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Current research at the ZAE Bayern – Testing, data representation and modelling of PCM

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Overview

- Ideal and non-ideal melting
- New method to compare different PCM
- Hysteresis and data representation
- Hysteresis and calorimetric measurements
- Experimental investigation of hysteresis
- Modelling of PCM with subcooling

Ideal and non-ideal melting

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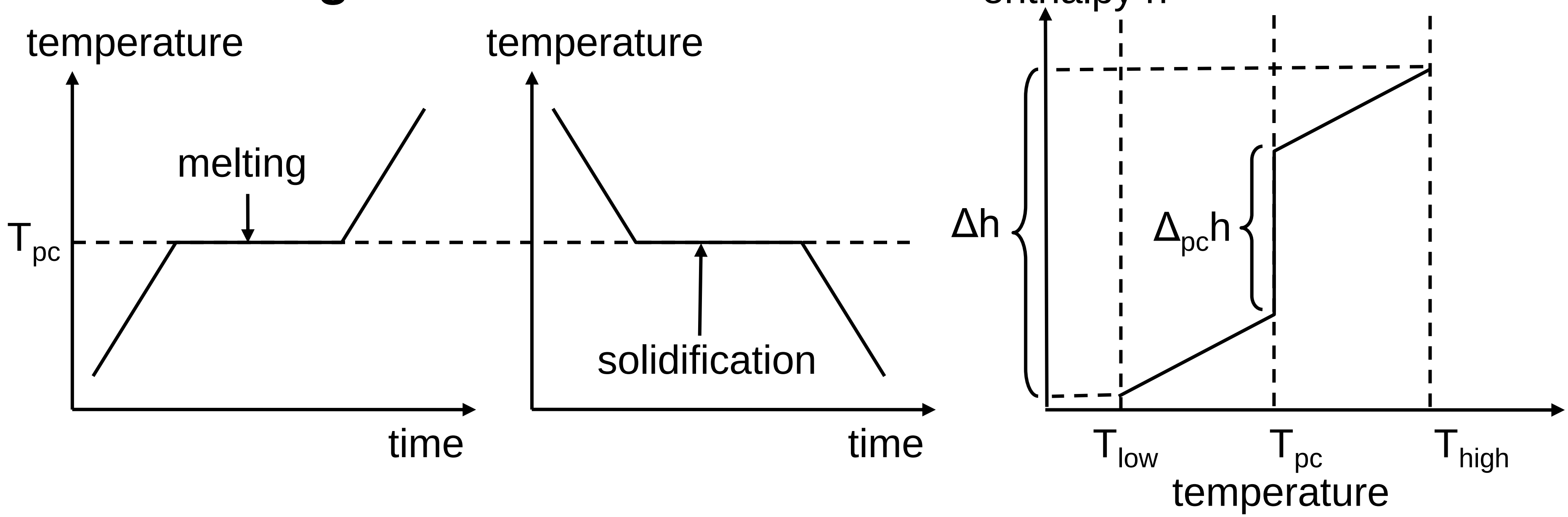
Ideal melting behaviour



Advantage of PCM

- Heat storage with high storage density in a small temperature interval
- Passive temperature stabilization

Data representation ⇒ Tabulation of T_{pc} and $\Delta_{pc}h$

Ideal and non-ideal melting

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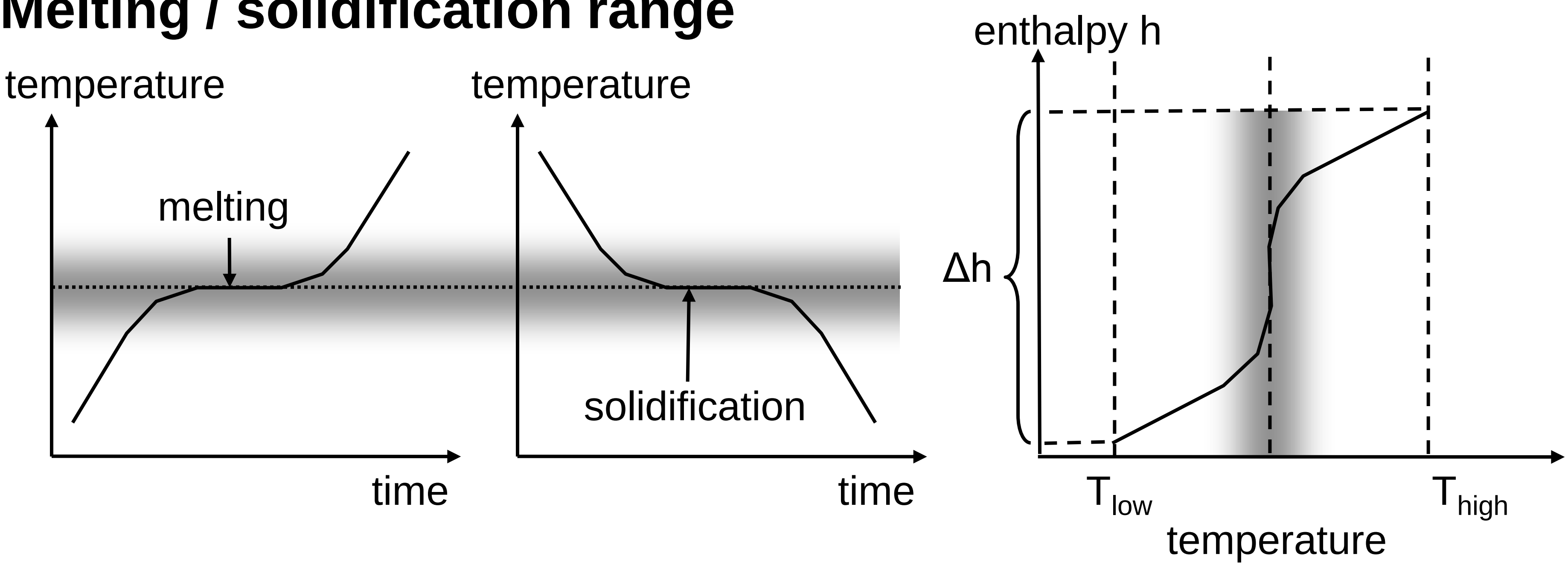
Melting / solidification range



Ideal and non-ideal melting

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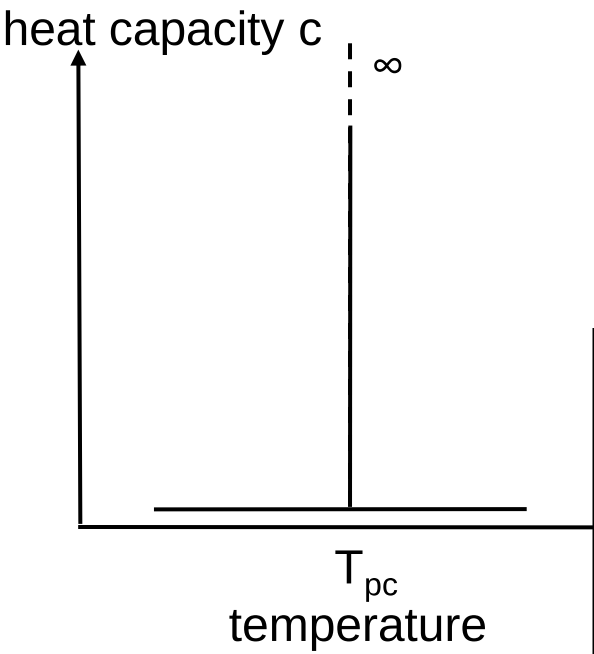
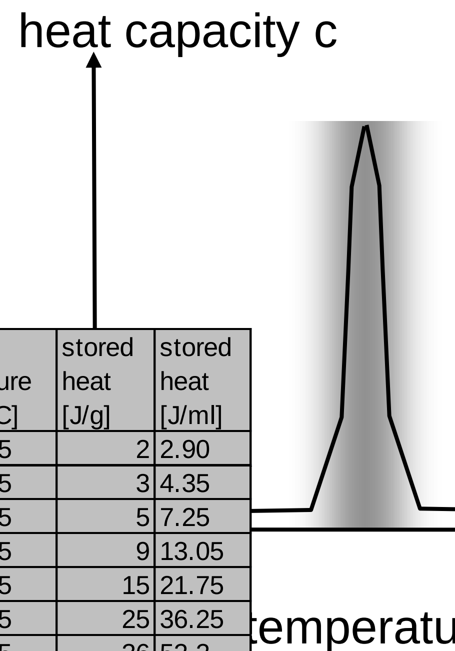
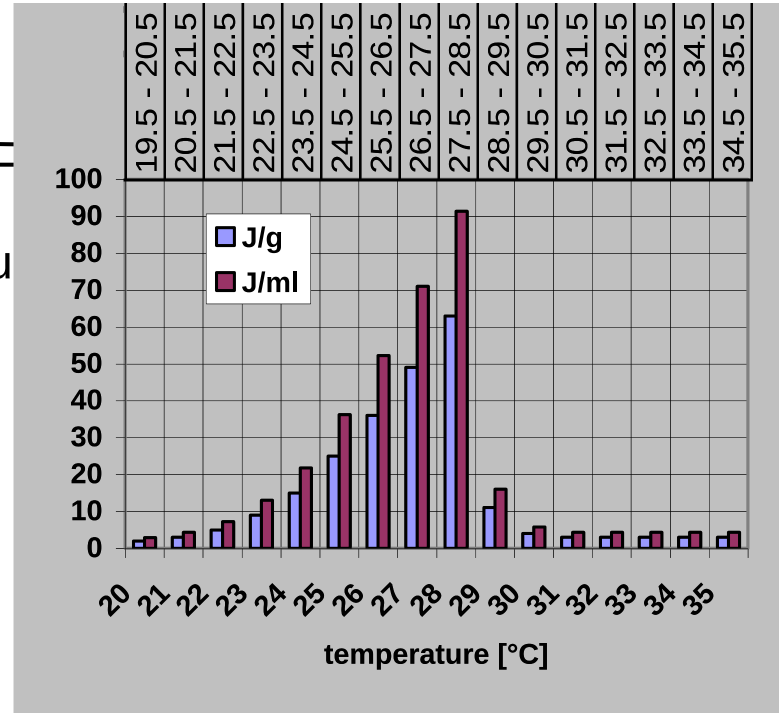
Ideal melting behaviour → Melting / solidification range





Temperature interval [°C]	stored heat [J/g]	stored heat [J/ml]
19.5 - 20.5	2	2.90
20.5 - 21.5	3	4.35
21.5 - 22.5	5	7.25
22.5 - 23.5	9	13.05
23.5 - 24.5	15	21.75
24.5 - 25.5	25	36.25
25.5 - 26.5	36	52.2
26.5 - 27.5	49	71.05
27.5 - 28.5	63	91.35
28.5 - 29.5	11	15.95
29.5 - 30.5	4	5.8
30.5 - 31.5	3	4.35
31.5 - 32.5	3	4.35
32.5 - 33.5	3	4.35
33.5 - 34.5	3	4.35
34.5 - 35.5	3	4.35
min. density [g/ml]	1.45	

Data representation
⇒ Tabulation of the stored heat (or enthalpy) in temperature intervals



New method to compare different PCM

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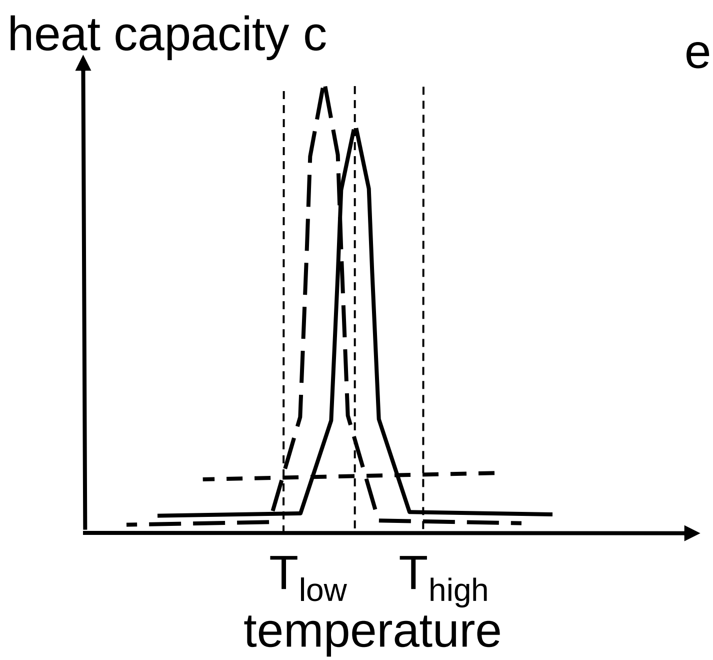
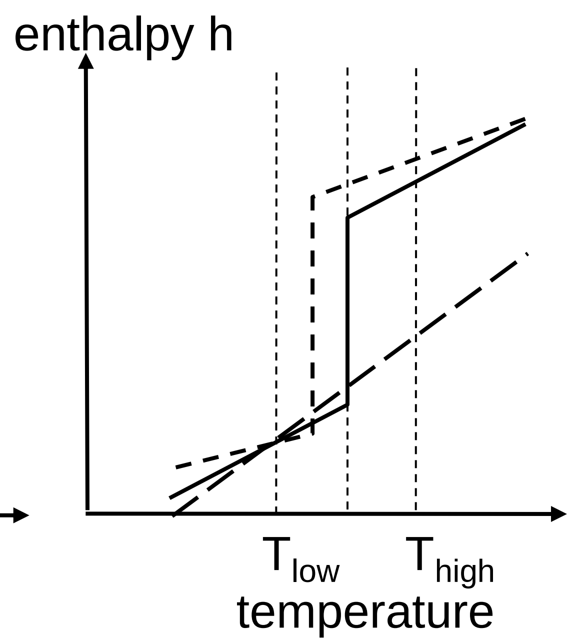
New method to evaluate the heat storage density in latent heat storage for arbitrary temperature ranges

Assumption: PCM with no hysteresis

Problem: which PCM has the higher storage density?





What if the temperature range changes?

New method to compare different PCM

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Solution:

Δh / kJ/kg

T_{high} / °C \ T_{low} / °C	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
15																
16	2															
17	4	2														
18	6	4	2													
19	8	6	4	2												
20	210	208	206	204	202											
21	212	210	208	206	204	2										
22	214	212	210	208	206	4	2									
23	216	214	212	210	208	6	4	2								
24	218	216	214	212	210	8	6	4	2							
25	220	218	216	214	212	10	8	6	4	2						
26	222	220	218	216	214	12	10	8	6	4	2					
27	224	222	220	218	216	14	12	10	8	6	4	2				
28	226	224	222	220	218	16	14	12	10	8	6	4	2			
29	228	226	224	222	220	18	16	14	12	10	8	6	4	2		
30	230	228	226	224	222	20	18	16	14	12	10	8	6	4	2	

Enthalpy difference $\Delta h = h(T_{high}) - h(T_{low})$ in kJ/kg between different upper and lower storage temperatures

Example: Comparison of two PCM

1. Calculate Δh table for both
2. Calculate table with ratio of Δh
3. Graphic result

Ratio of the enthalpy difference of PCM1 to PCM2 between different upper and lower storage temperatures.

T_high / °C \ T_low / °C	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
15																
16	0,53															
17	0,52	0,51														
18	0,51	0,51	0,5													
19	0,51	0,5	0,49	0,49												
20	0,52	0,52	0,52	0,53	0,56											
21	0,56	0,56	0,57	0,59	0,64	0,71										
22	0,64	0,65	0,68	0,71	0,78	0,87	1									
23	0,78	0,8	0,84	0,89	0,96	1,05	1,15	1,25								
24	0,98	1,02	1,06	1,11	1,18	1,26	1,35	1,43	1,54							
25	1,02	1,04	1,07	1,1	1,14	1,18	1,22	1,25	1,25	1,09						
26	0,73	0,73	0,74	0,75	0,76	0,77	0,77	0,76	0,7	0,52	0,44					
27	0,72	0,72	0,73	0,74	0,75	0,75	0,76	0,74	0,69	0,52	0,2	0,5				
28	0,71	0,72	0,73	0,73	0,74	0,75	0,75	0,74	0,69	0,52	0,23	0,55	0,63			
29	0,71	0,72	0,72	0,73	0,74	0,75	0,75	0,73	0,69	0,53	0,26	0,58	0,65	0,67		
30	0,71	0,72	0,73	0,73	0,74	0,75	0,75	0,74	0,69	0,54	0,28	0,61	0,69	0,73	0,8	

Figure 2: Heat capacity data of PCM1 (---) and PCM2 (——)

References

New method to evaluate the heat storage density in latent heat storage for arbitrary temperature ranges, H. Mehling, S. Hiebler, E. Günther, Applied Thermal Engineering 30 (2010) 2652e2657

Hysteresis and data representation

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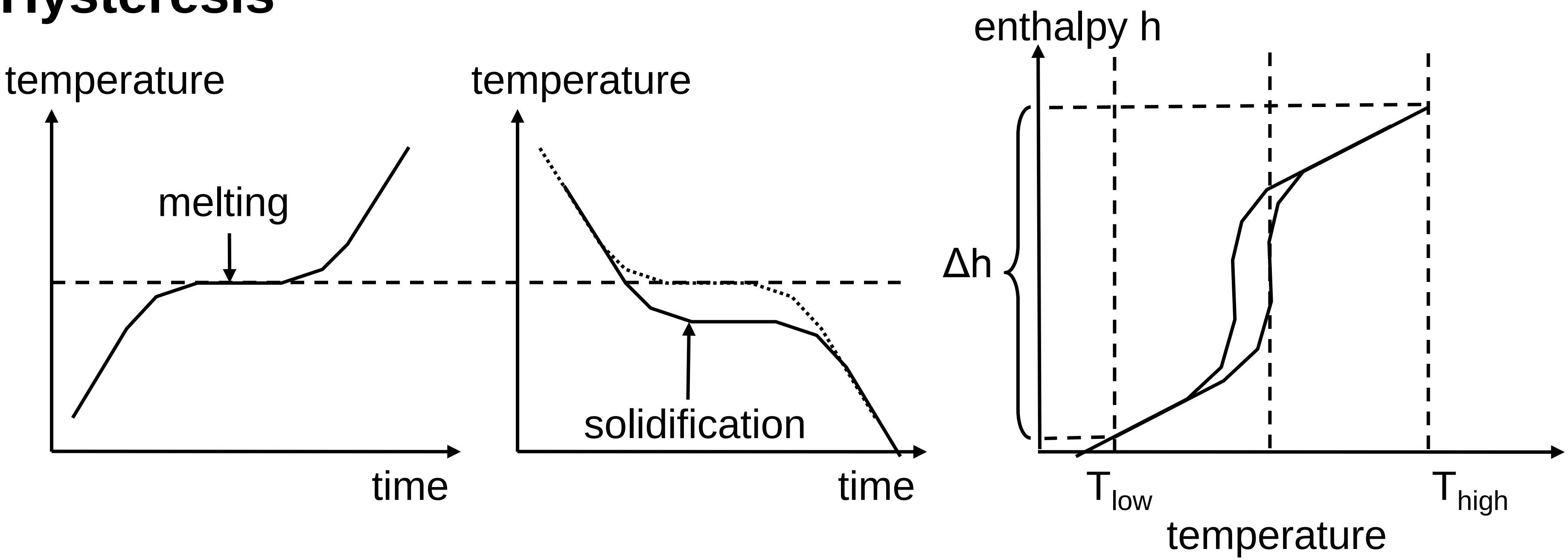
Hysteresis



Data representation
⇒ Tabulation of the stored heat in temperature intervals for the case of heating and for the case of cooling

Hysteresis and data representation

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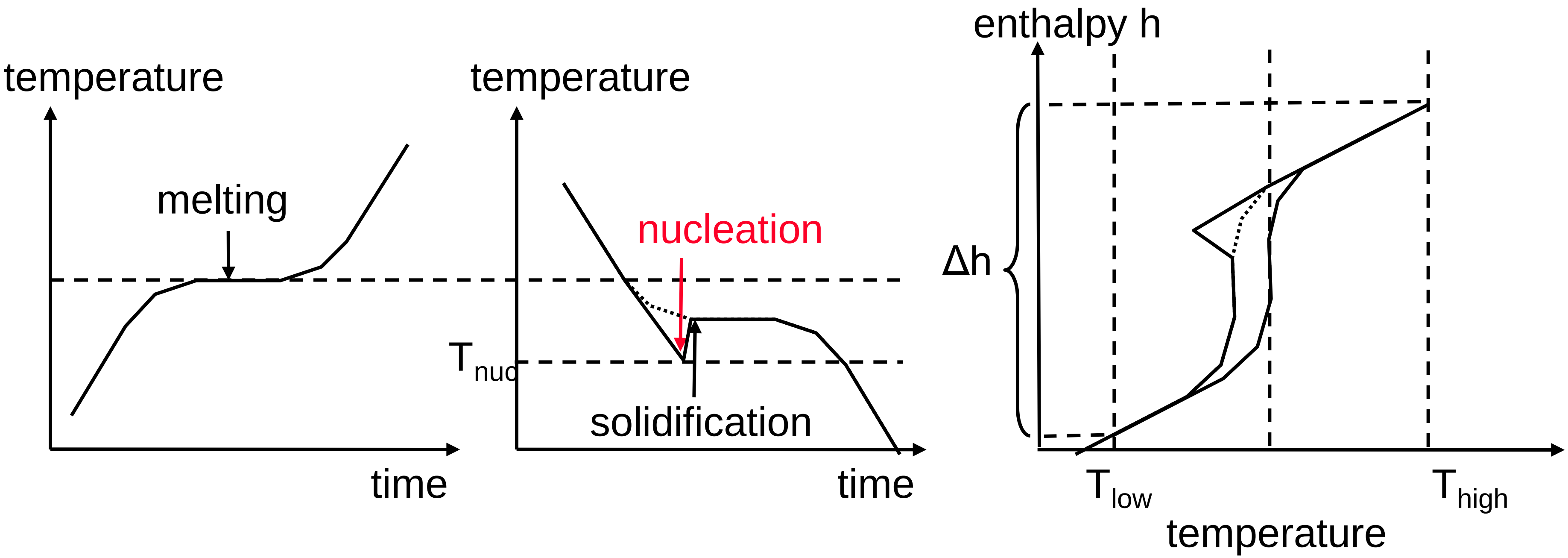
Hysteresis with subcooling (metastable)



Data representation
⇒ Tabulation of the stored heat in temperature intervals for the case of heating and for the case of cooling
+ nucleation temperature T_{nuc}

Hysteresis and calorimetric measurements

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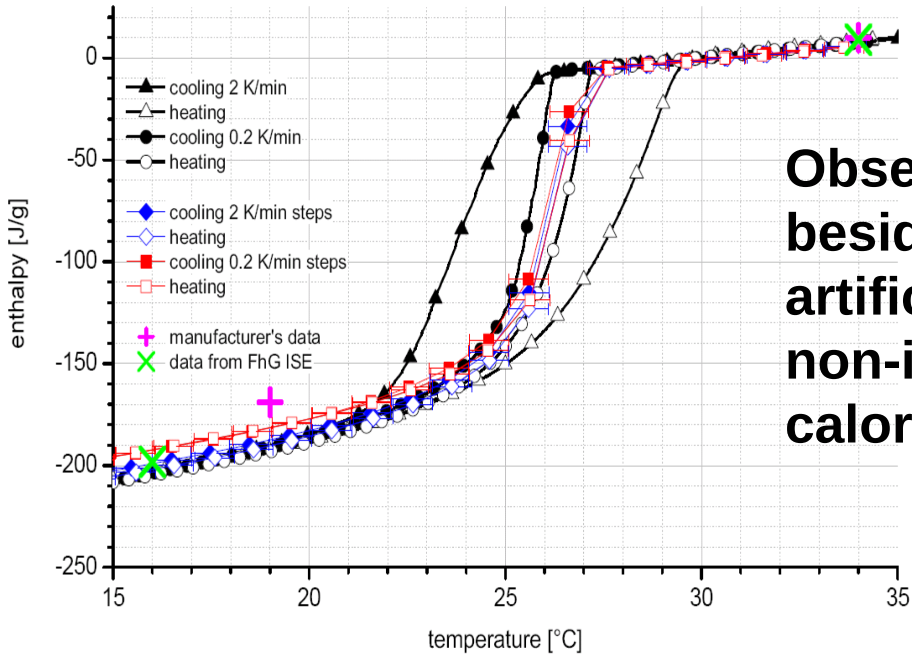
Test in hf-DSC on Commercial PCM paraffin RT27



Observation:
besides hysteresis of the material, artificial effects can be caused by a non-isothermal sample during a calorimetric measurement

How to avoid this problem is defined by the Gütegemeinschaft PCM e.V.

Observation: the material itself has a hysteresis ≤ 0.5 K (resolution of calorimetric measurement)

References

Enthalpy of Phase Change Materials as a Function of Temperature: Required Accuracy and Suitable Measurement Methods, E. Günther, S. Hiebler, H. Mehling, R. Redlich, Int J Thermophys, Int J Thermophys (2009) 30:1257–1269, DOI 10.1007/s10765-009-0641-z

Determination of the enthalpy of PCM as a function of temperature using a heat-flux DSC - A study of different measurement procedures and their accuracy, C. Castellón, E. Günther, H. Mehling, S. Hiebler, L. F. Cabeza, Int. J. Energy Research 32 (2008) 1258-1265

Development of standards for materials testing and quality control of PCM, H. Mehling, H.-P. Ebert, P. Schossig, Proc. of 7th Conference on Phase-Change-Materials and Slurries, Dinan, Frankreich, 2006

http://www.pcm-ral.de/en/quality-association.htm

Experimental investigation of hysteresis

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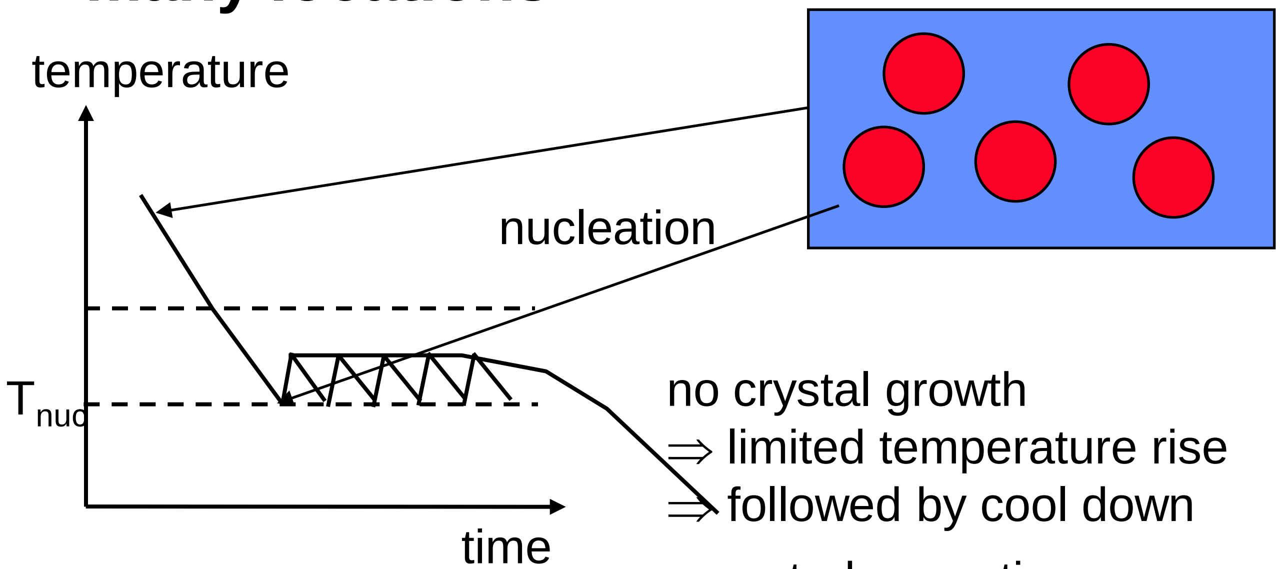
Possible origin of hysteresis:

Limited crystal growth, such that nucleation is necessary at many locations



no crystal growth
⇒ limited temperature rise
⇒ followed by cool down

repeated many times

leads to a lower solidification temperature than melting temperature

Experimental investigation of hysteresis

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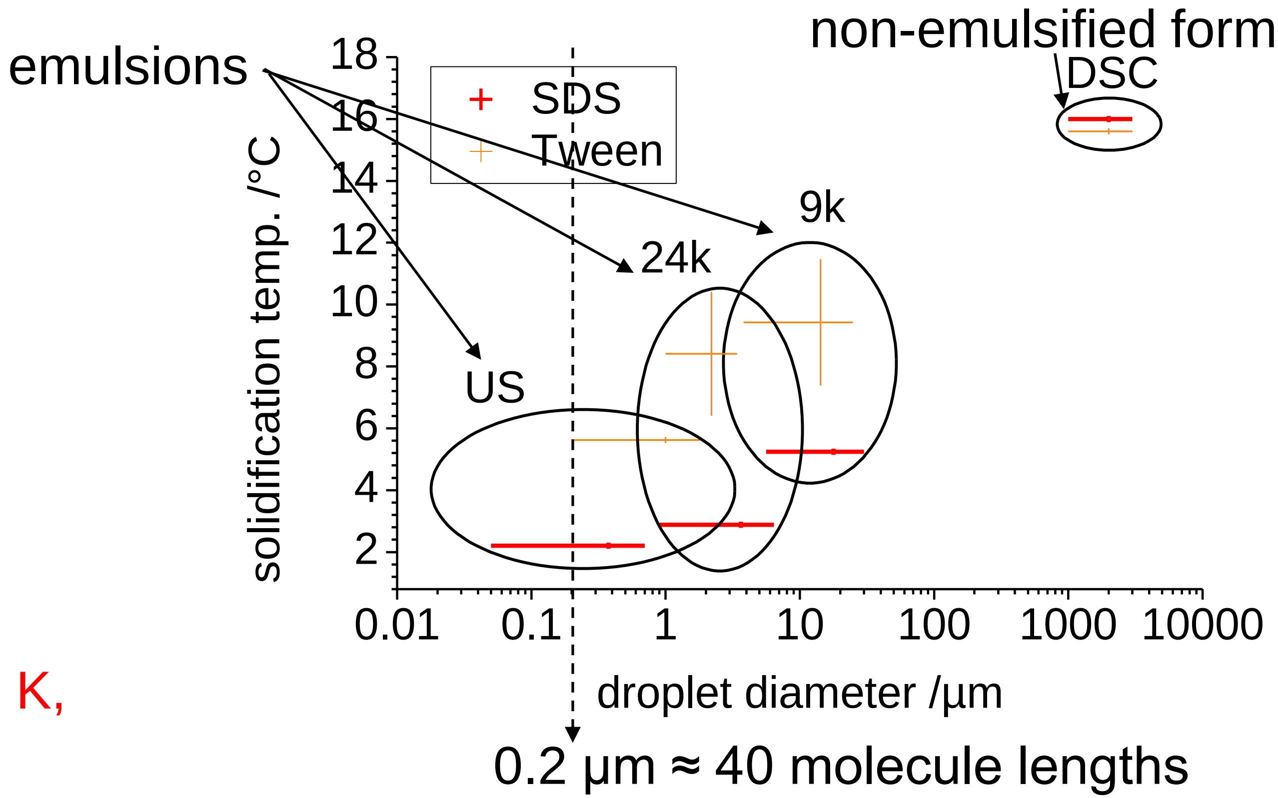
Investigation of T_{nuc} of hexadecane-water-emulsifier mixtures as a function of droplet size



subcooling up to 15 K,

References

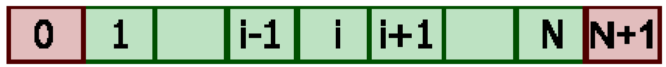
Subcooling in hexadecane emulsions, T. Schmid, E. Günther, H. Mehling, S. Hiebler, L. Huang, Proc. of 11th International Conference on Thermal Energy Storage, June 14-17, 2009, Stockholm

Subcooling in PCM emulsions—Part 1: Experimental, Li Huang, Eva Günther, Christian Doetsch, Harald Mehling, Thermochimica Acta 509 (2010) 93–99

Modelling of PCM with subcooling

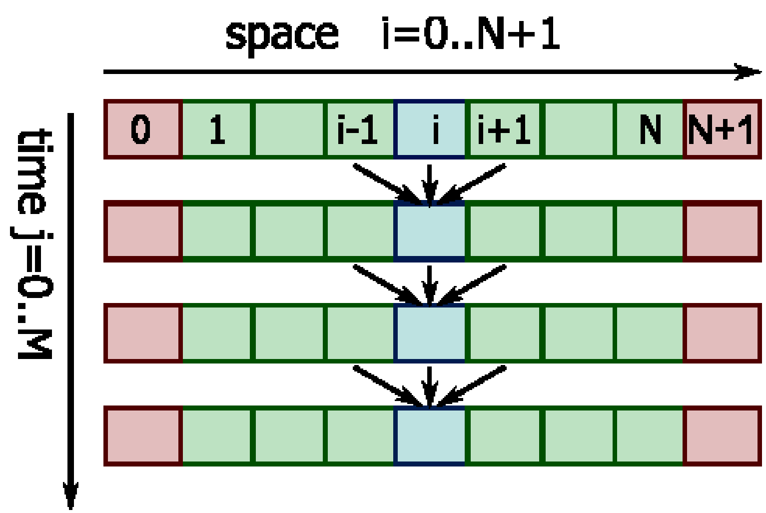
Conventional approach: Enthalpy method

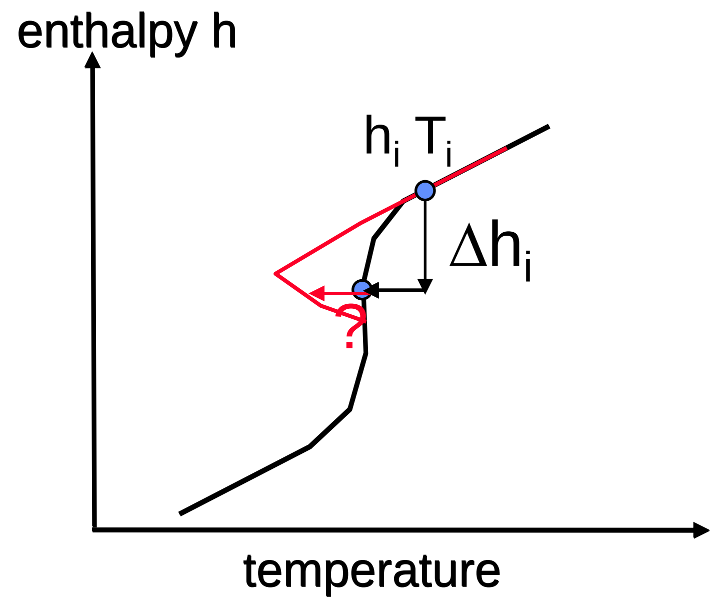
energy transport described using h = h(T)
in an explicit finite volume method



during one time step between neighboring volume elements

$\Delta h_i = \Delta t \cdot \sum_{i-1,\, i+1} \Delta T \cdot \lambda / \Delta x$





Idea: h=h(T, phase)

Modelling of solidification with subcooling

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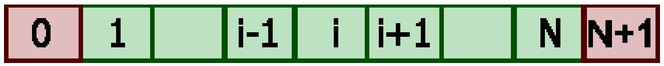
Idea: h=h(T, phase)

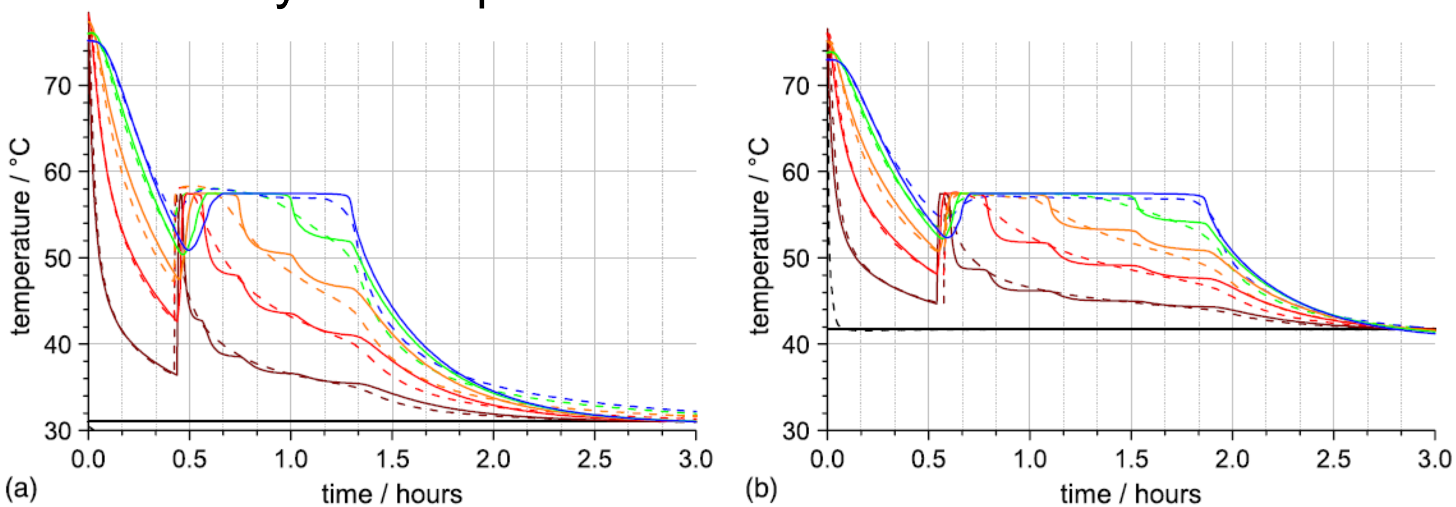
Nucleation of element i triggered by

- $T<T_{nuc}$



- crystal growth (neighbor element is solid)

to avoid fixed crystal growth speed of $\Delta x/\Delta t$ an appropriate number of Δt is necessary to set “phase” to “solid”



Results of simulation (——) and experiment (- - - -) for two different unloading temperatures. The original material parameters were slightly modified to fit the measured curves in (*a*) and then left unchanged for the second simulation (*b*).

Modelling of solidification with subcooling

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References

Modelling of subcooling and solidification of phase change materials; E. Günther, H. Mehling and S. Hiebler; Modelling Simul. Mater. Sci. Eng. 15 (2007) 879–892, doi:10.1088/0965-0393/15/8/005

Simulation of subcooling in latent heat storages, E. Günther, S. Hiebler, H. Mehling, Proc. of 11th International Conference on Thermal Energy Storage, June 14-17, 2009, Stockholm