

DTA and its historical development, thermodynamics and yet unsettled consequences of the sample heat inertia and temperature gradients

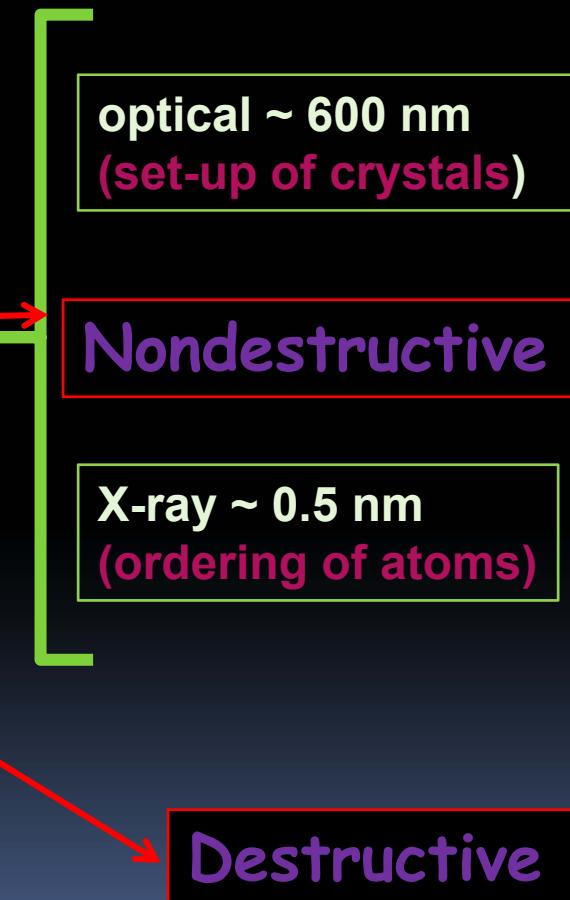
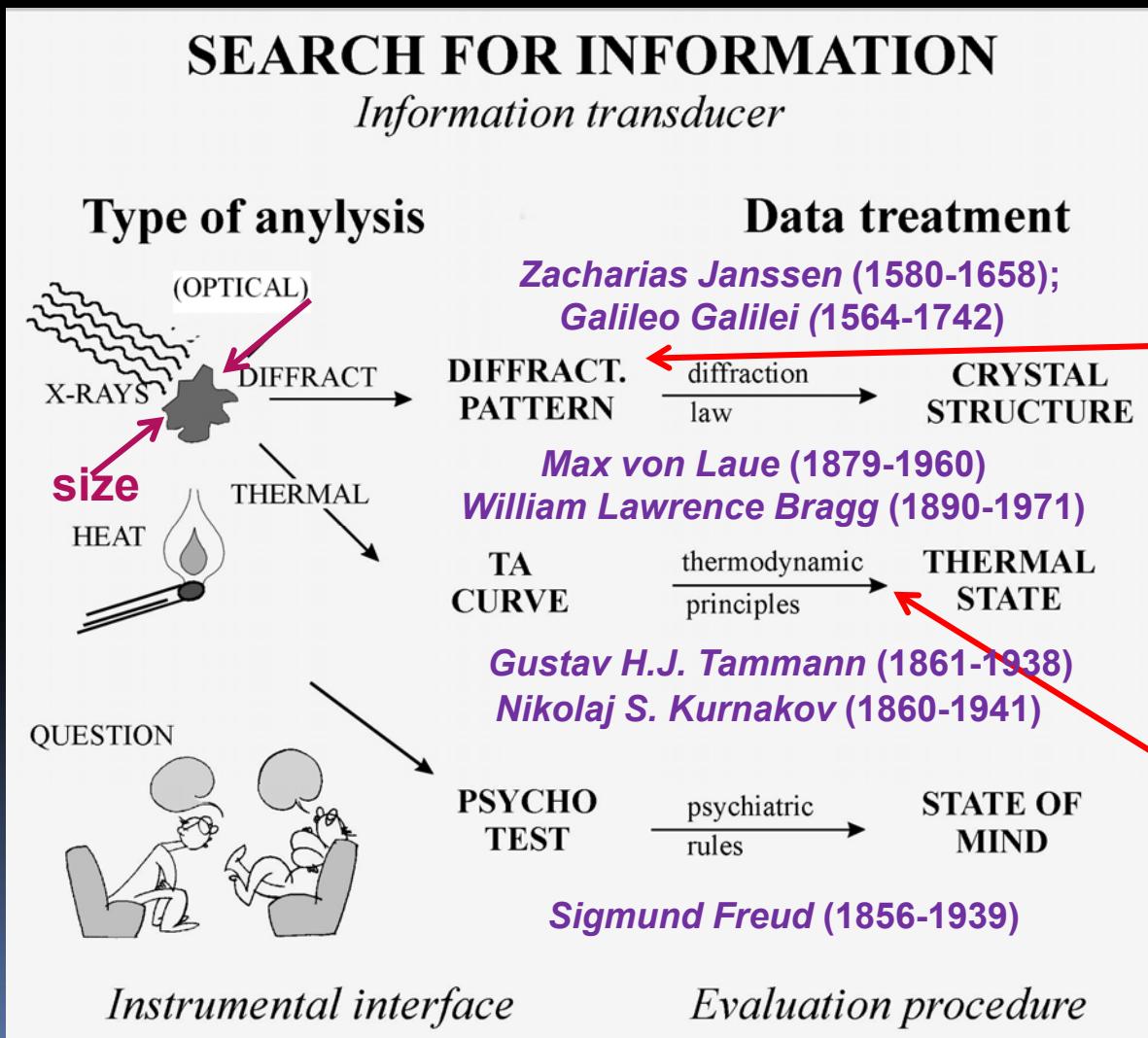
Jaroslav Šesták

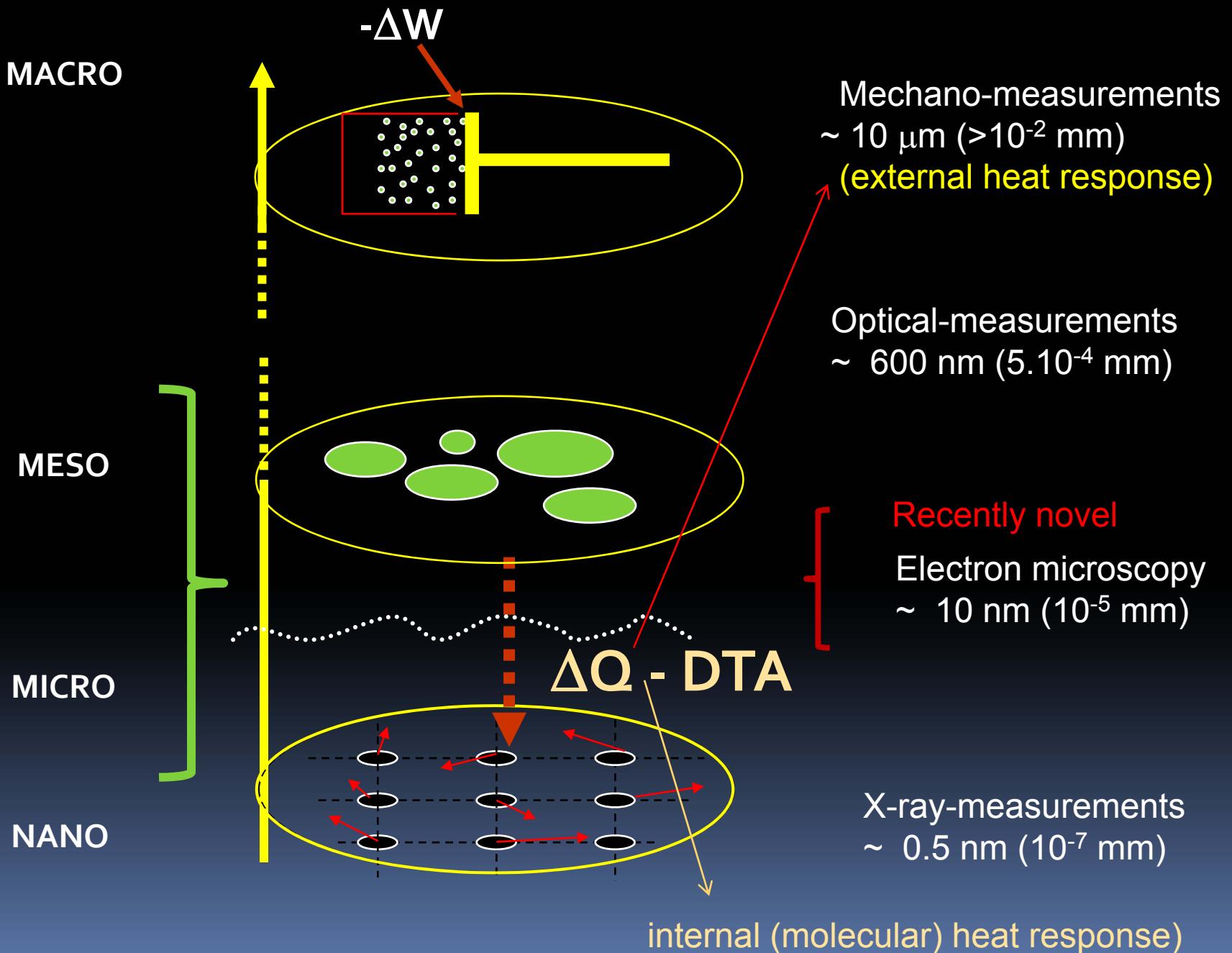
New Technology - Research Center in the Westbohemian Region, West Bohemian University, Universitní 8, CZ-30114 Plzeň;

Division of Solid-State Physics, Institute of Physics of the Academy of Sciences ČR, Cukrovarnická 10, CZ-16200 Praha, both Czech Republic; E-mail: sestak@fzu.cz

In cooperation with Pavel Holba and David Sedmidubský
prepared for NETZSCH-Gerätebau GmbH, Selb 17/12/12

ANALYSIS analogy





Spectroscopic methods

X-ray

Identity
“fingerprint”

Position
Symmetry
Quality

Quantity
Intensity
Area

Shape
Broadening
Crystal size

Heat transfer methods

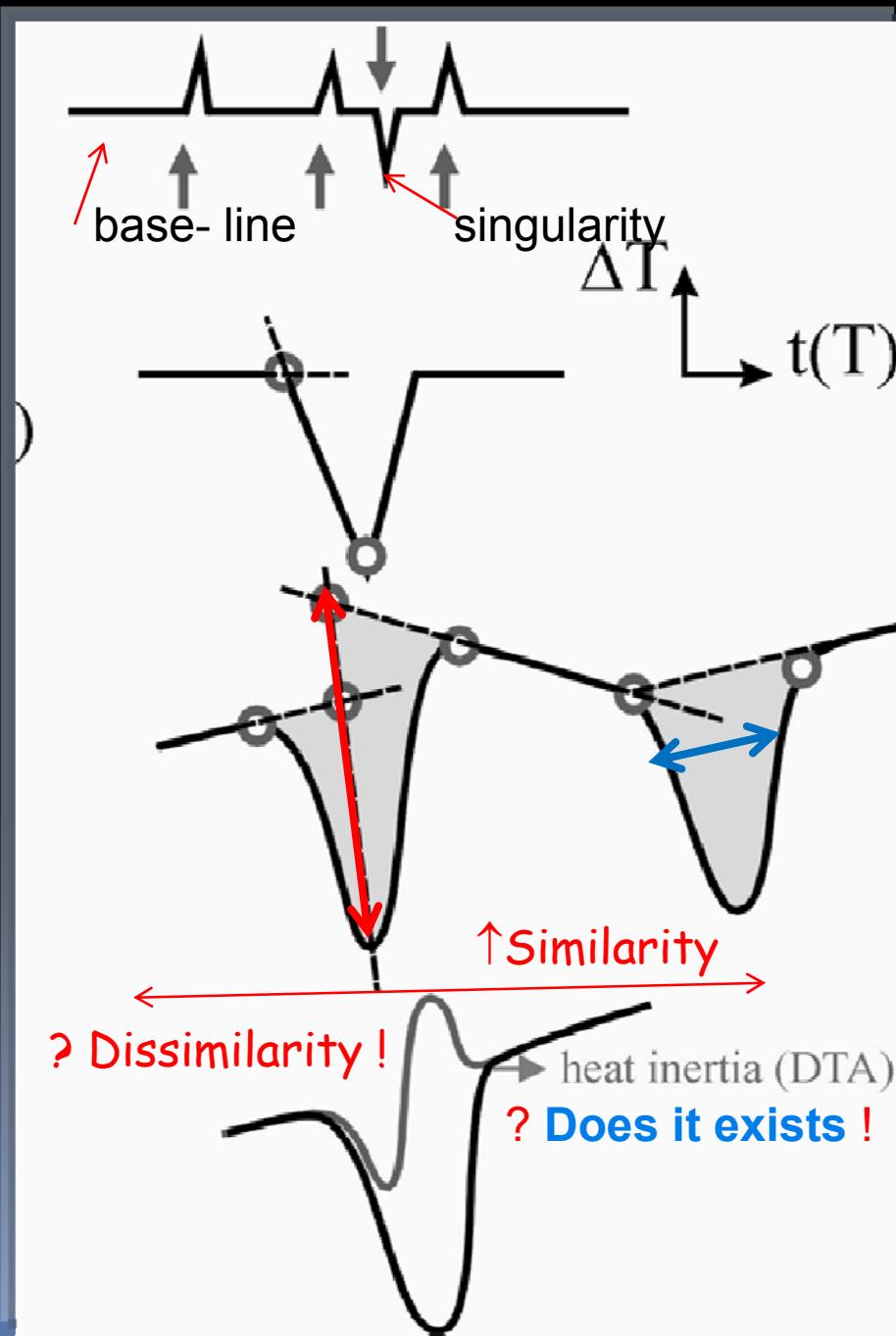
DTA

Identity
“fingerprint”

Position
Uniformity
Quality

Quantity
Size
Area

Shape
Structure
Kinetics



Thermal analysis determination of heat changes

MACRO
SOURCE

Impact of heat

MESO

MICRO

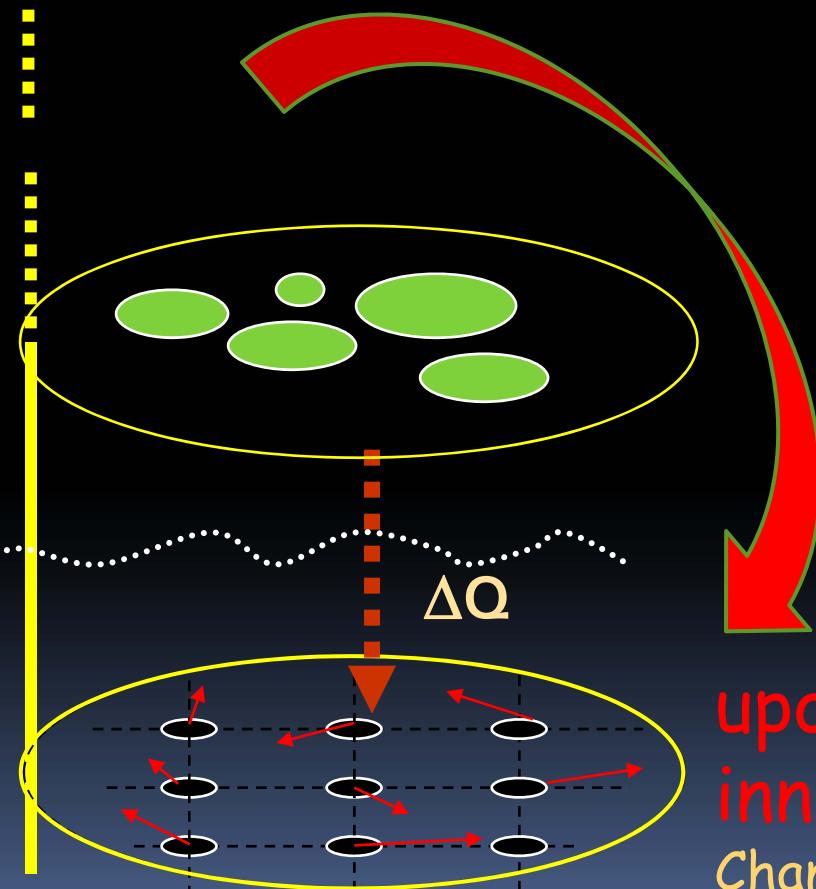
NANO

$$\Delta Q$$

and its sink

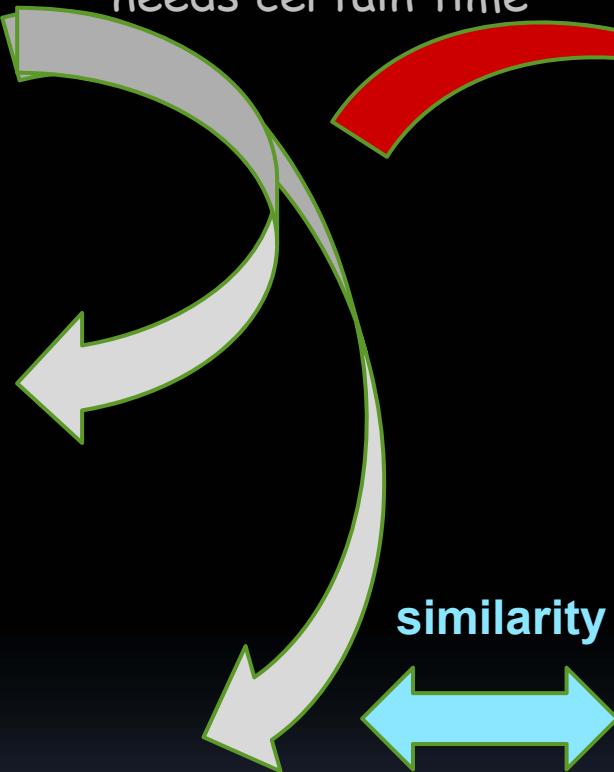
upon the sample
inner make up

Changes in vibrational
and positional structure



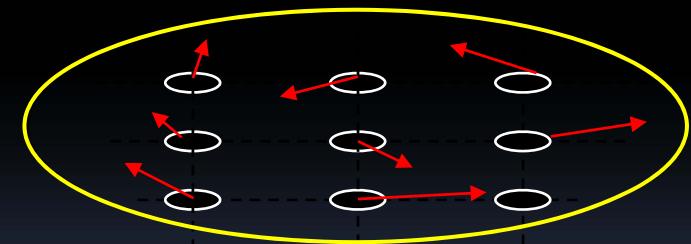


Pouring liquid and filling a bottle is not instantaneous but needs certain time



Fluid-like transfer

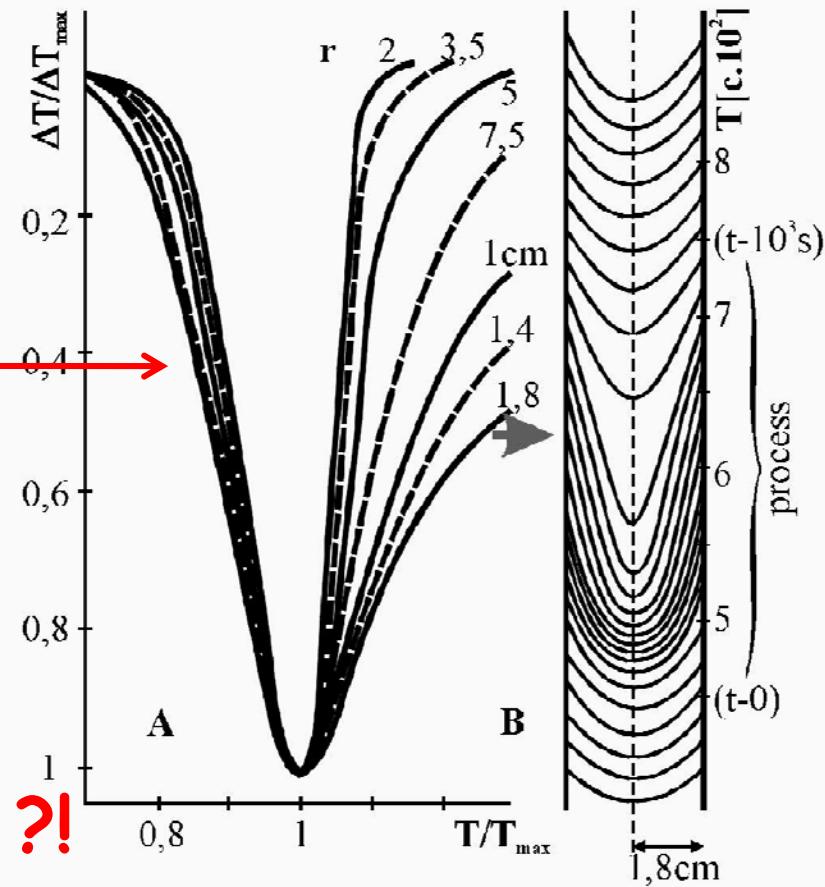
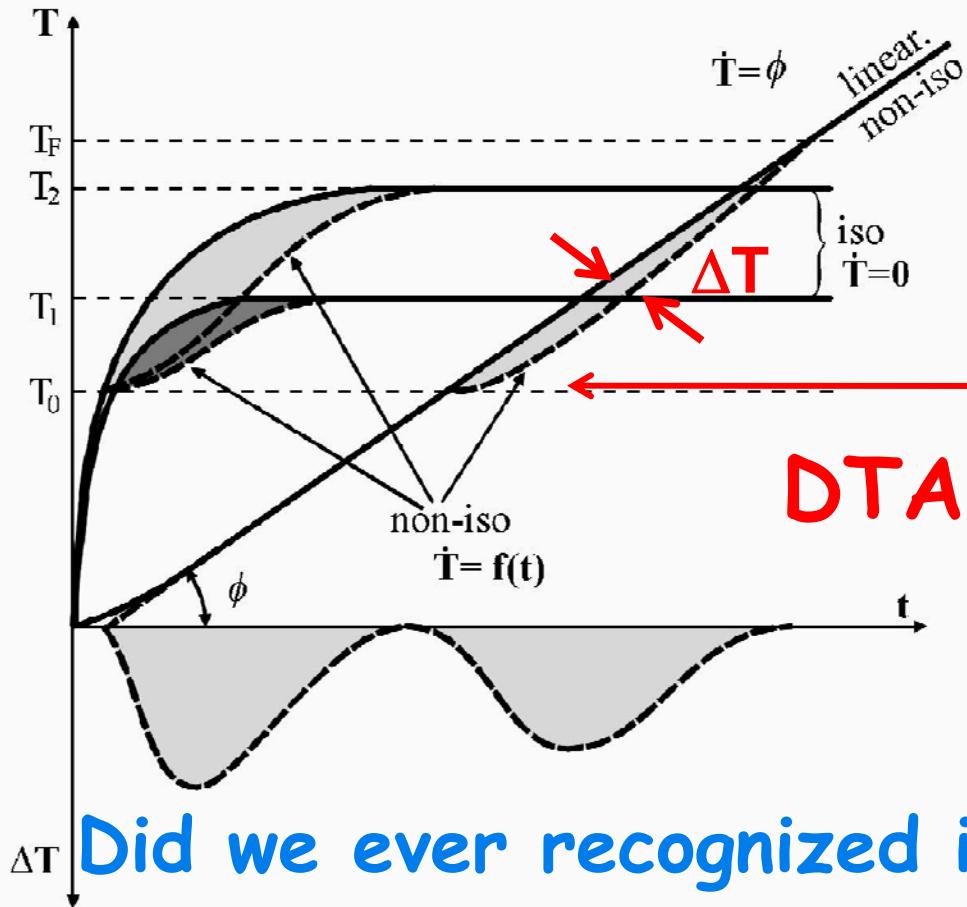
Inserting "heat" to the vibration and ordering modes is not immediate but needs explicit time



Any matter transport desires definite time lag

Heat sink within the sample thermal capacity

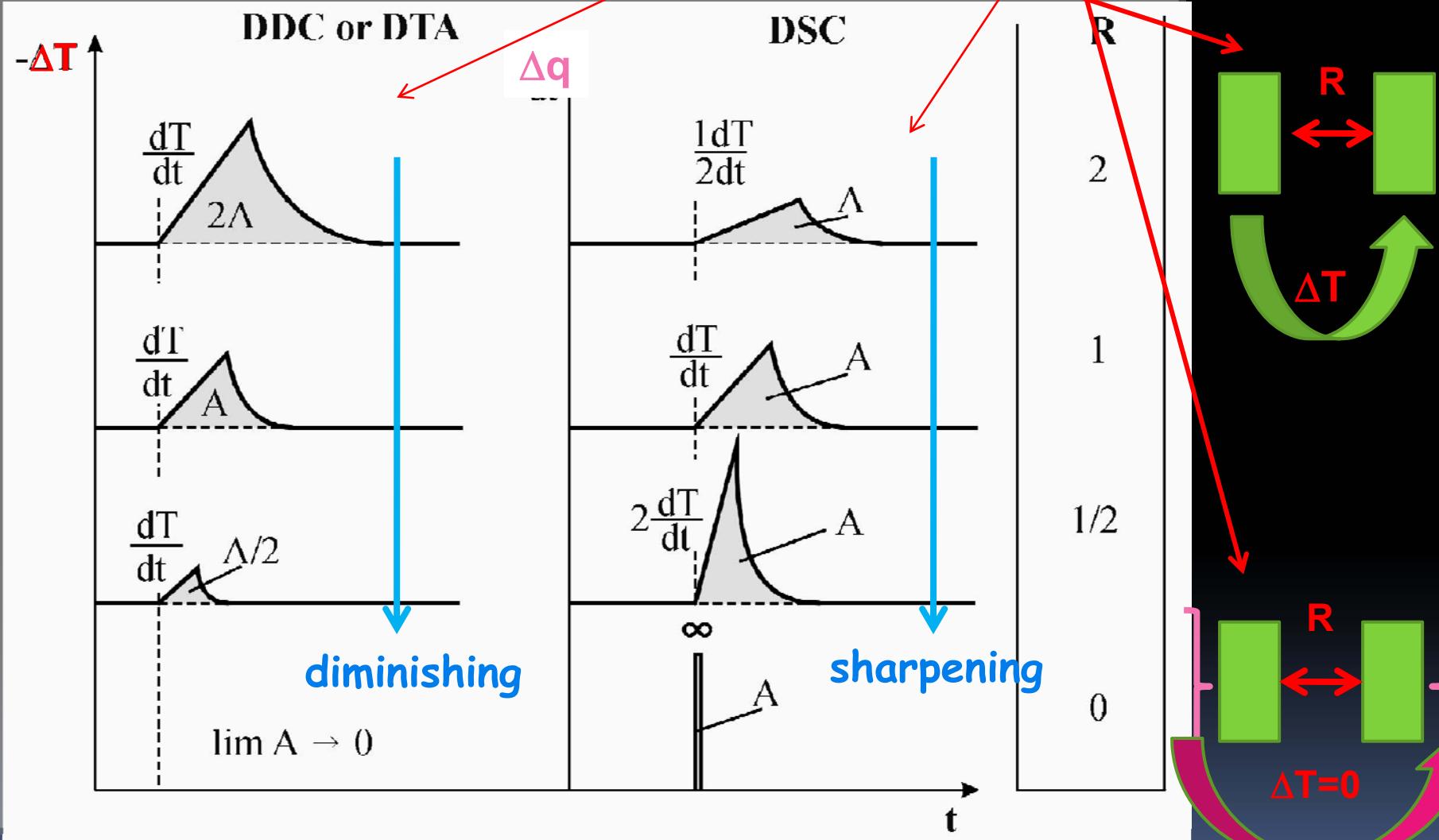
Isothermal and non-isothermal measurements: naturally involves thermal setups-gradients



Smyth HT. (1951) Temperature Distribution During Mineral Inversion and Its Significance in DTA. J.Amer.Cer.Soc 34:221-224.

Why are the curves/peak by DDC or DTA and DSC different ?

Mutual comparison of the sensitivity of measurements



Can we recognize its consequences ?!

CURVES

ANALOGY

Crystal order by
X-ray diffraction
screening

X-ray:
nondestructive
interaction

apparent



Thermal reordering
by thermal analysis

DTA: destructive
shift of ordered
species or modes

Acting through
crystal interface

What is the difference ?!

Nondestructive immediate response

Heat transfer destructive distortion

X-ray

Identity
“fingerprint”

Position
Symmetry
Quality

Quantity
Intensity
Area

Shape:
Broadening
Crystal size

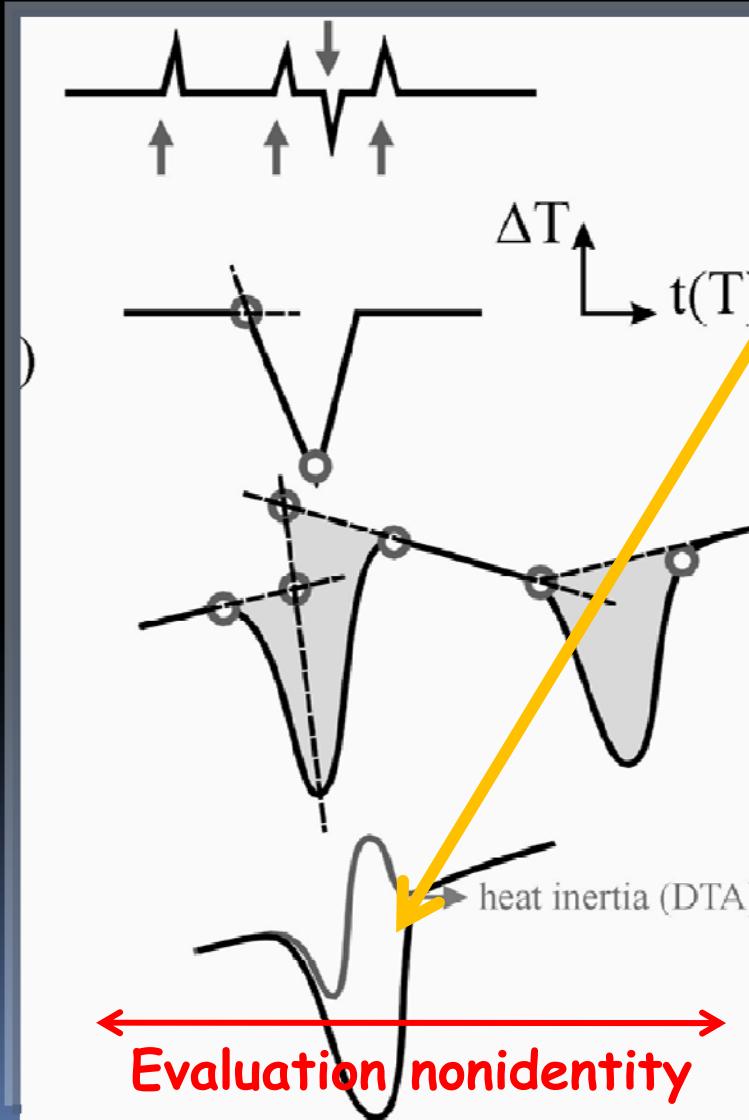
DTA

Identity
“fingerprint”

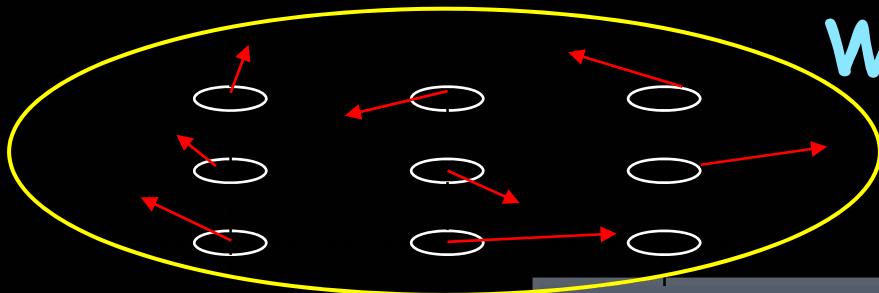
Position
Uniformity
Quality

Quantity
Size
Area

Shape:
Structure
Kinetics

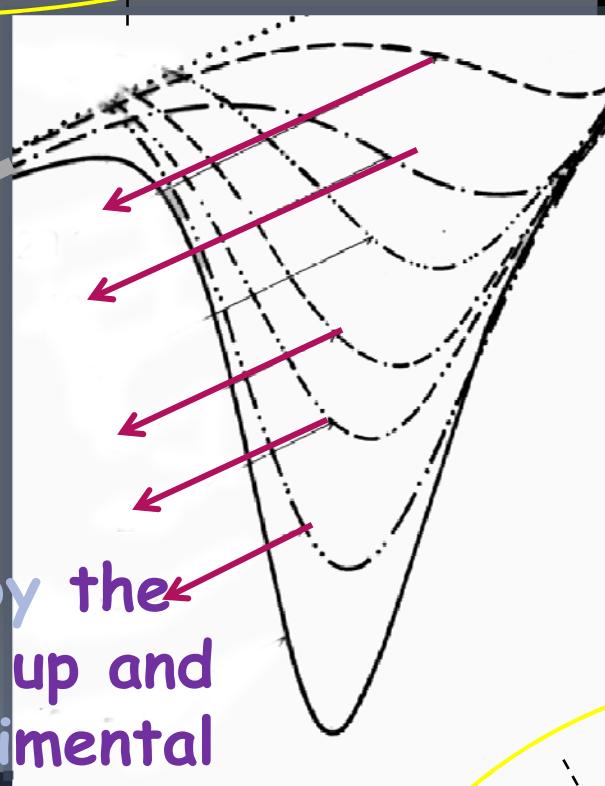


What reveals a DTA peak

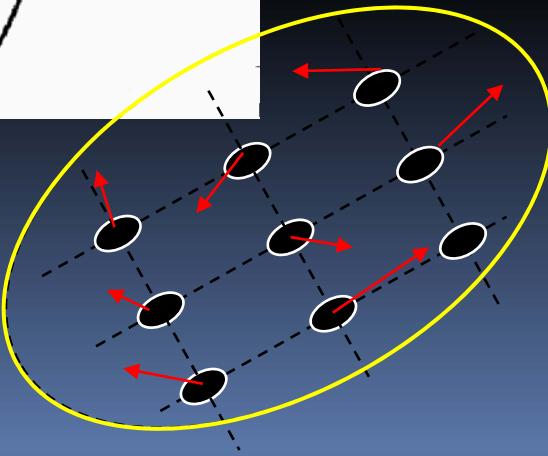


Base line - steady
thermal state of
structural makeup

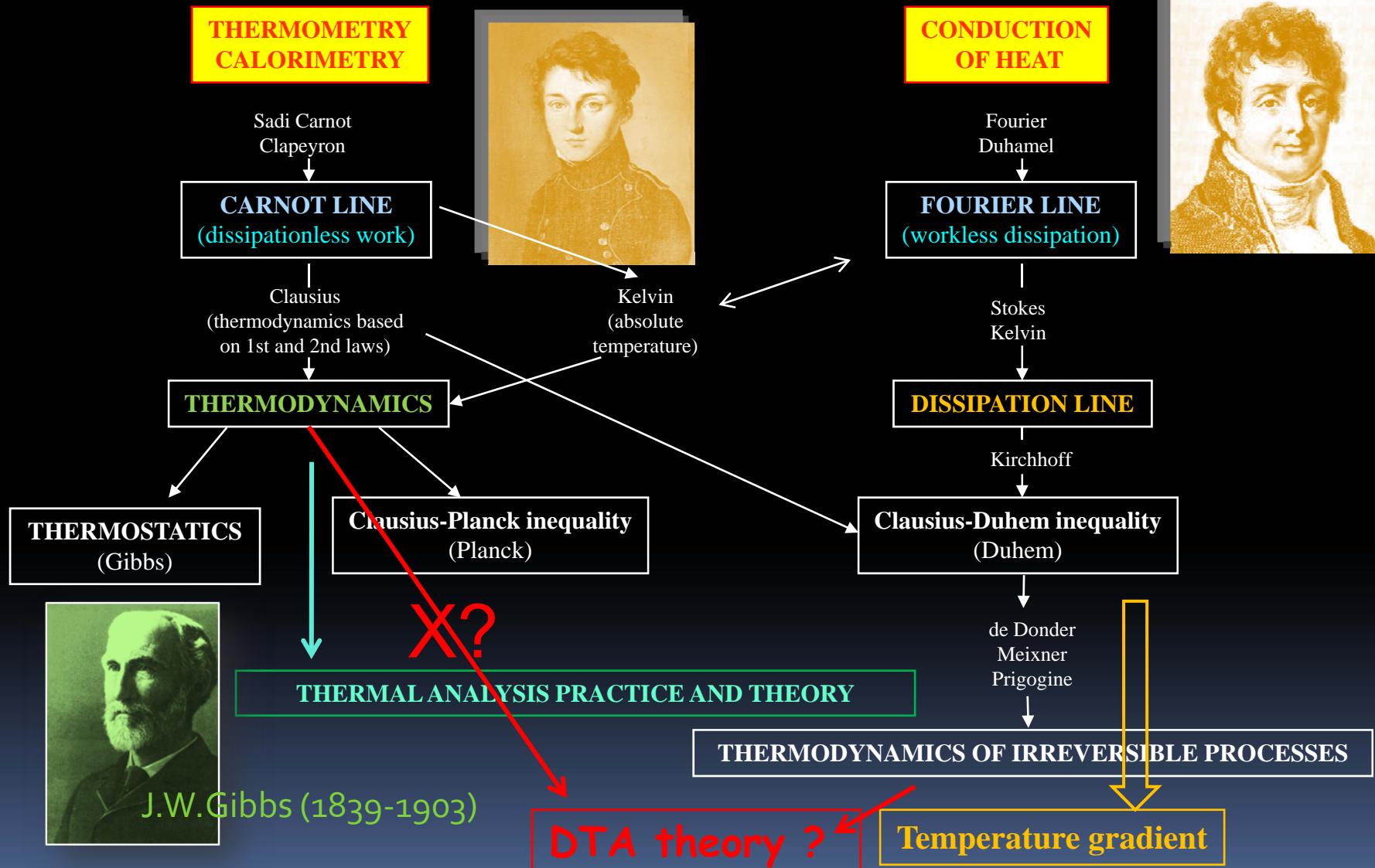
Affected by the
sample set up and
trial/experimental
arrangements



Peak, singularity:
due thermal state
response upon the
gradually integrated
structural changes



Thermodynamic approach through the detailed analysis of family tree of thermodynamic subdivisions:



Theoretical basis of thermal analysis

Thermal Methods of Analysis SECOND EDITION

1964

Wesley Wm Wendlandt

VOLUME 19 IN CHEMICAL ANALYSIS: A SERIES OF MONOGRAPHS ON ANALYTICAL CHEMISTRY AND ITS APPLICATIONS, EDITED BY P.J. ELVING AND I.M. KOLTHOFF

Edited by

G. SVEHLA, PH.D., D.Sc., F.R.S.C.
Reader in Analytical Chemistry
The Queen's University of Belfast

VOLUME XII

THERMAL ANALYSIS

PART D

THERMOPHYSICAL PROPERTIES OF SOLIDS

THEIR MEASUREMENTS AND THEORETICAL THERMAL ANALYSIS

by
JAROSLAV ŠESTÁK

Institute of Physics
of the Czechoslovak Academy of Sciences,
Prague



AMSTERDAM OXFORD NEW YORK TOKYO

1984

Šesták J., Šimon P.: *Thermal Analysis of Micro- nano- and non-crystalline Materials: transformation, kinetics and thermodynamics*; Springer, Berlin 2012

Thermal Analysis

Bernhard Wunderlich

1974

*The University of Tennessee at Knoxville, Knoxville, Tennessee
and
Oak Ridge National Laboratory, Oak Ridge, Tennessee*



ACADEMIC PRESS, INC.

BY BRUCE JOVANOVICH, JR.
IN SAN DIEGO



Jaroslav Šesták

Heat, Thermal Analysis and Society



KLAUS HEIDE

Dynamische thermische Analysenmethoden

1979

Generalised Approach to Thermal Analysis

Science of Heat and Thermophysical Study

by
Jaroslav Šesták



Institute of Physics of the Academy of Sciences of Czech Republic, Division of Solid-State Physics, Čukrovarnická 10, CZ - 162 53 Praha 6



University of Western Bohemia, Faculty of Applied Sciences, Univerzitní 8, CZ - 306 14 Pilsen, both Czech Republic

2005



Historical approaches toward theoretical basis of DTA

F. H. Norton. (1939) Critical study of the differential thermal methos for the identification of the clay minerals. J. Amer. Cer. Soc. 22. 54

Vold MJ. (1949) Differential Thermal Analysis. Anal. Chem. 21: 683-8

Speil S, Berkenhamer LH, Pask JA, Davies B. (1945) DTA, theory and its application to clays and other aluminous minerals. US. Bur. Mines, Tech. Paper. p. 664-745..

Sykes C. (1935) „Methods for Investigating Thermal Changes Occurring during Trans-formations in Solids”, Proc. Roy. Soc. (London) 148A:422-9.

Pask JA, Warner MF. (1954) Differential thermal analysis methods and techniques, Bull. Am. Ceram. Soc. 33: 168-175.

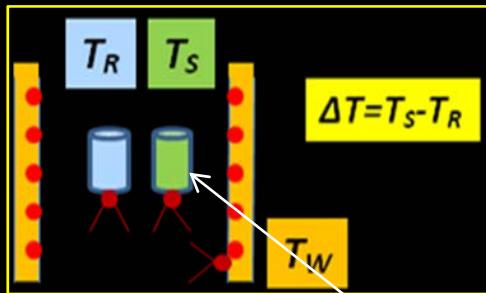
Boersma S.L. (1955) A theory of DTA and new methods of measurement and interpretation. J. Amer. Cer. Soc. 38: 281-284.

Borchadt HJ. (1956) Differential thermal analysis. J. Chem. Education 33: 103-109; and Borchard H.J., Daniels F.(1957): The application of DTA to the study of reaction kinetics. J. Amer. Chem. Soc. 79: 41-46.

Gray AP.: Simple Generalized Theory for Analysis of Dynamic Thermal Measurements. In: Porter R.S., Johnson J.F. (editors) Analytical Calorimetry, Vol. 1, p. 209. Plenum Press, New York 1968;. and: In: Proc. 4th ICTA, "Thermal Analysis", Akademiai Kiado, Budapest 1974

So far including theory of thermal inertia effects

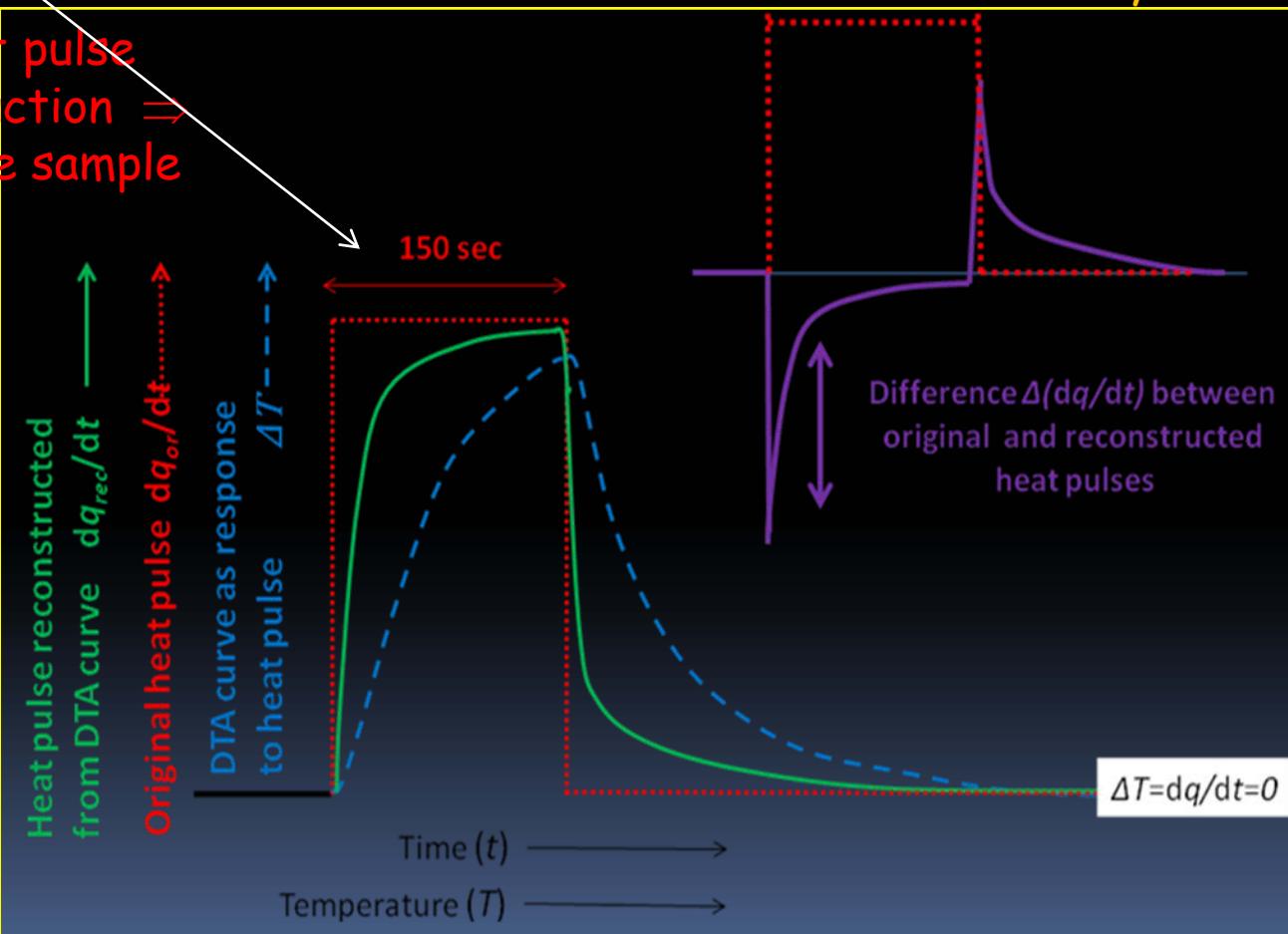
- Holba P, Šesták J., Bárta R. (1976) Teorie a praxe DTA/DSC. (Theory and practice of DTA/DSC). Silikáty (Prague) 20:, 83-95 (in Czech); and Šesták, J., Holba, P., Lombardi, G. (1977) Quantitative evaluation of thermal effects: theory and practice. Annali di Chimica (Roma) 67: 73-87.
- Nevřiva M, Holba P, Šesták J. (1976) Utilization of DTA for the determination of transformation heats. Silikaty (Prague) 29: 33-9 (in Czech); and On correct calorimetric measurements by means of DTA..In proceedings of 4th ICTA in Budapest, "Thermal Analysis", Akademia Kiado, Budapest 1974, pp. 981-990.
- Holba P, Nevřiva M., Šesták J. (1978) Analysis of DTA curve and related calculation of kinetic data using computer technique. Thermochim. Acta 23: 223-231.; and Thermal inertia accounte in DTA evaluation, Proceedings of. 2nd ESAC, "Thermal analysis" (D. Dollimore ed), Mc Millan, Salford 1976, pp. 33-37.
- Svoboda H, Šesták J. A new approach to DTA calibration by predetermined amount of Joule heat. In the proceedings of 4th ICTA, Thermal Analysis, Akademia Kiado, Budapest 1974, pp.726-731;
- Holba P., Šesták J. Sedmidubsky D. Heat transfer and phase transition at DTA experiments. Chapter 4 in the book: Thermal analysis of micro-, nano- and non-crystalline materials. (J. Šesták, P. Šimon. eds), Springer, Berlin 2012



- ↔ Macroscopic sample arrangement
- ↔ Response of a measuring device
- ↓ Analysis of the responded curves (peaks)
- ↓ Application of theoretical basis for

Heat transfer + Thermodynamics

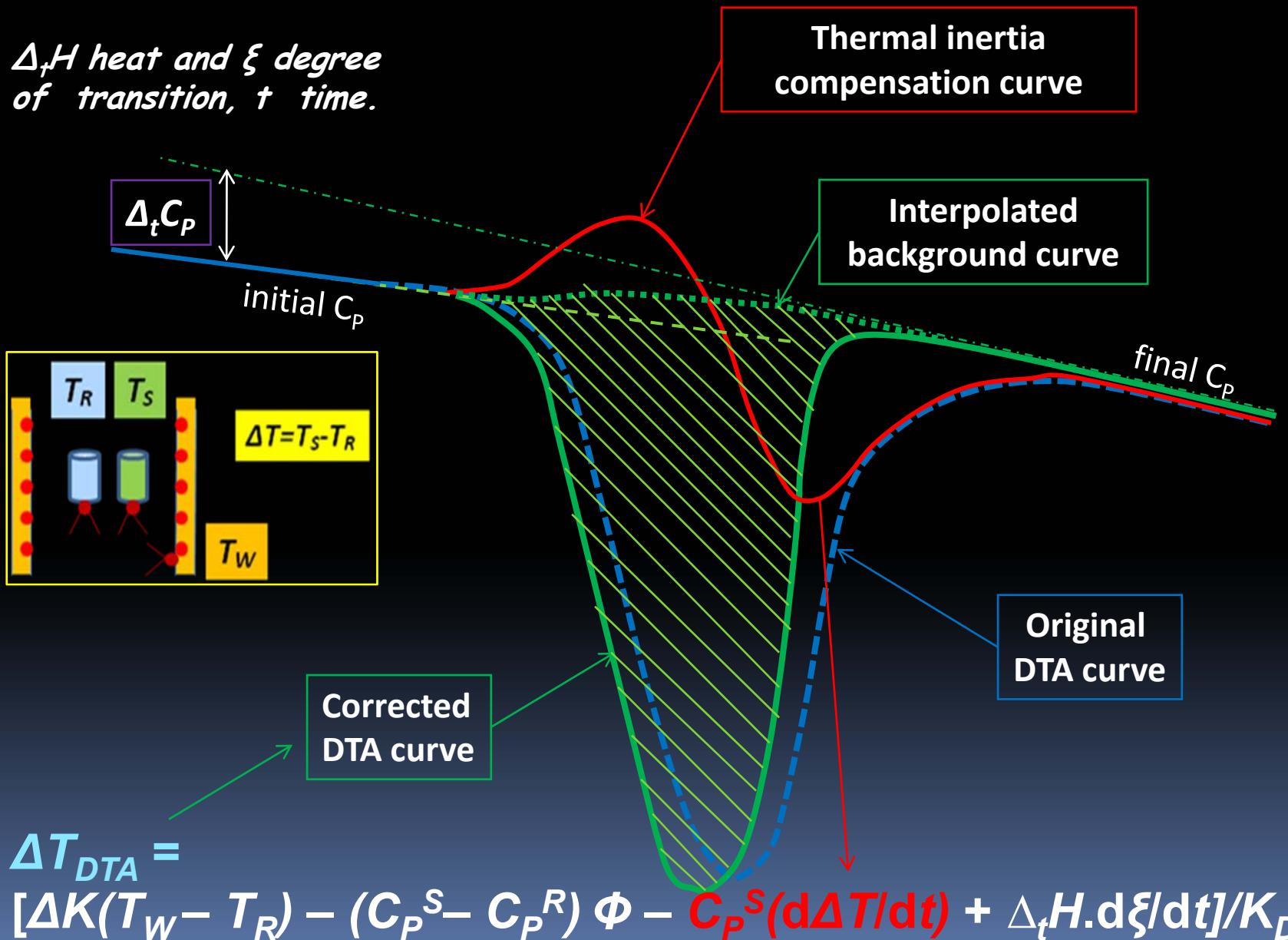
↑ Heat pulse introduction ⇒ into the sample



Surprising response: can we recognize its true meaning ?!

Original and corrected (rectified) DTA curve

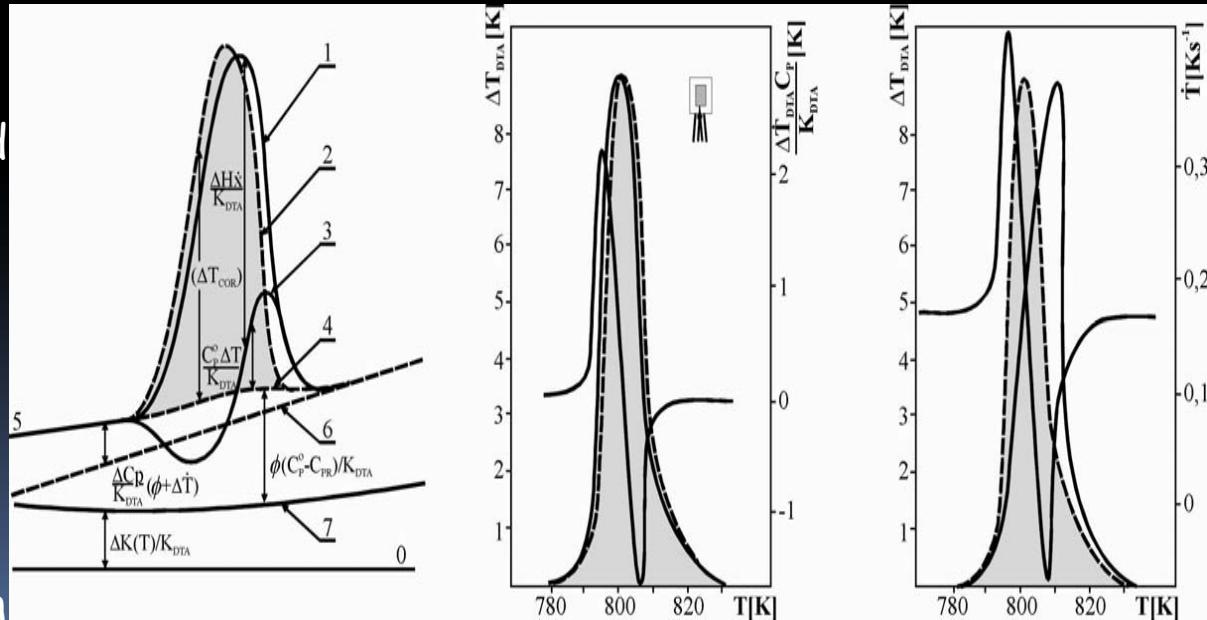
$\Delta_t H$ heat and ξ degree of transition, t time.



$$\begin{aligned}
& \Delta T K_{DTA} = \\
& + \Delta H_S \xi' \\
& - (Cp_{oS} - Cp_R) \phi \\
& - \Delta Cp_S (\phi + \Delta T/dt) \\
& - Cp_{oS} \Delta T/dt \\
& + \Delta K(T)
\end{aligned}$$

measured quantity
enthalpy evolved
heat capacity change
inertia
transient
experimental constant

- 1 - as-received DTA
- 2 - corrected DTA peak
- 3 - real (s-shaped) background
- 4 - approximated DTA peak baseline
- 5 - recorded i.e. actual DTA trace
- 6 - baseline shift due to the unequal heat capacities
- 7 - difference in the heat transfer coefficients between the sample and reference



Previous: M.J. Vold (125 citations) provided her equation 8 in above reference as

$$(\Delta H/C_S)(da/dt) = - (d\Delta T/dt) - A(\Delta T - \Delta_0 T)$$

where $\Delta_0 T$ means a level of signal background, C_S is heat capacity of sample and $A \approx K/C_S$. The equation (which is nearly equivalent to our equation) was obtained via a complicated derivation which is starting with a typing error " $dH/dt = (dH/dt)(dT/dt)$ " what could be a reason why the equation was not very credible for a majority of thermoanalysts. The results of Vold was detailed by I. Proks [42] who combined them with results of others authors to derive the dependences of peak area and of position and height of extreme deviation (on the DTA curve) upon heating rate.

In 1957 the mentioned inertia term was used by H.J. Borchard and F. Daniels (824 citations) who applied DTA to study kinetics of homogeneous reactions in well stirred liquid samples showing:

$$dH = C_p d\Delta T + K \Delta T dt$$

from which our equation can be obtained by substituting $dH = \Delta H da$ and then dividing their equation by dt . The correction with respect to heat inertia is included also in their equation expressing the rate constant k of homogeneous reaction

$$k = (C_p(d\Delta T/dt) + K\Delta T)/(K(A-a) - C_p\Delta T)$$

(where A is total area of peak and a is a part of this area for time

Effect of heat inertia on kinetic evaluations



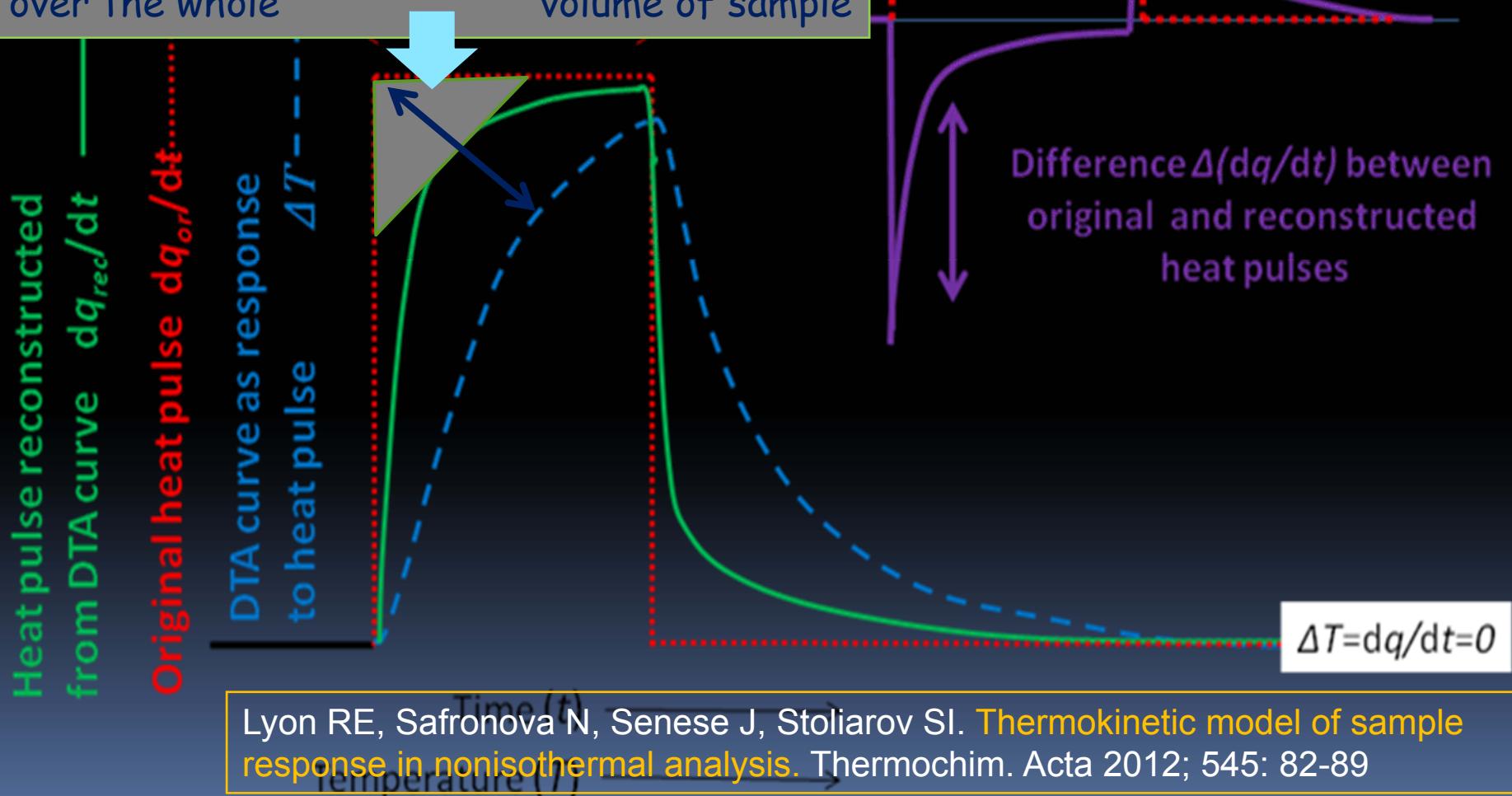
Evaluation of kinetics and mechanism by SQUEST
Škvára F, Šesták J. Computer calculation of the mechanism and associated kinetic data using a non-isothermal integral method. J. Thermal Anal. Calor. 1975; 8: 477-489

Phase transition of BaCO_3 at 810° C

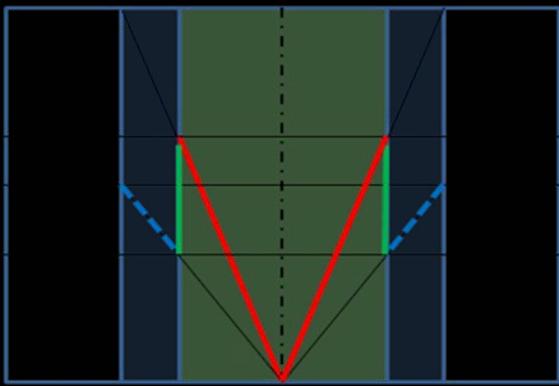
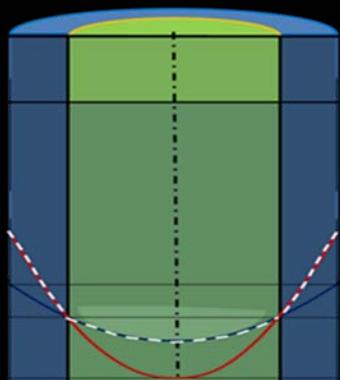
ΔH	E [cal]	mechanism
613	118	A3
617	52	A3

Inertia rectifying evaluation program by ALANTA :
Holba P, Nevřiva M., Šesták J. Analysis of DTA curve and related calculation of kinetic data using computer technique. Thermochim. Acta 1978; 23: 223-231.

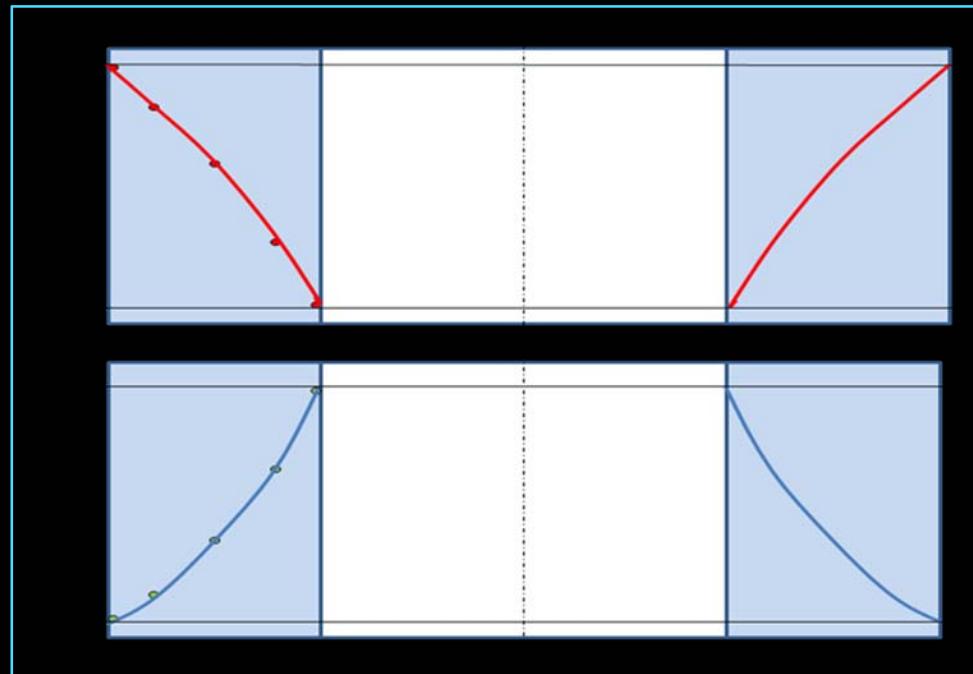
Gradient rectification by introducing an additional correction term respecting the changes in temperature field inside the sample $d\theta_{SM}/dt$, where θ_{SM} is the difference between the surface-measured temperature and the temperature averaged over the whole volume of sample



Practical approval and T-gradients



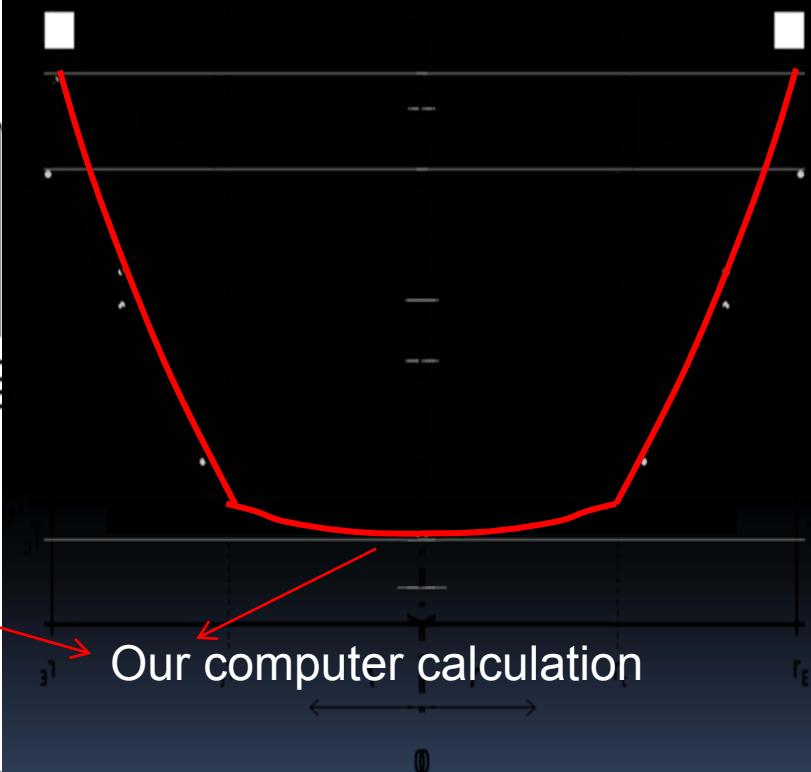
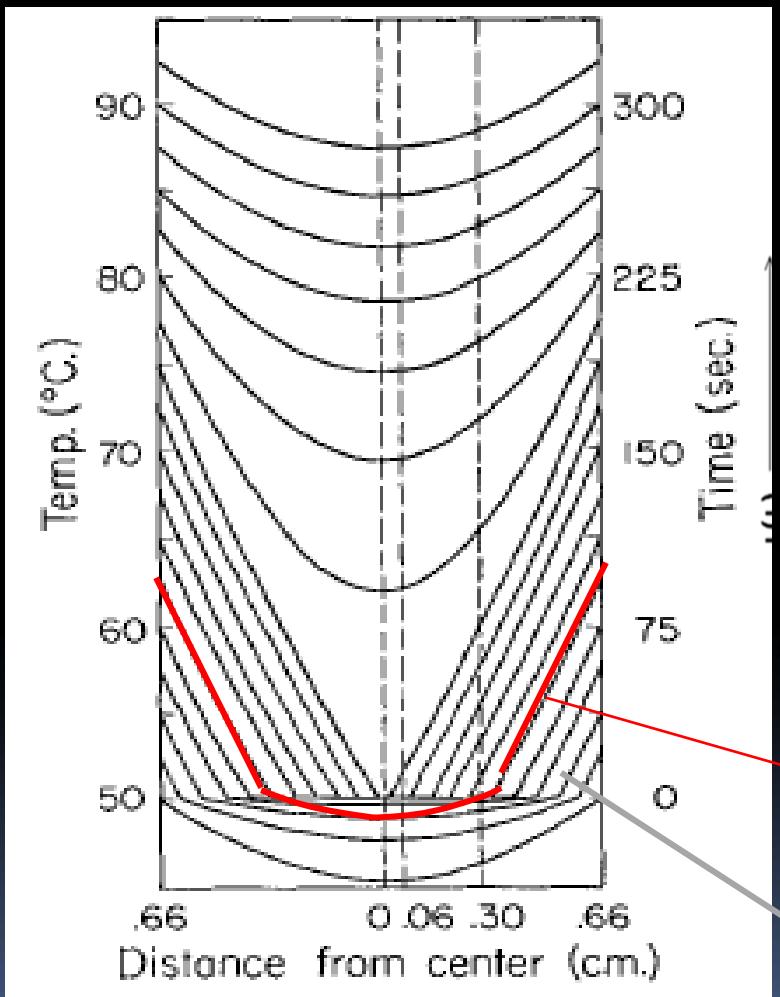
Temperature profiles



Stabilized temperature profiles $T_R(r)$, $T_H(r)$ and gradient profiles $g_R(r)$, $g_H(r)$ at linear heating ($\Phi_{RE} > 0$) in an infinite cylinder with external radius of holder (jacket) r_H and external radius of reference (core) r_E in the case when the thermal diffusivity of holder material α_H is greater than that of the reference material α_R ($\alpha_H > \alpha_R$).

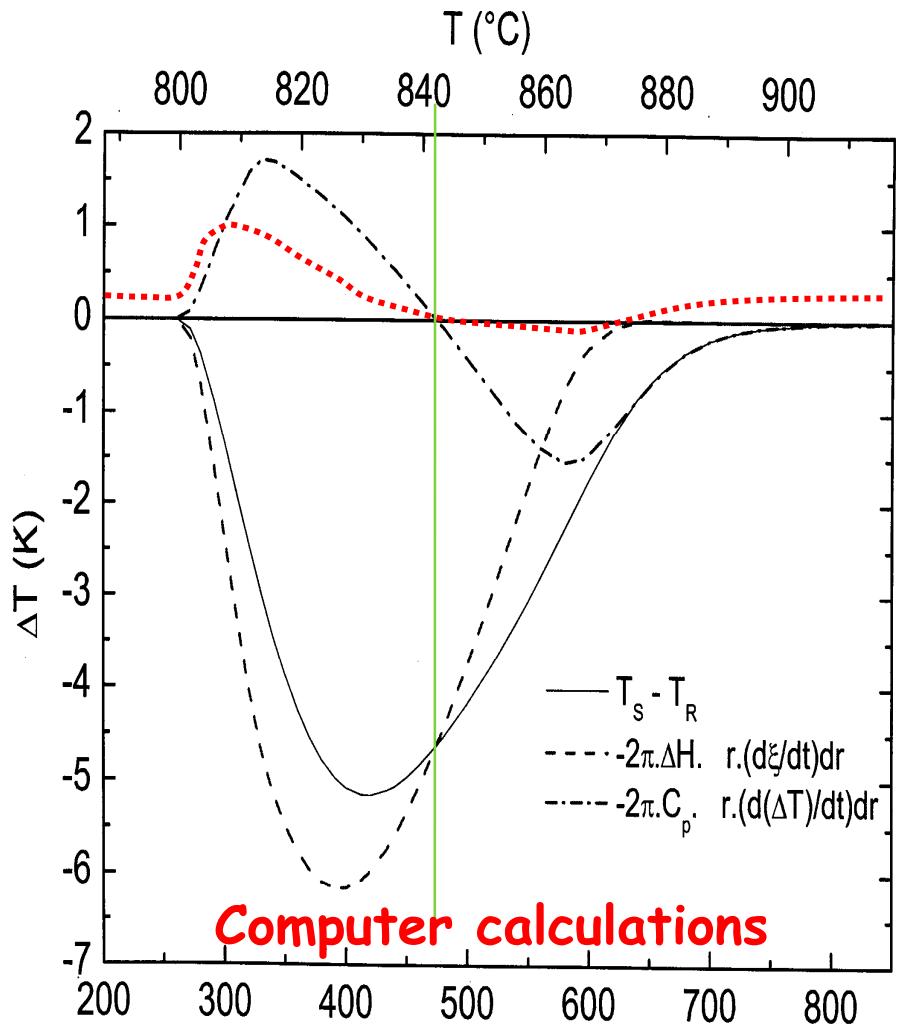
Stationary temperature profile $T_R(r)$ and gradient profile $g_R(r)$ in hollow cylinder with outer radius r_E and inner radius r_I separating outer reservoir with temperature T_E and inner reservoir with temperature T_I

Temperature profile according to Smyth compared with our continual model utilized by computer calculus

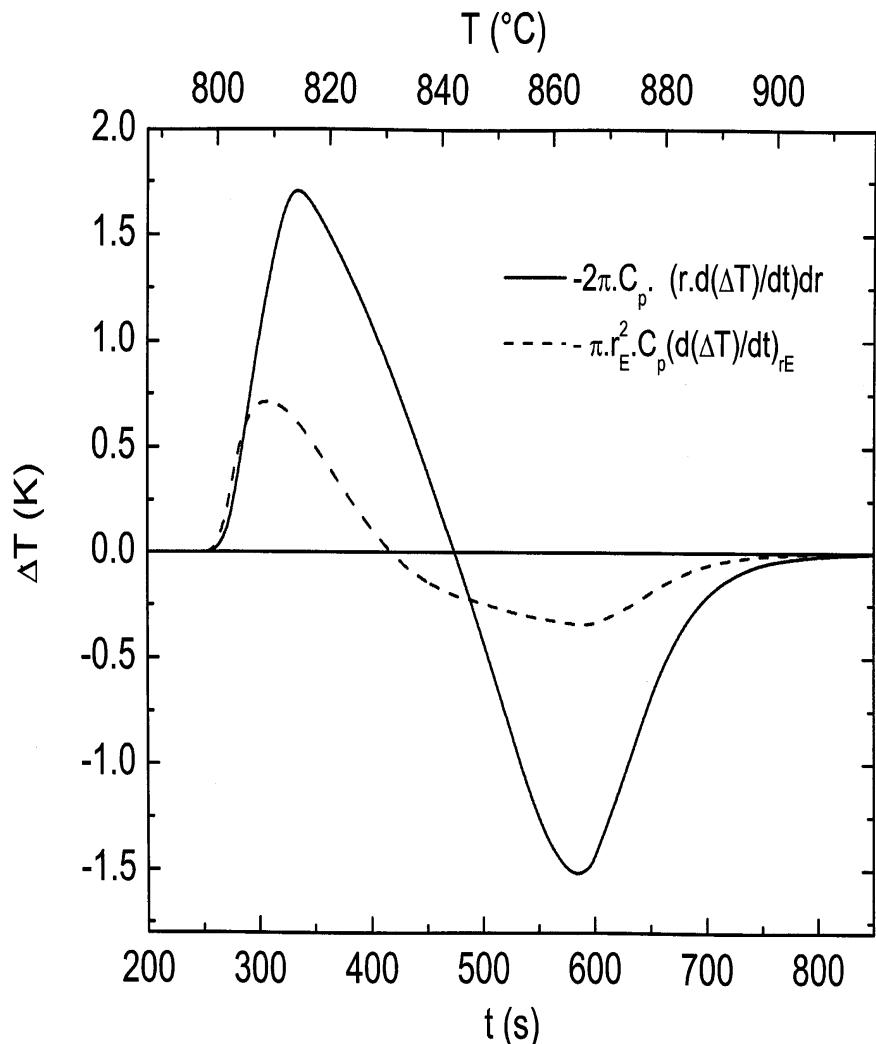


Smyth HT. Temperature Distribution during Mineral Inversion and Its Significance in DTA. J. Amer. Cer. Soc. 1951; 34: 221-224.

Real form of a DTA peak at the cylindrical location when integrating inherent temperature gradients



Computer calculations



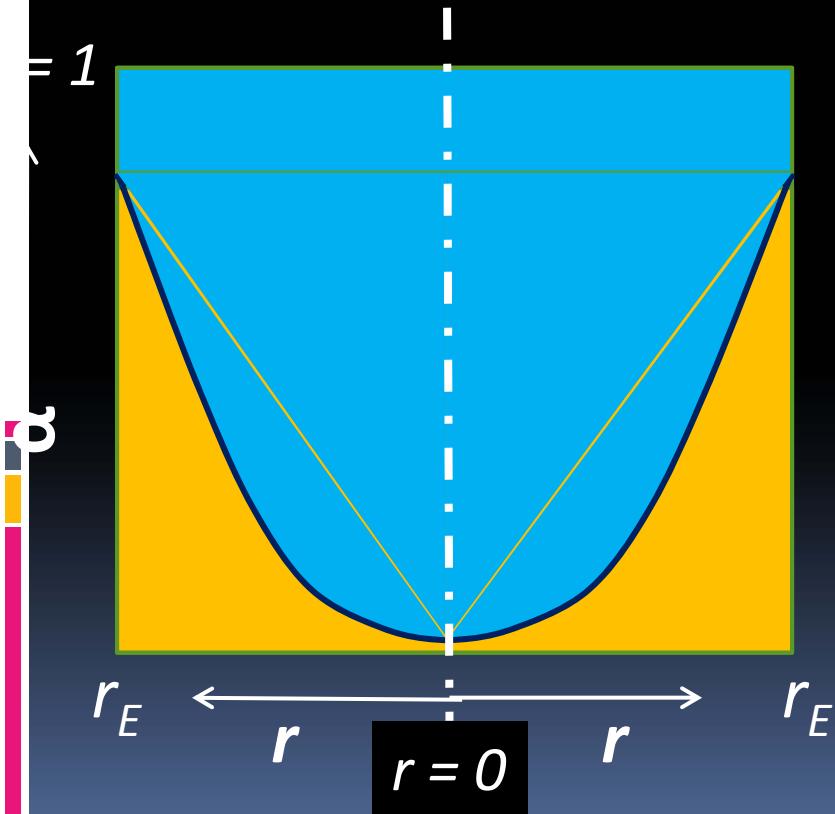
$$\Delta T_s = T_{S\bar{E}} - T_{SE} \text{ due to average gradients, } T_{S\bar{E}} = (2/r_E^2) \int_0^{r_E} T(r) r dr$$

Kinetic models of a phase transition

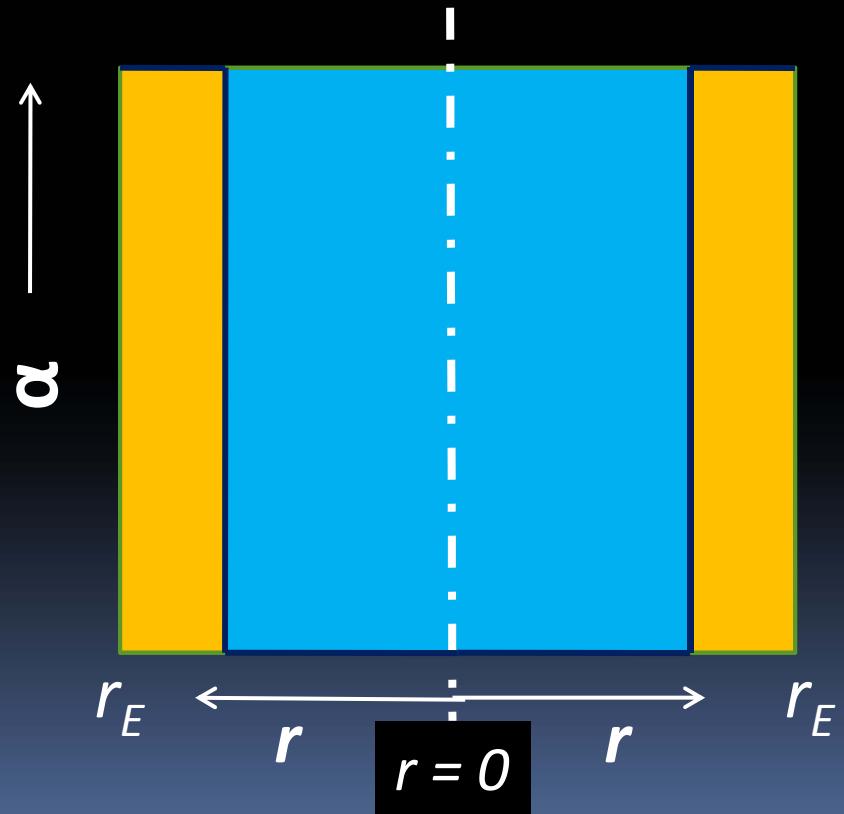
(initial)

(final)

Continual model:



Discontinual model:



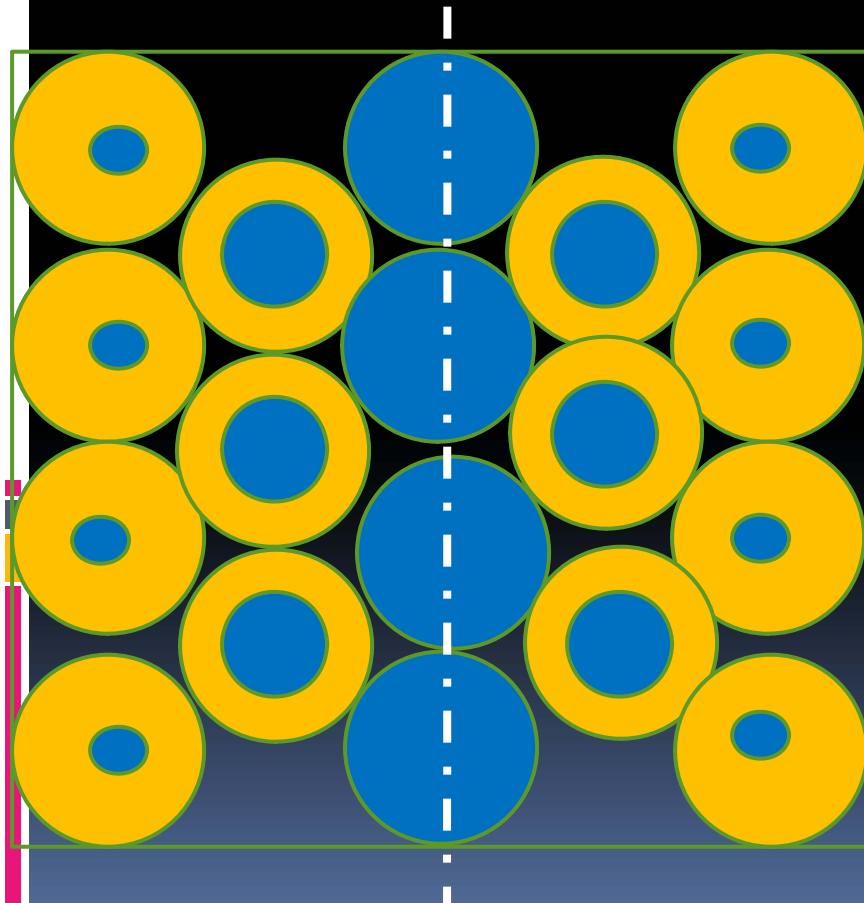
Variants of kinetic models of a phase transition

(initial)

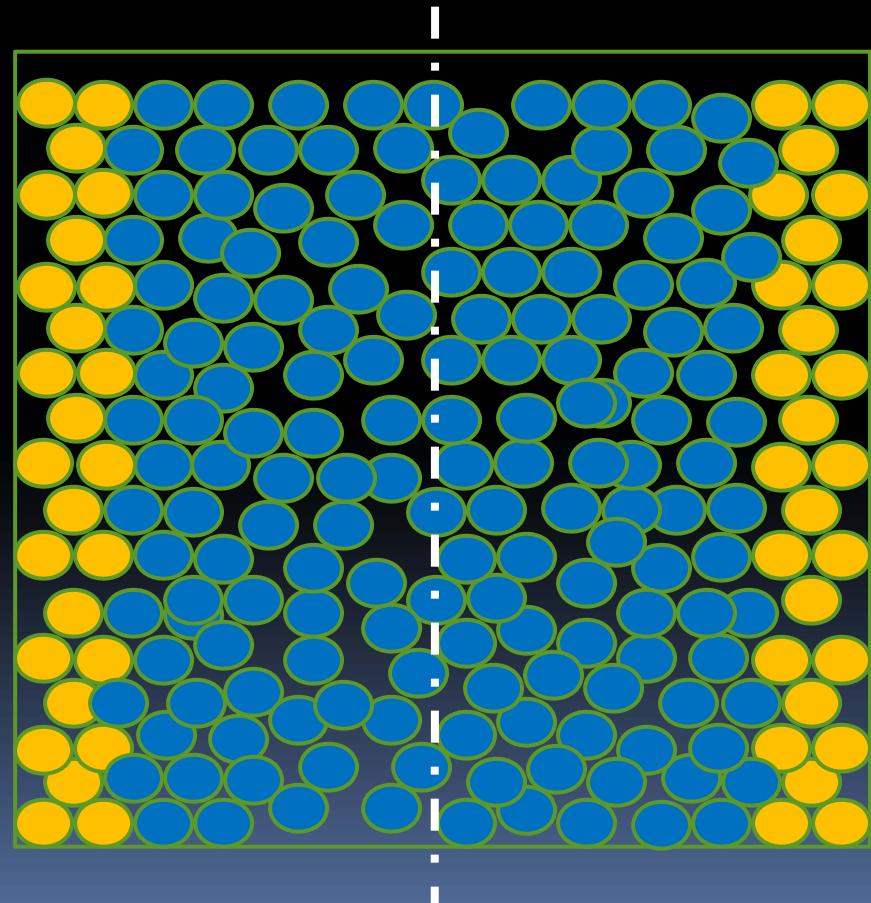
&

(final)

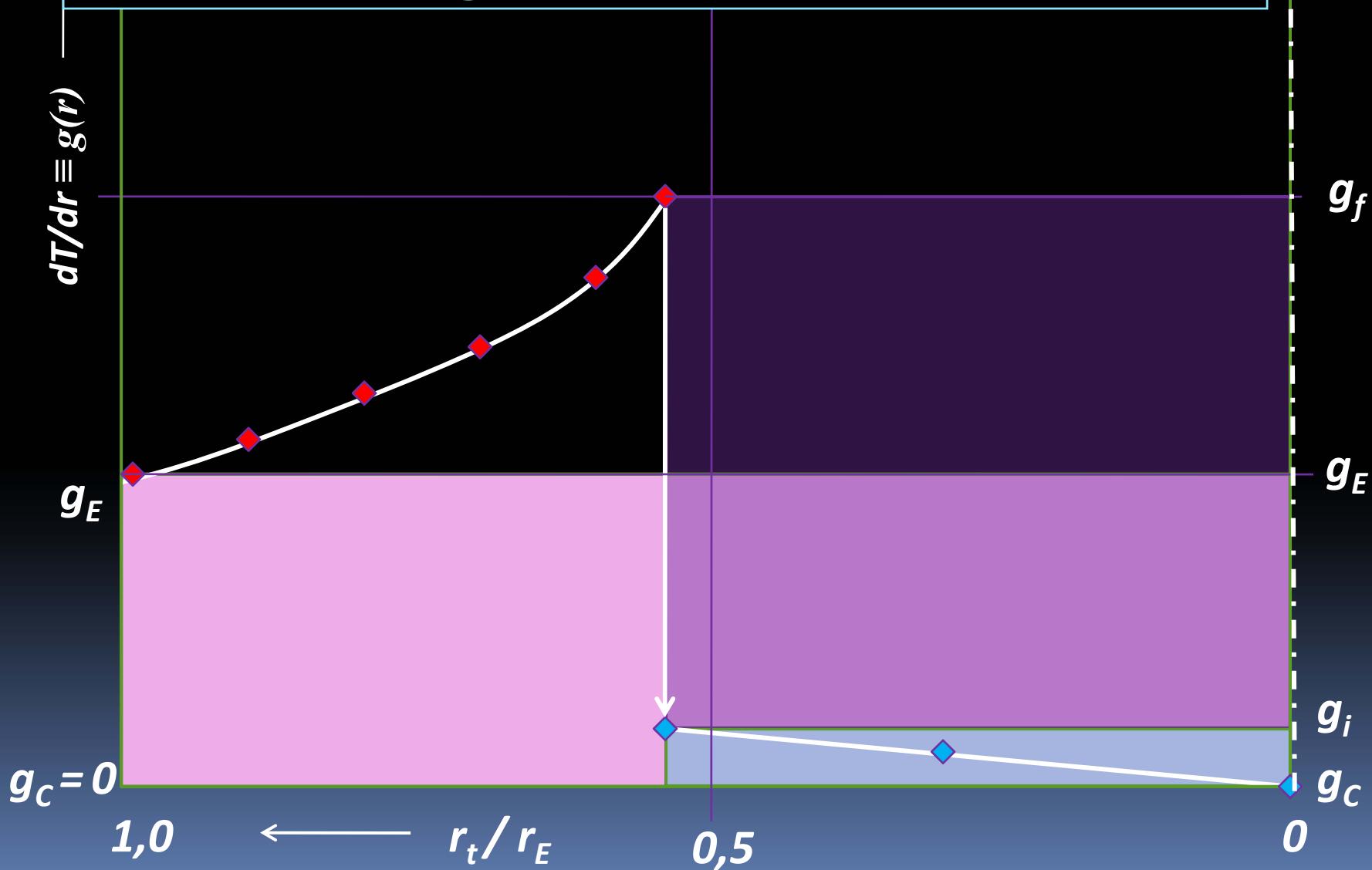
continual model:



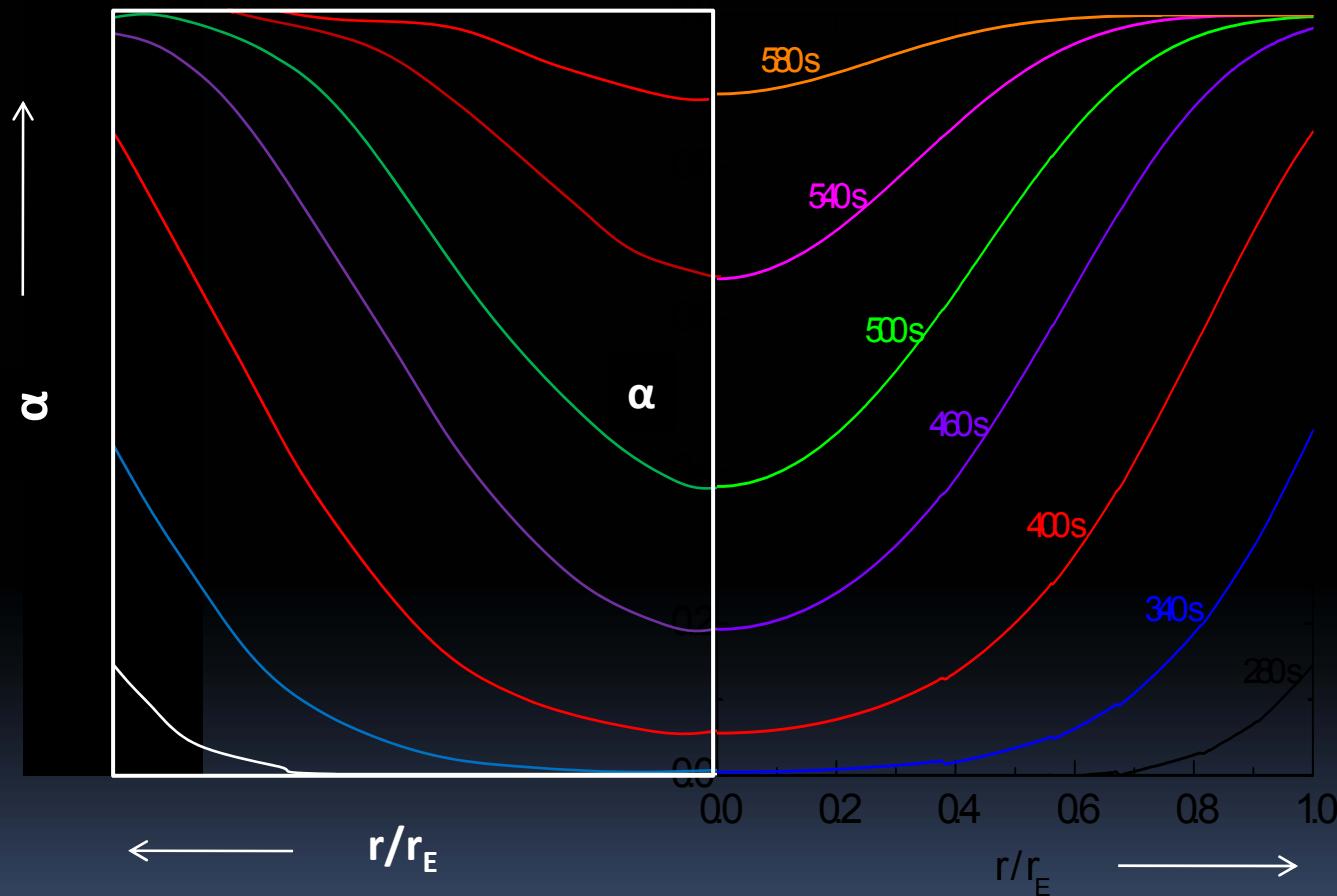
Discontinual model:



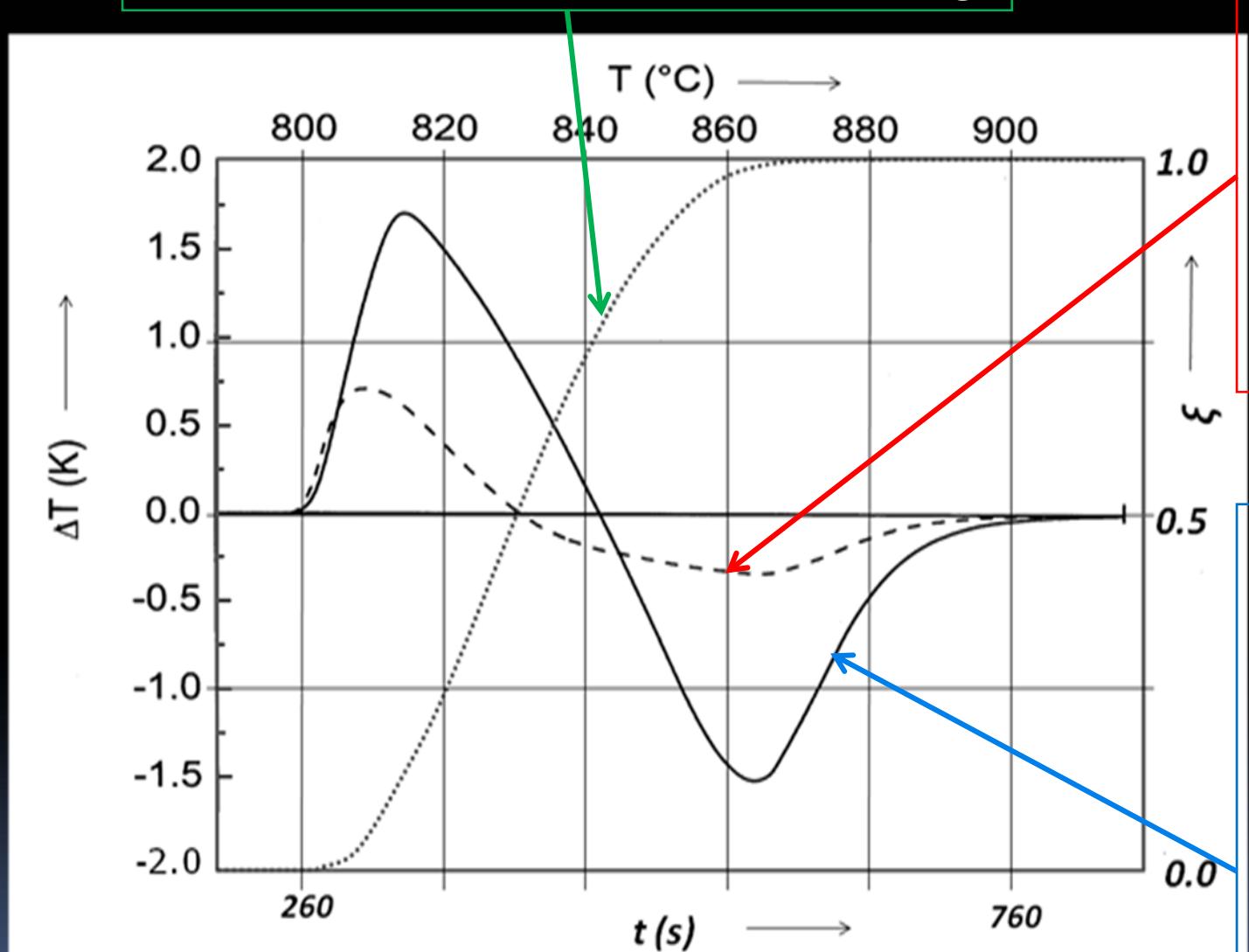
Profile of temperature gradient in the sample at the degree of transition $\xi = 0.7$ assuming a discontinued model



Continual model of a phase transition - computer calculated



Total (global) degree of transition: α_G

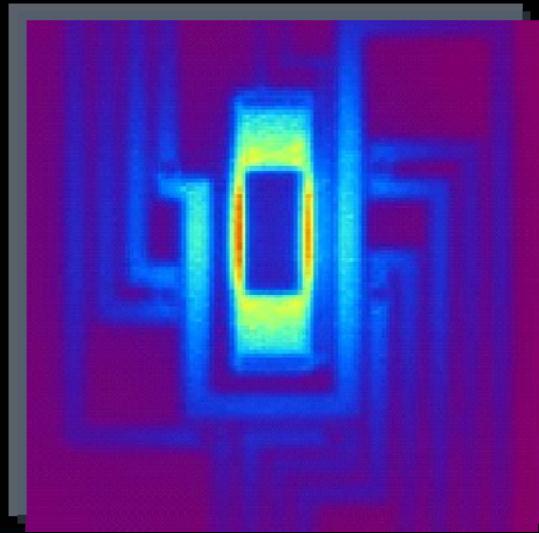
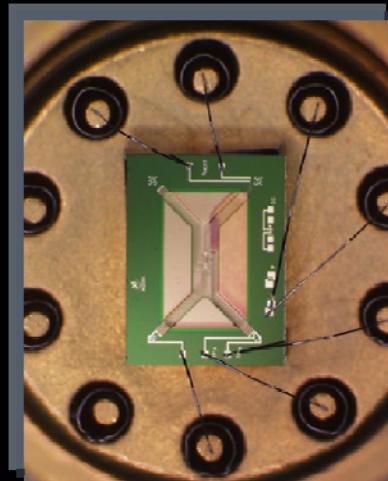
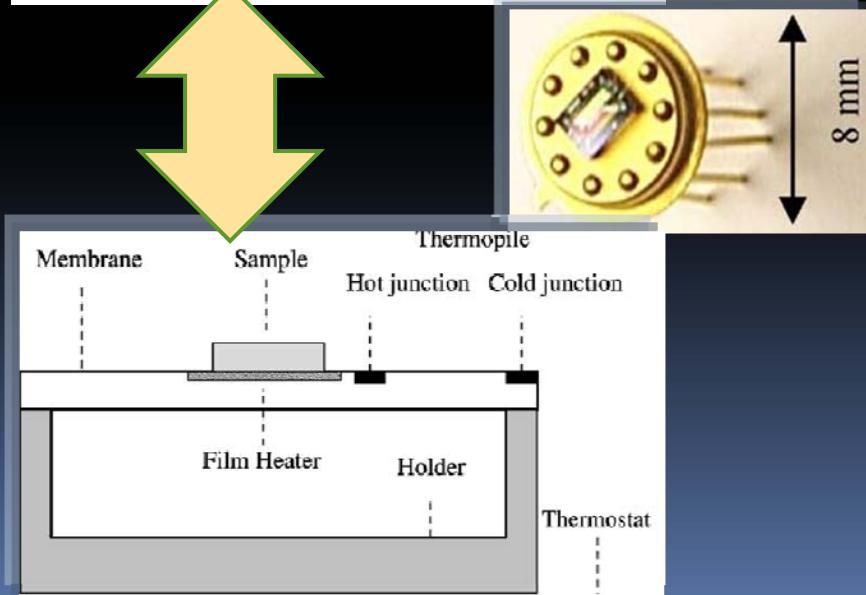
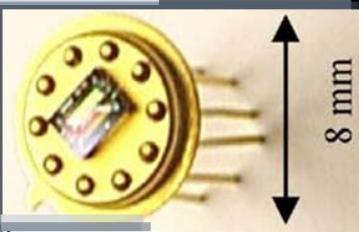
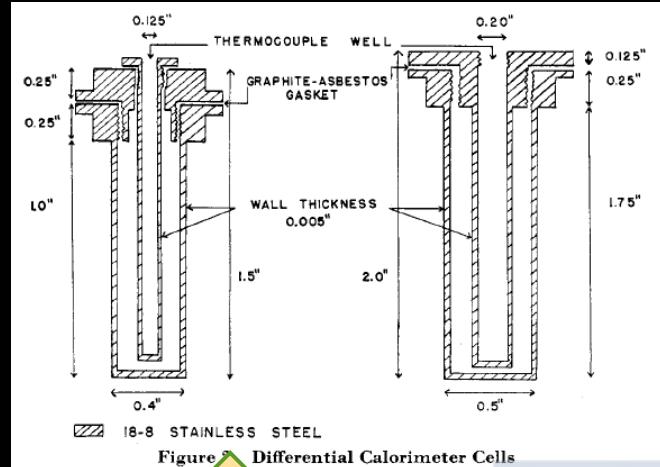


Thermal inertia from temperature changes T_{SE} on the sample surface

Thermal inertia from temperature changes $T_{S\phi}$ derived by integration over the thermal field inside the sample

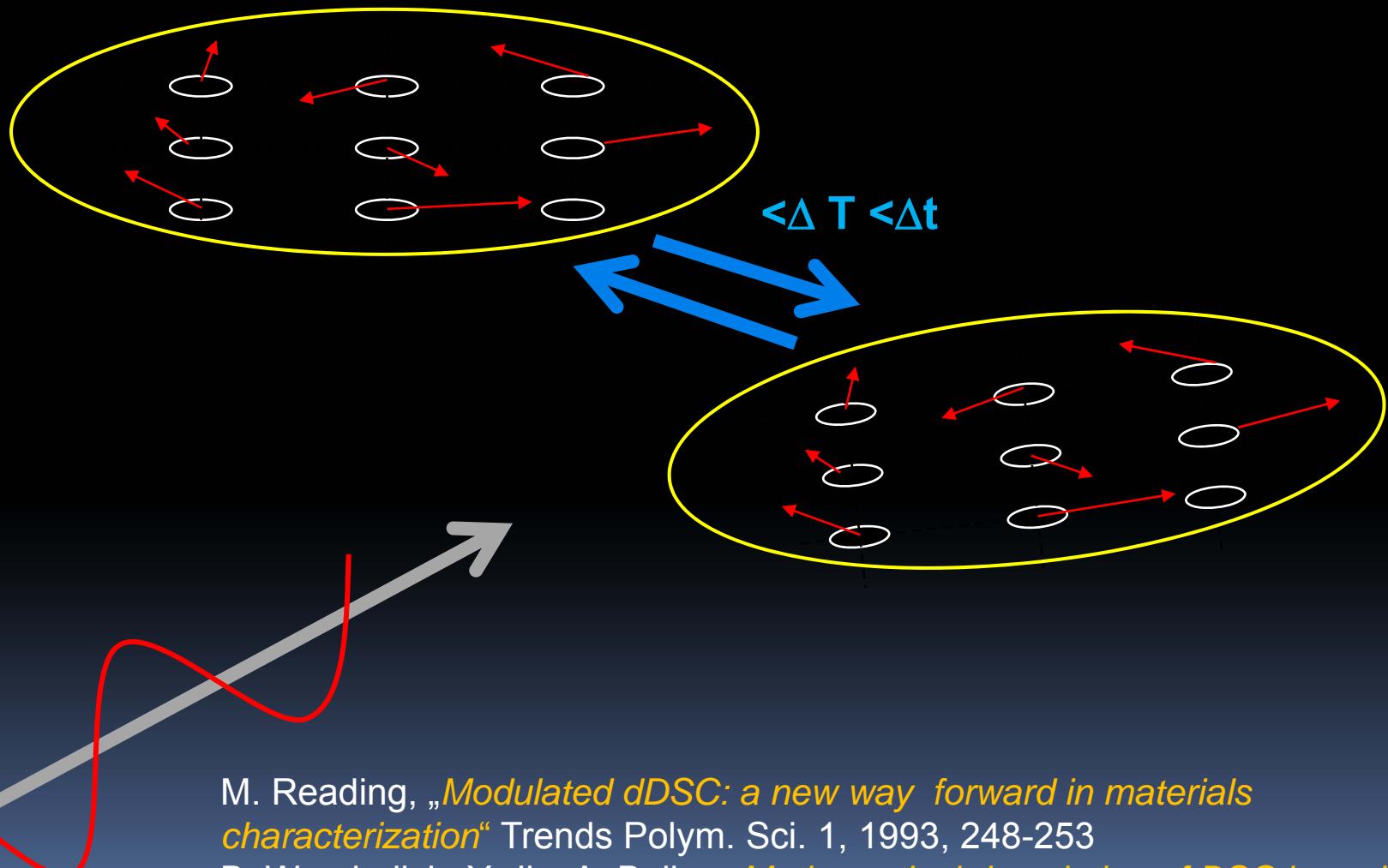
Approaching the reality - who cares ?

Not knowing well the thermal nature in a classically arranged sample we are seeking for yet novel methods applying more and more complex thermal regimes



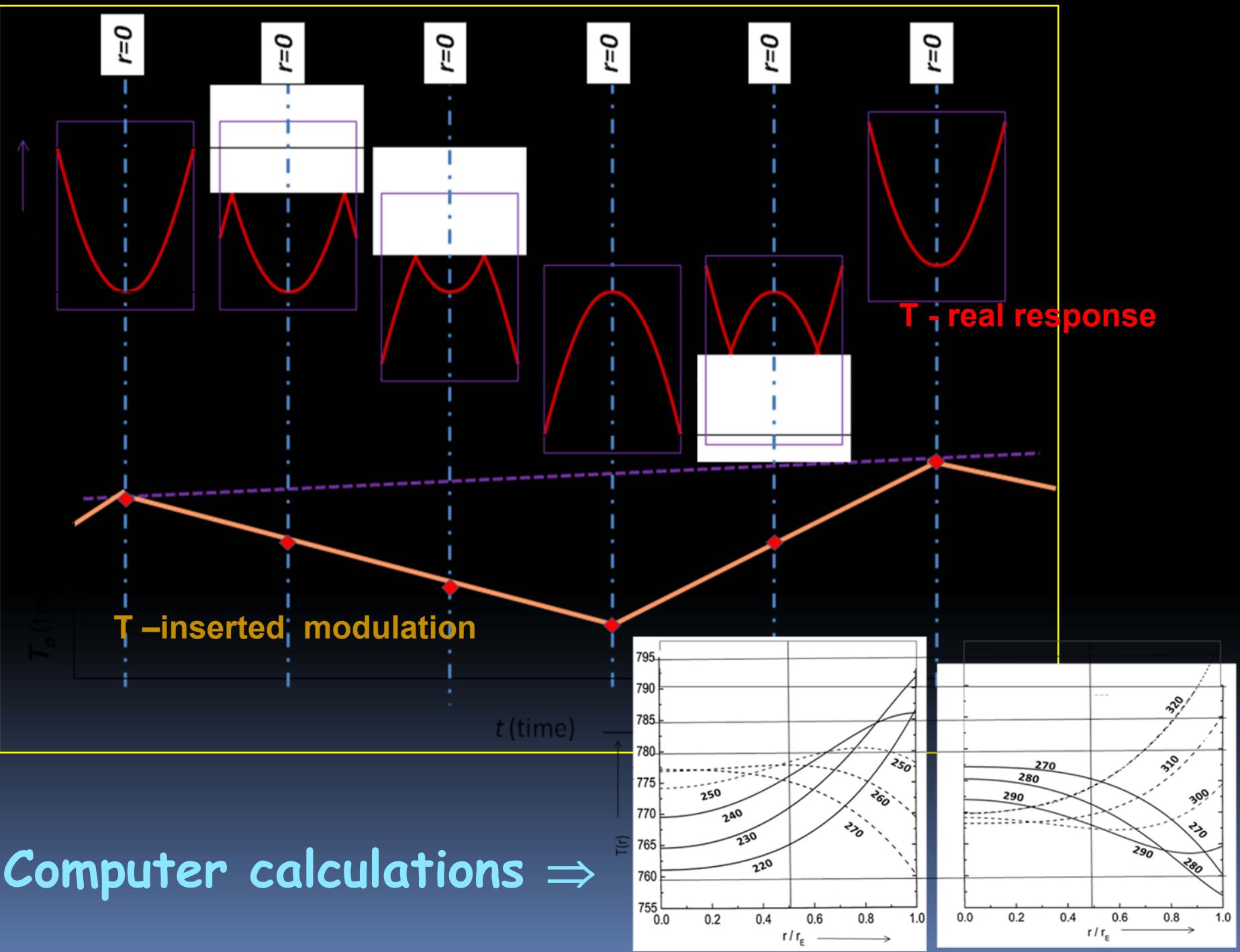
Amplitude of the radiation intensity $I(x, y)$ measured at ac heating (2 V, 1 Hz). Dashed line A indicates the direction at $y_1 = -24 \mu\text{m}$ along which the dependence $I(x, y_1)$ was measured.

Temperature modulation



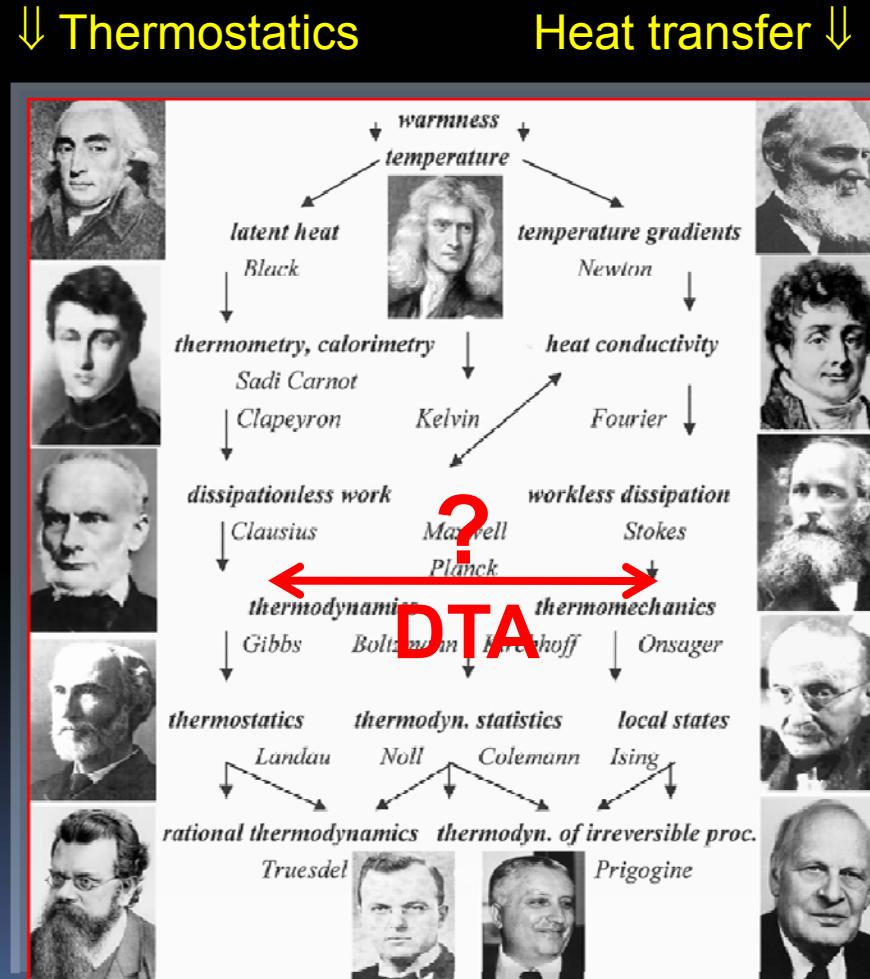
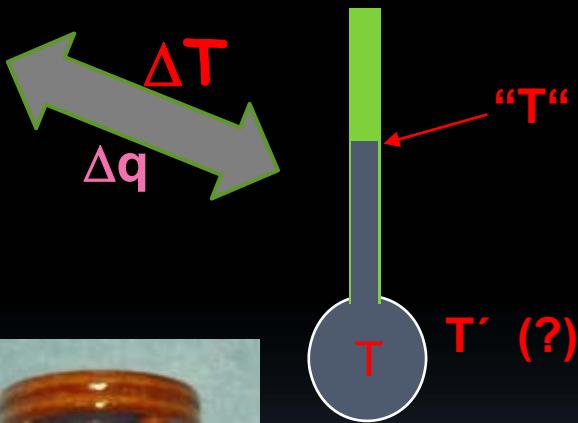
M. Reading, „*Modulated dDSC: a new way forward in materials characterization*“ Trends Polym. Sci. 1, 1993, 248-253

B. Wunderlich, Y. Jin, A. Boller, „*Mathematical description of DSC based on periodic temperature modulation*“, Thermochim. Acta 238 (1994) 277-293.



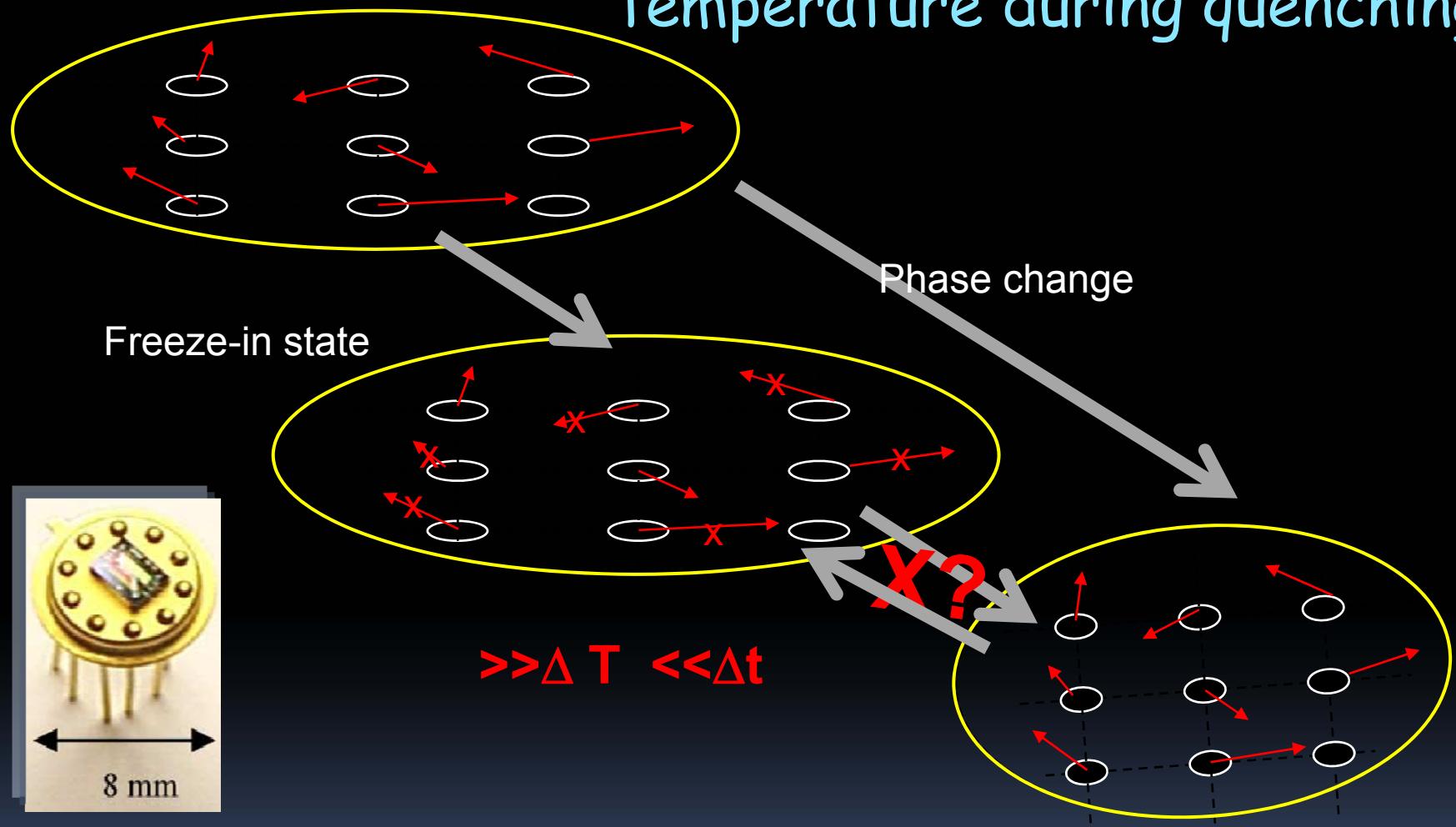
Ultra-fast processes - what is temperature contrivance of thermodynamics

What happens if there is no time for the system fast-enough equilibration?



what says "each thermodynamics" ?

Special case of a change: temperature during quenching



S.A. Adamovsky, A.A. Minakov, C. Schick. *Scanning microcalorimetry at high cooling rate*. Thermochimica Acta 403 (2003) 55–63; and: *Ultra-fast isothermal calorimetry using thin film sensors* Thermochimica Acta 415 (2004) 1–7

Temperature of ultrafast changes in nano-scale and its determinability

$$\Delta q \Delta T = ?\Delta?$$

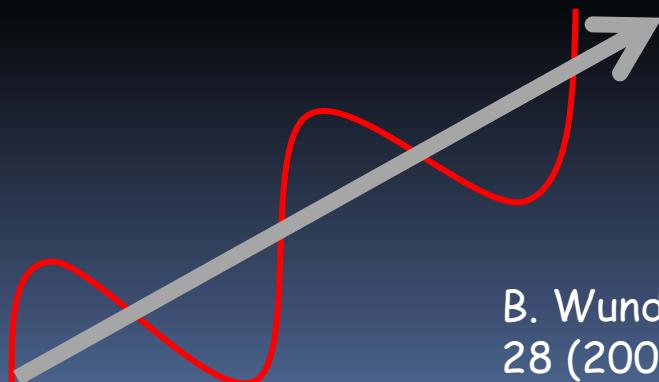
Where is the operate limit of uncertainty principle

$$\Delta T/\Delta t = ?\Delta?$$

Where is the operate limit of ever recordable temperature changes

$$\Delta T = ?\Delta?$$

Where is the limit of readable and reproducible temperature gradient



B. Wunderlich "Calorimetry of Nanophases" Int.J. Thermophysics 28 (2007) 958-96; M. Reading, A. Hammiche, H. M. Pollock, M. Song: Localized thermal analysis using a miniaturized resistive probe. Rev. Sci. Instrum. 67, 4268-4275 (1996)

Yet uncertain territory of thermodynamics

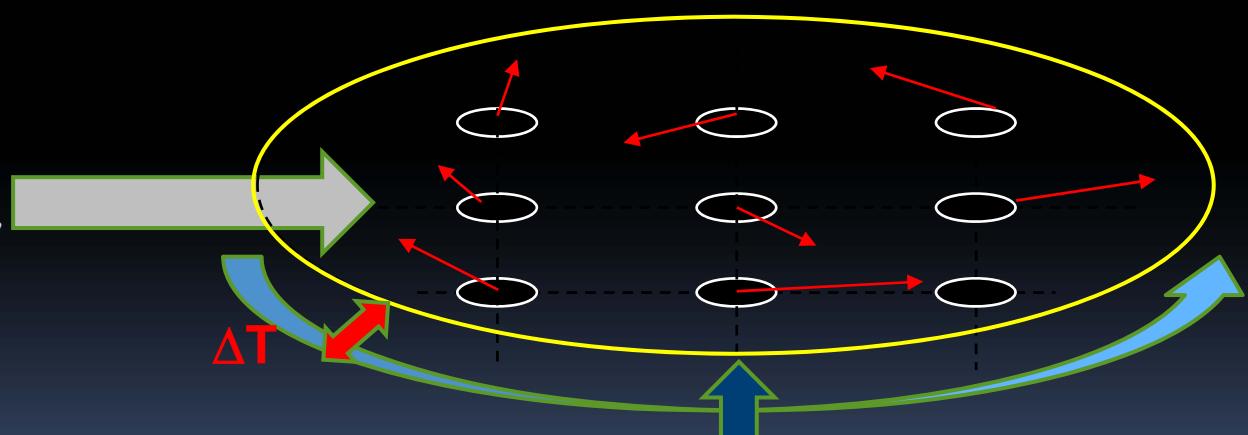
Corrections toward nano-scale?

At macroscopic scales:

the Laws are perfectly valid but

what happens at nano-scales (curved interfaces)?

Decreasing number of bulk molecules to a nano-limit narrowed by interface layer energy



Interaction between the sample holder (cell) and the entire sample surface (competition between the bulk $\sim r^3$ and surface $\sim r^2$)

Quandary for diminutive bringing on micro/nano-analysis methods by using:

- * ultra-small samples and
- * mili-second time scales .

It involves a further peculiarity of truthful temperature (T_r versus T_∞) measurements of nano-scale crystalline samples in the particle micro range with radius (r) which becomes size affected due to increasing role of the surface energy usually described by an universal equation:

$$T_r/T_\infty \approx (1 - C/r)^p$$

where ∞ portrays a standard state and C and p are empirical constants ranging $\approx 0.15 < C < 0.45$ and $p = 1$ and/or $\frac{1}{2}$

Micro/nano-analysis of materials

- Wunderlich, B.: Calorimetry of nanophases of macromolecules. Int. J. Thermophys. 2007; 28, 958-967
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Yet further problems at the nano-scale physics:

Heat transfer on submicro- and nano-scales differs from that at macro scale due to:

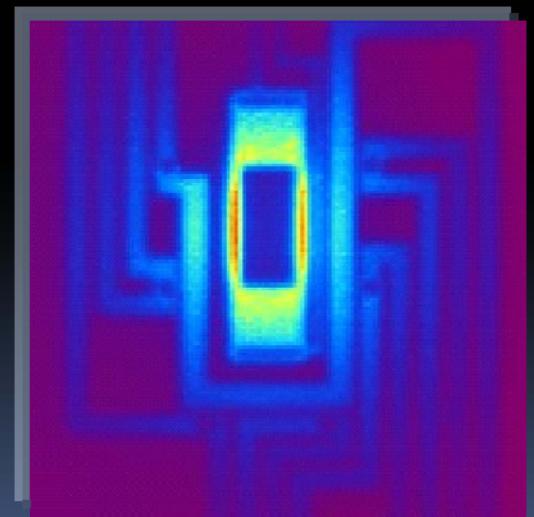
Finite size of gas gaps (molecules, species) : so called ballistic effect

Finite thickness of solid domains (photons, electrons) \Rightarrow ballistic effect

In narrow gaps heat flux limited by velocity and concentration of molecules

Destructing effects on phase interfaces
(including destructive interference -
phase interface does not have volume)

Thermal photon tunneling (evanescent waves)
Stationary versus dynamic heat capacity



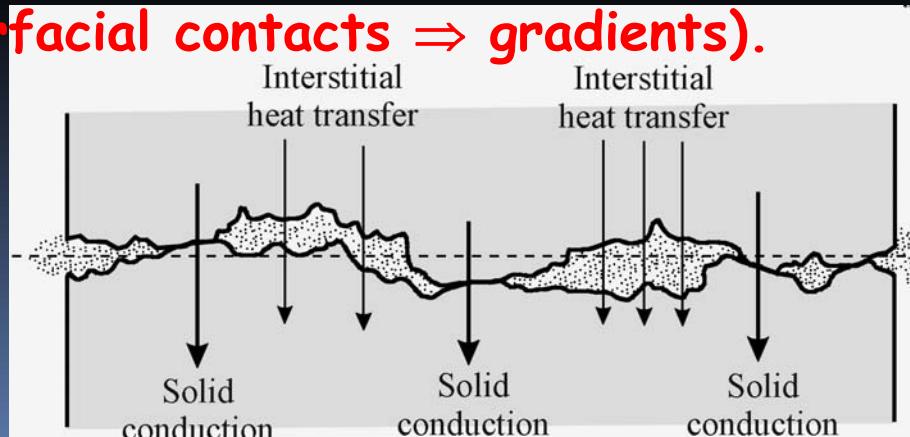
Careful when going behind the ordinary limits !

1. At small space scales we must be very careful when applying the first and second law of thermodynamics.
If we measure heat, for example, we should justify what we really do (modulated techniques and/or small samples)
2. The second law has a statistical character at small scales !
(needs a special application)
3. At fast processes seems the situation becomes alike that of quantum mechanics, i.e., **the coincident measure of accurate temperature and/or heat flow emerge awkward**
4. There are other open questions (gradients, interfaces, crystal size, contacts, fractal behavior, etc.) due to experimental set ups (**interfacial contacts \Rightarrow gradients**).

$$\Delta T \Delta q \Rightarrow \text{limit } ?\Delta?$$

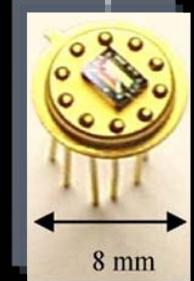
Uncertainty principle in quantum mechanics

$$\Delta p \Delta x = h$$



Any experiment **always** provides certain data on temperature and other measured variables!

It seems that thermoanalysts believe that a mere **replacement** of thermocouples by thermocouple batteries or by highly sensitive electronic chips moreover renaming DTA principle to variously termed DSC's is a sufficient solution toward theoretical rations.



It's the **responsibility** of researcher to know to what extent spans his true conscientiousness!

One never gets to see that his work is so **secret** that he does not even know what he is doing !
(~allied to blindness trust to instrumental outputs)

Various scientific views and practices compete each other: who is right in DTA?

Traditional evaluation should be changed but it would bring to many inconvenience in existing (software) practice (evaluations)

Traditional evaluation is necessary to be adjusted because it does not comply to modern theories of thermal gradients

Traditional evaluation is not necessary to modify; we are happy with our long lasting practice and both customary results and applicability thus not needing any troubles



It's not politics; is really the best the only one which is the easiest, loudest or most applauded one?



I appreciate that you kindly waited until the end of my long lecture
thank you

Worth of attention:



Series Editor J. Simon
Volume Editors J. Šesták, J.J. Mareš, P. Hubík

Glassy, Amorphous and Nano-Crystalline Materials

Glassy, Amorphous and Nano-Crystalline Materials: Thermal Physics, Analysis, Structure and Properties includes twenty-one chapter contributions from an international array of distinguished academics based in Asia, Australia, Eastern and Western Europe, Russia, and the USA. The book provides a coherent and authoritative overview of cutting-edge themes involving the thermal analysis, applied solid-state physics and the micro-crystallinity of selected materials and their macro- and microscopic thermal properties.

Selected chapters featured in the book include: Essential attributes of glassiness regarding the nature of non-crystalline solids; Aspects of vitrification, amorphization, disordering and the extent of nano-crystallinity; The basic role of thermal analysis in polymer physics; Classical and quantum diffusion and their application to the self-organized oscillatory reactions; Specificity of low temperature measurements applied to nanocrystalline diamante; Thermophysical properties of natural glasses at the extremes of the thermal history profile; Phenomenological meaning of temperature as background for the history and development of thermal analysis and calorimetry.

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Glassy, Amorphous and Nano-Crystalline Materials

Thermal Physics, Analysis, Structure and Properties

 Springer 2011

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