

Thermal Parameter Identification in Remote Heating

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In collaboration with: Facundo Altuna, Julieta Puig, Cristina Hoppe,
Fernando Otero and Gloria Frontini

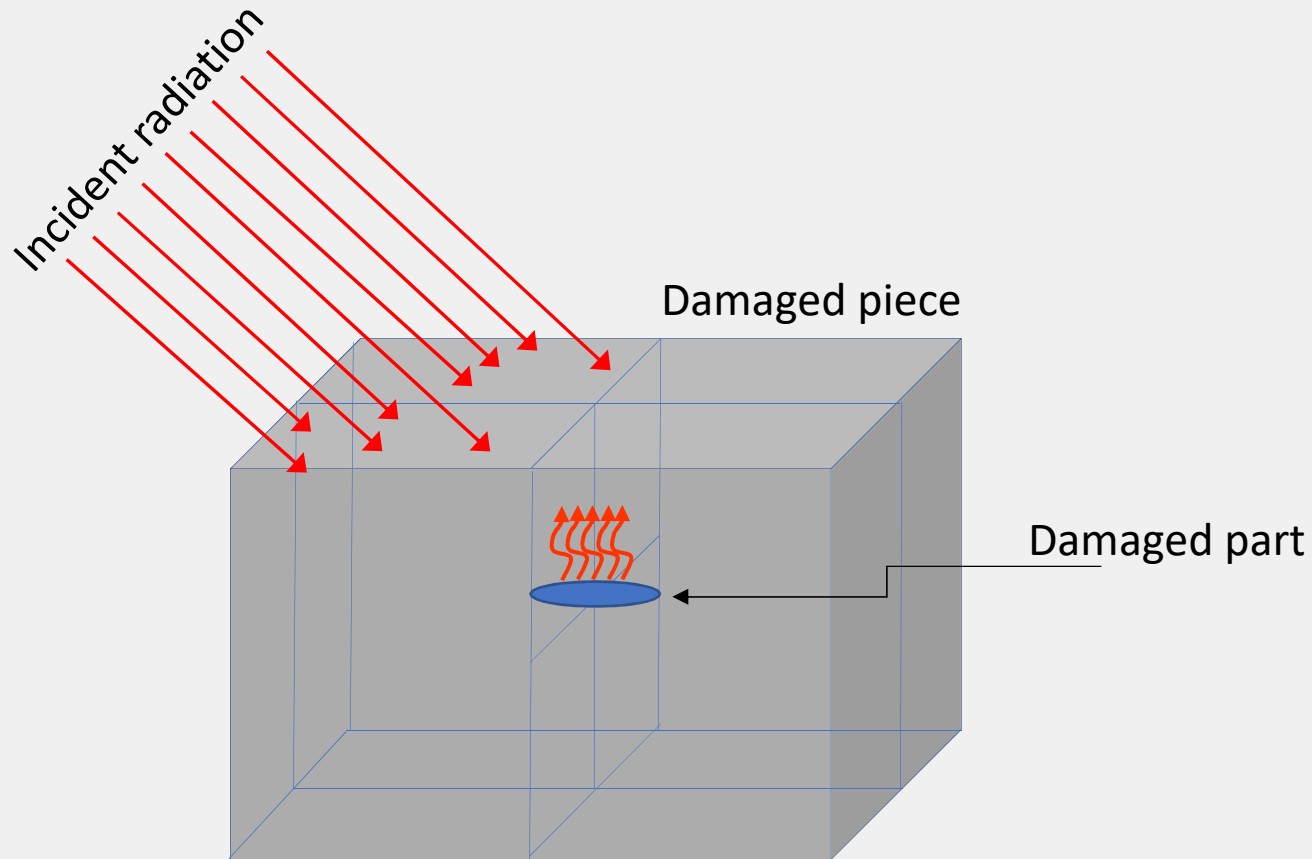


New Trends in Parameter Identification for Mathematical Model
IMPA, Rio de Janeiro, October 30th to November 3rd, 2017

What motivated this work?

- Diffusion of light
- Scattering and absorption by small particles
- Self healing polymers
- Previous and ongoing work in light diffusion problems in biomedical tissues:
 - Optical tomography for the detection of foreign bodies in live tissues (Guido Baez)
 - STATE ESTIMATION PROBLEM IN HYPERTHERMIA TREATMENT OF CÂNCER INDUCED BY NEAR-INFRARED DIODE LASER HEATING (Bernard Lamien)
- Ongoing work in the Polymer Group of INTEMA on:
 - Self-healing of polymers (Facundo Altuna, Julieta Puig, Cristina Hoppe)
 - Scattering and absorption of light by arrays of gold nanoparticles (Nancy Cativa)

Self-healing of polymers: Heating of the damaged part



- Local phase separation
- Localized reactions

Self-healable polymer networks based on the crosslinking of epoxidised soybean oil by an aqueous citric acid solution

Facundo I. Altuna,* Valeria Pettarin and Roberto J. J. Williams

Green Chem., 2013, 15, 3360

Abstract

Epoxidised soybean oil (ESO) was cross-linked with an aqueous citric acid (CA) solution without the addition of any other catalyst or solvent. Completely bio-based polymer networks were generated. The initial system was an emulsion, but it became a homogeneous and transparent polymer network by reaction. The ability of the final materials to self-heal without adding extrinsic catalysts was assessed by stress relaxation and lap-shear tests. This was achieved by molecular rearrangements produced by thermally activated transesterification reactions of β -hydroxyester groups generated in the polymerization reaction.

Fast optical healing of crystalline polymers enabled by gold nanoparticles.

Zhang H¹, Fortin D, Xia H, Zhao Y.

Macromol Rapid Commun, 2013 Nov, 34(22):1742-6

Abstract

A general method for very fast and efficient optical healing of crystalline polymers is reported. By loading a very small amount of gold nanoparticles (AuNPs) in either poly(ethylene oxide) ($T_m \approx 63\text{ }^{\circ}\text{C}$) or low-density polyethylene ($T_m \approx 103\text{ }^{\circ}\text{C}$), the heat released upon surface plasmon resonance (SPR) absorption of 532 nm light by AuNPs can melt crystallites in the interfacial region of two polymer pieces brought into contact; and the subsequent recrystallization of polymer chains on cooling merges the two pieces into one. The fracture strength of such repaired sample can reach the level of the undamaged polymer after 10 s laser exposure. Moreover, in addition to an ability of long-distance remote and spatially selective healing, the optical method also works for polymer samples immersed in water

Metal Nanoparticles Acting as Light-Activated Heating Elements within Composite Materials

Somsubhra Maity, Jason R. Bochinski and Laura I. Clarke

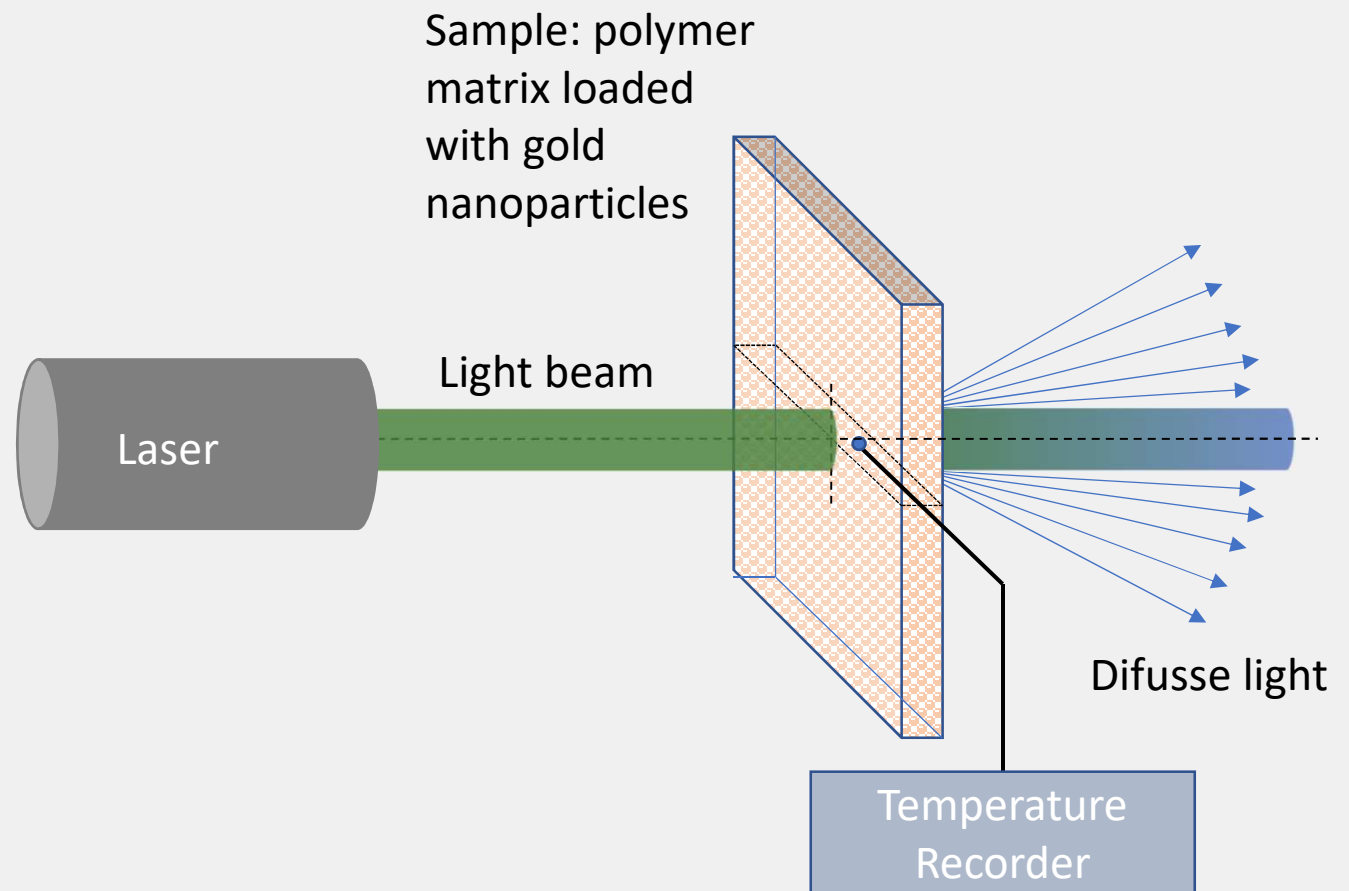
Advanced Functional Materials, Volume 22, Issue 24, December 19, 2012, Pages 5259–5270

Abstract

The photothermal effect of metal nanoparticles embedded in polymeric materials can be used to efficiently generate local heat for in situ thermally processing within an existing material. Fluorescent probes are employed as thermal sensors to allow dynamical measurement of the amplitude and rate of temperature change within the polymer matrix. The efficacy of this technique is demonstrated in polymer nanocomposite samples with different morphological characteristics, namely nanofibrous mats and thin film samples. For similarly thick materials and both types of sample morphology, average temperature increases on the order of $\approx 100^\circ\text{C}$ are readily obtained with dilute nanoparticle concentrations under relatively low irradiation intensity. Thus, the in situ photothermal heating approach has great potential for controllably driving a multitude of thermal processes, such as triggering phase transitions, generating site-specific cross-linking, or initiating chemical reactions from within a material.

Scope of the Problem

- Modelling the luminic and thermal variables in a slab of a polymer material loaded with plasmonic nanoparticles, and illuminated with a laser light.
- Estimating parameters and state variables from measurements in a few locations using the developed models.
- Proposing reduced models and analyzing validity and efficiency in estimating parameters and state variables.
- Analyzing simulated and experimental examples using the developed models.



Steps in the analysis:

1. Gold nanoparticles and their extreme light absorption characteristics.
 - . Distribution of electric field, power density and temperature for a gold nanoparticle in water.
 - . Light absorption: intuitive approach
 - . Gold nanoparticle: light absorption.
 - . High efficiency in absorbing the incident radiating energy
 - . Optical parameters of gold, cadmium selenide and aluminium alloy.
2. Radiative transfer theory as a tool to establish the heat generation terms all across the sample.
 - . Schematic of light propagation in the slab.
 - . Radiative transfer equation.
3. Heat transfer equation as a mean to calculate temperature profiles at all positions in the sample.
 - . Heat transfer equations.
 - . Assumptions in the model.

Steps in the analysis (cont.):

4. Experimental set-up.
 - . Sample.
 - . Operating conditions
5. Experimental evaluation of complete and reduced models through simulations.
 - . 3D model.
 - . 2D model.
 - . 1D model.

Distribution of electric field, power density and temperature for a gold nanoparticle in water

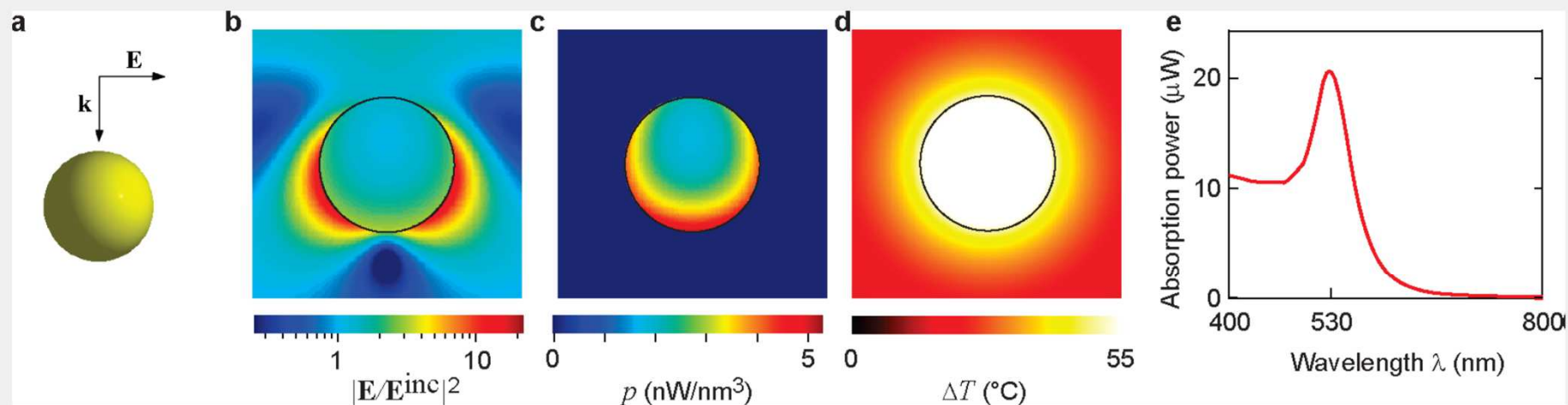
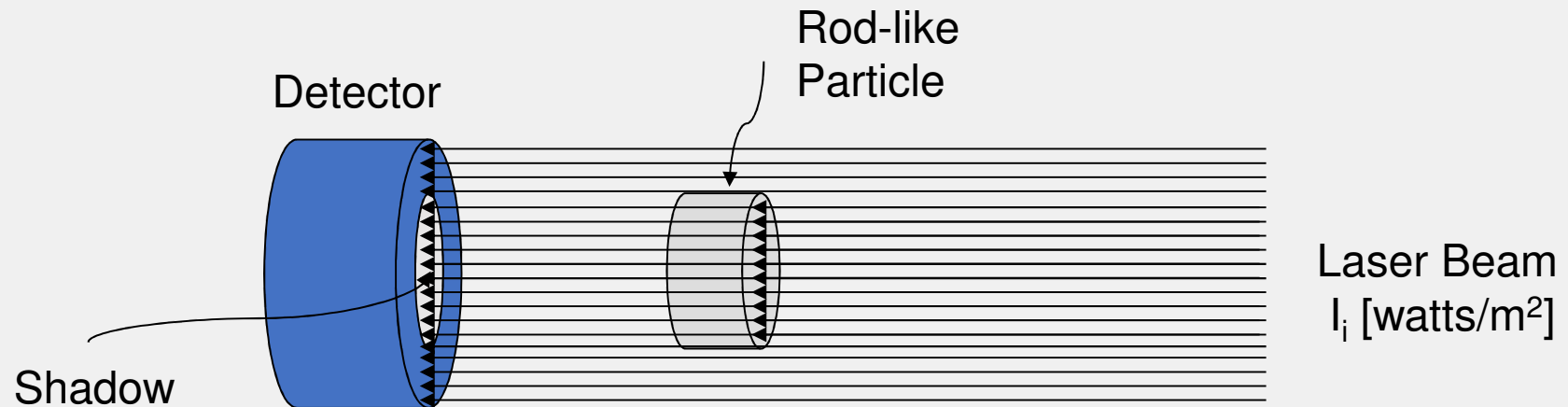


Figure 1. Photothermal heating of a 100 nm gold nanosphere placed in water. (a) Schematic representation of the sphere showing the orientation of the external electric field \mathbf{E} and the light wavevector \mathbf{k} . (b) Electric near-field intensity normalized to the incident field intensity, (c) heat generation density, and (d) equilibrium distribution of temperature increase for a light wavelength $\lambda = 530$ nm, tuned to the particle dipole plasmon. (e) Absorption power as a function of light wavelength. The incident light intensity is $1 \text{ mW}/\mu\text{m}^2$ in all cases.

Light extinction: intuitive approach



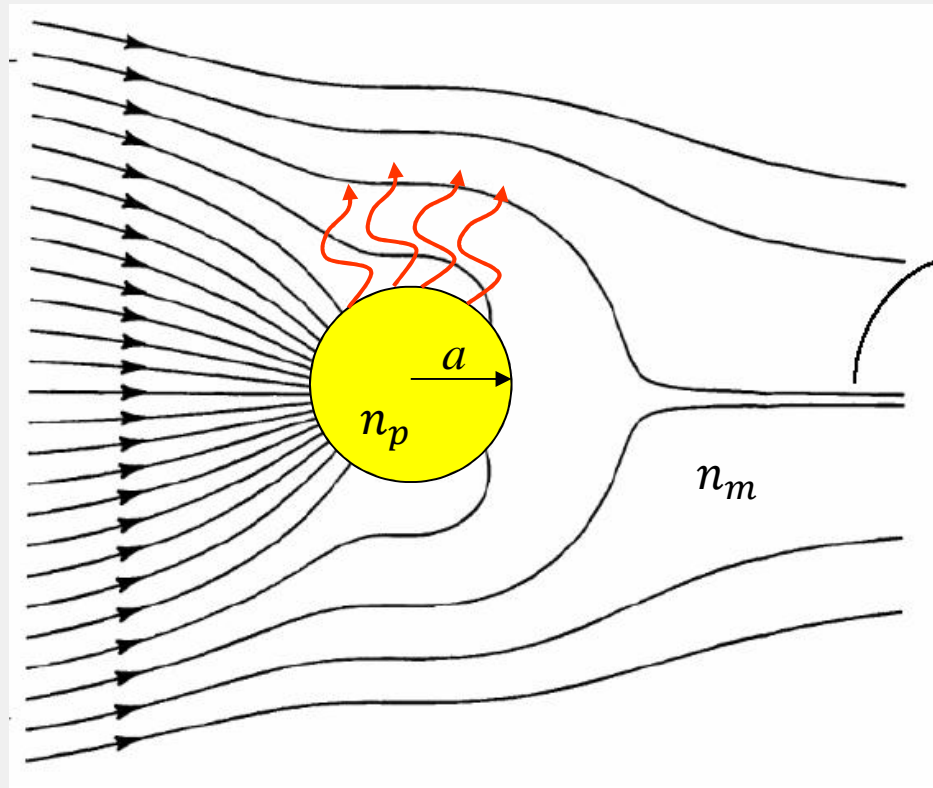
Detector area = A_d [m²]

Power at detector without particle = $P_d^- = A_d I_i$

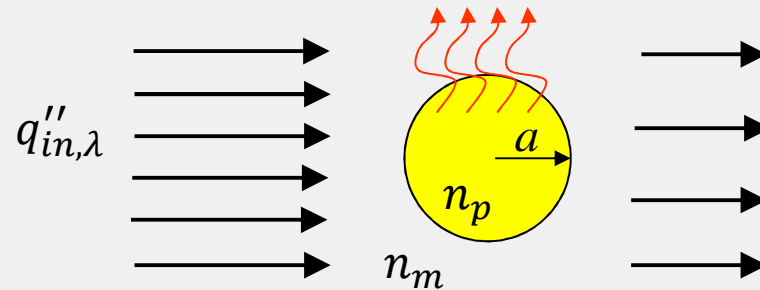
Power at detector with particle = $P_d^+ = (A_d - A_p) I_i$

$$A_p = C_{\text{ext}} = \pi R^2 \quad \text{and} \quad Q_{\text{ext}} = C_{\text{ext}} / \pi R^2 = 1$$

**High efficiency in absorbing
the incident radiating energy**



Gold nanoparticle: light absorption

$$W = q''_{in,\lambda} Q_{\kappa\lambda} \pi a^2 \text{ [watts]}$$


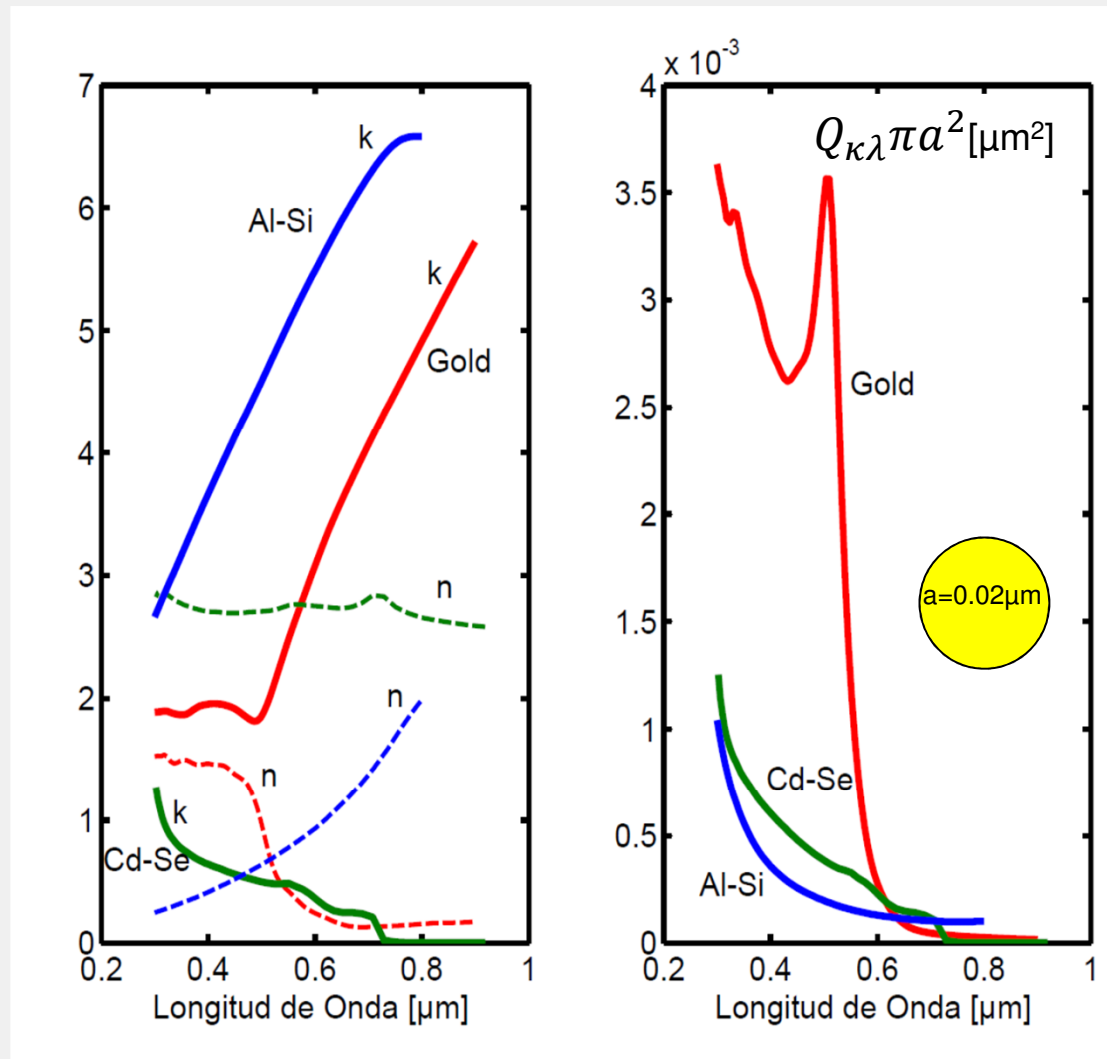
$$Q_{\kappa\lambda} = \frac{8\pi a n_m}{\lambda} \text{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\}$$

$$Q_{\sigma_{s\lambda}} = \frac{8}{3} \left(\frac{2\pi a n_m}{\lambda} \right)^4 \left| \frac{m^2 - 1}{m^2 + 2} \right|^2$$

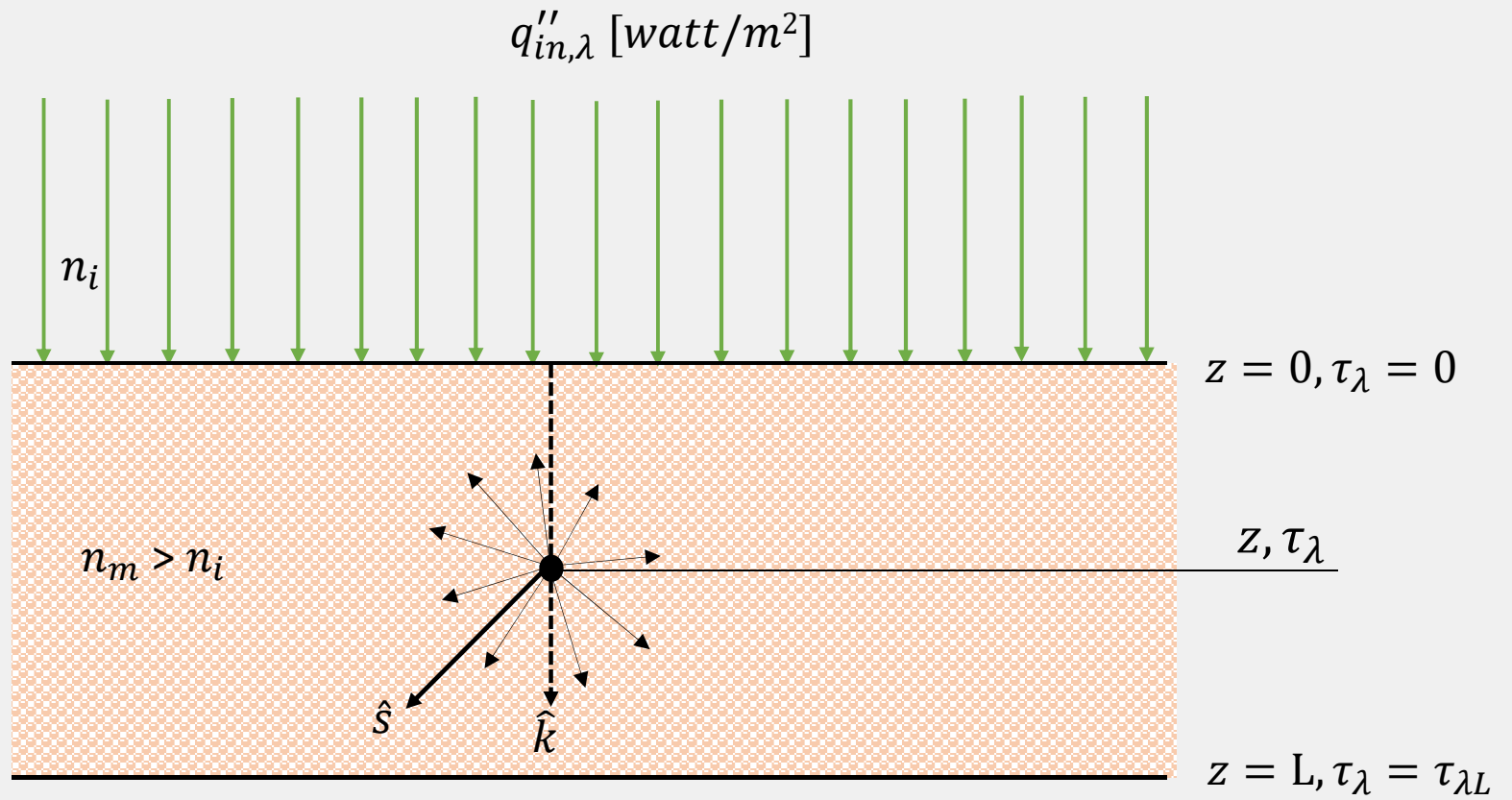
$$m = \frac{n_p}{n_m}$$

$$n_p = k + j n$$

Optical parameters of gold, cadmium selenide and aluminium alloy



Schematic of light propagation in the slab



Radiative transfer equation

$$\mu \frac{dI_{R\lambda}(\tau_\lambda, \hat{s})}{d\tau_\lambda} + I_{R\lambda}(\tau_\lambda, \hat{s}) = \frac{\omega_\lambda}{4\pi} \int_{4\pi} I_{R\lambda}(\tau_\lambda, \hat{s}) d\Omega$$

- Diffusion approximation
- One dimensional

$$\kappa_\lambda = \pi a^2 Q_{\kappa\lambda} N_T$$

$$\sigma_{s\lambda} = \pi a^2 Q_{\sigma_{s\lambda}} N_T$$

$$\omega_\lambda = \frac{\sigma_{s\lambda}}{\sigma_{s\lambda} + \kappa_\lambda}$$

$$\tau_\lambda = \beta_\lambda z$$

$$\beta_\lambda = \sigma_{s\lambda} + \kappa_\lambda$$

$$a=6.5nm$$

$$\lambda=532nm$$

$$n_p=0.54386+j2.2309 \text{ (Johnson \& Christy)}$$

$$n_m=1.53$$

$$Q_{ext}=1.36315$$

$$Q_{sca}=0.0046$$

$$N_T = 5.52 \times 10^{17}$$

$$Vf=6.358E-7$$

Radiative transfer equation (cont.)

$G_{R\lambda}(\tau_\lambda) = G_{d\lambda}(\tau_\lambda) + G_{c\lambda}(\tau_\lambda)$ *heat flux inside de sample as function of τ_λ*

$$G_{d\lambda}(\tau_\lambda) = -\frac{1}{(1 - \omega_\lambda)} [C_1 \xi_1 e^{\xi_1 \tau_\lambda} - C_2 \xi_1 e^{-\xi_1 \tau_\lambda} - B_1 e^{-\tau_\lambda} - \omega_\lambda G_{c\lambda}]$$

$$G_{c\lambda}(\tau_\lambda) = q''_{in,\lambda} e^{-\tau_\lambda}$$

$q''_{in,\lambda}$ *is the heat flux at the entry face*

C_1, C_2, B_1, ξ_1 *depend on $\tau_{L\lambda}, \omega_\lambda, q''_{in,\lambda}$*

Heat transfer equations

3 dimensional model

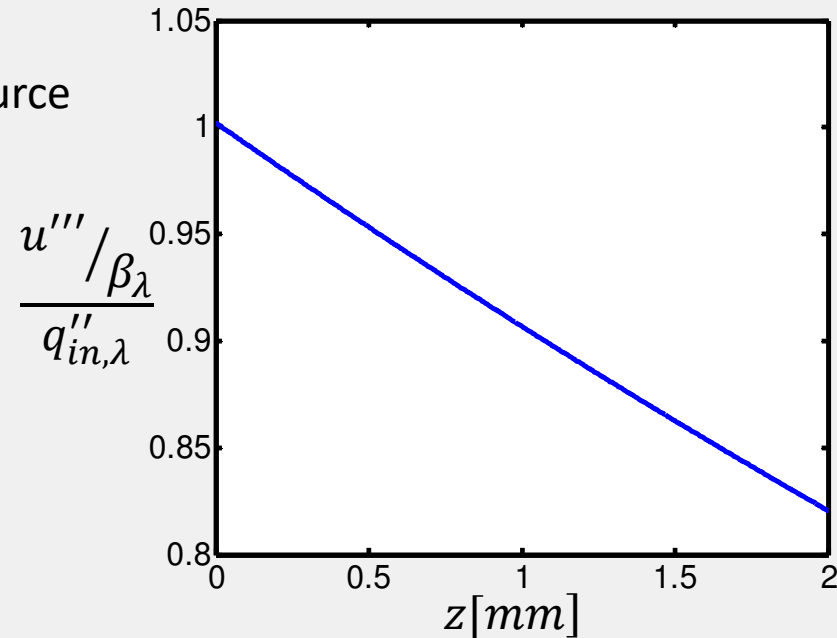
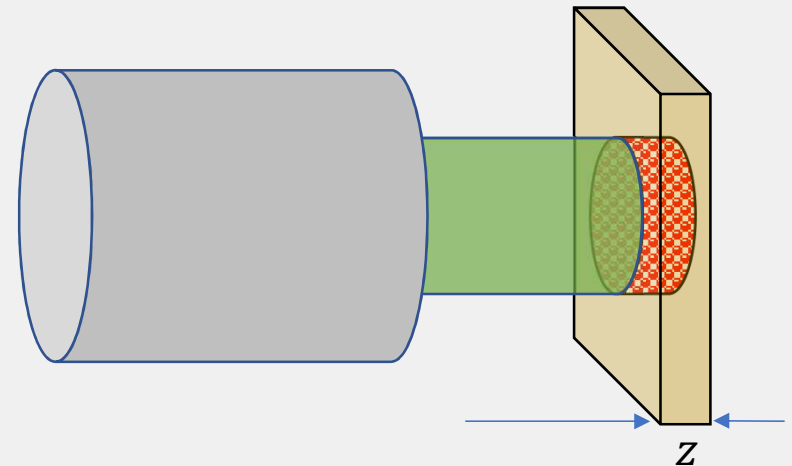
$$\rho c \frac{\partial T}{\partial t} = k_{md} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + u'''$$

$$k_{md} \frac{\partial T}{\partial t} = h(T_{ext} - T) \text{ on the 6 faces of the slab}$$

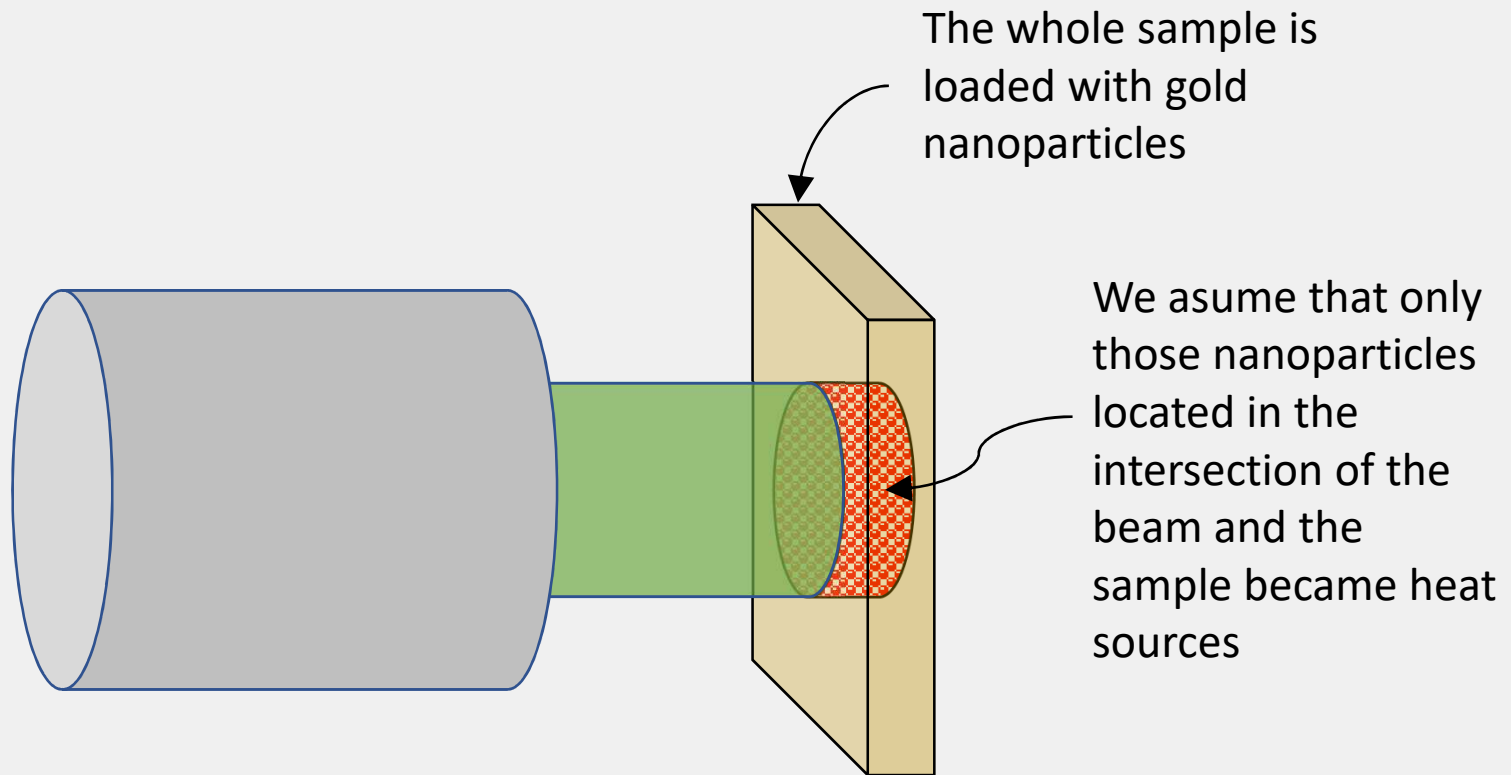
$$T(0) = T_i \text{ for all } x, y, z$$

$$u''' = -\kappa_\lambda G_{R\lambda}(z) \text{ [watt/m}^3\text{] Heat source}$$

$$\begin{aligned} \rho &= 1125 \text{ kg/m}^3 \\ K_{md} &= 0.13 \text{ watt/(m}^\circ\text{K)} \\ C &= 1900 \text{ J/(kg}^\circ\text{K)} \\ h &= 10 \text{ watt/(m}^\circ\text{K seg)} \\ T_{ext} &= 24^\circ\text{C} \\ T_i &= 25^\circ\text{C} \end{aligned}$$



Heat transfer equations: assumptions in the model



Experimental setup

Sample: polymer matrix embedded with spherical gold nanoparticles

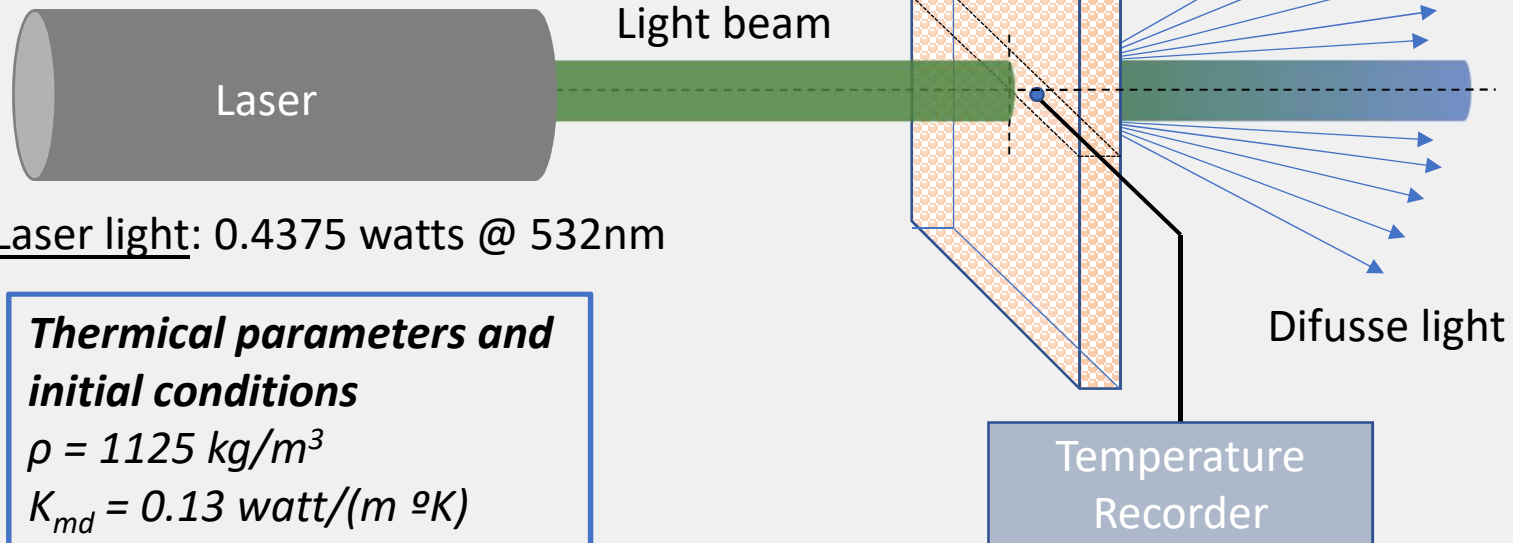
$$a=6.5\text{nm}$$

$$n_p=0.54386+j2.2309 \text{ (Johnson \& Christy)}$$

$$n_m=1.53$$

$$N_T = 5.52 \times 10^{17} \text{ particles/m}^3$$

$$V_f=6.358E-7$$



Laser light: 0.4375 watts @ 532nm

Thermal parameters and initial conditions

$$\rho = 1125 \text{ kg/m}^3$$

$$K_{md} = 0.13 \text{ watt/(m } ^\circ\text{K)}$$

$$C = 1900 \text{ J/(kg } ^\circ\text{K)}$$

$$h=10 \text{ watt/(m } ^\circ\text{K seg)}$$

$$T_{ext} = 24^\circ\text{C}$$

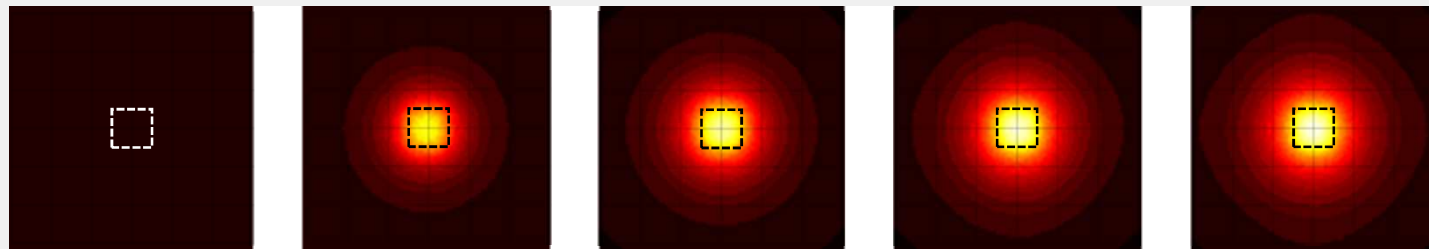
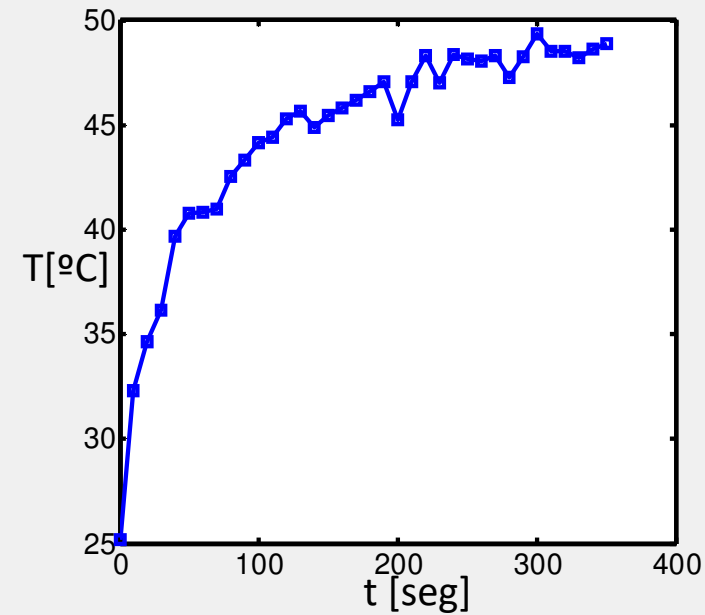
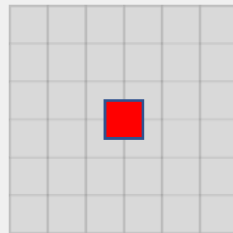
$$T_i=25^\circ\text{C}$$

Case A: partial illumination in two dimensions

Sample dimension: 18x18x2 mm

Illumination: 0.1575 watts
(0.0175watts/mm²) distributed
in 3x3mm² centered in the
center of the sample.

Measurement: in the center of
the sample

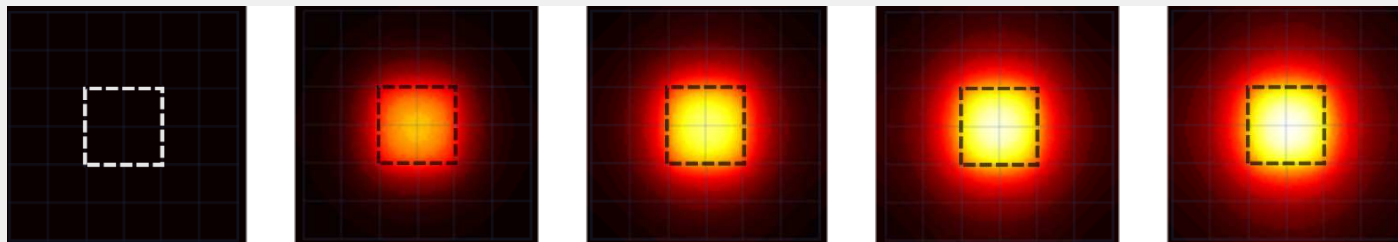
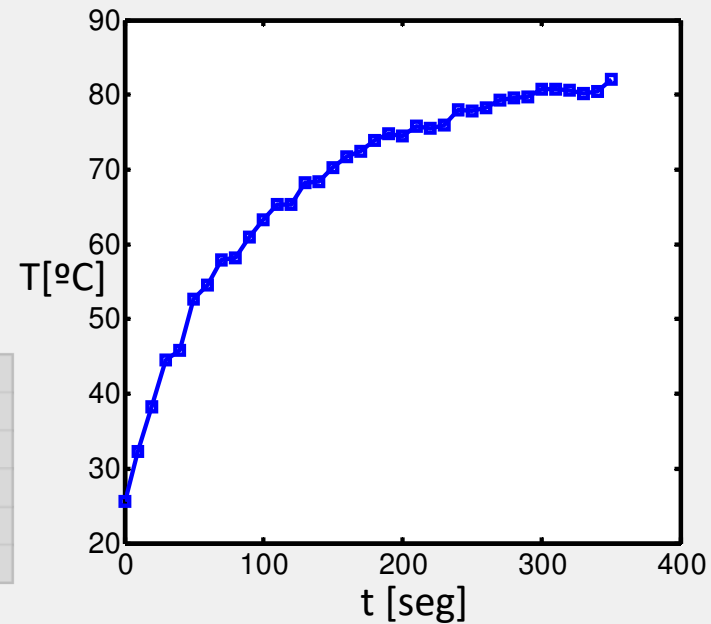
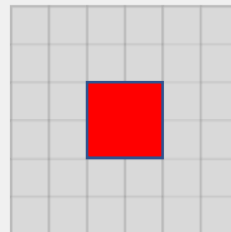


Case B: partial illumination in two dimensions

Sample dimension: 18x18x2 mm

Illumination: 0.63 watts
(0.0175watts/mm²) distributed
in 6x6mm² centered in the
center of the sample.

Measurement: in the center of
the sample

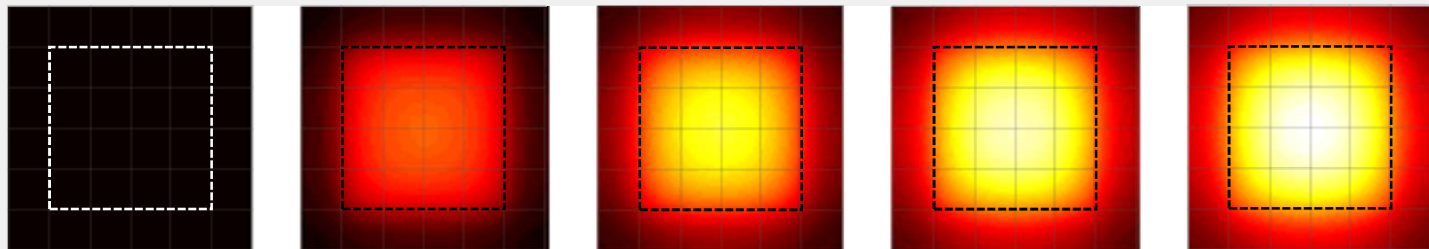
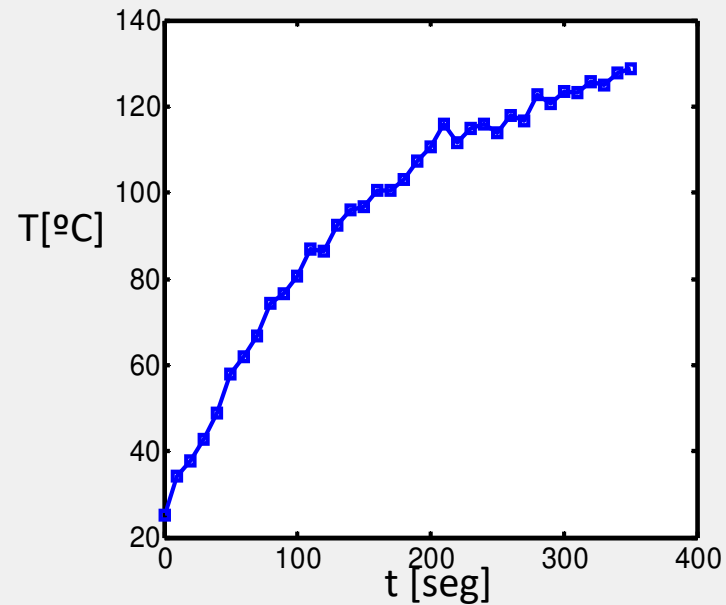
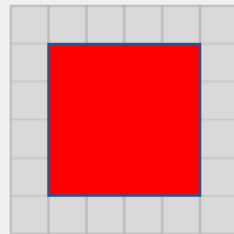


Case C: partial illumination in two dimensions

Sample dimension: 18x18x2 mm

Illumination: 2.52 watts,
(0.0175watts/mm²) distributed in
12x12mm² centered in the center
of the sample.

Measurement: in the center of the
sample

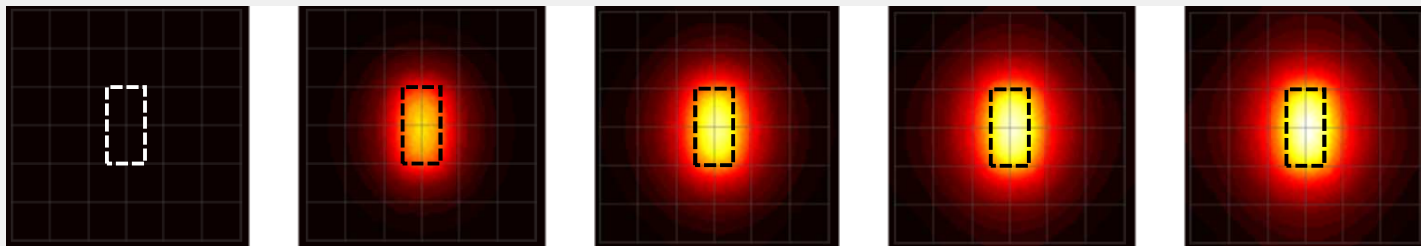
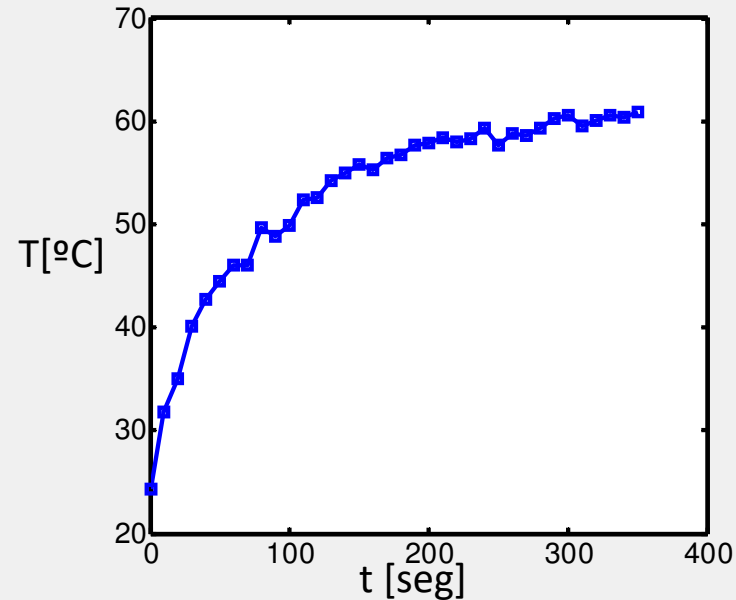
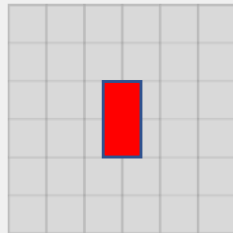


Case D: partial illumination in two dimensions

Sample dimension: 18x18x2 mm

Illumination: 0.315 watts,
(0.0175watts/mm²) distributed in
3x6mm² centered in the center of
the sample.

Measurement: in the center of the
sample

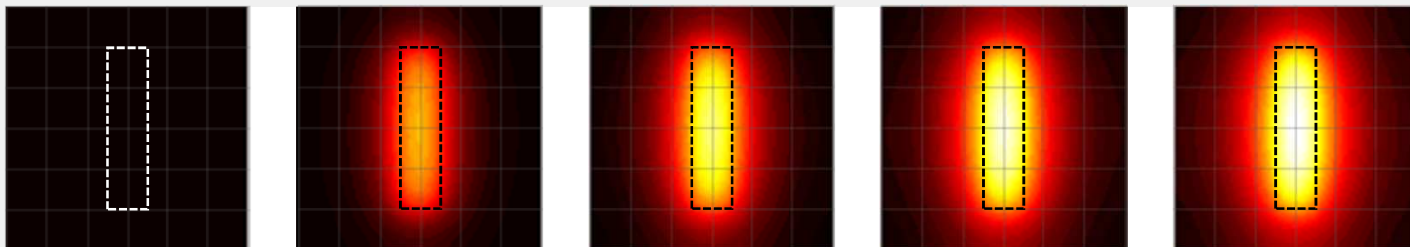
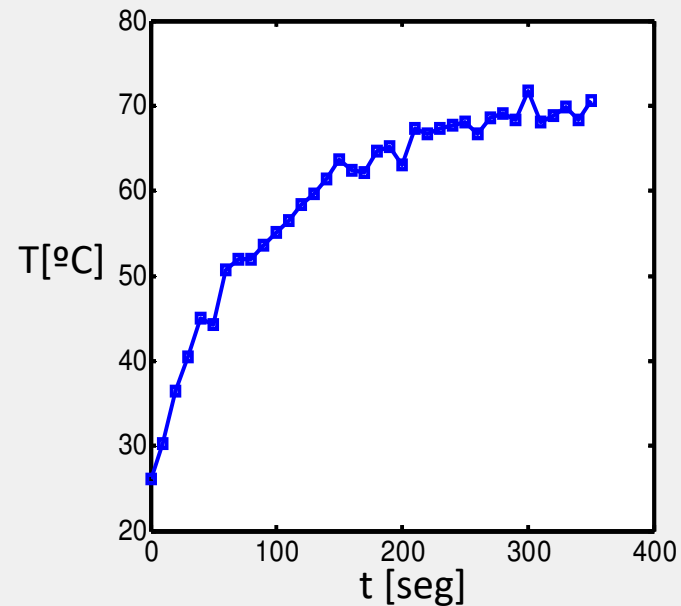
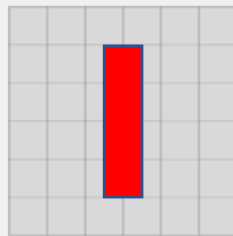


Case E: partial illumination in two dimensions

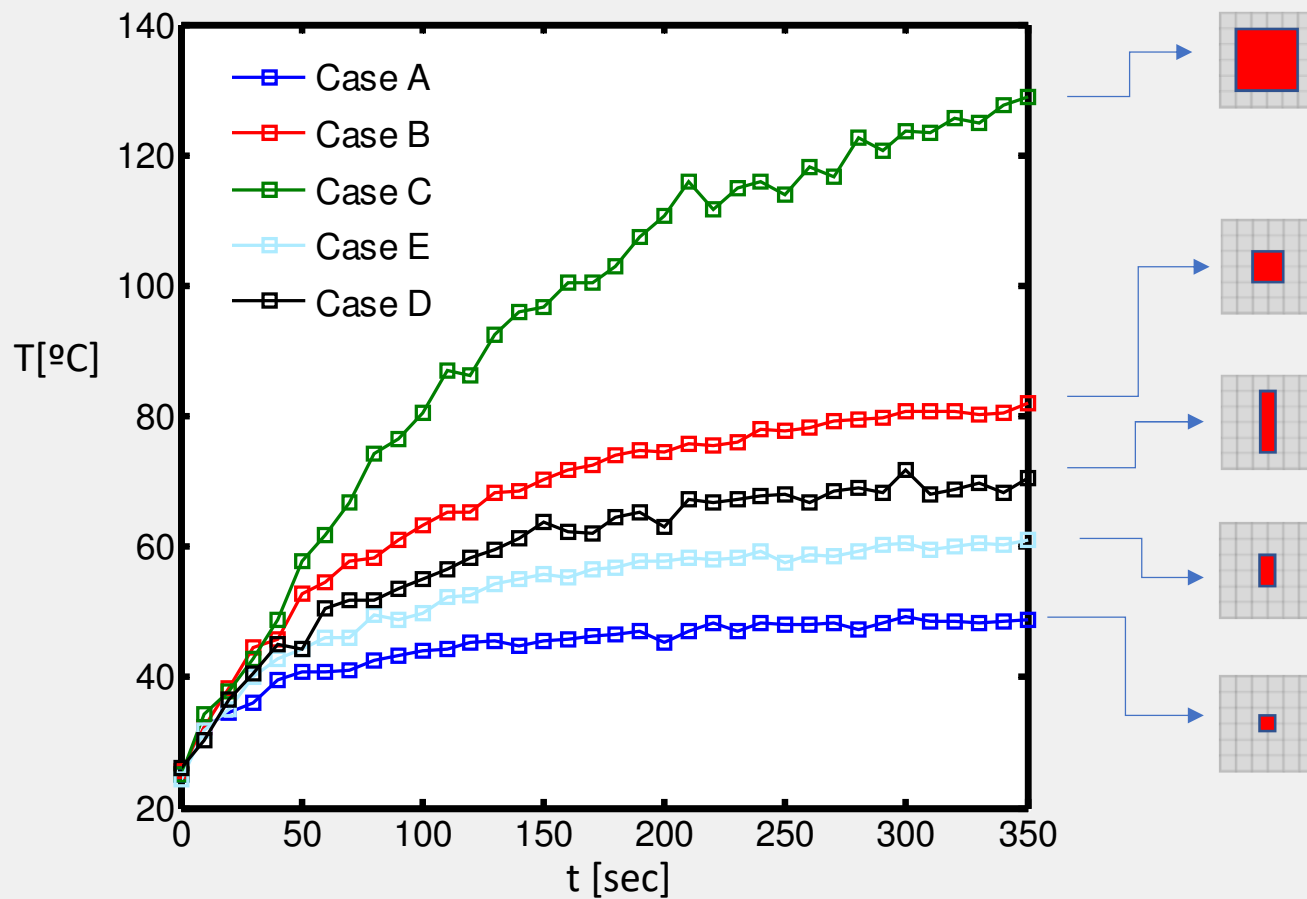
Sample dimension: 18x18x2 mm

Illumination: 0.63 watts,
(0.0175watts/mm²) distributed
in 3x12mm² centered in the
center of the sample.

Measurement: in the center of
the sample



Temperature evolutions for the different cases



Experimental Case 1

Polymer matrix: Epoxidized soybean oil – Citric acid Network

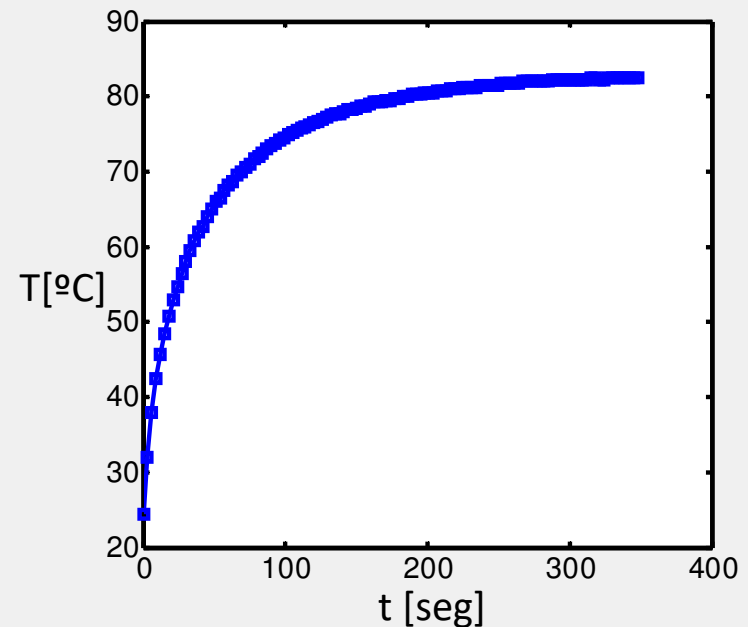
Gold nanoparticles: PVP capped Au nanoparticles where synthesized by post functionalization of gold nanoparticles obtained by the Turchevich method.

Nanocomposite: polymer matrix + gold nanoparticles

Sample dimension: 40x5x2 mm

Illumination: 0.7 watts, D=3mm centered in the center of the sample.

Measurement: in the center of the sample



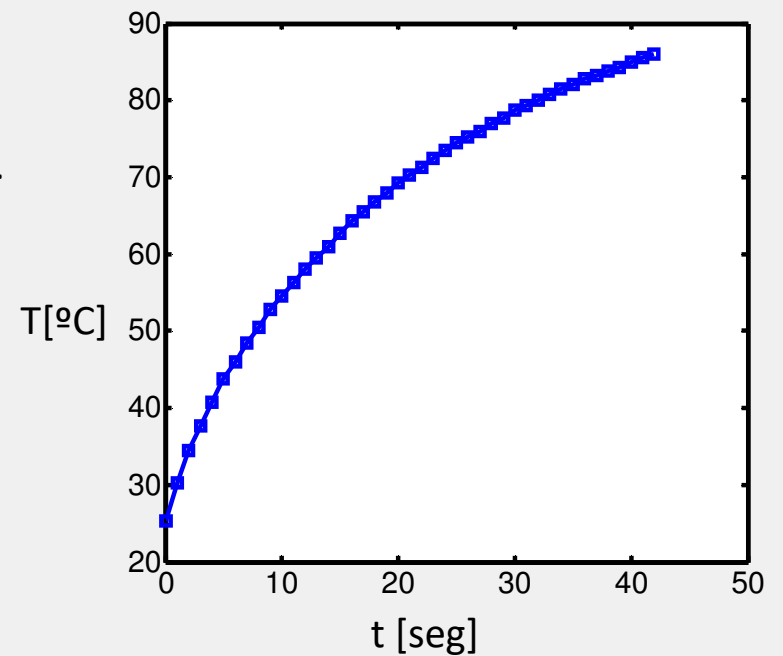
Experimental Case 2

Polymer matrix: DGEBA epoxi polymer

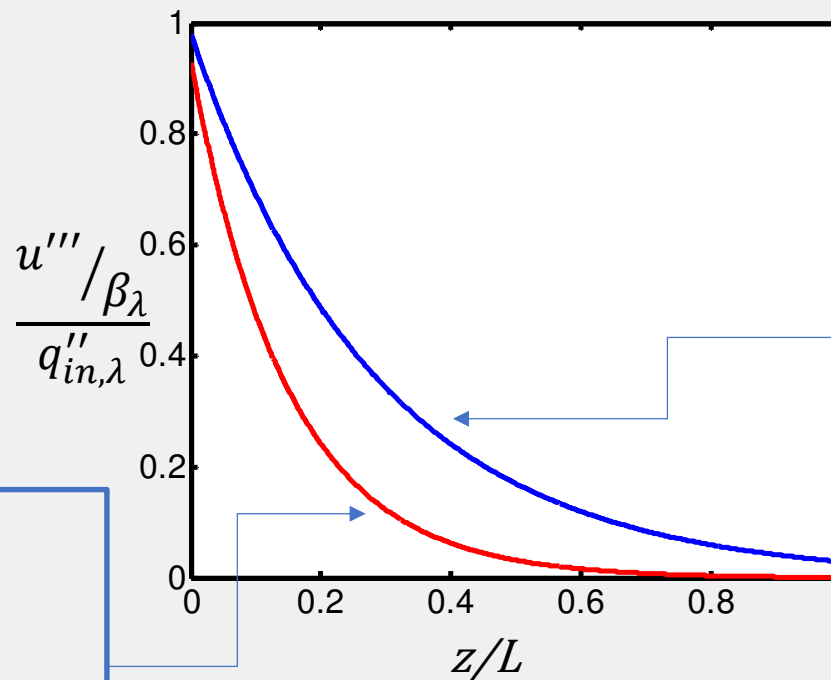
Gold nanoparticles: dodecanethiol capped gold nanoparticles

Nanocomposite: polymer matrix + gold nanoparticles

Sample dimension: 53x12x1.4 mm
Illumination: 0.7 watts, D=3mm
centered in the center of the sample.
Measurement: in the center of the sample



Heat source distribution along the thickness of the sample



Optical parameters

Experiment 2

$$a=1nm$$

$$\lambda=532nm$$

$$n_p=0.54386+j2.2309$$

$$n_m=1.53$$

$$N_T=2.18e22 \text{ part/m}^3 \text{ (weight concentration 0.05\%)}$$

Optical parameters

Experiment 1

$$a=6.5nm$$

$$\lambda=532nm$$

$$n_p=0.54386+j2.2309$$

$$n_m=1.568$$

$$N_T=2.03e21 \text{ part/m}^3$$

Some applications of the models

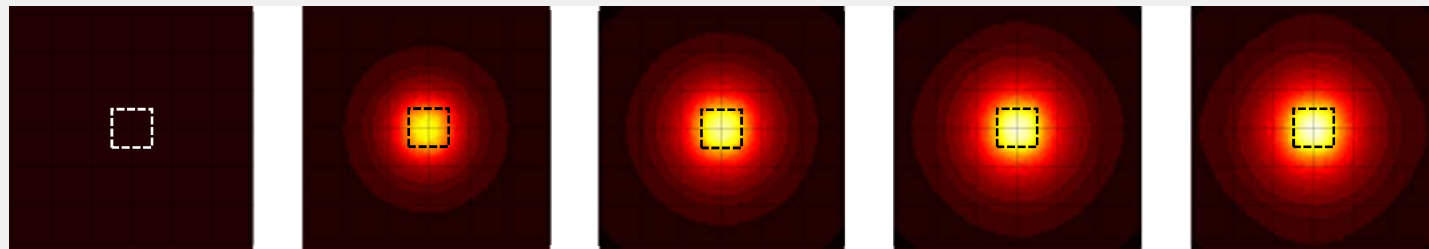
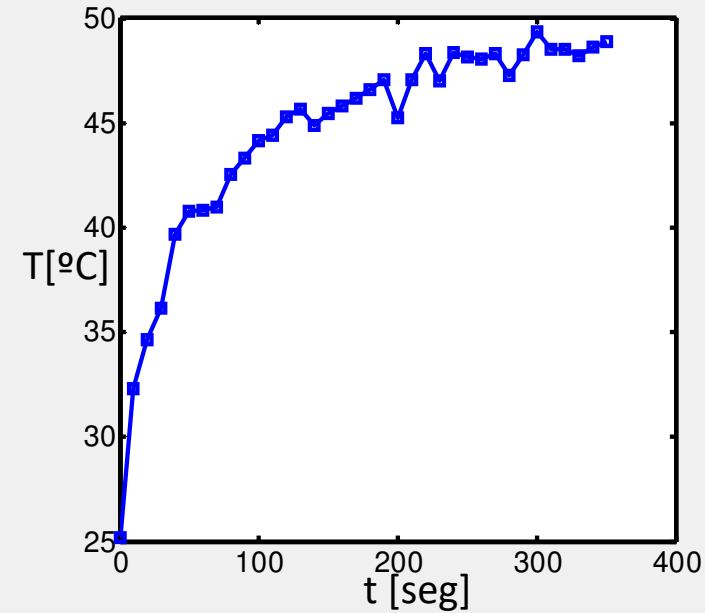
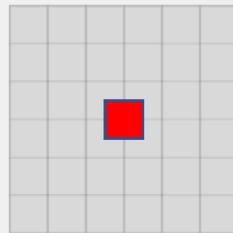
- The problem analyzed has several parameters and inputs that can be modified to produce different results on the output variables
- Parameter estimation, state estimation, optimization and control can be performed on the system with different objectives.
- Model reduction may be necessary in many of the previous tasks
- Model reduction is proposed here by reducing the dimensionality of the heat transfer problem.
- Model reduction is tested by analyzing how the 1 and 2 dimensional heat transfer models behave with respect to the 3 dimensional model.
- The analysis is performed by using the outputs of the system to estimate its parameters.
- The test is performed over samples with different types of illuminations in order to meet the assumptions of infinite dimensions for the dimensions not considered.
- The test is performed not only in terms of how much the state variables in the reduced models follow the real ones, but also on how the model parameters are close to the real parameters.
- To do so, the model parameters are estimated for the different reduced models using data from the full models to check the validity of the approximation.
- Some alternatives are explored in order to improve the way in which the reduced models see the parameters.

Case A: partial illumination in two dimensions

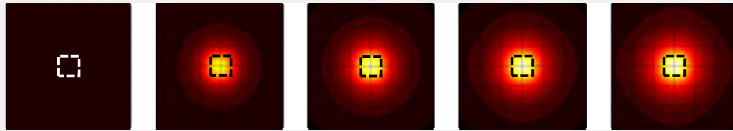
Sample dimension: 18x18x2 mm

Illumination: 0.1575 watts
(0.0175watts/mm²) distributed
in 3x3mm² centered in the
center of the sample.

Measurement: in the center of
the sample



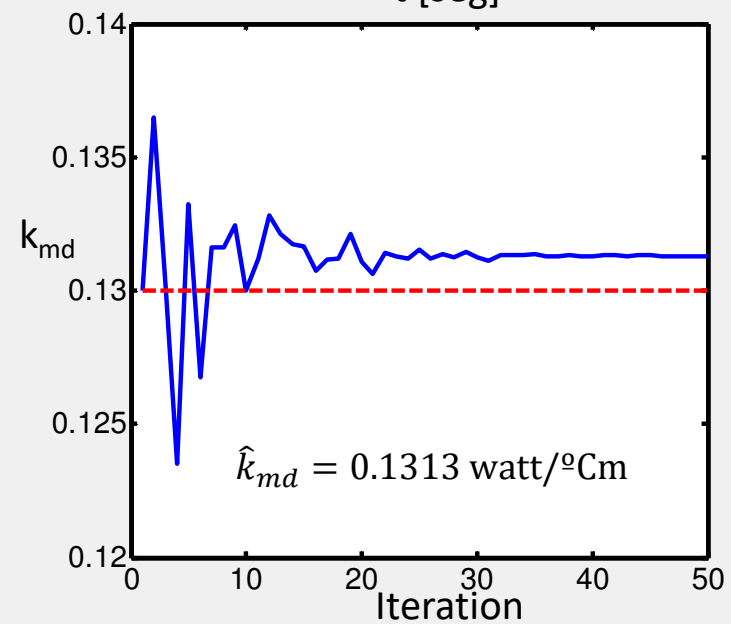
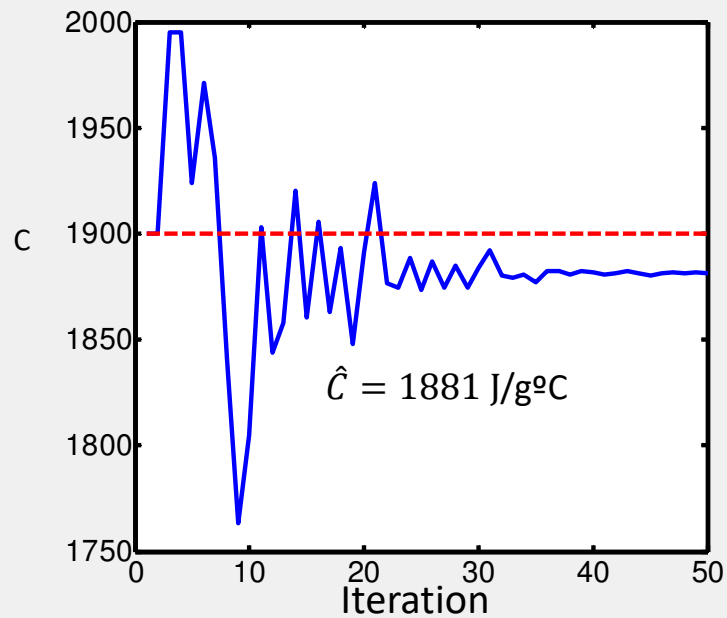
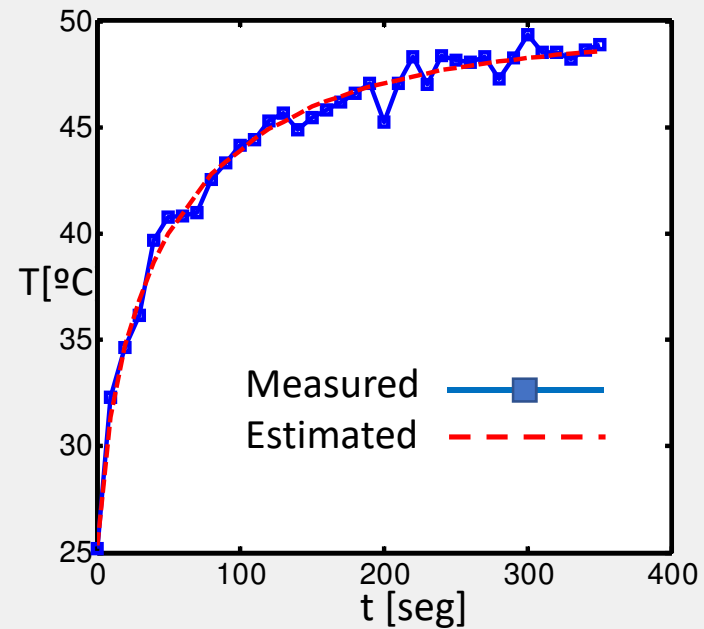
Case A: 3D



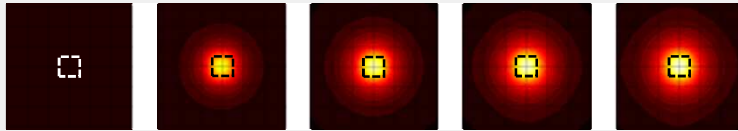
Measurements: 3D model + Noise

Estimation: 3D model

Number of measurements: 36



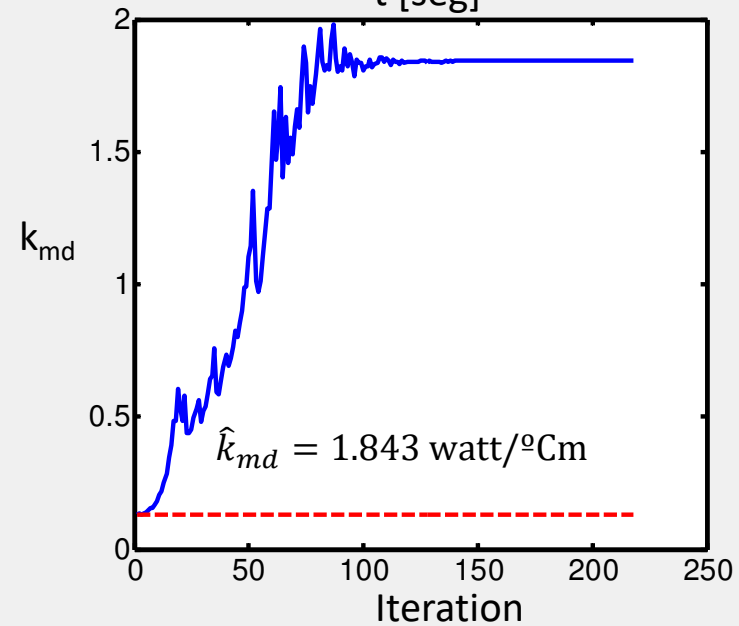
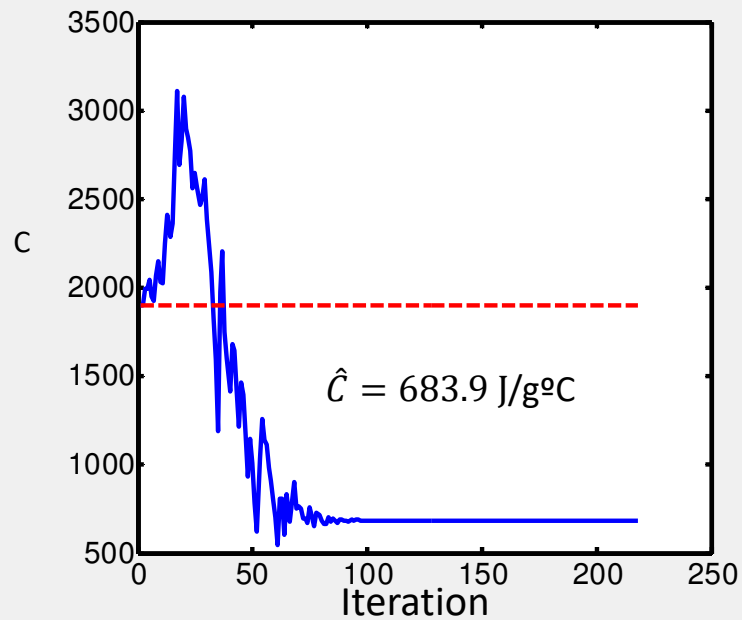
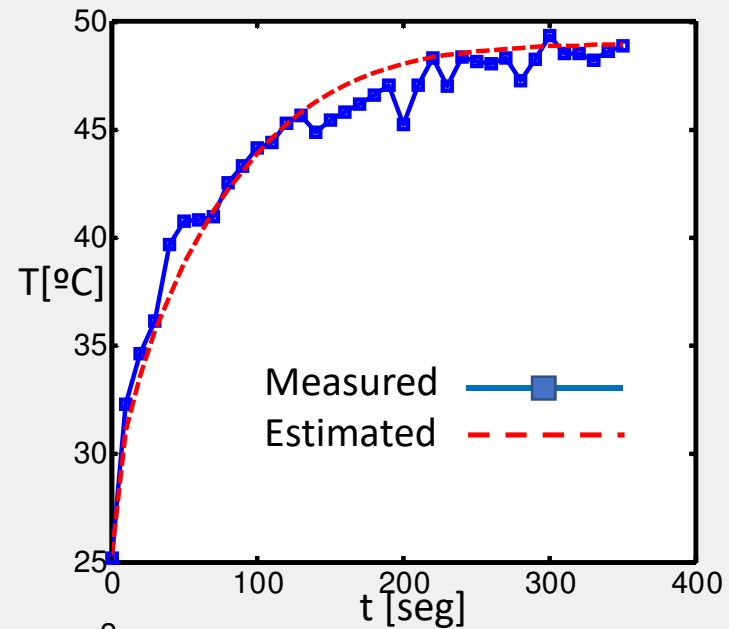
Case A: 2D



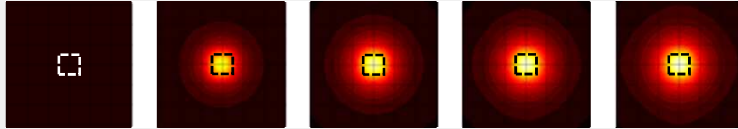
Measurements: 3D model + Noise

Estimation: 2D model

Number of measurements: 36



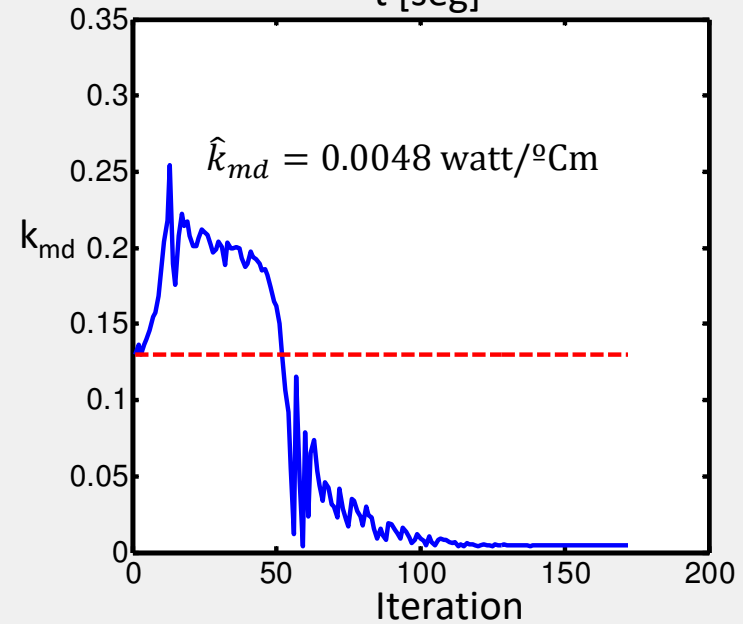
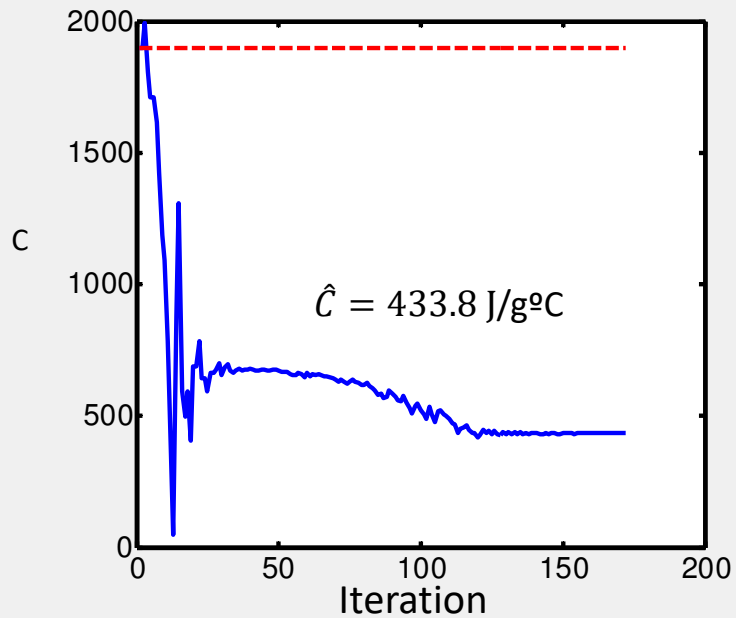
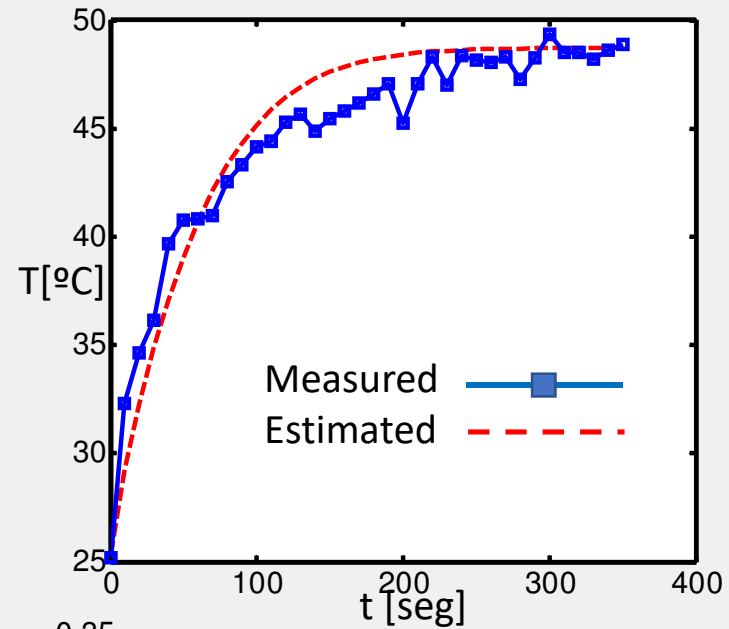
Case A: 1D



Measurements: 3D model + Noise

Estimation: 1D model

Number of measurements: 36

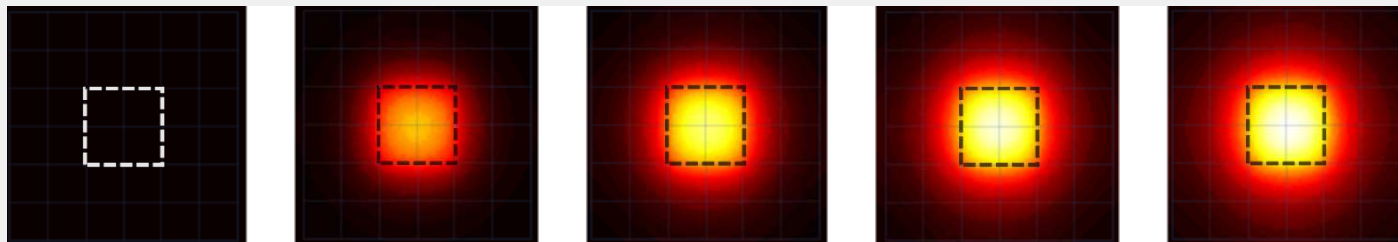
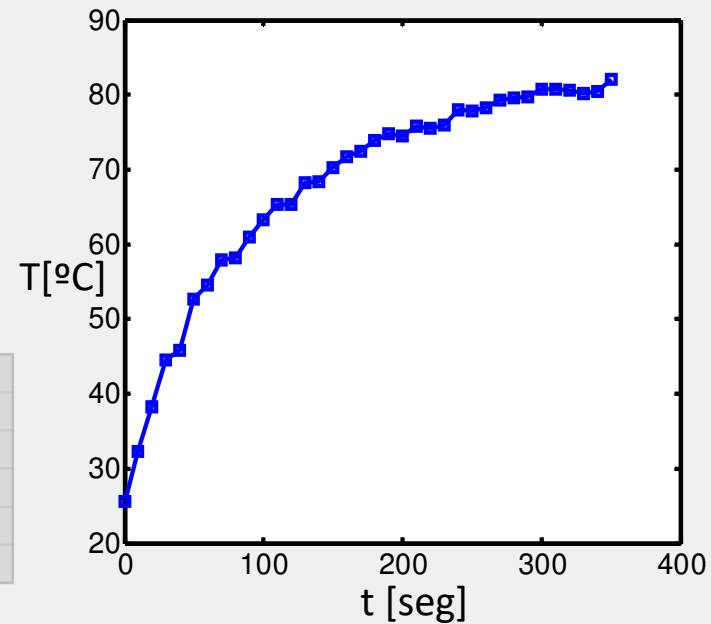
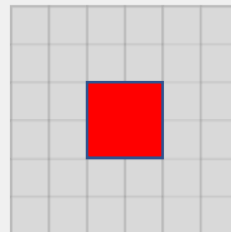


Case B: partial illumination in two dimensions

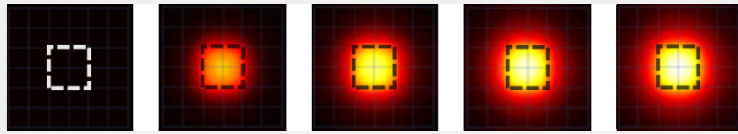
Sample dimension: 18x18x2 mm

Illumination: 0.63 watts
(0.0175watts/mm²) distributed
in 6x6mm² centered in the
center of the sample.

Measurement: in the center of
the sample



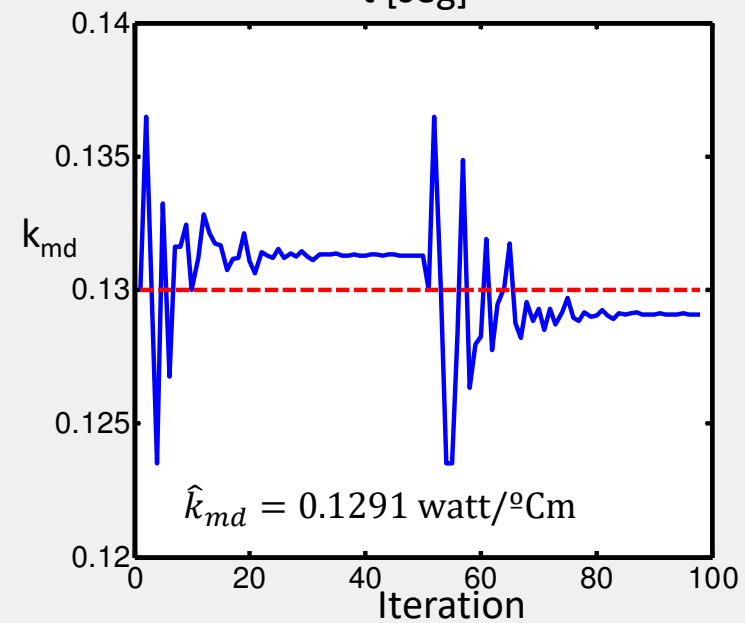
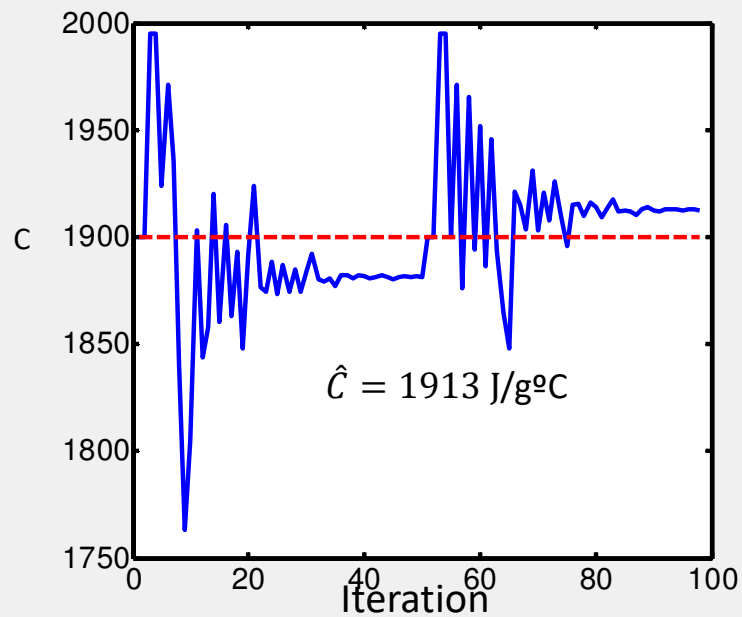
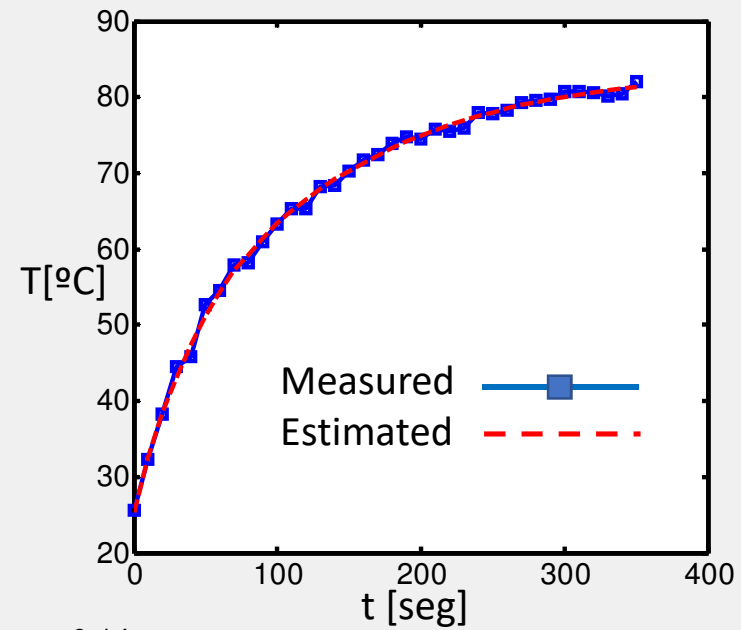
Case B: 3D



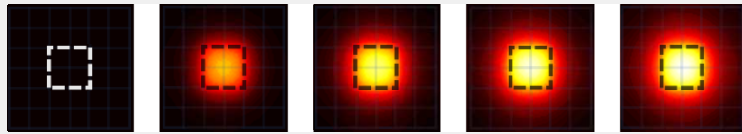
Measurements: 3D model + Noise

Estimation: 3D model

Number of measurements: 36



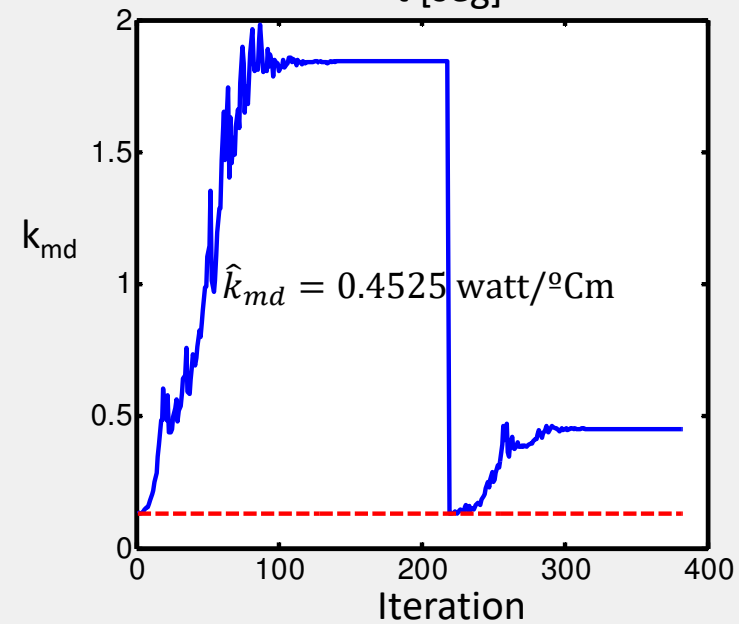
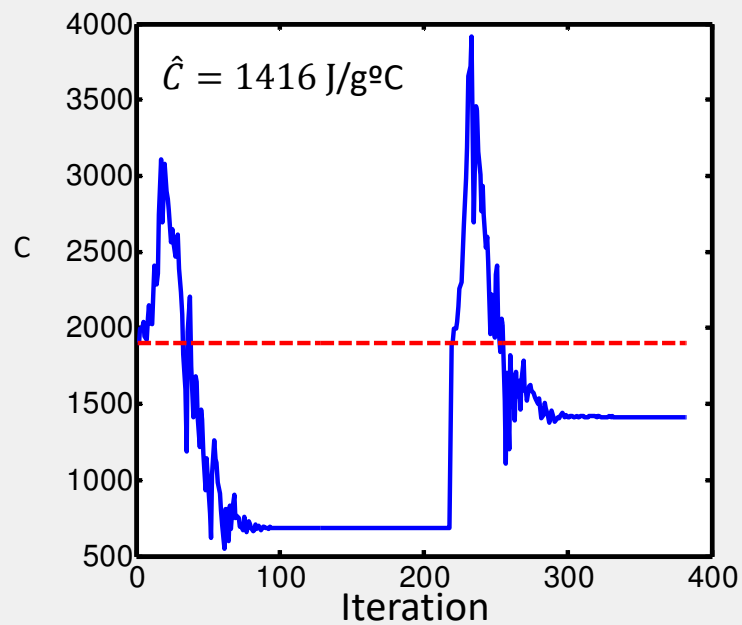
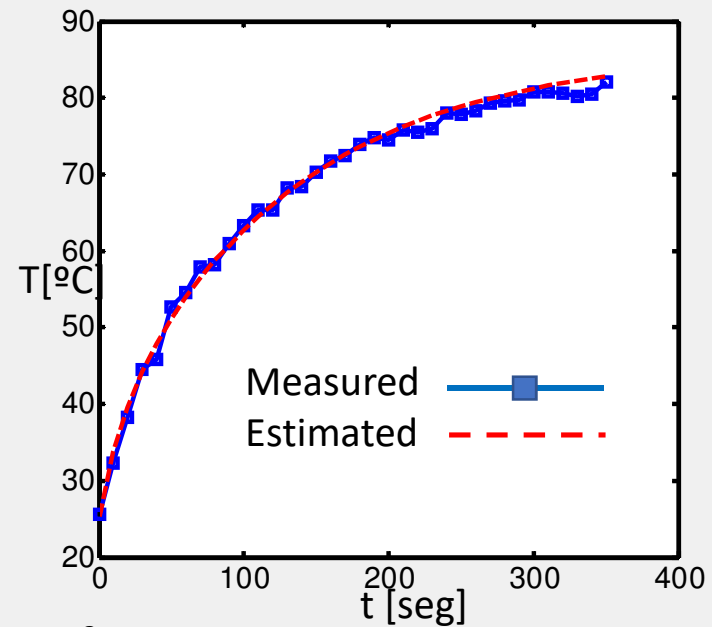
Case B: 2D



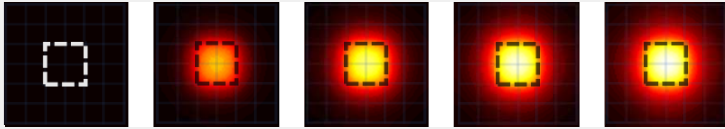
Measurements: 3D model + Noise

Estimation: 2D model

Number of measurements: 36



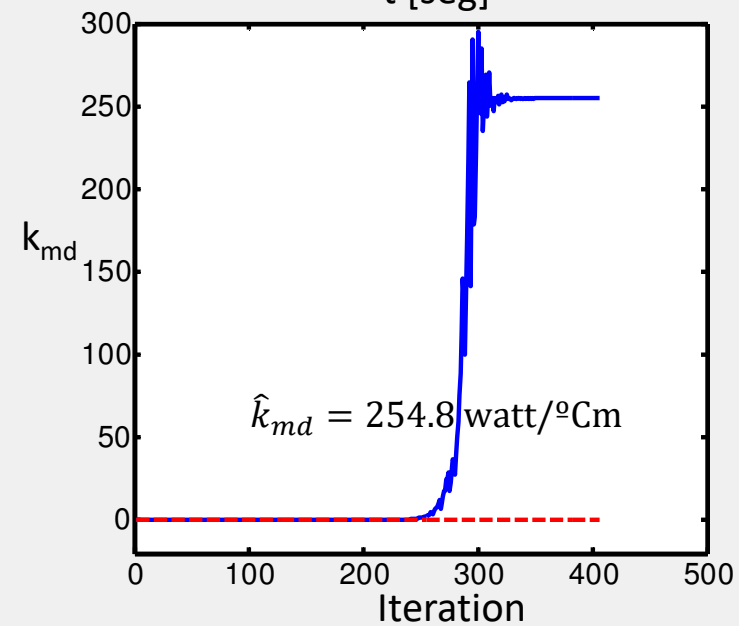
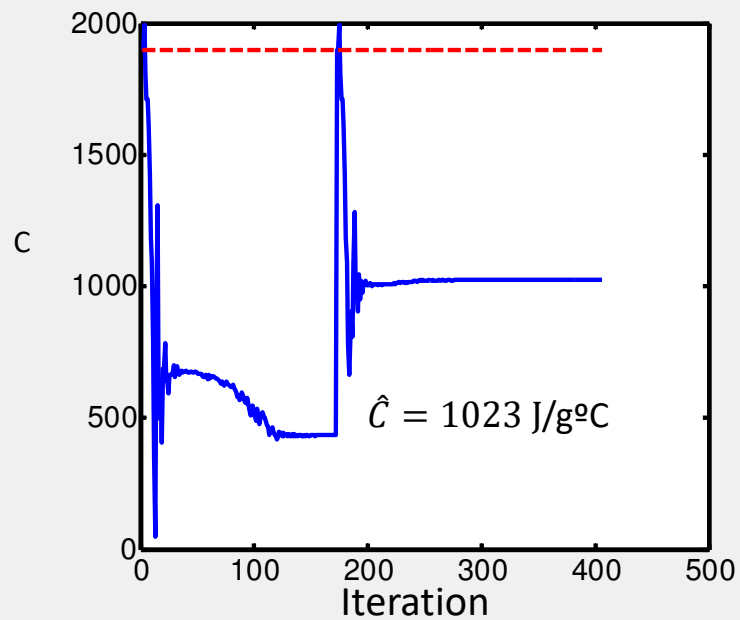
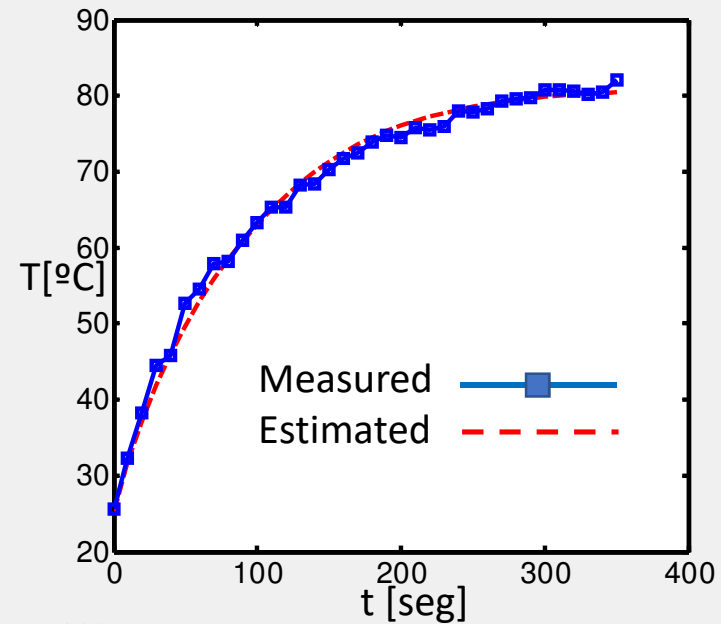
Case B: 1D



Measurements: 3D model + Noise

Estimation: 1D model

Number of measurements: 36

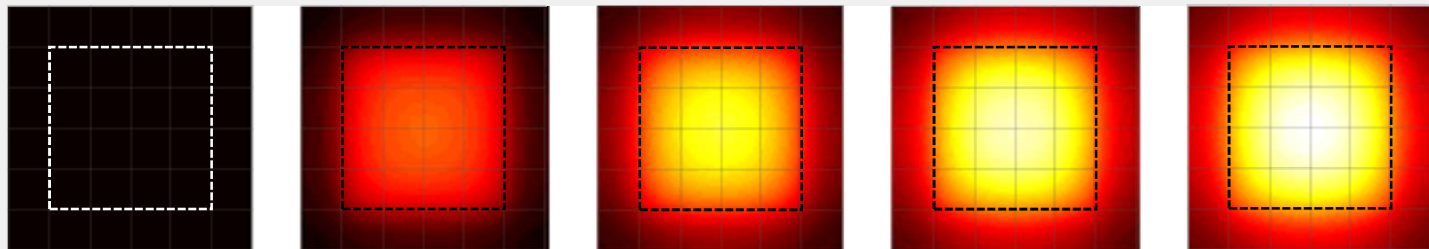
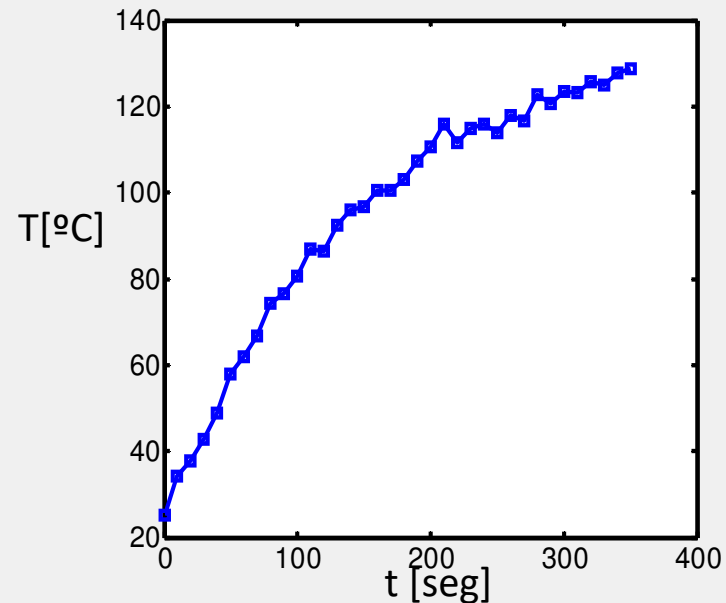
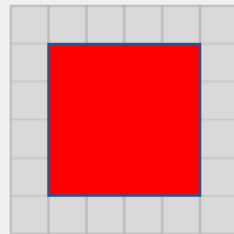


Case C: partial illumination in two dimensions

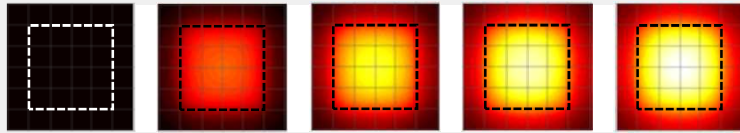
Sample dimension: 18x18x2 mm

Illumination: 2.52 watts,
(0.0175watts/mm²) distributed in
12x12mm² centered in the center
of the sample.

Measurement: in the center of the
sample



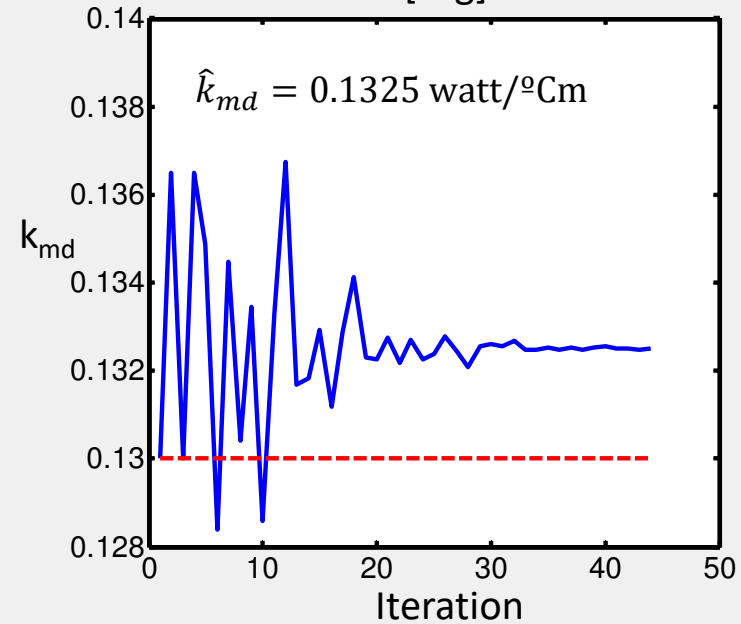
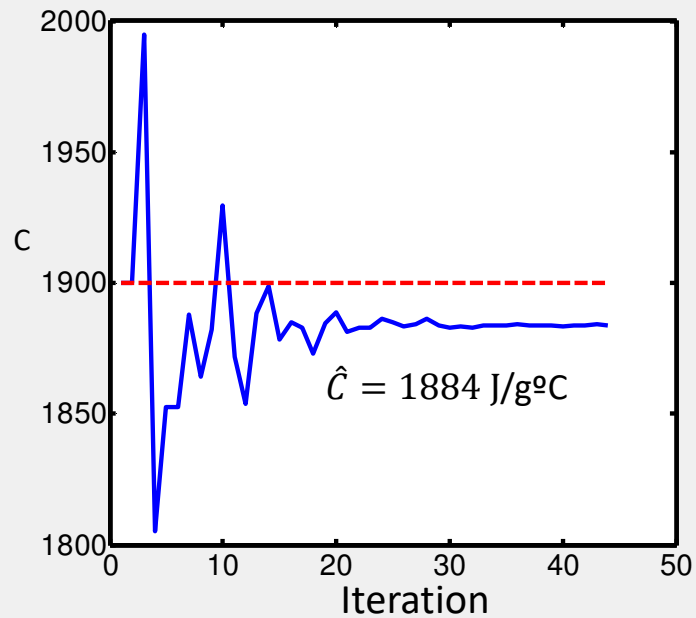
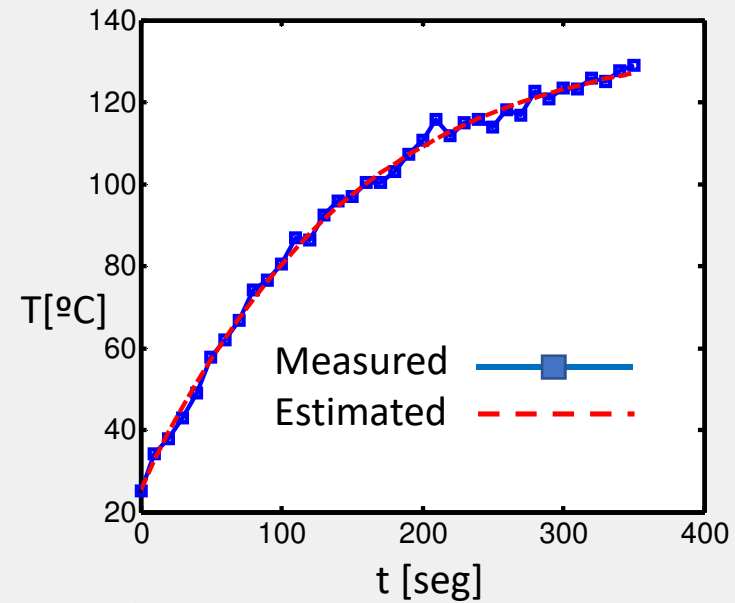
Case C: 3D



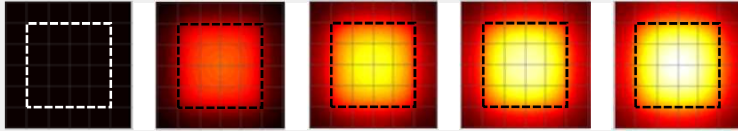
Measurements: 3D model + Noise

Estimation: 3D model

Number of measurements: 36



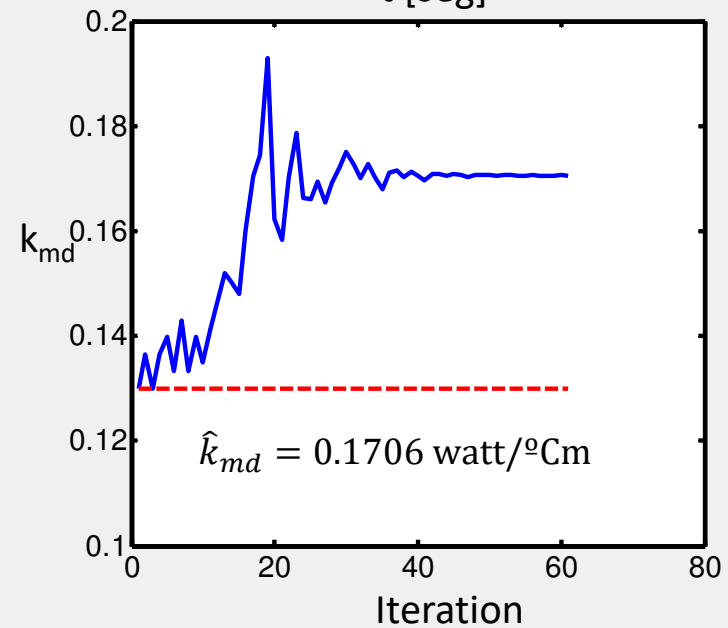
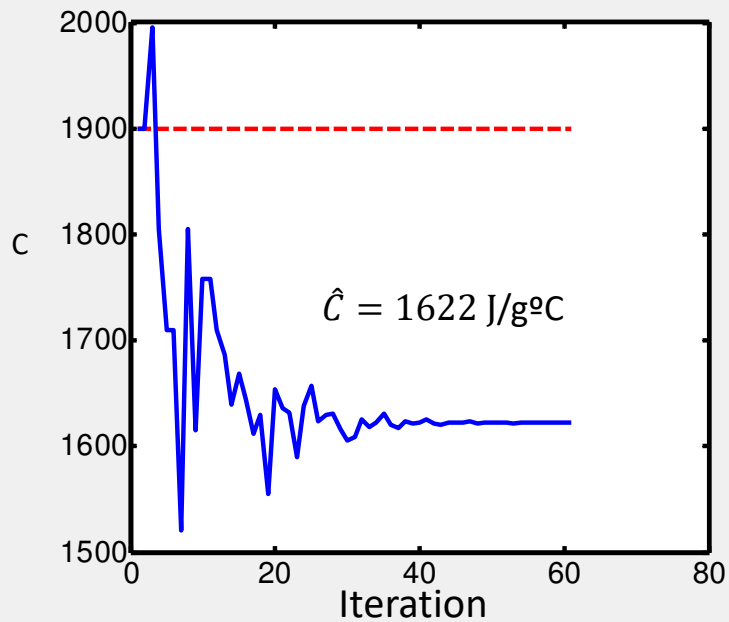
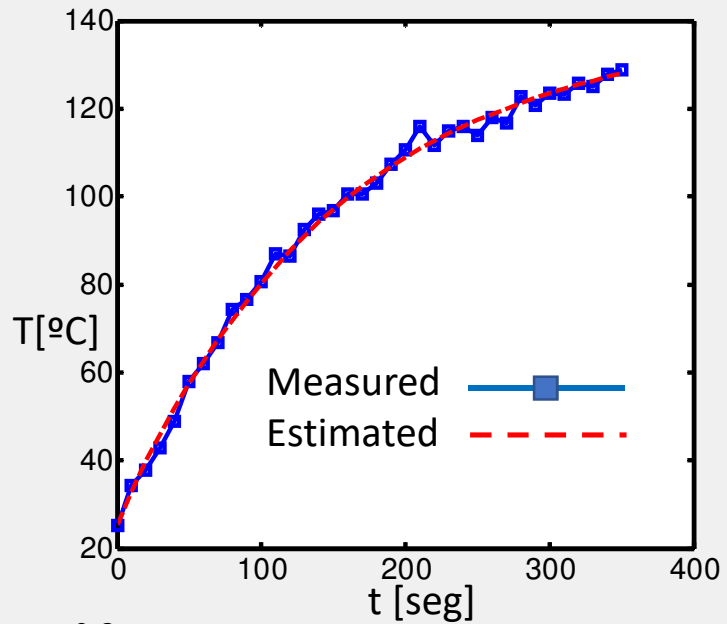
Case C: 2D



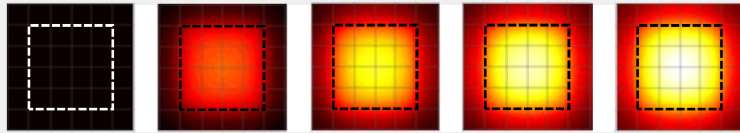
Measurements: 3D model + Noise

Estimation: 2D model

Number of measurements: 36



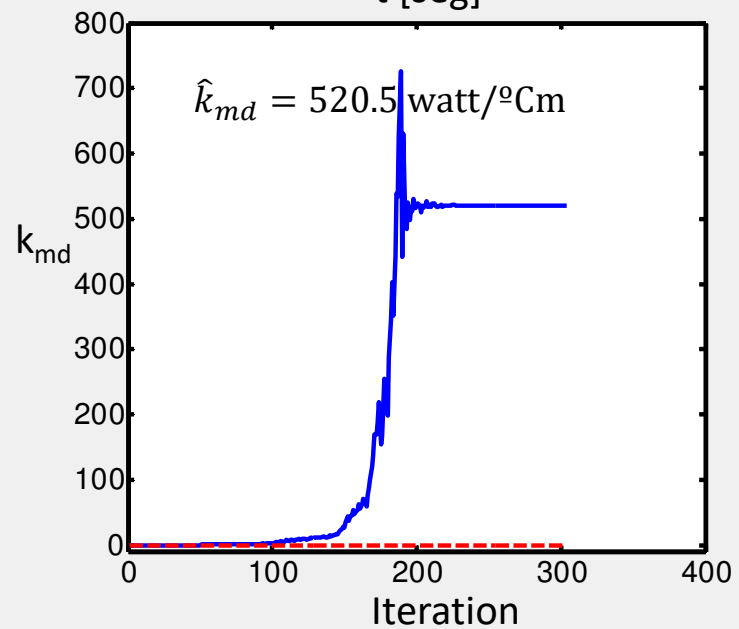
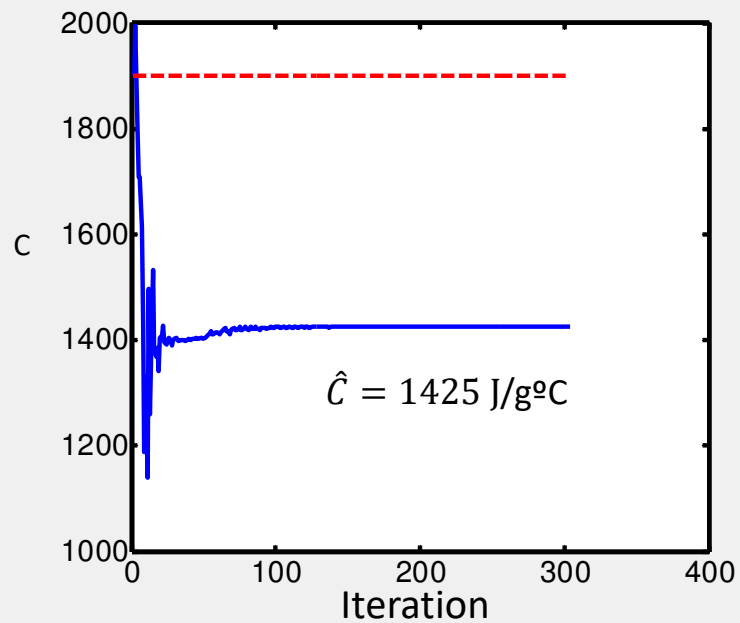
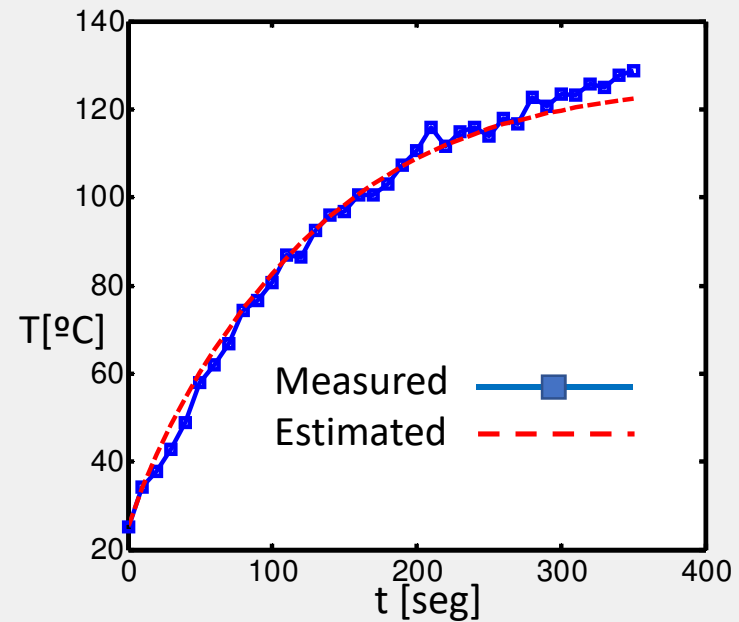
Case C: 1D



Measurements: 3D model + Noise

Estimation: 1D model

Number of measurements: 36

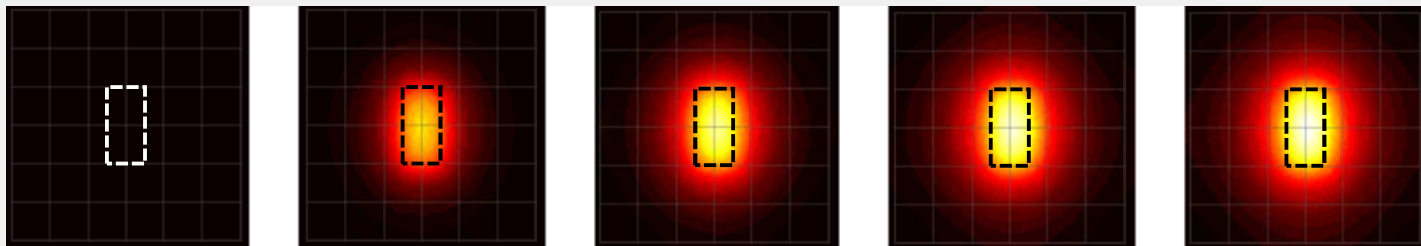
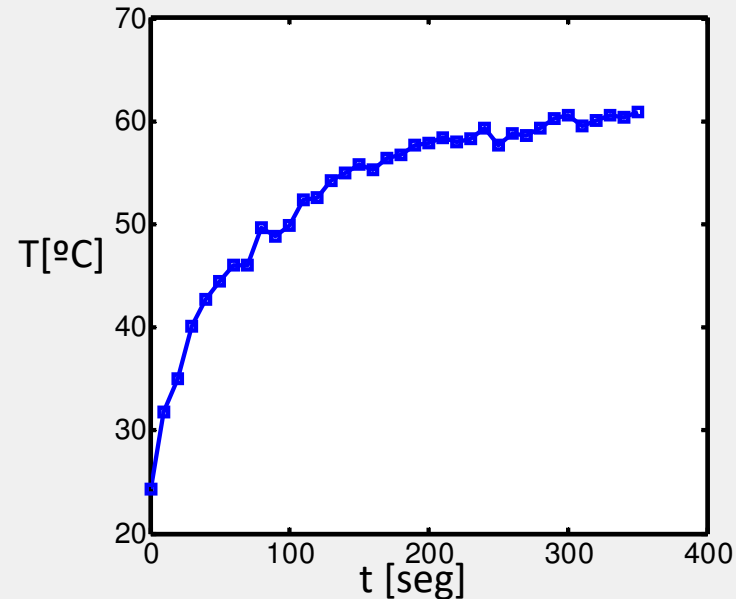
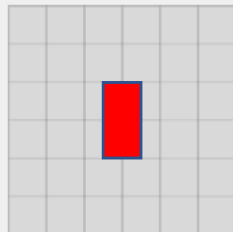


Case D: partial illumination in two dimensions

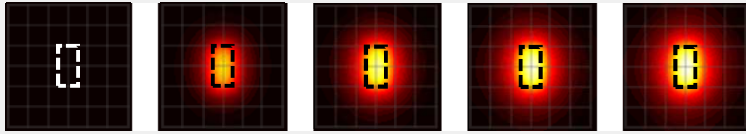
Sample dimension: 18x18x2 mm

Illumination: 0.315 watts,
(0.0175watts/mm²) distributed in
3x6mm² centered in the center of
the sample.

Measurement: in the center of the
sample



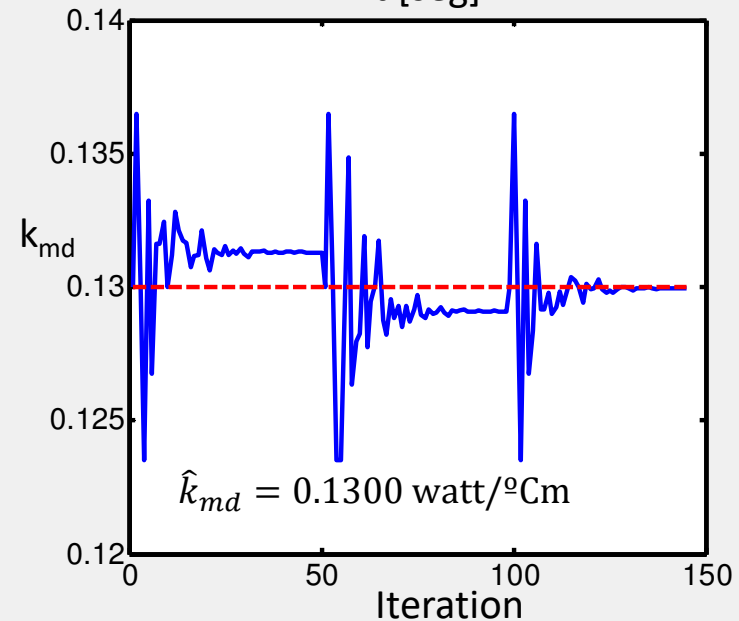
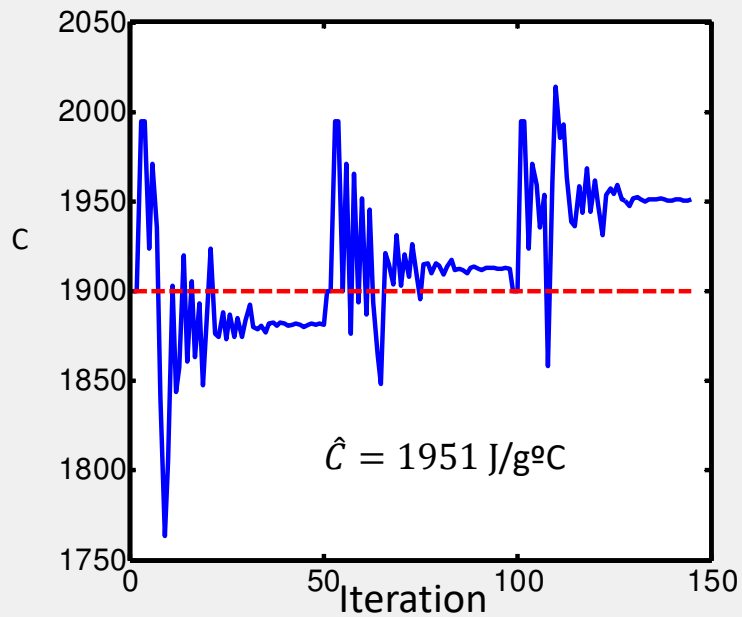
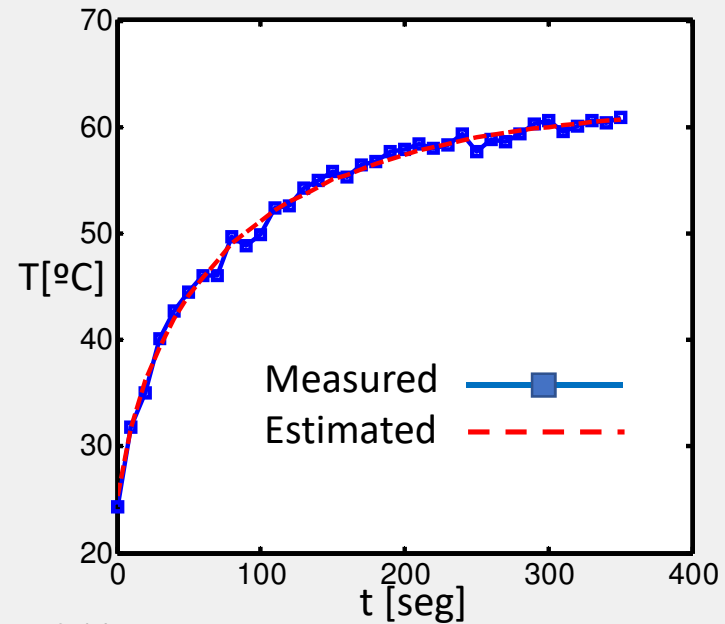
Case D: 3D



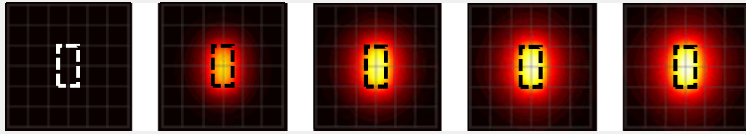
Measurements: 3D model + Noise

Estimation: 3D model

Number of measurements: 36



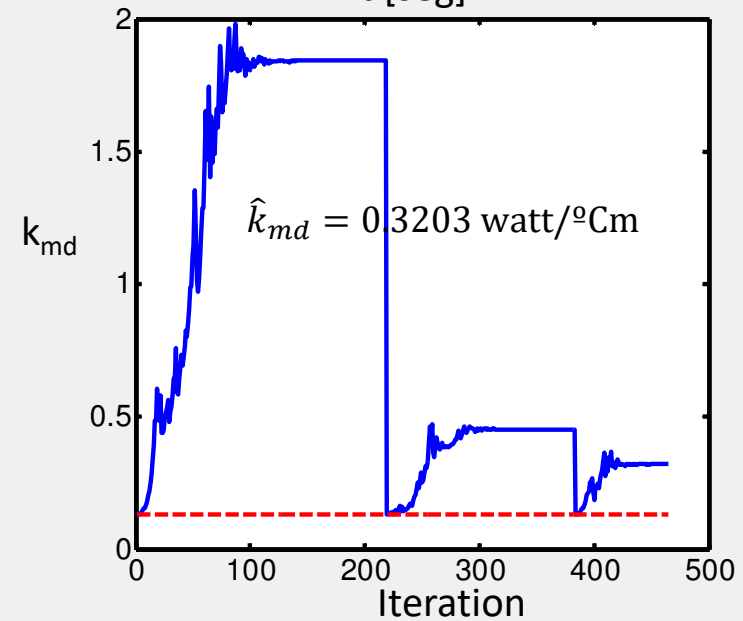
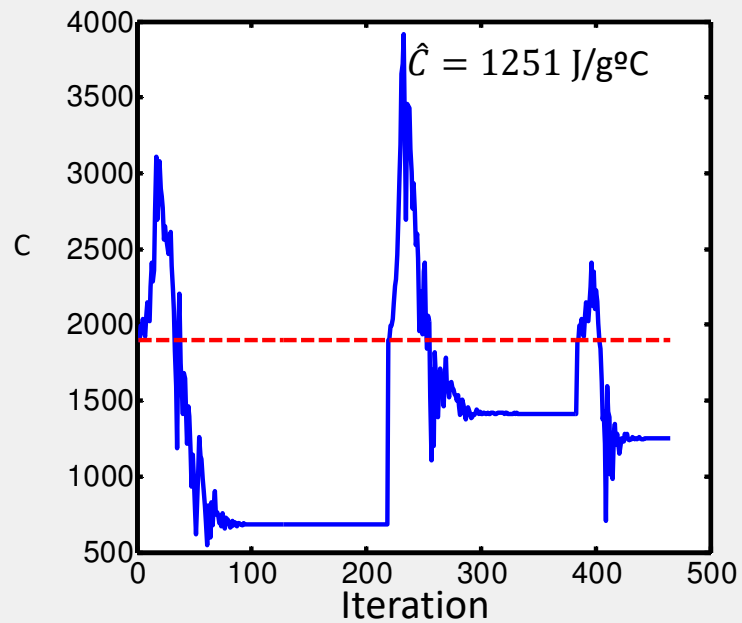
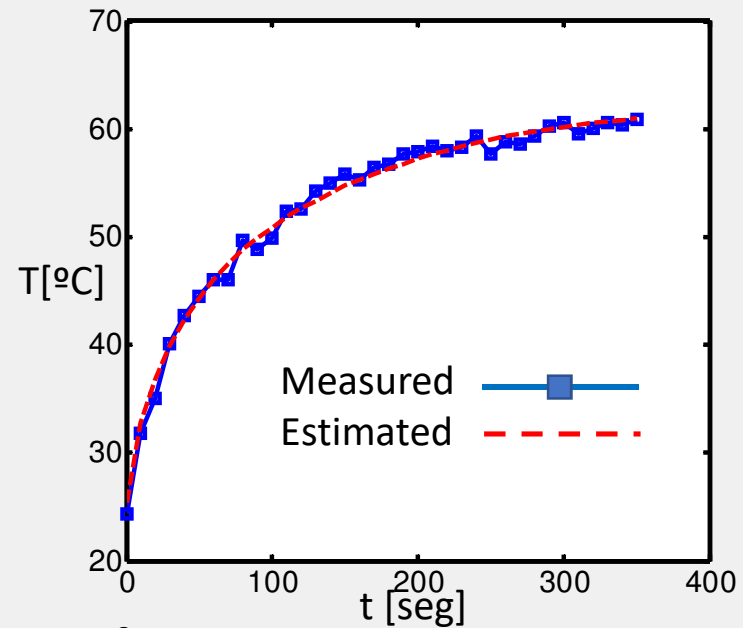
Case D: 2D



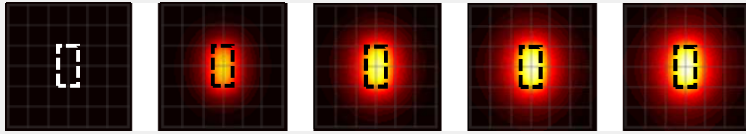
Measurements: 3D model + Noise

Estimation: 2D model

Number of measurements: 36



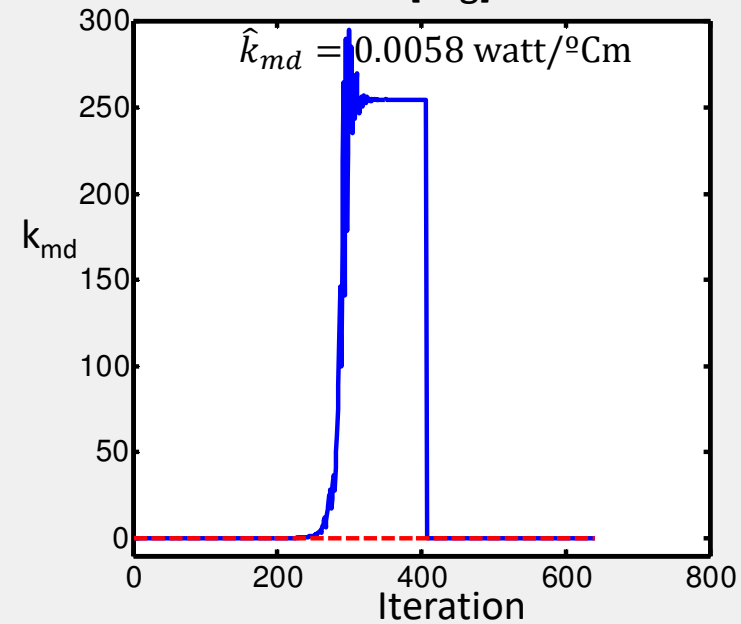
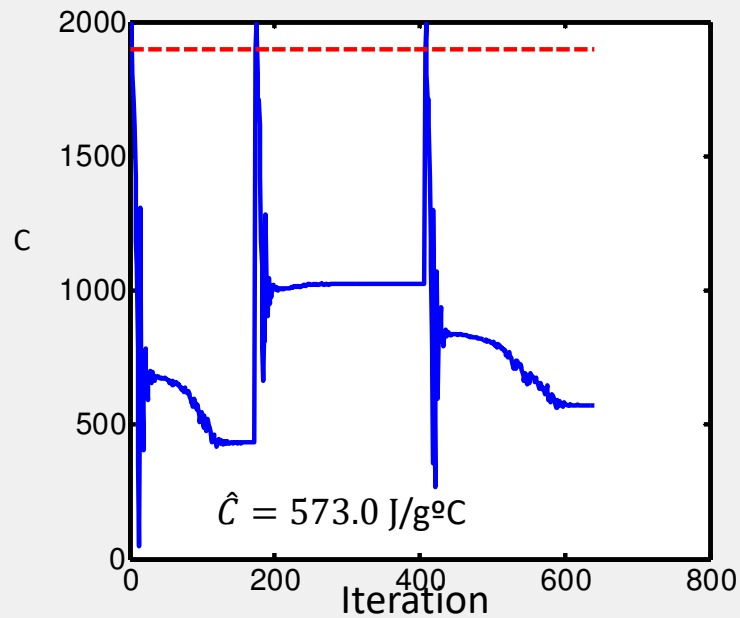
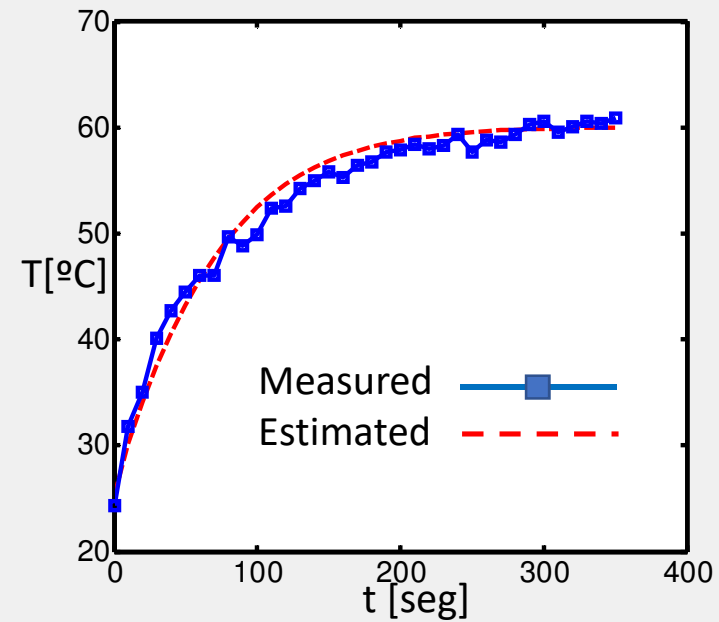
Case D: 1D



Measurements: 3D model + Noise

Estimation: 1D model

Number of measurements: 36

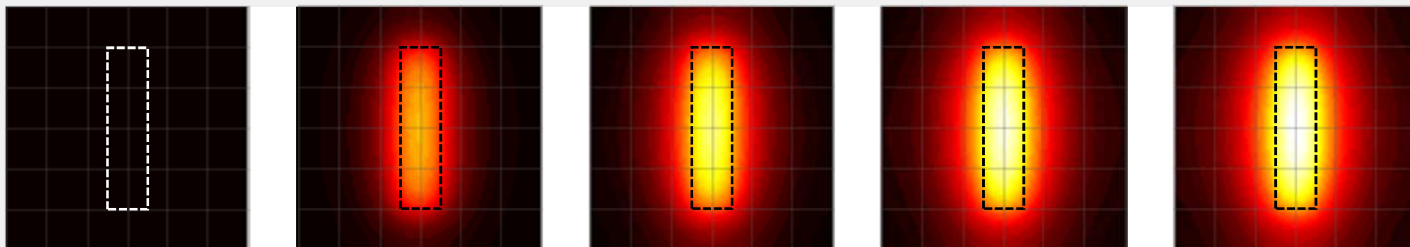
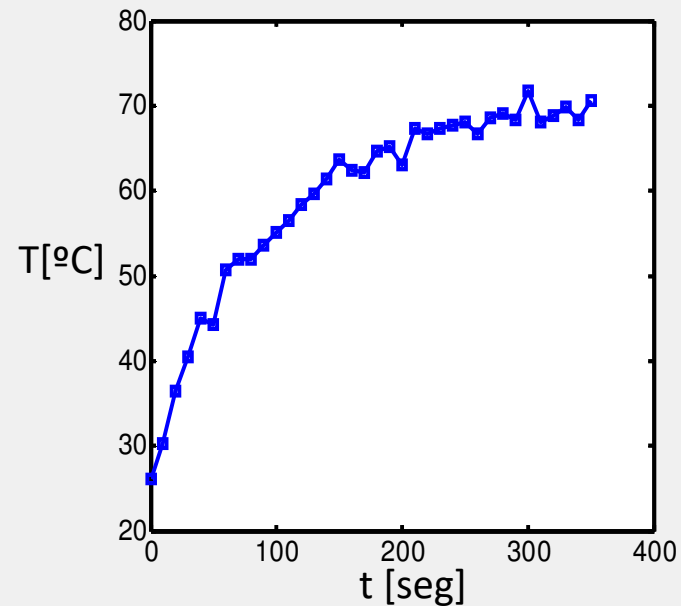
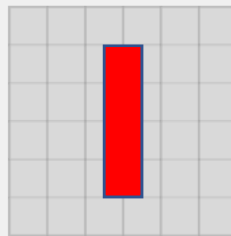


Case E: partial illumination in two dimensions

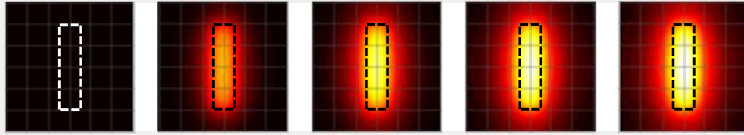
Sample dimension: 18x18x2 mm

Illumination: 0.63 watts,
(0.0175watts/mm²) distributed
in 3x12mm² centered in the
center of the sample.

Measurement: in the center of
the sample



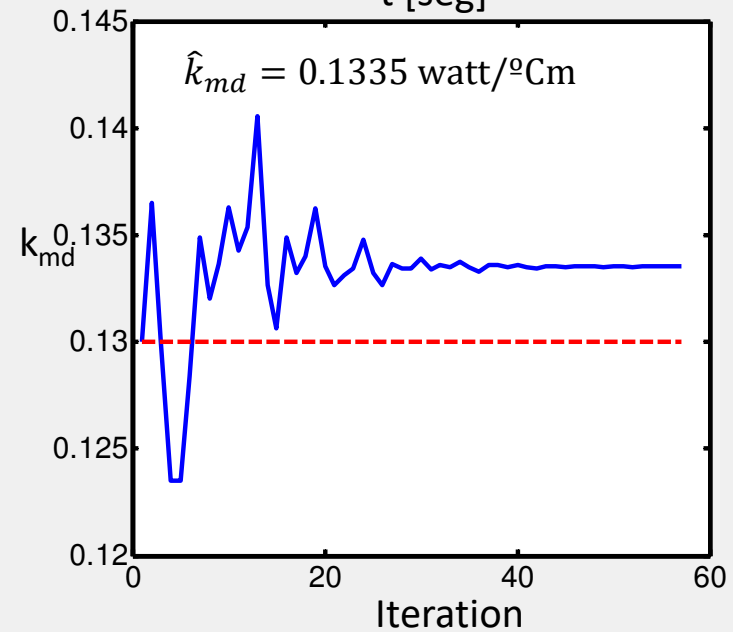
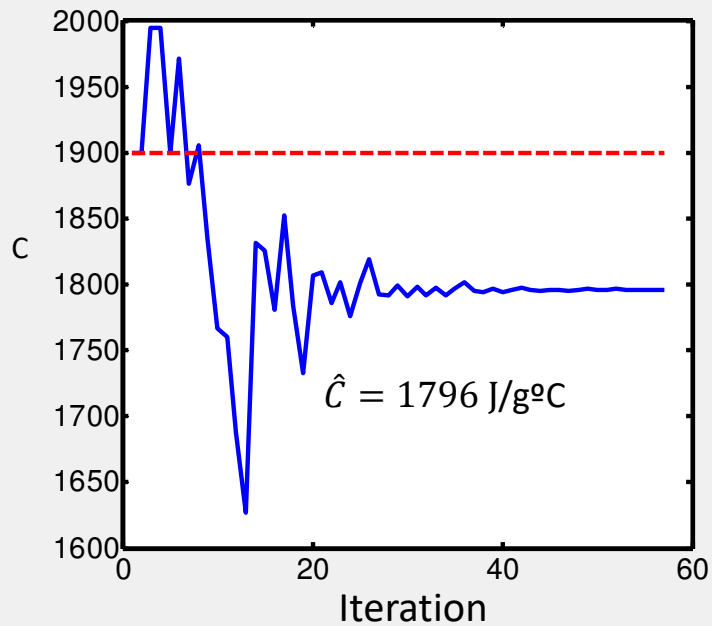
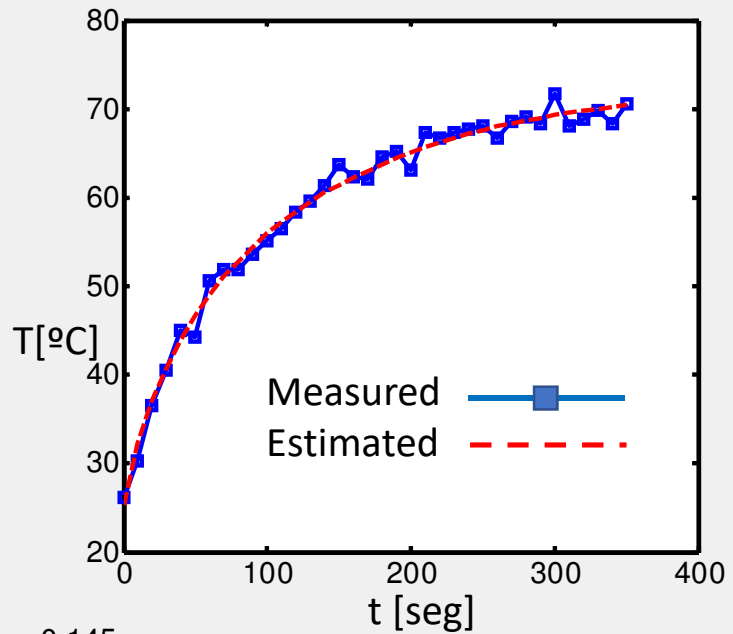
Case E: 3D



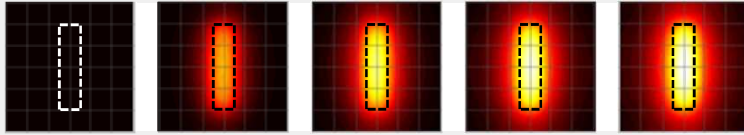
Measurements: 3D model + Noise

Estimation: 3D model

Number of measurements: 36



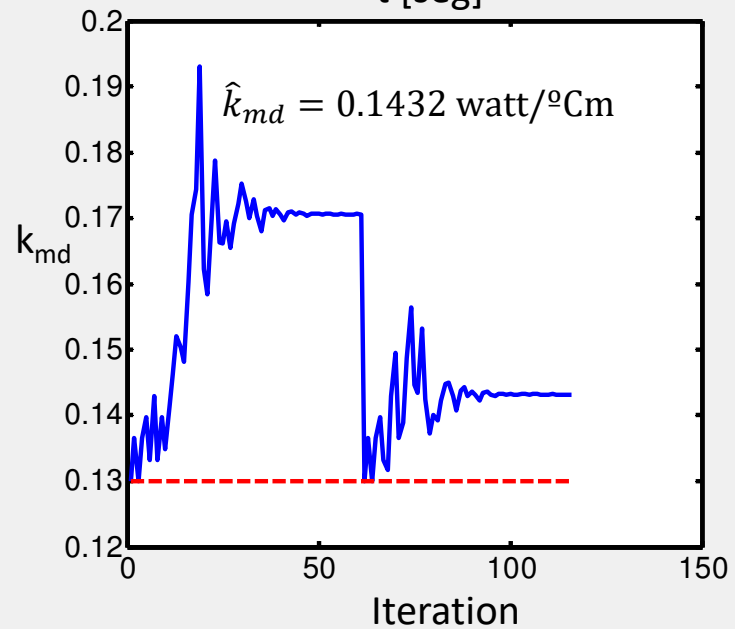
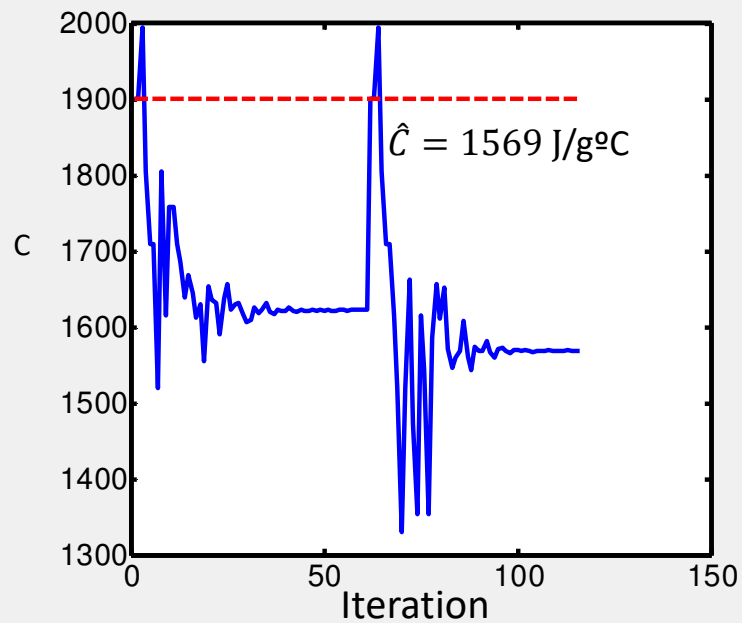
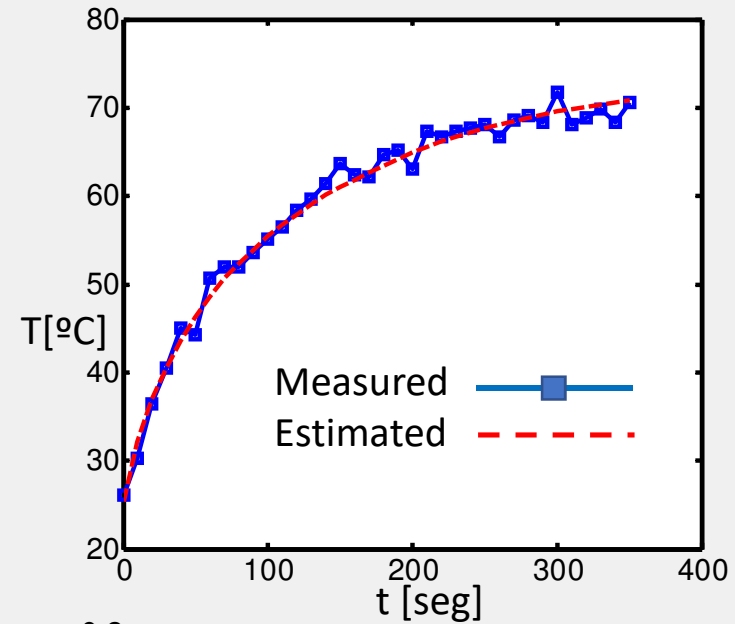
Case E: 2D



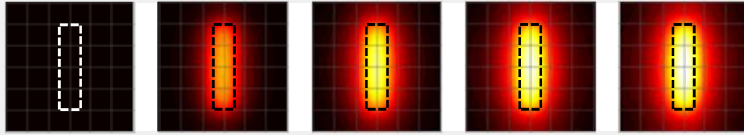
Measurements: 3D model + Noise

Estimation: 2D model

Number of measurements: 36



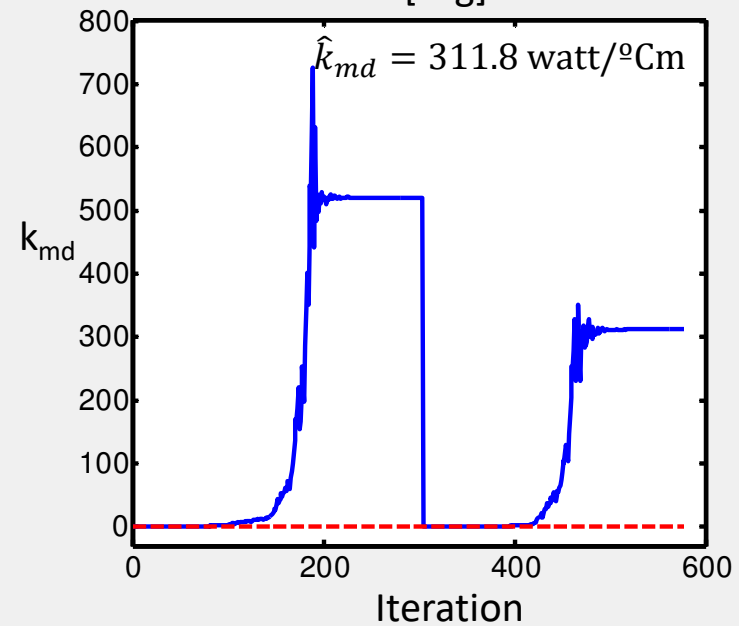
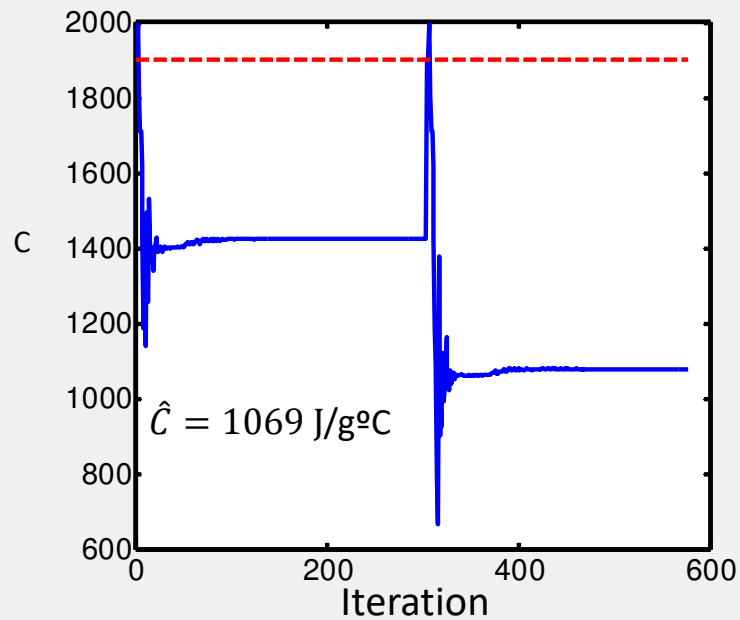
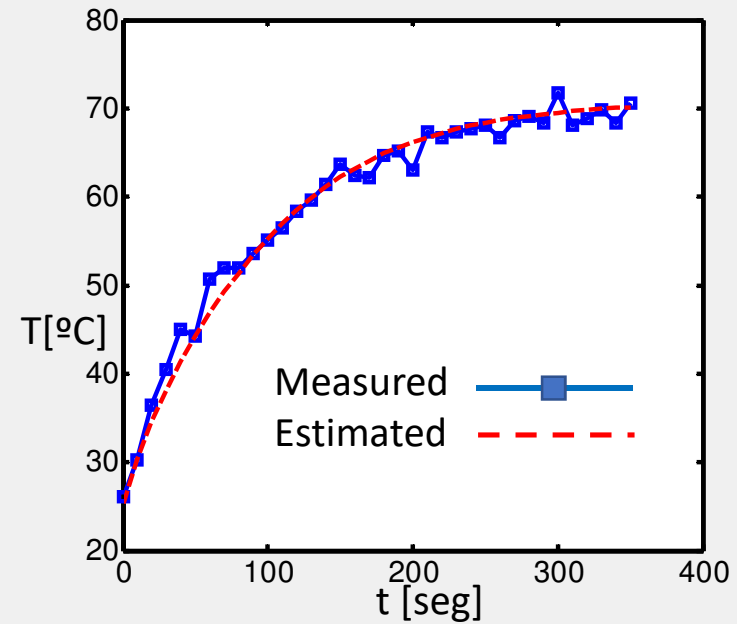
Case E: 1D



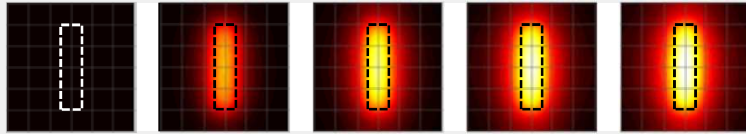
Measurements: 3D model + Noise

Estimation: 1D model

Number of measurements: 36

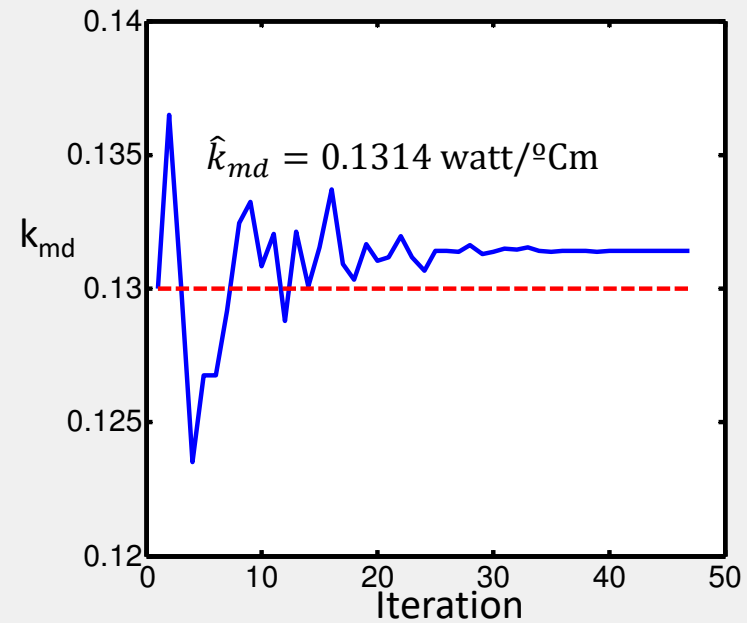
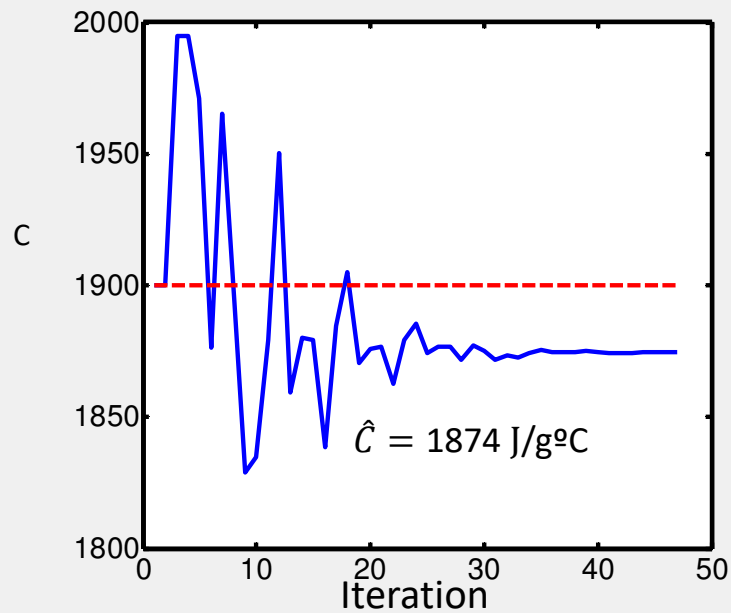
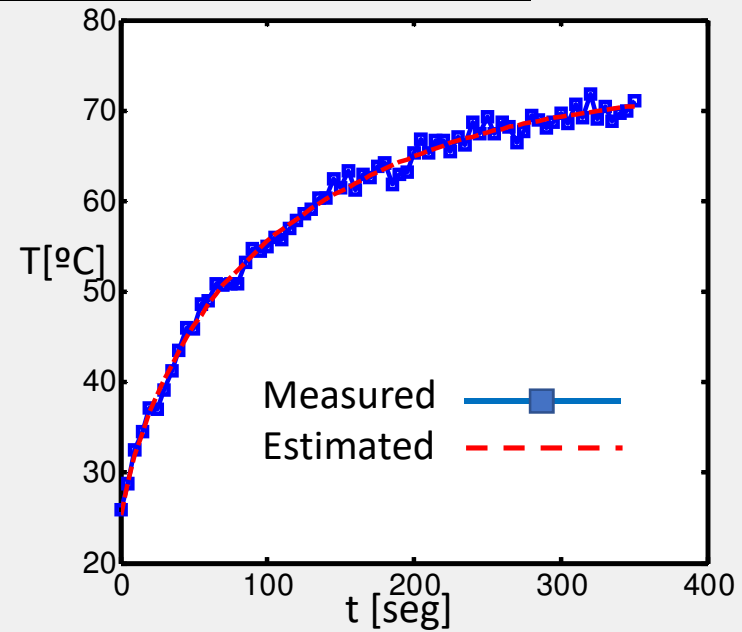


Case E: 3D (71 measurements)

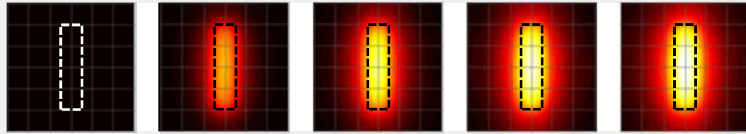


Measurements: 3D model + Noise

Estimation: 3D model

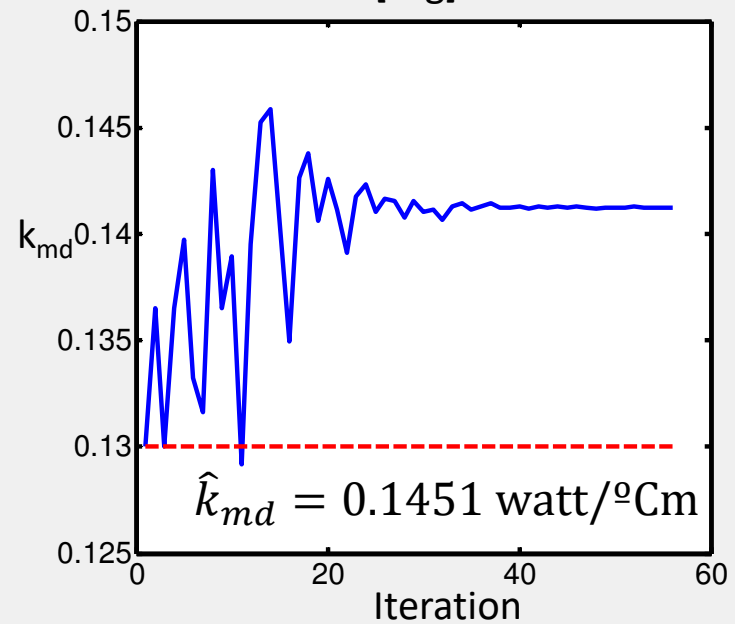
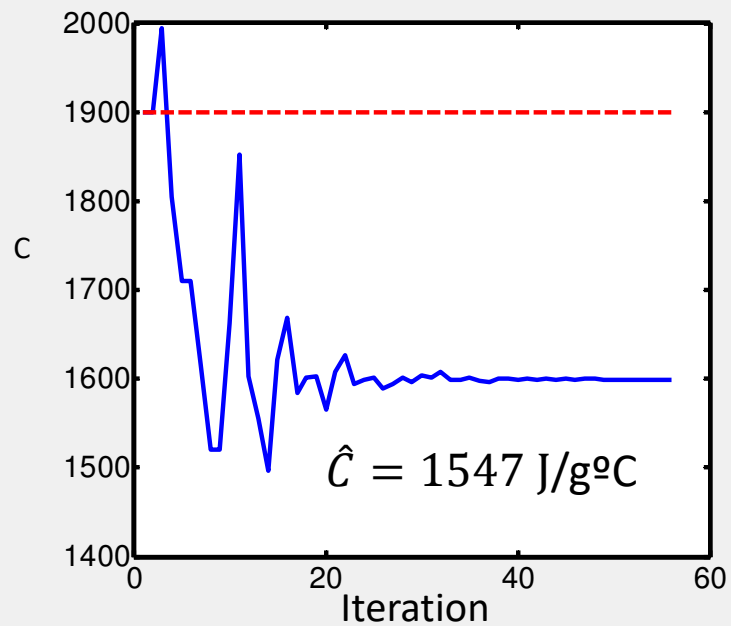
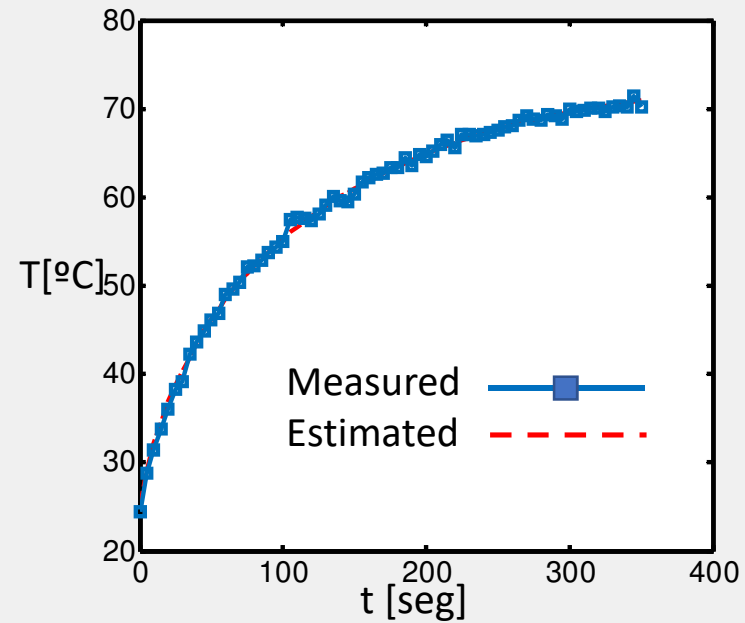


Case E: 2D (71 measurements)

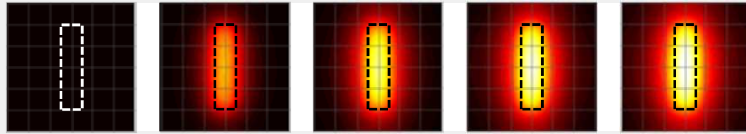


Measurements: 3D model + Noise

Estimation: 2D model

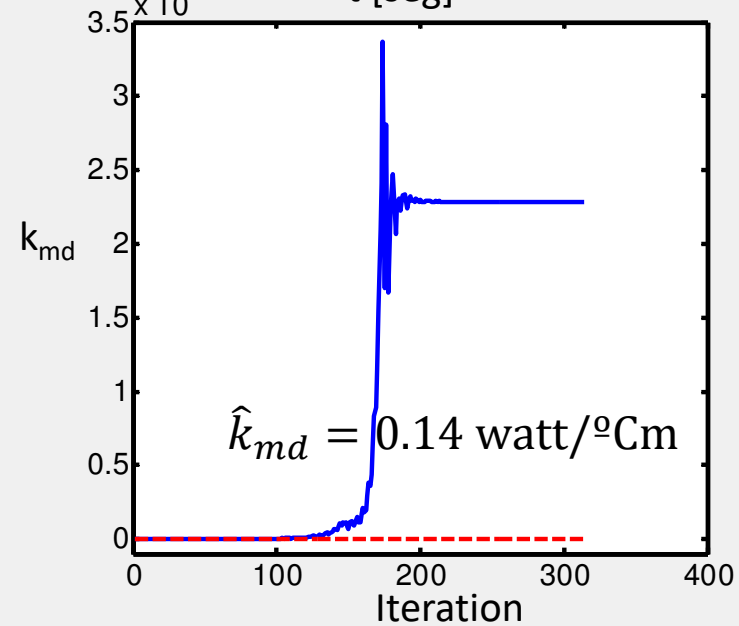
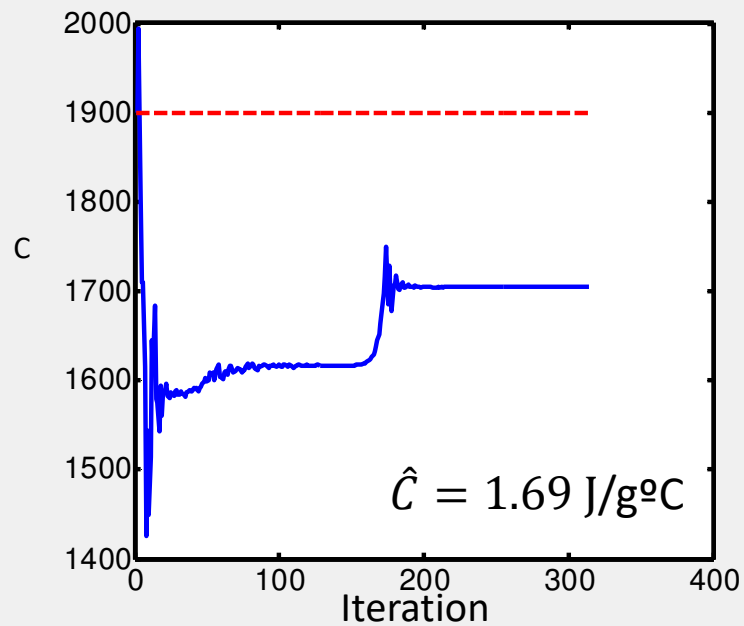
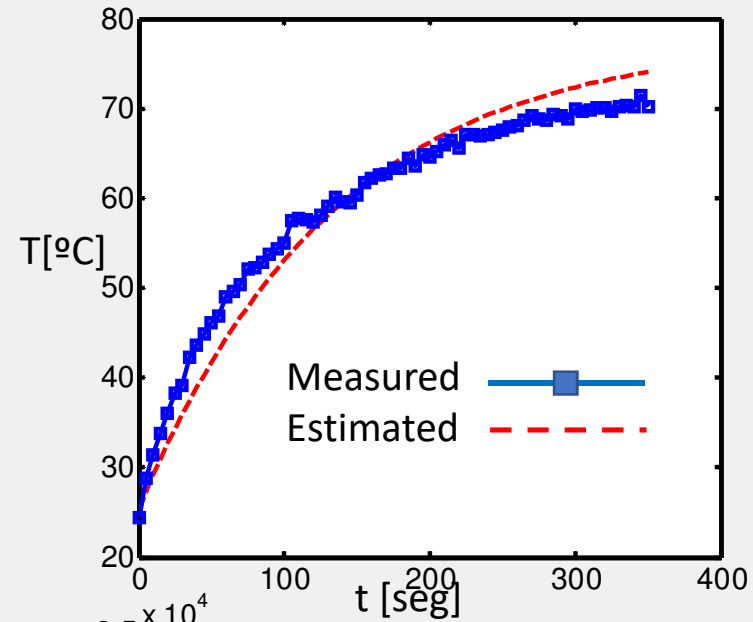


Case E: 1D (71 measurements)



Measurements: 3D model + Noise

Estimation: 1D model

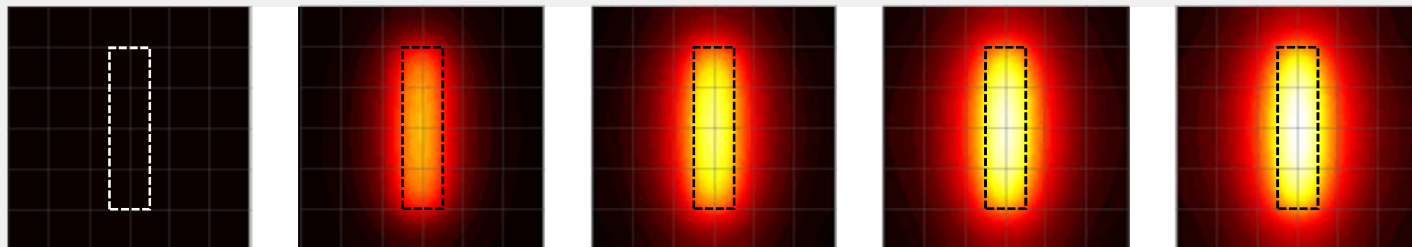
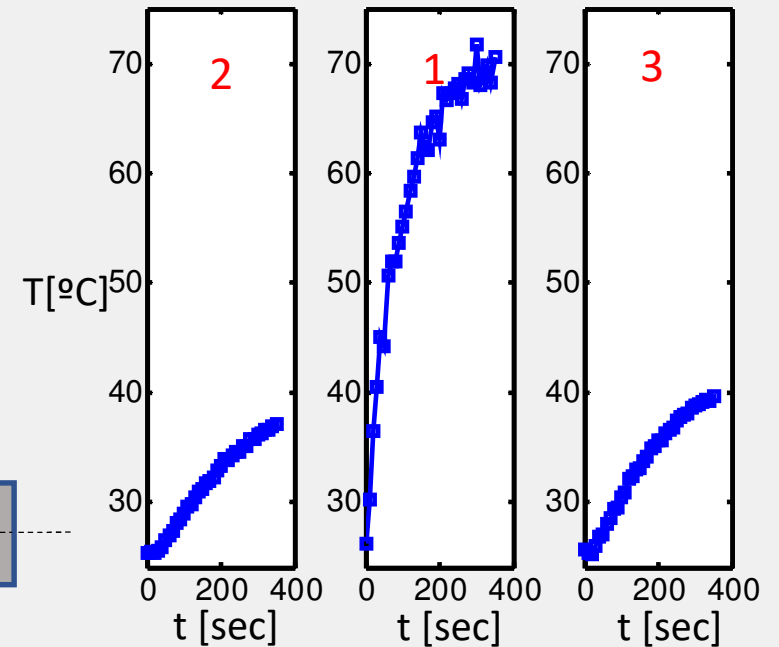
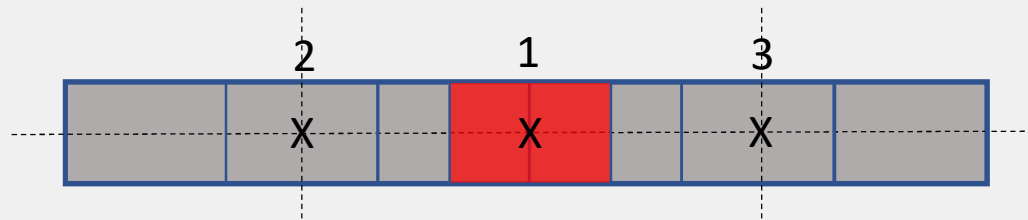
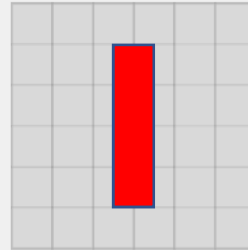


Case E: measurements in three places

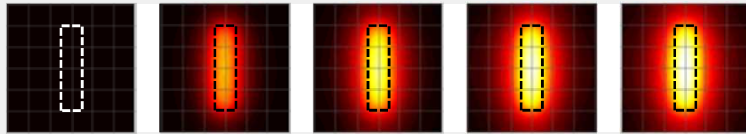
Sample dimension: 18x18x2 mm

Illumination: 0.63 watts,
(0.0175watts/mm²) distributed
in 3x12mm² centered in the
center of the sample.

Measurements: 36 in each place
1, 2 and 3



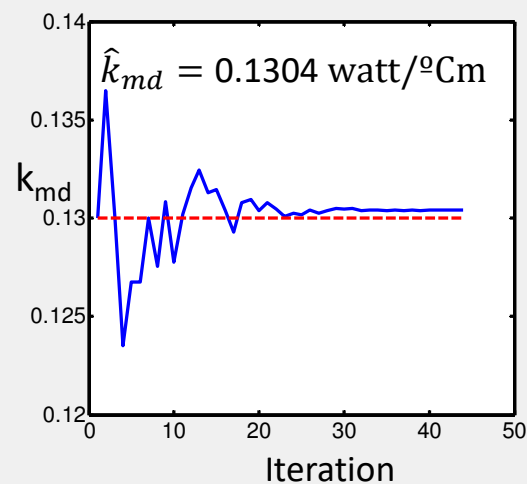
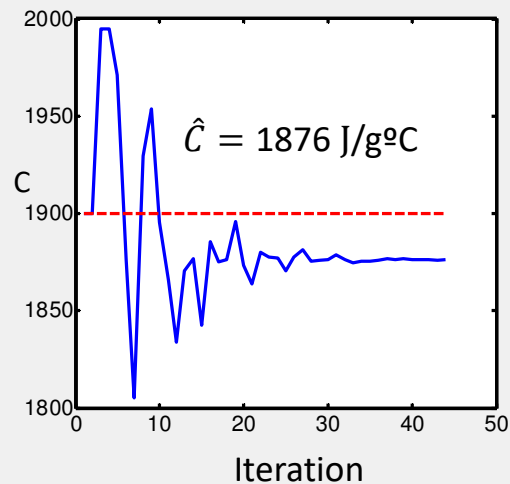
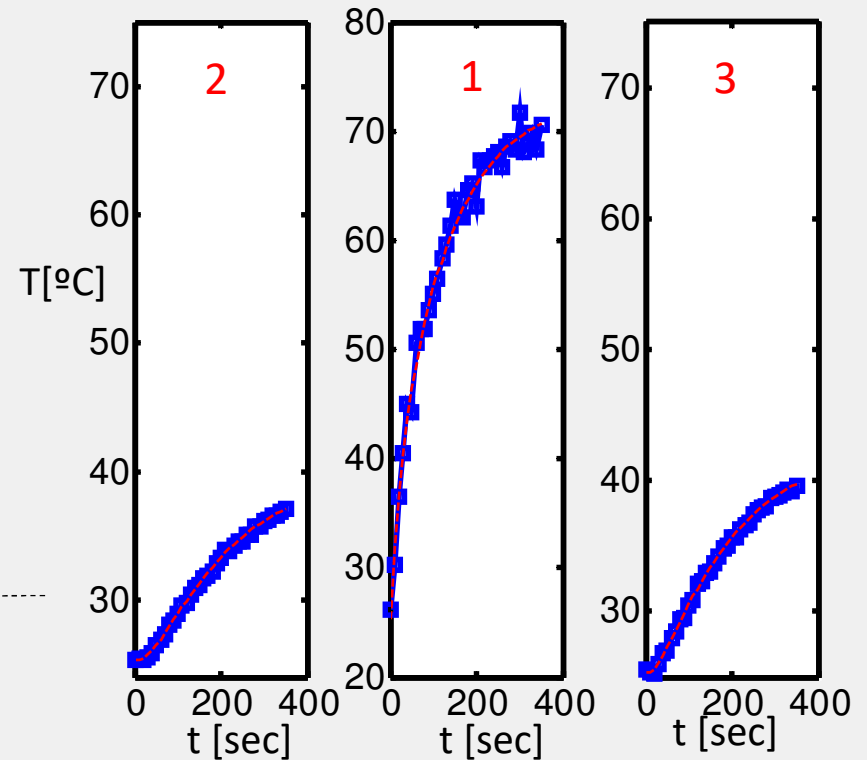
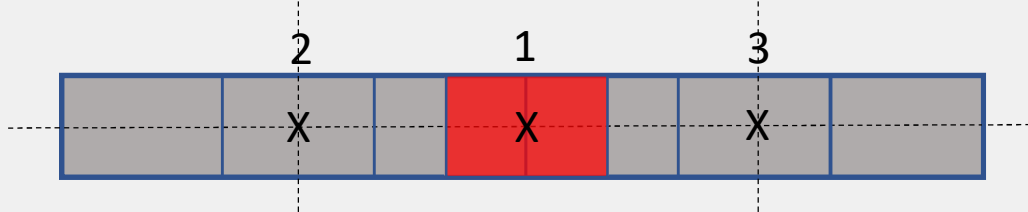
Case E: 3D (measurements in 3 places)



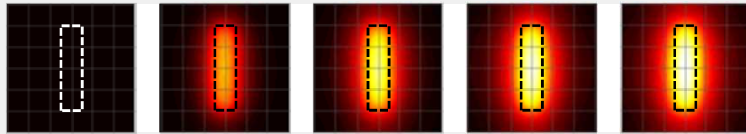
Measurements: 3D model + Noise

Estimation: 3D model

Number of measurements in each place: 36



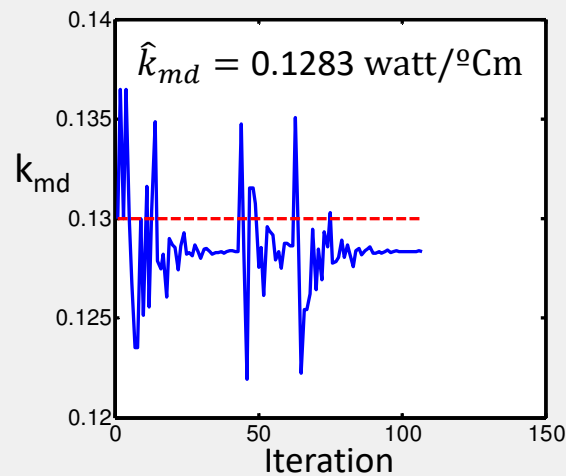
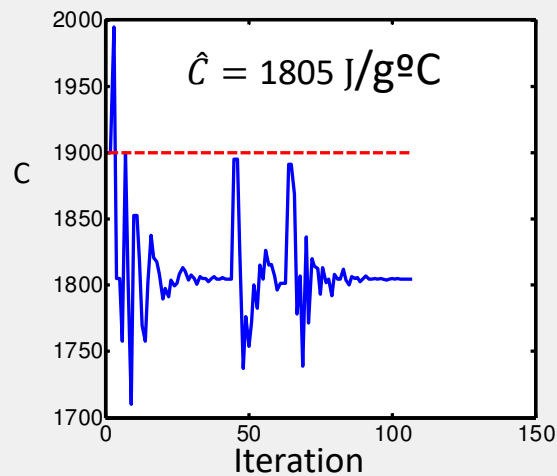
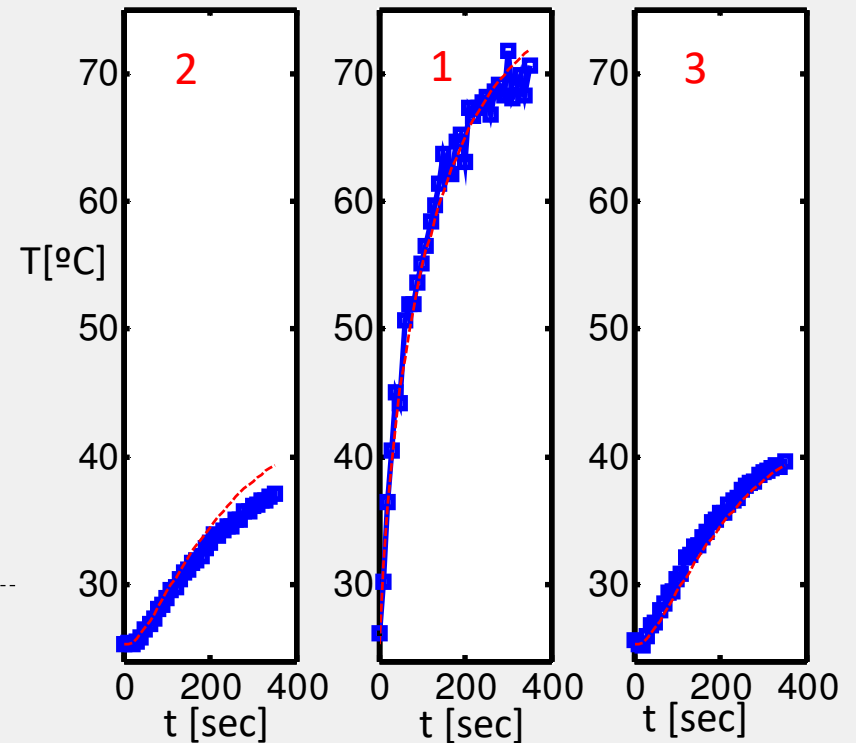
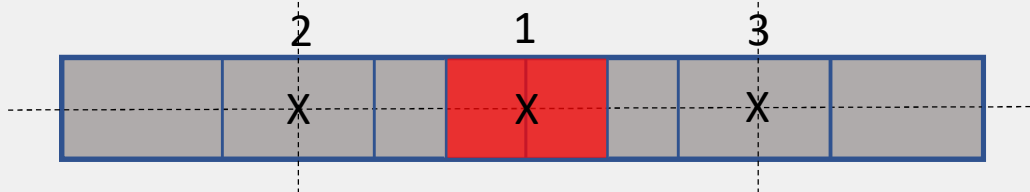
Case E: 2D (measurements in 3 places)



Measurements: 3D model + Noise

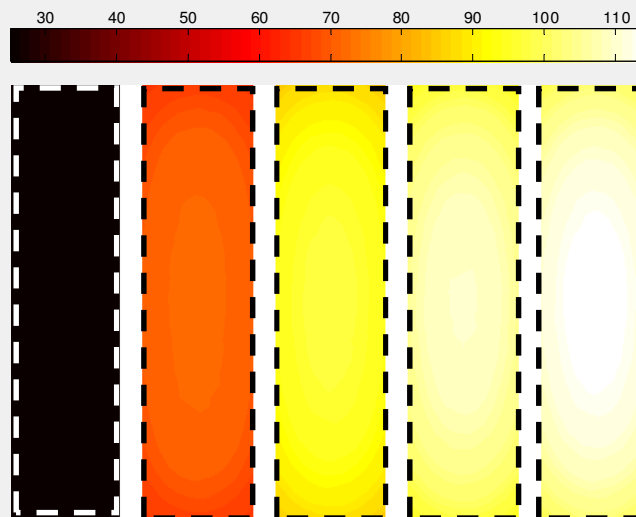
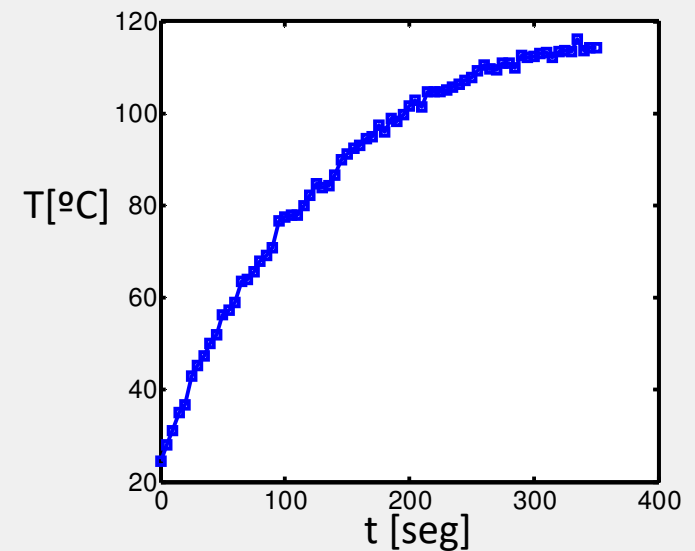
Estimation: 2D model

Number of measurements in each place: 36



Case E: total illumination

Sample dimension: 12x3x2 mm
Illumination: 0.63 watts,
(0.0175watts/mm²) distributed
in 3x12mm² centered in the
center of the sample.
Measurement: in the center of
the sample

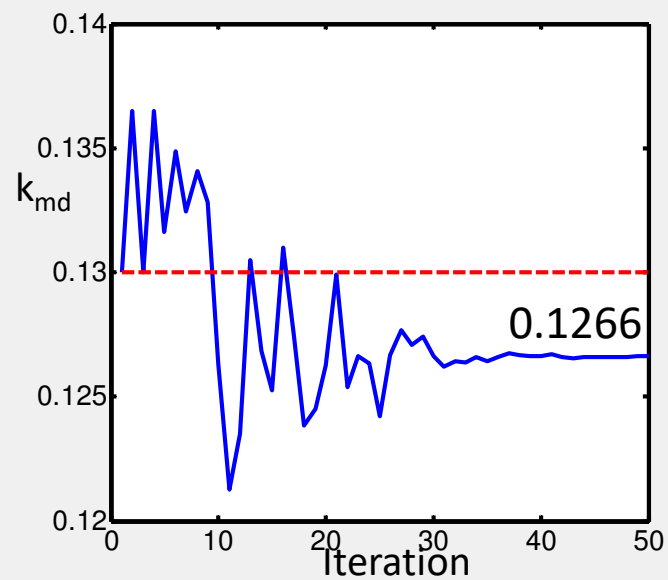
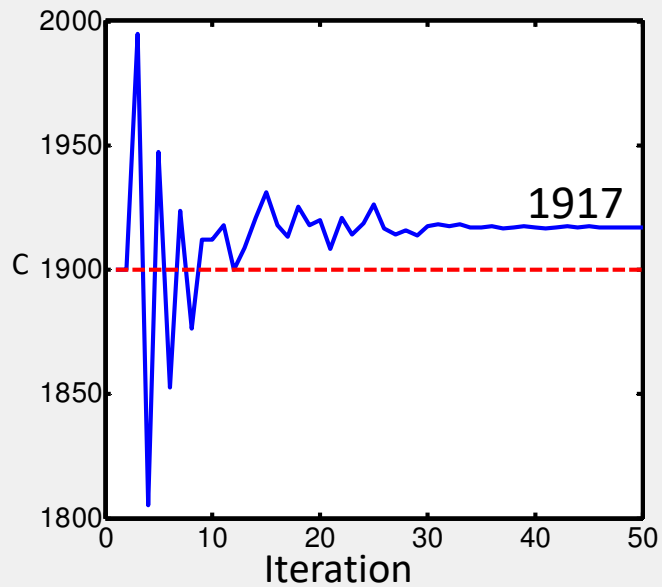
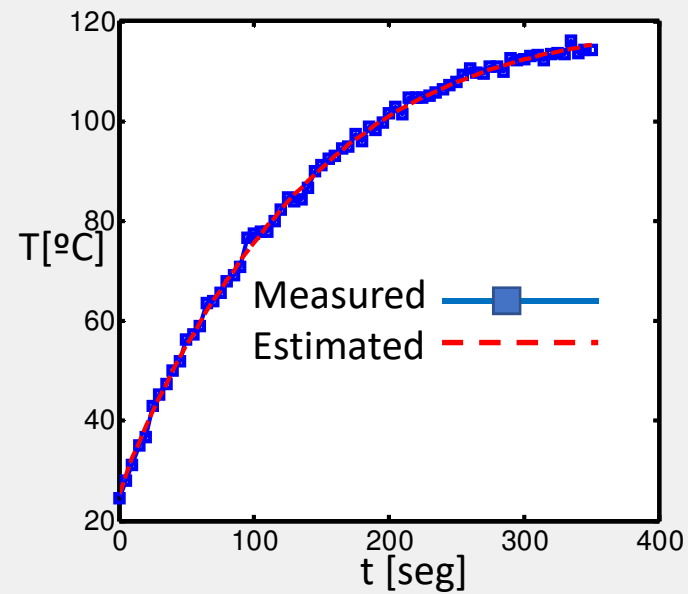


Case E: 3D (total illumination)



Measurements: 3D model + Noise

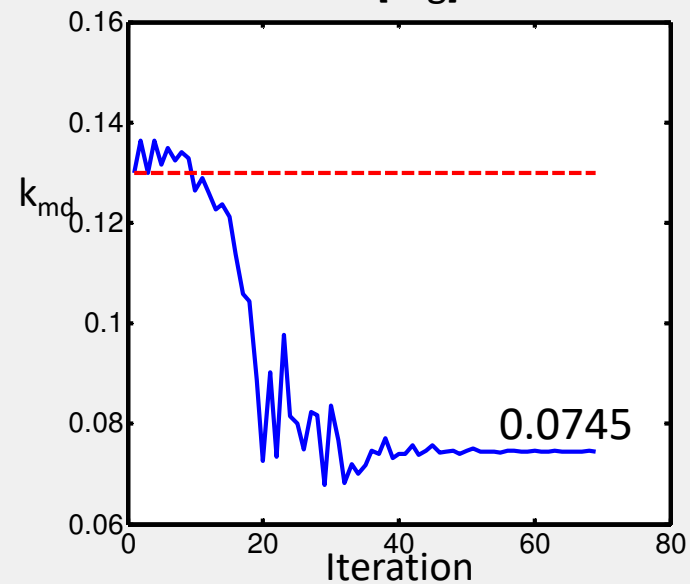
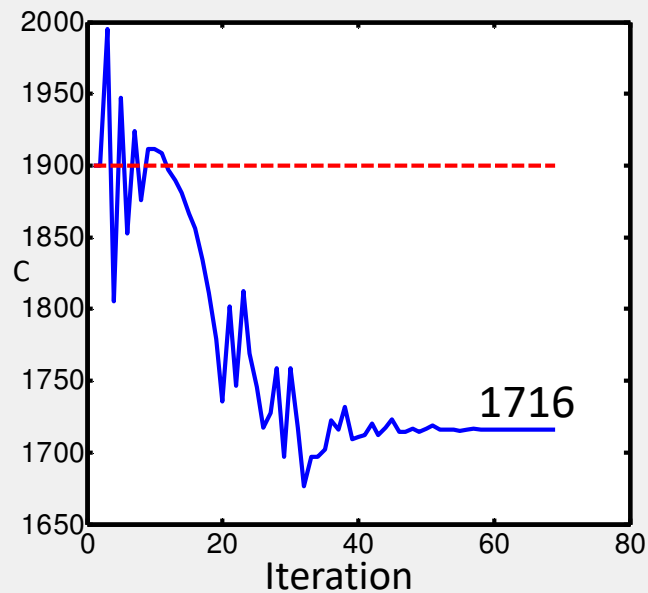
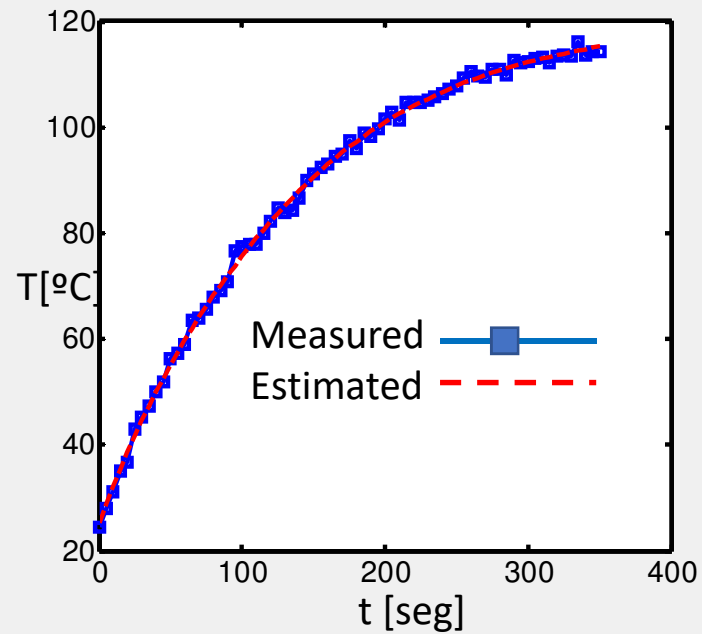
Estimation: 3D model



Case E: 2D (total illumination)



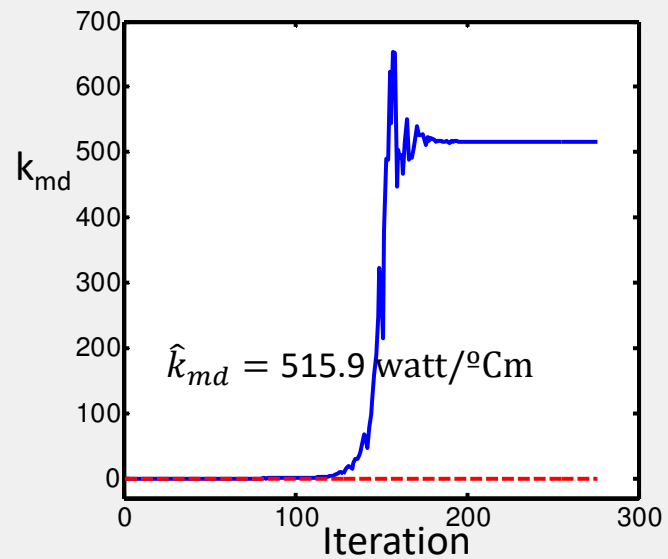
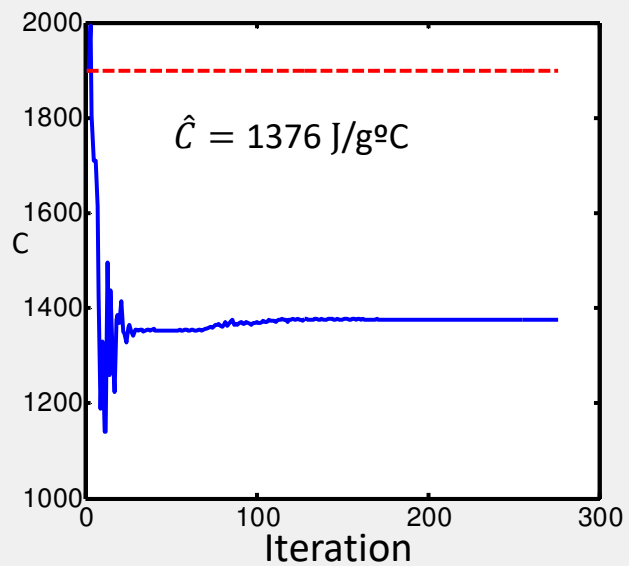
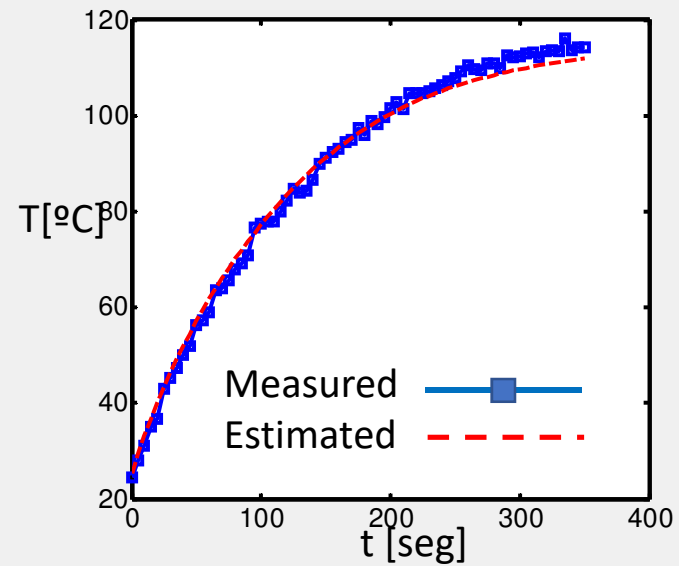
Measurements: 3D model + Noise
Estimation: 2D model



Case E: 1D (total illumination)



Measurements: 3D model + Noise
Estimation: 1D model



Estimated parameters for the different cases

		$c = 1900 \text{ J/(kg } ^\circ\text{K)}$ $k_{md} = 0.13 \text{ watt/(m } ^\circ\text{K)}$			
		\hat{c}	\hat{k}_{md}	<i>error</i>	
Caso A	1D	433.8	0.0048	0.0046	
	2D	683.9	1.843	0.0032	
	3D	1881	0.1313	0.0019	
Caso B	1D	1023	254.8	0.0034	
	2D	1416	0.4525	0.0030	
	3D	1913	0.1291	0.0020	
Caso C	1D	1425	520.5	0.0068	
	2D	1622	0.1706	0.0007	
	3D	1884	0.1325	0.0047	
Caso D	1D	573.0	0.0058	0.0041	
	2D	1251	0.3203	0.0023	
	3D	1951	0.1300	0.0021	
Caso E	1D	1079	311.8	0.0033	
	2D	1569	0.1432	0.0005	
	3D	1796	0.1335	0.0035	
Caso E (71 measurements)	1D	1519	1.692	0.0084	
	2D	1547	0.1451	0.0028	
	3D	1874	0.1314	0.0027	
Caso E (measurements in 3 locations)	1D				
	2D	1805	0.1283		
	3D	1876	0.1304		
Caso E (total illumination)	1D	1376	515.9	0.0056	
	2D	1716	0.0745	0.0026	
	3D	1917	0.1266	0.0027	

Experimental Case 1: Sample

Polymer matrix: Epoxidized soybean oil – Citric acid Network

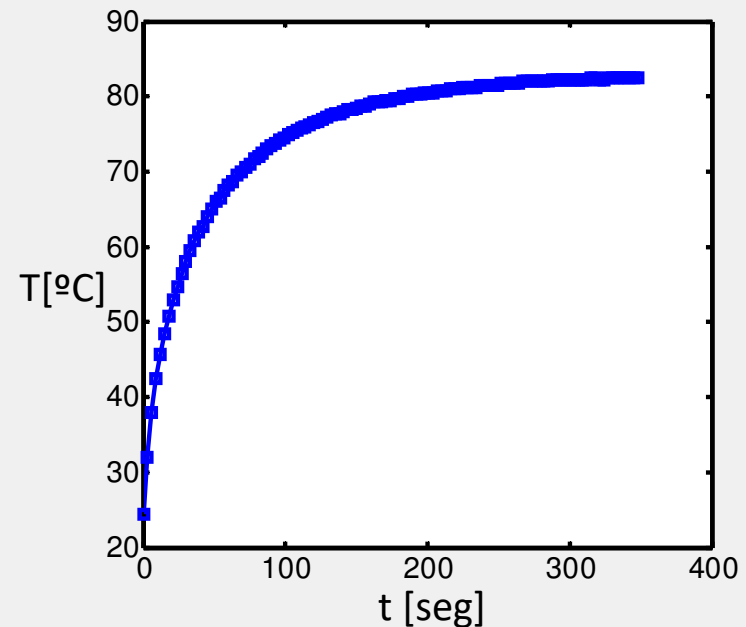
Gold nanoparticles: PVP capped Au nanoparticles where synthesized by post functionalization of gold nanoparticles obtained by the Turchevich method.

Nanocomposite: polymer matrix + gold nanoparticles

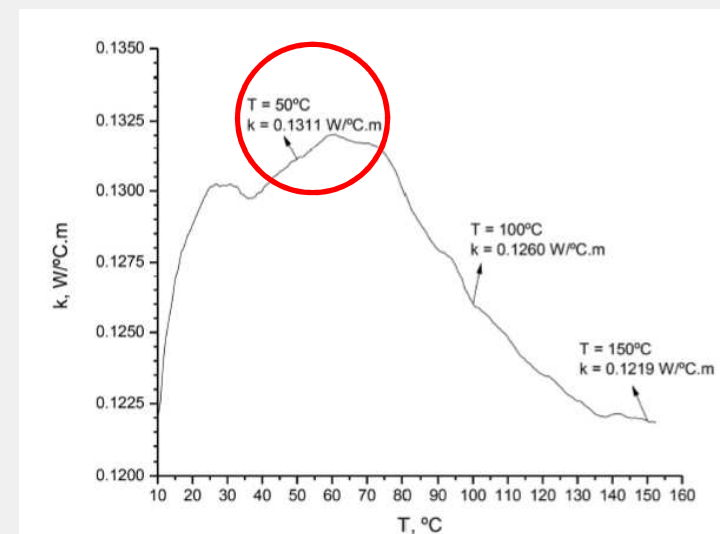
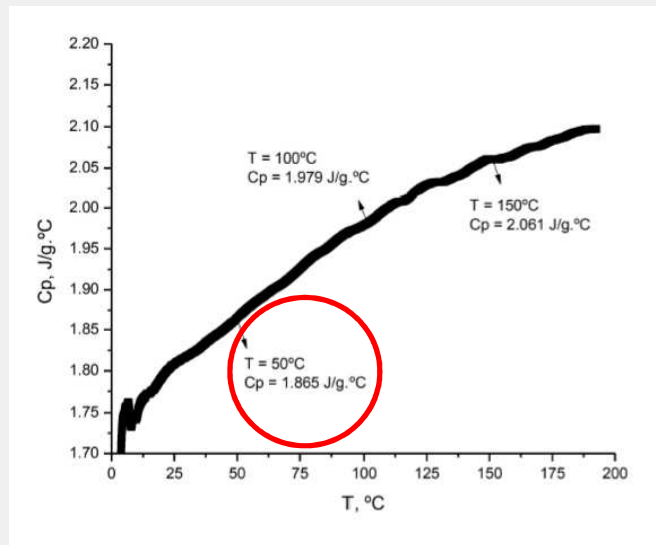
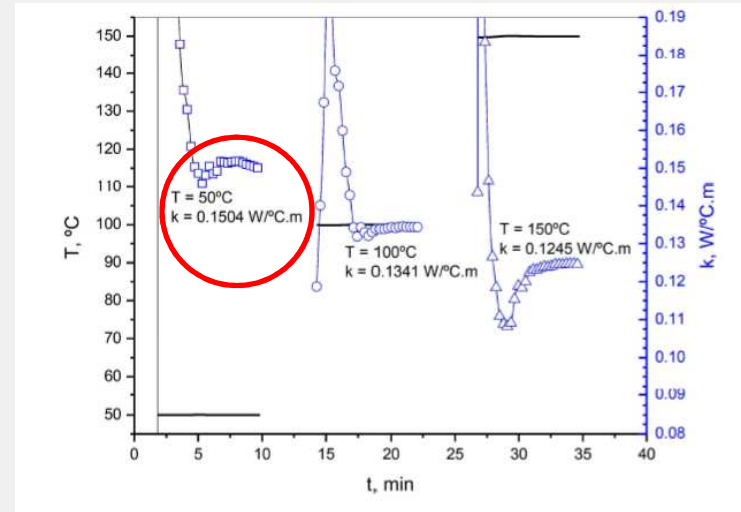
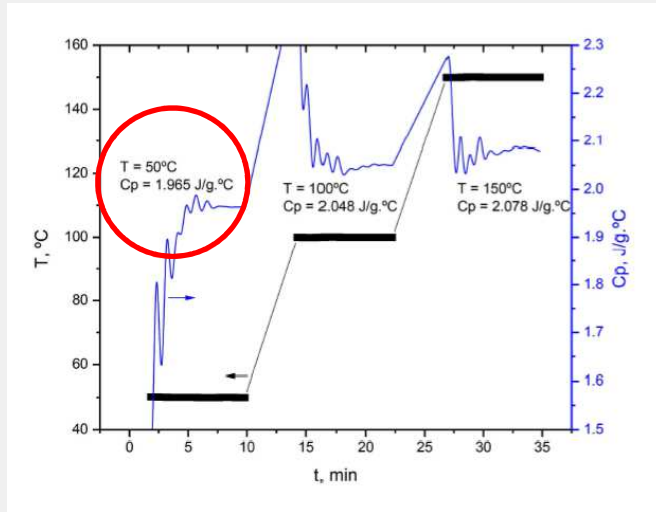
Sample dimension: 40x5x2 mm

Illumination: 0.7 watts, D=3mm centered in the center of the sample.

Measurement: in the center of the sample



Experimental Case 1: k_{md} and c measured statically and dynamically



Experimental Case 1: Parameters

Thermal parameters and initial conditions

$$C=1.865-1.965 \text{ J/g}^{\circ}\text{C}$$

$$K_{md} = 0.1311-0.1504 \text{ watt/}^{\circ}\text{Cm}$$

$$\rho = 1125 \text{ kg/m}^3$$

$$h=10 \text{ watt/(m }^{\circ}\text{K seg)}$$

$$T_{\text{ext}} = 24^{\circ}\text{C}$$

$$T_i = 25^{\circ}\text{C}$$

Optical parameters

$$a=6.5\text{nm}$$

$$\lambda=532\text{nm}$$

$$n_p=0.54386+j2.2309$$

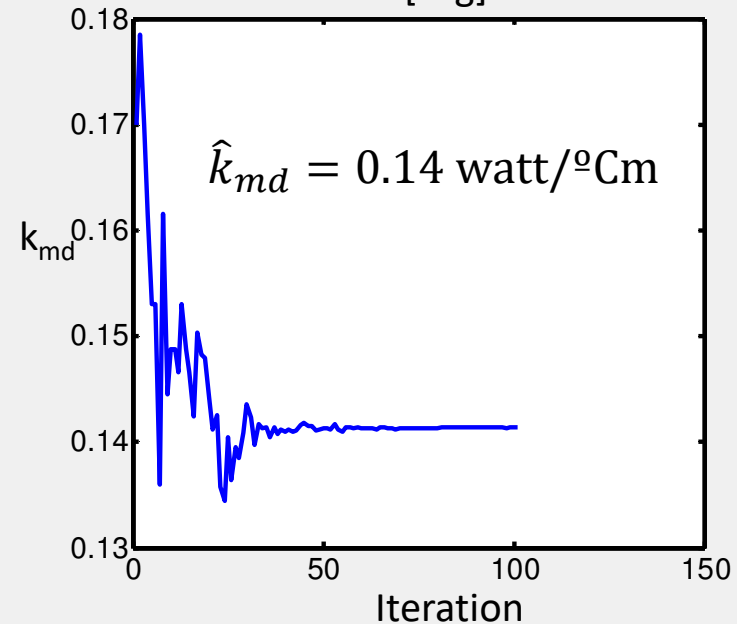
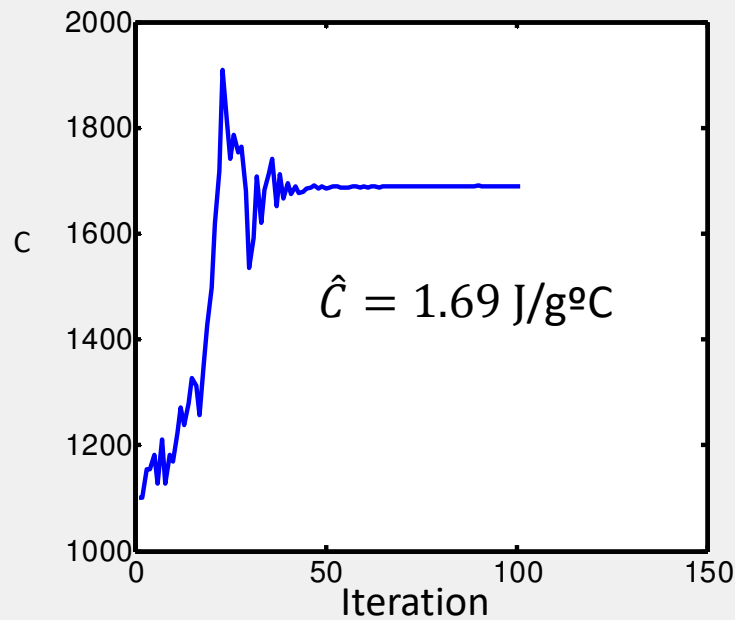
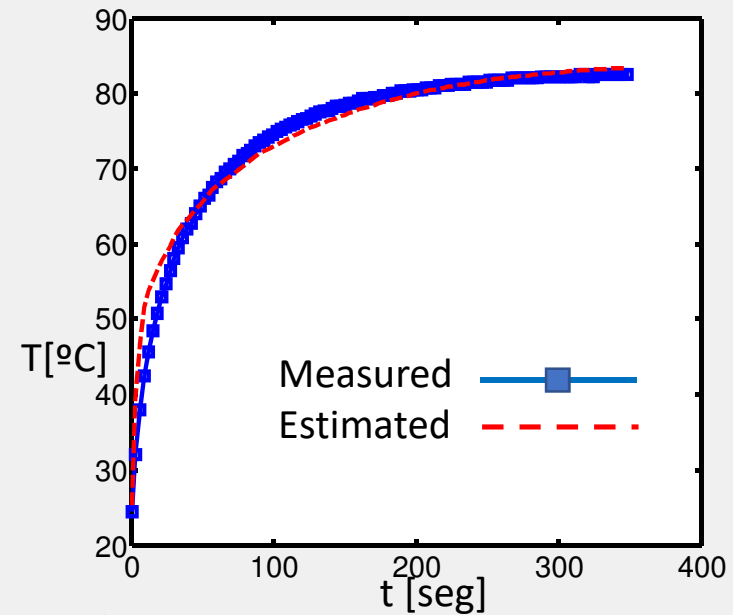
$$n_m=1.53$$

$$N_T = 2.03\text{e}21 \text{ part/m}^3$$

$$Vf=1.164\text{E-}5$$

Experimental Case 1: Estimation

Measurements: Experimental
Estimation: 3D model
117 measurements



Experimental

Materials

Epoxidized soybean oil (ESO; iodine value = 2.4; EEW = 241 g/eq; average molecular weight = 940 Da; average functionality = 3.9 epoxides per triglyceride) was kindly supplied by Unipox S.A. (Buenos Aires, Argentina). Citric acid (CA) monohydrate ($\text{C}_6\text{O}_7\text{H}_8\cdot\text{H}_2\text{O}$; $\geq 98.0\%$), hydrogen tetrachloroaurate (III) ($\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$; $\geq 49.0\%$ Au basis), sodium citrate tribasic dihydrate ($\text{C}_6\text{O}_3\text{H}_5\text{Na}_3\cdot 2\text{H}_2\text{O}$; 99%) and polyvinylpyrrolidone (PVP; number average molecular weight = 10 000 Da) were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification. A representative chemical structure of ESO and the chemical structures of CA, sodium citrate and PVP are shown in figure 1.

Synthesis of ESO-CA networks

The synthesis of ESO-CA networks with a stoichiometric ratio $R = (\text{carboxylic acid equivalents})/(\text{epoxy equivalents})$ of 0.5 was described and discussed elsewhere [13]. Typically, 2.178 g of an aqueous solution of CA (4 parts by weight of CA monohydrate with 1 part of distilled water) was prepared at 90 °C and added to 12.0 g of ESO at 90 °C, with continuous stirring. After 10 min, the solution was cast into a glass mold covered with anti-adherent paper, and it was placed in a convection oven (Yamato DKN400). The polymerization was performed for 6 h at 90 °C and 12 h at 120 °C. The post-curing step at 160 °C for 4 h was carried out outside the mold.

Synthesis of Au NPs

PVP capped Au NPs (Au@PVP) were synthesized by post-functionalization of gold NPs obtained by the Turkevich method [33]. Briefly, 3.40 ml of an aqueous HAuCl_4 solution ($0.036\ 52\ \text{mol l}^{-1}$) were diluted in 250 ml of water and heated until boiling. Subsequently, 12.5 ml of 1% (w/v) sodium citrate solution were added, and heating and stirring were maintained for 30 min. The dispersion was left to cool to room temperature before adding 10 ml of 26.5% (w/v) PVP aqueous solution. The mixture was stirred for 24 h, and Au@PVP NPs were separated by centrifugation (4 times; 1 h; 600 rpm) to obtain an aqueous dispersion of NPs with an average diameter of 13.1 nm and a standard deviation of 2.7 nm. A more detailed analysis of the NPs size distribution is available in the supplementary data file. **Polyvinylpyrrolidone (PVP)**

Synthesis of ESO-CA-Au@PVP nanocomposites

The incorporation of Au@PVP NPs to the ESO-CA matrix was performed in a two-steps procedure. First, an aqueous dispersion of Au@PVP NPs was added to 12.0 g of ESO at 90 °C. This mixture was stirred for 15 min at 90 °C to evaporate the water. The second step was the addition of an aqueous CA solution as it was done for the neat ESO-CA networks. For this system, the pre-polymerization step was performed for 15 min to assure a better elimination of water. The curing program was the same as that used for the neat polymers (6 h at 90 °C, 12 h at 120 °C and a post-curing of 4 h at 160 °C outside the mold). The obtained nanocomposites were labeled as ESO-CA-Au@PVP (0.08) and ESO-CA-Au@PVP (0.02), where the numbers between brackets indicate the Au content as wt%.

Experimental Case 2: Sample

Polymer matrix: DGEBA epoxi polymer

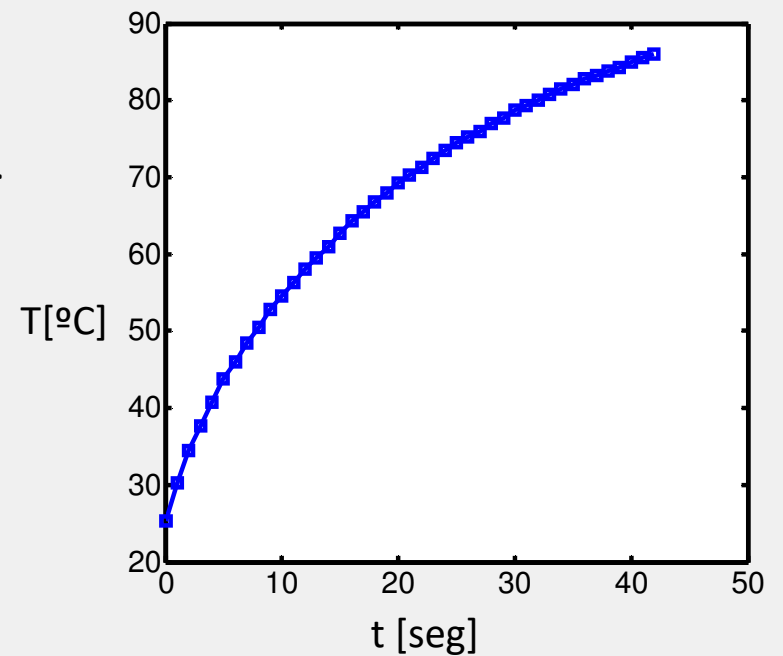
Gold nanoparticles: dodecanethiol capped gold nanoparticles

Nanocomposite: polymer matrix + gold nanoparticles

Sample dimension: 53x12x1.4 mm

Illumination: 0.7 watts, D=3mm
centered in the center of the sample.

Measurement: in the center of the sample



Experimental Case 2: Parameters

Optical parameters

$$a=1nm$$

$$\lambda=532nm$$

$$np=0.54386+j2.2309$$

$$nm=1.568$$

$$NT = 2.18e22 \text{ part/m}^3$$

$$Vf=2.91e-5$$

Thermal parameters and initial conditions

$$C=1110 \text{ J/kg}^\circ\text{C}$$

$$K_{md} = 0.17-0.35 \text{ watt/}^\circ\text{Cm}$$

$$\rho = 1125 \text{ kg/m}^3$$

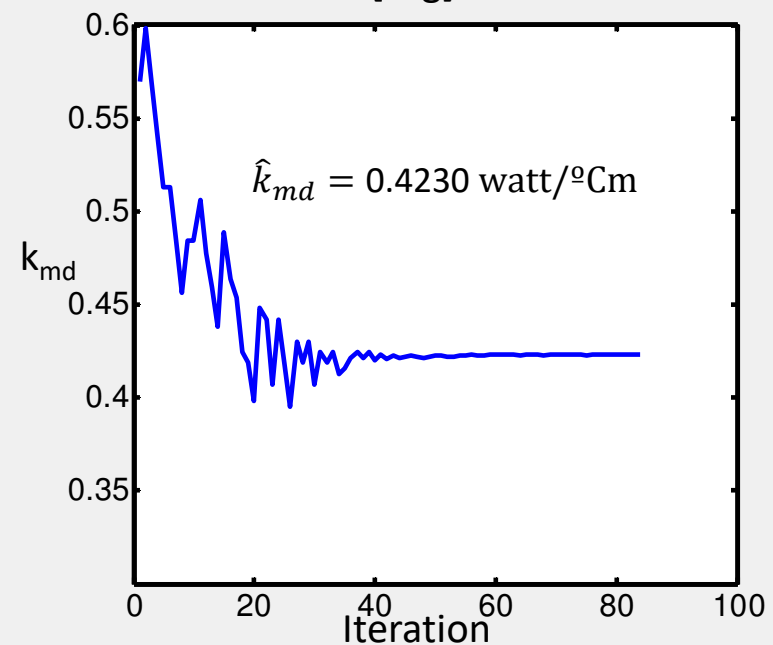
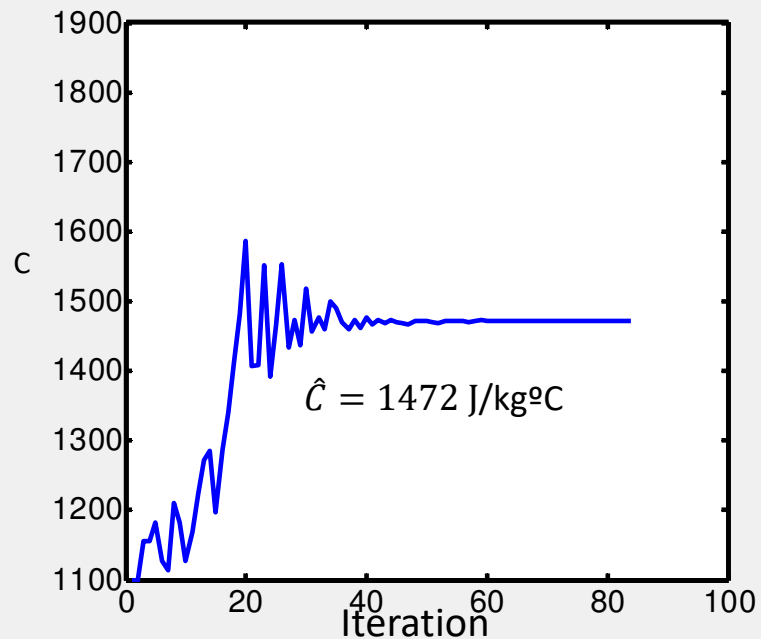
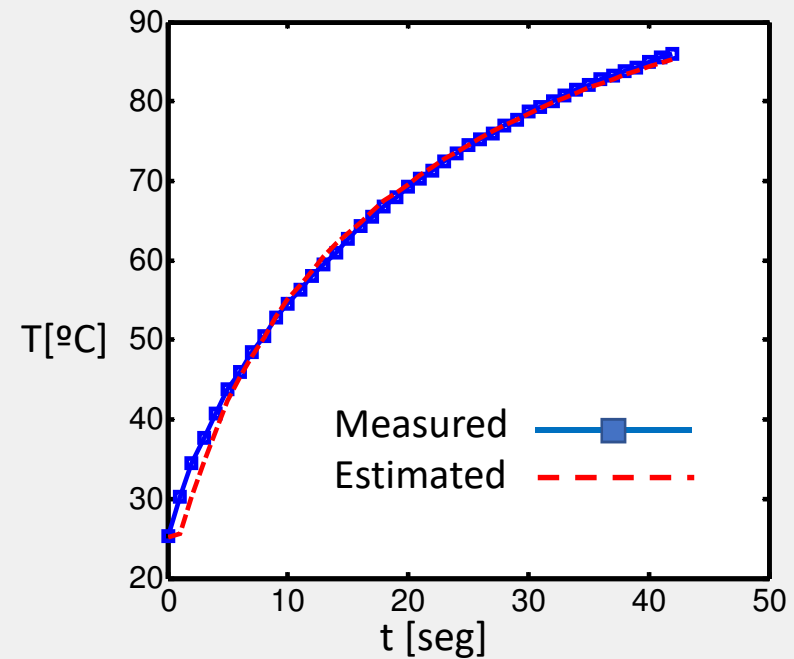
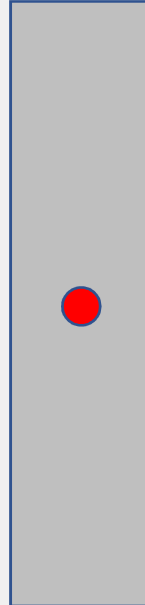
$$h=10 \text{ watt/(m }^\circ\text{K seg)}$$

$$T_{\text{ext}} = 24^\circ\text{C}$$

$$T_i=25^\circ\text{C}$$

Experimental Case 2: Estimation

Measurements: Experimental
Estimation: 3D model
36 measurements



Conclusions

- In this work we have proposed a 3 dimensional model that can be used to calculate the complete temperature map in a piece of material loaded with plasmonic nanoparticles and irradiated with laser light.
- The model is very appropriated to perform parameter and estate estimation, control and optimization with different objectives.
- We have used the model to estimate thermal parameters like the heat capacity and the heat diffusion coefficient, in simulated as well as in experimental examples.
- With the goal of reducing computational time for on-line and off-line computations we have proposed reduced models based on the assumption of infinite dimensionality in 1 or 2 of the 3 variables.
- We have checked the reduced models in their ability to recover the real parameters of the system through parameter estimation.
- Depending on the size of the illuminated area, the reduced models may recover or not reasonable values for the parameters.
- Some ideas were preliminary analyzed in order to improve the capability of the reduced models to asses, through parameter estimation, the right parameters.
- We concluded that adding measurements at specific locations in the sample may help to make the reduced model more robust with respect to its ability to track the real parameters.