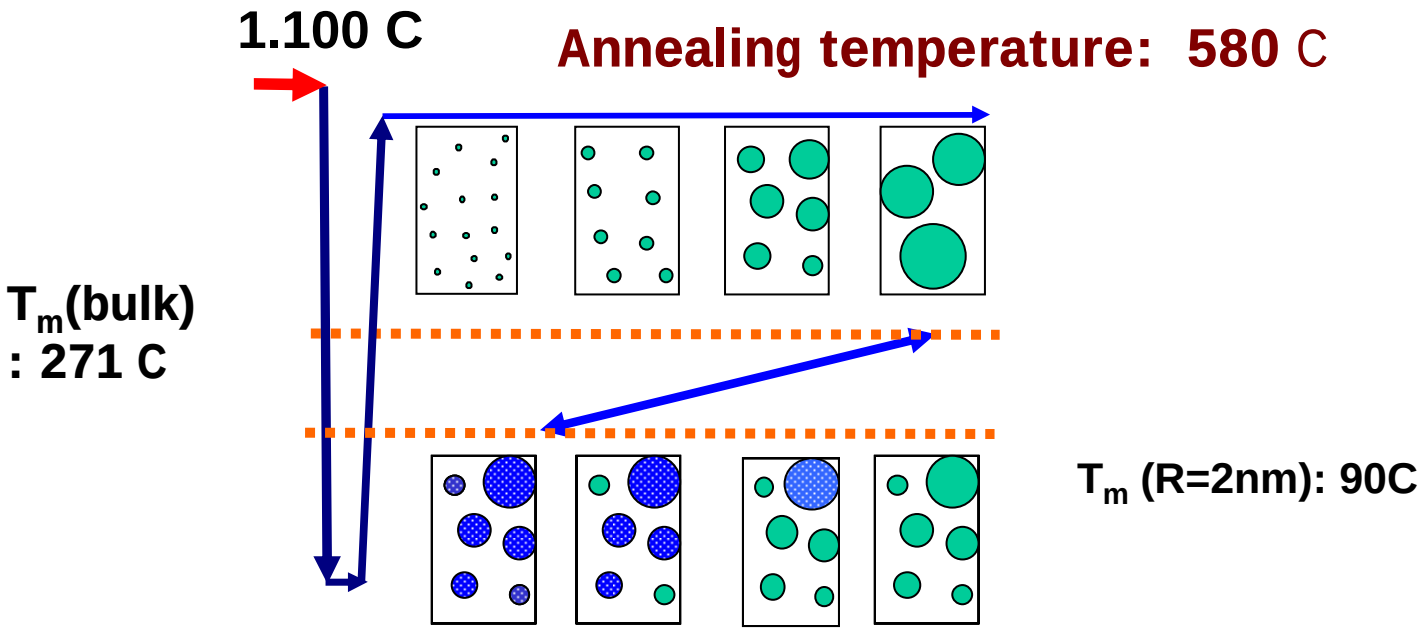
## Presence of elastic strain
(close to $T_g$ temperature)




J. Schmelzer and J. Moller, (1992)



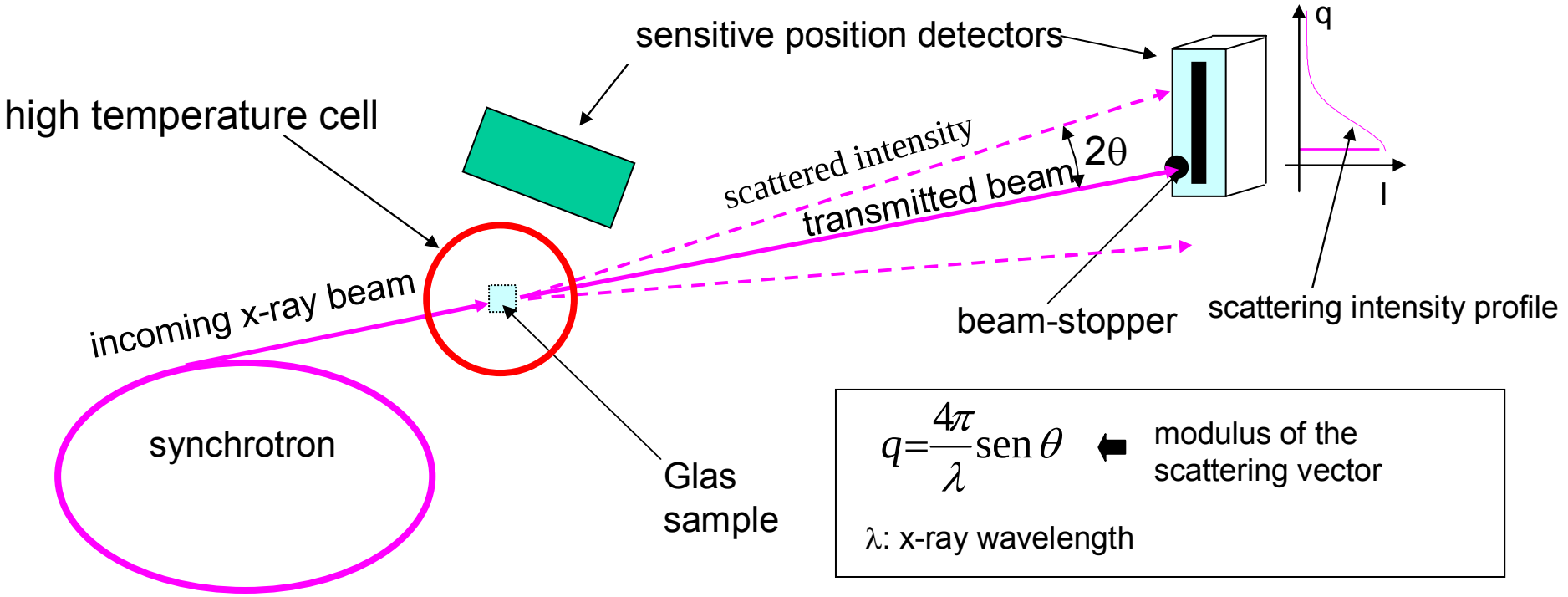
# MELTING OF NANOCRYSTALS




**Bi nanocrystals: Structure and melting.**
**(Precise determination of $T_m$)**
*Kellermann and Craievich, Phys Rev B, 65, 134204 (2002)*

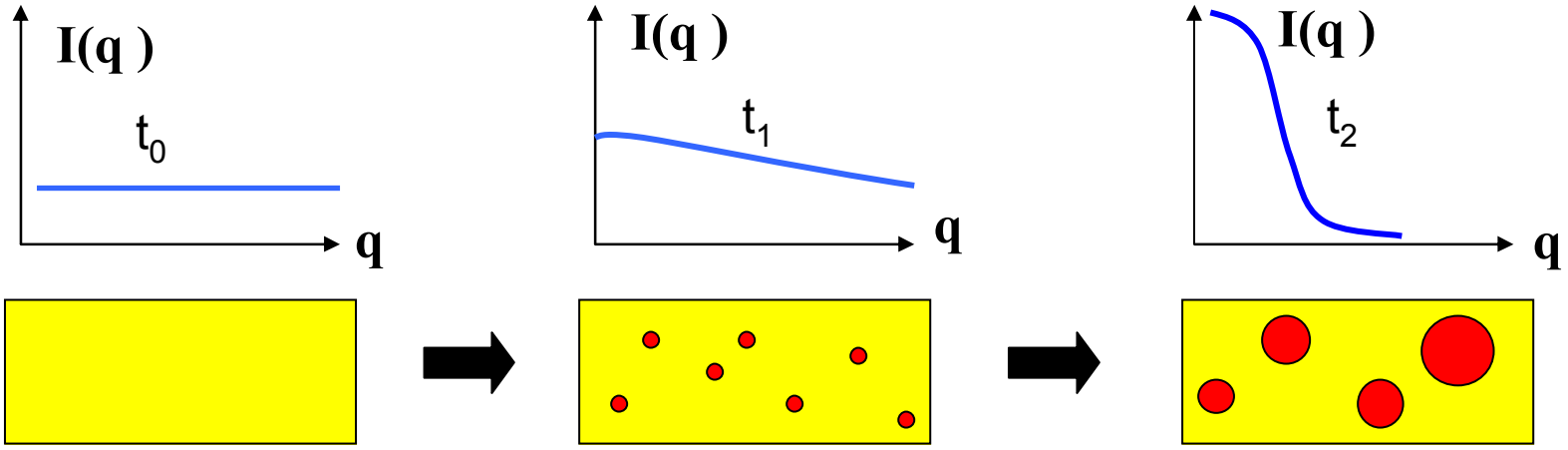
WAXS and SAXS

# Small-angle x-ray scattering - SAXS

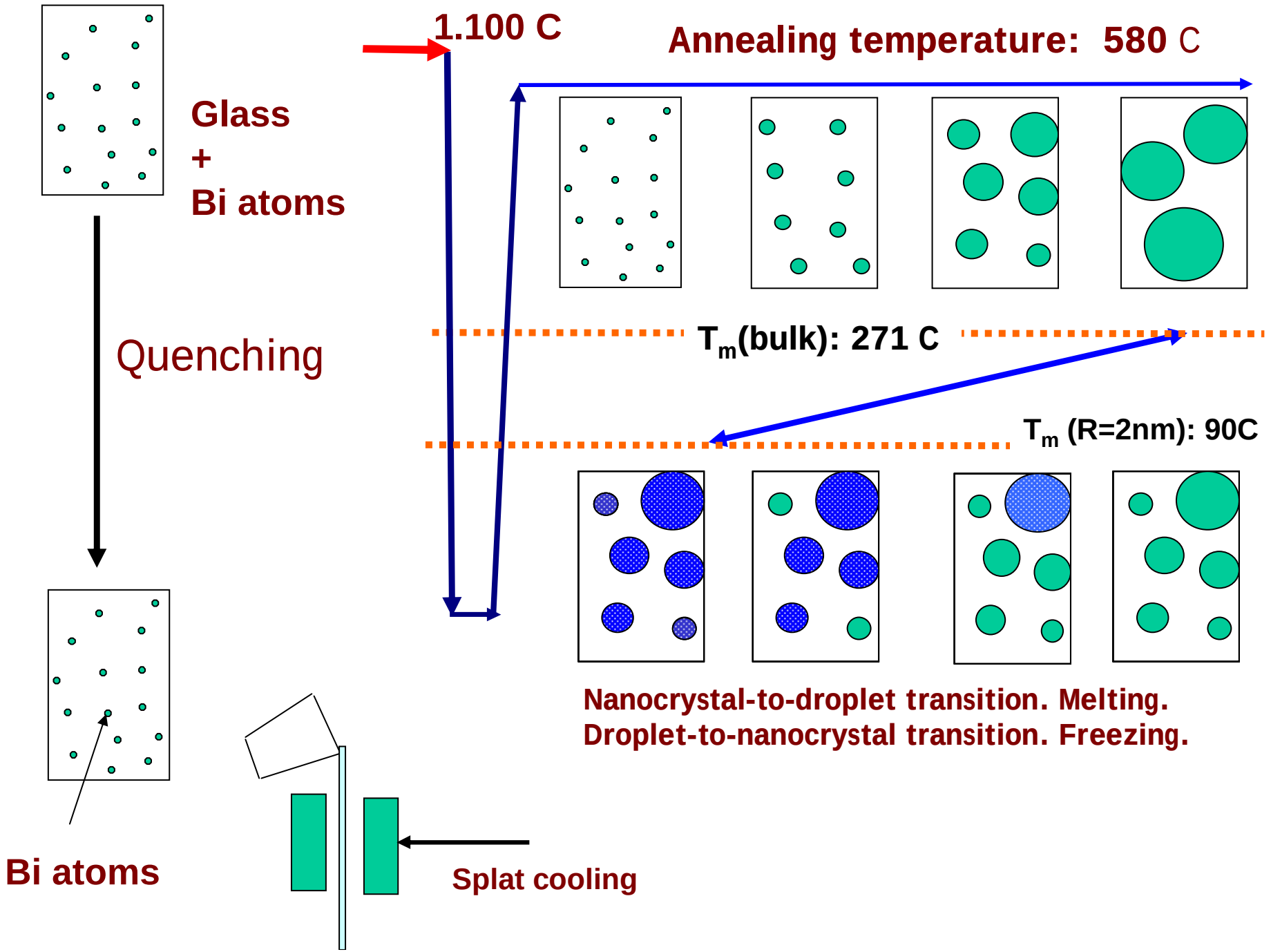



$$q = \frac{4\pi}{\lambda} \operatorname{sen}\theta$$ ⬅ modulus of the scattering vector

λ: x-ray wavelength

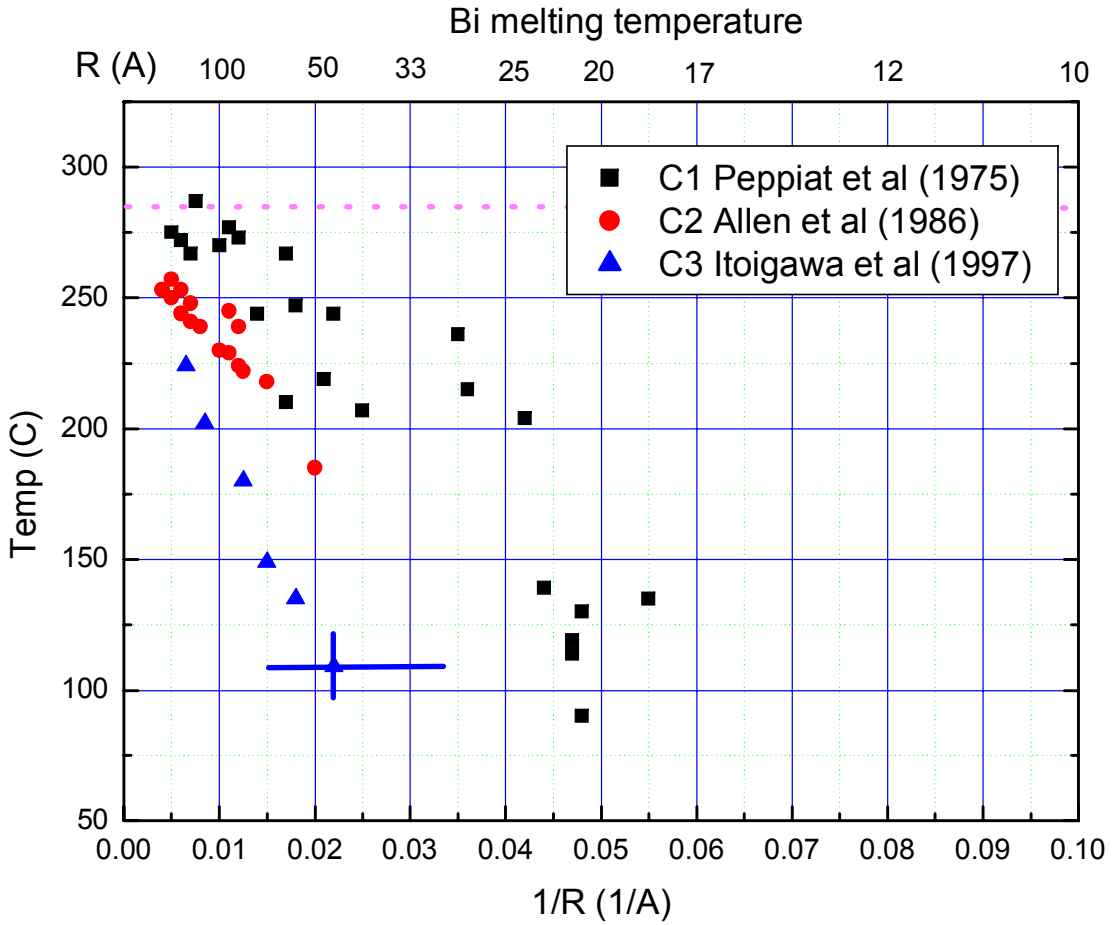



**Isothermal transformation** ⟶

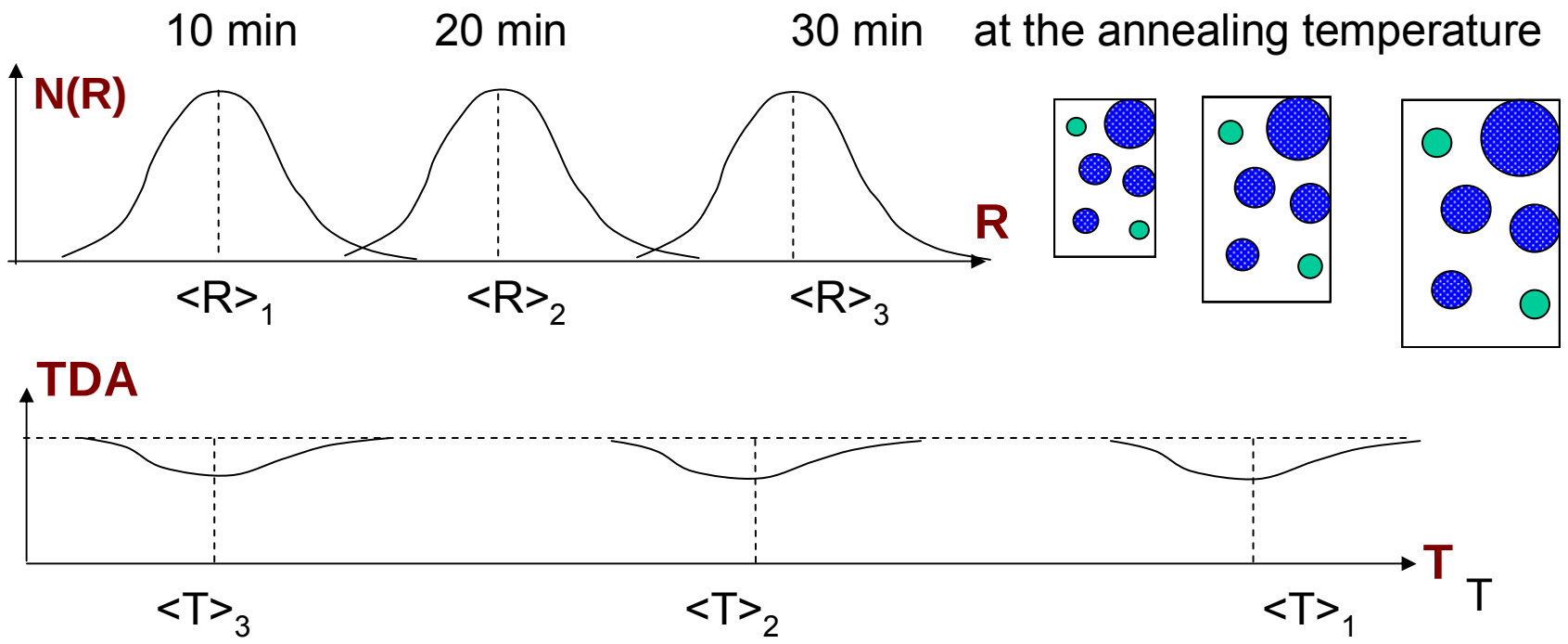

1.100 C
Annealing temperature: 580 C
Glass
+
Bi atoms
Quenching
$T_m$(bulk): 271 C
$T_m$ (R=2nm): 90C
Nanocrystal-to-droplet transition. Melting.
Droplet-to-nanocrystal transition. Freezing.
Bi atoms
Splat cooling

**How to check the validity of theoretical equations that predict $T_m(R)$ ??**

**-Determining experimentally a precise $T_m(R)$ function using a simple model system and combining in situ WAXS and SAXS technique using a S. R. set up.**

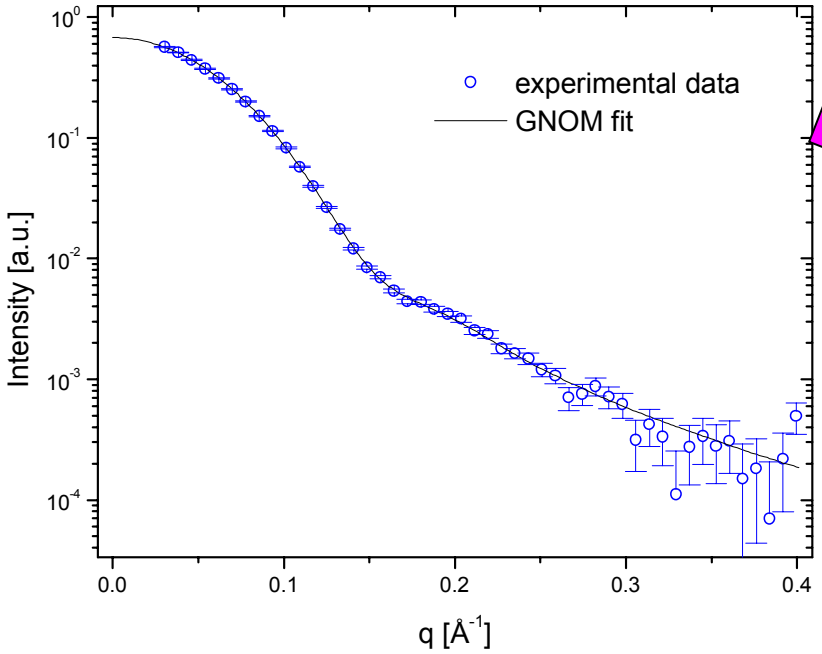


# Classical procedure for the determination of $T_m(R)$

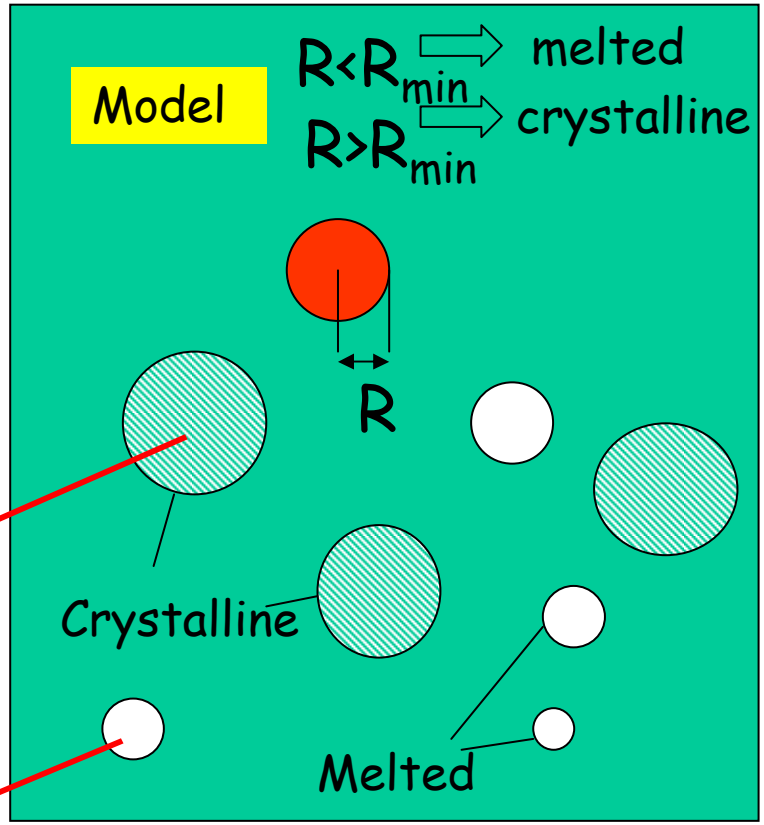


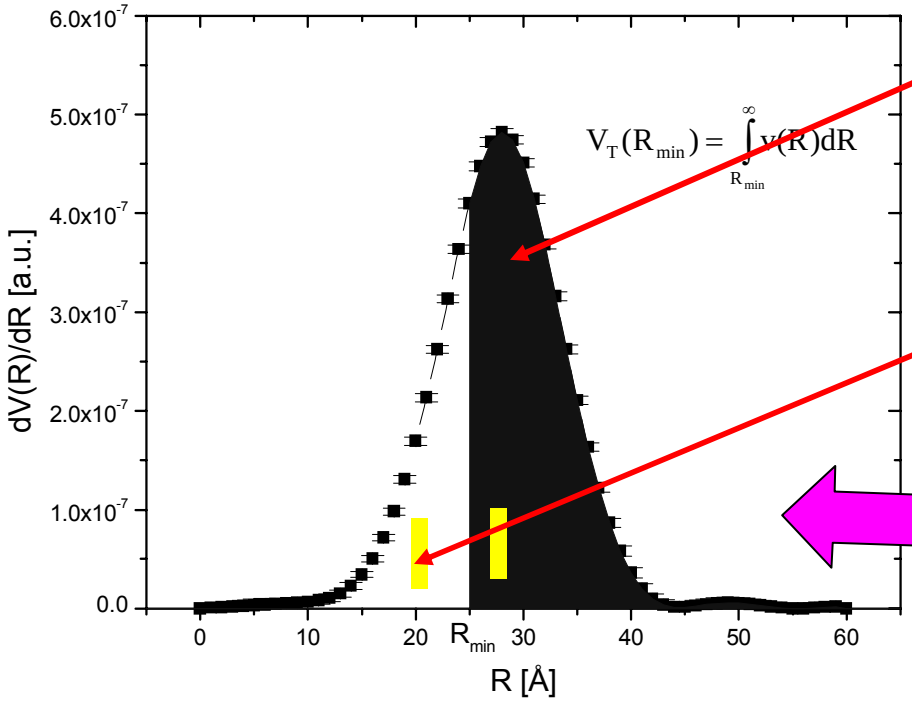

**$<T_m>(<R>)$** **TDA is a low precision procedure !**

**NEW PROCEDURE:**
**Use a SINGLE SAMPLE with a wide size distribution**
**and determine $T_m$ (R) by using combined IN SITU SAXS and WAXS results**




SAXS curve
at room temperature



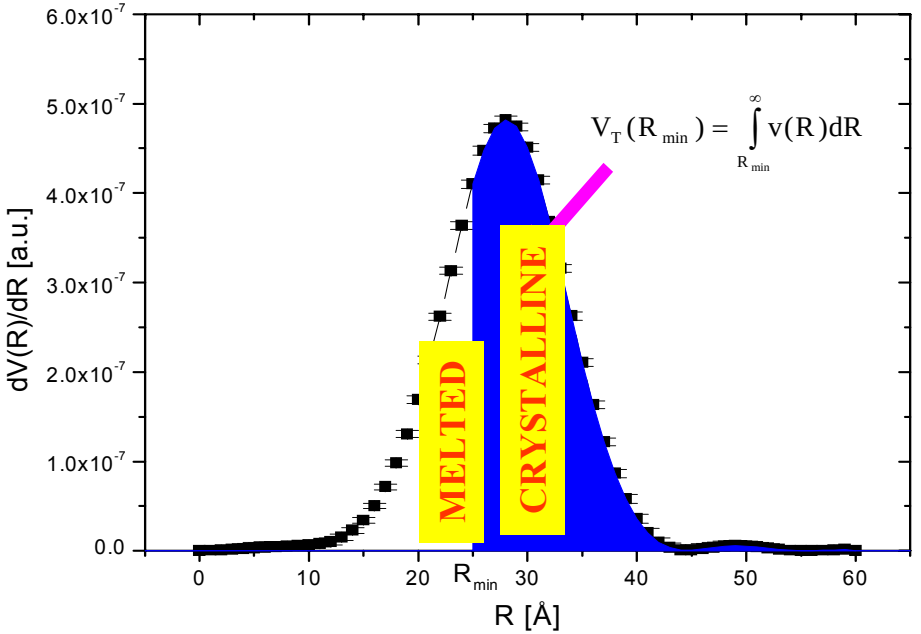



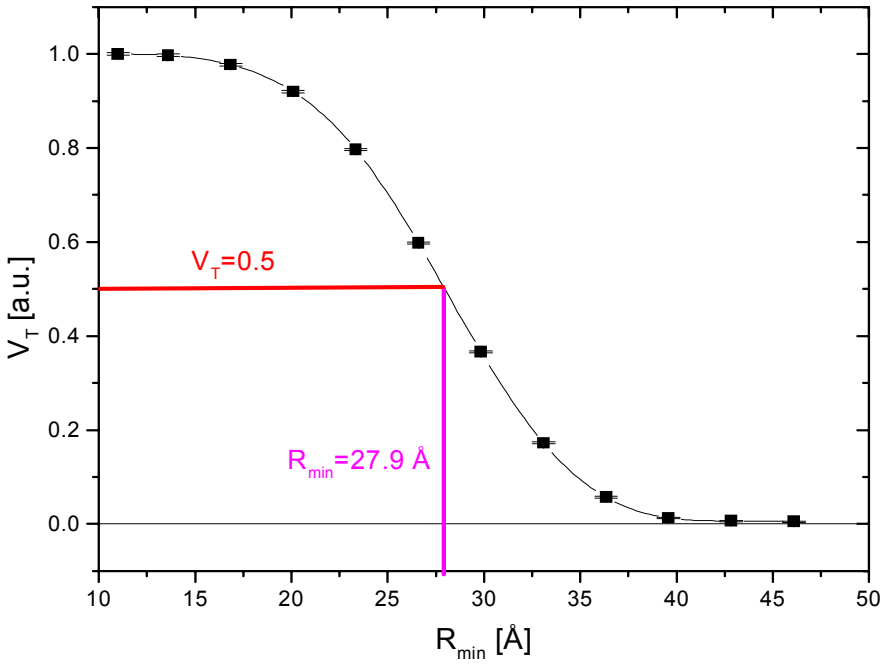

Volume distribution function
of the nanoparticles
(nanocrystals AND nanodroplets)

In our calculation we have considered that for a given temperature T all Bi nanoparticles with a radius R < $R_{min}(T)$ are completely melted and that the particles with R > $R_{min}(T)$ still remain crystalline.
The melting temperature was determined comparing the crystalline phase volume $V_{cry}(T)$ function, obtained by X-ray diffraction (XRD), with the function $V_T(R_{min})$ that describes the total volume occupied by the particles with radius $R>R_{min}$ :

$$V_T(R_{\min}) = \int_{R_{\min}}^{\infty} v(R)dR$$

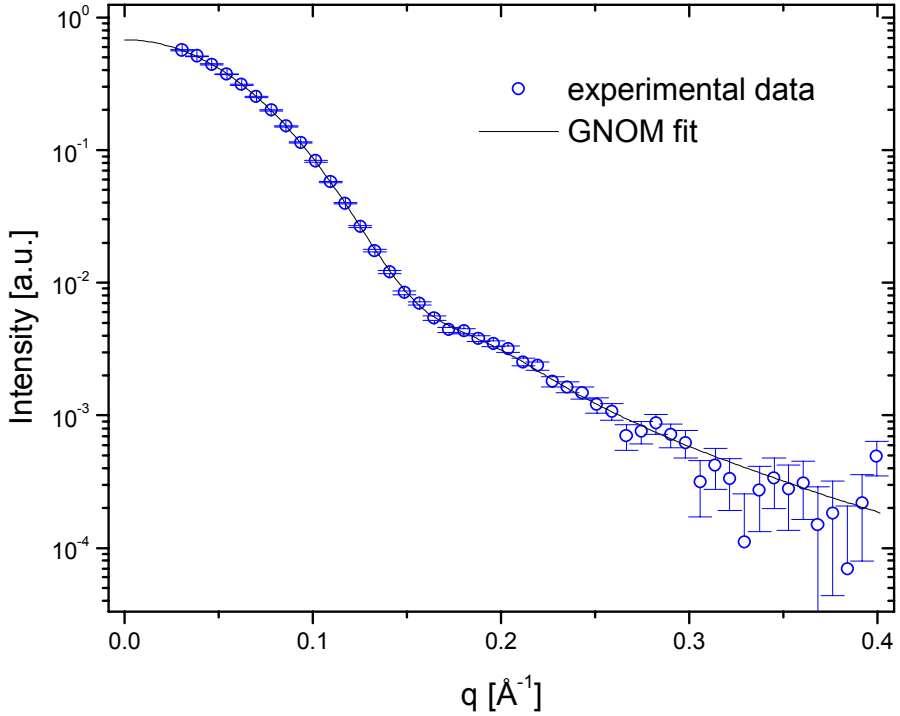
v(R) is the volume dispersion function calculated from small-angle X-ray scattering (SAXS) intensity.
The error bars in R corresponds to the range [$R_{min} - \sigma_R$, $R_{min} + \sigma_R$] for which $V_T$ falls between the $V_{cry} \pm \sigma_V$ (T) uncertain limits.



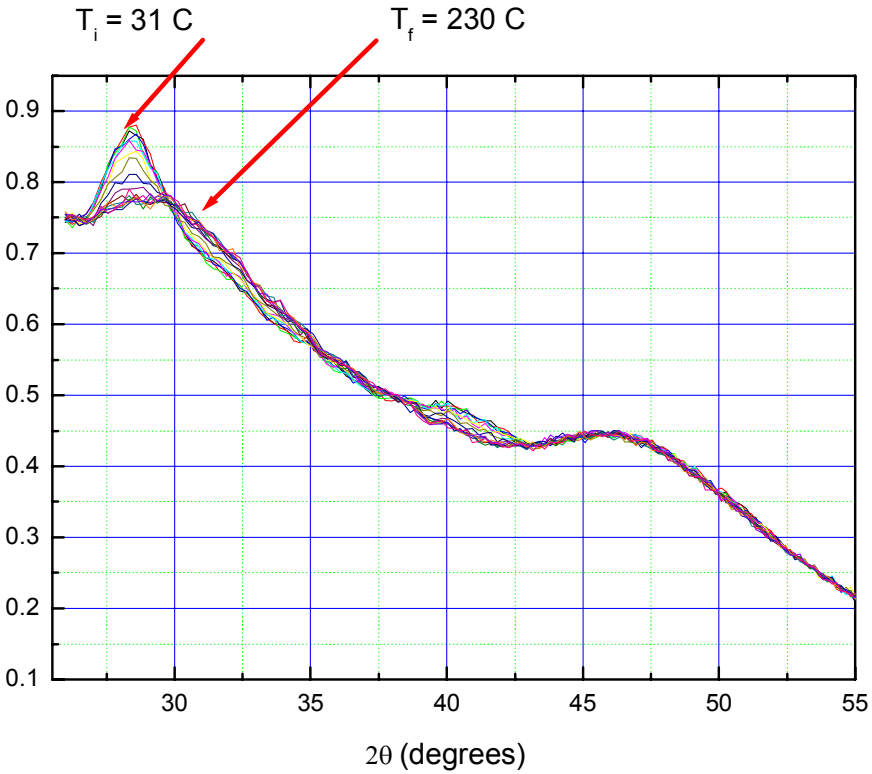
## SAXS

(The same spectrum at all temperatures)

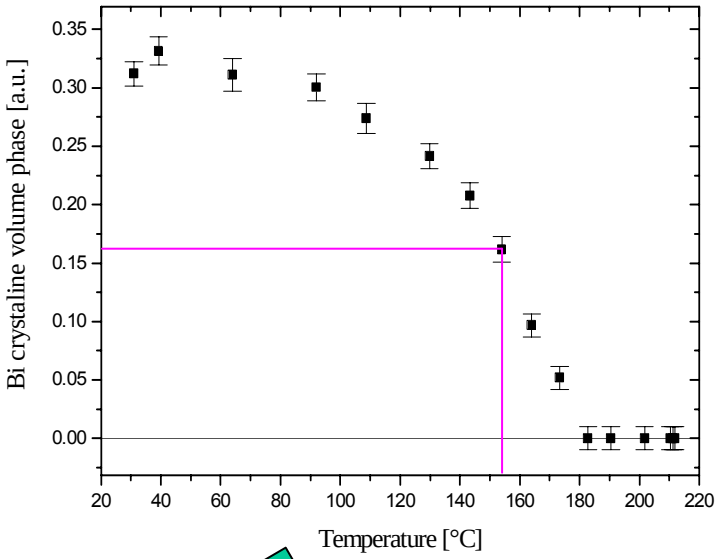



## WAXS

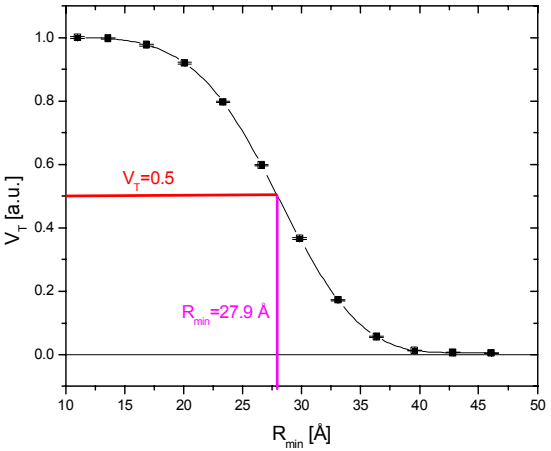
Different spectrum for temperatures increasing from 30 to 230C

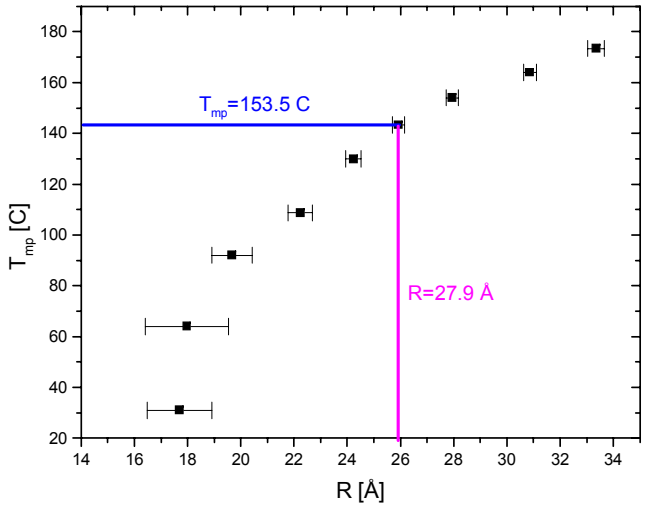


## WAXS results



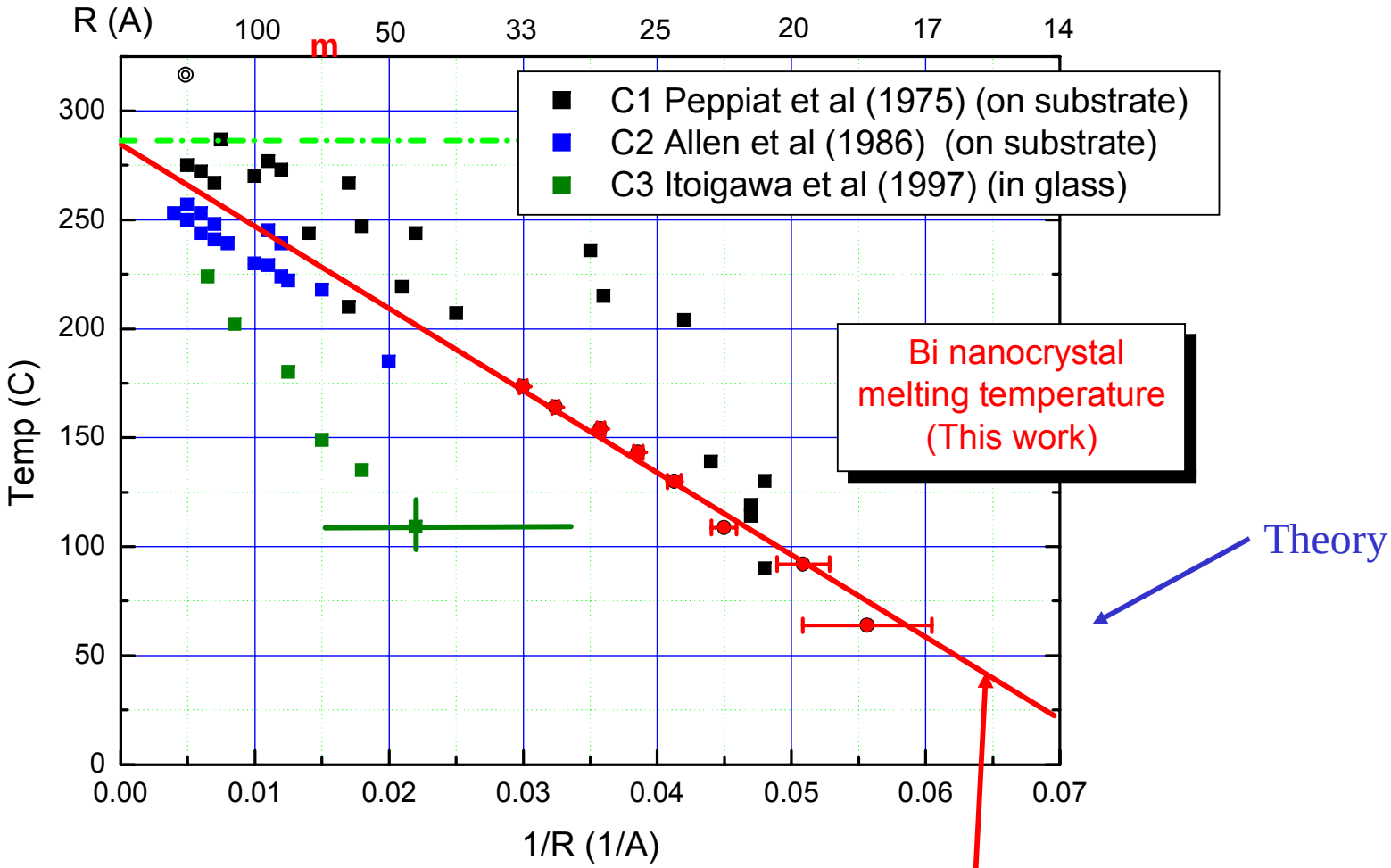

## From SAXS results




**Melting temperature as a function of nanocrystal radius**

# Melting temperature as a function of 1/R




$$T_m(R) = T_m(\text{bulk}) - \alpha\,(1/R)$$

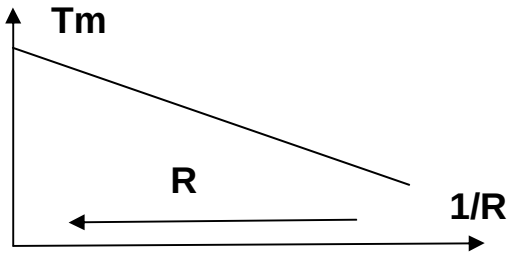
-The crystal lattice of Bi nanocrystals is rhombohedral, like those in bulk state. The nanocrystals have a contracted structure. Both lattice parameters (a and c, hexagonal unit cell) are smaller than in bulk crystals

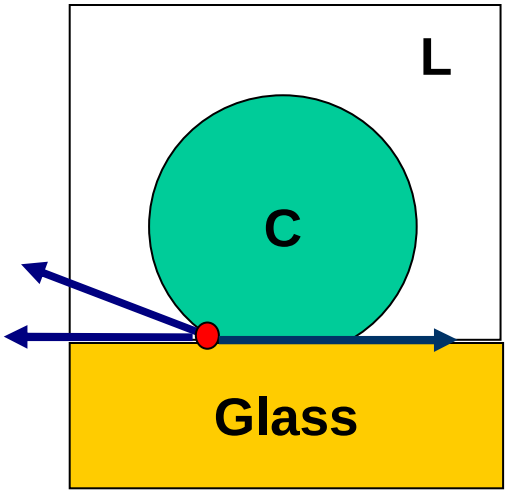
(<δV/V> = 1.3 ±0.1 % for <R>= 2.7 nm).

-The Tm(R) function obeys the law classical law of Couchman and Jesser:

$$T_m(R) = T_B - \frac{3(\sigma_{lg} - \sigma_{cg})}{(\rho_l + \rho_c)L_0}(1/R) = T_B - \alpha.(1/R)$$

$$\alpha = \frac{3(\sigma_{lg} - \sigma_{cg})}{(\rho_l + \rho_c)L_0}$$

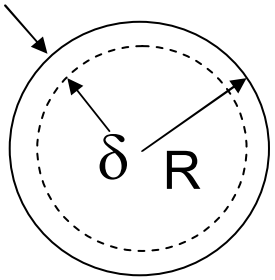



The difference of the surface energy of the interface crystal/glass and liquid/glass = **surface energy of the crystal-liquid interface:**

$$\sigma_{lg} - \sigma_{cg} = \sigma_{lc} = 116.10^{-3}\ \mathrm{J/m^2}.$$

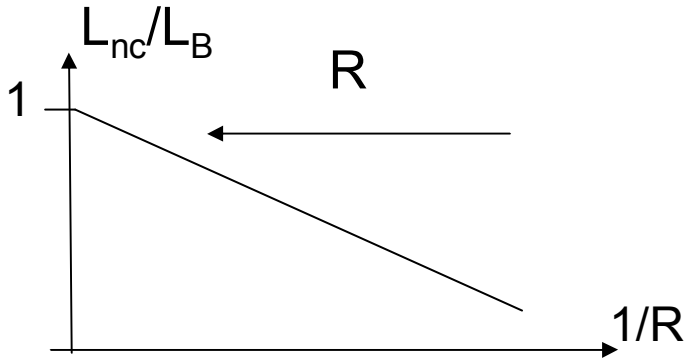
# Melting of Bi nanocrystals. Theoretical model

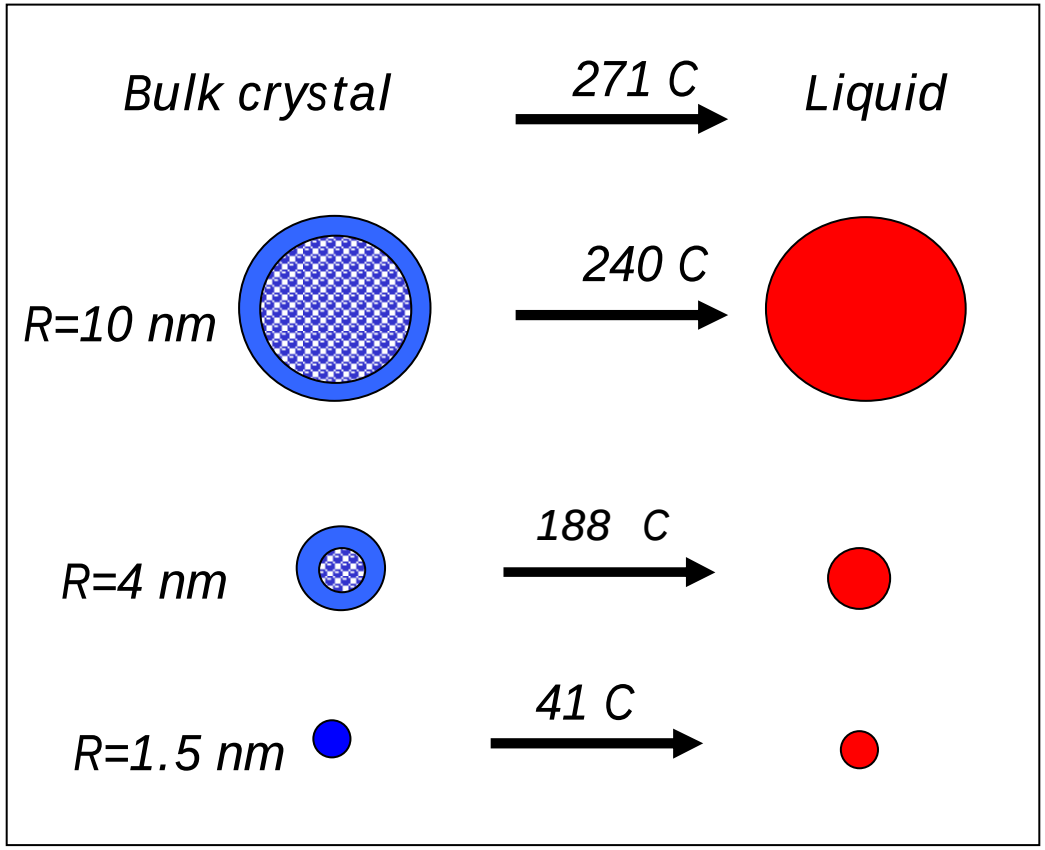



$$L_{nc} = x_{\text{int}}.L_{\text{int}} + (1 - x_{\text{int}})L_B$$

$$x_{\text{int}} \approx \frac{3\delta}{R}$$

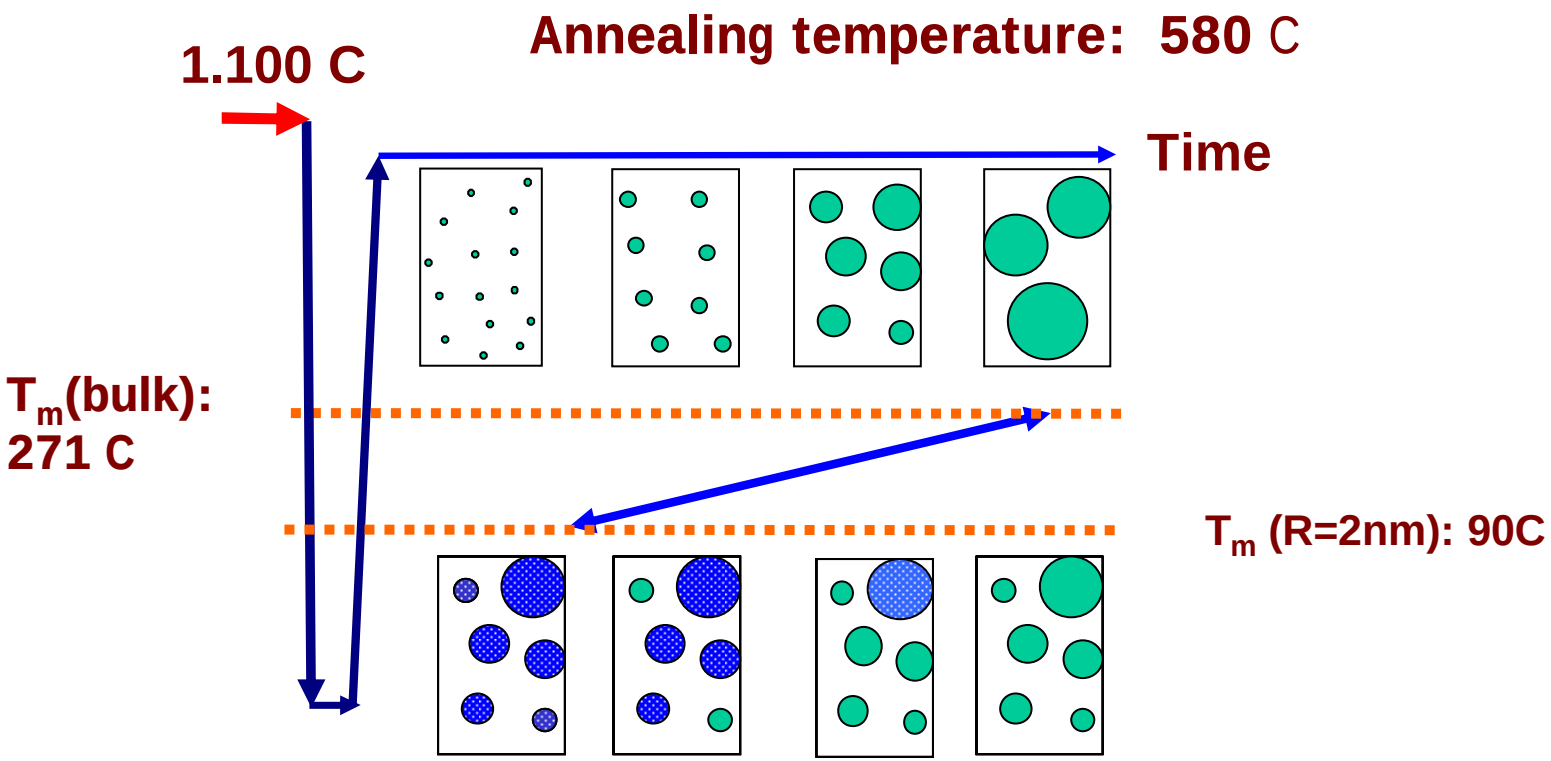
$$\frac{L_{nc}}{L_B} = 1 - \frac{3\delta(L_B - L_{\text{int}})}{L_B}\left(\frac{1}{R}\right)$$



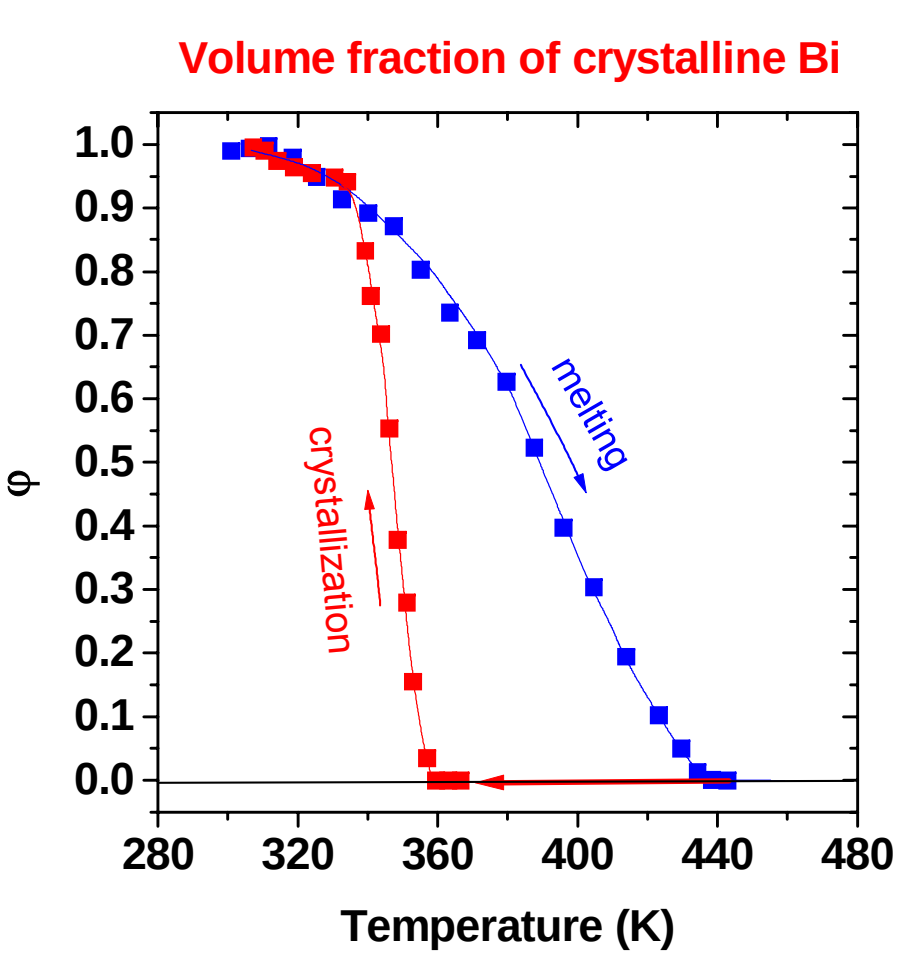



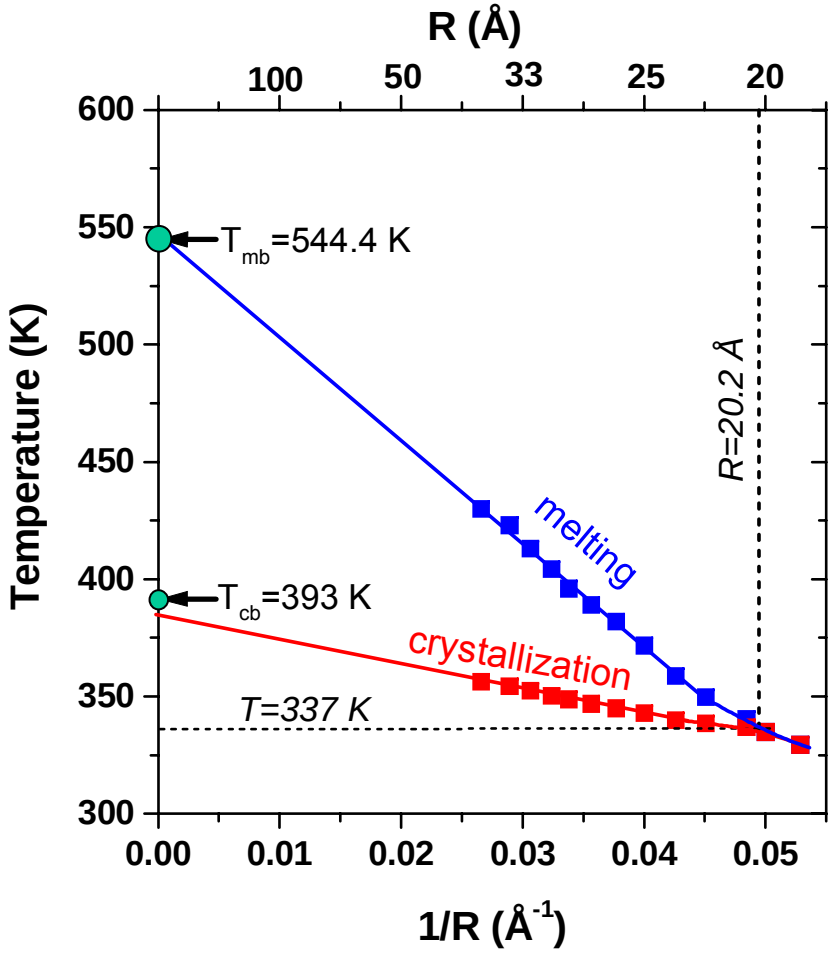
# FREEZING OF Bi LIQUID NANO-DROPLETS

*G. Kellermann and A. F. C. In preparation (2005)*



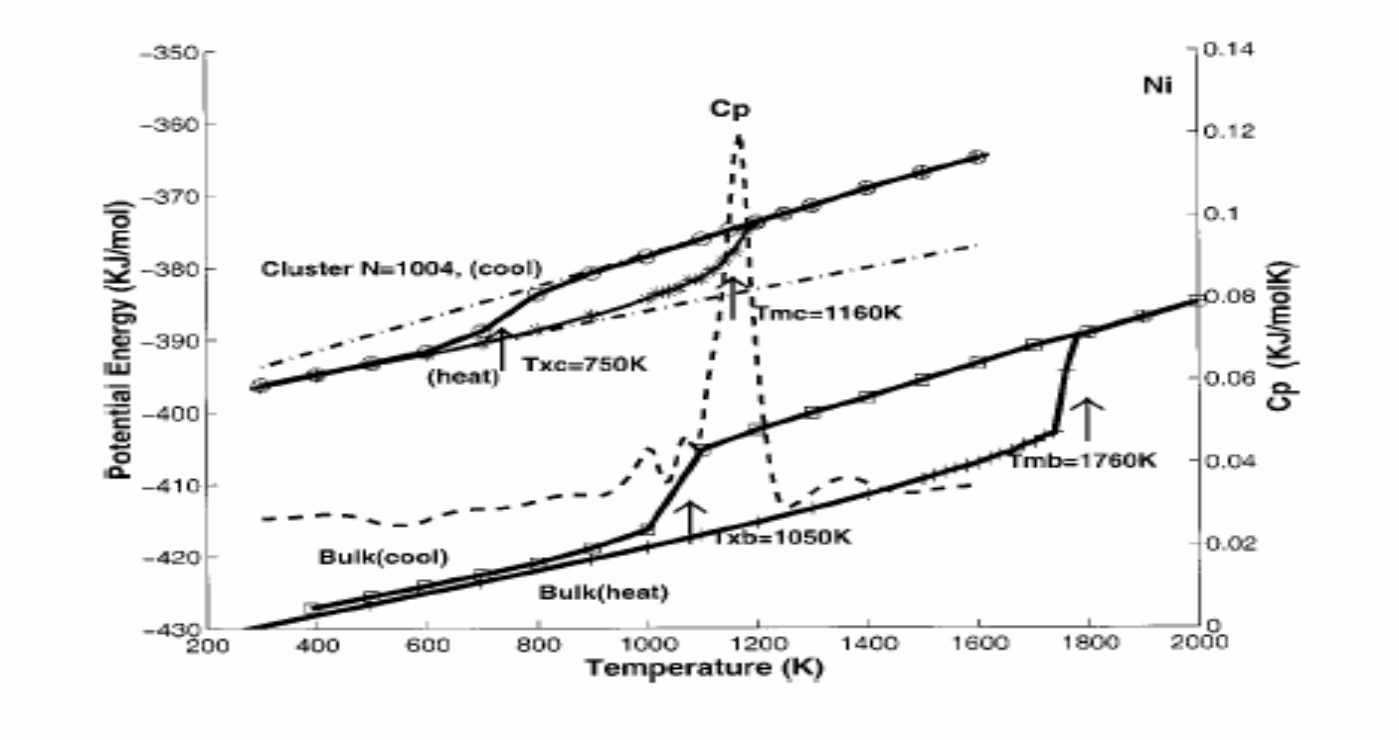
# Freezing of liquid Bi droplets
# Undercooling reduction (and suppression) for small nanodroplets

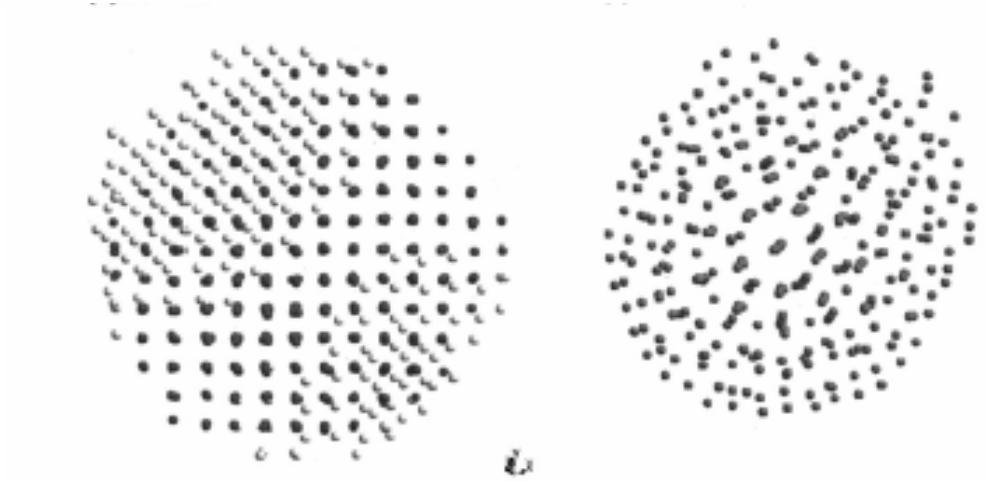


**Melting and crystallization in Ni nanoclusters: The mesoscale regime**

Y. Qi, Tahir C¸ W L. Johnson, W A. Goddard , J. Chem. Phys.,115, 385 (2001)



# CONCLUSIONS

**I - The melting temperature of Bi nanocrystals is a linear function of the reciprocal radius:**

$$T_m(R) = T_m(bulk) - a * (1/R)$$

**The melting temperature of Bi nanocrystals with R~2nm is 344K, i. e. 60 % lower than the melting temperature of bulk Bi (544K).**

**The surface energy of the solid-liquid Bi interface is equal to $116.10^{-3}$ $J/m^2$.**

**II - The frezing temperature of Bi nanodroplets is a linear function of the reciprocal radius:**

$$T_f(R) = T_f(bulk) - b * (1/R)$$

**This equation is similar to that corresponding to the melting temperature of Bi, but the magnitude of the slope b < a so as, for R~1.4 nm, we have $T_m = T_f$. This implies that, for nanodroplets with R<1.4 nm, undercooling effects are suppressed.**

# Self-organized nanomaterials. Current challenges

-*Precise in situ investigations, in real time, during the whole formation process.*

**A clever preparation of nanomaterials is guided by the precise knowledge of the mechanisms and conditions of formation of nanostructured materials with desired properties.**

**(In situ studies of structural transformations during the formation process)**

-*Simultaneous determination of properties and structure of the same final material*.

**Experimental determinations of the properties of nanomaterials accompannied by parallel and precise determinations of the relevant structural parameters (size, shape, density, spatial correlation) simultaneously, on the same samples.**

**(Precise evaluation of the correlation between structure and properties).**

-*Theoretical studies and computer simulations of complex systems.*

**Theoretical research in order to better understand the processes of formation and the properties of "real" nanostructured materials composed of bulding blocks with different shapes, sizes, size distributions, spatial correlation, etc.**

-*Reference books of physical properties*

**The properties of macroscopic materials are usually reported in tables and/or plots. They are usually published in reference handbooks.** *How to classify the properties of nanomaterials, which depend on sizes, shapes, spatial correlation of the nanometric building blocks? …*

*"When scientists have learned how to control the arrangment of matter at a very small scale, they will see materials take an enormously richer variety of properties"*

*Richard Feymman (1959)*

*Is this coloured glass a new material ?*

**LNLS**

*“When scientists have learned how to control the arrangment of matter at a very small scale, they will see materials take an enormously richer variety of properties”*

*Richard Feymman (1959)*

LNLS

*This is a Roman Calice, more than 2000 years old !!!*

*It is a nanostructured glass. A glass matrix in which Au and Ag nanocrystals are embedded*

## References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- G. Kellermann and A. F.C. In preparation (2005).


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LNLS staff