

Caractérisation par DSC: défauts intrinsèques et apports de la modélisation

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Généralités

Analyse thermique

Différents appareils / mesures

- Calorimètre: mesure chaleur
- Differential thermal analysis (DTA): mesure température
- Adiabatic scanning calorimetry (ASC): mesure température
- Differential scanning calorimetry (DSC): mesure variation de flux

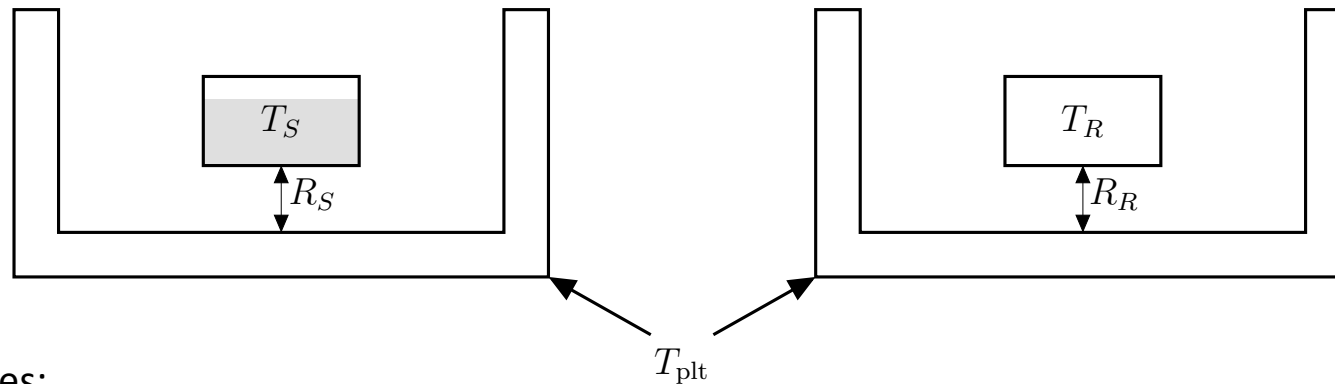
- méthode T – history...

- Thermo-gravimétrie
- Analyse thermo-mécanique...

Différents modes d'utilisation

- dynamique
- isotherme (step)

DSC

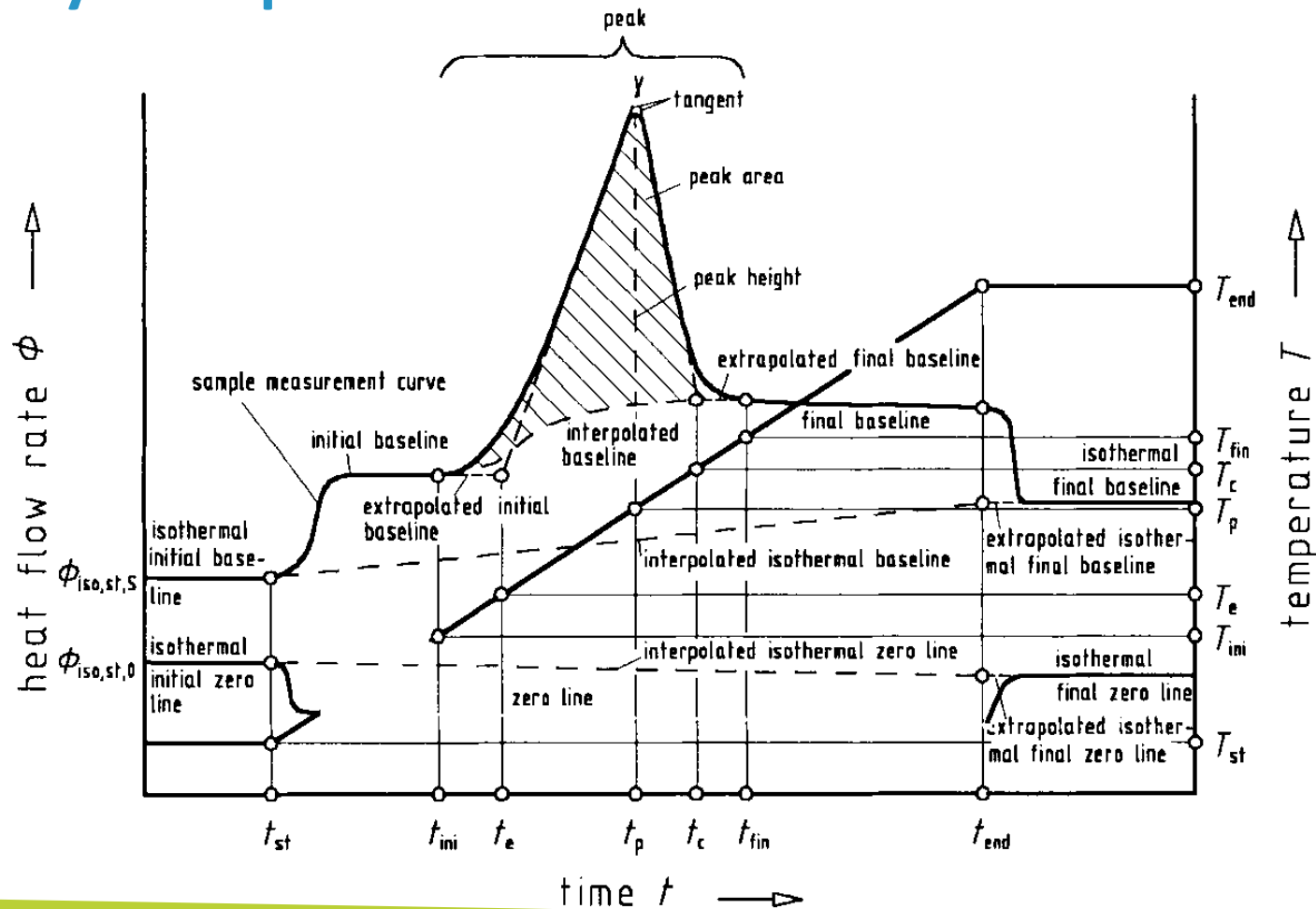


- Deux types:
 - Heat flux (ex: DSC131 de Setaram)
 - Power compensation (ex: Pyris Diamond de Perkin – Elmer)
- Imposition d'une sollicitation thermique
- Mesure d'un flux de chaleur
- Obtention d'un thermogramme (courbe DSC)
 - Mode dynamique
 - Mode isotherme (step)

$$T_{plt} = \beta t + T_0 \quad \longrightarrow \quad \phi(t)$$

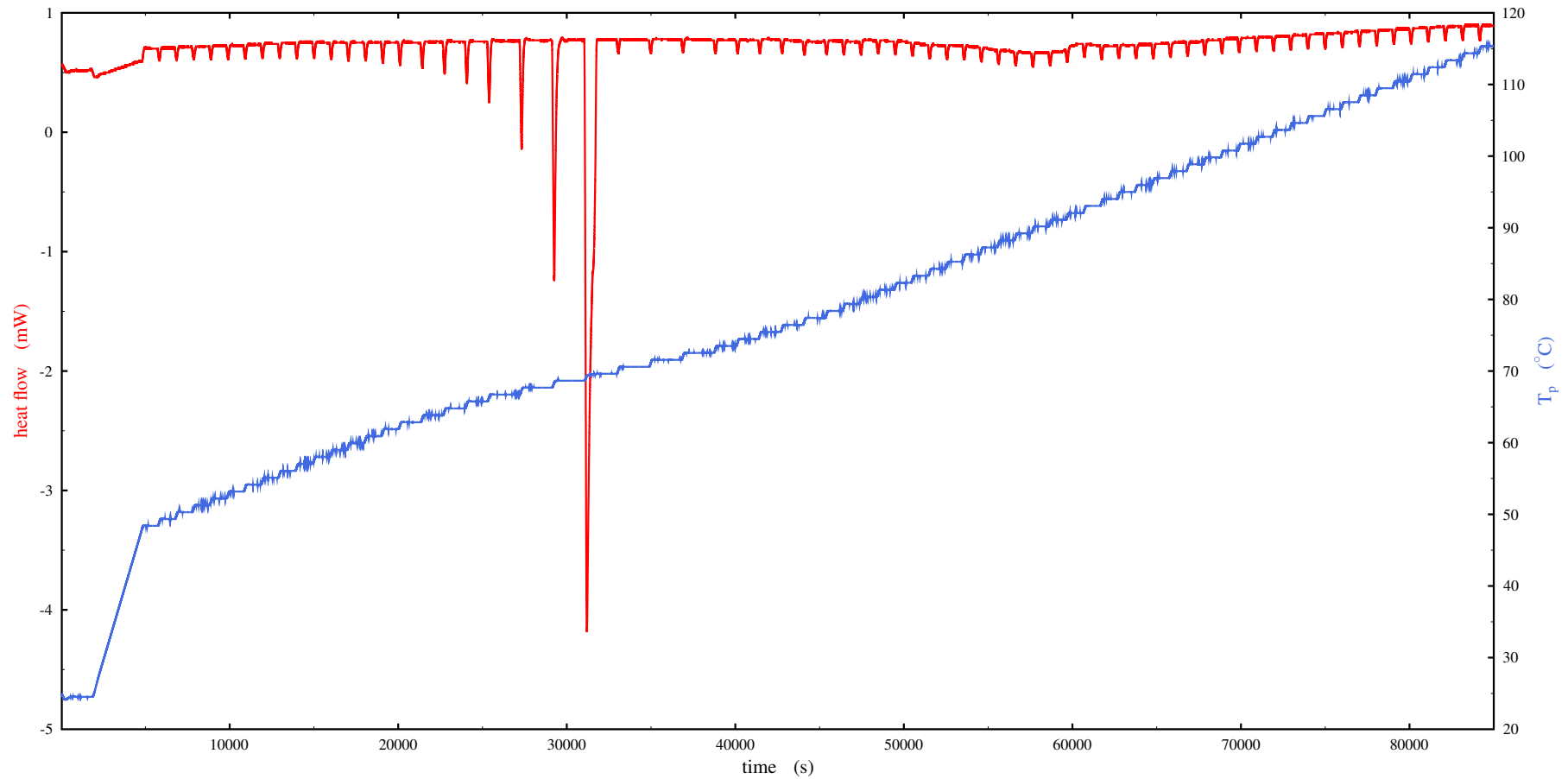
DSC

Mode dynamique



DSC

Mode isotherme



DSC

Informations liminaires

- Signal **temporel**
- Méthode relative:
 - Forte influence échantillon(s) calibration
 - Définition lignes de base / zéro
- Résultats dépendants:
 - Masse
 - Vitesse de chauffe/refroidissement

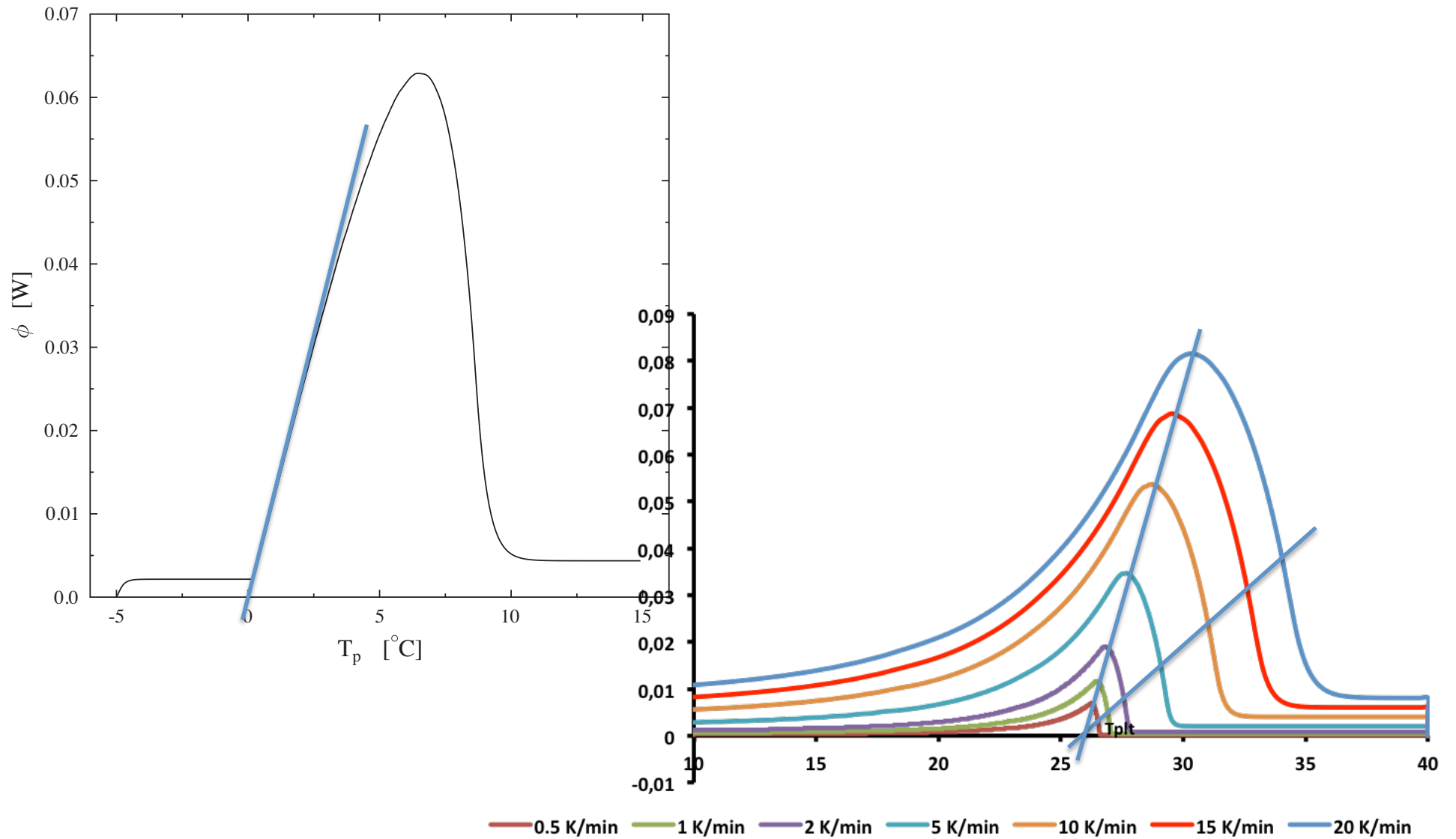
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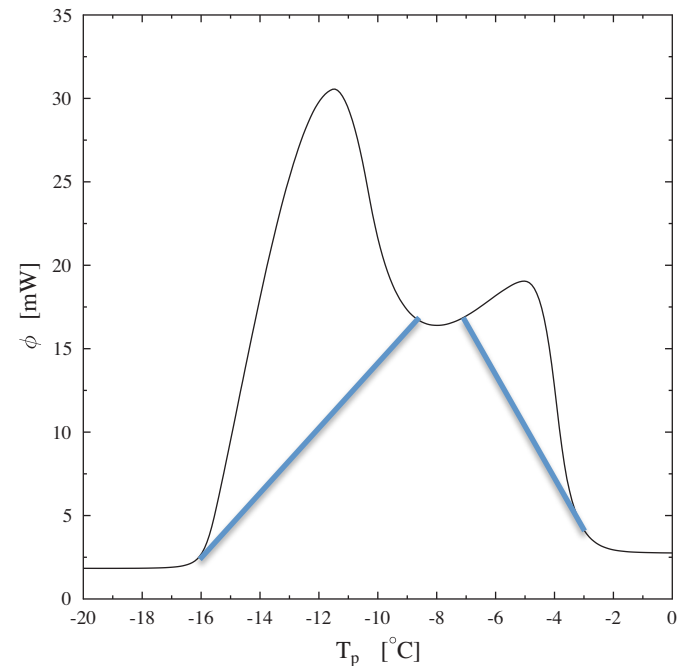
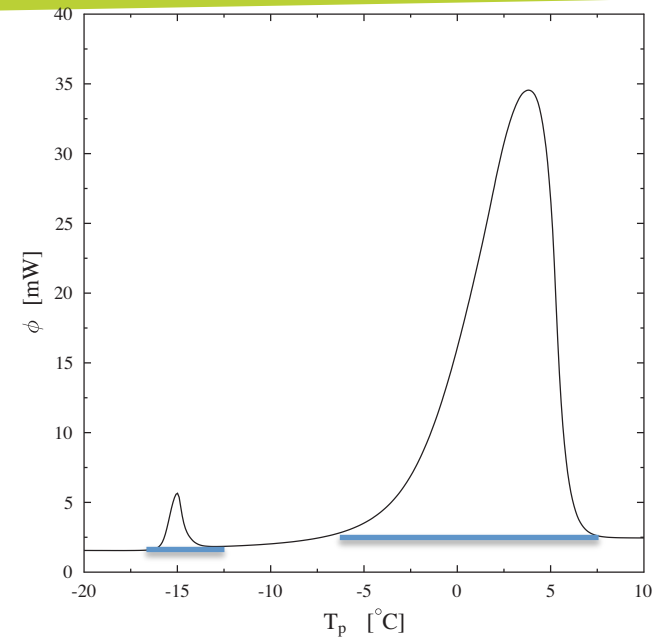
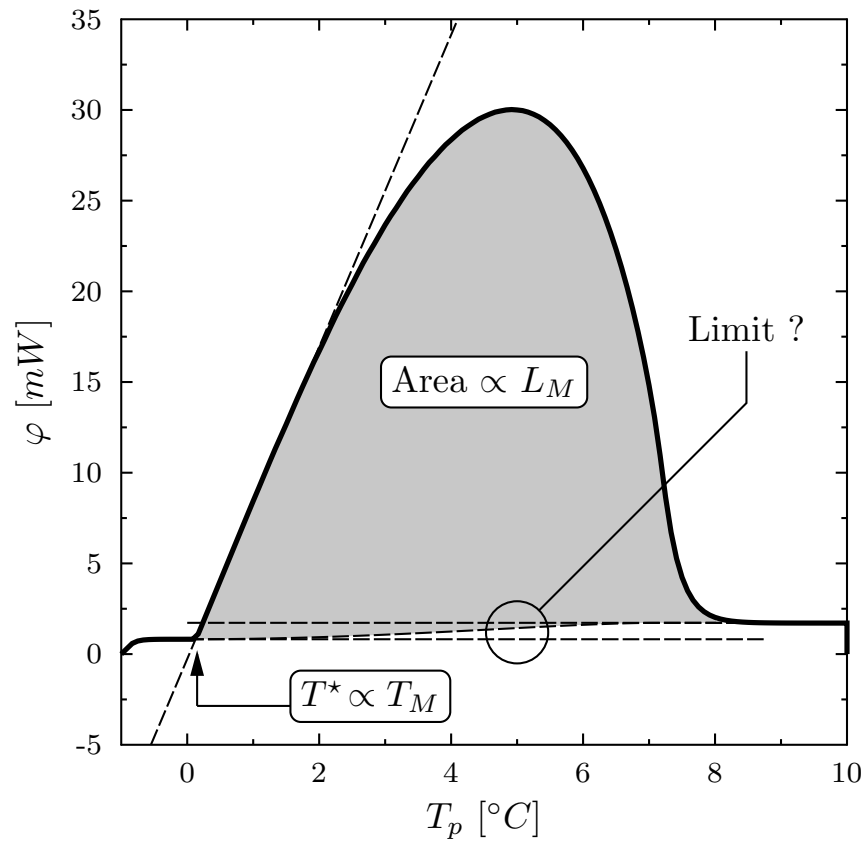
Grandeurs identifiables

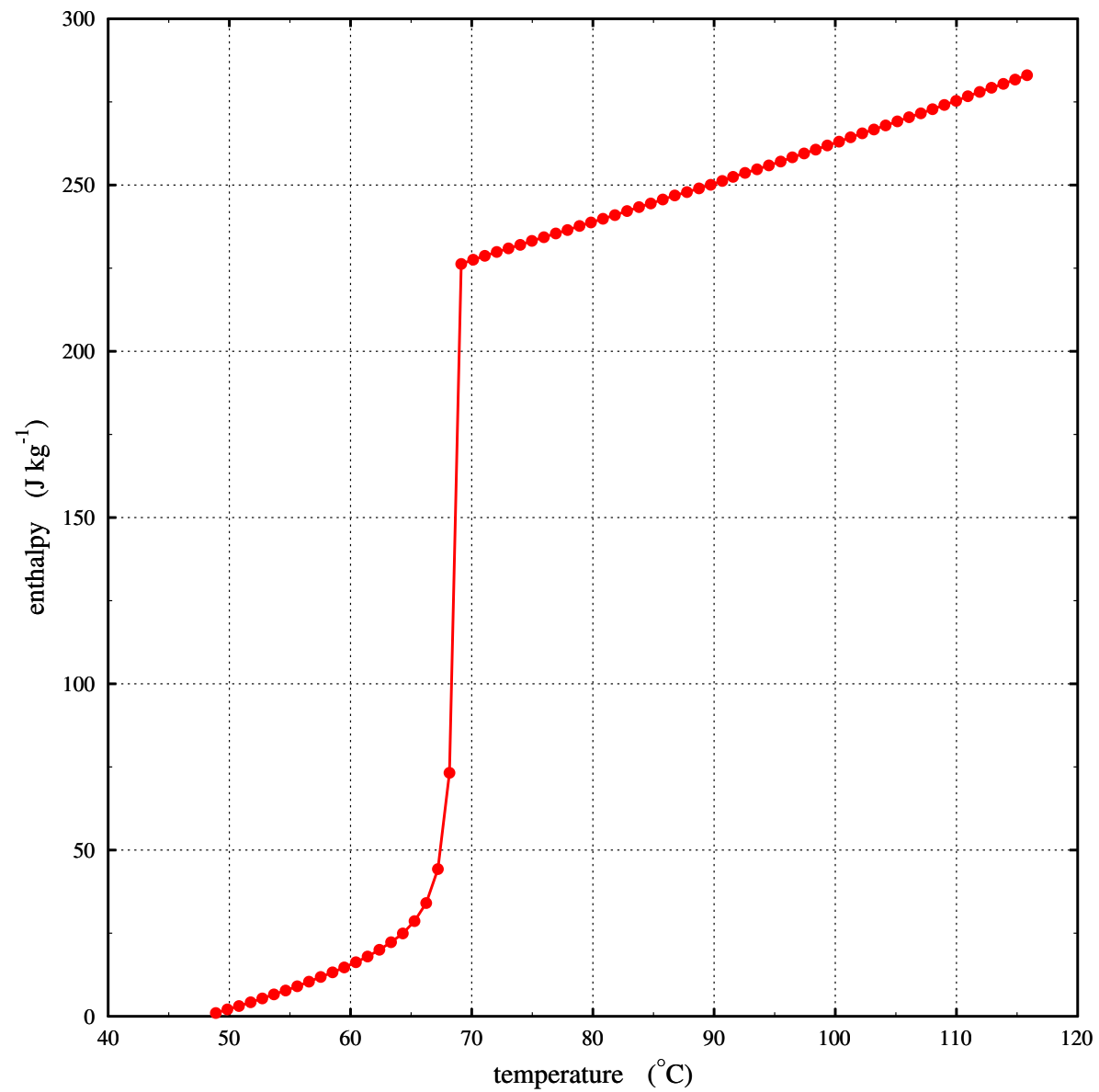
- Températures
 - Transitions de première espèce: T_{onset}
 - Transitions de seconde espèce: T_{solidus}

- Grandeurs énergétiques
 - Capacités calorifiques (i.e. dans les zones sensibles)
 - Chaleur latente (i.e. variations d'enthalpie)
 - Enthalpie (en mode isotherme)

- Données courante: la température de fusion et la chaleur latente
Implicitement, on considère donc un corps pur...



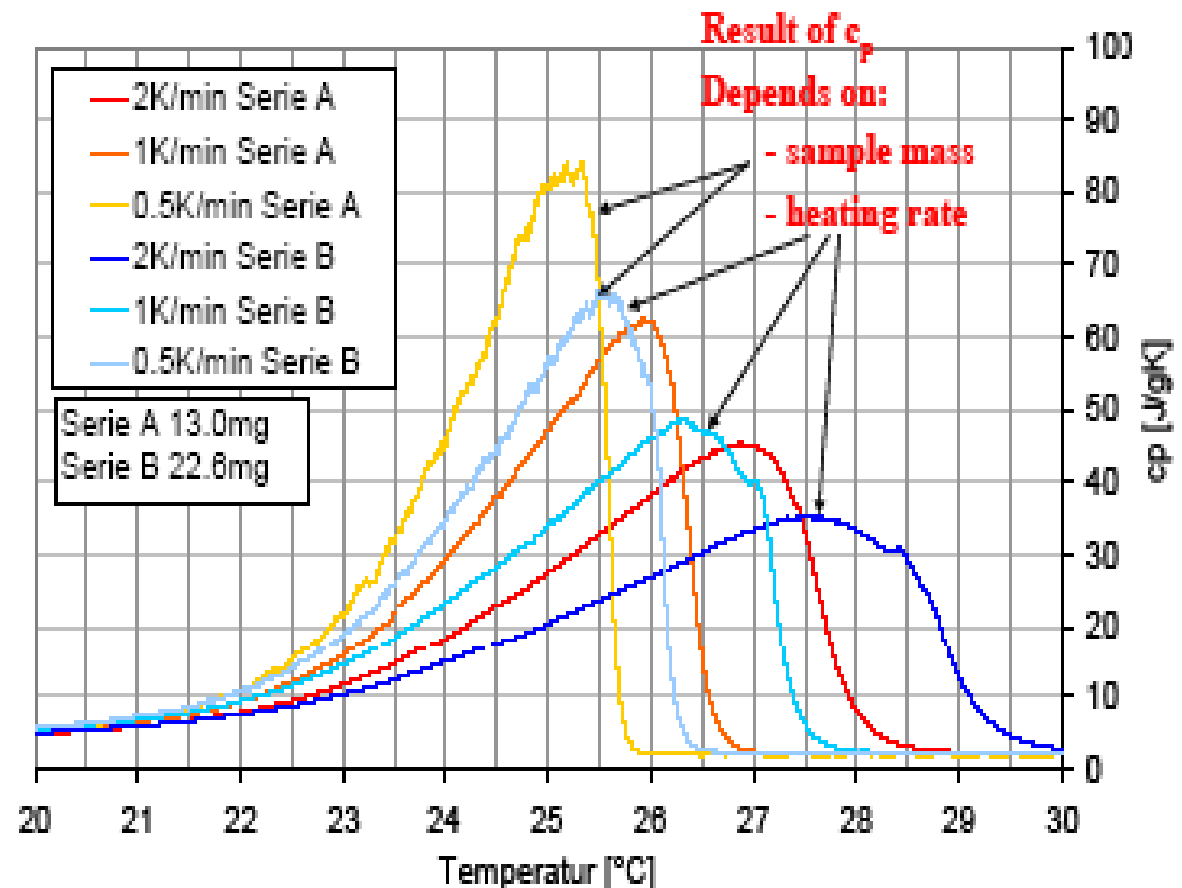


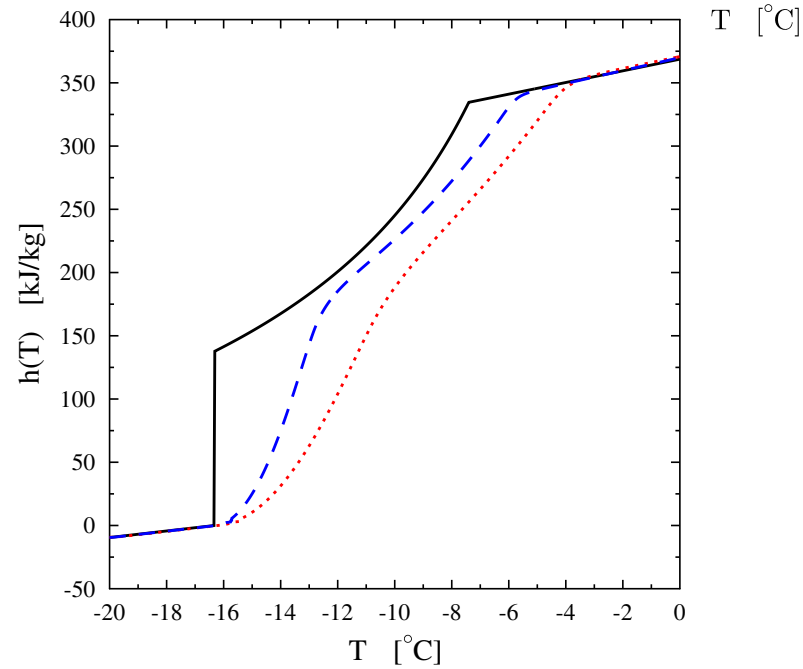
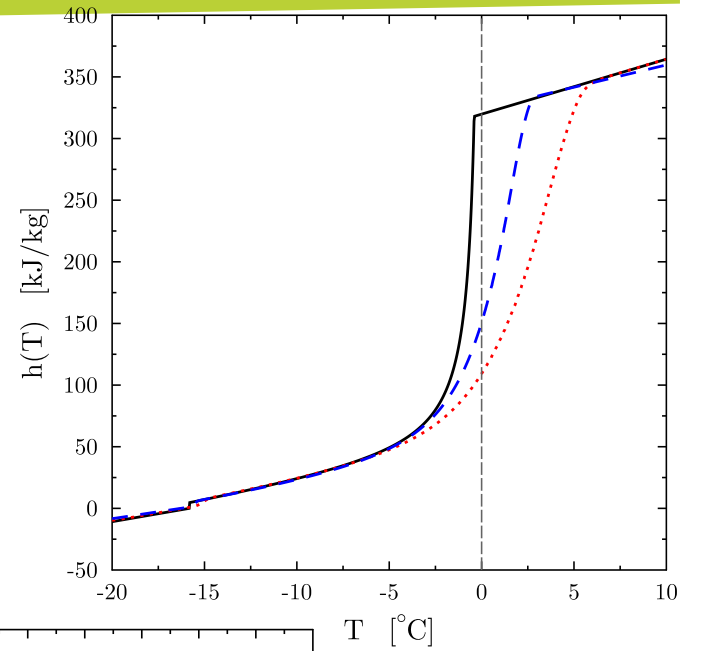
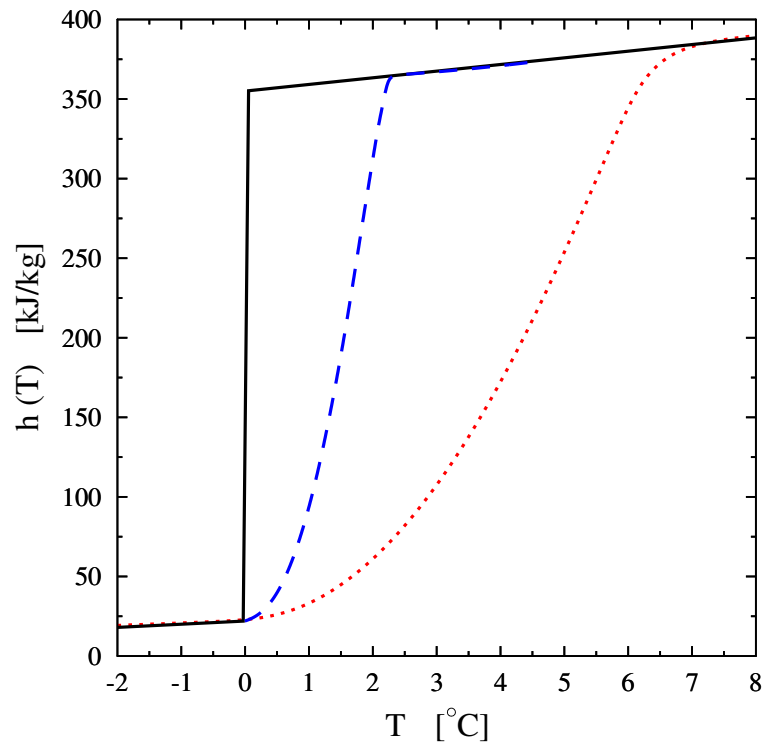


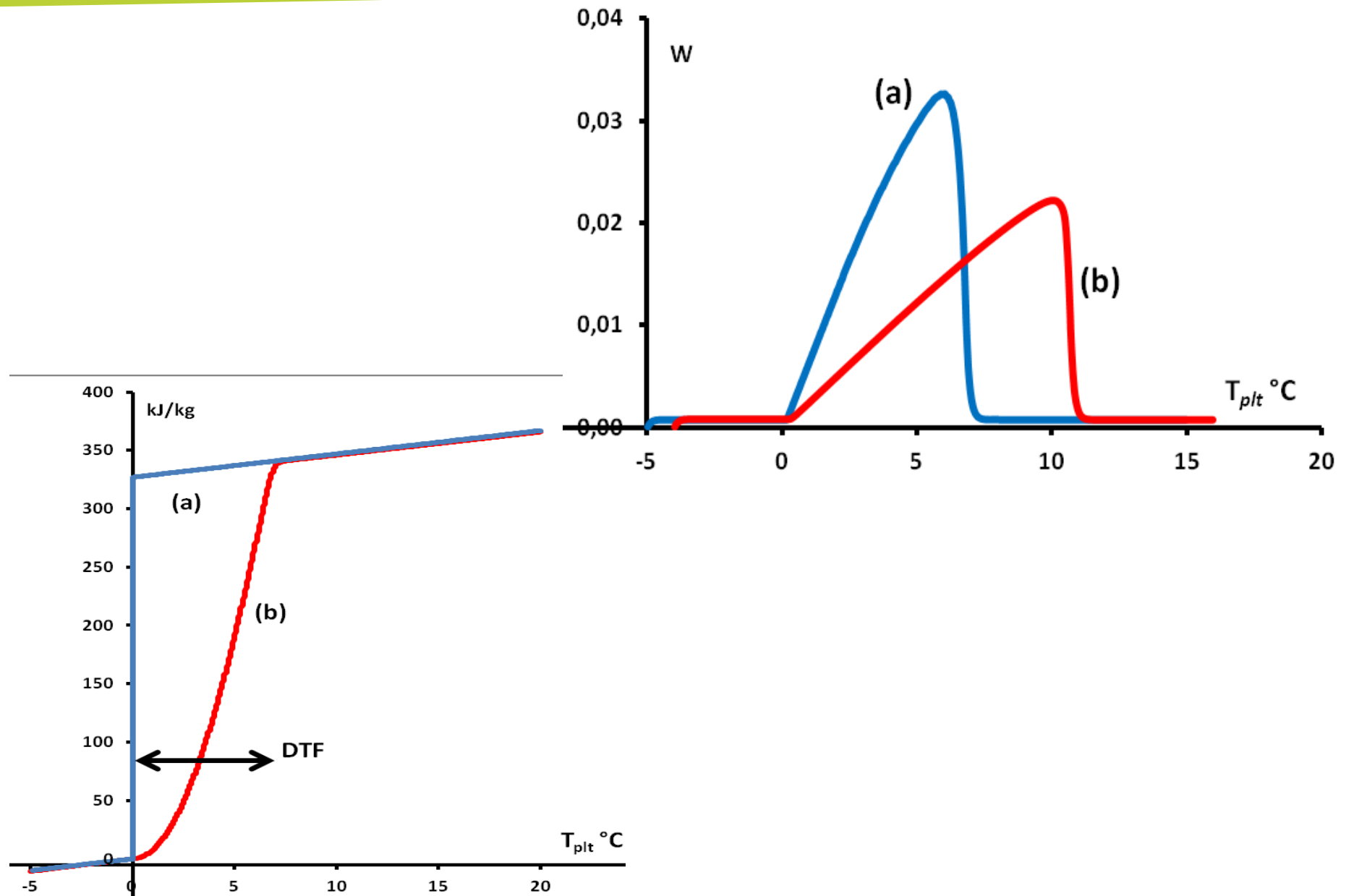
Erreur (très) courante

Enthalpies: $h=h(\beta)$

- Incohérence thermodynamique...
 - Variable d'état **indépendante** du chemin suivi
 - spécialistes obtiennent des valeurs éloignées de celles avancées par les fournisseurs (#10– 47%)
- [Lazaro2006, Barreneche2013, Lazaro2016]







Inconnues sur certains paramètres

Mode step

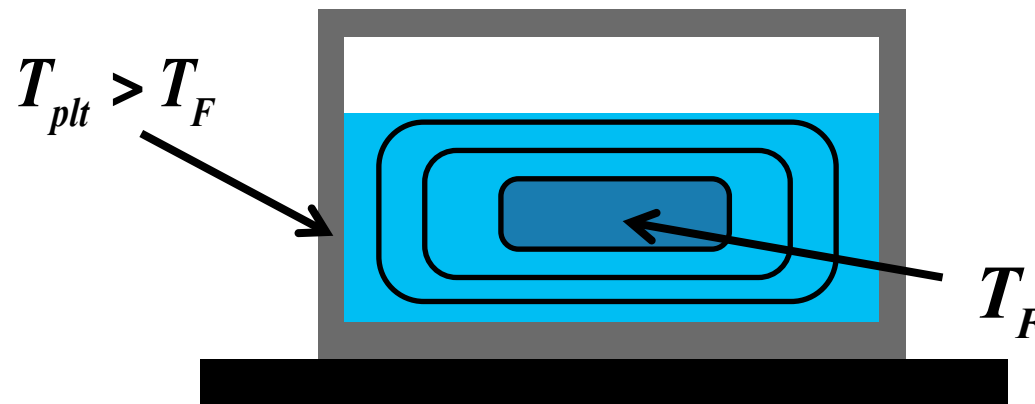
- Paramétrage et influence des différents steps:
 - Intervalle de température
 - Vitesse de chauffe
- Influence du bruit sur le signal
- Stabilité des conditions opératoires (cycle complet # jour)

Modélisation

Analyse théorique

Comportement de la cellule

- Présence de transferts thermiques pendant le changement de phase



Erreur commise

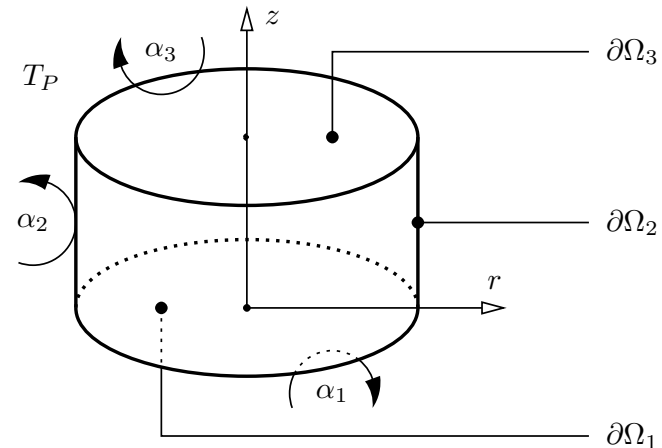
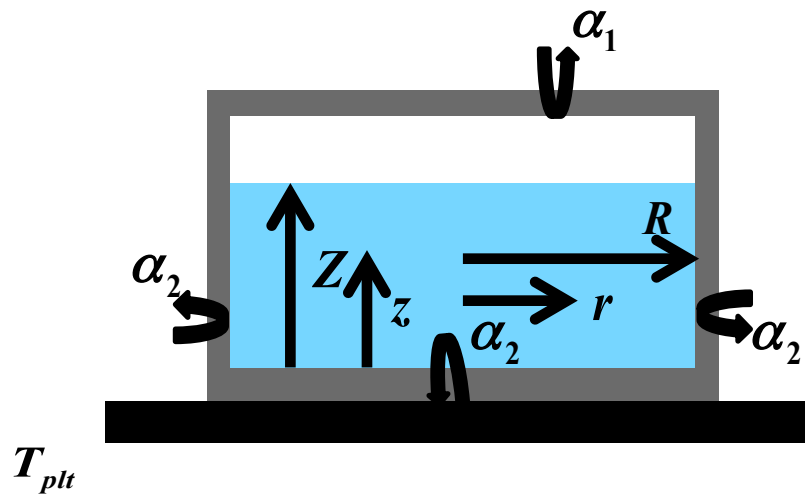
- Hypothèse de suite d'état à l'équilibre fautive lors de la transition

$$\phi(t) \cong \phi(T_P) \neq \frac{dh}{dT}$$

Modélisation / Simulation

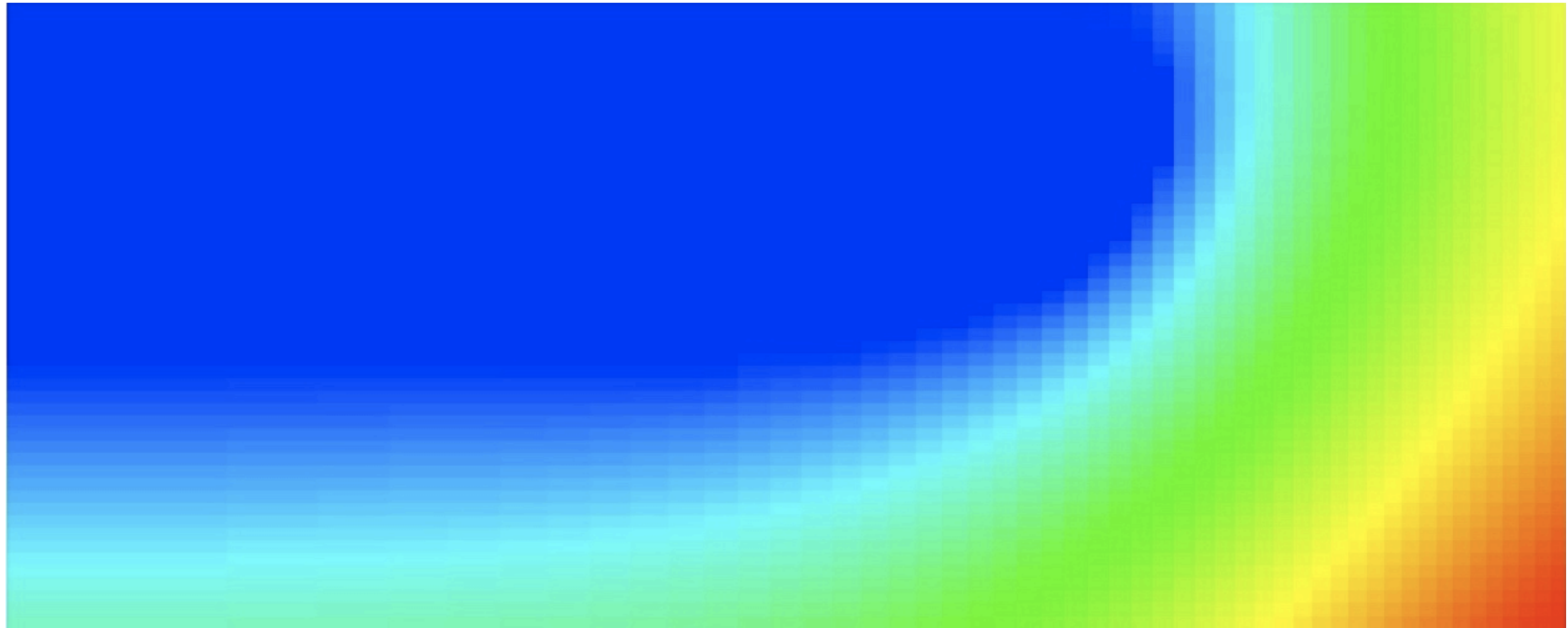
Solution

- Prendre en compte les phénomènes de transferts thermiques
- Bilan d'énergie complet du système en régime instationnaire



$$\frac{\partial \rho h}{\partial t} = \nabla \cdot (\lambda \nabla T)$$
$$\phi = \sum_i \alpha_i S_i (T_{plt} - T_i)$$

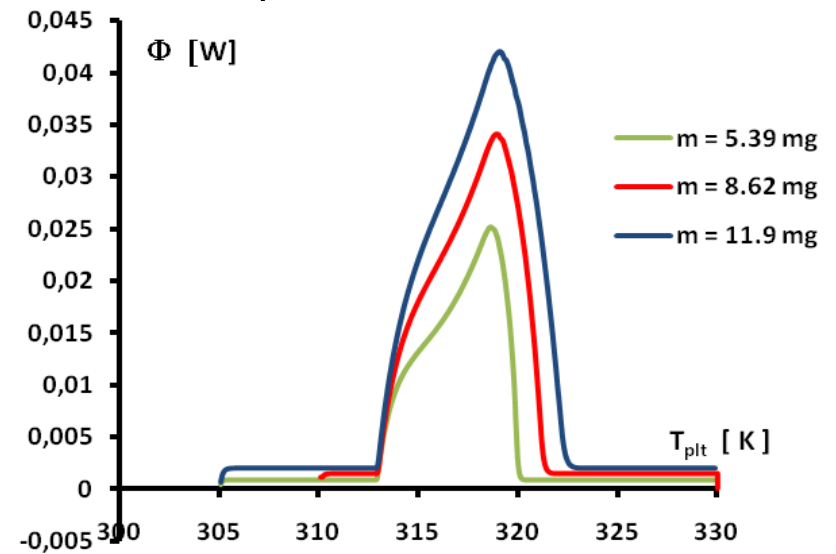
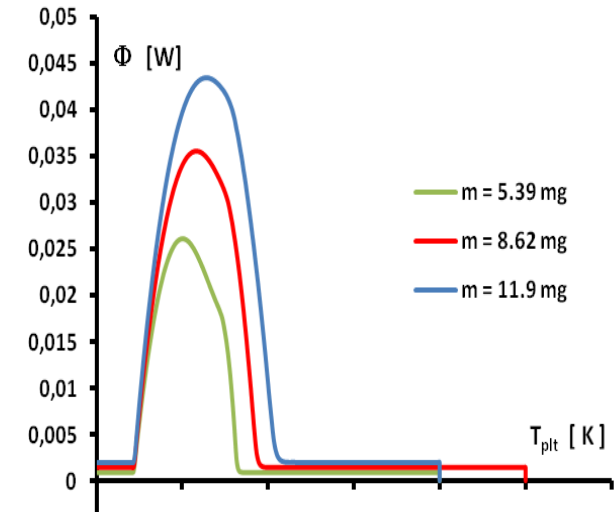
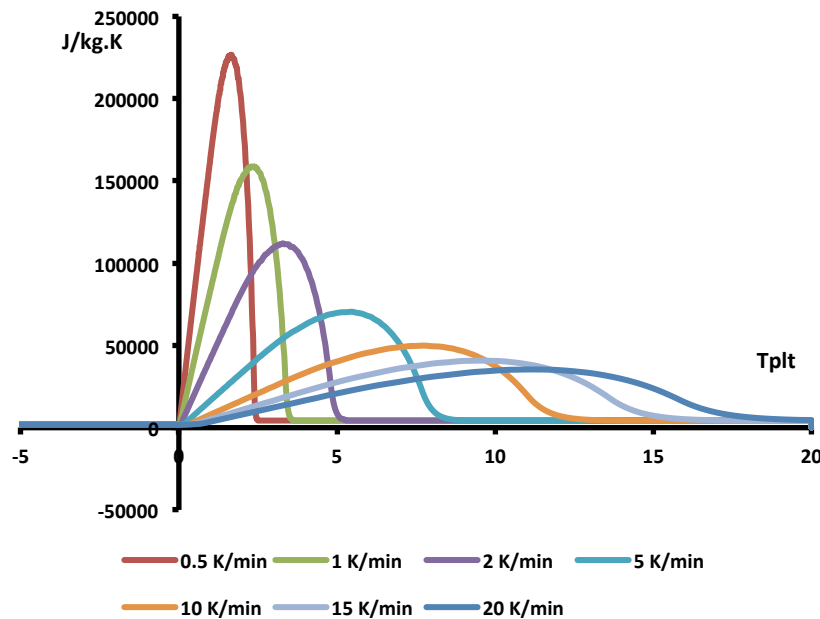
Modélisation / Simulation



Résultats

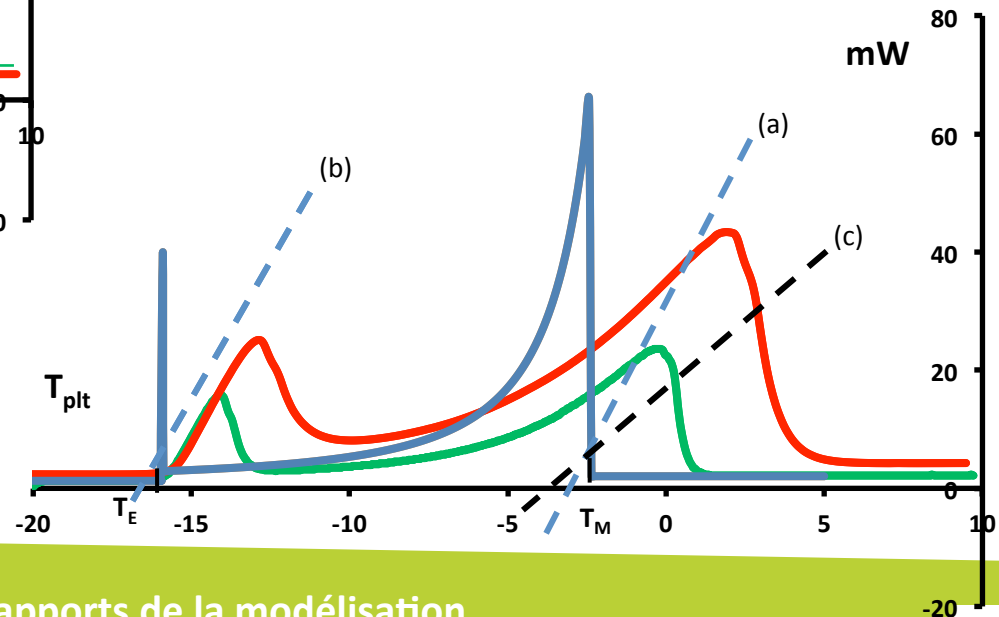
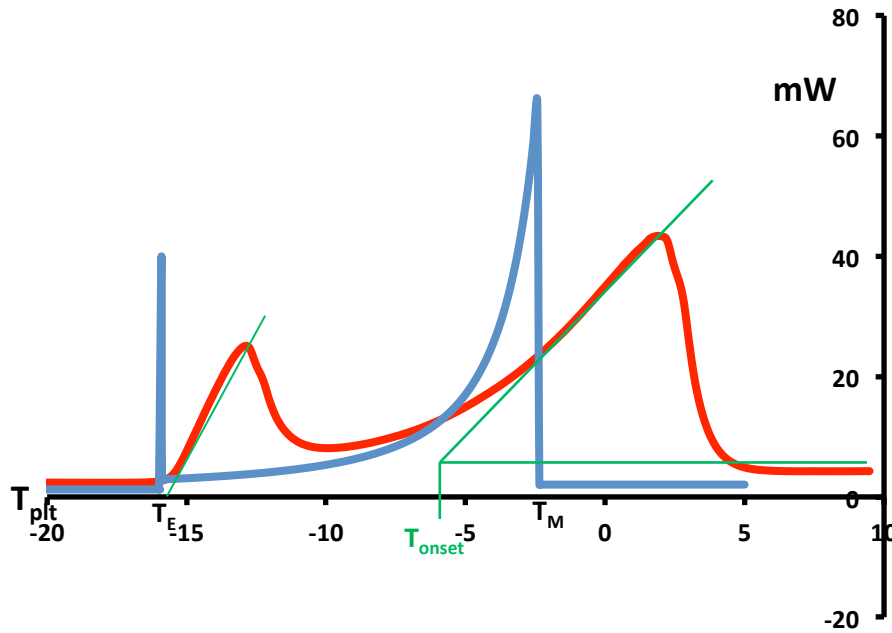
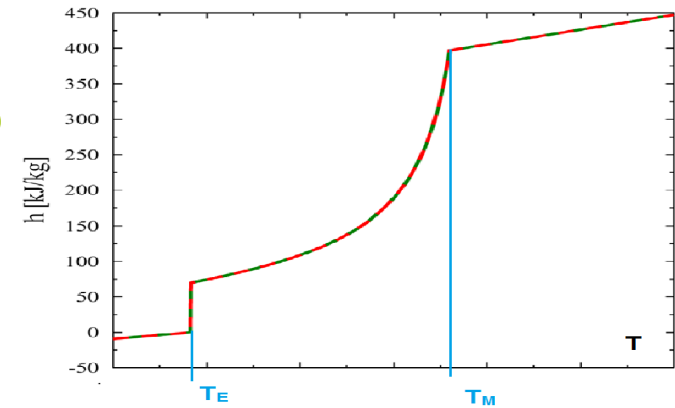
Influence des paramètres de base

- masse
- vitesse



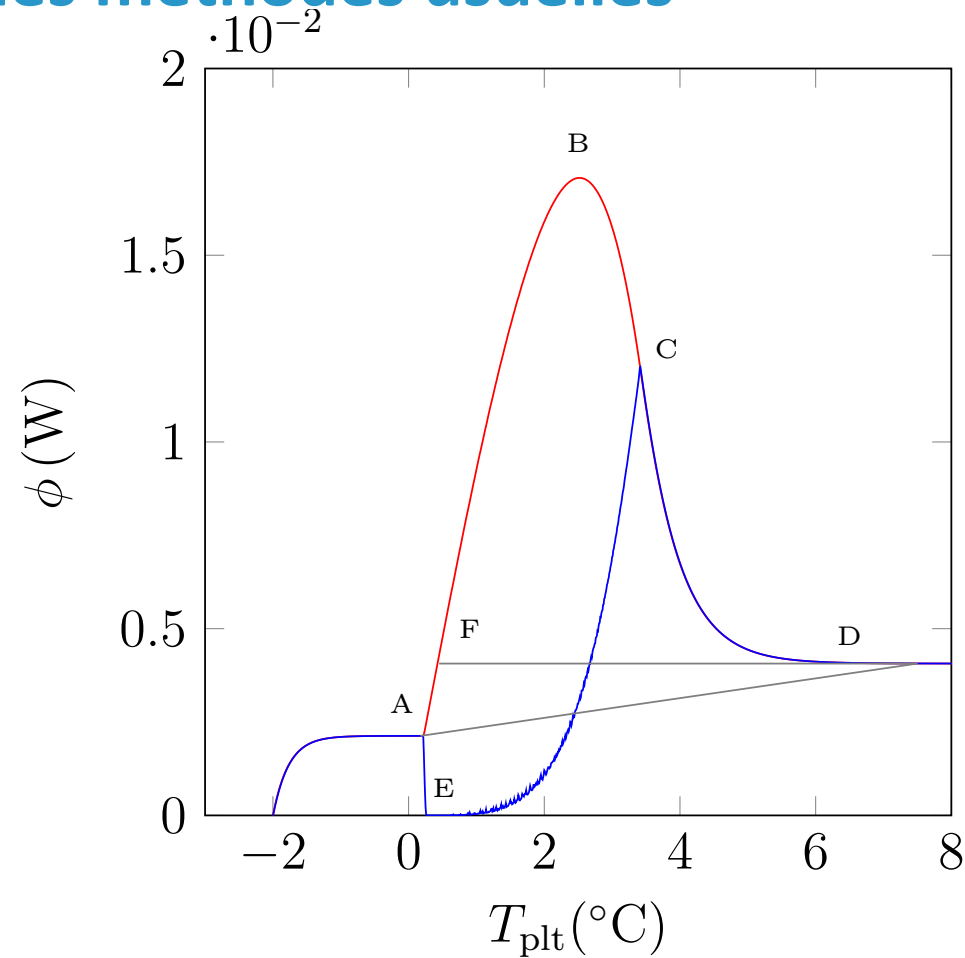
Résultats

Challenge des méthodes usuelles



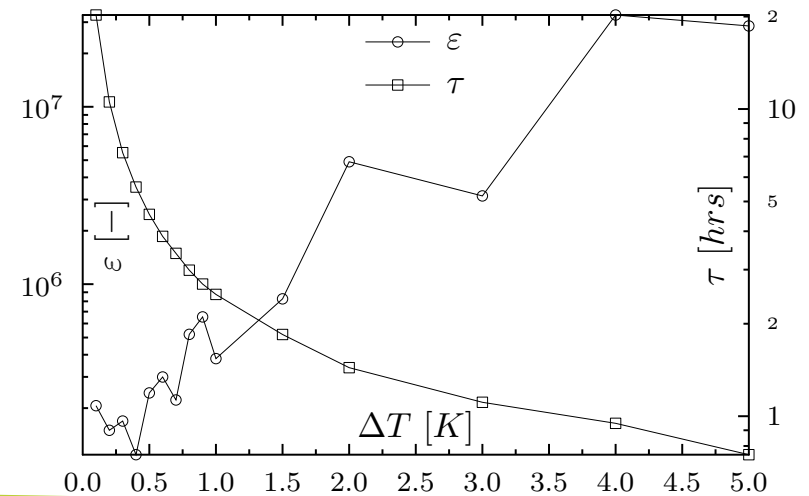
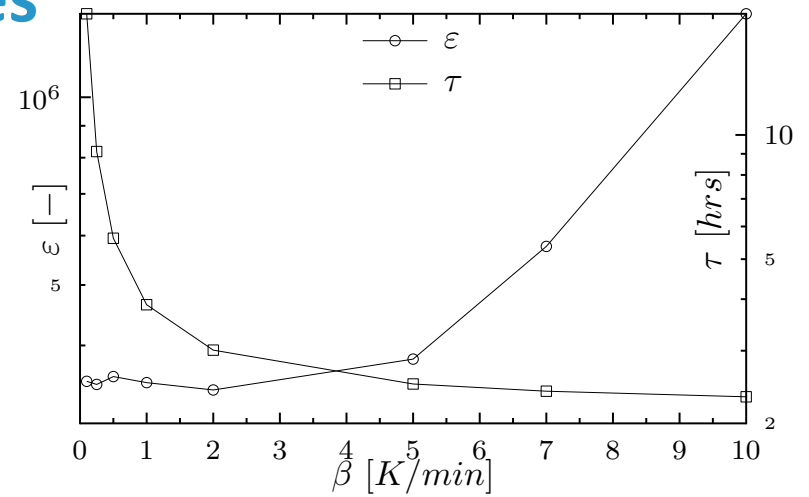
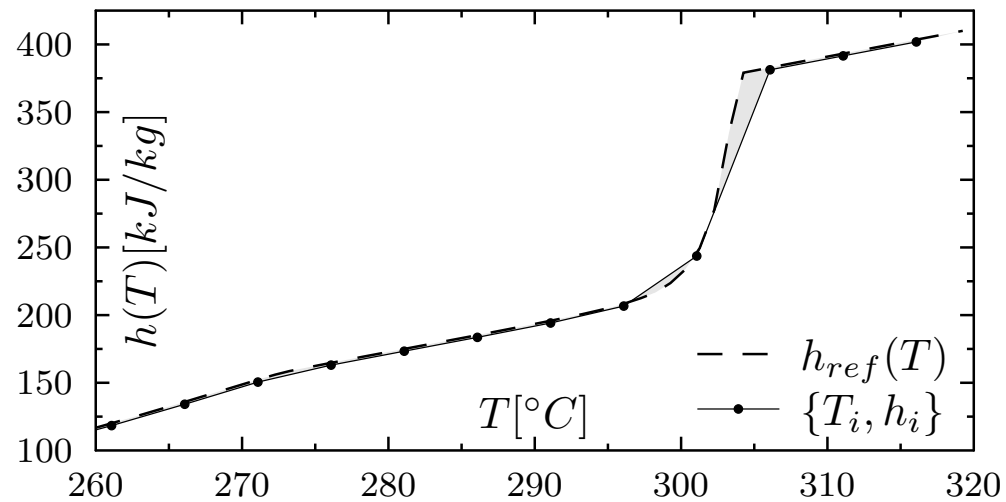
Résultats

Challenge des méthodes usuelles



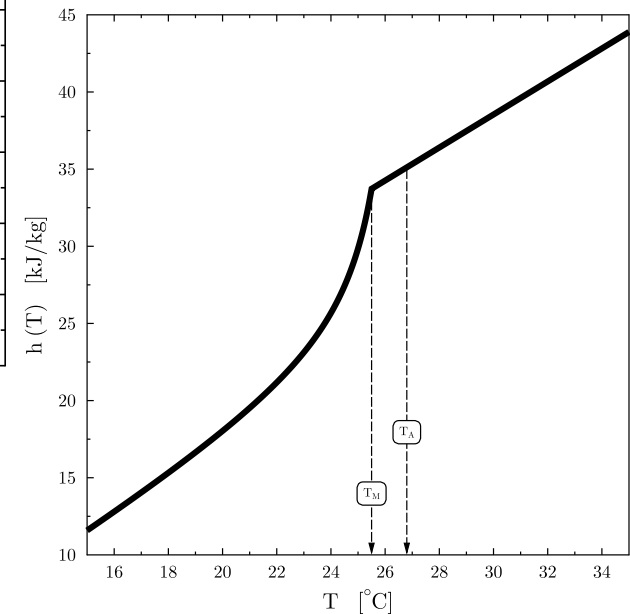
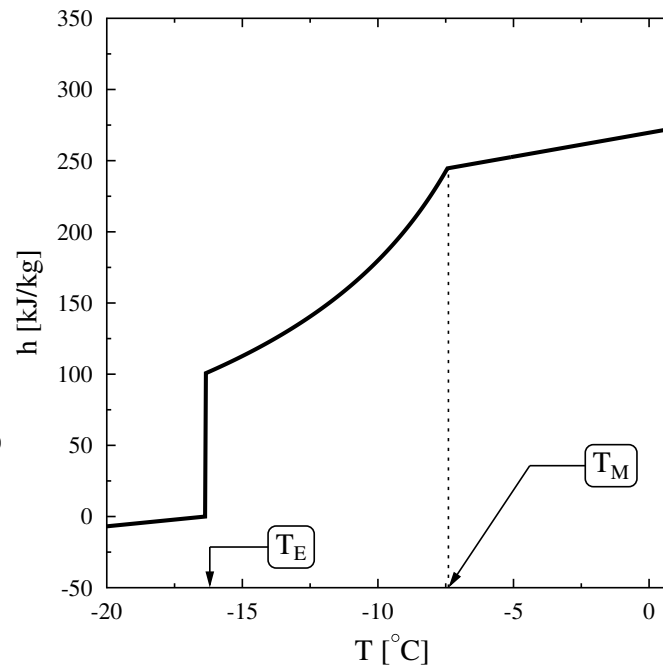
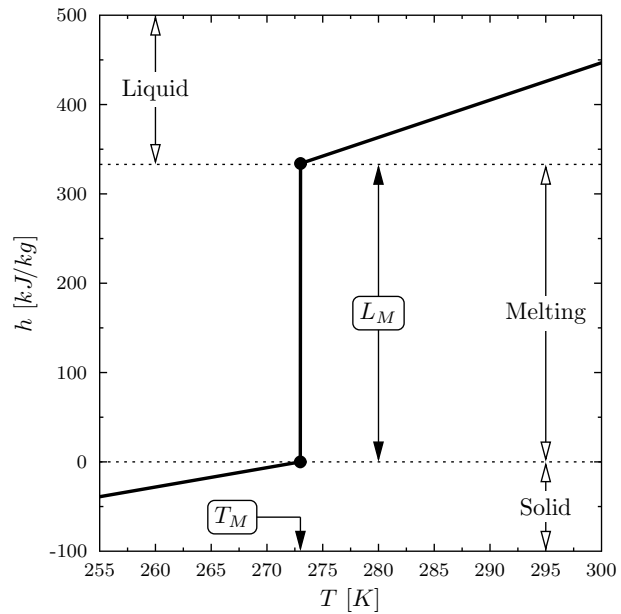
Résultats

Challenge des méthodes usuelles



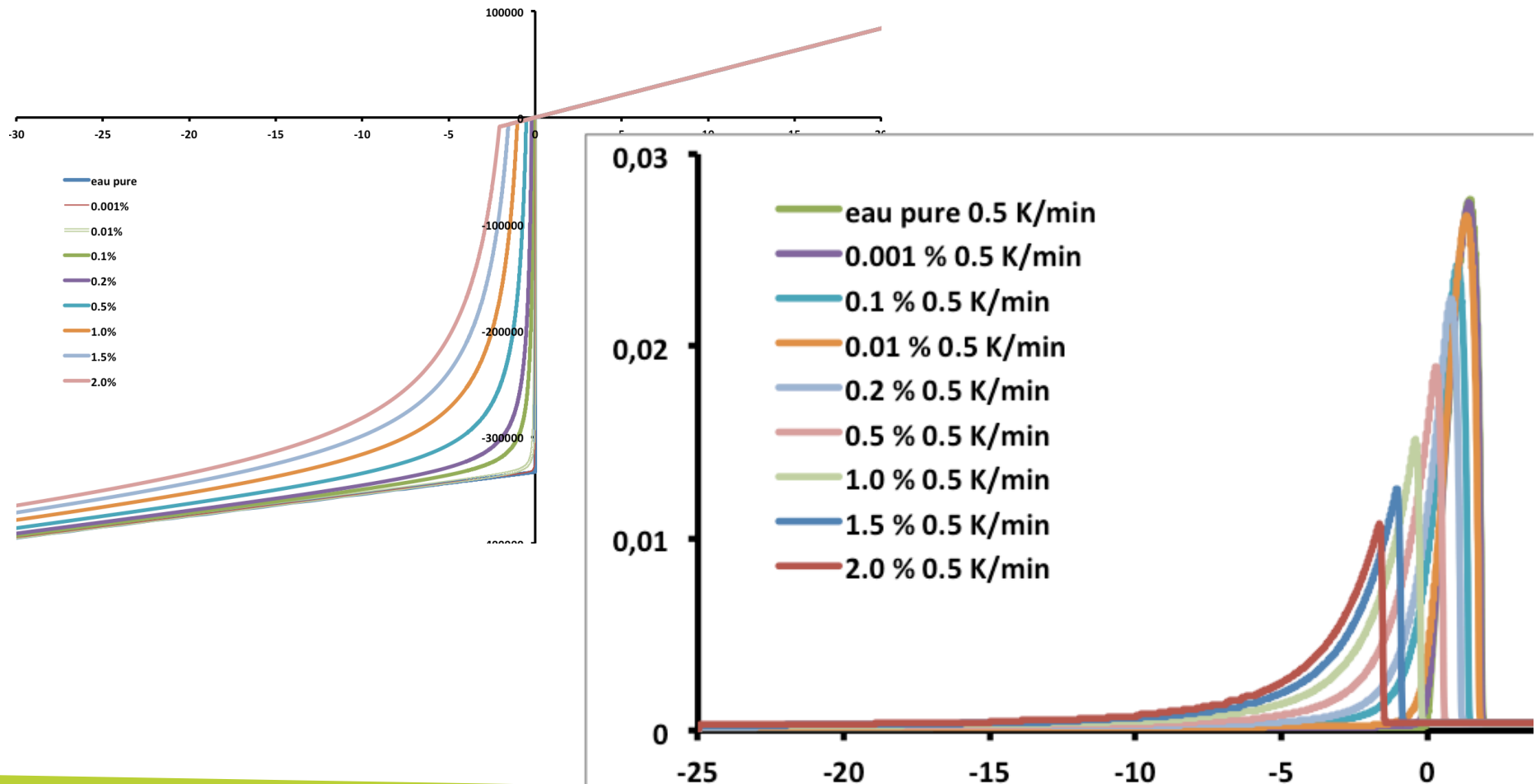
Résultats

Analyse de la fermeture thermodynamique



Résultats

Analyse de la fermeture thermodynamique



Caractérisation

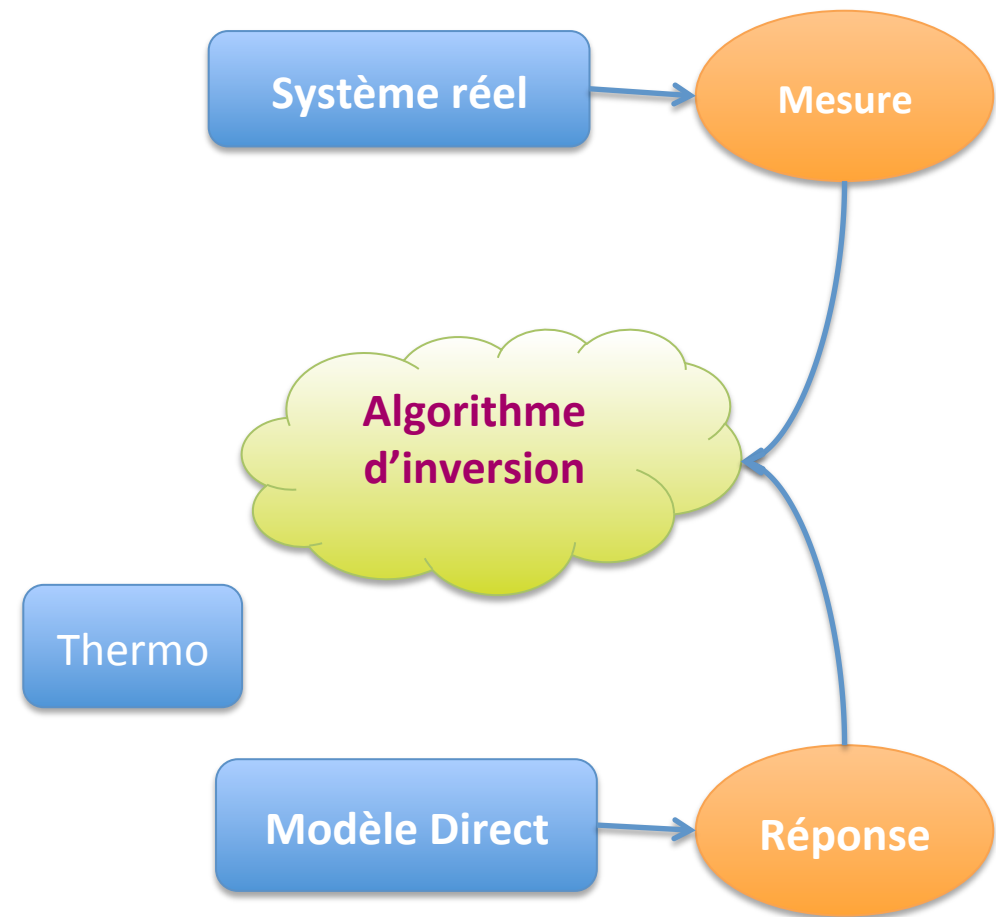
Identification: méthodes inverses

Combinaison exp./num.

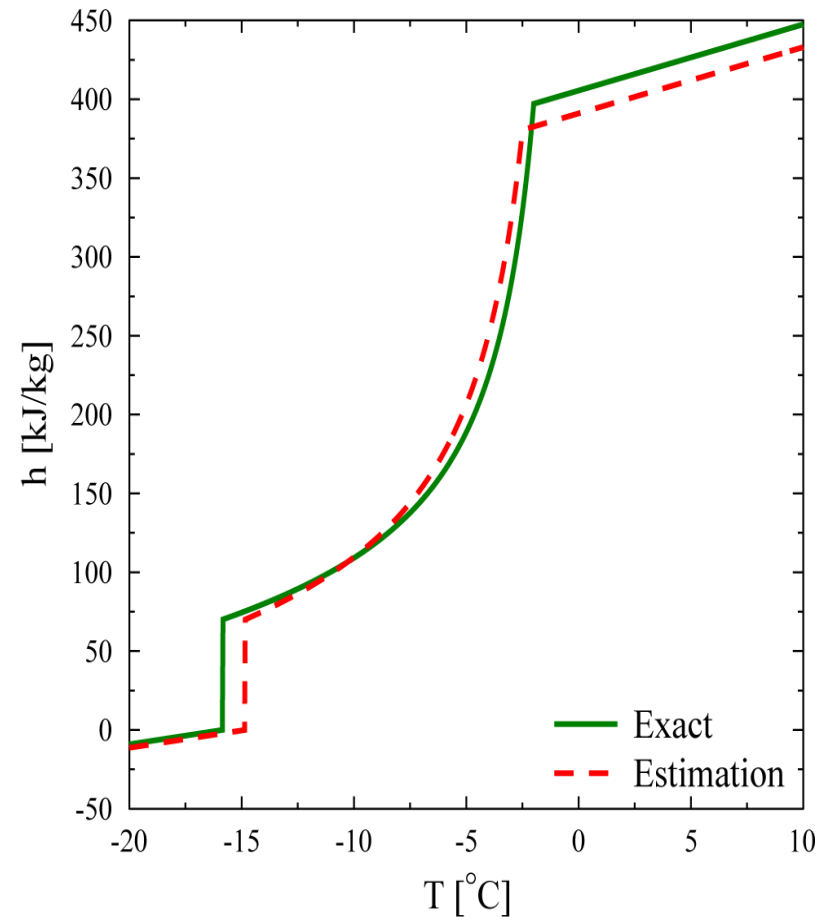
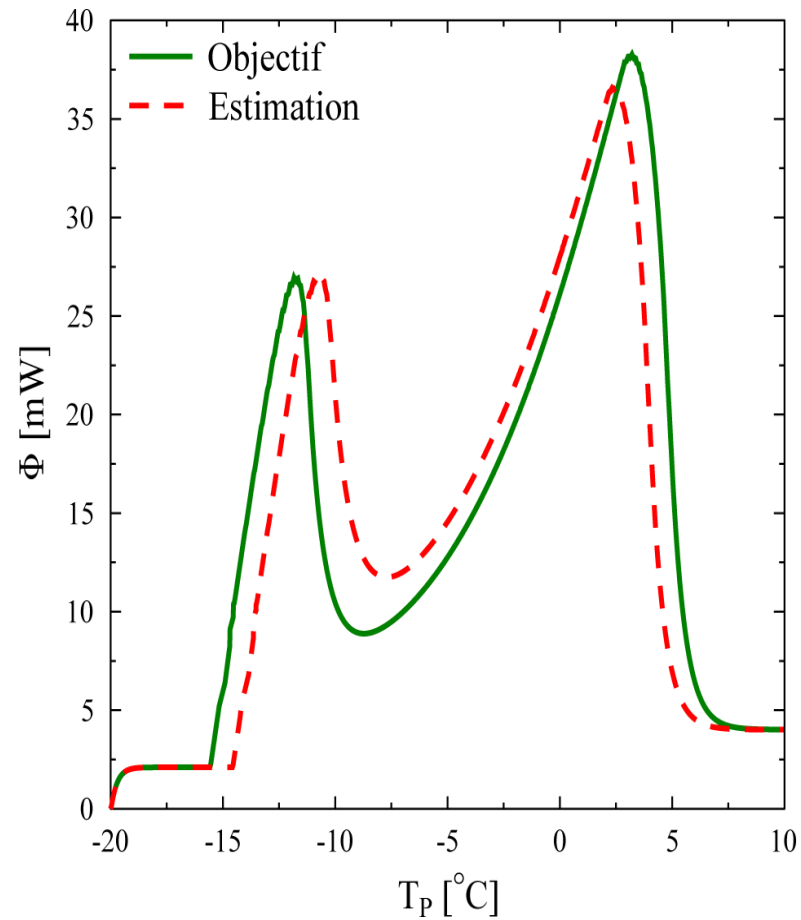
- Mesure du flux de chaleur en fonction du temps
- Modélisation et simulation de la cellule sollicitée

Couplage

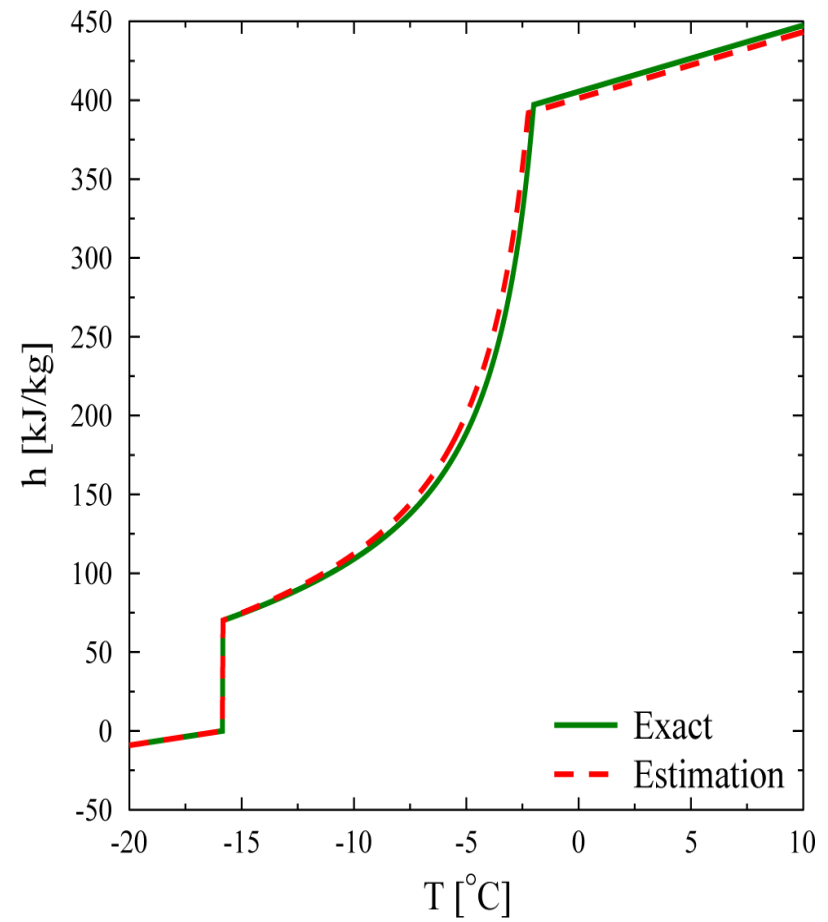
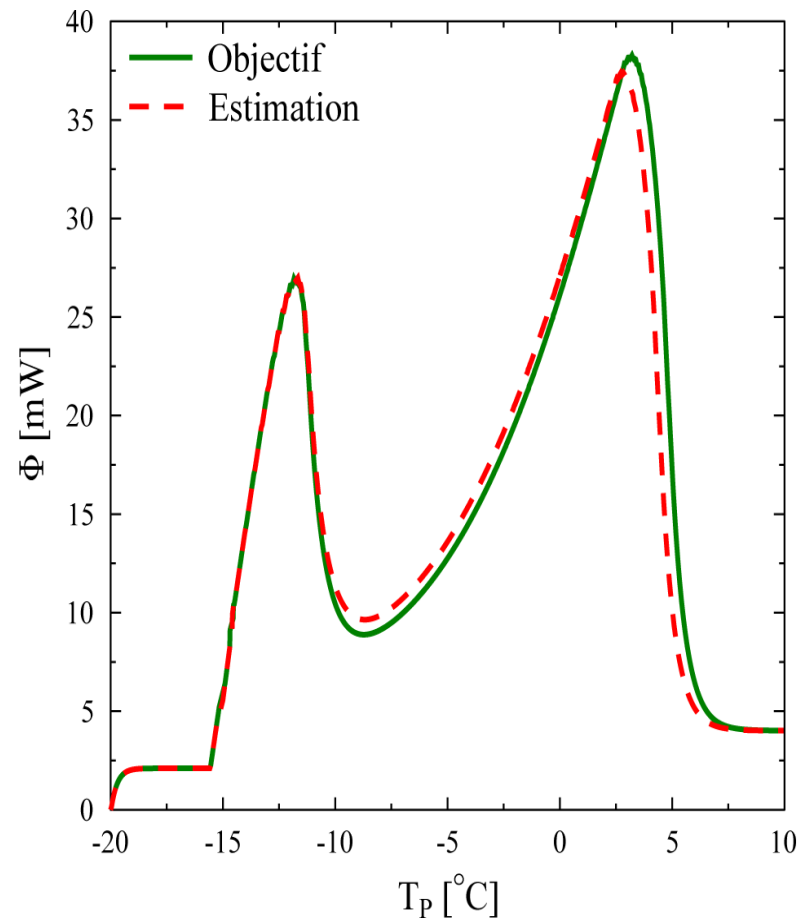
- Définition d'un critère de comparaison (fonction objectif)
- Modification des paramètres d'entrée, dont les paramètres thermodynamiques, pour minimiser la fonction objectif
 - Simplex...
 - Algorithmes génétiques



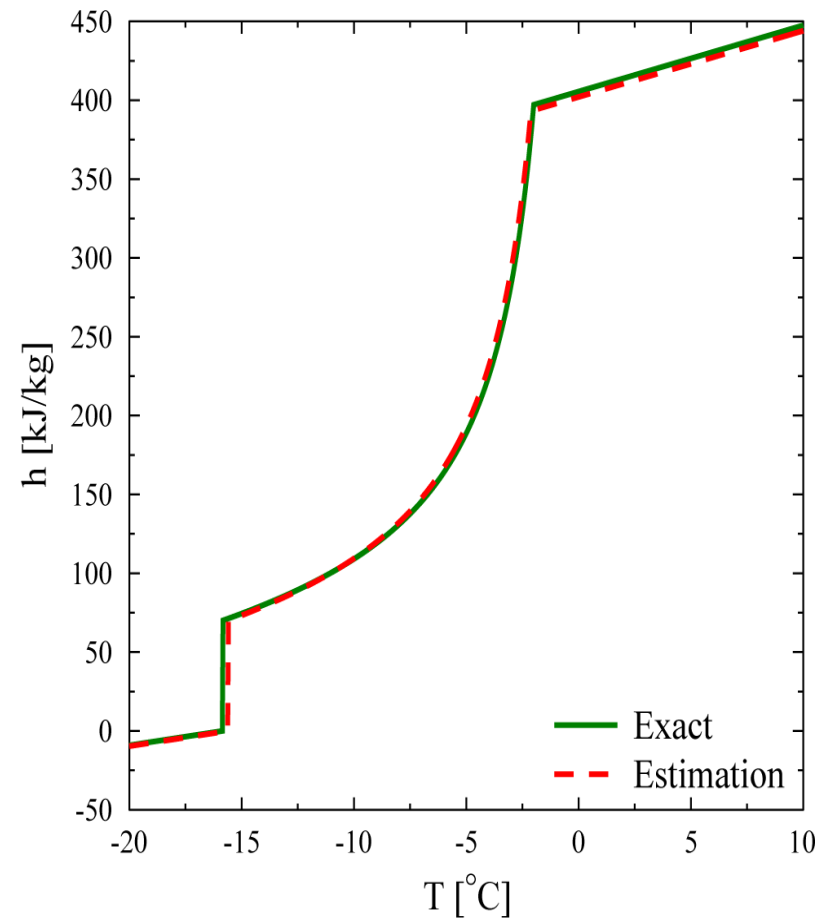
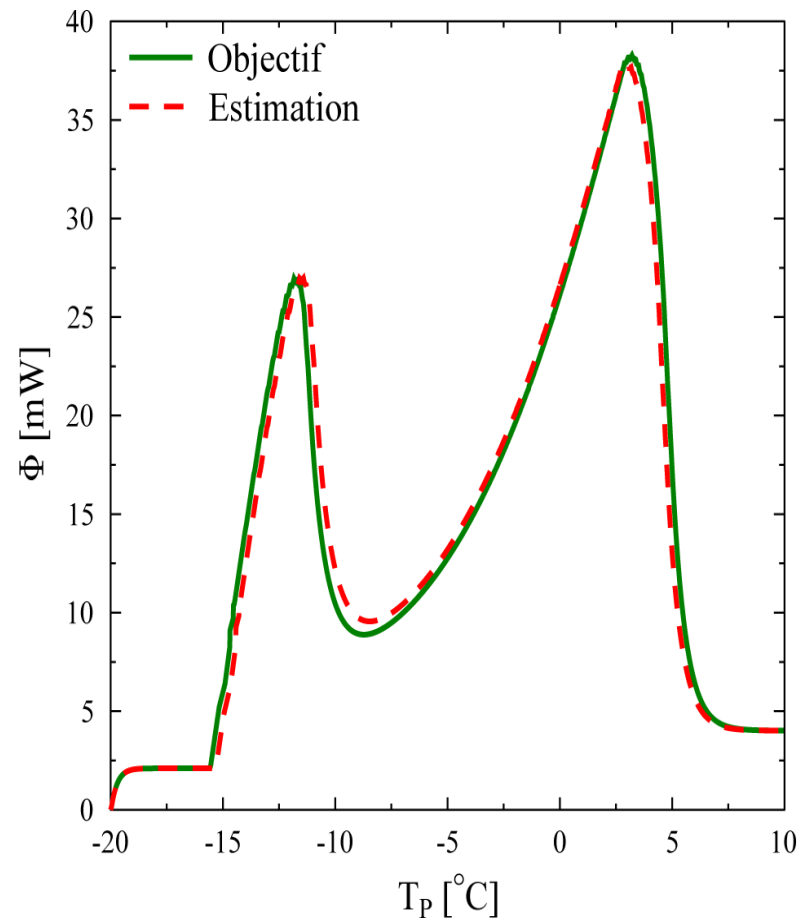
Processus d'inversion



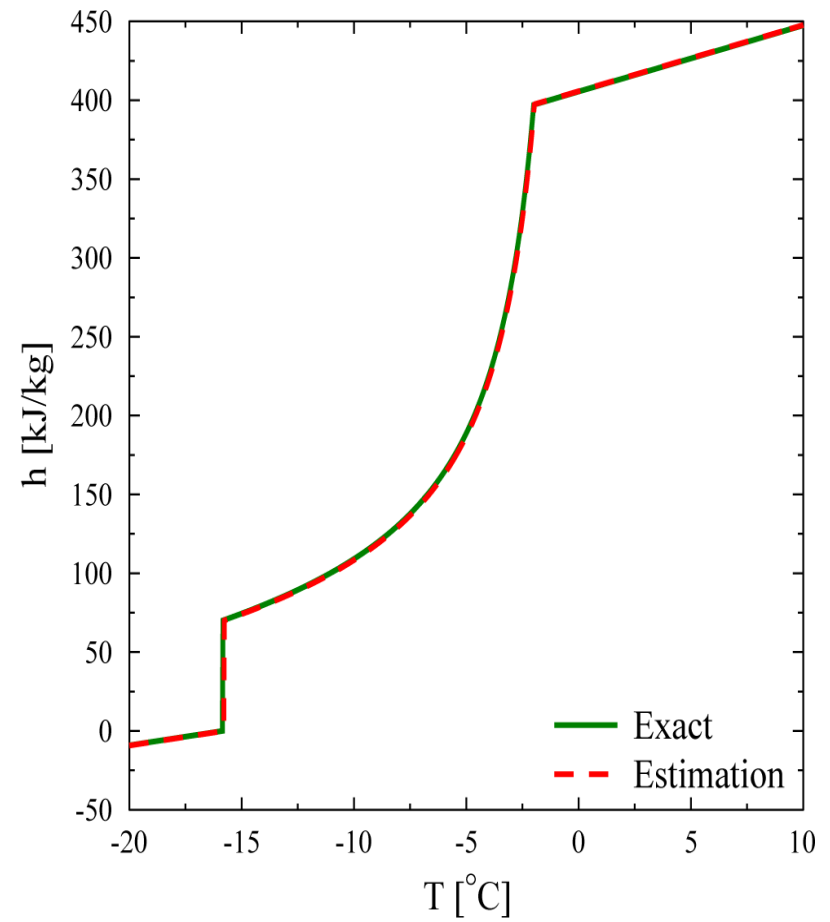
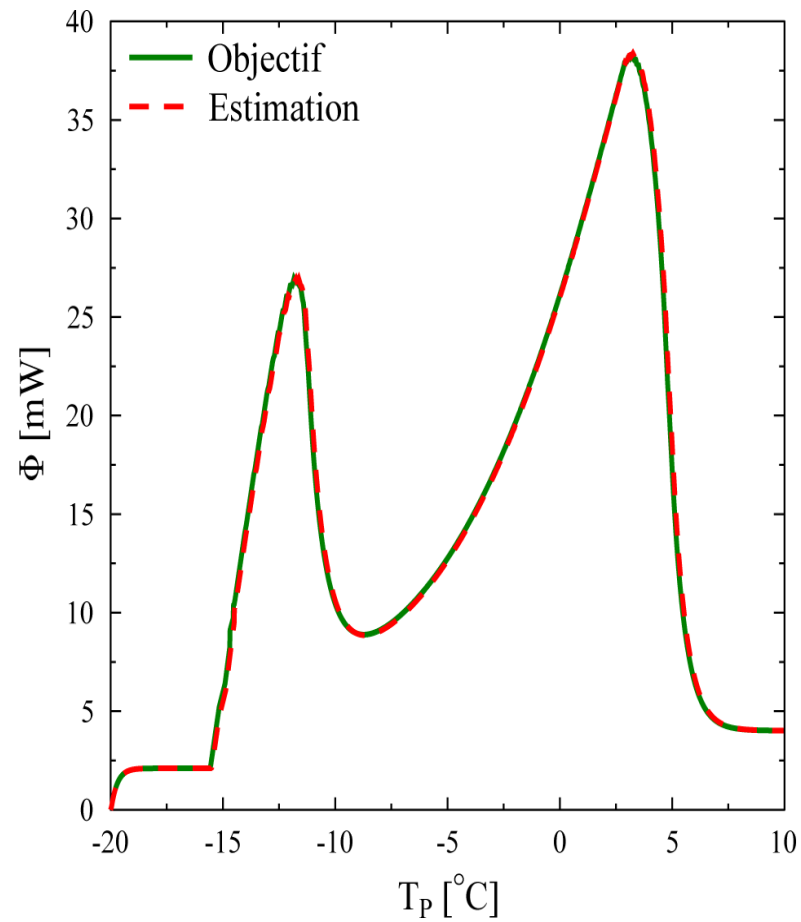
Processus d'inversion



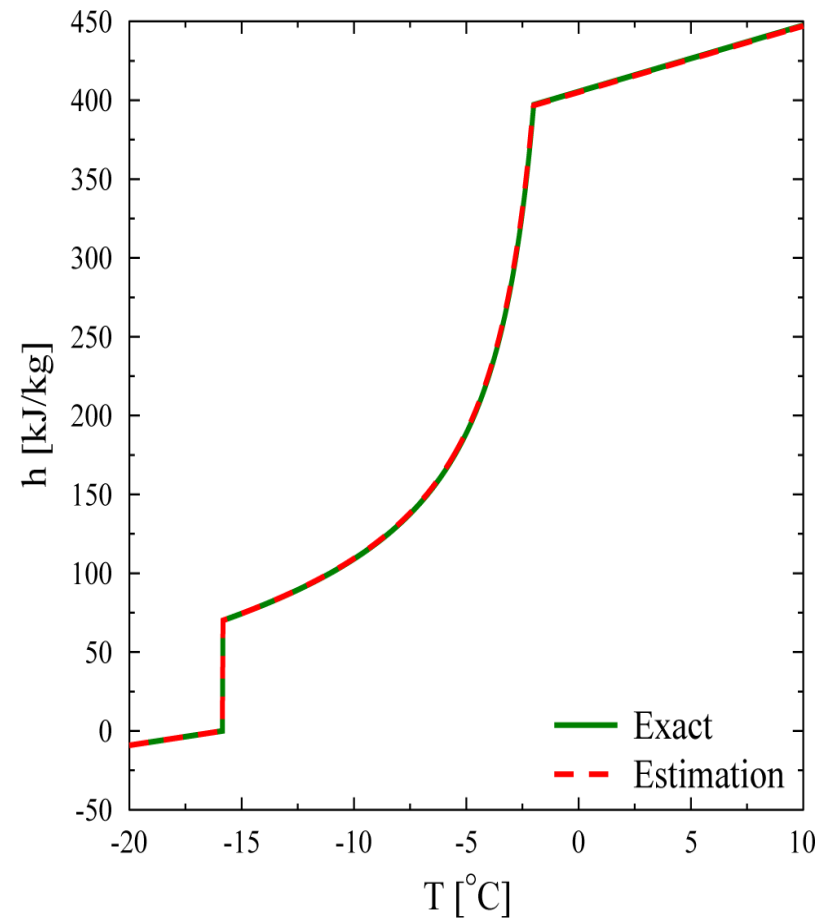
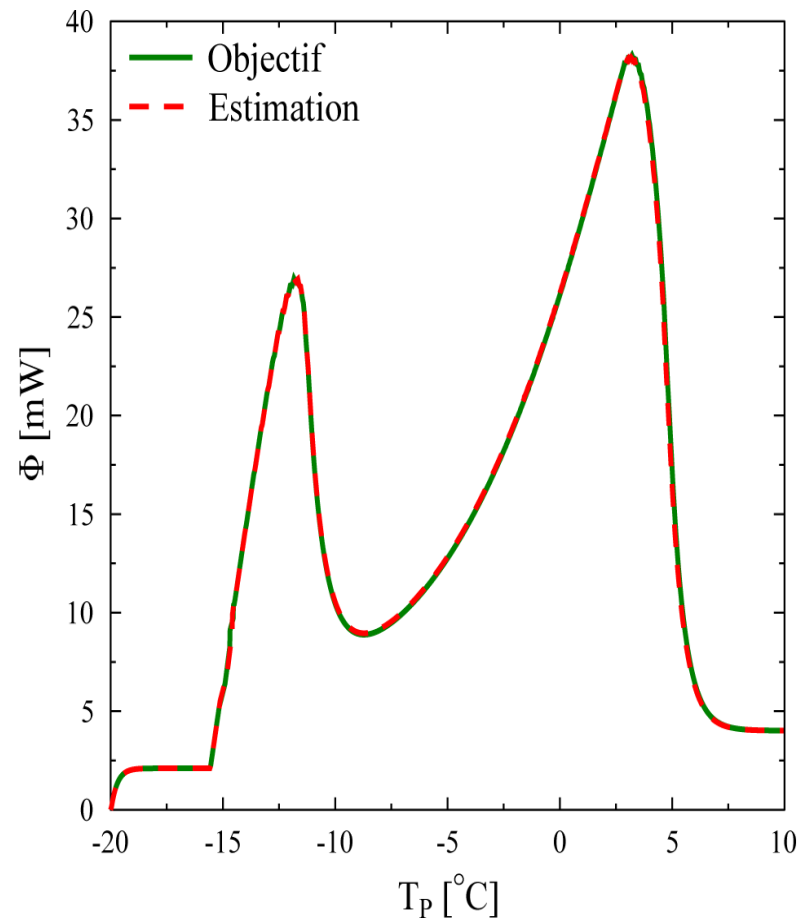
Processus d'inversion



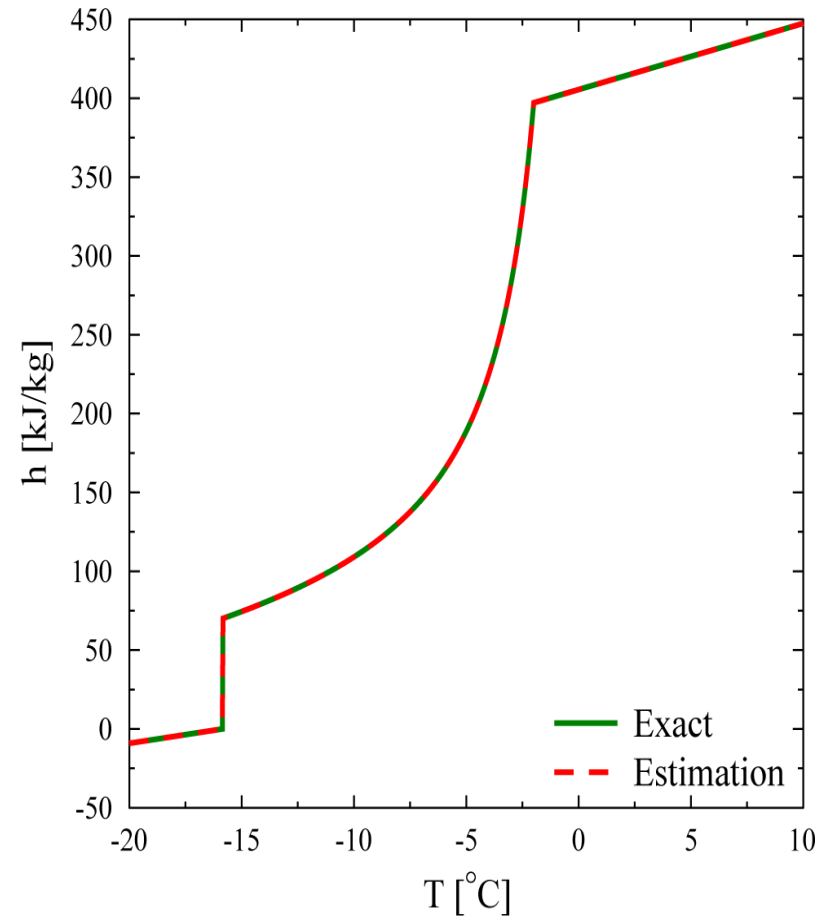
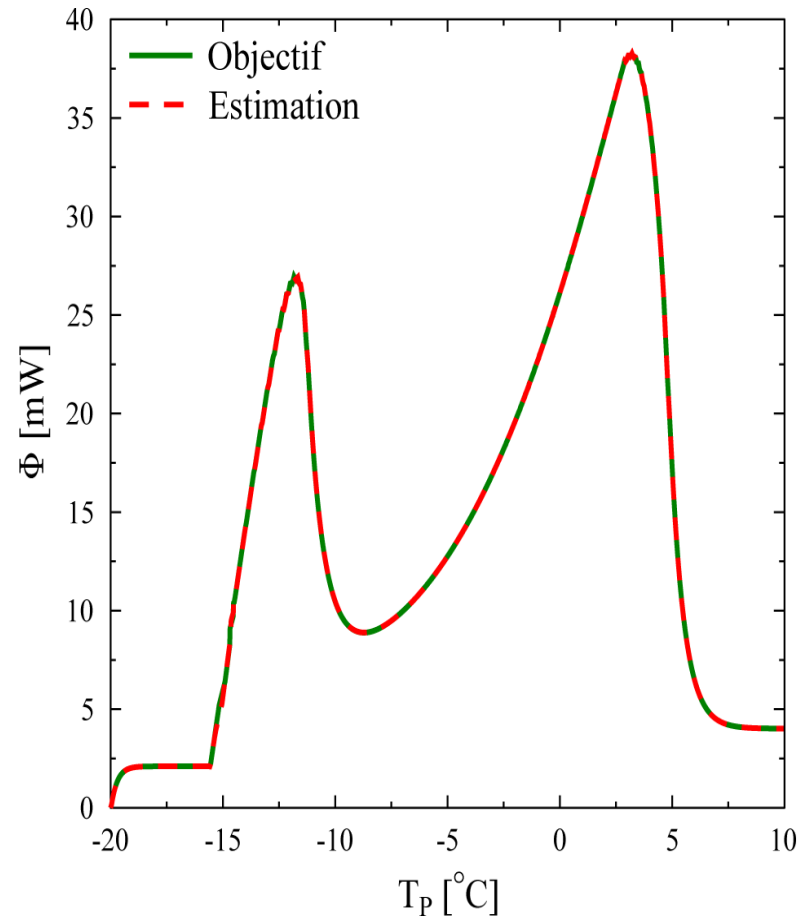
Processus d'inversion



Processus d'inversion

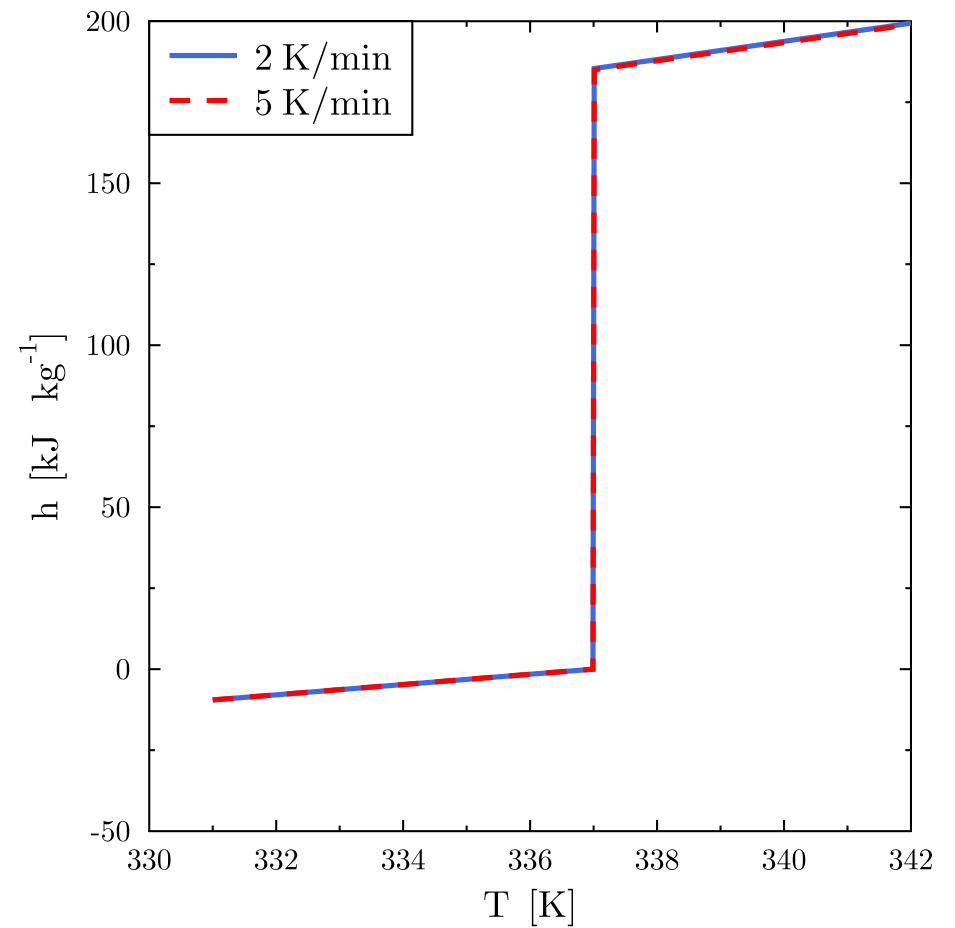
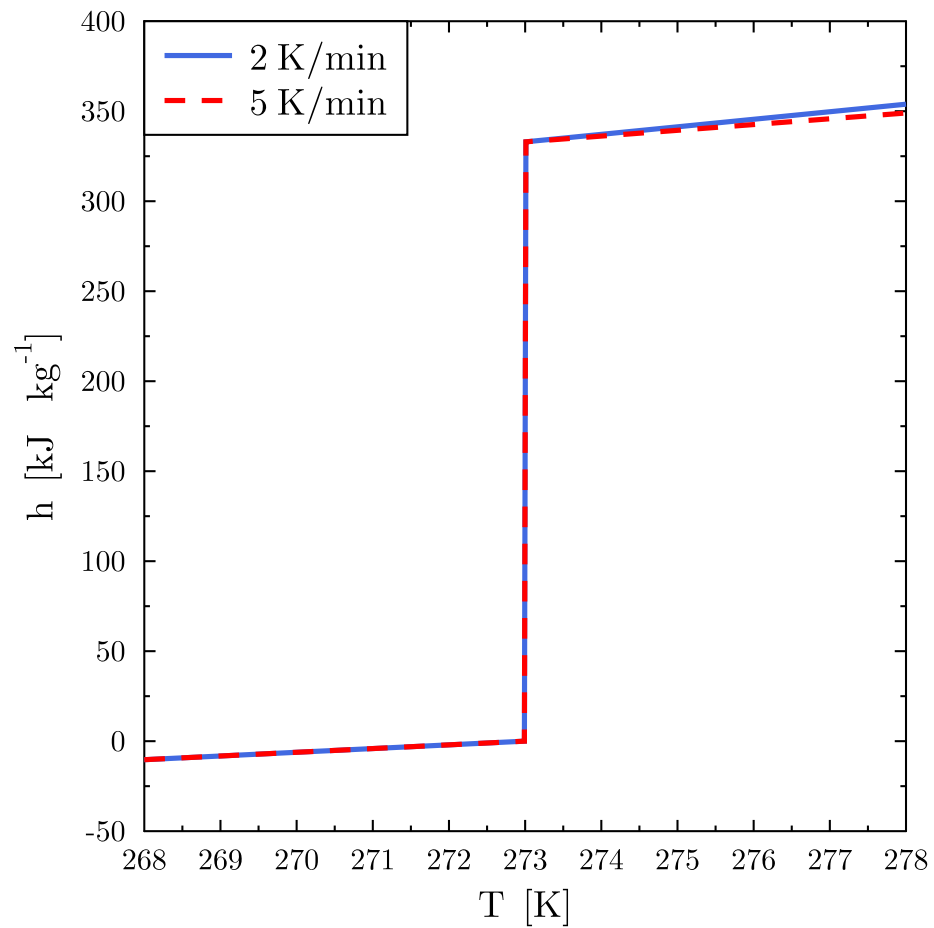


Processus d'inversion



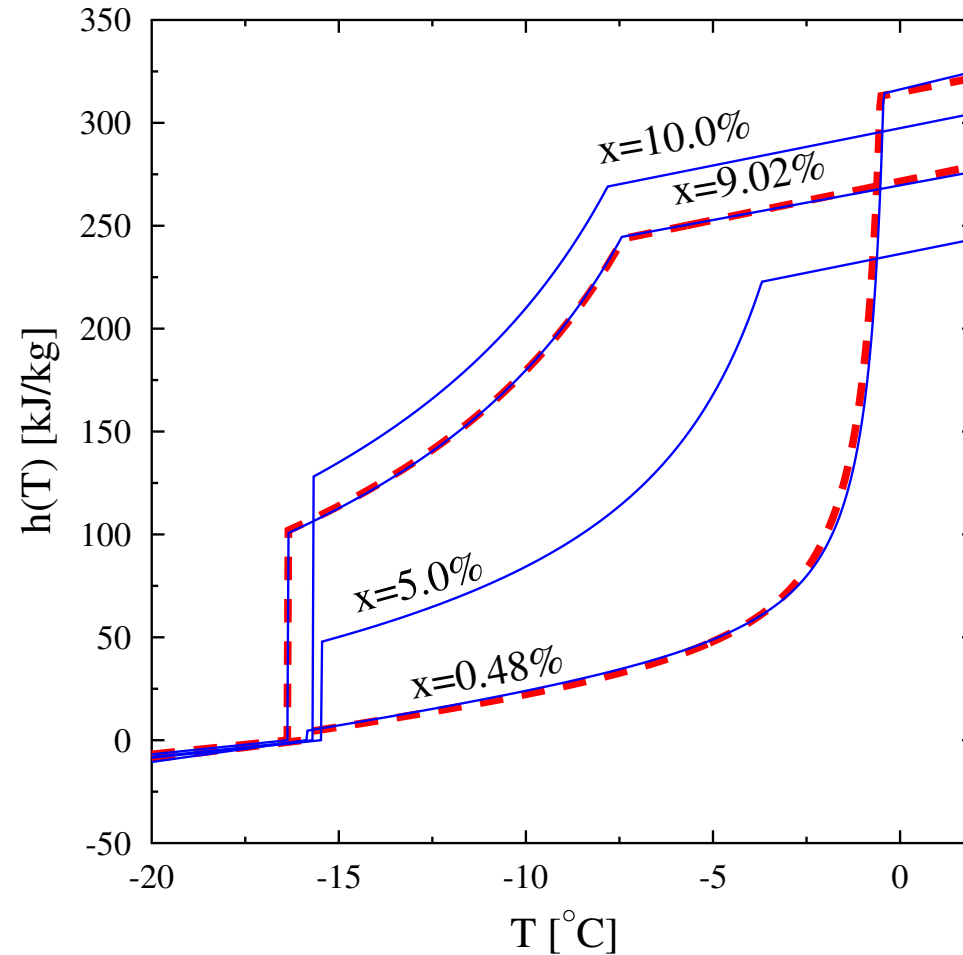
Résultats

Corps purs



Résultats

Mélanges



Conclusion

Conclusion

Méthode pratique

- Informations parcellaires
- Biais de mesure courant
- Interprétation erronée (**très**) répandue

Numérique indispensable

- Meilleure compréhension des phénomènes impliqués, et de **leurs conséquences**
- Challenge et amélioration des méthodes usuelles
- Aide à la mise en place de nouvelles méthodes et/ou protocoles
- Caractérisation plus poussée
 - Thermodynamique consistante
 - Tout type de loi d'état

That's all folks

CONTACT

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Annexes

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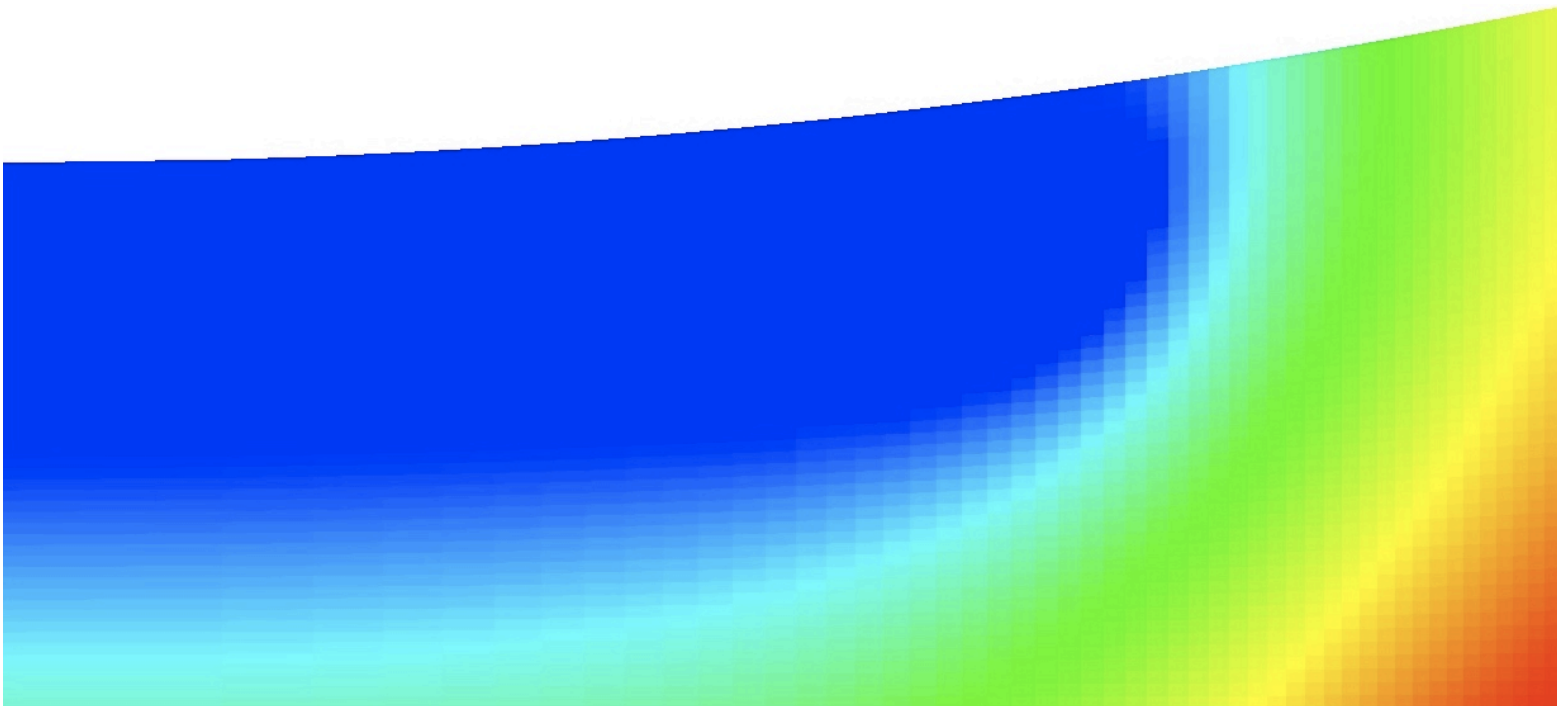
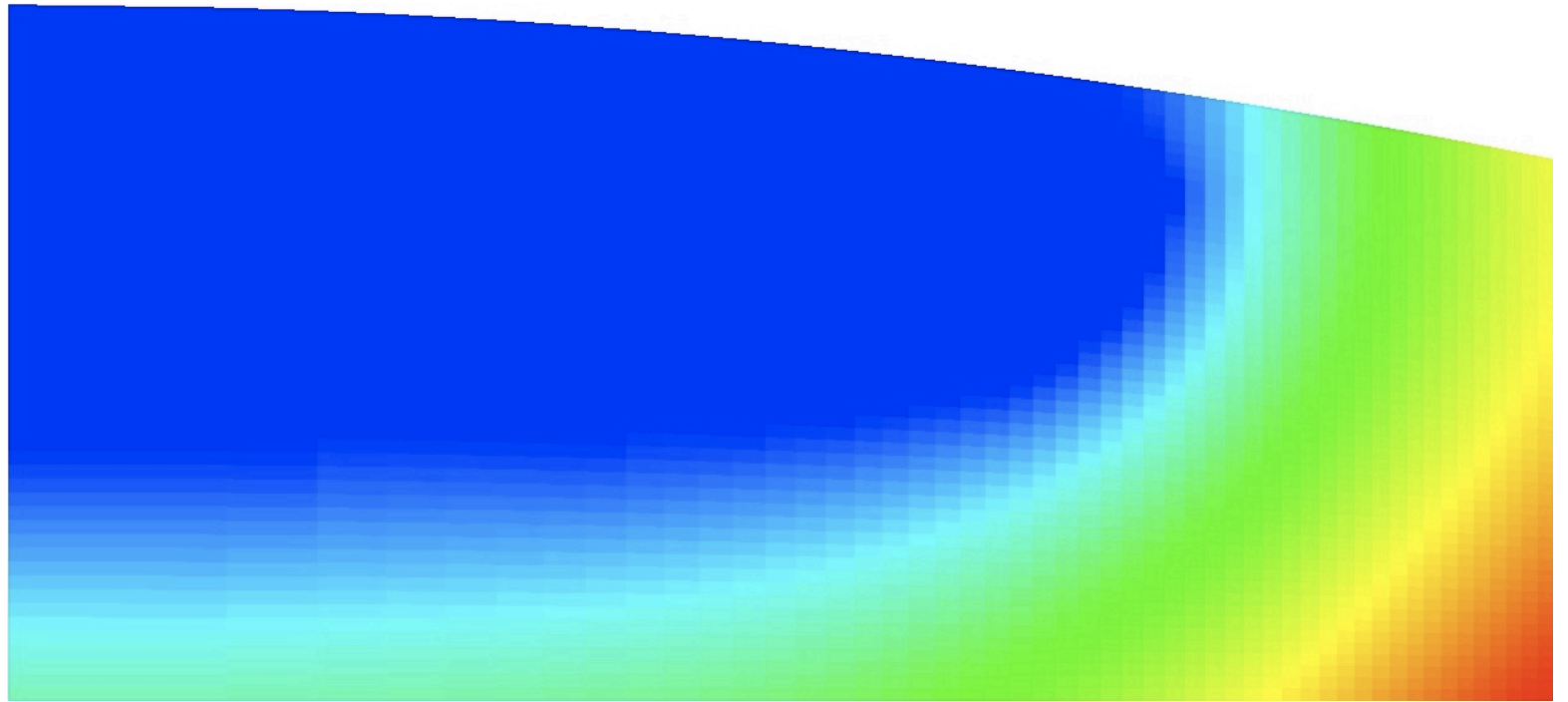
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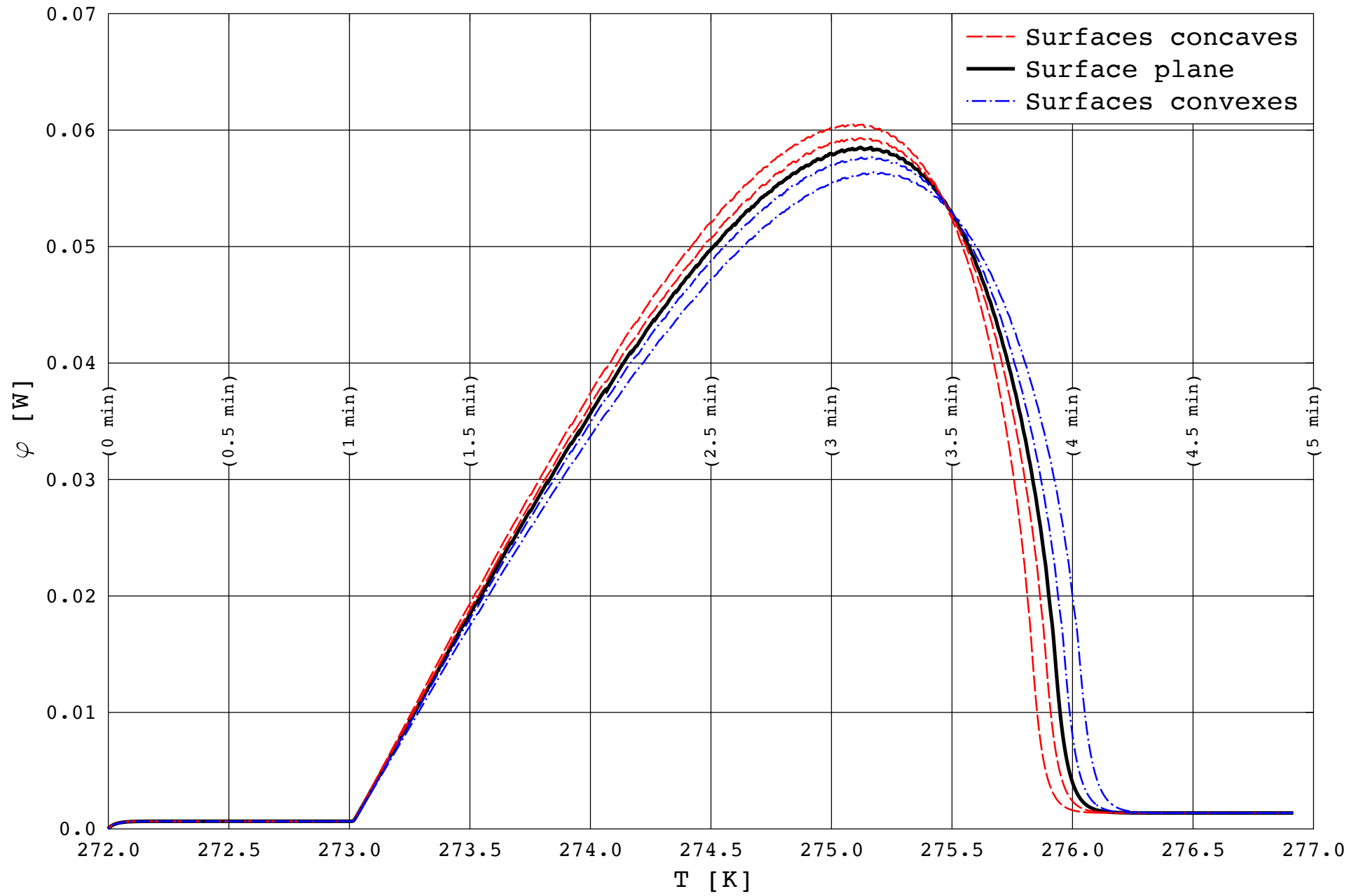
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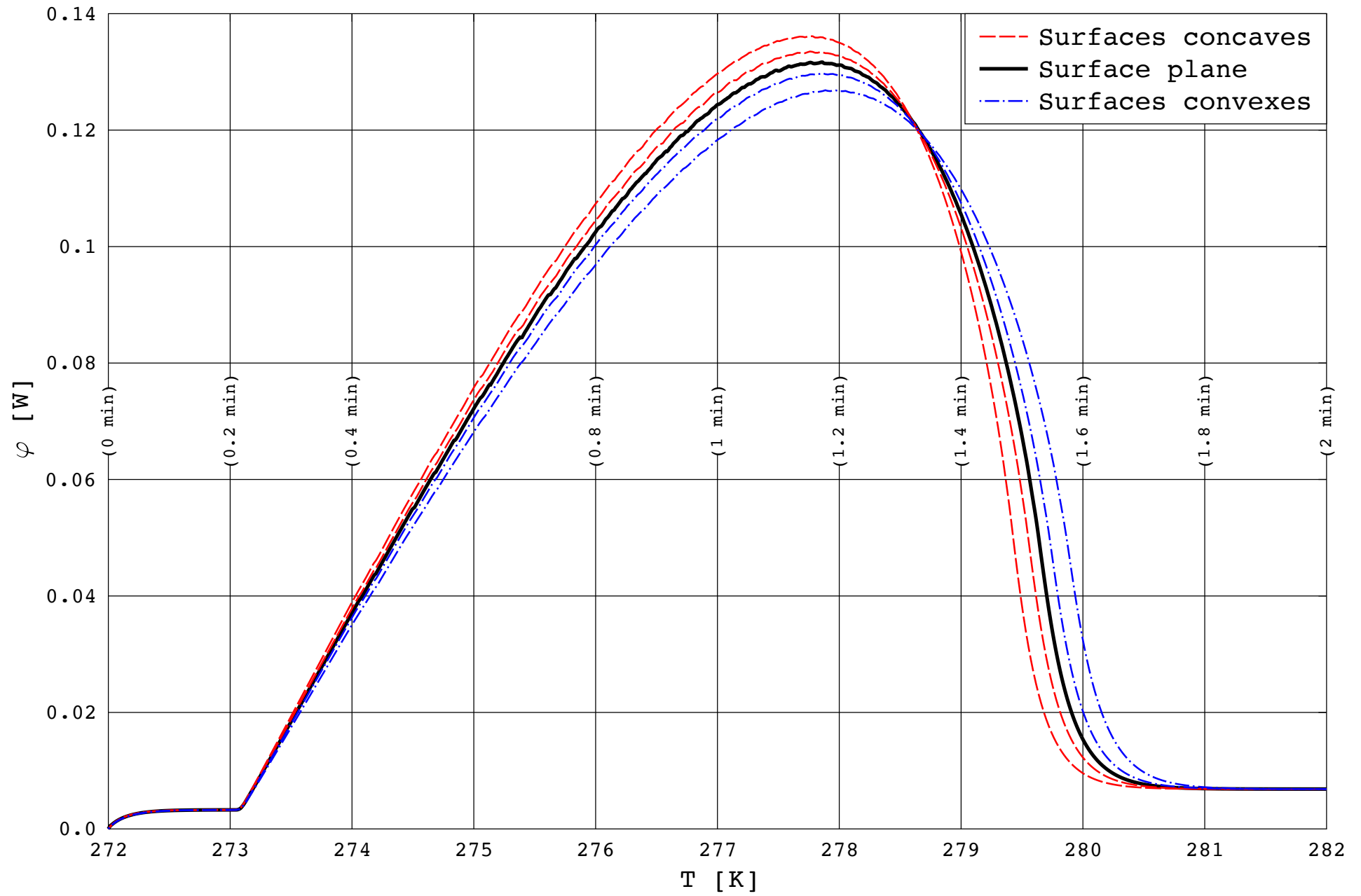
[[Sarge1999](#)] Stefan M. Sarge, Eberhard Gmelin, Günther W.H. Höhne, Heiko K. Cammenga, Wolfgang Hemminger, and Walter Eysel. The caloric calibration of scanning calorimeters. Thermochimica Acta, 247(2) :129 – 168, 1994.

[[Utschick1988](#)] H. Utschick, B. Gobrecht, C. Fleischhauer, A. Treffurth, and H. Müller. On the complex influence of the experimental parameters and the properties of the substances on the representaiton of solid-liquid transitions studied with a differential scanning calorimeter.

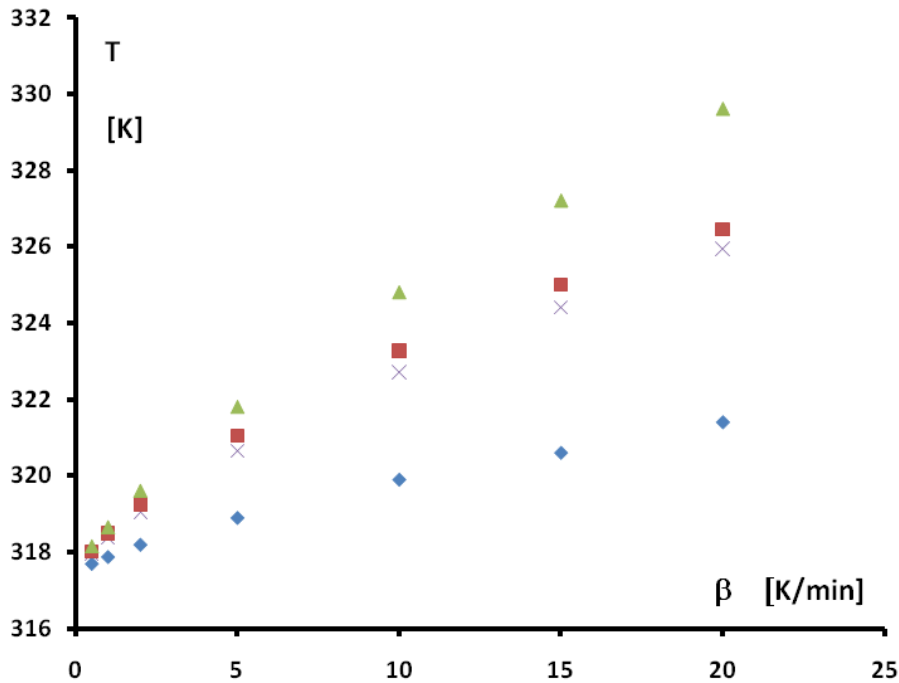
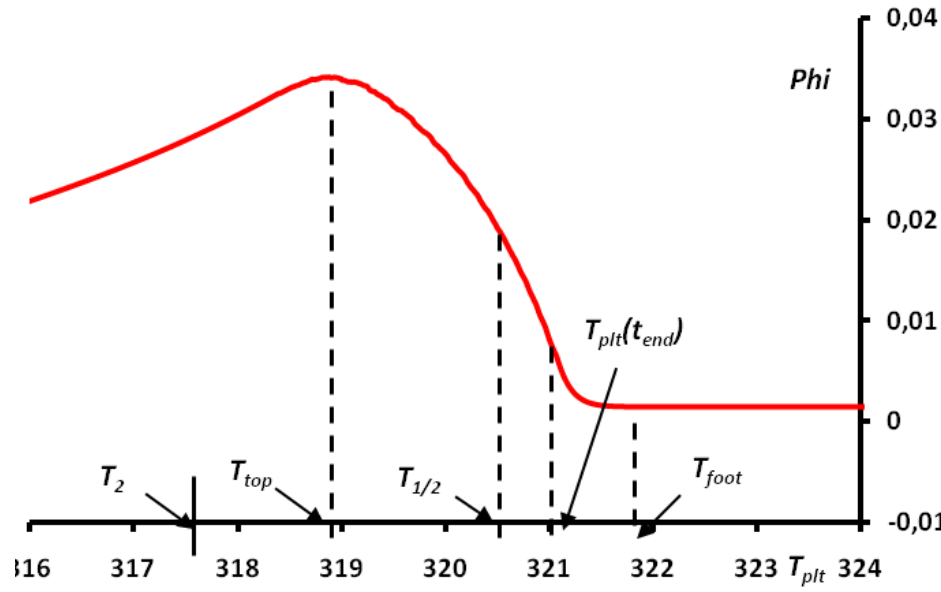
J. Thermal Analysis, 33 :297–304, 1988







Limite « vitesse nulle »



◆ T_{top} × $T_{1/2}$ ■ T_{end} ▲ T_{foot}

