

Thermal hysteresis and its impact on the efficiency of first-order caloric materials

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Cooling with caloric materials could be an option to replace compressor-based cooling systems in the future. In addition to the advantage of avoiding dangerous liquid coolants, one often cites a possible higher efficiency of the caloric cooling systems compared to compressor-based systems. But is that true? The aim of this work is to assess the efficiency potential of caloric cooling systems on a very basic material level. We placed our focus on materials with a first-order phase change since they generally show a large caloric response. We derive a relation between thermal hysteresis and the dissipative losses due to hysteresis. To predict the efficiency this relation is integrated in a Carnot-like cycle. This approach was chosen to get access to the efficiency reduction due to hysteresis without any further losses due to other non-idealities of the thermodynamic cycle. As a main finding we present a direct relation between thermal hysteresis and the expected maximum exergy or second-law efficiency of a caloric cooling device. These results indicate that for many caloric materials, the thermal hysteresis needs to be further reduced to be able to compete with the efficiency of compressor based system.

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Nomenclature	
a	working-point variable [-]
β	model parameter corresponding to the shift of the peak per applied field [K [F] ⁻¹]
c	specific heat capacitance [J kg ⁻¹ K ⁻¹]
c_0	specific baseline heat capacitance at T_0 [J kg ⁻¹ K ⁻¹]
c_F	specific heat capacitance at a defined applied magnetic field [J kg ⁻¹ K ⁻¹]
COP	coefficient of performance [-]
COP_{carnot}	coefficient of performance of a Carnot cycle [-]
E	electric field [V m ⁻¹]
ε	strain [-]
$f(x)$	generalized distribution function [-]
F	generalized field parameter [-]
H	magnetic field [A m ⁻¹]
κ	model parameter for simplification [-]
M	magnetization [A m ⁻¹]
η	exergy efficiency i.e. COP/COP_{carnot} [-]
p	pressure [pa]
P	electric polarization [A s m ⁻²]
$\phi(x)$	generalized density function [A s m ⁻²]
Δq_{hyst}	specific dissipative heat per cycle due to hysteresis [J kg ⁻¹]
$\Delta q_h, \Delta q_c$	heat transferred per cycle and caloric material form/to the cold/hot side [J kg ⁻¹]
ρ	density [kg m ⁻³]
s	specific entropy [J kg ⁻¹ K ⁻¹]
Δs_0	specific entropy transferred from the cold side to the first stage of a cascaded heat pump [J kg ⁻¹ K ⁻¹]
$\Delta s_{\text{iso,max}}$	maximum specific isothermal entropy change of the caloric material [J kg ⁻¹ K ⁻¹]
Δs_{hyst}	specific entropy generation per cycle due to hysteresis [J kg ⁻¹ K ⁻¹]
σ	stress [N]
T	temperature [K]
T_0	peak temperature of specific heat capacitance with no external field [K]
T_h, T_c	temperature at the hot/cold side [K]
$\Delta T_{\text{ad,max}}$	maximum adiabatic temperature change of the caloric material [K]
ΔT_{hyst}	thermal hysteresis [K]
ΔT_{irr}	irreversibility of the adiabatic temperature change [K]
w	applied work to the heat pump per cycle and caloric material [J kg ⁻¹]
X	generalized order parameter [-]

1 Introduction

There are predictions in the literature that caloric materials can outperform the efficiency of compressor-based systems by 20 % [1] or even more [2,3]. This estimation – alongside the option of avoiding hazardous liquid coolants [4] – motivates material scientists worldwide to identify, synthesize and characterize caloric materials and engineers to build refrigeration systems with these materials. Many demonstrators show the general feasibility of refrigeration systems based on caloric materials as solid-state coolants [5–7].

However, the measured efficiency values of those demonstrators still fall short in comparison to state of the art compressor-based systems with exergy efficiencies higher than 50 % [8]. One important aspect for the improvement of the efficiency of caloric systems is how the hysteresis of the caloric materials affects the thermodynamic performance of a refrigeration system. Hysteresis of caloric materials generally appears in two different ways. First the hysteresis of the corresponding order parameter (magnetization, polarization, deformation) versus the corresponding field parameter (magnetic, electric, pressure), which is defined as »isothermal field hysteresis«. The closed curve integral of the isothermal field hysteresis loop for a phase change corresponds to the dissipative heat produced when undergoing this phase change. A second form of hysteresis the transition temperature varies depending on the direction of the phase change (from the low temperature phase to the high temperature phase or from high to low). This effect can be measured by a shift of the heat capacitance peak for a heating and cooling measurement protocol [9,10]. This is defined as »thermal hysteresis«.

For the comparison of different caloric materials, a figure of merit is desirable. A detailed review on different figures of merit for caloric materials is given by Griffith *et al.* [11]. Moya *et al.* [12] for example introduced a material parameter, which can be used to sort the caloric materials with respect to their expected performance but cannot be used to predict the system performance. Qian *et al.* [13] proposed the material specific value COP_{mat} to predict the potential thermodynamic efficiency of different caloric materials. They calculate the dissipative losses from the experimentally determined closed curve integral of the isothermal field hysteresis and thereby derive its performance in a thermodynamic cycle.

In the present work, we derive an expression for the coupling between thermal hysteresis and the area of the isothermal field hysteresis loop for materials with a first order phase transition. The derivation is based on a generalized material model for first order materials, in which the state description of the caloric material is purely defined by the heat capacitance as function of field and temperature [14]. This approach ensures thermodynamic consistency. The resulting expression for the coupling supports an approximation for the irreversible entropy change introduced by Basso *et al* [15] and is compared with data from the literature. The expression for the closed curve integral of the isothermal field hysteresis loop (dissipative losses) is used to predict the potential efficiency of a caloric cooling device. Similar to Qian *et al.* [13], we introduce a Carnot-like thermodynamic cycle including dissipative losses. With the expression for the dissipative losses, we derive an expression for the second-law efficiency of a potential cooling device as a function of the thermal hysteresis. Additionally the model is used to predict the reversibility of the adiabatic temperature change under cyclic conditions.

2 Field hysteresis and thermal hysteresis

For a generalized description of magneto-, mechano- and electrocalorics, F is the field variable, which corresponds to the magnetic field H , to the mechanical stress σ or to the electric field E is introduced. Furthermore, X is the order parameter corresponding to the magnetization M , the strain ϵ or the electric polarization P . An overview of these parameters for the different caloric materials as well as for fluidic refrigerants is given in table 1.

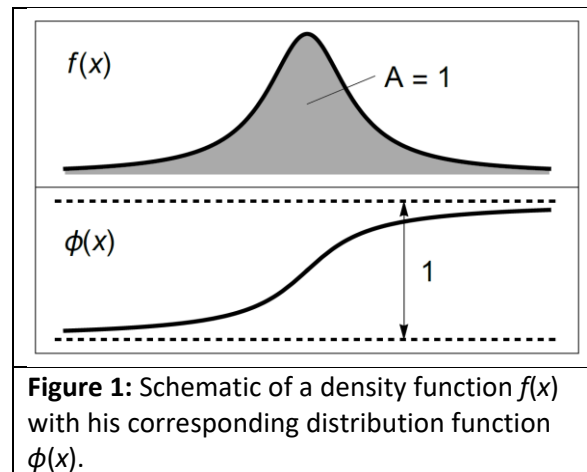
Table 1: Generalized Parameter for the different caloric effects

	field variable F	order parameter X	low temperature phase	high temperature phase
magnetocalorics	magnetic field H	magnetization M	ferromagnetic	paramagnetic
mechanocalorics	mechanical stress σ	strain ϵ	e.g. martensitic	e.g. austenitic
electrocalorics	electric field E	polarization P	ferroelectric	paraelectric
fluidic refrigerants	pressure p	density δ	liquid	gaseous

A generalized density function $f(x)$ with its corresponding distribution function $\phi(x)$ is introduced, where

$\phi(x) = \int_{-\infty}^x f(x') dx'.$	1
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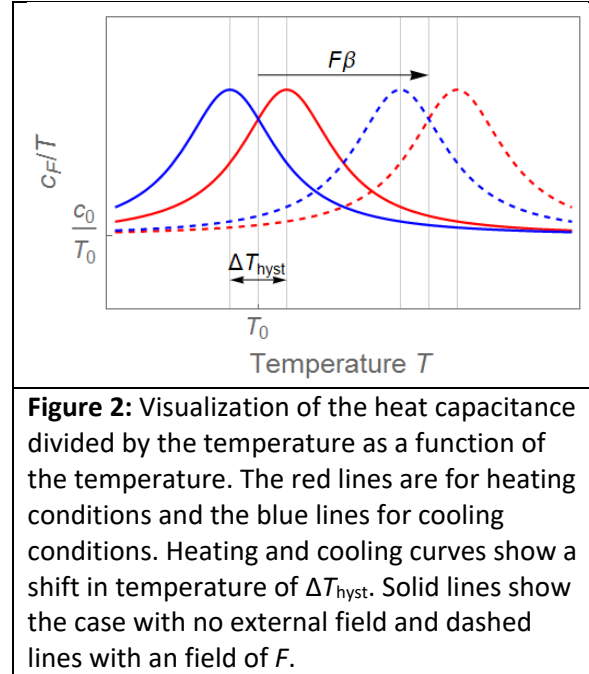
The generalized density function f has the following properties: It is strictly positive, converges to zero for $\pm\infty$ and its integral from $-\infty$ to $+\infty$ is 1. For the distribution function $\phi(-\infty) = 0$ and $\phi(+\infty) = 1$ must be fulfilled. Figure 1 shows an exemplary pair of density and distribution function. Simple examples of pairs of f and ϕ are a Cauchy–Lorentz density function with an arcus tangent as distribution function or a Gaussian density function with an error function as distribution function.



In [14] a consistent and validated material model for a first order magnetocaloric material neglecting hysteresis is introduced. Here, the specific heat capacitance c_F divided by temperature T is modelled by a Cauchy–Lorentz function. In this present work, this approach is generalized by the inclusion of hysteretic behavior into the model. Thus, the specific heat capacitance c_F divided by temperature T is given by

$\frac{c_F(T)}{T} = \Delta s_{\text{iso,max}} f\left(T - T_0 - \beta F \pm \frac{1}{2} \Delta T_{\text{hyst}}\right) + \frac{c_0}{T_0} \text{ with } \begin{cases} +\frac{1}{2} \Delta T_{\text{hyst}} \text{ for cooling} \\ -\frac{1}{2} \Delta T_{\text{hyst}} \text{ for heating} \end{cases}.$	2
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The parametrization function for c_F/T has an offset of c_0/T_0 . $\Delta s_{\text{iso,max}}$ is the area under the peak function without offset and T_0 is the center peak position with no applied field and without hysteresis. Applying a field F shifts the function to higher temperatures, whereby β defines the shift in temperature per applied field. The parameter β is analogous to the inverse Clausius-Clapeyron coefficient. To account for the thermal hysteresis the c_F/T curve is shifted by $\pm \frac{1}{2} \Delta T_{\text{hyst}}$ with respect to T_0 , with $-\frac{1}{2} \Delta T_{\text{hyst}}$ for heating (low temperature phase $\rightarrow$ high temperature phase) and $+\frac{1}{2} \Delta T_{\text{hyst}}$ for cooling (high temperature phase $\rightarrow$ low temperature phase). Hereby it is assumed, that ΔT_{hyst} is not a function of the applied field, regardless the fact, that e.g. Basso and Skokov showed a slight decrease of ΔT_{hyst} with an increasing field for magnetocaloric samples. Figure 2 shows c_F/T as a function of temperature for heating (red) and cooling (blue), with (dashed lines) and without applied field F (solid lines).



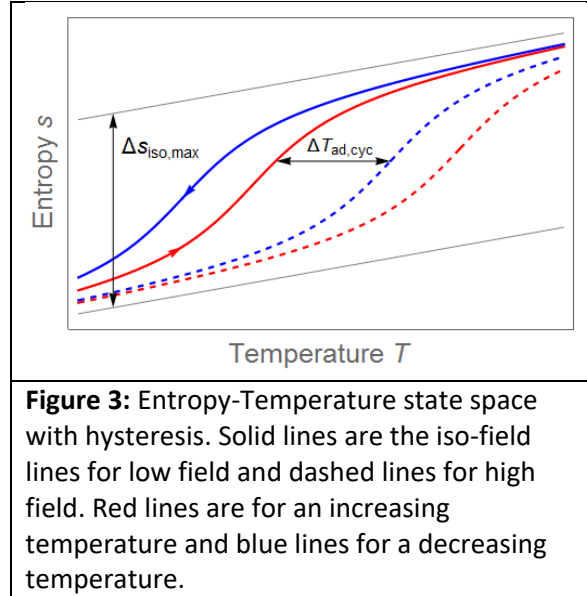
In the following it is assumed that a full phase transition takes places. This means there is no discontinuity at the turning point for the heating and the cooling curve and the Maxwell relations can be applied. Using equation 2 in combination the Maxwell relations, the link between thermal hysteresis and field hysteresis can be derived. Integrating c_F/T over the temperature yields the specific entropy s :

$s = \int_{0K}^T \frac{c_F(T)}{T} dT.$	3
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Using equation 2, this leads to

$s = \Delta s_{\text{iso,max}} \phi \left(T - T_0 - \beta F \pm \frac{1}{2} \Delta T_{\text{hyst}} \right) + \frac{c_0}{T_0} T.$	4
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The specific entropy as a function of the temperature is shown in figure 3. This graph can also be used to explain the phenomena that caloric materials can show a larger temperature change at a first stimulation compared to a stimulation under cyclic conditions. The temperature change under cyclic conditions is marked as $\Delta T_{\text{ad,cyc}}$. This phenomena is explained in detail in [16,17].



From the generalized Maxwell relation

$\left(\frac{\delta s}{\delta F} \right)_T = \left(\frac{\delta X}{\delta T} \right)_F$	5
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the order parameter X can be expressed as

$X = \int_{0K}^T \frac{\delta s}{\delta F} dT.$	6
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From equation 4, $\frac{\delta s}{\delta F}$ can be derived as

$\frac{\delta s}{\delta F} = -\beta \Delta s_{\text{iso,max}} f \left(T - T_0 - \beta F \pm \frac{1}{2} \Delta T_{\text{hyst}} \right).$	7
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Thus, the relative order parameter X is approximated as

$X \approx \beta \Delta s_{\text{iso,max}} \phi \left(T_0 - T + \beta F \mp \frac{1}{2} \Delta T_{\text{hyst}} \right),$	8
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whereby the lower bound of the integral of equation 6 is ignored, because this term can be assumed independent of F and ΔT_{hyst} for T_0 around room temperature. For isothermal case, a constant temperature $T=T_0$ is assumed, resulting in an expression for the order parameter as a function of the applied field

$X \approx \beta \Delta s_{\text{iso,max}} \varphi \left(\beta F \mp \frac{1}{2} \Delta T_{\text{hyst}} \right) \text{ with } \begin{cases} -\frac{1}{2} \Delta T_{\text{hyst}} & \text{for field up} \\ +\frac{1}{2} \Delta T_{\text{hyst}} & \text{for field down} \end{cases}.$	9
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This is shown in figure 4 a. The blue curve describes the transition from high to low temperature phase – corresponding to an increasing field F . The red curve describes the transition from the low to the high temperature phase – equivalent to a decreasing field. Figure 4 b shows the same functions as Figure 4 a with exchanged abscissa and ordinate.

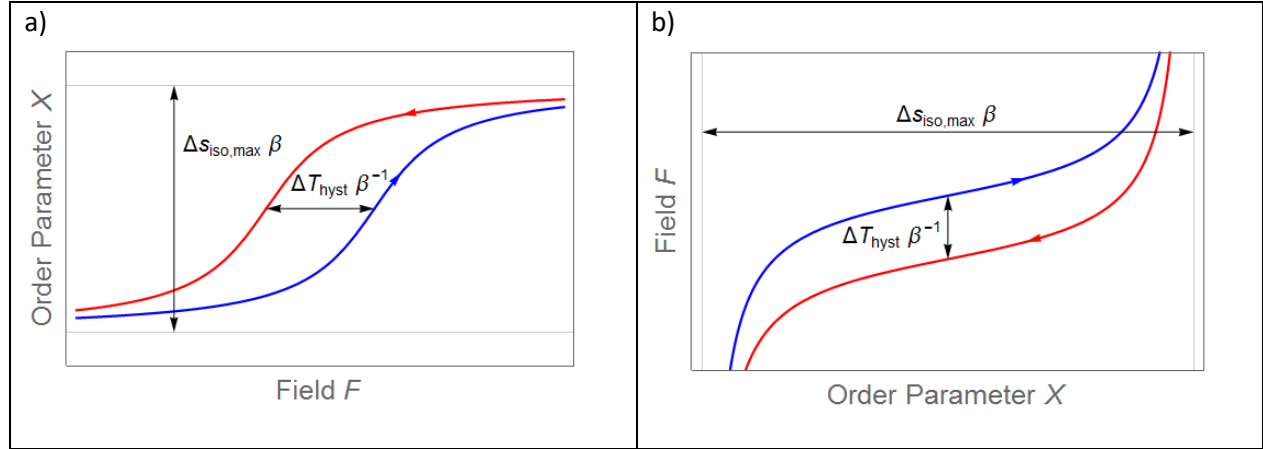


Figure 4: Visualization of the field hysteresis.

a) Order parameter X as a function of the applied field F corresponding to equation 9.

b) Axis exchanged compared to a), which corresponds e.g. to a stress-strain diagram.

The work that has to be applied to the caloric material in one cycle is the difference between the applied and released energy and therefore given by the area between the red and blue curve in Figure 4 a and Figure 4 b. This area is geometrically determined by a parallelogram with the height of $\Delta s_{\text{iso,max}} \beta$ and a width of $\Delta T_{\text{hyst}} \beta^{-1}$. Since the process is isothermal, no work is required to pump heat from a hot to a cold reservoir. Thus this area corresponds to the dissipative losses Δq_{hyst} for undergoing the phase change back and forth in a hysteretic process, and is given by

$\Delta q_{\text{hyst}} = \int X_{\text{heating}} dF - \int X_{\text{cooling}} dF = \Delta T_{\text{hyst}} \Delta s_{\text{iso,max}}.$	10
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This means the area of the hysteresis loop is defined by the product of the thermal hysteresis ΔT_{hyst} and the maximum entropy change $\Delta s_{\text{iso,max}}$ that is given by the phase change. This remarkably simple connection between field hysteresis and thermal hysteresis is verified with data from the literature. As shown in Table 2, the derived approximation fits measured data with less than a factor of two. This discrepancy can be explained by the simplified assumption of a field independent thermal hysteresis ΔT_{hyst} or for elastocalorics by the presence of the R -phase that is not implemented in the present model or by measurement uncertainties.

Table 2: Exemplary material parameters to examine the approximation derived in equation 10. The values for the dissipative heat Δq_{hyst} , thermal hysteresis ΔT_{hyst} , isothermal entropy change $\Delta s_{\text{iso,max}}$, and adiabatic temperature change $\Delta T_{\text{ad,max}}$ are taken from the referenced publication.

Material	Δq_{hyst} [J kg ⁻¹]	ΔT_{hyst} [K]	$\Delta s_{\text{iso,max}}$ [J kg ⁻¹ K ⁻¹]	$\Delta T_{\text{ad,max}}$ [K]	$(\Delta T_{\text{hyst}} \Delta s_{\text{iso,max}}) / \Delta q_{\text{hyst}}$ [-]	Reference
MnFe(P,As)	5	0.6	12	6.5	1.4	[18]
Nitinol	600	10	35	30	0.58	[9]
LaFe _{11.6} Si _{1.4}	20	1.1	31	10	1.7	[19]
Gd ₅ Si ₂ Ge ₂	40	3.5	17		1.5	[18]

From this dissipative heat Δq_{hyst} the corresponding entropy change Δs_{hyst} is derived as

$\Delta s_{\text{hyst}} = \frac{\Delta q_{\text{hyst}}}{T} = \frac{\Delta T_{\text{hyst}}}{T} \Delta s_{\text{iso,max}}.$	11
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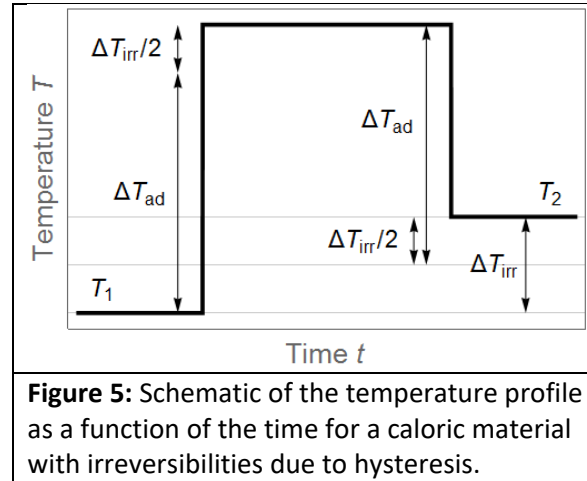
This entropy change was also derived in the work of Basso *et al.* [15], however they use geometric relations in the sT -diagram. Due to the factor $\Delta T_{\text{hyst}}/T$, which is in the order of 1%, it seems that this entropy change is negligible. In section 4 however, this entropy change is analyzed within a thermodynamic cycle, and it is shown that it is not negligible.

3 Irreversibility of the adiabatic temperature change

When applying a field to a caloric material under adiabatic conditions, its temperature rises by ΔT_{ad} . Without any irreversibilities, the caloric material cools down by the same amount when the field is removed, returning to the same temperature T_1 after the stimulation as it had before. However, when the material shows irreversibilities due to hysteresis, the material attains a larger temperature $T_2 = T_1 + \Delta T_{\text{irr}}$ than it had before the stimulus due to the dissipative losses, where ΔT_{irr} denotes the increase in temperature after one cycle. This irreversible temperature change is here in equal parts assigned to heating and to the cooling process. For the full phase change $\Delta T_{\text{irr,max}}$ is determined by the hysteresis-induced dissipative losses Δq_{hyst} and is given by

$\Delta T_{\text{irr,max}} = \frac{\Delta q_{\text{hyst}}}{c_F} = \frac{\Delta T_{\text{hyst}} \Delta S_{\text{iso,max}}}{c_F} = \frac{\Delta T_{\text{hyst}} \Delta T_{\text{ad,max}}}{T}$	12
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with $\Delta T_{\text{ad,max}} = \frac{T \Delta S_{\text{iso,max}}}{c_F}$. This is schematically shown in figure 5.



Therefore, the ratio of ΔT_{irr} over ΔT_{ad} is given by:

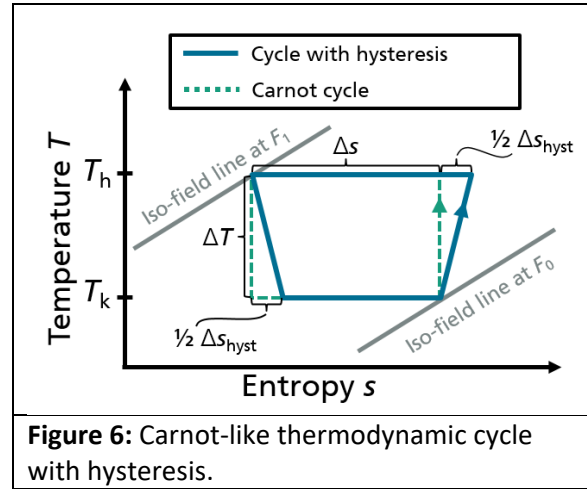
$\frac{\Delta T_{\text{irr}}}{\Delta T_{\text{ad}}} = \frac{\Delta T_{\text{hyst}}}{T}.$	13
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For most caloric materials being active around room temperature, this ratio is very small and in the order of 0.1 – 1% and is therefore very difficult to quantify experimentally. Thus, even very small deviations in the loading and unloading ΔT_{ad} can still encounter significant thermodynamic losses due to hysteresis.

4 Cycle efficiency of caloric materials with thermal hysteresis

In the following, the impact of this hysteresis on the thermodynamic cycle is analyzed. As a thermodynamic cycle a Carnot-like cycle is assumed, since here the determined efficiency is not reduced by cycle dependent additional losses and gives the efficiency potential that is possible with a given material.

The resulting Carnot-like cycle incorporating the hysteresis losses is shown in figure 6. It is assumed that the dissipative losses occur in equal parts while increasing and decreasing the field and that a field is applied to drive a full phase change. The two iso-field lines at F_0 and F_1 correspond to a full phase change and have a spacing in temperature of $\Delta T_{ad,max}$ and in entropy of $\Delta s_{iso,max}$. The dashed green rectangle shows a Carnot cycle between the hot side temperature T_h and the cold side temperature T_c without hysteretic effects. The blue lines however show the cycle under the consideration of dissipative losses due to hysteresis.



For the cycle with hysteresis, the heat transferred to the hot side Δq_h is given by

$\Delta q_h = T_h \left(\Delta s + \frac{\Delta s_{hyst}}{2} \right)$	14
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and the heat taken from the cold side Δq_c is given by

$\Delta q_c = T_c \left(\Delta s - \frac{\Delta s_{hyst}}{2} \right).$	15
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Due to energy conservation, it is $\Delta q_h = \Delta q_c + w$, where w is the work applied to the system. Using equations 14 and 15, this gives

$w = \Delta q_h - \Delta q_c = \Delta T \Delta s + T_c \Delta s_{hyst} + \frac{\Delta T \Delta s_{hyst}}{2}.$	16
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Since $\Delta s \gg \Delta s_{hyst}$ and $T_c \gg \Delta T$ the last term can be neglected. Using equations 10 and 11 and, this results in

$w \approx \Delta T \Delta s + \Delta q_{\text{hyst}}$	17
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This equation supports the consistency of the model – the applied work is given by the sum of the work of the Carnot cycle ($\Delta T \Delta s$) and the work of the isothermal field-hysteresis loop Δq_{hyst} , which corresponds to the dissipative losses. For a cooling system, the coefficient of performance COP is given by

$COP = \frac{\Delta q_c}{w} = \frac{T_c \left(\Delta s - \frac{\Delta s_{\text{hyst}}}{2} \right)}{\Delta s \Delta T + \Delta q_{\text{hyst}}}$	18
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For $\Delta s \gg \Delta s_{\text{hyst}}$ this can be simplified as

$COP \approx \frac{T_c \Delta s}{\Delta s \Delta T + \Delta q_{\text{hyst}}}$	19
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When the state lines are parallel, ΔT and Δs can be expressed as factors of their corresponding spacing and a working-point variable a as introduced in [20]:

$\begin{aligned} \Delta T &= a \Delta T_{\text{ad,max}} \\ \Delta s &= (1 - a) \Delta s_{\text{iso,max}} \end{aligned}$	20
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For a close to one a cooling system shows a relatively large temperature span with a relatively low cooling power and for an a close to zero vice versa. With the coefficient of performance for a Carnot cycle of $COP_{\text{carnot}} = T_c / \Delta T$ and by inserting equations 20 into equation 19, the second-law (or exergy) efficiency η is derived as

$\frac{COP}{COP_{\text{carnot}}} = \eta \approx \frac{\Delta s \Delta T}{\Delta s \Delta T + \Delta q_{\text{hyst}}} = \frac{a(1 - a) \Delta s_{\text{iso,max}} \Delta T_{\text{ad,max}}}{a(1 - a) \Delta s_{\text{iso,max}} \Delta T_{\text{ad,max}} + \Delta q_{\text{hyst}}}$	21
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This expression is further simplified using the previous considerations. Inserting equation 10 ($\Delta q_{\text{hyst}} = \Delta T_{\text{hyst}} \Delta s_{\text{iso,max}}$), this fraction is reduced to be independent of $\Delta s_{\text{iso,max}}$ as

$\eta \approx \frac{a(1 - a) \Delta T_{\text{ad}}}{a(1 - a) \Delta T_{\text{ad}} + \Delta T_{\text{hyst}}} = \frac{1}{1 + \frac{1}{(1 - a)a} \frac{\Delta T_{\text{hyst}}}{\Delta T_{\text{ad,max}}}}$	22
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This equation has a maximum at $a = 0.5$. This is plausible, since $a = 0.5$ results in the rectangular with the largest area that fits between the two parallel iso-field lines. With $a = 0.5$, this gives

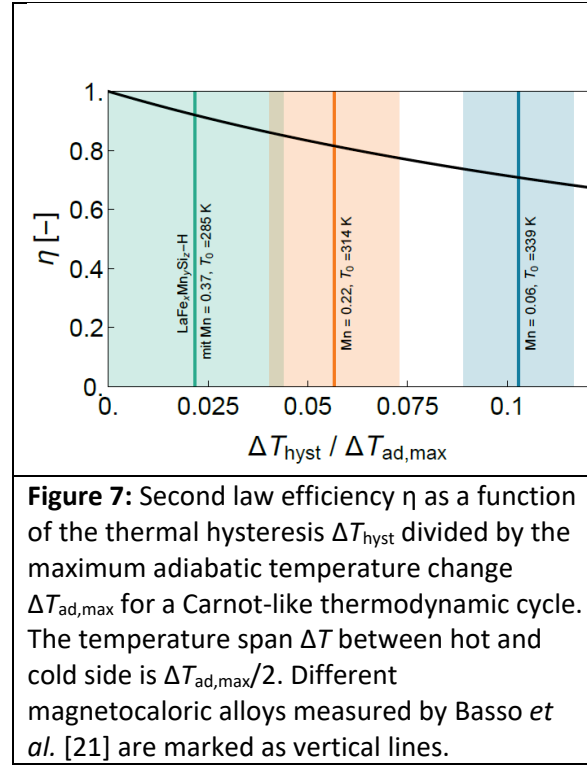
$\eta \approx \frac{1}{1 + 4 \frac{\Delta T_{\text{hyst}}}{\Delta T_{\text{ad,max}}}}$	23
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This is a slight overestimation of the second law efficiency for a system with a temperature span of $\Delta T_{\text{ad,max}}/2$, due to the approximation from equation 18 to 19. In Figure 7 the efficiency of different magnetocaloric alloys from the $\text{La}(\text{FeSiMn})_{13}\text{-H}$ material family determined using equation 23 are shown as vertical lines. The values and the confidence regions are extracted from measurements by Basso *et al.* [21]. A higher manganese content lowers the transition temperature T_0 and the phase change transforms to a more second order transition resulting in an increases of the expected exergy efficiency. The exergy efficiency of these materials are generally in the range of the exergy efficiency of compressor based system on their refrigerant level ($\eta \approx 0.85$ [22]).

Efficiency values for Nitinol as a elastocaloric material are estimated from Tusek *et al.* [9]. With a maximum adiabatic temperature of $\Delta T_{\text{ad,max}} \approx 40$ K and a thermal hysteresis of $\Delta T_{\text{ad,max}} \approx 10$ K the exergy

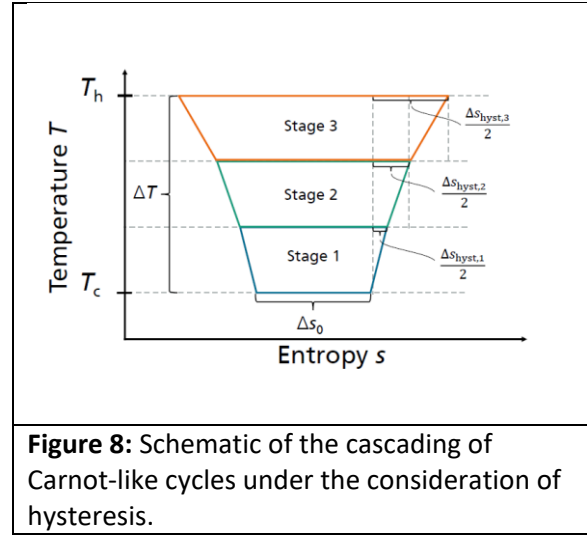
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efficiency is $\eta \approx 0.5$. However, due to the influence of the *R*-phase, these results require further investigations and should be interpreted with caution. One promising approach to reduce the hysteresis of Nitinol is the addition of copper, palladium or manganese [23,24]. For electrocalorics with many newly emerging materials, it seems that ferroelectric relaxors (generally more second-order) are required to reach competitive efficiencies.



5 Cascading

Since most caloric materials show an adiabatic temperature change of only a few Kelvin, a cascaded system needs to be taken into account in order to attain relevant temperature lifts. Therefore, in the following the impact of hysteretic losses are investigated for a cascaded system. It is assumed that the additional entropy due to hysteresis of one stage of a cascaded system is a factor of the total transported entropy of the stage. A second stage for example receives the entropy of the first stage that the first stage received from the cold side and the entropy that the first stage generated due to hysteresis. Therefore the second stage creates more entropy due to hysteresis than the first stage since it receives more entropy than the first stage and therefore carries on more entropy as shown in figure 8.



To transport more entropy at the same temperature span as the first stage, the second stage needs to contain more caloric material or material with a higher caloric effect. The additional hysteresis created by the first stage is given by

$\Delta s_{\text{hyst},1} = \frac{\Delta T_{\text{hyst}}}{T(1-a)} \Delta s_0,$	24
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with Δs_0 as the entropy detracted from the cold side. The additional hysteresis that is passed on of an n_{th} stage compared to the hysteresis detracted from the cold side can be written as recursive expression as

$\Delta s_{\text{hyst},n} = \kappa(\Delta s_0 + \Delta s_{\text{hyst},n-1}) + \Delta s_{\text{hyst},n-1},$	25
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with

$\kappa = \frac{\Delta T_{\text{hyst}}}{T(1-a)}.$	26
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The first summand is the entropy created by the n_{th} stage. The recursive expression can be solved as

$\Delta s_{\text{hyst},n} = ((1 + \kappa)^n - 1) \Delta s_0.$	27
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For relatively small κ and n it is $((1 + \kappa)^n - 1) \approx n\kappa$, which gives

$\Delta s_{\text{hyst},n} \approx n\kappa \Delta s_0.$	28
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The exergy efficiency of a system with n stages is derived by the work w applied to a hysteretic system and by the work w_{carnot} applied to a Carnot cycle with the same cooling power and temperature span as the hysteretic cycle as

$\eta_n = \frac{w_{\text{carnot}}}{w} = \frac{n a \Delta T_{\text{ad,max}} \Delta s_0}{n a \Delta T_{\text{ad,max}} \Delta s_0 + T_h \Delta s_{\text{hyst},n}}.$	29
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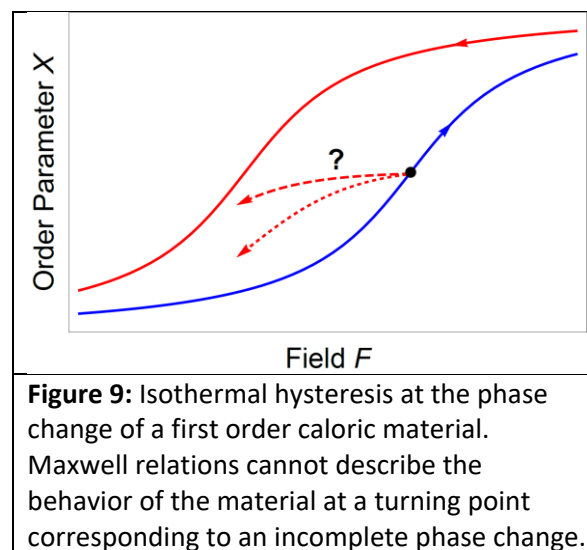
Inserting the simplified expression for $\Delta s_{\text{hyst},n}$ the n cancels out and the exergy efficiency of a multi-stage system is approximately the same as for a single stage system:

$\eta_n \approx \eta.$	30
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Therefor we conclude that cascading of multiple stages to increase the temperature span has no significant effect on the exergy efficiency losses due to hysteresis.

6 Incomplete phase change

In the previous derivation, we assumed a complete phase change to allow the application of the Maxwell relations. If the phase change is incomplete the change of direction in the corresponding state space takes place at a state where the direction dependent state lines are not converged. This is shown schematically in figure 9, where the turning point is marked as a black dot. To describe the behavior at this turning point neither Maxwell relations nor a Preisach approach lead to satisfying results. At the turning point, the system is a critical phenomenon and the special coupling of neighboring phase domains has to be taken into account. This is not investigated in the present work, however some general thoughts about the influence of an incomplete phase change to the efficiency of a cooling system are presented.



In a very basic approximation the adiabatic temperature change and the isothermal entropy change scale linearly with the applied field until they reach their value of saturation. Therefor the product of Δs_{iso} times ΔT_{ad} scales approximately quadratic with the applied field (alternatively a scaling of $\propto F^{2/3}$ can be assumed for ΔT_{ad} and Δs_{iso} resulting in a scaling of their product in $\propto F^{4/3}$). The fraction of the cooling capacitance and the isothermal hysteresis area are proportional to the exergy efficiency. Which leads to the following question: How does the isothermal hysteresis area scales with the applied field? This strongly depends on the behavior at the turning point. If the state trajectory is horizontal after the turning point (dashed line in figure 8) and merges with the red solid line, the area scales approximately linear with the applied field. Then the following expression for the scaling of the exergy efficiency with the applied field F can be set up:

$\eta(F) \approx \frac{F^2 \Delta s \Delta T}{F^2 \Delta s \Delta T + F \Delta q_{\text{hyst}}} \text{ or } \frac{F^{4/3} \Delta s \Delta T}{F^{4/3} \Delta s \Delta T + F \Delta q_{\text{hyst}}}$	31
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Both functions are extremely monotonic increasing with F and therefore it would be beneficial for the exergy efficiency if the complete phase change of the caloric material were undergone. However, if the hysteretic losses show a lower order scaling with the applied field (dotted line in figure 9) this might be different. Measurements of Skokov *et al.* [16] show for a magnetocaloric material a behavior similar to the dashed line suggesting a more complete phase change might be beneficial. Additionally, some caloric materials show a decrease of the thermal hysteresis with the applied external field. Considering this effect, using e.g. an elastocaloric material with a lower austenite finish temperature and applying a pre-strain can lower the hysteresis. The influence of a partial phase change and the effect of an offset field (e.g. pre-strain) requires further investigations.

7 Conclusion

A phenomenological material model incorporating thermal hysteresis is introduced which is used to derive the dependence between thermal hysteresis and field hysteresis. These results are compared to experimental data from the literature and show very good agreement. Based on this expression, an expression for the second law efficiency as a function of the ratio thermal hysteresis over adiabatic temperature change is given. Furthermore an approximation for the reversibility of the adiabatic temperature change is shown. Based on the results obtained, the following can be concluded:

- The irreversible entropy change due to hysteresis, although seeming very small (entropy generation due to hysteresis of about ~1 % of the entropy change due to the phase change), has a significant influence on the second law efficiency of a caloric cooling system.
- Although hysteresis does not influence the reversibility of the adiabatic temperature change in a measurable quantity, it still can have a major influence on the thermodynamic efficiency of a caloric cooling system.
- Cascading of multiple stages of caloric material has no significant influence on the losses due to hysteresis.
- Only undergoing an incomplete phase change seems to be not beneficial for the efficiency of a caloric cooling system. Further investigations are required here.

In order to show similar or even better exergy efficiencies compared to compressor-based systems, the ratio of $\Delta T_{\text{hyst}}/\Delta T_{\text{ad}}$ needs to be smaller than 10%, and thus for many caloric materials, the thermal hysteresis needs to be further reduced.

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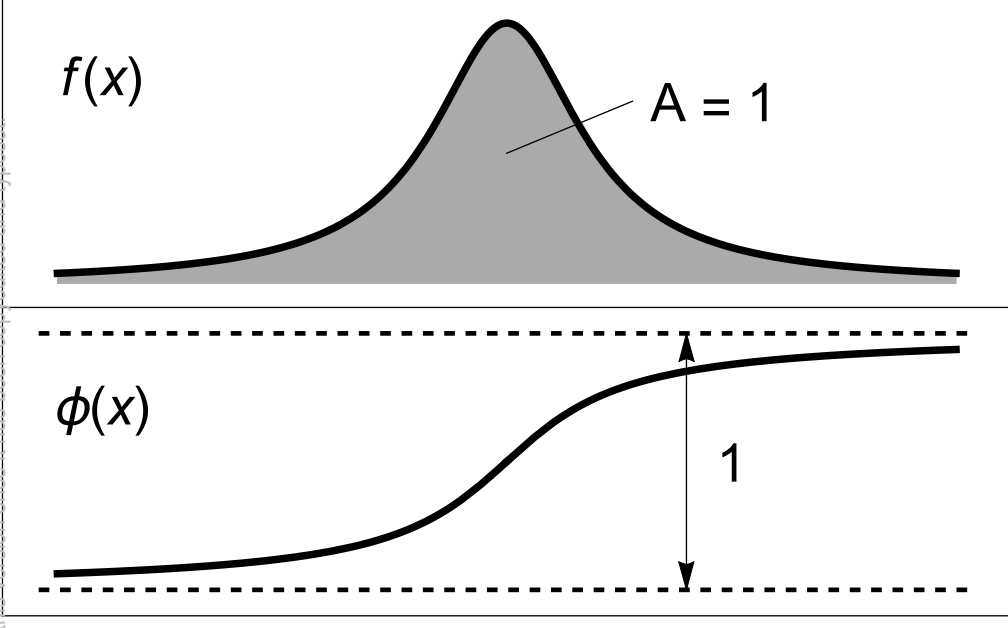
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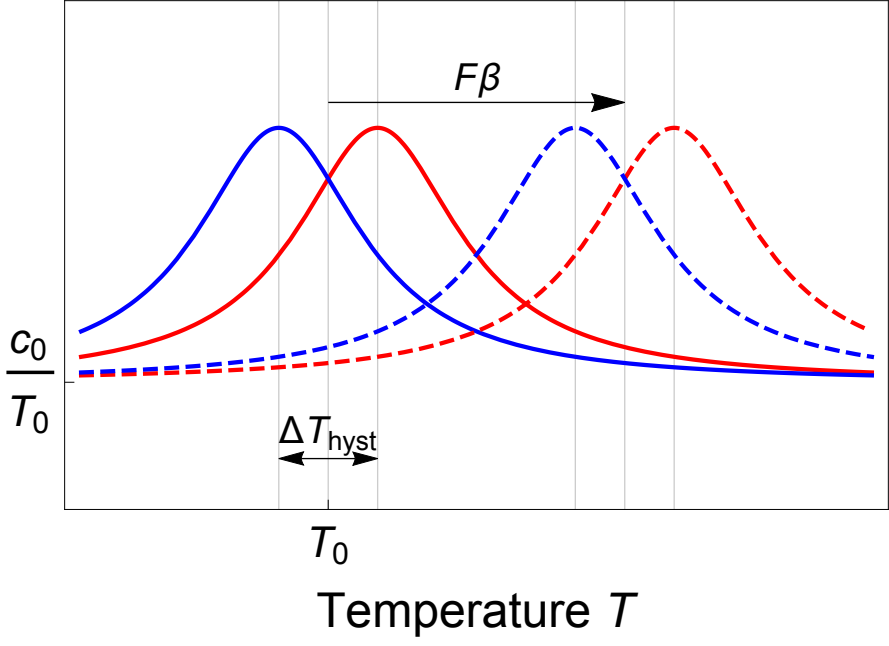
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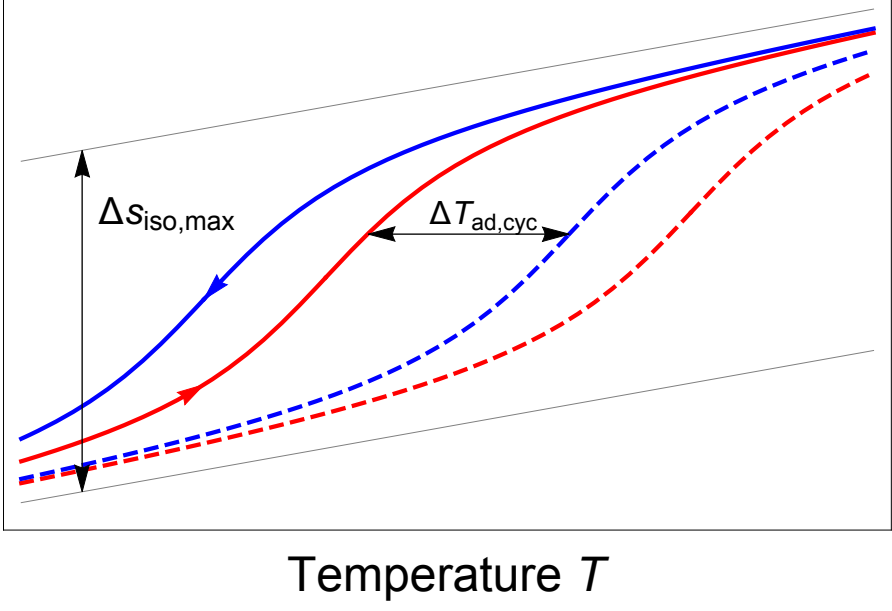


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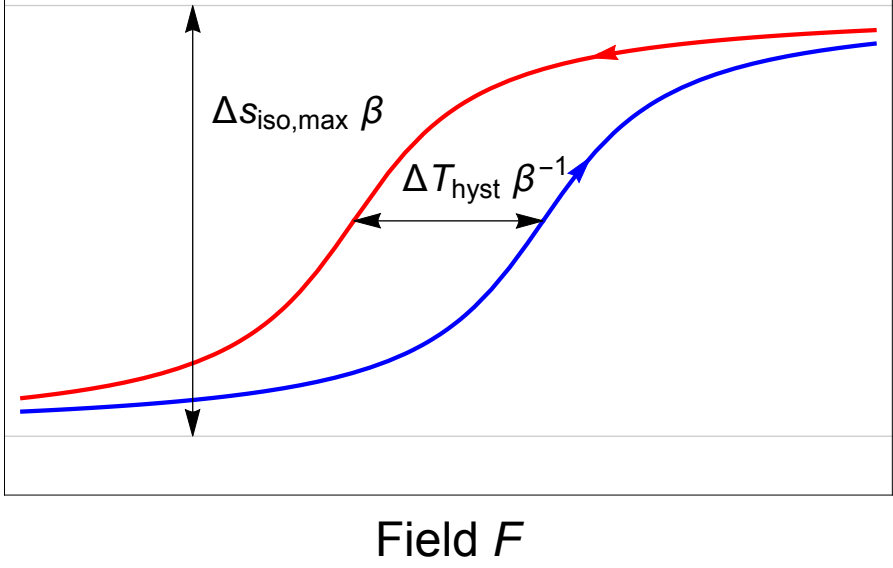
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Entropy s



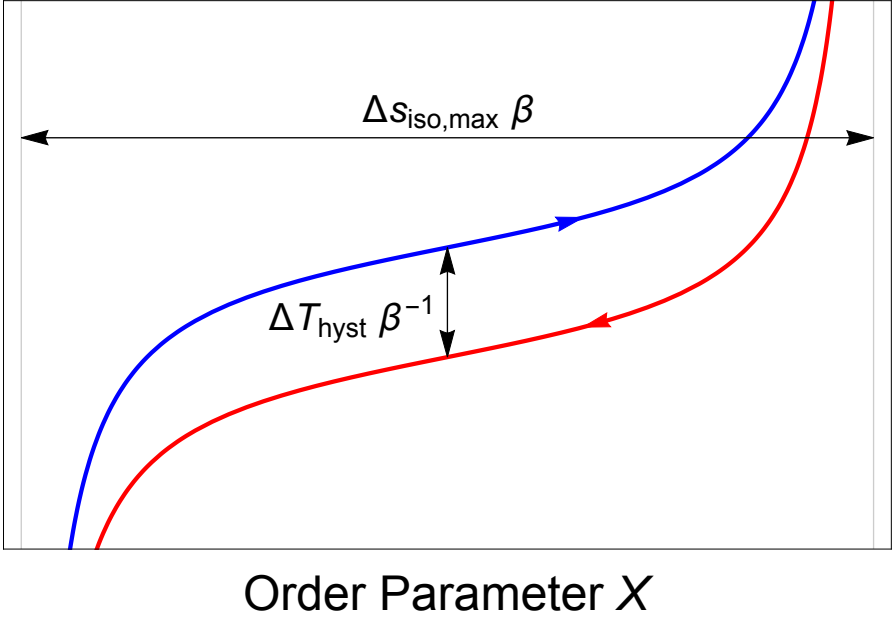
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Order Parameter X



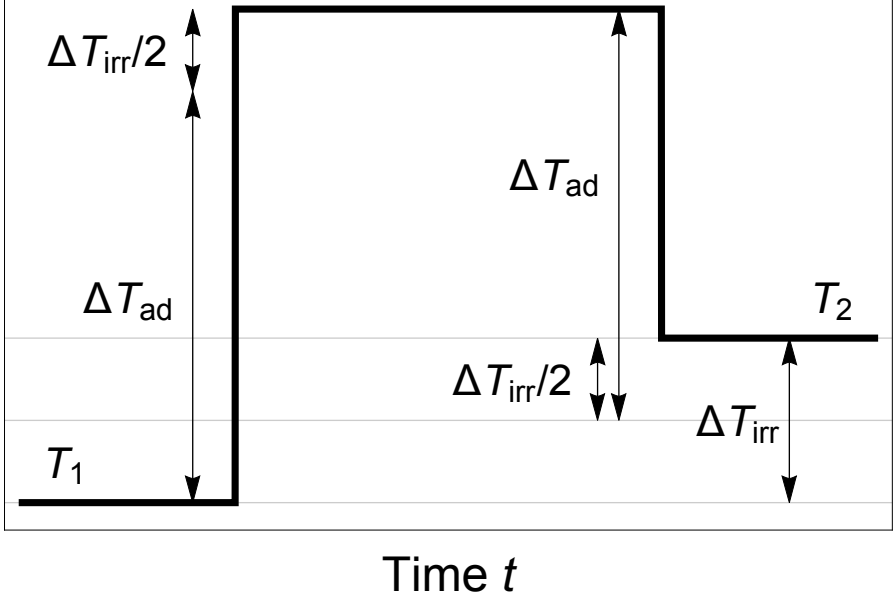
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Field F

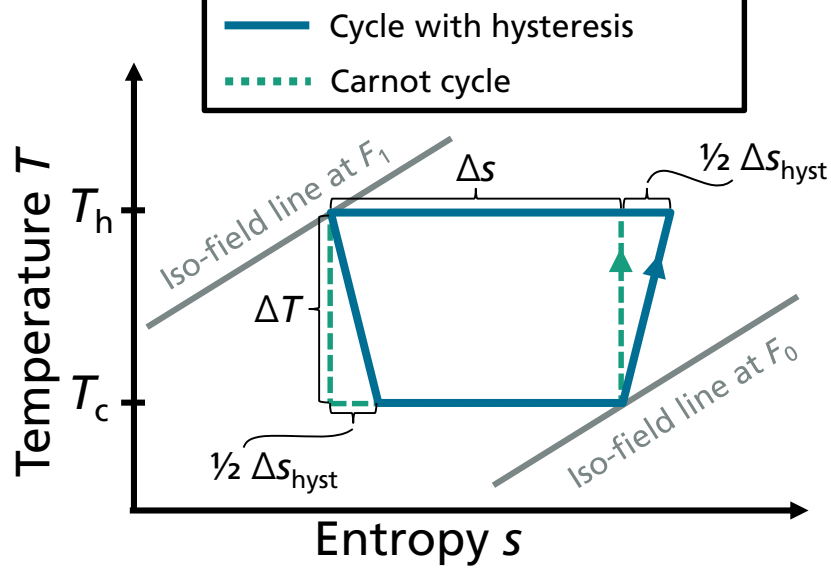


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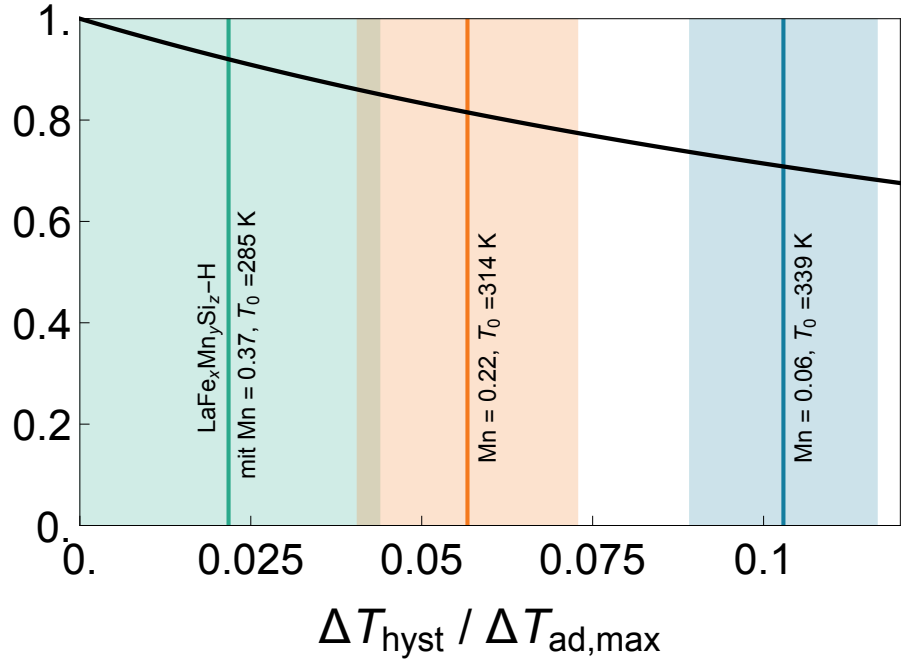
Temperature T



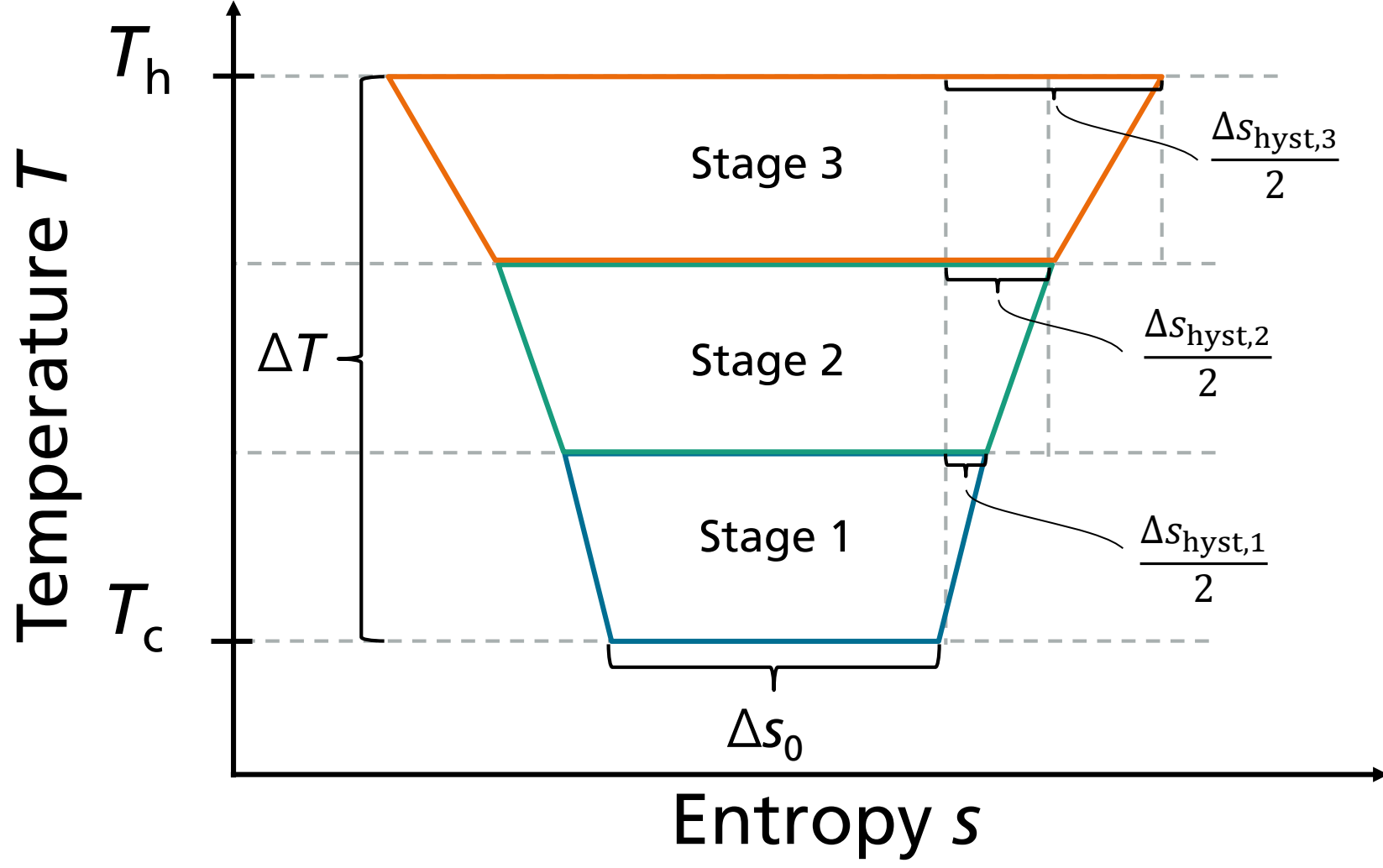
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Order Parameter X

