Modeling thermodynamical properties by segmented non-linear regression

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In memory of my grandfather, Pavel.
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A novel thermodynamic physically-based model is proposed for the description of temperature dependence of solid phases from 0K up to the melting point. It considers several physical effects that appear in different temperature regions. To take such phenomena into account, a segmented regression approach is applied for modeling of the heat capacity of solids by using a bent-cable model.

The bent-cable model has been applied for the decomposition of several physical effects of the heat capacity which depends linearly in low and high temperatures. Since the bent-cable model is one the key components of the newly proposed segmented model, the asymptotic theory for the least-squares estimates of the bent-cable model parameters under non-standard assumptions has been developed. In particular we prove the consistency and asymptotic normality of the nonlinear least-squares estimator for independent not identically distributed random errors and a not twice differentiable regression function.

The new segmented model is applied for the description of thermodynamic properties of several pure elements and compared to the existing alternative physically-based models based on the evaluation of several statistical criteria. It is demonstrated that the proposed segmented model provides a better description regarding the physical relation, than all models which have been developed so far. Moreover, the parameter estimates obtained from the new model have been successfully validated from a physical point of view with respect to the relevant thermodynamic properties.

In order to further improve the statistical inference, a locally $D$-optimal design is constructed for the segmented model and its benefits are illustrated analyzing heat capacity data of pure chromium. In particular, we formulate recommendations how heat capacity measurements should be collected from different literature sources to estimate the parameters of segmented model as accurately as possible.
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Since the early ages of mankind, people try to discover materials with specific and desirable properties in order to utilize them according to their needs. Usually this process of the design and development of new materials has been performed by a so-called "trial-and-error" approach which requires a significant amount of time, human and financial recourses. Such a way of the discovering of new materials, methods or technologies is sometimes also called the Edisonian approach”. "I haven't failed - I've just found 10,000 that won't work.” - Thomas Edison. Nowadays, due to the enormous progress in the theoretical and applied science, the design of new materials transforms into a problem of the multi-disciplinary research field and its solution is usually supported by computer simulations.

Currently, there are several fundamental initiatives to accelerate the development and design of new materials using computer simulations and multi-scale modeling approaches, for example, the Materials Genome Initiative [Warren (2012)] or the Integrated Computational Mechanical Engineering (ICME) approach [Allison et al. (2006)]. The main goal of these initiatives is to be able to model the entire chain of industrial processes from the design and production of novel materials till their utilization under certain conditions in a shorter period of time with less costs. The first and critical step in such complex material design chains is the modeling of microstructures which define important material properties. However, the accurate modeling and prediction of microstructures requires a reliable thermodynamic model for the various phases depending on the alloy composition [Perrut (2015)]. Consequently, the thermodynamic models become a key component for a successful and robust design of new materials.

In practice, under such a thermodynamic model is usually understood the Gibbs energy function depending on the temperature, pressure and composition. A set of Gibbs energy
functions for all stable and metastable phases of an alloy or material is called a thermodynamic database. These databases are used to predict phases in the studied materials which determine microstructures and therefore the material properties. From a mathematical point of view, the construction of Gibbs energy databases is an inverse problem as the available experimental information complies with derivatives of Gibbs energies, such as, for example, the heat capacity and the relative enthalpy.

Traditionally in thermodynamic applications, the temperature dependence of the heat capacity is described by high-order polynomials with adjustable parameters fitted to experimental data \cite{Dinsdale(1991)}. This modeling approach has been developed to cover high temperatures above 298.15K, but it should not be used to describe any low temperature data. Moreover, an application of the high-order polynomials often can lead to the so-called overfitting problem, which results in highly unstable models. This means that even a successful application of polynomials within the range of available experimental data cannot guarantee that the evaluated models will correctly extrapolate the thermodynamic properties and phase boundaries beyond these regions. Therefore, an effort to extend the current thermodynamic description to the low temperatures requires a more physical modeling which should take into account recently available theoretical and experimental data.

Currently, several attempts to propose an alternative physically-based model for the description of the heat capacity data down to 0K have been performed (see, \cite{Chase et al. (1995)}, \cite{Chen and Sundman (2001)} and \cite{Palumbo et al. (2014)}). Despite of significant improvement in the modeling of experimental heat capacity data reported in these works, an accurate description of the low temperatures from 298K down to 0K is still an issue. Moreover, for several engineering application, for example, development of the thermoelectric materials, the accurate modeling of temperature-dependent material properties is a key factor for the successful design of novel materials. Therefore, following these ideas, a new model for the temperature dependence in the heat capacity of solids which consider several physical effects (e.g. electronic, vibrational, etc.) is proposed in this thesis. Since these contributions appear in different temperature ranges and can be described by different functions, the segmented regression methodology is applied for the development of a mathematical model for heat capacity data.

The work presented in this thesis considers the development of a new physically-based model from different perspectives. Chapter\textsuperscript{2} gives an introduction on the segmented regression approach where the main part is devoted to the linear segmented models with continuous changes between the intervals, and in particular, to the bent-cable model. This model is one of the main components of the proposed segmented heat capacity model that allows us to decompose the linearly dependent physical effects in temperatures, that have to be estimated from the data. The asymptotic theory for the bent-cable model is developed in Chapter\textsuperscript{3}. In particular, consistency and asymptotic normality of the nonlinear least-squares estimator is proved under non-standard assumptions on the error distribution and the regression function. Chapter\textsuperscript{4} is devoted to the theoretical and practical aspects of the modeling of
thermophysical properties using the CALPHAD method (CALPHAD = CALculation of PHASE Diagram). Here, the new thermodynamic model based on the segmented regression approach is introduced and its advantages are demonstrated on several pure elements. The asymptotic theory developed in Chapter 3 is used in Chapter 5 to construct locally $D$-optimal designs for the segmented heat capacity model. In particular we provide practical recommendations how to choose experimental conditions in order to estimate the parameters of the segmented heat capacity model as accurately as possible. Finally, Chapter 6 summarizes the results and benefits of proposed methodology and provides a discussion of future research directions.
Segmented regression: literature overview

In many applications it is not possible to describe experiments by a single parametric function throughout the entire domain of analysis. To model such a complex behavior it is necessary to consider regression models which have a different analytical form for different regions of the domain. Regression models of this type are called segmented regression models [Feder (1975a)], i.e. we observe data from the following nonlinear regression model

\[ y_i = f(x_i; \theta, \tau) + \epsilon_i, \quad i = 1, \ldots, n, \tag{2.1} \]

where \( f \) denotes the regression function, \( \theta \) is the unknown parameter vector, \( \epsilon_i \) are random errors and the experimental domain is assumed to be an interval \([\tau_0, \tau_r]\) such that \( \tau_0 < \tau_1 < \ldots < \tau_{r-1} < \tau_r \) is a partition of this interval represented as the vector \( \tau = (\tau_0, \tau_1, \ldots, \tau_r) \). Here segmented regression function with \( r \) segments is defined by

\[
    f(x; \theta, \tau) = \begin{cases} 
    f_1(x; \theta_1), & x \leq \tau_1 \\
    f_2(x; \theta_2), & \tau_1 < x \leq \tau_2 \\
    \vdots \\
    f_r(x; \theta_r), & \tau_{r-1} > x,
    \end{cases} \tag{2.2}
\]

where \( f_j(x; \theta_j) \) are regression models with unknown parameters \( \theta_j \), \( j = 1, 2, \ldots, r \). The function \( f(x; \theta, \tau) \) is then defined by different \( f_j(x; \theta_j) \) on different intervals \([\tau_{j-1}, \tau_j]\). In addition, the end points of intervals \( \tau_j \) are unknown and have also to be estimated [Seber and Wild (1989)].

The points \( \tau_j \) are called change points and the neighborhoods delimited by the joint points are called regimes, phases, stages, intervals or segments. These points are usually of particular interest because they represent shifts in the pattern of the data. The segmented regression
Chapter 2

problem is also known as change point regression, multistage or multiphase regression, piecewise regression [Piegorsch and Bailer (2005)]. Segmented regression is usually applied if the number of intervals are small and the behavior of the regression function for each interval can be well described by simple parametric functions [Seber and Wild (1989)].

A segmented model (2.2) is continuous if the submodels \( f_j(x, \theta_j) \) are subject to constraints

\[
f_j(\tau_j, \theta_j) = f_{j+1}(\tau_j, \theta_{j+1}), \quad \text{for all } j = 1, ..., r - 1.
\]

When the model is discontinuous at the change points \( \tau_j \), a sudden jump occurs in the mean response. If additionally to the conditions (2.3) the submodels \( f_j(x, \theta_j) \) are also subject to smoothness constraints, i.e.

\[
\frac{\partial}{\partial x} f_j(\tau_j, \theta_j) \big|_{x=\tau_j} = \frac{\partial}{\partial x} f_{j+1}(x, \theta_{j+1}) \big|_{x=\tau_j}, \quad \text{for all } j = 1, ..., r - 1,
\]

then the segmented model is called continuous segmented model with a smooth transition between two intervals.

The segmented regression problem has been the subject of intensive research since the second half of the past century. If the function for one of the segment is nonlinear or at least one change point is unknown and has to be estimated then the segmented regression problem becomes a nonlinear problem. There are usually three main points of the interest: estimation of the change point and model parameters, testing if the underlying regression model truly exhibits a change and development of the asymptotic theory [Seber and Wild (1989)].

The first time the segmented regression problem has been introduced by Quandt (1958), Quandt (1960), where the regression model with two linear segments that do not necessarily intersect for normally distributed data has been considered. Quandt proposed maximum likelihood estimation for the unknown model parameters. He suggested asymptotic and small-sample tests of the hypothesis that two regression lines are, in the fact, the same. The power of these tests depends on the location of the true change point \( \tau_0 \). The closer \( \tau_0 \) is to the end point of the interval, the smaller is the power of the tests. Blischke (1961) was the first who investigated the linear-linear model with the continuity constraint at the change point. Such a segmented model can be defined as

\[
f(x; \theta, \tau) = \begin{cases} 
\beta_{10} + \beta_{11}x, & x \leq \tau, \\
\beta_{20} + \beta_{21}x, & x > \tau,
\end{cases}
\]

under continuity constraint (2.3) at the change point \( \tau \) given by

\[
\beta_{10} + \beta_{11}\tau = \beta_{20} + \beta_{21}\tau,
\]

where \( \tau \) is the unknown change point to be estimated from the data together with the vector of unknown parameters \( \theta = (\beta_{10}, \beta_{11}, \beta_{20}, \beta_{21}) \). This model is often called a broken-stick model [Bacon and Watts (1971)].
Application of this model for the analysis of biological data has been demonstrated by Sprent (1961). More development of the linear-linear segmented model is provided by Hinkley (1969), where the problem of estimating and making inference about the intersection has been studied. Hinkley (1971) described the procedure for the calculation of the likelihood confidence regions and discusses the associated problems of testing hypothesis about the intersection. He suggested the empirical evidence of an asymptotic distribution for the classic F-test statistic. An alternative formulation of the two-segments regression problem is proposed by Quandt (1972) where it has been assumed that nature chooses between two segments with probabilities $p$ and $1 - p$ respectively.

A major difficulty of the estimation of the unknown change point in regression models with linear segments is the non-smoothness of the likelihood function with respect to the change point considered as a model parameter. Several researches tried to overcome this problem by using other type of functions such as quadratic or cubic functions. This resulted in the natural extension of the linear-linear model as a segmented model comprising general continuous functions which are not necessary a straight lines. Robison (1964) is the first who exchanged linear functions in the segmented problem with polynomials and derived the maximum likelihood estimators and confidence intervals around the change point between two intersecting polynomials. However, under the formulation proposed by Robinson, it is possible to obtain a non-real solution. Hudson (1966) expanded this methodology to more than two polynomial segments, distinguish between four types of change points and derived the overall least squares solution for the unknown model parameters, which is based on a local solution for each fitted submodel. The idea to use polynomials instead of linear functions has been also considered by Fuller (1969) and Gallant and Fuller (1973). They studied $r$-segments model consisting of grafted polynomial submodels with a continuous first derivative of the modeling function at $r - 1$ change points. In order to be able to apply the modified Gauss-Newton method, the re-parameterization approach of such a type of segmented function was introduced. This approach has been demonstrated on quadratic-quadratic, linear-quadratic and quadratic-quadratic-linear models. Gallant and Fuller (1973) also suggested a test statistic for the choice between quadratic-linear and quadratic-quadratic-linear model based on the notation of an asymptotically F-distributed deviance statistic. Poirier (1973) related theory of splines and segmented models and designed tests to identify structural changes in the model.

Alternative solution for the estimation problem in linear-linear models is an application of the smooth transition models. Such kind of segmented models is preferable in compare to the linear-linear model with abrupt change because of the two reasons. First of all, we suppose that the considering phenomenon can be described more accurately by a smooth transition model. The second reason is a computational one. Smooth maximum likelihood or least squares allows to use the gradient technique for the estimation [Seber and Wild (1989)].

Bacon and Watts (1971) were the first who introduced a segmented model with a smooth transition function between two linear intervals. They provided an alternative formulation of
the broken-stick model \([2.4]-[2.5]\) using the signum function, \(\text{sgn}\),
\[
f(x; \theta, \tau) = \beta_0 + \beta_1(x - \tau) + \beta_2|x - \tau| \\
= \beta_0 + \beta_1(x - \tau) + \beta_2(x - \tau)\text{sgn}(x - \tau),
\]
(2.6)
where the parameter \(\beta_1 = (\beta_{11} + \beta_{21})/2\) is the average slope, and \(\beta_2 = (\beta_{21} - \beta_{11})/2\) is the half of difference in slopes.

Using the formulation (2.6) of the broken-stick model, the transition between two linear segments can be modeled from gradual to fairly abrupt. Therefore, Bacon and Watts (1971) proposed to replace the \(\text{sgn}(\cdot)\) in (2.6) by a general smooth function, say \(\text{trn}(\cdot): \mathbb{R} \to \mathbb{R}\),
\[
f(x; \theta) = \beta_0 + \beta_1(x - \tau) + \beta_2(x - \tau)\text{trn}\left(\frac{x - \tau}{\gamma}\right),
\]
(2.7)
which satisfies following conditions:
\[
[C_1] \lim_{z \to \pm \infty} [z\text{trn}z - |z|] = 0,
[C_2] \lim_{\gamma \to \infty} \text{trn}(z/\gamma) = \text{sgn}(x),
[C_3] \text{trn}(0) = \text{sgn}(0) = 0.
\]
The condition \([C_1]\) guaranties the asymptotic linearity in (2.7). The condition \([C_2]\) ensures that the piecewise linear model (2.6) is a limiting form of the smooth transition model. Finally, the condition \([C_3]\) ensures that the smooth model passes through \((\tau, \beta_0)\) the intersection between the two lines, which are the asymptotes to the curve Seber and Wild (1989).

One of the many functions that satisfies condition \([C_1]-[C_3]\) is the hyperbolic tangent
\[
\tanh(z) = \frac{e^z - e^{-z}}{e^z + e^{-z}}.
\]
(2.8)
Then the smooth segmented model (2.7) can be described by following equation
\[
f(x; \theta) = \beta_0 + \beta_1(x - \tau) + \beta_2(x - \tau)\tanh\left(\frac{x - \tau}{\gamma}\right),
\]
(2.9)
In contrast to model (2.6), the smooth segmented model (2.9) contains an additional parameter, \(\gamma\). As \(\gamma\) approaches zero, \(\text{trn}(z/\gamma)\) produces an abrupt transition between two linear models (see \([C_2]\)) and a gradual transition if \(\gamma > 1\) Bacon and Watts (1971). The Figure 2.1a plots the linear segmented model (2.9) for various values of \(\gamma\).

The condition \([C_3]\) forces the segmented model (2.9) to bulge on the outside of the corner created by the intersection of the two lines (see Figure 2.1a). For this reason Griffiths and Miller (1973) decided to drop the condition \([C_3]\) and replace \(\tanh(z)\) by the hyperbolic function
\[
\text{hyp}(z, \gamma) = \frac{1}{z} \sqrt{z^2 + \gamma},
\]
(2.10)
which satisfies only the first two conditions [C₁] and [C₂]. This leads to the model
\[ f(x; \theta) = \beta_0 + \beta_1 (x - \tau) + \beta_2 \sqrt{(x - \tau)^2 + \gamma}. \]  
(2.11)

The model (2.11) for different values of \( \gamma \) is plotted on the Figure 2.1b. Both smooth transition models, (2.11) and (2.9), have asymptotes (2.6) as \( \gamma \to 0 \) (see Figure 2.1).

A different approach for the re-parametrization of the linear segmented regression model (2.4)-(2.5) was proposed by Tishler and Zang (1981b) and it is based on the properties of max-function (see Figure 2.2)
\[ f(x, \theta) = \max(\beta_{10} + \beta_{11}x, \beta_{20} + \beta_{21}x), \]
\[ f(x, \theta) = \min(\beta_{10} + \beta_{11}x, \beta_{20} + \beta_{21}x). \]  
(2.12)

In this case, the continuity of the modeling function \( f(x, \theta) \) is implicit and the location of the change point \( \tau \) does not need to be represented. Since \( \min(b_1, b_2) = -\max(-b_1, -b_2) \), the method should be developed only for the max-formulation (2.12) and the modeling function \( f(x, \theta) \) can be rewritten as
\[ f(x, \theta) = \beta_{10} + \beta_{11}x + u(\beta_{20} - \beta_{10} + (\beta_{21} - \beta_{11})x), \]  
(2.13)

where \( u(z) = \max(0, z), z \in \mathbb{R} \) is a transition function which is continuously differentiable except at \( z = 0 \).

Tishler and Zang (1981b) proposed to replace \( u(z) \) by a smooth approximation
\[ q_\gamma(z) = \begin{cases} 
0, & z \leq -\gamma, \\
(z + \gamma)^2/4\gamma, & -\gamma \leq z \leq \gamma, \\
z, & z \geq \gamma. 
\end{cases} \]  
(2.14)
Figure 2.2: The linear segmented model (2.12) proposed by Tishler and Zang (1981b).

Clearly, $\lim_{\gamma \to 0} q_\gamma(z) = u(z)$ and $q_\gamma(z)$ has continuous first, but not second derivatives. The smooth transition function (2.14) with $z = x - \tau$, where $\tau$ is the unknown change point, can be written in the following compact form [Chiu (2002)]

$$q_\gamma(x - \tau) = q(x; \tau, \gamma) = \frac{(x - \tau + \gamma)^2}{4\gamma} 1\{|x - \tau| \leq \gamma\} + (x - \tau) 1\{x > \tau + \gamma\}, \quad (2.15)$$

where $1\{\cdot\}$ is an indicator function, e.g. $1\{x > \tau + \gamma\} = 1$ if $x > \tau + \gamma$ and 0 otherwise. The model (2.15) is called the basic bent-cable model and plotted in Figure 2.3.

Figure 2.3: The basic bent-cable model (2.15) with different $\gamma$-values.

Using the approximation (2.15) instead of the $u(z)$-function in (2.13) the linear segmented model transforms into

$$f(x, \theta) = \beta_0 + \beta_1 x + \beta_2 q(x; \tau, \gamma), \quad (2.16)$$

where $\theta = (\beta_0, \beta_1, \beta_2, \tau, \gamma)$ is the vector of parameters. Here, $\beta_0$ and $\beta_1$ are the intercept and slope of the incoming linear segment, $\beta_2$ is the scaling factor associated with the location
of the transition, $\beta_1 + \beta_2$ is the slope of the outgoing segment and the function $q(x; \tau, \gamma)$ is defined in (2.15). The model (2.16) is called the full bent-cable model or simply, the bent-cable model. Such formulation of the bent-cable model (2.16) was proposed by Chiu (2002) and it allows to distinguish parameters which appear linearly and nonlinearly in the model.

In contrast to the both previous formulation (2.9) and (2.11), the bent-cable model (2.16) has a non-asymptotic behavior and is identically to the broken-stick model (2.13) except the transition region $[\tau - \gamma, \tau + \gamma]$. The differences between these smooth transition segmented models are illustrated in Figure 2.4.

![Figure 2.4: The models (2.16), (2.11) and (2.9) with different $\gamma$-values.](image)

The three appealing features - flexibility, greatly interpretability of regression coefficients and clear characterization of the transition region using the parameters $\tau$ and $\gamma$ distinguish the bent-cable model (2.16) from the two other smooth transition segmented models (2.9), (2.11) described above. Therefore, based on above facts, the bent-cable model (2.16) has been selected to be one of the main components of a novel thermodynamic modeling strategy proposed in Chapter 4 of this thesis.

Several methodological approaches have been applied for the parameter estimation in segmented regression models. Bacon and Watts (1971) were the first that applied a Bayesian estimation method. They derived a posterior estimators for the linear-linear model using an improper change point. The estimation of the model parameters for the linear segmented model from Bayesian perspective have been also studied by Ferreira (1975), Smith and Cook (1980), Lubrano (1985) and Pole and Smith (1985). Ferreira (1975) considered the linear-linear model without the continuity constraints on the modeling function at the change point. He analyzed the data studied by Quandt (1958) and showed that the Bayesian estimator has a smaller mean-square error than the maximum likelihood estimator. Smith and Cook
applied the Bayesian method to both constrained and unconstrained linear segmented models. Lubrano (1985) studied segmented models in the parameterization form with the min-operator proposed by Tishler and Zang (1981a). Pole and Smith (1985) provided the extension of segmented models to the linear time series.

Different methodology for the parameters estimation in segmented regression has been suggested by Bellman and Roth (1969) and Hawkins (1976). They considered methods for the fitting of segmented regression based on dynamical programing. Bellman and Roth (1969) minimized the maximum absolute deviation between the modeling function and the data. Hawkins (1976) considered maximum likelihood estimation procedure. Alternatives approach for the maximum likelihood methods has been considered by Lerman (1980). He proposed a grid-search method in the change point parameter space as a way to ensure that the global minimum has been found.

Most of these earlier articles mentioned above deal with the estimation procedure without providing much details on asymptotic properties of the estimators. Some asymptotic theory for the segmented regression models has been established by Feder (1975a), Feder (1975b), Gallant (1974), Gallant (1975), and Ivanov (1997) as a set of assumptions to ensure model regularity.

Feder (1975a) provided the consistency and asymptotic normality of the least squares estimator for the regression coefficients and the change points of the general underlying model with \( r \) segments. For the simplicity, the case where all segments of the modeling function are described by linear models has been considered. Also it has been noted that by using an appropriate Taylor expansion this technique can be extended to the nonlinear segments. The continuity of the underlying function is a principle and only one assumption on the modeling regression function. Since there are no other smoothness constrains imposed on the modeling function, a kinked fit is possible for a true relationship that happens to be smooth. In some practical cases, it is not trivial to identify if underlying function is smooth or kinked. Therefore, Feder established separately the asymptotic theory for the segmented models with odd and even order of smoothness. Here, the order of smoothness is defined as number of continuous derivatives plus one. His results showed that the asymptotic properties are very different, if the underlying model has an odd order of smoothness in comparison to the case with the even one. Feder (1975a) introduced a definition for the well-identified, identified and not identified estimator based on the location of the design point for the underlying modeling function and demonstrated it with several examples. Feder (1975b) studied the asymptotic distribution of the likelihood ratio statistic in regression model with \( r \) segments. He showed that if the true number of segments is less as the number assumed in the model, then the least square estimates are not asymptotically normal and the log-likelihood ratio statistic does not follow asymptotically \( \chi^2 \) distribution. In this case, the asymptotic behavior is more complicated and depends on location of the design points.

Gallant (1974), Gallant (1975) showed that the consistency and asymptotic normality of the least-squares estimator for the unknown change point in a quadratic-quadratic model
can be established if requirements on the location of the design points are fulfilled. Also the search for candidate change points should be restricted to be between two consecutive covariate design values. Both, Gallant (1975) and Ivanov (1997), established the consistency of the least squares estimator under the assumption that the parameter space is compact. Ivanov (1997) also proved the asymptotic normality by assuming twice-differentiability of the regression function.

Based on the asymptotic results for segmented models provided by Feder (1975b), Feder (1975a), Gallant (1974), Gallant (1975), and Ivanov (1997), the asymptotic theory for the bent-cable model (2.16) has been established by Chiu (2002). This compact and simple formulation allows to split all parameter models into linear and nonlinear ones. Therefore, the asymptotic theory has been developed first for the basic bent-cable model (2.15), which represents a nonlinear part of the modeling function. Afterward, these results have been extended to the full bent-cable model (2.16). In both cases, the set of design conditions on the covariates have been formulated, which guarantee the identifiability of the unknown model parameters.

In case of the basic bent-cable regression problem, Chiu (2002) assumed the errors $\epsilon_i$, $i = 1, \ldots, n$, where $n$ is a sample size, to be independent and identically normally distributed random variables with mean zero and a known finite constant variance $\text{Var}(\epsilon_i^2) = \sigma^2 < \infty$. The unknown parameters $\tau, \gamma$ have been estimated by the maximum likelihood method. The asymptotic results show that the maximum likelihood estimator is consistent ($\gamma \geq 0$) and it follows a asymptotically bivariate normal distribution ($\gamma > 0$). The case with the abrupt change between two linear segments ($\gamma = 0$) is an irregular boundary problem and it has been studied separately in Chiu et al. (2002]. The obtained results showed that the maximum likelihood estimation error converges either at a rate $n^{-1/3}$ and to an impractically complex limiting distribution. Due to these negative results, the asymptotic theory for the full bent-cable model (2.16) has been developed only for $\gamma > 0$ (see Chiu (2002), Chiu et al. (2006]). Here, the normality assumption on the errors has been relaxed together with the unrealistic assumption of a known error variance and the unknown model parameters has been estimated by least-squares.

An easy computational algorithm for the parameter estimation of the full bent-cable model has been proposed by Chiu (2009) and it has been implemented in R-package called bentcableAR that also can be applied to the data with autoregressive noise. The algorithmic and mathematical details for the bent-cable regression with AR($p$)-noise are reported in Chiu and Lockhart (2008) and the asymptotic theory for this regression problem is established in Chiu and Lockhart (2010]. The asymptotic results for the bent-cable model with the mixture longitudinal data has been developed by Khan (2010). In this thesis, a further extension of the asymptotic theory for the bent-cable model is developed under more realistic assumptions and these results are presented in Chapter 3.
Asymptotic theory for the bent-cable model under non-standard assumption

During the last decade, the asymptotic theory for the bent-cable model has been developed extensively and this type of segmented regression problem has been applied in many fields (see, for example, [Toms and Lesperance (2003), Chiu et al. (2006)] and [Roslyakova et al. (2016a)]). Taking into account that real data very seldom satisfy the classical assumptions on the error distribution, the asymptotic theory for the bent-cable models with $\gamma > 0$ under non-standard assumptions is developed in this chapter and the results are presented in the following manner. First, the consistency and asymptotic normality of the least-squares estimator are established for the basic bent-cable model. Then, the asymptotic theory for the full bent-cable model is formulated based on the results for the basic bent-cable model.

### 3.1 Basic bent-cable model

The basic bent-cable model is defined in (2.15) as

$$q(x; \tau, \gamma) = \frac{(x - \tau + \gamma)^2}{4\gamma} \mathbb{1}\{|x - \tau| \leq \gamma\} + (x - \tau) \mathbb{1}\{x > \tau + \gamma\}, \quad (3.1)$$

where $x$ is covariate, $\tau$ and $\gamma$ are parameters. The parameter space is defined as a compact set $\Theta = [-M_1, M] \times [0, M_2]$, where $M, M_1, M_2$ are some large positive but finite upper bounds for the candidate $\tau$ and $\gamma$-values.

The basic bent-cable model consists of three elements: incoming and outgoing linear phases with fixed slopes of 0 and 1, respectively, and a smooth quadratic transition, the
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so-called bent. The center $\tau$ and half-width of the bent $\gamma$ are unknown parameters. The bent-cable model with $\gamma = 0$ reduces to a non-differentiable broken stick. If $\gamma > 0$, the bent-cable model has a transition region over $[\tau - \gamma, \tau + \gamma]$, see Figure 3.1 and the resulting function is continuously differentiable with respect to each argument.

![Figure 3.1: A basic bent-cable model (solid line) and broken-stick model (dotted line).](image)

We consider observations $\{y_{ij} | i = 1, ..., p, j = 1, ..., n_i\}$ generated by a basic bent-cable regression model (3.1), that is

$$y_{ij} = q(x_i; \theta_0) + e_{ij}, \quad i = 1, ..., p, \quad j = 1, \cdots, n_i,$$

(3.2)

where $\theta_0 = (\tau_0, \gamma_0)$ is the “true” (two-dimensional) vector of regression parameters and $e_{ij}$ are independent random variables with mean $\mathbb{E}(e_{ij}) = 0$ and unknown variance $\text{Var}(e_{ij}) = \sigma_i^2 < \infty, \ i = 1, ..., p$. The least-squares estimator of $\theta$ based on data $\{x_i, y_{ij}\}, \ i = 1, ..., p, \ j = 1, \cdots, n_i$ is defined to be any vector $\hat{\theta}_n \in \Theta$ which minimizes the sum of squares

$$Q_n(\theta) = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} (y_{ij} - q(x_i, \theta))^2.$$  

(3.3)

Note, that the regression function (3.1) is not twice differentiable at the points $\tau - \gamma, \tau + \gamma$ and for this reason standard asymptotic theory is not directly applicable. In the following we will show that under appropriate assumptions the least squares estimate $\hat{\theta}_n$ is a strongly consistent estimator of $\theta_0$.

Through this chapter several assumptions on the error distribution and design points are considered to show asymptotic properties of the least-square estimates for the parameters $\tau$ and $\gamma > 0$ of the basic bent-cable model (3.1).

**Assumption [A0] (error distribution)**

$$\mathbb{E}|e_{ij}|^{2+\delta} \leq c < \infty, \quad \text{for some} \ \delta > 0.$$  

(3.4)
Asymptotic theory for the bent-cable model under non-standard assumption

We will also frequently use the matrix $Q$

The following result is one of the key components in the proof of consistency of the least-squares estimates in the basic bent-cable model, we introduce following notations

$$q_i(\theta) = q(x_i, \theta),$$

$$g_i(\theta) = \left(\frac{\partial q_i(\theta)}{\partial \tau}, \frac{\partial q_i(\theta)}{\partial \gamma}\right)^T = \left(-\alpha_{1i}(\theta) - \alpha_{2i}(\theta), \alpha_{3i}(\theta)\right)^T,$$

where $\alpha_{1i}(\theta), \alpha_{2i}(\theta), \alpha_{3i}(\theta)$ and $\alpha_{4i}(\theta)$ are functions of the parameters $\theta = (\tau, \gamma)$

$$\alpha_{1i}(\theta) = 1 \{x_i > \tau + \gamma\}, \quad \alpha_{2i}(\theta) = \frac{1}{2} \left(1 + \frac{x_i - \tau}{\gamma}\right) 1 \{|x_i - \tau| \leq \gamma\}, \quad \alpha_{3i}(\theta) = \frac{1}{4} \left[1 - \left(\frac{x_i - \tau}{\gamma}\right)^2\right] 1 \{|x_i - \tau| \leq \gamma\}. \quad (3.8)$$

We will also frequently use the matrix

$$A_n(\theta) = \sum_{i=1}^{p} n_i \cdot g_i(\theta)g_i^T(\theta) = \sum_{i=1}^{p} n_i \cdot \left(\alpha_{1i}(\theta) + \alpha_{2i}^2(\theta) - \alpha_{2i}(\theta)\alpha_{3i}(\theta)\right)$$

and introduce the matrix of the second derivatives (which exist whenever $x_i \neq \tau \pm \gamma$)

$$H_i(\theta) = \begin{pmatrix}
\frac{\partial^2 q_i(\theta)}{\partial \tau^2} & \frac{\partial^2 q_i(\theta)}{\partial \tau \partial \gamma} \\
\frac{\partial^2 q_i(\theta)}{\partial \tau \partial \gamma} & \frac{\partial^2 q_i(\theta)}{\partial \gamma^2}
\end{pmatrix} = \frac{1}{2\gamma} \left(1 + \frac{x_i - \tau}{\gamma}\right) 1 \{|x_i - \tau| \leq \gamma\}. \quad (3.10)$$

The distance between two bent-cable models both evaluated at $x_i$ is denoted by

$$d_{\theta_1, \theta_2}(x_i) = q_i(\theta_1) - q_i(\theta_2), \quad i = 1, \ldots, p. \quad (3.11)$$

With these notations the function, $Q_n(\theta)$, defined in $[3.3]$ with $[3.11]$ can be written as

$$Q_n(\theta) = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} \left(y_{ij} - q(x_i, \theta)\right)^2 = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} \left(e_{ij} + d_{\theta_0, \theta}(x_i)\right)^2. \quad (3.12)$$

### 3.1.1 Consistency

Before we start with the formulation and the proof of consistency theorem as the least-squares estimate we investigate the identifiability of the parameters in the basic bent-cable model. The following result is one of the key components in the proof of consistency of the least squares estimates $\hat{\theta}_n$ in the basic bent-cable model.
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Lemma 3.1.1 (Identifiability) Given two points \((x_1, y_1)\) and \((x_2, y_2)\) such that

\[ x_1 \in (\tau_0 - \gamma_0, \tau_0 + \gamma_0), \quad x_2 \in (\tau_0 + \gamma_0, \infty), \quad (3.13) \]
\[ y_i = q_i(\theta_0) \quad \forall i = 1, 2. \quad (3.14) \]

If for some parameter \(\theta\) the conditions

\[ q_i(\theta) = y_i, \quad \forall i = 1, 2 \quad (3.15) \]

are satisfied, then \(\theta = \theta_0\).

The conditions (3.13) of Lemma 3.1.1 are directly related to the assumptions on the design points \([A1]\) required for consistency of the least-squares estimates \(\hat{\theta}_n\). Moreover, they provide an indirect condition for identifiability of the unknown parameters of the considered model (3.1). We will show that for any candidate basic bent-cable \(q_i(\theta)\) which passes through the points \((x_1, y_1)\) and \((x_2, y_2)\) satisfying (3.13)–(3.15) guarantee that \(\theta = \theta_0\). In other words, this means that the candidate basic basic bent-cable \(q_i(\theta)\) is indeed the underlying model \(q_i(\theta_0)\).

Proof of Lemma 3.1.1 First not that any basic bent-cable model \(q_i(\theta)\) has a non-decreasing slope from 0 to 1 as \(x\) increases. This means that for any points \(x_1 \in (\tau - \gamma, \tau + \gamma)\) and \(x_2 \in (\tau + \gamma, \infty)\)

\[
\left. \frac{\partial q(x, \theta)}{\partial x} \right|_{x=x_1} \in (0, 1), \quad \left. \frac{\partial q(x, \theta)}{\partial x} \right|_{x=x_2} = 1, \quad (3.16)
\]

where \(\frac{\partial q(x, \theta)}{\partial x}\) is a partial derivative with respect to \(x\) given by

\[
\frac{\partial q(x, \theta)}{\partial x} = \frac{(x - \tau + \gamma)^2}{2\gamma} \{ |x - \tau| \leq \gamma \} + 1 \{ x > \tau + \gamma \}. \quad (3.17)
\]

This property of basic bent-cable model is one of the essential components in the proof of Lemma 3.1.1 which based on the following idea.

Taking into account (3.13)–(3.15) we will search for a solution of system of equations

\[ q_i(\theta) = q_i(\theta_0), \quad i = 1, 2 \quad (3.18) \]

under conditions (3.16)–(3.17) with respect to the parameters \(\tau\) and \(\gamma\).

The points \((x_1, y_1), (x_2, y_2)\) satisfy (3.13)–(3.14). Each of the point must lie on either the bend or the slope-one phase of a candidate basic bent-cable, \(q_i(\theta)\), and therefore we have to investigate three different cases.

Case 1: If \(x_1 \in (\tau - \gamma, \tau + \gamma), x_2 \in (\tau + \gamma, \infty)\), then the system of equations (3.18) transforms into

\[
\begin{cases}
\frac{(x_1 - \tau_0 + \gamma_0)^2}{4\gamma_0} = \frac{(x_1 - \tau + \gamma)^2}{4\gamma} \\
x_2 - \tau_0 = x_2 - \tau
\end{cases} \quad (3.19)
\]
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which directly shows \( \tau = \tau_0 \). Substituting this into the first equation and solving it with respect to \( \gamma \), gives two roots \( \gamma_1 = \gamma_0 \) and \( \gamma_2 = (x_1 - \tau_0)^2/\gamma_0 \), and we have two solutions of the system (3.19), \( \theta_1 = (\tau_0, \gamma_0) \) and \( \theta_2 = (\tau_0, (x_1 - \tau_0)^2/\gamma_0) \) respectively.

Now for the parameter vectors \( \theta_1 \) and \( \theta_2 \) we verify if the inequality \( |x_1 - \tau| < \gamma \) is valid for \( x_1 \) satisfying (3.13) and the conditions (3.16)-(3.17) are fulfilled. It is obvious true for \( \theta_1 \). However, substituting \( \theta_2 \) in the inequality above we obtain that \( |x_1 - \tau_0| > \gamma_0 \) which contradicts to the condition (3.13) on \( x_1 \) and the conditions (3.16)-(3.17). Therefore, we conclude that the parameter vector \( \theta_1 \) and it is unique solution of the system (3.19) under considered conditions.

**Case 2:** If \( x_1, x_2 \in (\tau + \gamma, \infty) \), then the system of equations (3.18) transforms into

\[
\begin{aligned}
\frac{(x_1 - \tau_0 + \gamma_0)^2}{4\gamma_0} &= x_1 - \tau \\
x_2 - \tau_0 &= x_2 - \tau
\end{aligned}
\]  
(3.20)

and again from the second equation we directly obtain \( \tau = \tau_0 \). Substituting this result in the first equation of the system (3.20) we have

\[
\frac{(x_1 - \tau_0 + \gamma_0)^2}{4\gamma_0} = x_1 - \tau_0.
\]

However, the unique solution of this equation is given by \( x_1 = \tau_0 + \gamma_0 \) which contradicts to (3.13) and we conclude that the system (3.20) does not have a solution different for \( (\tau_0, \gamma_0) \) under the considered conditions.

**Case 3:** If \( x_1, x_2 \in (\tau - \gamma, \tau + \gamma) \), then the system of equations (3.18) transforms into

\[
\begin{aligned}
\frac{(x_1 - \tau_0 + \gamma_0)^2}{4\gamma_0} &= (x_1 - \tau + \gamma)^2 \\
x_2 - \tau_0 &= (x_2 - \tau + \gamma)^2
\end{aligned}
\]

which has a unique solution given by

\[
\begin{aligned}
\tau &= \frac{1}{4} \left( y_1 + y_2 \right) \left( x_1 - x_2 \right)^2 + 4 \left( y_2 - y_1 \right) \left( x_1 y_2 - x_2 y_1 \right) + 2 \sqrt{y_2 y_1 \left( x_1 - x_2 \right)^2 a^2},
\\
\gamma &= \frac{1}{4} \left( x_1 - x_2 \right) \left( 2 \sqrt{y_2 y_1 \left( x_1 - x_2 \right)^2 a^2} + \left( y_1 + y_2 \right) \left( x_1 - x_2 \right) a \right) \left( y_2 - y_1 \right)^2
\\&\quad \left( \left( y_2 - y_1 \right)^2 a \right).
\end{aligned}
\]

where \( a = x_1 - x_2 + 2 \left( y_2 - y_1 \right) > 0 \) and \( y_1, y_2 \) are defined in (3.14) (note that \( y_2 > y_1 \)).

Verifying the condition (3.16) at the point \( x_2 \) we obtain

\[
\left. \frac{\partial q(x, \theta)}{\partial x} \right|_{x = x_2} = 2 \frac{\sqrt{y_1 y_2} \left( x_1 - x_2 \right)^2 a^2 + y_2 \left( x_1 - x_2 \right) a \left( y_1 - y_2 \right)}{y_2 - y_1} \left( x_1 - x_2 \right) \left( 2 \sqrt{y_1 y_2} \left( x_1 - x_2 \right) a + \left( y_1 + y_2 \right) \left( x_1 - x_2 \right) a \right)
\]

\[
= \left( x_1 - x_2 \right) a \cdot \left( 2 \sqrt{y_1 y_2} + y_1 + y_2 \right)
\]

\[
= 2 \sqrt{y_2 \left( \sqrt{y_1} + \sqrt{y_2} \right)} \left( y_1 - y_2 \right)
\]

\[
= \frac{2 \sqrt{y_2 \left( \sqrt{y_1} + \sqrt{y_2} \right)^2}}{x_1 - x_2}
\]

\[
= \frac{2 \sqrt{y_2 \left( x_2 - x_1 \right)}}{x_2 - x_1}.
\]
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Using the conditions (3.13) and (3.14) this expression can be rewritten as

\[
\frac{\partial q(x, \theta)}{\partial x} \bigg|_{x=x_2} = 2 \frac{y_2 - \sqrt{y_1 y_2}}{x_2 - x_1} = 2 \frac{x_2 - \tau_0 - \sqrt{\frac{(x_1 - \tau_0 + \gamma_0)^2}{4 \gamma_0}} (x_2 - \tau_0)}{x_2 - x_1}
\]

\[
= 2 \frac{x_2 - \tau_0 - \frac{(x_1 - \tau_0 + \gamma_0)}{2} \sqrt{\frac{x_2 - \tau_0}{\gamma_0}}}{x_2 - x_1} = 2 \frac{x_2 - x_1 + \frac{(x_2 + \tau_0 - \gamma_0)}{2} \sqrt{\frac{x_2 - \tau_0}{\gamma_0}}}{x_2 - x_1}
\]

\[
= 2 \left( \frac{1}{2} + (x_2 - x_1)(x_2 + \tau_0 - \gamma_0) \sqrt{\frac{x_2 - \tau_0}{\gamma_0}} \right) = 1 + (x_2 - x_1)(x_2 + \tau_0 - \gamma_0) \sqrt{\frac{x_2 - \tau_0}{\gamma_0}} > 1
\]

and thus it contradicts to the condition (3.16).

**Theorem 3.1.1** (Consistency) Under conditions \([A0]\) and \([A1]\), the least-squares estimator of parameters in the model (3.2) with \(\gamma_0 > 0\) is strongly consistent, that is

\[\hat{\theta}_n \xrightarrow{a.s.} \theta_0, \text{ as } n \to \infty.\]

**Proof.** Let \(\hat{\theta}_n\) be a least-squares estimator of \(\theta_0\) obtained by minimizing the function \(Q_n\) defined in (3.3). To prove that \(\hat{\theta}_n\) is a strongly consistent estimator of \(\theta_0\) under assumptions \([A0]\) and \([A1]\), it is enough to show that

\[
\liminf_{n \to \infty} \inf_{|\theta - \theta_0| \geq \delta} \left[ Q_n(\theta) - Q_n(\theta_0) \right] > 0 \quad \text{a.s.} \quad (3.21)
\]

for all \(\delta > 0\) (see Lemma 1 in [Wu (1981)]).

Taking into account the parameter space \(\Theta = [-M_1, M] \times [0, M_2]\), where \(M, M_1, M_2\) are some large positive but finite upper bounds for the candidate \(\tau\) and \(\gamma\)-values, the condition (3.21) transforms into

\[
\liminf_{n \to \infty} \inf_{\theta \in D_\delta} \left[ Q_n(\theta) - Q_n(\theta_0) \right] > 0 \quad \text{a.s.},
\]

where \(D_\delta = \{\theta : \delta \leq |\theta - \theta_0| \leq M^*\}\) and \(M^*\) is a finite positive constant.

First note that

\[
Q_n(\theta) - Q_n(\theta_0) = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} \left( (y_i - q_i(\theta))^2 - e_{ij}^2 \right)
\]

\[
= \frac{1}{n} \sum_{i=1}^{p} n_i \cdot \left( q_i(\theta_0) - q_i(\theta) \right)^2 + \frac{2}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} e_{ij} \left( q_i(\theta_0) - q_i(\theta) \right) + \frac{1}{n} \sum_{i=1}^{p} n_i \cdot d_{\theta, \theta}^2(x_i) + \frac{2}{n} \sum_{i=1}^{p} d_{\theta, \theta}(x_i) \cdot \sum_{j=1}^{n_i} e_{ij}. \quad (3.22)
\]
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Therefore

\[
\liminf_{n \to \infty} \inf_{\theta \in D_3} \left[ Q_n(\theta) - Q_n(\theta_0) \right] \geq \liminf_{n \to \infty} \inf_{\theta \in D_3} \frac{1}{n} \sum_{i=1}^{p} n_i \cdot d_{\theta_i,\theta}(x_i) \\
+ 2 \liminf_{n \to \infty} \inf_{\theta \in D_3} \sum_{i=1}^{p} d_{\theta_i,\theta}(x_i) \cdot \frac{1}{n} \sum_{j=1}^{n} e_{ij}
\]

and the condition (3.21) is fulfilled if we can show that

\[
\liminf_{n \to \infty} \inf_{\theta \in D_3} \frac{1}{n} \sum_{i=1}^{p} n_i \cdot d_{\theta_i,\theta}(x_i) > \epsilon_1 > 0, \tag{3.23}
\]

\[
\liminf_{n \to \infty} \inf_{\theta \in D_3} \sum_{i=1}^{p} d_{\theta_i,\theta}(x_i) \cdot \frac{1}{n} \sum_{j=1}^{n} e_{ij} \xrightarrow{a.s.} 0, \tag{3.24}
\]

where \(\epsilon_1 > 0\) is some finite constant. Here (3.23) and (3.24) are non-stochastic and stochastic parts of (3.22) respectively.

**Proof of (3.23).** Note that

\[
\liminf_{n \to \infty} \inf_{\theta \in D_3} \frac{1}{n} \sum_{i=1}^{p} n_i \cdot d_{\theta_i,\theta}(x_i) \geq \lim_{n \to \infty} \left\{ \inf_{\theta \in D_3} T_n(x_1, x_2, \theta) \right\},
\]

where \(x_1, x_2\) satisfying (3.13) and \(T_n(x_1, x_2, \theta)\) is defined as

\[
T_n(x_1, x_2, \theta) = \frac{n_1}{n} |d_{\theta_1,\theta}(x_1)|^2 + \frac{n_2}{n} |d_{\theta_2,\theta}(x_2)|^2.
\]

For all \(n \geq N_0\) according to the assumption [A1], \(\frac{m_i}{n} \geq c > 0\) for \(i = 1, 2\). Then

\[
\lim_{n \to \infty} \left\{ \inf_{\theta \in D_3} T_n(x_1, x_2, \theta) \right\} \geq \inf_{\theta \in D_3} T(x_1, x_2, \theta),
\]

where \(T(x_1, x_2, \theta)\) satisfies

\[
T(x_1, x_2, \theta) \geq c \left( |d_{\theta_1,\theta}(x_1)|^2 + |d_{\theta_2,\theta}(x_2)|^2 \right).
\]

Now, assume that \(\inf_{\theta \in D_3} T(x_1, x_2, \theta) = 0\). Then there exists a sequence \(\theta_n\) such that \(T(x_1, x_2, \theta_n) \to 0\) and this sequence \(\theta_n\) is bounded. Now, according to the Bolzano - Weierstrass theorem, there exists a convergent subsequence \(\theta_{n_k} \to \theta' \in D_3\) and \(T(x_1, x_2, \theta') = 0\). From the last argument it follows that \(q_i(\theta_0) = q_i(\theta')\) for all \(i = 1, 2\). Therefore, using Lemma 3.1.1 we obtain that \(\theta_0 = \theta'\) which contradicts with the definition of \(D_3\) given above, where \(\theta_0 \neq \theta'\).

**Proof of (3.24).** Applying the Kolmogorov’s strong law of large number [Chung (2001), Chapter 5.4], we have

\[
\frac{1}{n} \sum_{j=1}^{n} e_{ij} \xrightarrow{a.s.} 0 \quad \forall i = 1, \ldots, p.
\]

(3.25)
It is can be shown that for all \( x_i \in \mathbb{R} \) and \( \theta_1, \theta_2 \in \Theta \)
\[
|d_{\theta_1,\theta_2}(x_i)| \leq \max \{|\tau_1 - \tau_2|, |\gamma_1 - \gamma_2|\}.
\] (3.26)

Then, for all \( i = 1, \ldots, p \), we have
\[
|d_{\theta_0, \theta}(x_i)| \leq M^*, \quad \forall \theta \in \Theta,
\] (3.27)

where \( M^* \) is a finite positive constant. Taking into account (3.25)-(3.27), we have
\[
\lim_{n \to \infty} \inf_{\theta \in D} \frac{1}{n} \sum_{i=1}^{p} d_{\theta_0, \theta}(x_i) \cdot \frac{a_{ij}}{n} \to 0,
\]
and thus we showed (3.24).

### 3.1.2 Asymptotic normality

The proof of the asymptotic normality of the least squares estimate for the model (3.1) is established in this section under assumptions [A0] and [A1]. Note, the basic bent-cable model (3.1) does not fulfill the common assumptions considered for heteroskedastic nonlinear regression models (see, for example, [Shao (1990)]). Therefore, the existing results cannot be directly applied in this case.

**Theorem 3.1.2** (Asymptotic normality) Under conditions [A0] and [A1], we have
\[
\sqrt{n}(\theta_0 - \hat{\theta}_n) \xrightarrow{D} N(0, A^{-1}(\theta_0) \sum_{i=1}^{p} \xi_i \sigma_i^2 g_i(\theta_0) g_i^T(\theta_0) A^{-1}(\theta_0)),
\] (3.28)

where the matrix \( A(\theta) \) and the vector \( g_i(\theta) \) are defined in (3.9) and (3.7) respectively.

**Proof.** Let \( Q_n(\theta) = \left( \frac{\partial Q_n(\theta)}{\partial \tau}, \frac{\partial Q_n(\theta)}{\partial \gamma} \right)^T \) be the gradient of \( Q_n(\theta) \). Writing the representation component-wise we have
\[
\frac{\partial Q_n(\theta)}{\partial \tau} = \frac{2}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} \left( q_i(\theta) - q_i(\theta_0) - e_{ij} \right) \frac{\partial q_i}{\partial \tau}(\theta),
\]
\[
\frac{\partial Q_n(\theta)}{\partial \gamma} = \frac{2}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} \left( q_i(\theta) - q_i(\theta_0) - e_{ij} \right) \frac{\partial q_i}{\partial \gamma}(\theta).
\]

We will apply the second fundamental theorem of calculus for a Lebesgue integral component-wise to the functions \( h_\tau, h_\gamma(t) : [0, 1] \to \mathbb{R} \) defined as a composition of the functions
\[
h_\tau(t) = f_\tau(\theta(t)),
\]
\[
h_\gamma(t) = f_\gamma(\theta(t)),
\]

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where \( \theta(t) = \theta_t = \theta_0 + t(\hat{\theta}_n - \theta_0), t \in [0, 1] \) and \( f_\tau(\theta_t) = \frac{\partial Q_n}{\partial \tau}(\theta_t), f_\gamma(\theta_t) = \frac{\partial Q_n}{\partial \gamma}(\theta_t) : \mathbb{R}^2 \to \mathbb{R} \).

As the functions \( h_\tau(t), h_\gamma(t) \) are almost everywhere differentiable, we obtain

\[
\frac{\partial Q_n}{\partial \tau}(\theta_n) - \frac{\partial Q_n}{\partial \tau}(\theta_0) = h_\tau(1) - h_\tau(0) = \int_0^1 h'_\tau(t) dt
\]

\[
= \int_0^1 \left[ \frac{\partial^2 Q_n}{\partial \tau^2}(\theta_t)(\hat{\tau}_n - \tau_0) + \frac{\partial^2 Q_n}{\partial \tau \partial \gamma}(\theta_t)(\hat{\gamma}_n - \gamma_0) \right] dt
\]

\[
= \int_0^1 \nabla_\theta \frac{\partial Q_n}{\partial \tau}(\theta_t) dt \cdot (\hat{\theta}_n - \theta_0),
\]

\[
\frac{\partial Q_n}{\partial \gamma}(\hat{\theta}_n) - \frac{\partial Q_n}{\partial \gamma}(\theta_0) = h_\gamma(1) - h_\gamma(0) = \int_0^1 h'_\gamma(t) dt
\]

\[
= \int_0^1 \left[ \frac{\partial^2 Q_n}{\partial \gamma^2}(\theta_t)(\hat{\tau}_n - \gamma_0) + \frac{\partial^2 Q_n}{\partial \gamma \partial \tau}(\theta_t)(\hat{\gamma}_n - \gamma_0) \right] dt
\]

\[
= \int_0^1 \nabla_\theta \frac{\partial Q_n}{\partial \gamma}(\theta_t) dt \cdot (\hat{\theta}_n - \theta_0).
\]

where \( \nabla_\theta \frac{\partial Q_n}{\partial \tau}(\theta_t) \) and \( \nabla_\theta \frac{\partial Q_n}{\partial \gamma}(\theta_t) \) correspond to the first and second row of the matrix

\[
Q''_n(\theta_t) = \frac{2}{n} \left[ A_n(\theta_t) + \sum_{i=1}^p \sum_{j=1}^{n_i} (q_i(\theta_t) - q_i(\theta_0) - e_{ij}) H_i(\theta_t) \right],
\]

and \( A_n(\theta_t) \) and \( H_i(\theta_t) \) are defined in \( \text{(3.3)} \) and \( \text{(3.10)} \) respectively. Therefore, we can write

\[
Q'_n(\hat{\theta}_n) - Q'_n(\theta_0) = \left[ \int_0^1 Q''_n(\theta_t) dt \right] (\hat{\theta}_n - \theta_0).
\]

Since \( Q''_n(\hat{\theta}_n) = 0 \), we have

\[
Q'_n(\theta_0) = \left[ \int_0^1 Q''_n(\theta_t) dt \right] (\hat{\theta}_n - \hat{\theta}_n).
\]

Thus, using the expressions \( \text{(3.29)} \) and \( \text{(3.30)} \) in \( \text{(3.31)} \) gives

\[
\left[ \int_0^1 Q''_n(\theta_t) dt \right] \cdot \sqrt{n} (\theta_0 - \hat{\theta}_n) = \frac{1}{\sqrt{n}} \sum_{i=1}^p \sum_{j=1}^{n_i} e_{ij} g_i(\theta_0).
\]

Then the assertion \( \text{(3.28)} \) follows if we can show that

\[
\left[ \int_0^1 Q''_n(\theta_t) dt \right] \overset{p}{\longrightarrow} A(\theta_0)
\]

and

\[
X_n = \frac{1}{\sqrt{n}} \sum_{i=1}^p \sum_{j=1}^{n_i} e_{ij} g_i(\theta_0) \overset{p}{\longrightarrow} N(0, \sum_{i=1}^p \xi_i \sigma_i^2 g_i(\theta_0) g_i^T(\theta_0)),
\]

where \( A(\theta_0) \) is positive definite nonsingular matrix.
Proof of (3.33). We can rewrite $X_n$ defined from (3.33) in the form

$$X_n = \sum_{i=1}^{p} \sqrt{\frac{n_i}{n}} \cdot X_{n,i},$$

(3.34)

where $X_{n,1}, \ldots, X_{n,p}$ are independent random variables defined by

$$X_{n,i} = \frac{1}{\sqrt{n_i}} \sum_{j=1}^{n_i} e_{ij} g_i(\theta_0)$$

with mean value $E(X_{n,i}) = 0$ and variance

$$\text{Var}(X_{n,i}) = \text{Var} \left( \frac{1}{\sqrt{n_i}} \sum_{j=1}^{n_i} e_{ij} g_i(\theta_0) \right) = \frac{1}{n_i} \sum_{j=1}^{n_i} \sigma_i^2 g_i(\theta_0) g_i^T(\theta_0) = \sigma_i^2 g_i(\theta_0) g_i^T(\theta_0).$$

We now apply the Cramer-Wold device and verify the conditions of the Lyapunov central limit theorem for $X_{n,i}$, that is

$$\lambda^T X_{n,i} = \frac{1}{\sqrt{n_i}} \sum_{j=1}^{n_i} e_{ij} \cdot \lambda^T g_i(\theta_0) = \frac{1}{\sqrt{n_i}} \sum_{j=1}^{n_i} e_{ij} \cdot (\lambda_1 g_i(\theta_0) + \lambda_2 g_i(\theta_0)),$$

where $g_i(\theta_0)$ and $g_i^T(\theta_0)$ are the components of the gradient vector $g_i(\theta)$ defined in (3.7). Then

$$s_i^2 = \text{Var} (\lambda^T X_{n,i}) = \sigma_i^2 \cdot (\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0))^2$$

and for some $\delta > 0$

$$s_i^{2+\delta} = (\sigma_i^2 \cdot (\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0))^2)^{\frac{2+\delta}{2}} = (\sigma_i^2)^{\frac{2+\delta}{2}} \cdot (\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0))^{2+\delta}.$$

On the other hand we have

$$\sum_{j=1}^{n_i} \mathbb{E}|\lambda^T X_{n,i}|^{2+\delta} = \sum_{j=1}^{n_i} \mathbb{E} \left[ \frac{1}{\sqrt{n_i}} |e_{ij}| |\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0)| \right]^{2+\delta}$$

$$= \left( \frac{1}{\sqrt{n_i}} \right)^{2+\delta} |\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0)|^{2+\delta} \cdot \sum_{j=1}^{n_i} \mathbb{E} |e_{ij}|^{2+\delta}.$$

Taking into account that $\mathbb{E}|e_{ij}|^{2+\delta} < \infty$ (assumption [A0]), we obtain

$$\sum_{j=1}^{n_i} \mathbb{E}|X_{n,i}|^{2+\delta} = \Delta \cdot n_i \left( \frac{1}{\sqrt{n_i}} \right)^{2+\delta} |\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0)|^{2+\delta}$$

$$= \Delta \cdot \left( \frac{1}{\sqrt{n_i}} \right)^{\delta} |\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0)|^{2+\delta}.$$

Combining the results of these calculations we obtain

$$\lim_{n_i \to \infty} \frac{1}{s_i^{2+\delta}} \sum_{j=1}^{n_i} \mathbb{E}|X_{n,i}|^{2+\delta} = \lim_{n_i \to \infty} \frac{\Delta \cdot |\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0)|^{2+\delta}}{(\sigma_i^2)^{\frac{2+\delta}{2}} \cdot (\lambda_1 g_i^T(\theta_0) + \lambda_2 g_i^T(\theta_0))^{2+\delta}} \cdot \left( \frac{1}{\sqrt{n_i}} \right)^{\delta} = 0.$$
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Therefore, the Lyapunov condition of the central limit theorem is fulfilled and we have

\[ X_{n,i} \overset{D}{\to} N(0, \xi_i \sigma_i g_i(\theta_0) g_i^T(\theta_0)), \quad \forall i = 1, \ldots, p. \tag{3.35} \]

Finally define

\[ \bar{X}_n = \sum_{i=1}^p \sqrt{\xi_i} \cdot X_{n,i}. \]

Since the random variables \( X_{n,i} \) are independent and asymptotically normal distributed, we obtain that

\[ \bar{X}_n \overset{D}{\to} N(0, \sum_{i=1}^p \xi_i \sigma_i g_i(\theta_0) g_i^T(\theta_0)). \]

Now our object of interest \( X_n \) defined in (3.34) can be represented as

\[ X_n = \bar{X}_n - \sum_{i=1}^p \left( \sqrt{\xi_i} - \sqrt{\frac{n_i}{n}} \right) \cdot X_{n,i}. \tag{3.36} \]

Taking into account a definition of \( \xi_i \) given in (3.5) we obtain

\[ \sqrt{\xi_i} - \sqrt{\frac{n_i}{n}} \to 0, \quad \forall i = 1, \ldots, p \]

and together with (3.35), (3.36) we have the weak convergence and proved (3.33).

**Proof of (3.37).** The three summands of \( \int_0^1 Q_n''(\theta_t)dt \) will be considered separately to show that

\[ \int_0^1 \frac{1}{n} A_n(\theta_t)dt \overset{a.s.}{\longrightarrow} A(\theta_0), \tag{3.37} \]

\[ \int_0^1 \frac{1}{n} \sum_{i=1}^p \sum_{j=1}^n e_{ij} H_i(\theta_t)dt \overset{p}{\longrightarrow} 0, \tag{3.38} \]

\[ \int_0^1 \frac{1}{n} \sum_{i=1}^p n_i \cdot (q_i(\theta_t) - q_i(\theta_0)) H_i(\theta_t)dt \overset{a.s.}{\longrightarrow} 0. \tag{3.39} \]

**Proof of (3.37).** We will calculate \( \int_0^1 \frac{1}{n} A_n(\theta_t)dt \) component-wise using the Lebesgue’s Dominated Convergence Theorem (DCT). For this purpose we verify the conditions of the DCT separately for each component of the matrix \( \frac{1}{n} A_n(\theta_t) \)

\[ \frac{1}{n} A_{n,rr}(\theta_t) = \frac{1}{n} \sum_{i=1}^p n_i (\alpha_{1i}(\theta_t) + \alpha_{2i}^2(\theta_t)), \]

\[ \frac{1}{n} A_{n,ry}(\theta_t) = \frac{1}{n} A_{n,yr}(\theta_t) = -\frac{1}{n} \sum_{i=1}^p n_i \alpha_{2i}(\theta_t) \alpha_{3i}(\theta_t), \]

\[ \frac{1}{n} A_{n,yy}(\theta_t) = \frac{1}{n} \sum_{i=1}^p n_i \alpha_{3i}^2(\theta_t). \]
First we calculate the upper bound for each element of the matrix $\frac{1}{n}A_n(\theta_t)$. From the obvious estimates

$$|\alpha_{1\alpha}(\theta_t)| \leq |\{x_i > \tau_t + \gamma_t\}| \leq 1,$$

$$|\alpha_{2\alpha}(\theta_t)| \leq \frac{1}{2} \left( 1 + \frac{x_i - \tau_t}{\gamma_t} \right) \{\{x_i - \tau_t\} \leq \gamma_t\} \leq 1,$$

$$|\alpha_{3\alpha}(\theta_t)| \leq \frac{1}{4} \left( 1 - \left( \frac{x_i - \tau_t}{\gamma_t} \right)^2 \right) \{\{x_i - \tau_t\} \leq \gamma_t\} \leq \frac{1}{2},$$

it follows

$$\left| \frac{1}{n} A_{n,\tau\tau}(\theta_t) \right| \leq \frac{1}{n} \sum_{i=1}^{p} n_i |\alpha_{1\alpha}(\theta_t)| + \frac{1}{n} \sum_{i=1}^{p} n_i |\alpha_{2\alpha}(\theta_t)| \leq \frac{1}{n} \sum_{i=1}^{p} n_i + \frac{1}{n} \sum_{i=1}^{p} n_i = 1 + 1 = 2,$$

(3.40)$$\left| \frac{1}{n} A_{n,\tau\gamma}(\theta_t) \right| \leq \frac{1}{n} \sum_{i=1}^{p} n_i |\alpha_{2\alpha}(\theta_t)| |\alpha_{3\alpha}(\theta_t)| \leq \frac{1}{n} \sum_{i=1}^{p} n_i \frac{n_i}{2} = \frac{1}{2},$$

(3.41)$$\left| \frac{1}{n} A_{n,\gamma\gamma}(\theta_t) \right| \leq \frac{1}{n} \sum_{i=1}^{p} n_i |\alpha_{3\alpha}(\theta_t)| \leq \frac{1}{n} \sum_{i=1}^{p} n_i \frac{1}{4} = \frac{1}{4},$$

(3.42)

The equations (3.40)-(3.42) show that each component of the matrix $\frac{1}{n}A_n(\theta_t)$ is dominated by an integrable function.

Next note that each component of the matrix $\frac{1}{n}A_n(\theta_t)$ contains at least one of the two indication functions of the form

$$\{x_i > \tau_t + \gamma_t\}, \quad \{\{|x_i - \tau_t| \leq \gamma_t\},$$

where either $x_i \in (\tau_0 - \gamma_0, \tau_0 + \gamma_0)$ or $x_i \in (\tau_0 + \gamma_0, \infty)$ and $\tau_t = \tau_0 + t(\hat{\tau}_n - \tau_0), \gamma_t = \gamma_0 + t(\hat{\gamma}_n - \gamma_0)$. Therefore, we begin investigating the asymptotic properties of these two indicator functions. The following Lemma will be shown at the end of this section.

**Lemma 3.1.2** If $x_i \in (\tau_0 - \gamma_0, \tau_0 + \gamma_0)$ or $x_i \in (\tau_0 + \gamma_0, \infty)$ then

$$F_n = \{x_i > \tau_t + \gamma_t\} \xrightarrow{a.s.} \{x_i > \tau_0 + \gamma_0\},$$

(3.43)$$V_n = \{\{|x_i - \tau_t| \leq \gamma_t\} \xrightarrow{a.s.} \{\{|x_i - \tau_0| \leq \gamma_0\},$$

(3.44)

where $\tau_t = \tau_0 + t(\hat{\tau}_n - \tau_0), \gamma_t = \gamma_0 + t(\hat{\gamma}_n - \gamma_0)$ and $t \in [0, 1]$.

Now the limit of each component of the matrix $\frac{1}{n}A_n(\theta_t)$ will be calculated by an application
of Lemma 3.1.2. For example,

\[
\lim_{n \to \infty} \frac{1}{n} A_{n, \tau\gamma}(\theta_t) = \lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{p} n_i \mathbb{1} \{x_i > \tau_t + \gamma_t\} \\
+ \lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{p} n_i \left(1 + \frac{x_i - \tau_t}{\gamma_t}\right)^{2} \mathbb{1} \{|x_i - \tau_t| \leq \gamma_t\} \\
= \lim_{n \to \infty} \left(\sum_{i=1}^{p} n_i \mathbb{1} \{x_i > \tau_t + \gamma_t\} \cdot \sum_{i=p+1}^{n} n_i \mathbb{1} \{x_i > \tau_t + \gamma_t\}\right) \\
+ \frac{1}{4} \lim_{n \to \infty} \sum_{i=1}^{p} n_i \left(1 + \frac{x_i - \tau_t}{\gamma_t}\right)^{2} \mathbb{1} \{|x_i - \tau_t| \leq \gamma_t\} \\
+ \frac{1}{4} \lim_{n \to \infty} \sum_{i=p+1}^{n} n_i \left(1 + \frac{x_i - \tau_t}{\gamma_t}\right)^{2} \mathbb{1} \{|x_i - \tau_t| \leq \gamma_t\} \\
\xrightarrow{a.s.} \sum_{i=p+1}^{p} \xi_i + \frac{1}{4} \sum_{i=1}^{p} \xi_i \left(1 + \frac{x_i - \tau_0}{\gamma_0}\right)^{2}. 
\]

Analogously, we obtain

\[
\lim_{n \to \infty} \frac{1}{n} A_{n, \tau\gamma}(\theta_t) = \lim_{n \to \infty} \frac{1}{n} A_{n, \gamma\tau}(\theta_t) \\
= \lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{n} \frac{1}{8} \left(1 + \frac{x_i - \tau_t}{\gamma_t}\right) \left(1 - \left(\frac{x_i - \tau_t}{\gamma_t}\right)^2\right) \mathbb{1} \{|x_i - \tau_t| \leq \gamma_t\} \\
\xrightarrow{a.s.} -\frac{1}{8} \sum_{i=1}^{p} \xi_i \left(1 + \frac{x_i - \tau_0}{\gamma_0}\right) \left(1 - \left(\frac{x_i - \tau_0}{\gamma_0}\right)^2\right), 
\]

and

\[
\lim_{n \to \infty} \frac{1}{n} A_{n, \gamma\gamma}(\theta_t) = \lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{n} \frac{1}{16} \left(1 - \left(\frac{x_i - \tau_t}{\gamma_t}\right)^2\right) \mathbb{1} \{|x_i - \tau_t| \leq \gamma_t\} \\
\xrightarrow{a.s.} \frac{1}{16} \sum_{i=1}^{p} \xi_i \left(1 - \left(\frac{x_i - \tau_0}{\gamma_0}\right)^2\right)^2. 
\]

By an application of the DCT, we can calculate component-wise the integral of the matrix \(\frac{1}{n} A_n(\theta_t)\), that is

\[
\lim_{n \to \infty} \int_0^1 \frac{1}{n} A_n(\theta_t) dt = A(\theta_0) \\
:= \begin{pmatrix}
\sum_{i=p+1}^{p} \xi_i + \frac{1}{4} \sum_{i=1}^{p} \xi_i \left(1 + \frac{x_i - \tau_0}{\gamma_0}\right)^2 - \frac{1}{8} \sum_{i=1}^{p} \xi_i \left(1 + \frac{x_i - \tau_0}{\gamma_0}\right) \left(1 - \left(\frac{x_i - \tau_0}{\gamma_0}\right)^2\right) \\
- \frac{1}{8} \sum_{i=1}^{p} \xi_i \left(1 + \frac{x_i - \tau_0}{\gamma_0}\right) \left(1 - \left(\frac{x_i - \tau_0}{\gamma_0}\right)^2\right) & \frac{1}{16} \sum_{i=1}^{p} \xi_i \left(1 - \left(\frac{x_i - \tau_0}{\gamma_0}\right)^2\right)^2
\end{pmatrix}
\]

We finally verify that the matrix \(A(\theta_0)\) is nonsingular and positive definite. For this
purpose we first calculate the determinant

$$\det \mathbf{A}(\theta_0) = A_{\tau\tau}(\theta_0) \cdot A_{\gamma\gamma}(\theta_0) - (A_{\tau\gamma}(\theta_0))^2$$

$$= \left[ \sum_{i=p_1+1}^{p} \xi_i + \frac{1}{4} \sum_{i=1}^{p_1} a_i^2 \right] \cdot \frac{1}{16} \sum_{i=1}^{p_1} b_i^2 - \frac{1}{64} \left[ \sum_{i=1}^{p_1} a_i \cdot b_i \right]^2$$

$$= \frac{1}{16} \sum_{i=p_1+1}^{p} \xi_i \cdot \sum_{i=1}^{p_1} b_i^2 + \frac{1}{64} \left( \sum_{i=1}^{p_1} a_i^2 \cdot \sum_{i=1}^{p_1} b_i^2 - \left[ \sum_{i=1}^{p_1} a_i \cdot b_i \right]^2 \right),$$

where we use the notation

$$a_i = \sqrt{\xi_i} \left( 1 + \frac{x_i - \tau_0}{\gamma_0} \right), \quad b_i = \sqrt{\xi_i} \left( 1 - \left( \frac{x_i - \tau_0}{\gamma_0} \right)^2 \right).$$

Applying the Cauchy-Schwarz Inequality to the second summand of the equation (3.45) we obtain (note that $$x_i \neq \tau_0 \pm \gamma_0$$)

$$\det \mathbf{A}(\theta_0) \geq \frac{1}{16} \sum_{i=p_1+1}^{p} \xi_i \cdot \sum_{i=1}^{p_1} b_i^2 > 0.$$

As the element $$A_{\tau\tau}$$ in the position $$(1, 1)$$ of the matrix $$\mathbf{A}(\theta_0)$$ is positive, it follows that $$\mathbf{A}(\theta_0)$$ is positive definite.

**Proof of (3.38).** Since $$H_{i,k}(\theta_t), k = \{(\tau, \tau), (\tau, \gamma), (\gamma, \tau), (\gamma, \gamma)\}$$ is a matrix, all calculations during this step will be performed component-wise. For each component of the matrix $$H_{i,k}(\theta_t)$$ we consider the decomposition

$$Y_n = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n} e_{ij} \int_{0}^{1} H_{i,k}(\theta_t) dt = Z_n + (Y_n - Z_n),$$

where

$$Z_n = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n} e_{ij} \int_{0}^{1} H_{i,k}(\theta_t) dt = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n} e_{ij} H_{i,k}(\theta_0),$$

$$Y_n - Z_n = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n} e_{ij} \int_{0}^{1} (H_{i,k}(\theta_t) - H_{i,k}(\theta_0)) dt.$$ 

The mean and the variance of the random variable $$Z_n$$ are given by

$$\mathbb{E}[Z_n] = 0,$$

$$\text{Var}[Z_n] = \frac{1}{n^2} \sum_{i=1}^{p} \sum_{j=1}^{n} \text{Var}(e_{ij}) \cdot H_{i,k}^2(\theta_0) \leq \frac{\rho}{n} \cdot \frac{1}{n} \sum_{i=1}^{p} n_i \cdot H_{i,k}^2(\theta_0) = \frac{\rho}{n} \sum_{i=1}^{p} \frac{n_i}{n} \cdot H_{i,k}^2(\theta_0) \to 0,$$

where $$\rho$$ is a constant and we used [A1] and the definition of the matrix $$\mathbf{H}_i$$ in (3.10).
Then

\[
|Y_n - Z_n| = \left| \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} e_{ij} \cdot \int_0^1 (H_{i,k}(\theta_t) - H_{i,k}(\theta_0)) \, dt \right|
\]

\[
= \sum_{i=1}^{p} \int_0^1 \left( H_{i,k}(\theta_t) - H_{i,k}(\theta_0) \right) dt \, \left( \frac{1}{n} \sum_{j=1}^{n_i} e_{ij} \right) \left( \frac{1}{n} \sum_{j=1}^{n_i} e_{ij} \right) ^T \left( \frac{1}{n} \sum_{j=1}^{n_i} e_{ij} \right) \right| 
\]

\[
\leq \sum_{i=1}^{p} \frac{n_i}{n} \left| \int_0^1 \left( H_{i,k}(\theta_t) - H_{i,k}(\theta_0) \right) dt \right| \cdot \frac{1}{n_i} \sum_{j=1}^{n_i} \left| e_{ij} \right| .
\]

(3.46)

We now show that the integral \( \int_0^1 \left| H_{i,k}(\theta_t) - H_{i,k}(\theta_0) \right| dt \) converges to 0 by an application of the DCT. For the first component we have

\[
|H_{i,\tau\tau}(\theta_t) - H_{i,\tau\tau}(\theta_0)| = \frac{1}{2} \cdot \left| \frac{1}{\gamma_t} \{x_i - \tau_t \leq \gamma_t \} - \frac{1}{\gamma_0} \{x_i - \tau_0 \leq \gamma_0 \} \right|
\]

\[
\leq \frac{1}{2} \cdot \left( \frac{1}{\gamma_t} \{x_i - \tau_t \leq \gamma_t \} + \frac{1}{\gamma_0} \{x_i - \tau_0 \leq \gamma_0 \} \right) \leq \frac{1}{2} \cdot \left( \frac{1}{\gamma_t} + \frac{1}{\gamma_0} \right) .
\]

(3.47)

Taking into account that \( \gamma_t = \gamma_0 + t(\bar{\gamma}_n - \gamma_0), \ t \in [0,1] \) and \( \bar{\gamma}_n \overset{a.s.}{\rightarrow} \gamma_0 \), it follows that there is exist an \( n_0 \in \mathbb{N} \) and that for \( n \geq n_0 \)

\[
0 < \frac{\gamma_0}{2} \leq \gamma_t \leq \frac{3\gamma_0}{2}, \ \text{a.s. } \forall t \in [0,1].
\]

(3.48)

Then with (3.48) the upper bound of (3.47) is

\[
|H_{i,\tau\tau}(\theta_t) - H_{i,\tau\tau}(\theta_0)| \leq \frac{3}{2\gamma_0}.
\]

Similar calculation can be performed for other components

\[
|H_{i,\tau\gamma}(\theta_t) - H_{i,\tau\gamma}(\theta_0)| = \frac{1}{2\gamma_t} \left( \frac{x_i - \tau_t}{\gamma_t} \right) \{x_i - \tau_t \leq \gamma_t \} - \frac{1}{2\gamma_0} \left( \frac{x_i - \tau_0}{\gamma_0} \right) \{x_i - \tau_0 \leq \gamma_0 \} \leq \frac{3}{2\gamma_0},
\]

\[
|H_{i,\tau\gamma}(\theta_t) - H_{i,\tau\gamma}(\theta_0)| \leq \frac{1}{2} \left( \frac{x_i - \tau_t}{\gamma_t} \right)^2 \{x_i - \tau_t \leq \gamma_t \} - \frac{1}{2\gamma_0} \left( \frac{x_i - \tau_0}{\gamma_0} \right)^2 \{x_i - \tau_0 \leq \gamma_0 \} \leq \frac{3}{2\gamma_0}.
\]

(3.49)

By Theorem 3.1.1 the estimator \( \hat{\theta}_n \) is strongly consistent. Since each component of the matrix \( H_i(\theta) \) is a continuous function, an application of the Continuous Mapping Theorem yields

\[
H_{i,k}(\theta_t) \overset{a.s.}{\rightarrow} H_{i,k}(\theta_0)
\]

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consequently by the DCT $|Y_n - Z_n|$ defined as (3.46) converges in probability to 0. Therefore,

$$
\frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} c_{ij} \int_{0}^{1} H_{i,k}(\theta_i) dt \xrightarrow{P} 0.
$$

**Proof of (3.39).** For each component of the matrix $H_i(\theta_i)$

$$
\left| \frac{1}{n} \sum_{i=1}^{p} n_i \left( q_i(\theta_i) - q_i(\theta_0) \right) H_{i,k}(\theta_i) \right| \leq \frac{1}{n} \sum_{i=1}^{p} n_i \left( |q_i(\theta_i) H_{i,k}(\theta_i)| + |q_i(\theta_0) H_{i,k}(\theta_i)| \right). \tag{3.49}
$$

For the first component we obtain

$$
|q_i(\theta_i) H_{i,\tau\tau}(\theta_i)| = \left| \left( \frac{(x_i - \tau_{i} + \gamma_{i})^2}{4\gamma_{i}} \right) \mathbb{1}\{ |x_i - \tau_{i}| \leq \gamma_{i} \} + (x_i - \tau_{i}) \mathbb{1}\{ x_i > \tau_{i} + \gamma_{i} \} \right|.
$$

Similarly we obtain an upper bound for $|q_i(\theta_0) H_{i,k}(\theta_i)|$ from (3.49), that is

$$
|q_i(\theta_0) H_{i,\tau\tau}(\theta_i)| = \left| \left( \frac{(x_i - \tau_{i} + \gamma_{i})^2}{4\gamma_{i}} \right) \mathbb{1}\{ |x_i - \tau_{i}| \leq \gamma_{i} \} + (x_i - \tau_{i}) \mathbb{1}\{ x_i > \tau_{i} + \gamma_{i} \} \right|.
$$

Analogously, we have for other components

$$
|q_i(\theta_i) H_{i,\tau\gamma}(\theta_i)| = \left| \left( \frac{(x_i - \tau_{i} + \gamma_{i})^2}{4\gamma_{i}} \right) \mathbb{1}\{ |x_i - \tau_{i}| \leq \gamma_{i} \} + (x_i - \tau_{i}) \mathbb{1}\{ x_i > \tau_{i} + \gamma_{i} \} \right|.
$$

$$
|q_i(\theta_i) H_{i,\gamma\gamma}(\theta_i)| = \left| \left( \frac{(x_i - \tau_{i} + \gamma_{i})^2}{4\gamma_{i}} \right) \mathbb{1}\{ |x_i - \tau_{i}| \leq \gamma_{i} \} + (x_i - \tau_{i}) \mathbb{1}\{ x_i > \tau_{i} + \gamma_{i} \} \right|.
$$

$$
|q_i(\theta_0) H_{i,\tau\gamma}(\theta_i)| = \left| \left( \frac{(x_i - \tau_{i} + \gamma_{i})^2}{4\gamma_{i}} \right) \mathbb{1}\{ |x_i - \tau_{i}| \leq \gamma_{i} \} + (x_i - \tau_{i}) \mathbb{1}\{ x_i > \tau_{i} + \gamma_{i} \} \right|.
$$

Similarly we obtain an upper bound for $|q_i(\theta_0) H_{i,k}(\theta_i)|$ from (3.49), that is

$$
|q_i(\theta_0) H_{i,\tau\tau}(\theta_i)| = \left| \left( \frac{(x_i - \tau_{0} + \gamma_{0})^2}{4\gamma_{0}} \right) \mathbb{1}\{ |x_i - \tau_{0}| \leq \gamma_{0} \} + (x_i - \tau_{0}) \mathbb{1}\{ x_i > \tau_{0} + \gamma_{0} \} \right|.
$$

$$
\leq \frac{1}{2|\gamma_{i}|} \cdot \left( \frac{(x_i - \tau_{0} + \gamma_{0})^2}{4\gamma_{0}} \mathbb{1}\{ |x_i - \tau_{0}| \leq \gamma_{0} \} + (x_i - \tau_{0}) \mathbb{1}\{ x_i > \tau_{0} + \gamma_{0} \} \right) \leq \frac{1}{2|\gamma_{i}|} \cdot (\gamma_{0} + M),
$$

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Asymptotic theory for the bent-cable model under non-standard assumption

where $M < \infty$ is a finite positive constant defined such that $|x_i - \tau_0| \leq M$ according to the conditions [A1] of the design points. Taking into account (3.48) we have

$$|q_i(\theta_0) H_{i, \tau_\gamma}(\theta_i)| \leq 1 + \frac{M}{\gamma_0}$$

if $n$ is sufficiently large. Analogously, we have for other components

$$|q_i(\theta_0) H_{i, \gamma}(\theta_i)| = \left| \left( \frac{x_i - \tau_0 + \gamma_0}{4\gamma_0} \right)^2 \mathbb{1}\{|x_i - \tau_0| \leq \gamma_0\} + (x_i - \tau_0) \mathbb{1}\{x_i > \tau_0 + \gamma_0\} \right|$$

and

$$|q_i(\theta_0) H_{i, \gamma}(\theta_i)| = \left| \left( \frac{x_i - \tau_0 + \gamma_0}{4\gamma_0} \right)^2 \mathbb{1}\{|x_i - \tau_0| \leq \gamma_0\} + (x_i - \tau_0) \mathbb{1}\{x_i > \tau_0 + \gamma_0\} \right|$$

Taking into account (3.50)-(3.56) we obtain the upper bound of (3.49) for each $k$-th component

$$\left| \frac{1}{n} \sum_{i=1}^{p} n_i (q_i(\theta_i) - q_i(\theta_0)) H_{i,k}(\theta_i) \right| \leq \frac{1}{2} + 1 + \frac{M}{\gamma_0} = \frac{3}{2} + \frac{M}{\gamma_0}.$$

By Theorem 3.1.1 the estimator $\hat{\theta}_n$ is strongly consistent. Since $q_i(\theta)$ and each component of the matrix $H_{i,k}(\theta_0)$ are continuous functions, by an application of the Continuous Mapping Theorem $q_i(\theta_i) - q_i(\theta_0) \overset{a.s.}{\rightarrow} 0$ and $H_{i,k}(\theta_i) \overset{a.s.}{\rightarrow} H_{i,k}(\theta_0)$. Therefore

$$\lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{p} n_i (q_i(\theta_i) - q_i(\theta_0)) H_{i,k}(\theta_i) = 0$$

and by the DCT

$$\int_0^1 \frac{1}{n} \sum_{i=1}^{p} n_i (q_i(\theta_i) - q_i(\theta_0)) \mathcal{H}_i(\theta_i) dt \overset{a.s.}{\rightarrow} 0.$$
3.1.3 Proof of Lemma 3.1.2.

With the notations $Z_n = (\hat{\tau}_n + \hat{\gamma}_n) - (\gamma_0 + \tau_0)$ we have $Z_n \overset{a.s.}{\rightarrow} 0$. Define $F_n = 1\{x_i > \tau_0 + \gamma_0 + t \cdot Z_n\}$.

Denote by $(Z^+_n)_{n \in \mathbb{N}}$ and $(Z^-_n)_{n \in \mathbb{N}}$ the subsequences of $(Z_n)_{n \in \mathbb{N}}$ with $Z_n \geq 0$ and $Z_n < 0$ respectively and define

$$F^+_n = 1\{x_i > \tau_0 + \gamma_0 + t \cdot Z^+_n\}, \quad F^-_n = 1\{x_i > \tau_0 + \gamma_0 + t \cdot Z^-_n\}.$$  

If $\tau_0 - \gamma_0 < x_i < \tau_0 + \gamma_0$ then $F^+_n = 0$ and there exists an $n_1 \in \mathbb{N}$ such that for all $n \geq n_1$, $x_i < \tau_0 + \gamma_0 + t \cdot Z^-_n$. This implies for all $n \geq n_1$ that $F^-_n = 0$ which means that for $t \in [0, 1]$ $F_n \overset{a.s.}{\rightarrow} 0$. On the other hand, if $x_i > \tau_0 + \gamma_0$ then $F^-_n = 1$ and there exists an $n_0 \in \mathbb{N}$ and that for all $n \geq n_0$, $x_i > \tau_0 + \gamma_0 + t \cdot Z^+_n$ which yields $F^+_n = 1$, and consequently $F_n \overset{a.s.}{\rightarrow} 1$ in this case. Combining these arguments yields the first assertion of Lemma 3.1.2. For the proof of (3.44) we introduce the representation

$$V_n = 1\{|x_i - \tau_i| \leq \gamma_i\} = 1\{\tau_0 - \gamma_0 + t \cdot Z_{1,n} \leq x_i \leq \tau_0 + \gamma_0 + t \cdot Z_{2,n}\},$$

where $Z_{1,n} = (\hat{\tau}_n - \hat{\gamma}_n) - (\gamma_0 - \tau_0) \overset{a.s.}{\rightarrow} 0$ and $Z_{2,n} = (\hat{\tau}_n + \hat{\gamma}_n) - (\gamma_0 + \tau_0) \overset{a.s.}{\rightarrow} 0$.

Note that

$$V_n = V^L_n \cdot V^R_n, \quad (3.57)$$

where $V^L_n = 1\{\tau_0 - \gamma_0 + t \cdot Z_{1,n} \leq x_i\}$ and $V^R_n = 1\{x_i \leq \tau_0 + \gamma_0 + t \cdot Z_{2,n}\}$. We will now discuss these two terms separately and then combine the results.

For the investigation of the term $V^L_n$ let $(Z^+_{1,n})_{n \in \mathbb{N}}$ and $(Z^-_{1,n})_{n \in \mathbb{N}}$ denote the subsequences of $(Z_{1,n})_{n \in \mathbb{N}}$ with $Z_{1,n} \geq 0$ and $Z_{1,n} < 0$ respectively and define

$$V^{L+}_n = 1\{x_i \geq \tau_0 - \gamma_0 + t \cdot Z^+_{1,n}\}, \quad V^{L-}_n = 1\{x_i \geq \tau_0 - \gamma_0 + t \cdot Z^-_{1,n}\}.$$  

If $\tau_0 - \gamma_0 < x_i < \tau_0 + \gamma_0$ then $V^{L-}_n = 1$ and there exists $n_2 \in \mathbb{N}$ such that for all $n \geq n_2$, $x_i > \tau_0 - \gamma_0 + t \cdot Z^+_{1,n}$. This implies for all $n \geq n_2$ that $V^{L+}_n = 1$ which means for all $t \in [0, 1]$ $V^L_n \overset{a.s.}{\rightarrow} 1$. On the other hand, if $x_i > \tau_0 + \gamma_0$ then $V^{L+}_n = 1$ and $V^{L-}_n = 1$ which mean for all $t \in [0, 1]$ $V^L_n \overset{a.s.}{\rightarrow} 1$. Combining these arguments yields that $V^L_n \overset{a.s.}{\rightarrow} 1\{\tau_0 - \gamma_0 < x_i\}$. Similarly we can show that $V^R_n \overset{a.s.}{\rightarrow} 1\{x_i < \tau_0 + \gamma_0\}$.

Combining the results for $V^L_n$, $V^R_n$ for the sequence $V_n$ defined in (3.57), we obtain

$$V_n = V^L_n \cdot V^R_n \overset{a.s.}{\rightarrow} 1\{\tau_0 - \gamma_0 < x_i < \tau_0 + \gamma_0\},$$

which implies the second assertion of the Lemma 3.1.2.

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3.2 Full bent-cable model

In this section we present results for the full bent-cable model defined in (2.16) as
\[
f(x, \theta) = \beta_0 + \beta_1 x + \beta_2 q(x; \tau, \gamma),
\]
where \( x \) is a covariate, \( q(x; \tau, \gamma) \) is the basic bent-cable model (3.1) and \( \theta = (\beta_0, \beta_1, \beta_2, \tau, \gamma) \) is the vector of unknown model parameters. The parameter space is defined as
\[
\Theta = [-M_1, M_1] \times \mathbb{R} \times [-M_3, -\epsilon_3] \cup [\epsilon_3, M_3] \times [-M_4, M_4] \times [0, \infty),
\]
where \( M_1, M_3, M_4 \) are some large positive but finite upper bounds for the candidate values of the parameters \( \beta_0, \beta_2 \) and \( \tau \) respectively, \( \epsilon_3 > 0 \) is a small positive value [Chiu (2002)]. The full bent-cable model is presented in Figure 3.2 below.

![Figure 3.2: The full bent-cable model (2.16).](image)

We consider the observations \( \{x_i, y_{ij}\} \) satisfying assumptions \([A2]\) and generated by a full bent-cable regression model
\[
y_{ij} = f(x_i, \theta_0) + \epsilon_{ij}, i = 1, \ldots, p, j = 1, \ldots, n_i,
\]
where \( \theta_0 = (\beta_{0,0}, \beta_{1,0}, \beta_{2,0}, \tau_0, \gamma_0) \in \Theta \) is the underlying vector of regression parameters and \( \epsilon_{ij} \) are independently distributed random variables with mean \( \mathbb{E}(\epsilon_{ij}) = 0 \) and unknown variance \( \text{Var}(\epsilon_{ij}) = \sigma_i^2 < \infty, i = 1, \ldots, p \) satisfying the assumption \([A0]\) defined in (3.4).

The least-squares estimator of \( \theta \) based on data \( \{x_i, y_{ij}\}, i = 1, \ldots, p, j = 1, \ldots, n_i \) is defined to be any vector \( \hat{\theta}_n \in \Theta \) which minimizes
\[
Q_n(\theta) = \frac{1}{n} \sum_{i=1}^{p} \sum_{j=1}^{n_i} \left( y_{ij} - f(x_i, \theta) \right)^2.
\]

It can be shown in the same way as for the basic bent-cable model that under the assumptions \([A0], [A2]\) the least-squares estimate \( \hat{\theta}_n \) is a strongly consistent estimator of \( \theta_0 \) and
asymptotically follows a multivariate normal distribution. The proofs are omitted for the sake of brevity.

The asymptotic theory for least-squares estimates of the model parameters of the full bent-cable model (3.58) can be extended from the results obtained in previous section for the regression problem with the basic bent-cable model. Here the assumption on the error distribution $\mathcal{A}_0$ is exactly the same as for the basic bent-cable model. However, we have to consider slightly different conditions on the design points $x_i, i = 1, ..., p$.

**Assumption [42] (design points)**

The different experimental conditions $x_1, ..., x_n$ satisfy $x_1, ..., x_{p_1} \in (-\infty, \tau_0 - \gamma_0)$, $x_{p_1+1}, ..., x_{p_2} \in (\tau_0 - \gamma_0, \tau_0 + \gamma_0)$ and $x_{p_2+1}, ..., x_p \in (\tau_0 + \gamma_0, \infty)$ and the sample sizes $n_1, ..., n_p$ at these points satisfy

$$n = \sum_{i=1}^{p} n_i \quad \text{and} \quad \frac{n_i}{n} \to \xi_i > 0,$$

where $n$ is a total number of observations and $p_1 \geq 2, p - p_2 \geq 2$.

The full bent-cable model (3.58) contains five parameters $\beta_0, \beta_1, \beta_2, \tau, \gamma$ to be estimated from the data $\{x_i, y_{ij}\}, i = 1, ..., p, j = 1, ..., n_i$. Therefore, in this case the minimum number of observation $n_{\min} = 5$. Moreover, we consider \{2-1-2\}-configuration of the design space which means that it requires at least two distinct observations for the incoming and outgoing linear segments and at least one observation from the smooth quadratic region. For more details see [Chiu (2002)].

### 3.2.1 Consistency

The asymptotic results on the consistency of the least-squares estimator of the parameter vector of the full bent-cable model (3.58) are presented in the similar manner as the results for the basic bent-cable model. First, the Identifiability Lemma 3.2.1 is formulated and then the consistency results are reported in form of the Theorem 3.2.1.

**Lemma 3.2.1** (Identifiability) Given five points $(x_i, y_i)_{i=1}^5$ such that

$$x_1, x_2 \in (-\infty, \tau_0 - \gamma_0), \quad x_3 \in (\tau_0 - \gamma_0, \tau_0 + \gamma_0), \quad x_4, x_5 \in (\tau_0 + \gamma_0, \infty),$$

$$y_i = f_i(\theta_0) \quad \forall i = 1, ..., 5.$$

If for some parameter $\theta$ the conditions

$$f_i(\theta) = y_i, \quad \forall i = 1, ..., 5$$

are satisfied, then $\theta = \theta_0$.

**Theorem 3.2.1** (Consistency) Under conditions $[A0]$ and $[A2]$, the least-squares estimator of the model (3.58) with $\gamma_0 > 0$ is strongly consistent, that is

$$\hat{\theta}_n \overset{a.s.}{\to} \theta_0, \text{ as } n \to \infty.$$
3.2.2 Asymptotic normality

To formulate the asymptotic normality theorem for the least-squares estimates in the full bent-cable model, we introduce following notations

Vector of partial derivatives of the model (3.58) with respect to the parameters

\[
\nabla f_i(\theta) = \begin{pmatrix}
\frac{\partial f_i(\theta)}{\partial \beta_0} & \frac{\partial f_i(\theta)}{\partial \beta_1} & \frac{\partial f_i(\theta)}{\partial \beta_2} & \frac{\partial f_i(\theta)}{\partial \tau} & \frac{\partial f_i(\theta)}{\partial \gamma}
\end{pmatrix}^T
\]

(3.62)

where \( \alpha_{1i}(\theta), \alpha_{2i}(\theta), \alpha_{3i}(\theta) \) are defined in (3.8) and \( q(x; \tau, \gamma) \) is the basic bent-cable model defined in (3.1).

Matrix \( A(\theta) \) can be calculated using the relationship

\[
A(\theta) = \sum_{i=1}^{p} \xi_i \cdot \nabla f_i(\theta) \nabla f_i^T(\theta),
\]

(3.63)

where \( \xi_i \) is defined as [3.59].

**Theorem 3.2.2 (Asymptotic normality)** Under conditions \([A0]\) and \([A2]\), we have

\[
\sqrt{n}(\hat{\theta}_n - \theta_0) \xrightarrow{D} N(0, A^{-1}(\theta_0) \sum_{i=1}^{p} \xi_i \sigma_i^2 \nabla f_i(\theta_0) \nabla f_i^T(\theta_0) A^{-1}(\theta_0)),
\]

where \( \nabla f_i(\theta) \) and \( A(\theta) \) are defined in (3.62) and (3.63) respectively.
Modeling of thermophysical properties: theory and application

One of the key tools for the modeling of thermophysical material properties is the CALPHAD method which is used to calculate phase diagrams from modeled Gibbs energies of the different phases as functions of temperature, composition, and pressure. The knowledge of phase diagrams and thermodynamic properties of multicomponent alloys is important for the understanding of processes taking place in complex materials. Therefore, robust models of the Gibbs energy are required for the correct prediction of phases and reliable modeling of multicomponent and multiphase materials.

An attempt to improve the description of the temperature dependence of the Gibbs energy, $G(T)$, of the stable phases of solids that covers the temperature range from 0 Kelvin up to the melting point, $T_m$, is presented in this chapter which organized as following. First, a definition of phase diagram is given together with two examples of binary and ternary systems. Then, a short introduction into the CALPHAD method and its main components is presented. For more details see, for example, [Saunders and Miodownik (1998)] or [Lukas et al. (2007)]. The remaining part of this chapter is devoted to the extension of CALPHAD methodology to the low temperatures by a newly proposed physically-based segmented model and its application to pure Cr, Al and Fe. The materials and results presented in Sections 4.3-4.5 have been recently published in [Roslyakova et al. (2016a)].

4.1 Phase diagram

Phase diagrams are visual representation of the state of a material as a function of two or more variables like temperature, pressure or concentrations of the components.
Phase diagrams are used in many industrial applications as a very powerful tool for predicting the state of the system under different conditions, alloy design, development of new materials, processing and teaching.

The state of a two-component material at constant pressure can be presented in the well-known graphical form of binary phase diagrams. As an example, the Fe-Cr binary phase diagram obtained by Xiong et al. (2011) is presented in Figure 4.1 in comparison to one of the previous thermodynamic assessment of this binary system performed by Andersson and Sundman (1987). Both phase diagrams contain four phases: liquid, bcc, fcc and \(\sigma\)-phase. Between the single phase regions there are regions with two stable phases. The horizontal line represents a three phase equilibrium at constant temperature. However, the four phases presented on both phase diagrams of Fe-Cr binary systems appear at slightly different composition and temperature ranges. Mathematical models of the Gibbs energy and experimental data considered in thermodynamic assessments are two main reasons for these differences. Therefore, any thermodynamic assessment of a multicomponent system is started with the selection of key experiments and a mathematical model for the Gibbs energy function. Both these components are essential for a successful and robust thermodynamic modeling.

![Figure 4.1: Phase diagrams of Fe-Cr obtained by Andersson and Sundman (1987) (red dotted lines) and Xiong et al. (2011) (black solid lines) Xiong (2012).](image)

The phase diagram of the three component system is usually presented as series of sections or projections. Examples of a ternary phase diagrams at temperatures 1073K and 973K are presented in Figure 4.2. It is very challenging task to provide a useful graphical representation for the phase diagram with more than three components. An additional difficulty is the lack of experimental information available for the higher order systems. However, the problems with graphical representation for the systems with many components can be handled by software for the calculation of phase diagrams, for example, PANDAT Cao et al. (2009) or ThermoCalc Andersson et al. (2002).
4.2 Introduction to CALPHAD Method

The reason to model the Gibbs energy and not any other thermodynamic function is that most experimental data are obtained at known temperature and pressure. Furthermore, all other thermodynamic properties can be derived from the Gibbs energy.\cite{Lukas2007}

\begin{align*}
\text{Gibbs energy} \\
\quad G &= G(T,p,N_i), \\
\text{Helmholtz energy} \\
\quad A &= G - pV, \\
\text{Entropy} \\
\quad S &= -\left(\frac{\partial G_m}{\partial T}\right)_{p,N_i}, \\
\text{Enthalpy} \\
\quad H &= G + TS = G - T\left(\frac{\partial G_m}{\partial T}\right)_{p,N_i}, \\
\text{Volume} \\
\quad V &= \left(\frac{\partial G}{\partial p}\right)_{T,N_i}, \\
\text{Heat capacity} \\
\quad C_p &= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N_i}, \\
\text{Chemical potential of component } i \\
\quad \mu_i &= \left(\frac{\partial G}{\partial N_i}\right)_{T,N_i,p,j,p}, \\
\text{Thermal expansion} \\
\quad \alpha &= \frac{1}{V}\left(\frac{\partial^2 G}{\partial p\partial T}\right)_{N_i}, \\
\text{Isothermal compressibility} \\
\quad k &= -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N_i}, \\
\text{Bulk modulus} \\
\quad B &= \frac{1}{k},
\end{align*}

where $T$ is the temperature in Kelvin, $p$ is the pressure in Pascal, $N_i$ is the number of type $i$ particles in mole.
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The CALPHAD method is a semi-empirical technique for calculation of phase diagrams based on evaluation of experimental data and theoretical estimates related to the thermodynamic properties of the materials. The basic principle behind the CALPHAD approach is a modeling "from bottom to top" and it can be graphically illustrated as so-called "inverse pyramid" presented in Figure 4.3.

![Figure 4.3: Inverse pyramid of the CALPHAD method.](image)

Accurate description of pure elements forms the basis for consistent estimation of parameters for phase models of binary systems. A ternary system can be calculated based on available knowledge of binary and unary systems, and a few estimated ternary parameters. For system with more than three components the CALPHAD method relies on the estimation of the basic ternary systems. This principle stands behind different type of solution model which will be highlighted in detail below [Kattner (1997)].

The traditional thermodynamic optimization technique based on the CALPHAD method consists of following main steps [Balakumar (2008)]:

**Step 1:** Investigation of selected system starts with a literature survey and collection of all experimental information on phase equilibria of a system. The different types of experimental data include both thermochemical and thermophysical studies and phase diagram data.

**Step 2:** At the next step, a mathematical model for Gibbs energy of each phase for the system should be selected. These models could be either polynomials [Dinsdale (1991)] or related to the crystal structure [Chase et al. (1995), Chen and Sundman (2001), Roslyakova et al. (2016a)]. Selection of the phase model generally depends on the knowledge and experience of the researcher and the application. The phase models usually contain parameters which have to be estimated based on the collected experimental information.

**Step 3:** The model of the Gibbs energy and corresponding parameters are estimated by a non-linear least-squares method. The least-squares estimates of model parameters provide the best match between collected experiments and the calculated quantities with respect to quadratic loss function. There are several optimization tools available for calculation based on CALPHAD method, for example, BINGSS [Lukas et al. (1977), Lukas and Fries (1992)], PARROT [Jansson (1984)], TERGSS [Lukas and Fries (1992)].
Step 4: Now it is possible to calculate the phase diagram of studied system and all thermodynamic properties of all phases. Often several runs of the optimization are necessary to give different weights to the available data and provide an estimation of extrapolations to metastable regions. Successfully accessed thermodynamic systems can be stored in thermodynamical databases. These databases contain critically assessed unary, binary and ternary and sometimes high-order systems with thermochemical model parameters for studied elements, species, and phases in their stable and metastable states from room temperature, 298.15K, up to their liquid and gaseous state. The main purposes of performing CALPHAD optimization is the creation of multicomponent thermodynamic databases for industrial applications. Today many different types of databases are available depending on the application, for example, pure element database [Dinsdale (1991)] or light metal alloys database [Ansara et al. (1998)].

Only the main steps in CALPHAD method are described above, but in reality the thermodynamic optimization is a quite complicated and iterative process, because the experimental data are incomplete and scattered. For more details see [Lukas et al. (2007)].

During thermodynamic assessment, the selection of phase models for all phases that may exist in the selected system is one of the critical factors for the success of the CALPHAD method. Therefore, a review of available models of phases with fixed and variable composition is given in next section.

4.2.1 Models of phases with fixed composition

Models of phases with fixed composition are used for the description of pure elements or stoichiometric compounds and they depend only on temperature and pressure.

It is not possible to do any kind of measurements on the Gibbs energy directly and thus such phases are modeled in terms of their heat capacity and the heat of formation. The reason for the use of the heat capacity for the modeling of phases with fixed composition is that it is the most sensitive property and can be measured experimentally for the stable phases. Generally, the model for temperature dependence of the heat capacity is based on a polynomial description proposed by Maier and Kelley (1932) of the form

\[ C_p(T) = a + bT + cT^{-2} + dT^2 + \ldots \] (4.1)

The Gibbs energy function can be derived from equation (4.1) by using the Gibbs-Helmholtz equation

\[ G(T) = H(T) - T \cdot S(T), \] (4.2)

where \( H(T) \) and \( S(T) \) are the enthalpy of formation and the entropy respectively, which are related to the heat capacity by two well-known identities given by

\[ H(T) = H_{298} + \int_{298}^{T} C_p(T) dT, \quad S(T) = S_{298} + \int_{298}^{T} \frac{C_p(T)}{T} dT. \] (4.3)
Here $H^{298}$ and $S^{298}$ are the standard enthalpy and entropy of the substance respectively at 298.15K. By substituting equations (4.3) in (4.2) using the polynomial description of the heat capacity (4.1), we obtain the following form of the Gibbs energy for a phase with fixed composition

$$G(T) = A + BT + CT \ln(T) + DT^2 + ET^{-1} + FT^3 + ..., \quad (4.4)$$

where coefficients $C$, $D$ etc. can be derived from the coefficients $a$, $b$ etc. in equation (4.1). The constants $A$ and $B$ are determined from $H^{298}$ and $S^{298}$.

The Gibbs energy model presented by equation (4.4) is valid only for phases with fixed composition and when pressure dependence and magnetic contributions are not considered.

The magnetic contribution of the Gibbs energy is described by

$$G^{\text{magn}}(T) = RT \cdot g(\tau) \ln(\beta + 1), \quad (4.5)$$

where $R = 8.314$, $J/(\text{mol} \cdot \text{K})$ is the gas constant, $\tau = T/T^*$, $T^*$ is the Curie temperature $T_C$ for ferromagnetic materials or the Neel temperature $T_N$ for antiferromagnetic materials, and $\beta$ is the average magnetic moment per atom. The function, $g(\tau)$ is based on the model for the heat capacity proposed by Inden (1976), which has been modified by Hillert and Jarl (1978) and it is defined as

$$g(\tau) = \begin{cases} 
1 - \frac{1}{A} \left[ \frac{79r^{-1}}{140p} + \frac{424}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{r^3}{6} + \frac{r^5}{135} + \frac{r^{15}}{600} \right) \right], & \tau \leq 1, \\
-\frac{1}{A} \left( \frac{1}{10} \tau^{-5} + \frac{1}{315} \tau^{-15} + \frac{1}{1500} \tau^{-25} \right), & \tau > 1,
\end{cases} \quad (4.6)$$

where $A$ is given by

$$A = 0.46044444 + 0.73189358 \left( \frac{1}{p} - 1 \right) \quad (4.7)$$

and $p$ is the structure factor, which is the ratio of the magnetic enthalpy in the paramagnetic state to the total magnetic enthalpy. For the body-central cubic (bcc) structure, the accepted value is $p = 0.4$, while for the face-centered cubic (fcc) and hexagonal closed-packed (hcp) structure $p = 0.28$ is used.

The magnetic contribution to the other thermodynamic properties can be described in similar way. For example, the heat capacity according to the Inden-Hillert-Jahr model is defined by following equation

$$C^{\text{magn}}_p(T) = RT \cdot g(\tau) \ln(\beta + 1), \quad (4.8)$$

$$g(\tau) = \begin{cases} 
\frac{1}{A} \left[ \frac{424}{497} \left( \frac{1}{p} - 1 \right) \left( 2\tau^3 + \frac{2\tau^5}{3} + \frac{3\tau^{15}}{5} \right) \right], & \tau \leq 1, \\
\frac{1}{A} \left( 2\tau^{-5} + \frac{2\tau^{-15}}{3} + \frac{2\tau^{-25}}{5} \right), & \tau > 1,
\end{cases} \quad (4.9)$$

where $A$ is defined above by (4.7).

The Inden-Hillert-Jahr model (4.5)-(4.7) is currently used for description of magnetic contribution within CALPHAD databases [Dinsdale (1991)]. Dinsdale established SGTE
Pressure dependence of the Gibbs energy

In order to include a pressure contribution to the Gibbs energy, the model for condensed phases proposed by Murnaghan (1944) can be used for pressures up to 20GPa:

\[
G_{\text{pressure}} = V^0 \exp \left( \int_{298}^{T} \alpha(T) dT \right) \frac{[1 + n \cdot k(T)P]^{1-\frac{1}{n}} - 1}{(n - 1)k(T)},
\]

where \(V^0\) is the molar volume at room temperature, \(\alpha(T)\) is the thermal expansion, \(k(T)\) is the compressibility at 1 bar, and \(n\) is the pressure derivative of the bulk modules \(B = 1/k(T)\).

The thermal expansion, \(\alpha(T)\), and compressibility, \(k(T)\), depend on the temperature as

\[
\alpha(T) = A_0 + A_1T + A_2T^2 + A_3T^{-2},
\]

\[
k(T) = K_0 + K_1T + K_3T^2.
\]

4.2.2 Models of phases with variable composition

In a phase with variable composition mixing of the various components takes place. Such a phase is also called a "solution" phase. The Gibbs energy of a solution phase, \(\phi\) can be divided into three parts as:

\[
G^\phi = G^{ref} + G^{ideal} + G^{excess}.
\]

The first term of equation (4.10), \(G^{ref}\) is the Gibbs energy arising from contribution of the pure components to the phase defined as

\[
G^{ref} = \sum_i x_i^0 G_i^\phi,
\]

where \(x_i\) is the mole fraction of component \(i\) and \(^0G_i^\phi\) represents standard molar Gibbs energy of component \(i\) in the phase \(\phi\).

The second term \(G^{ideal} = RT \sum_i x_i \ln(x_i)\) is called the ideal mixing term and describes the solution properties by assuming random mixing of atoms, where \(T\) is the temperature and \(R\) is the gas constant.

The third term in equation (4.10), describes the deviation of solution properties from ideal mixing by a mathematical model which for a binary system is based on the Redlich-Kister polynomial description given by Redlich and Kister (1948) in the form

\[
G^{excess} = \sum_i \sum_{j \neq i} x_i x_j \sum_\nu L_{ij}^{\nu=0} (x_i - x_j)^\nu,
\]

where \(L_{ij}^\nu\) is the Redlich-Kister binary interaction parameter for different integer powers of \(\nu\). This parameter is usually described by a linear function of temperature

\[
L_{ij}^\nu = a_{ij}^\nu + b_{ij}^\nu T.
\]
Equation (4.11) considers the Gibbs energy of a multicomponent solution phase to be a product of the summarized binary interactions and \( L'_{ij} \) is an optimized interaction parameter. In real applications, the values of \( \nu \) are usually not larger than 3. One of the advantages of the excess term of the Gibbs energy in form of Redlich-Kister polynomials is that these models can be easily extended to multicomponent systems without changing the shape of the excess Gibbs energy of the binary system in the multicomponent system [Kattner (1997)].

Additionally, excess parameters can be added in ternary systems. The non-ideal solution model with excess term described by equation (4.11) is extensively used in metallic systems for substitutional phases such as liquid, bcc, fcc. More complex models including chemical ordering, interstitial solutions and intermetallics are described in [Lukas et al. (2007)].

### 4.3 Low temperature CALPHAD

Currently in CALPHAD applications the temperature dependence of the heat capacity is described by high-order polynomials (4.1) with adjustable parameters fitted to experimental data. This approach to fit coefficients has been proposed by Dinsdale (1991) to cover high temperatures above 298.15K and should not be used to describe any low temperature data. The effort to extend that description to low temperatures demands more physical modeling which takes into account the available experiments and theoretical data.

The CALPHAD community discussed this problem during a Ringberg Workshop’1995 and proposed a “universal” model to describe the thermodynamic properties over the whole temperature range down to 0K [Chase et al. (1995)]. This model considers several physical effects of the heat capacity. Such modeling approach should improve the present thermodynamic models of pure elements and the predictive capability of the CALPHAD method.

An attempt in this direction was performed by Chen and Sundman (2001) applied to bcc, fcc, liquid and amorphous phases for the pure Fe. The more recent work in development of physical-sounded models for the crystalline phase of pure elements was performed during a Ringberg Workshop’2013 by Palumbo et al. (2014).

Despite of an improvement in the description of the temperature dependencies of the experimental heat capacity data by the models proposed in [Chase et al. (1995), Chen and Sundman (2001)], the low temperature range from 298K down to 0K is still an issue. Both these models are based on combination of the Einstein function and several different power terms, the low temperature regime could not be described precisely enough. Therefore, following the ideas from [Chase et al. (1995), Chen and Sundman (2001) and Palumbo et al. (2014)] a new model for the heat capacity of pure elements is proposed in this thesis and it has been recently published in [Roslyakova et al. (2016a)]. The proposed model considers several physical effects in the heat capacity and it based on the combination of the Debye model with a segmented function. Applying such a modeling approach, a better agreement with the experimental data below 298K down to 0K has been reached.
4.3.1 The heat capacity of pure elements

The heat capacity is a fundamental state property and describes the amount of energy needed to increase the temperature of a known quantity of material by 1 K. The heat capacity is usually measured in J/(mole K). Various physical contributions of the heat capacity are presented in Figure 4.4. Overview of these physical effects is given in [Grimvall (1986)].

Figure 4.4: Physical contributions of the heat capacity: A - electronic heat capacity, B - phonon contribution, C - harmonic vibrational phonon contribution, D - $C_P - C_V$ contribution, E - explicit anharmonic contribution to $C_V$, F - electronic contribution, G - correction factor, H - vacancies formation, M - magnetic heat capacity.

From a mathematical point of view we are interested in the analytical form of the functions which can be used to describe temperature dependence of each physical effect drawn in Figure 4.4 and the range where this effect could appear. Therefore, according to the review given in [Grimvall (1986)], three different types of the mathematical functions can be applied for the modeling of the various contributions to the heat capacity.

The main part of the heat capacity can be explained by phonon contributions (B) and the harmonic vibrational phonon contribution (C). Such effects can be described using the Debye (4.12) or the Einstein model (4.13) and with increase of the temperature asymptotically will reach value of $3R$ according to the Dulong-Petit law (see Figure 4.5).

\[
C_P^{Deb}(T, \theta_D) = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4e^x}{(e^x-1)^2} dx,
\]

(4.12)

\[
C_P^{Ein}(T, \theta_E) = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2},
\]

(4.13)

where $\theta_D$ and $\theta_E$ are the Debye and Einstein temperatures respectively.
Figure 4.5: Debye vs. Einstein. Predicted heat capacity as a function of temperature.

The Debye model (4.12) reproduces the correct temperature dependence proportional to \( T^3 \) at very low temperatures, but it has more complicated mathematical form and should be approximated by some series expansion [Guseinov and Mamedov (2007), Dubinov and Dubinova (2008)]. In contrast to the Debye model (4.12), the Einstein model (4.13) can be easily implemented in thermodynamic databases, but it does not deliver such an accurate description at the low temperatures (see Figure 4.5). To plot the Debye and Einstein models of the same set of axes, the relationship \( \theta_E \approx 0.714 \theta_D \) has been used [Chen and Sundman (2001)].

The contributions to the heat capacity, (A), (D), (E), (F), and (G), presented in Figure 4.4 can be modeled using a linear function depending on the temperature. Two of these contributions (A) and (F) describe the effect of the electronic heat capacity at low and high temperatures correspondingly. Therefore, the linear function used for the description of the electronic heat capacity at low temperatures cannot be applied for the modeling of the high temperature range.

The magnetic contribution (M) to the heat capacity should be considered for elements with magnetic ordering as, for example, Iron or Nickel. This physical effect is currently described by the model (4.8) [Hillert and Jarl (1978)]. A more accurate approximation for the magnetic heat capacity has been proposed by Chen and Sundman (2001) and its further improvement by Xiong et al. (2012),

\[
C_P^{\text{magn}}(T) = RT \cdot g(\tau) \ln(\beta + 1),
\]

\[
g(\tau) = \begin{cases} 
  \frac{0.63570895}{A} (\frac{1}{p} - 1) \bigg( 2\tau^3 + 2\tau^2 + 2\tau + 2\tau^5 \bigg), & \tau \leq 1, \\
  \frac{1}{A} \bigg( 2\tau^{-7} + 2\tau^{-21} + 2\tau^{-35} + 2\tau^{-49} \bigg), & \tau \geq 1,
\end{cases}
\]
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where

\[ A = 0.33471979 + 0.49649686 \left( \frac{1}{p} - 1 \right). \]  \hspace{1cm} (4.16)

Here the parameters \( \tau \), \( \beta \) and \( p \) have been already defined above in Section 4.2.1. Chen and Sundman (2001) re-optimized the structure parameter \( p \) for the bcc phase and set its value to 0.37.

### 4.3.2 Model proposed during Ringberg Workshop’1995

The main idea behind the model proposed during a Ringberg Workshop in 1995, in the following abbreviation "RW", is based on consideration of physical contributions to the heat capacity which were shortly described above. The RW model is defined as

\[ C_{P}^{RW}(T, \theta_{RW}) = C_{P}^{Deb/Ein}(T) + aT + bT^2 + C_{P}^{magn}(T), \]  \hspace{1cm} (4.17)

where \( T \) is the temperature, \( \theta_{RW} = (\theta_{D}/\theta_{E}, a, b) \) is the vector of the unknown model parameters to be estimated, \( C_{P}^{Deb/Ein}(T) \) is the heat capacity describing phonon contribution using Debye (4.12) or Einstein model (4.13), \( C_{P}^{magn}(T) \) is the magnetic contribution of the heat capacity. The parameters \( \theta_{D} \) (or \( \theta_{E} \)), \( a \) and \( b \) are physically motivated.

The first term \( C_{P}^{Deb/Ein}(T) \) in the proposed model (4.17) is used to model the contribution from harmonic vibrations. There was no concrete recommendation whether the Debye or Einstein model should be used. The second \( aT \) term in (4.17) is related to electronic excitations and low order anharmonic corrections. The third term \( bT^2 \) contains the next order anharmonic corrections. The last term in equation (4.17), \( C_{P}^{magn}(T) \), considers the contribution from magnetic ordering.

The model (4.17) was applied to five pure elements Ag, Cu, Mo, Ti, Sn and one compound CaCl\(_2\) and its application showed significant improvement of prediction quality at low temperatures [Chase et al. (1995)].

### 4.3.3 Chen-Sundman model

Chen and Sundman (2001) applied a modeling concept proposed by Chase et al. (1995) to the lattice stability of pure Fe based on the Einstein model, in the following abbreviation "CS", and described \( C_{P} \) of the bcc phase at low temperatures by further modification of (4.17) into

\[ C_{P}^{CS}(T, \theta^{CS}) = C_{P}^{Ein}(T, \theta_{E}) + aT + bT^4 + C_{P}^{magn}(T), \]  \hspace{1cm} (4.18)

where \( \theta^{CS} = (\theta_{E}, a, b) \) is the vector of the unknown model parameters to be estimated and \( C_{P}^{magn}(T) \) is the magnetic contribution to the heat capacity modeled by (4.14)-(4.16). They found that the 4th power of the third term would make it easier to fit the high temperature experimental data of the heat capacity for the pure Fe.
The first attempt to improve the thermodynamic description of a binary system by adoption of the Chen-Sundman model \((4.18)\) has been performed by Xiong et al. (2011) and binary Fr-Cr phase diagram has been calculated down to 0K. The most recent application of Chen-Sundman model \((4.18)\) are the calculated Fe-C binary system [Naraghi et al. (2014)], pure Mn and Fe [Bigdeli et al. (2015), Bigdeli et al. (2016)], and pure Co [Li et al. (2016)].

### 4.3.4 Segmented regression model for the heat capacity of pure elements

Following recommendations of the Ringberg Workshop’1995 [Chase et al. (1995)] and results of the work performed by Chen and Sundman (2001), a new model, in the following abbreviation "SR", is proposed here for describing temperature dependence of the heat capacity of the pure elements, which considers relevant physical effects. Since these contributions appear in different temperature ranges and can be described by different functions, the segmented regression methodology described in Section 2 was applied to develop a mathematical model. The proposed model for the temperature dependence of the heat capacity for pure elements consists of three terms

\[
C_{P}^{SR}(T, \theta^{SR}) = C_{P}^{Deb/Ein}(T) + C_{P}^{bcm}(T; \beta_1, \beta_2, \tau, \gamma) + C_{P}^{mag}(T),
\]

(4.19)

where the first term \(C_{P}^{Deb/Ein}(T)\) is described by \((4.12)\) or \((4.13)\), \(\theta^{SR} = (\theta_D \text{ or } \theta_E, \beta_1, \beta_2, \tau, \gamma)\) is the vector of the unknown parameters to be estimated. The second term \(C_{P}^{bcm}(T; \beta_1, \beta_2, \tau, \gamma)\) is used for the decomposition of physical effects described by linear functions at low and high temperatures. For this purpose we used the full bent-cable model defined in \((2.16)\) with parameter \(\beta_0 = 0\) of the form

\[
C_{P}^{bcm}(T; \beta_1, \beta_2, \tau, \gamma) = \beta_1 T + \beta_2 \cdot q(T; \tau, \gamma),
\]

(4.20)

where the term \(q(T; \tau, \gamma)\) is the basic bent-cable model \((2.15)\). The components of the SR model are shown in Figure (4.6).

![Figure 4.6: The components of SR model (4.19).](image-url)
4.3.5 Statistical approach for the model selection

Usually, physical based models, such as (4.17), (4.18) and (4.19), are preferred to any formal mathematical description. In the ideal case, the investigator who collects or generates the data should use an appropriate model for the specific experiment. If it is not possible to decide which model is the most appropriate based on the expert knowledge, some kind of quantitative statistical measure can be applied to compare competing models.

We model the data by a nonlinear regression model of the form

\[ y_i = C_p(T_i, \theta) + \epsilon_i, \quad i = 1, \ldots, n, \]  

(4.21)

where \( \theta \in \Theta \subseteq \mathbb{R}^p \) is the underlying vector of unknown parameters, \( \Theta \) is the parameter space, \( n \) is a number of observations and \( y_i \) and \( C_p(T_i, \theta) \) are experimental and estimated values of the heat capacity at the temperature \( T_i, i = 1, \ldots, n \). We assume that \( \epsilon_i \) are independent normal distributed random variables with mean 0 and variance \( \sigma^2 \). Alternative distributions can be considered by a similar approach.

The parameters in a given model are estimated by the least squares method, which determines parameter values, say \( \hat{\theta}_n \), minimizing the residual sum of squares over parameter space \( \Theta \) that is

\[ \hat{\theta}_n = \arg \min_{\theta \in \Theta} \sum_{i=1}^{n} (y_i - C_p(T_i, \theta))^2. \]  

(4.22)

The goodness-of-fit statistics are calculated for each considered model (4.17), (4.18) and (4.19). One of such statistics that are quite often used for a comparison of different fits is the residual standard error (RSE), which is a measure between the data and fitted regression curve defined as

\[ RSE^j = \sqrt{\frac{\sum_{i=1}^{n} (y_i - C^j_p(T_i, \hat{\theta}^j_n))^2}{n - p^j - 1}}. \]  

(4.23)

Here \( C^j_p(T_i, \hat{\theta}^j_n) \) is the estimated heat capacity at temperature \( T_i \) with \( j \)th model, \( p^j \) is the number of the parameters and \( \hat{\theta}^j_n \) is the vector of the estimated parameters in the \( j \)th model. The upper index \( j \in \{SR, CS, RW\} \) denotes the model under consideration introduced above.

Alternative measures of goodness-of-fit are Akaike’s information criteria (AIC) and the Bayesian information criteria (BIC) defined as

\[ AIC^j = n \ln \sum_{i=1}^{n} (y_i - C^j_p(T_i, \hat{\theta}^j_n))^2 + p^j, \]  

(4.24)

\[ BIC^j = n \ln \sum_{i=1}^{n} (y_i - C^j_p(T_i, \hat{\theta}^j_n))^2 + p^j \ln n. \]  

(4.25)

Compared to the RSE-criterion the AIC and BIC criteria have the advantage that the model complexity (here the number of parameters \( p^j \)) is taken into account as penalty term.
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Thus one tries to find a model with a small residual standard error and a small number of parameters. This could prevent the so-called the effect of overfitting [Ritz and Streibig (2008)].

The decision rule is quite simple for all these criteria. The model with the smallest value of statistic is the most appropriate one. The measures RSE (4.23), AIC (4.24) and BIC (4.25) have been used in this work as objective goodness-of-fit measures for the selection of the most appropriate model from a statistical points of view.

4.4 Test of the segmented regression approach

The results for each selected pure element, Cr, Al and Fe, will be reported in following manner. The estimates of the model parameters with the corresponding confidence intervals are displayed in several tables. The 95%-confidence interval for \( r \)th component of the parameter vector \( \theta = (\theta_r) \), \( r = 1, ..., p \) is of the form

\[
\text{CI}[\theta_r] = \hat{\theta}_r \pm t_{n-p}^{0.975} \cdot \hat{s}_{\theta_r},
\]

(4.26)

where \( t_{n-p}^{0.975} \) is the upper 0.975 quantile of the \( t \)-distribution with \( n - p \) degrees of freedom and \( \hat{s}_{\theta} \) is the standard error of \( \hat{\theta}_r \) [Seber and Wild (1989)].

The width of the confidence region is closely related to the sample size. Roughly speaking, a large confidence interval means that absolute error of estimate is large. Conversely a narrow confidence interval means that the absolute error of the parameter is small. If a confidence interval contains the value 0 this means that the corresponding parameter is not significant. In regression analysis this means that corresponding parameter could be eliminated from the considered model.

Analogously to the confidence intervals for the parameters \( \theta_r, r = 1, ..., p \) of the regression model, a 95% pointwise confidence interval for the modeling function \( C_P(T_i, \theta) \) can be computed as follows

\[
\text{CI}[C_P(T_i, \theta)] = C_P(T_i, \hat{\theta}) \pm t_{n-p}^{0.975} \cdot \hat{s}_{C_P},
\]

(4.27)

where \( \hat{s}_{C_P} \) is the standard error of the estimate \( C_P(T_i, \hat{\theta}) \).

For a prediction of a new observation at temperature \( T_i \) one usually uses a prediction interval which is defined by

\[
\text{PI}[C_P(T_i, \theta)] = C_P(T_i, \hat{\theta}) \pm t_{n-p}^{0.975} \left( (\text{RSE})^2 + \hat{s}_{C_P}^2 \right)^{1/2},
\]

(4.28)

where \( \text{RSE} \) is defined in (4.23).

Similar calculations and analysis of the reported results have been performed also with the models (4.17) and (4.18). In a second step the obtained fits have been compared visually
on the basis of the RSE, AIC and BIC criteria in order to find the most appropriate model. This is defined as model for which at least two of the three criteria are minimal.

Moreover, taking into account that some of the estimated parameters of the proposed model (4.19) are physically motivated, the validation of their values has been performed based on available experimental values.

### 4.4.1 General modeling remarks

Although, it is a well-known fact that the Debye model delivers a more accurate description in low temperatures, we should take into account that it is still an issue to implement Debye model in its integral form or even as a series representation in the currently used TDB format. For this reason we include both models in our comparison and fitted the heat capacity data for each considered model with Debye and Einstein functions respectively. This allows to obtain the differences in the enthalpies between the fits with Debye and Einstein for low temperatures and to justify the analytical expression of the Gibbs energy function obtained with the SR including Einstein model (see Section 4.5).

For pure Cr the results for the SR model are reported including the Debye and Einstein functions to demonstrate the differences in low temperatures. Finally, for pure Al and Fe results will only reported for the Debye function.

### 4.4.2 Programming implementation and computational remarks

The models (4.17), (4.18) and (4.19) have been implemented in the software language R and their parameters have been estimated using nonlinear least squares method. R is a open-source software for statistical computing and graphics [R Core Team (2017)]. Calculations have been performed using three R-packages: *nls2* [Grothendieck (2013)], *nlstool* [Baty and Delignette-Muller (2013)] and *investr* [Brandon (2015)].

The numerical integration procedure already implemented in R allows us to use the Debye model for the phonon contribution of the heat capacity directly in its integral form. This is not a first attempt that the Debye model is involved directly in thermodynamic calculations (see [Palumbo et al. (2014), Shang et al. (2010)]). However, the main difference of the proposed modeling approach from the work presented in [Shang et al. (2010)] is that we do not need any predefined value of the Debye temperature to estimate other model parameters. The whole set of the unknown model parameters including the Debye temperature is determined simultaneously form the considered experiments using least-squares method. Another approach to consider phonon contributions using tabulated values of the Debye functions has been proposed by [Palumbo et al. (2014)].
4.4.3 Pure chromium (Cr)

The SR model has been used for a fit of the heat capacity data for the pure Cr. Here the term $C_p^{mag}(T)$ has not been considered, because a contribution from magnetic ordering in case of the pure Cr according to [Andersson (1985)] is not significant. The most recent investigation of the magnetic properties for the pure Cr using ab-initio calculations is performed by [Koermann et al (2013)].

A comparison between the experimental and predicted heat capacities from SR model is shown in Figure 4.7. The fits from the SR model show a good agreement with the experimental data over the entire temperature region (see Figure 4.7a). These two fitted lines coincide almost everywhere except low temperatures (see Figure 4.7b), where the combination of the bent-cable model (4.20) and Debye function (4.12) delivers more accurate description. This agrees with the classical theory on the physical effects in the heat capacity [Grimvall (1986)]. Moreover, an analysis of the measures RSE, AIC and BIC reported in Table 4.3 confirms this fact as well. The minimal values of all calculated goodness-of-fit measures are achieved for the SR model. The values of estimated models parameters with their confidence intervals for the SR model (4.19) are given in Table 4.2. To evaluate the uncertainties of the fitted SR model with the Debye function, the confidence and prediction intervals defined in (4.27) and (4.28) are displayed on Figure 4.8a and Figure 4.8b respectively.

The obtained values for such physical parameters as the Debye $\theta_D$ temperature together with several collected experimental data are reported in Table 4.1. The Einstein temperature $\theta_E$ has been evaluated using the well-known relationship $\theta_D \approx 0.714\theta_E$ [Chen and Sundman].
(a) Confidence band  
(b) Prediction band

**Figure 4.8:** Fitted by SR model (4.19) heat capacity of pure Cr with the confidence and prediction intervals.

**Table 4.1:** Fitted by SR (4.19) and experimental values of $\theta_D$, K of pure Cr.

The contributions of each component of the SR model is illustrated in Figure 4.9.

In addition to the fitting of the experimental heat capacity data by the SR model (4.19), the RW (4.17) and CS (4.18) models have been applied and compared with results for pure Cr.
Chapter 4

Figure 4.9: Components of the SR model for pure Cr. Blue line: $C_{p}^{Deb}(T, \theta_{D}) + C_{p}^{chem}(T; \hat{\beta}_{1}, \hat{\beta}_{2}, \hat{\tau}, \hat{\gamma})$, green line: $C_{p}^{Deb}(T, \hat{\theta}_{D})$, red line: $C_{p}^{chem}(T; \hat{\beta}_{1}, \hat{\beta}_{2}, \hat{\tau}, \hat{\gamma})$ (solid red lines: linear segments, dashed red line: quadratic segment).

Cr reported above. The estimated parameters values with corresponding confidence intervals for CS and RW models are presented in Table 4.2.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>incl. Debye term</th>
<th>incl. Einstein term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>Confidence Interval</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.5%</td>
</tr>
<tr>
<td>SR</td>
<td>$\hat{\theta}<em>{D}$ (or $\hat{\theta}</em>{E}$)</td>
<td>493.20</td>
<td>484.34</td>
</tr>
<tr>
<td></td>
<td>$\hat{\beta}_{1} \cdot 10^{3}$</td>
<td>5.456</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>$\hat{\beta}_{2} \cdot 10^{2}$</td>
<td>1.942</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>$\hat{\tau}$</td>
<td>1072</td>
<td>982.09</td>
</tr>
<tr>
<td></td>
<td>$\hat{\gamma}$</td>
<td>372.60</td>
<td>225.29</td>
</tr>
<tr>
<td>CS</td>
<td>$\hat{\theta}<em>{D}$ (or $\hat{\theta}</em>{E}$)</td>
<td>492.20</td>
<td>484.54</td>
</tr>
<tr>
<td></td>
<td>$\hat{a} \cdot 10^{3}$</td>
<td>5.325</td>
<td>5.045</td>
</tr>
<tr>
<td></td>
<td>$\hat{b} \cdot 10^{12}$</td>
<td>1.569</td>
<td>1.463</td>
</tr>
<tr>
<td>RW</td>
<td>$\hat{\theta}<em>{D}$ (or $\hat{\theta}</em>{E}$)</td>
<td>463.70</td>
<td>454.56</td>
</tr>
<tr>
<td></td>
<td>$\hat{a} \cdot 10^{3}$</td>
<td>1.244</td>
<td>0.640</td>
</tr>
<tr>
<td></td>
<td>$\hat{b} \cdot 10^{6}$</td>
<td>6.183</td>
<td>5.704</td>
</tr>
</tbody>
</table>

Table 4.2: Pure Cr: The estimated parameters values with corresponding confidence intervals of SR, CS and RW models.

In Figure 4.10 and Figure 4.11 the SR model is compared with the two alternative physically-based models (4.18) and (4.17). The CS and RW models could not provide the same level of the accuracy as the proposed SR model, in particular, in the medium and high temperature range (see Figure 4.10b and Figure 4.11b). On the other hand, in the
low temperatures all models yield similar results. The calculated heat capacity is slightly

Figure 4.10: Comparison of the fitted SR and CS models for pure Cr. Blue line: the SR model, red line: the CS model.

Figure 4.11: Comparison of the fitted SR and RW models for pure Cr: Blue line: the SR model, red line: the RW model.

underestimated by the RW model in the middle and high temperature range (see Figure 4.11) and the CS model overestimates in the high temperature region (see Figure 4.10a). The visual advantages of the new SR model are confirmed by a quantitative comparison on the basis of the goodness-of-fit measures RSE, AIC and BIC introduced in Section 4.3.5, which are summarized in Table 4.3. We observed that the SR model (4.19) with Debye term is
most appropriate for modeling the heat capacity of pure Cr. The second most appropriate model is the SR with Einstein function.

For completeness the SR model with Einstein function has been included in Table 4.3. We observed a larger RSE that compared to the SR model with Debye term, which is consistent with the fact that the Einstein model cannot describe the low temperatures regime correctly. Only the RW model shows a lower RSE with Einstein instead of Debye in general, which shall not be analyzed here further. In the future we will only consider the Debye model as the "optimal" choice. Only for reason of numeric efficiency the use of Einstein model might be justified in high temperature regime if the low temperature error is considered in the integration constant of the Gibbs energy.

<table>
<thead>
<tr>
<th>Statistics</th>
<th>SR</th>
<th>CS</th>
<th>RW</th>
<th>MA-Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Debye</td>
<td>Einstein</td>
<td>Debye</td>
<td>Einstein</td>
</tr>
<tr>
<td>RSE</td>
<td>0.90</td>
<td>0.91</td>
<td>0.92</td>
<td>0.94</td>
</tr>
<tr>
<td>AIC</td>
<td>1170</td>
<td>1183</td>
<td>1194</td>
<td>1210</td>
</tr>
<tr>
<td>BIC</td>
<td>1194</td>
<td>1207</td>
<td>1210</td>
<td>1226</td>
</tr>
</tbody>
</table>

Table 4.3: Calculated RSE, AIC, BIC statistics for the SR, CS and RW models and the selected most appropriate model (MA-Model) for pure Cr.

### 4.4.4 Pure aluminum (Al)

The performance of the different models is investigated here by analyzing the heat capacity data for pure Al. As pure Al is nonmagnetic, the term $C_{\text{magn}}^p(T) = 0$ for all models. It can be observed from Figure 4.12 that the new SR model provides a very good fit of the experimental data for the entire temperature range (Figure 4.12a) and the main part of the low temperature region (Figure 4.12b). The estimated parameter values with corresponding confidence intervals for the fitted SR are reported in Table 4.4. The different components $C_{\text{Deb}}^p$ and $C_{\text{bcm}}^p$ of the SR are displayed in Figure 4.13 while the corresponding confidence and prediction intervals are shown on Figure 4.14a and Figure 4.14b respectively.

In Figure 4.15 and 4.16 the new SR model is compared with the CS and RW models respectively. The fitted heat capacity with the RW and SR models deliver similar results and describe experimental data well over entire temperature range (see Figure 4.16a). In contrast, the CS model slightly overestimates the experimental heat capacity data in the high temperatures which is demonstrated on Figure 4.15a. This fact also has been confirmed by analysis of the selected goodness-of-fit measures, RSE, AIC and BIC (see Table 4.5). The minimal values of all selected measures belong to the SR model. The estimated parameters with the corresponding confidence intervals for the RW and CS models are reported in Table 4.4.
Table 4.5: The calculated goodness-of-fit measures, RSE, AIC and BIC, for the SR, CS and RW models fitted to pure Al data.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>incl. Debye term</th>
<th>incl. Einstein term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Confidence Interval</td>
<td>Value</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5%</td>
<td>97.5%</td>
</tr>
<tr>
<td>SR</td>
<td>$\theta_D$ (or $\theta_E$)</td>
<td>390.30</td>
<td>382.84</td>
</tr>
<tr>
<td></td>
<td>$\hat{\beta}_1 \cdot 10^3$</td>
<td>2.724</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>$\hat{\beta}_2 \cdot 10^3$</td>
<td>6.090</td>
<td>4.084</td>
</tr>
<tr>
<td></td>
<td>$\hat{\tau}$</td>
<td>227.00</td>
<td>164.56</td>
</tr>
<tr>
<td>CS</td>
<td>$\theta_D$ (or $\theta_E$)</td>
<td>403.80</td>
<td>399.24</td>
</tr>
<tr>
<td></td>
<td>$\hat{a} \cdot 10^3$</td>
<td>5.315</td>
<td>4.959</td>
</tr>
<tr>
<td></td>
<td>$\hat{b} \cdot 10^6$</td>
<td>3.304</td>
<td>2.423</td>
</tr>
<tr>
<td>RW</td>
<td>$\theta_D$ (or $\theta_E$)</td>
<td>396.50</td>
<td>391.48</td>
</tr>
<tr>
<td></td>
<td>$\hat{a} \cdot 10^3$</td>
<td>3.047</td>
<td>2.246</td>
</tr>
<tr>
<td></td>
<td>$\hat{b} \cdot 10^6$</td>
<td>5.191</td>
<td>3.914</td>
</tr>
</tbody>
</table>

Table 4.4: Pure Al: The estimated parameters values with corresponding confidence intervals of SR, CS and RW models.

Table 4.5: The calculated goodness-of-fit measures, RSE, AIC and BIC, for the SR, CS and RW models fitted to pure Al data.
Figure 4.13: Components of the SR model for pure Al. Blue line: $C_p^{Deb}(T, \hat{\theta}_D) + C_p^{bcm}(T; 3, \beta_1, \beta_2, \gamma, \gamma)$, green line: $C_p^{Deb}(T, \hat{\theta}_D)$, red line: $C_p^{bcm}(T; 3, \beta_1, \beta_2, \gamma, \gamma)$ (solid red lines: linear segments, dashed red line: quadratic segment).

Figure 4.14: Fitted by SR model heat capacity of pure Al with the corresponding confidence and prediction intervals.
Figure 4.15: Comparison of the fitted SR and CS models. Blue line: the SR model, red line: the CS model.

Figure 4.16: Comparison of the fitted SR and RW models. Blue line: the SR model, red line: the RW model.
4.4.5 Pure iron (Fe)

In this section the different approaches modeling the heat capacity data for pure Fe are analyzed, where a magnetic effect in all models has been described by equations (4.14)-(4.16).

In Figure 4.17 the results for the new SR model is shown and a reasonable fit in the low and high temperature regions is observed. The estimated parameter values together with their confidence intervals in the SR model are reported in Table 4.6.

![Figure 4.17](image)

**Figure 4.17:** Fitted heat capacity of pure Fe using the SR model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>incl. Debye term</th>
<th>incl. Einstein term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Confidence Interval</td>
<td>Value</td>
</tr>
<tr>
<td></td>
<td>2.5%</td>
<td>97.5%</td>
<td>2.5%</td>
</tr>
<tr>
<td>SR</td>
<td>$\theta_D$ (or $\theta_E$)</td>
<td>421.50</td>
<td>393.05-449.93</td>
</tr>
<tr>
<td></td>
<td>$\tilde{\beta}_1 \cdot 10^3$</td>
<td>7.177</td>
<td>6.770-7.584</td>
</tr>
<tr>
<td></td>
<td>$\tilde{\beta}_2 \cdot 10^6$</td>
<td>1.683</td>
<td>0.242-3.124</td>
</tr>
<tr>
<td></td>
<td>$\tau$</td>
<td>1526</td>
<td>1333.40-1719.11</td>
</tr>
<tr>
<td></td>
<td>$\gamma$</td>
<td>85.72</td>
<td>-530.68-702.13</td>
</tr>
<tr>
<td>CS</td>
<td>$\theta_D$ (or $\theta_E$)</td>
<td>417.60</td>
<td>389.08-446.11</td>
</tr>
<tr>
<td></td>
<td>$a \cdot 10^3$</td>
<td>6.668</td>
<td>6.121-7.215</td>
</tr>
<tr>
<td></td>
<td>$b \cdot 10^6$</td>
<td>4.237</td>
<td>2.459-6.013</td>
</tr>
<tr>
<td>RW</td>
<td>$\theta_D$ (or $\theta_E$)</td>
<td>412.50</td>
<td>383.50-441.59</td>
</tr>
<tr>
<td></td>
<td>$a \cdot 10^3$</td>
<td>5.422</td>
<td>4.211-6.632</td>
</tr>
<tr>
<td></td>
<td>$b \cdot 10^6$</td>
<td>1.822</td>
<td>0.892-2.751</td>
</tr>
</tbody>
</table>

**Table 4.6:** Pure Fe: The estimated parameters values with corresponding confidence intervals of the SR, CS and RW models.
The parameter values from the fit of the SR model with Debye term do not differ substantially from these SR model with Einstein function which confirms a consistency of our calculations. The different components of the SR model are displayed in Figure 4.18 while the confidence and prediction intervals are shown on Figure 4.19a and Figure 4.19b respectively.

**Figure 4.18:** Components of the SR model. Black line: $C_p^\text{Deb}(T; \hat{\theta}_D) + C_p^\text{thcm}(T; \hat{\beta}_1, \hat{\beta}_2, \hat{\tau}, \hat{\gamma}) + C_p^\text{magn}(T)$, blue line: $C_p^\text{Deb}(T, \hat{\theta}_D) + C_p^\text{cm}(T; \hat{\beta}_1, \hat{\beta}_2, \hat{\tau}, \hat{\gamma})$, green line: $C_p^\text{Deb}(T, \hat{\theta}_D)$, red line: $C_p^\text{cm}(T; \hat{\beta}_1, \hat{\beta}_2, \hat{\tau}, \hat{\gamma})$ (solid red lines: linear segments, dashed red line: quadratic segment).

**Figure 4.19:** Fitted heat capacity by SR model with the corresponding confidence and prediction intervals.
The confidence interval presented in Figure 4.19a is narrow and the fitted SR has been estimated precisely. The prediction intervals covers almost all experimental heat capacity data of pure Fe and shows a range where a new data point could appear. Since the experimental data used for the fitting are strongly heterogeneous and in some cases even contradictory to each other, it is not surprising that we obtain larger prediction interval for pure Fe as in case of Cr and Al.

Next the CS and RW models are compared with the new SR model. The estimated parameters with the confidence intervals for these models are reported in Table 4.6 and the corresponding fits are shown in Figure 4.21 and Figure 4.20. The CS model and the SR deliver similar results and describe experimental data well in low and high temperature ranges (see Figure 4.20). In contrast, the RW model slightly underestimates heat capacity data in middle temperature range (see Figure 4.20a). The analysis of the RSE, AIC and BIC for the different models confirms this conclusion from the visual inspection. The SR model has been selected as the most appropriate model for the fitting of the heat capacity data of pure Fe according to the minimal values of the RSE and AIC measures. However, according to the analysis of the obtained BIC values, the CS model also has been identified as a reasonable function. However, this is not a surprising observation as initially the CS model has been developed for modeling the heat capacity of pure Fe. It is therefore remarkable that the SR model provides the same accuracy as the CS model.

![Graphs showing heat capacity vs temperature for different models](image)

**Figure 4.20:** Comparison of the fitted SR and CS models for pure Fe: Blue line: the SR model, red line: the CS model.
4.5 Modeling Gibbs energy by segmented regression

According to the analysis of the obtained fitted results for pure Cr, Al and Fe, the proposed SR model has been selected as the most appropriate model in comparison to other two physically-based models, CS and RW. For the considered physically-based models a more accurate description of the experimental heat capacity is provided by the Debye function. The difference between the formulations with Debye \(4.12\) and Einstein \(4.13\) is significant for low temperatures. For middle and high temperatures the Debye and Einstein functions yield similar results. Therefore, since it is still an issue to implement the Debye model into TDB format, the explicit expression for thermodynamic quantities, enthalpy \(H(T)\), entropy \(S(T)\) and Gibbs energy \(G(T)\) will be derived for the SR model where the Einstein function is used for the description of the phonon contribution in the heat capacity.
4.5.1 Analytical expression of Gibbs energy, $G(T)$, for segmented regression model

The thermodynamic functions $G(T)$, $S(T)$, $H(T)$ and $C_p(T)$ provide the starting point for the construction and theoretical investigation of unary and binary phase diagrams. These properties are related by the well-known Gibbs-Helmholtz equation defined in (4.2) as

$$G(T) = H(T) - T \cdot S(T),$$

where the enthalpy $H(T)$ and the entropy $S(T)$ can be derived from the heat capacity through the formulas

$$H(T) = \int C_p(T) dT \quad \text{and} \quad S(T) = \int \frac{C_p(T)}{T} dT. \quad (4.29)$$

The proposed segmented model for the heat capacity (4.19) contains three terms

$$C_p^{SR}(T) = C_p^{Ein}(T) + C_p^{bcm}(T) + C_p^{magn}(T),$$

where $C_p^{Ein}(T)$ and $C_p^{bcm}(T)$ are defined by (4.13) and (4.20) respectively as

$$C_p^{Ein}(T) = 3R \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2},$$

$$C_p^{bcm}(T) = \begin{cases} \beta_1 T, & T < \tau - \gamma, \\ \beta_1 T + \beta_2 (T - \tau + \gamma)^2, & \tau - \gamma \leq T \leq \tau + \gamma, \\ \beta_1 T + \beta_2 (T - \tau), & \tau + \gamma < T. \end{cases}$$

The magnetic contribution to the heat capacity, $C_p^{magn}(T)$, is modeled by (4.14)-(4.16). Since the analytical expression for magnetic $G^{magn}(T)$ and Einstein $G^{Ein}(T)$ terms of the Gibbs energy are provided in [Chen and Sundman (2001)], here only the mathematical expression for the bent-cable term of the enthalpy, $H(T)$, is obtained using the relations given in (4.29)

$$H(T) = \begin{cases} \beta_1 \frac{T^2}{2}, & T < \tau - \gamma, \\ \beta_1 \frac{T^2}{2} + \beta_2 \frac{(T - \tau + \gamma)^3}{12\gamma}, & \tau - \gamma \leq T \leq \tau + \gamma, \\ \beta_1 \frac{T^2}{2} + \beta_2 \frac{T(T - \tau)}{2} + \beta_2 \left( \frac{2^2}{6} + \frac{T^2}{2} \right), & \tau + \gamma < T. \end{cases}$$

After the collection of the coefficients according to the same order of power for the $T$ terms, the bent-cable part of $H(T)$ will have the following form

$$H^{bcm}(T) = \begin{cases} c_1^{(H)} T^2, & T < \tau - \gamma, \\ a_2^{(H)} T + c_2^{(H)} T^2 + d_2^{(H)} T^3, & \tau - \gamma \leq T \leq \tau + \gamma, \\ a_3^{(H)} + b_3^{(H)} T + c_3^{(H)} T^2, & \tau + \gamma < T. \end{cases} \quad (4.30)$$
where the coefficients $c_1^{(H)}, a_1^{(H)}, b_2^{(H)}, c_2^{(H)}, d_2^{(H)}, a_3^{(H)}, b_3^{(H)}, c_3^{(H)}$ are connected with the estimated parameters of the bent-cable model $\beta_1, \beta_2, \tau, \gamma$ by the relationship

$$
\begin{align*}
    c_1^{(H)} &= \frac{\beta_1}{2}, \\
    a_2^{(H)} &= -\frac{\beta_2}{12\gamma}(\tau - \gamma)^3, \\
    b_2^{(H)} &= \frac{\beta_2}{4\gamma}(\tau - \gamma)^2, \\
    c_2^{(H)} &= \frac{\beta_1}{2} - \frac{\beta_2}{4\gamma}(\tau - \gamma), \\
    d_2^{(H)} &= \frac{\beta_2}{12\gamma}, \\
    a_3^{(H)} &= \frac{\beta_2}{2}\left(\frac{\gamma^2}{3} + \tau^2\right), \\
    b_3^{(H)} &= -\beta_2\tau, \\
    c_3^{(H)} &= \frac{\beta_1 + \beta_2}{2}.
\end{align*}
$$

Analytical expression for the entropy $S(T)$ can be derived in similar way and the second term in the expression is given for the Gibbs energy (4.2) by

$$
T \cdot S(T) = \begin{cases} 
    c_1^{(s)} T^2, & T < \tau - \gamma, \\
    b_2^{(s)} T + c_2^{(s)} T^2 + d_2^{(s)} T^3 + e_2^{(s)} T \ln(T), & \tau - \gamma \leq T \leq \tau + \gamma, \\
    b_3^{(s)} T + c_3^{(s)} T^2 + e_3^{(s)} T \ln(T), & \tau + \gamma < T,
\end{cases}
$$

where the coefficients $c_1^{(s)}, b_2^{(s)}, c_2^{(s)}, d_2^{(s)}$, $e_2^{(s)}$, $b_3^{(s)}, c_3^{(s)}, e_3^{(s)}$ are connected with the estimated parameters of the bent-cable model $\beta_1, \beta_2, \tau, \gamma$ by the relationship

$$
\begin{align*}
    c_1^{(s)} &= \beta_1, \\
    b_2^{(s)} &= (\tau - \gamma)^2\left(\frac{3k_2}{8\gamma} - \frac{k_2}{4\gamma} \ln(\tau - \gamma)\right), \\
    c_2^{(s)} &= \beta_1 - \frac{k_2(\tau - \gamma)}{2\gamma}, \\
    d_2^{(s)} &= \frac{\beta_2}{8\gamma}, \\
    e_2^{(s)} &= \frac{\beta_2}{4\gamma}(\tau - \gamma)^2, \\
    b_3^{(s)} &= -\frac{3\beta_2 \tau}{2} - \frac{\beta_2}{4\gamma}(\tau - \gamma)^2 \ln(\tau - \gamma) - (\tau + \gamma)^2 \ln(\tau + \gamma), \\
    e_3^{(s)} &= \beta_1 + \beta_2, \\
    e_3^{(s)} &= -\beta_2 \tau.
\end{align*}
$$

Therefore, the bent-cable part of the total Gibbs energy $G(T)^\text{bcm}$ at 101,325Pa can be evaluated from the the heat capacity $C_p(T)^\text{bcm}$ expression using equations (4.2), (4.29) as

$$
G(T) = \begin{cases} 
    c_1 T^2, & T < \tau - \gamma, \\
    a_2 + b_2 T + c_2 T^2 + d_2 T^3 + e_2 T \ln(T), & \tau - \gamma \leq T \leq \tau + \gamma, \\
    a_3 + b_3 T + c_3 T^2 + e_3 T \ln(T), & T > \tau + \gamma,
\end{cases}
$$

Here coefficients $c_1, a_2, b_2, c_2, d_2, e_2, a_3, b_3, c_3, e_3$ in expression for the $G^\text{bcm}(T)$ (4.32) can be derived directly from the estimated values of parameters $\beta_1, \beta_2, \tau, \gamma$

$$
\begin{align*}
    c_1 &= -\frac{\beta_1}{2}, \\
    a_2 &= -\frac{\beta_2}{12\gamma}(\tau - \gamma)^3, \\
    b_2 &= (\tau - \gamma)^2\left(-\frac{\beta_2}{8\gamma} + \frac{\beta_2}{4\gamma} \ln(\tau - \gamma)\right), \\
    c_2 &= -\frac{\beta_1}{2} + \frac{\beta_2}{4\gamma}(\tau - \gamma), \\
    d_2 &= -\frac{\beta_2}{24\gamma}, \\
    e_2 &= -\frac{\beta_2}{4\gamma}(\tau - \gamma)^2, \\
    a_3 &= \frac{1}{6}\beta_2 \gamma^2 + \frac{1}{2}\beta_2 \tau^2, \\
    b_3 &= \frac{\beta_2 \tau}{2} + \frac{\beta_2}{4\gamma}(\tau - \gamma)^2 \ln(\tau - \gamma) - (\tau + \gamma)^2 \ln(\tau + \gamma), \\
    c_3 &= -\frac{1}{2}(\beta_1 + \beta_2), \\
    e_3 &= \beta_2 \tau.
\end{align*}
$$
4.5.2 Verification of results from physical point of view

The consistency of underlying fitting results from a physical point of view has been performed by calculating the relative enthalpy \( H - H_{298.15} \) that can be derived directly from the fitted heat capacity \( C_p(T) \) \cite{Lukas et al. (2007)} using a relationship

\[
H(T) - H_{298.15} = \int_{298.15}^{T} C_P(T) dT. \tag{4.33}
\]

Since the proposed SR model with the Debye term (4.12) has been selected as the most-appropriate model for the description of the heat capacity data, we calculate relative enthalpies using equation (4.33) and compare it with the collected experimental data. The predicted relative enthalpies and experimental results for pure Cr, Al and Fe are presented in Figure 4.22a, Figure 4.22b and Figure 4.22c, respectively. In all cases we observe good predictions by the SR model. No data on the relative enthalpy at the temperatures below 298.15K were found in the literature.

![Graphs showing calculated and experimental relative enthalpy](image)

**Figure 4.22:** Calculated and experimental relative enthalpy \( H - H_{298.15} \).
Additionally, the enthalpy $H_{298.15}$ and entropy $S_{298.15}$ at the room temperature has been calculated and compared with the values reported in [Dinsdale (1991)] and [Palumbo et al. (2014)]. The corresponding results are presented in Table 4.8 which also gives a comparison with the values from SGTE description [Dinsdale (1991)] for pure Al, Cr and Fe. We can observed slightly higher values of $H_{298.15}$ for all considered models (4.17), (4.18), (4.19). The values of standard enthalpy calculated with segmented regression model (4.19) are in good agreement with current SGTE data.

<table>
<thead>
<tr>
<th>Reference</th>
<th>model</th>
<th>Cr bcc</th>
<th>Fe bcc</th>
<th>Al fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dinsdale (1991)</td>
<td>SGTE</td>
<td>4050.0</td>
<td>4489.0</td>
<td>4540.0</td>
</tr>
<tr>
<td>Present work</td>
<td>SR with Debye</td>
<td>4064.34</td>
<td>4583.94</td>
<td>4557.89</td>
</tr>
<tr>
<td></td>
<td>SR with Einstein</td>
<td>4068.93</td>
<td>4598.39</td>
<td>4565.24</td>
</tr>
<tr>
<td></td>
<td>CS with Debye</td>
<td>4064.46</td>
<td>4584.97</td>
<td>4579.18</td>
</tr>
<tr>
<td></td>
<td>CS with Einstein</td>
<td>4059.18</td>
<td>4596.36</td>
<td>4583.12</td>
</tr>
<tr>
<td></td>
<td>RW with Debye</td>
<td>4096.48</td>
<td>4576.04</td>
<td>4567.47</td>
</tr>
<tr>
<td></td>
<td>RW with Einstein</td>
<td>4089.82</td>
<td>4585.27</td>
<td>4564.81</td>
</tr>
</tbody>
</table>

Table 4.8: Calculated standard enthalpy $H_{298.15}$.

<table>
<thead>
<tr>
<th>Reference</th>
<th>method</th>
<th>details</th>
<th>Cr bcc</th>
<th>Fe bcc</th>
<th>Al fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dinsdale (1991)</td>
<td>assessed</td>
<td></td>
<td>23.54</td>
<td>27.28</td>
<td>28.30</td>
</tr>
<tr>
<td>Palumbo et al. (2014)</td>
<td>QE</td>
<td>calc.QHA</td>
<td>23.07</td>
<td>26.58</td>
<td>27.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>calc.QHA+el.</td>
<td>23.72</td>
<td>27.41</td>
<td>27.70</td>
</tr>
<tr>
<td></td>
<td>VASP</td>
<td>calc.QHA</td>
<td>23.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>calc.QHA+el.</td>
<td>23.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>NLS</td>
<td>SR with Debye</td>
<td>24.02</td>
<td>28.18</td>
<td>28.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SR with Einstein</td>
<td>23.34</td>
<td>27.51</td>
<td>27.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CS with Debye</td>
<td>24.03</td>
<td>28.24</td>
<td>28.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CS with Einstein</td>
<td>23.24</td>
<td>27.54</td>
<td>27.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RW with Debye</td>
<td>24.41</td>
<td>28.23</td>
<td>28.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RW with Einstein</td>
<td>23.60</td>
<td>27.51</td>
<td>27.66</td>
</tr>
</tbody>
</table>

Table 4.9: Calculated standard entropy $S_{298.15}$.

The calculated standard entropies $S_{298.15}$ for Cr bcc, Fe bcc and Al fcc in comparison with first-principles and assessed standard entropy $S_{298.15}$ from [Palumbo et al. (2014)] are presented in Table 4.9. Here assessed values are from current SGTE description [Dinsdale (1991)], QE are values computed using Quantum Espresso software and density functional perturbation theory, VASP are values computed using VASP (VASP = the Vienna Ab initio Simulation Package) and the supercell method. QHA refers to the quasiharmonic approximation, QHA+el to the quasiharmonic approximation including the electronic contribution. For more details and description of these methods we refer to [Palumbo et al. (2014)]. Calculations performed
by integration of the SR model (4.19) for $C_p(T)$ from 0K up to 298 K (NLS) provide reliable results for the thermodynamic properties such as the entropy and show good agreement with first-principle calculation reported by Palumbo et al. (2014). Slightly higher values for the relative entropy are obtained by application of the models (4.17), (4.18) and (4.19) with the Debye function for description of the phonon contributions. Comparison between experimental and calculated relative enthalpy $H(T) - H_{298.15}$ is shown in Figure 4.22a and delivers good agreement from the room temperature, 298.15K, up to the high temperatures.
In practice, usually the parameters of thermodynamic models are estimated using experimental data that have been collected with the goal to cover an entire temperature range $0 \leq T \leq T_m$ by as much data as possible. However, such a data collection process is a very time consuming and tedious process which can take up to several months depending on the complexity of the element or system under study. Moreover, under some conditions, for example, metastable or unstable phases, it is impossible to perform experimental investigations. In such a case the material properties can be obtained using Density Functional Theory (DFT) calculations which in turn are time consuming and are performed on big computational clusters. Therefore, the time required for the data collection has become one of the key issues for the development of novel thermodynamic models.

A properly designed experiment can not only reduce the time and cost of the model development process, but also maximize the accuracy of the resulting parameter estimates. In terms of the experimental design, this means that an optimal design allows to estimate the unknown model parameters with minimal variance (with high precision), but requires fewer number of observations to achieve the same precision as a non-optimal design. Therefore, the goal of this chapter is to construct optimal designs for the proposed SR model (4.19), which will provide recommendations for the data collection process for the heat capacity data. Our interest is in estimating all parameters of the SR model as precisely as possible and therefore, the well-known $D$-optimality criterion is considered for the construction of the optimal designs. As an illustrative example the heat capacity of solid phase of pure Cr will be considered. Similarly, this method can be applied for stable, metastable and liquid phases of other pure elements and compounds.

First, the basic concepts of the optimal design theory for nonlinear regression models
is introduced and some well-known theoretical results relevant to $D$-optimal designs are presented without any formal proof. The remaining part of the chapter is devoted to the construction of locally $D$-optimal designs for the SR model of the heat capacity data of pure Cr. In particular, two alternative designs based on a constructed $D$-locally optimal design are proposed for the data collection process of the heat capacity and their influence on the accuracy of the least-squares estimates of the SR model parameters is investigated by simulations. Based on the obtained results, a set of practical recommendations for the data collection process is formulated.

5.1 Introduction to optimal design theory

Consider the univariate nonlinear regression model of the form

$$y_{ij} = f(T_i, \theta) + e_{ij}, \quad i = 1, \ldots, p; j = 1, \ldots, n_i, \sum_{i=1}^{p} n_i = n,$$

where $n_1, \ldots, n_p$ are the numbers of repeated observations taken at each one of the distinct experimental conditions $T_1, \ldots, T_p$, $n$ denotes the total sample size, $\theta = (\theta_1, \ldots, \theta_m)^T$ is the vector of the unknown model parameters and the errors $e_{ij} (i = 1, \ldots, p, j = 1, \ldots, n_i)$ are assumed to be independent and identically normally distributed with zero mean and variance $\sigma^2$.

The information of the total of $n$ observations at the points $T_1, \ldots, T_p$, organized in the form

$$\xi_n = \begin{pmatrix} T_1 & \cdots & T_p \\ n_1 & \cdots & n_p \end{pmatrix},$$

is called exact design. The set $T$ of possible values for the support points $T_i$ is called the design space [Fedorov and Leonov (2013)].

The goal of the optimal experimental design is to choose the experimental conditions $T_1, \ldots, T_p \in T$ and the corresponding numbers of replicated observations $n_1, \ldots, n_p$ to be taken at each $T_i$, such that the unknown model parameters $\theta = (\theta_1, \ldots, \theta_m)^T$ are estimated with minimal variance.

However, it is difficult to find the solution of such a discrete optimization problem. Therefore, the optimal design problem is typically considered under the approximate designs framework, where instead of exact designs $\xi_n$ with integer number of observations $n_i$ at points $T_i, (i = 1, \ldots, p)$, approximate designs [Kiefer (1974)] of the form

$$\xi = \begin{pmatrix} T_1 & \cdots & T_p \\ w_1 & \cdots & w_p \end{pmatrix}$$

are considered. These are probability measures of the design space $T$ with finite support. The weights $w_1, \ldots, w_p$ take values in the interval $(0, 1)$ such that $\sum_{i=1}^{p} w_i = 1$ and they represent the proportions of observations to be taken at each support point $T_1, \ldots, T_p$ of the design.
Therefore, the approximate design problem is that of choosing the conditions \( T_1, \ldots, T_p \) and weights \( w_1, \ldots, w_p \) in an optimal manner, that is, so that the parameters are estimated with minimal variance.

The approximate designs are preferred to the exact designs since they are independent of the total number of observations \( n \) and thus their use avoids the discrete optimization problem which may be extremely tedious from a computational point of view [Atkinson et al. (2007)]. Moreover, the formulation of the optimal design problem in terms of approximate designs allows one to apply the powerful tools of convex optimization theory [Fedorov and Leonov (2013)]. Therefore, a solution of the optimal design problem is usually constructed in terms of an approximate design of the form (5.3) and then the corresponding exact design can be obtained using an efficient rounding method [Pukelsheim and Rieder (1992)].

The minimization of the asymptotic variance-covariance matrix of the least-squares (or the maximum likelihood) estimator is equivalent to the maximization of the information matrix given by

\[
M(\xi, \theta) = \sum_{i=1}^{p} w_i g(T_i, \theta) g^T(T_i, \theta),
\]

for nonlinear models of the form (5.1) [Fedorov and Leonov (2013)], where

\[
g(T, \theta) = \left( \frac{\partial f(T, \theta)}{\partial \theta_1}, \ldots, \frac{\partial f(T, \theta)}{\partial \theta_m} \right)^T
\]

is the vector of partial derivatives with respect to the model parameters \( \theta_1, \ldots, \theta_m \).

Since we cannot directly optimize a matrix, a real-valued functional say \( \Phi \) of the information matrix \( M(\xi, \theta) \) will be optimized with respect to arbitrary approximate designs \( \xi \). An optimal (approximate) design is defined as

\[
\xi^* = \arg \max_{\xi} \Phi (M(\xi, \theta)),
\]

where \( \Phi \) is a scalar function which corresponds to an optimality criterion.

The most widely used optimality criteria are defined for positive definite information matrices as the matrix mean \( \Phi_p \) given by [Pukelsheim (1993)]

\[
\Phi_p(M(\xi, \theta)) = \begin{cases} 
\lambda_{\text{min}}(M(\xi, \theta)), & p = -\infty \\
\frac{1}{m} \text{trace}(M(\xi, \theta)), & p = 1 \\
\det(M(\xi, \theta))^{1/m}, & p = 0 \\
\left( \frac{1}{m} \text{trace}(M^{-1}(\xi, \theta)) \right)^{-1}, & p = -1,
\end{cases}
\]

where \( \lambda_{\text{min}}(M(\xi, \theta)) \) is the minimal eigenvalue of the information matrix \( M(\xi, \theta) \) and \( \text{trace}(M(\xi, \theta)^p) \) and \( \det(M(\xi, \theta)) \) denote the trace and determinant respectively of the information matrix.
Some of the special cases of such criteria are the $D$, $A$- and $E$-optimality criteria corresponding to $p = 0, -1, -\infty$ respectively. The choice of the appropriate optimality criterion to be used depends on the goal of the experiment. If all the model parameters have to be estimated as accurately as possible then the $D$-optimality criterion has to be used since it corresponds to the minimization of the generalized variance of the parameter estimates. In terms of designs, $D$-optimal designs minimize the volume of the confidence ellipsoid for the vector of parameter estimators and they are very popular for practical applications [Dean et al. (2015)]. Moreover, $D$-optimal designs are invariant with respect to nondegenerate transformations of model parameters such as changes in parameter scale [Fedorov and Leonov (2013)]. Based on the above arguments, the rest of the chapter is devoted to $D$-optimal designs.

The necessary and sufficient condition for the optimality of an approximate design is formulated in the form of the general equivalence theorem. The equivalence theorem for the $D$-optimality criterion [Fedorov and Leonov (2013)] states that the design $\xi$ is $D$-optimal for estimation of the parameter vector $\theta$ if and only if the inequality

$$d(\xi, T, \theta) = g^T(T, \theta)M^{-1}(\xi, \theta)g(T, \theta) - m \leq 0,$$

holds for all $T \in \mathcal{T}$ with equality at the support points of $\xi$. The information matrix $M(\xi, \theta)$ is defined in (5.4) [Pukelsheim (1993)]. For the formulation of the general equivalence theorem for other optimality criteria see, for example, Atkinson et al. (2007).

An upper bound for the number of support points of an optimal design is provided by Caratheodory’s theorem [Pukelsheim (1993)] which states that an optimal design contains at most $m(m + 1)/2$ points, where $m$ is the number of model parameters. If an optimal design has exactly $m$ points, then such a design is called minimally supported or saturated design [Dean et al. (2015)]. In the next section the general equivalence theorem (5.7) will be applied to show that the obtained locally $D$-optimal design for the segmented heat capacity model (4.19) of pure Cr is indeed $D$-optimal.

Note that for nonlinear models, the information matrix and therefore the optimal designs depend on the unknown model parameters to be estimated. Following Chernoff (1953) such designs are referred to as locally optimal designs. Since the parameters are unknown, a best guess of the parameter values in required in order for the locally optimal designs to be used in practice and this approach can result in inefficient designs if the parameters are misspecified. However, locally optimal designs play an important role in the study of optimal designs since they are usually used as a benchmarks for the construction of designs that are robust to parameter misspecification. Such robust design strategies include the construction of Bayesian optimal designs (see, for example, Pronzato and Walter (1985) and Chaloner and Larntz (1989)) and standardized maximin optimal designs (see Dette (1997) and Dette and Biedermann (2003) for further details).
5.2 Locally \( D \)-optimal designs for the SR model

In this section locally optimal designs are constructed for the physically-based SR model \(^{(4.19)}\) proposed in Chapter \(^{[4]}\) for the description of the temperature dependence of the heat capacity, \( C_P(T) \), of solids for temperatures in the interval \([0, T_m]\). The SR has been developed based on the analysis of several physical effects which could appear at low and high temperatures. Two alternative formulations of the SR model either with the Debye \(^{(4.12)}\) or Einstein \(^{(4.13)}\) function are available. Both functions are typically used for the modeling of phonon vibrations in solids \(^{[Einstein (1906), Debye (1912)]}\). Since the Debye function is an integral that cannot be expressed using elementary functions, we construct a locally \( D \)-optimal design for the SR model with Einstein function and use the following abbreviation "SRE". The SRE model is given by

\[
f(T, \theta) = C_P(T, \theta) = 3R \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{e^{\theta_E/T} - 1} + \beta_1 T + \beta_2 q(T; \tau, \gamma),
\]

where \( T \in [0, T_m] \) is the temperature in Kelvin, \( \theta = (\theta_E, \beta_1, \beta_2, \tau, \gamma)^T \) is the vector of model parameters and \( q(T; \tau, \gamma) \) is the basic bent-cable model \(^{[Chiu (2002)]}\) defined in \(^{(3.1)}\) as

\[
q(T; \tau, \gamma) = \frac{(T - \tau + \gamma)^2}{4\gamma} \mathbb{1}\{|T - \tau| \leq \gamma\} + (T - \tau) \mathbb{1}\{T > \tau + \gamma\},
\]

where \( \mathbb{1}\{\cdot\} \) is the identity function.

Suppose that we would like to estimate all parameters \( \theta = (\theta_E, \beta_1, \beta_2, \tau, \gamma)^T \) of the SRE model \(^{(5.8)}\) with minimum variance. Then, according to the \( D \)-optimality criterion, the determinant of the information matrix, \( M(\xi, \theta) \), defined by \(^{(5.4)}\) has to be maximized in terms of a design \( \xi \). The vector of the partial derivatives \( g(T_i, \theta) \) with respect to the model parameters is

\[
g(T_i, \theta) = \frac{\partial f_i}{\partial \theta_j} = \left( \frac{\partial f(T_i, \theta)}{\partial \theta_E}, \frac{\partial f(T_i, \theta)}{\partial \beta_1}, \frac{\partial f(T_i, \theta)}{\partial \beta_2}, \frac{\partial f(T_i, \theta)}{\partial \tau}, \frac{\partial f(T_i, \theta)}{\partial \gamma} \right)^T,
\]

where the components are given by

\[
\begin{align*}
\frac{\partial f(T_i, \theta)}{\partial \theta_E} &= 3R \left( \frac{\theta_E}{T_i} \right)^2 \frac{e^{\theta_E/T_i}}{(e^{\theta_E/T_i} - 1)^2} \left( \frac{2}{\theta_E} + \frac{1}{T_i} - \frac{2}{T_i} e^{\theta_E/T_i} \right), \\
\frac{\partial f(T_i, \theta)}{\partial \beta_1} &= T_i, \\
\frac{\partial f(T_i, \theta)}{\partial \beta_2} &= q(T_i; \tau, \gamma), \\
\frac{\partial f(T_i, \theta)}{\partial \tau} &= -\beta_2 (\alpha_1(\theta) + \alpha_2(\theta)),
\end{align*}
\]

(5.10)

The functions \( \alpha_1(\theta), \alpha_2(\theta), \alpha_3(\theta) \) are defined in \(^{(3.8)}\).

5.2.1 Choice of the design space

The SRE model \(^{(5.8)}\) is defined on the design space \( \mathcal{T} = [0, T_m] \) and it consists of two nonlinear models: the Einstein function \(^{(4.13)}\) and the bent-cable model \(^{(3.58)}\) with the
parameter \( \beta_0 = 0 \). Based on the asymptotic theory for the bent-cable model established in Chapter 3 and the analysis of the Einstein function we formulate several requirements on the design points \( T_i, i = 1, ..., p \) and slightly modify the definition of \( \mathcal{T} \).

First, we consider the properties of the Einstein function, which is a continuous differentiable function asymptotically reaching the \( 3R \) value, where \( R \) is the gas constant, according to the Dulong-Petit law (see Figure 4.5a) and it is unidentified at 0K temperature. Therefore, we will exclude the temperature of 0K from the considered design space and set up a lower bound for \( \mathcal{T} \) equal to a small positive constant \( \delta_0 > 0 \). The upper bound of the design space is assumed to be \( T_m \) except for the elements and compounds whose melting temperature is extremely high. In this case the highest experimentally accessible temperature \( T_f (< T_m) \) is considered instead of \( T_m \).

The bent-cable (3.58) is a segmented part of the SRE model. The form of this model requires the assumptions (3.59) on the design points such that \( x_i \neq \tau_0 \pm \gamma_0 \), where \( \tau_0, \gamma_0 \) are the true but unknown parameter values. These conditions together with the so-called "2-1-2" configuration of the design space \( \mathcal{T} \) presented in Figure 5.1 guarantee the identifiability of the model parameters. They also have been used to establish the asymptotic theory of the bent-cable model presented in Chapter 3. These results can be extended to the SRE model (5.8).

Taking into account the properties of the Einstein function and the identifiability conditions for the bent-cable parameters we define the design space of the SRE model as

\[
\mathcal{T} = [\delta_0, \tau_0 - \gamma_0] \cup (\tau_0 - \gamma_0, \tau_0 + \gamma_0) \cup (\tau_0 + \gamma_0, T_f],
\]

where \( \delta_0 > 0 \) is a small positive constant. Note, that true values \( \tau_0, \gamma_0 \) will be replaced by the estimates \( \hat{\tau}, \hat{\gamma} \) in order to construct a locally \( D \)-optimal design for the SRE of pure Cr.

### 5.2.2 Numerical results

The SRE model (5.8) has been successfully applied to fit the collected heat capacity data of pure Cr and the results are shown in Figure 5.2. For more details see Chapter 4.
The least-squares estimates of the SRE model parameters for the heat capacity of pure Cr

\[ \hat{\theta}_E = 356.40, \quad \hat{\beta}_1 = 4.779 \times 10^{-3}, \quad \hat{\beta}_2 = 2.010 \times 10^2, \quad \hat{\tau} = 1035, \quad \hat{\gamma} = 441.5, \quad (5.12) \]

together with the corresponding confidence intervals are reported in Table 4.2. Based on the validation of the obtained results from a physical point of view presented in section 4.5, the estimates (5.12) are used to construct a locally D-optimal design for the considered segmented model (5.8).

Taking into account that no experiments on the heat capacity of pure Cr have been found in the literature for temperatures \( T > 1800 \) and setting up \( \delta_0 = 0.01 \), the design space \( \mathcal{T} \) (5.11) for the SRE model of pure Cr with respect to the estimates (5.12) is defined as

\[ \mathcal{T} = [0.01, 593.33) \cup (593.33, 1476.41) \cup (1476.41, 1800]. \quad (5.13) \]

Due to the complexity of model (5.8) the locally D-optimal design

\[ \xi_D^* = \begin{bmatrix} 159.93 & 593.31 & 1034.87 & 1476.43 & 1800 \\ 0.2 & 0.2 & 0.2 & 0.2 & 0.2 \end{bmatrix} \quad (5.14) \]

is found numerically using the particle swarm optimization (pso) algorithm (see, for example, Clerc (2006)) from R-package psoptim Bendtse (2015).

We can check that the design \( \xi_D^* \) (5.14) is D-optimal using the general equivalence theorem (5.7). The plot in Figure 5.3 shows that the function \( d(\xi, T, \hat{\theta}) \) defined in (5.7) is equal to zero at the support points of the design \( \xi_D^* \) and negative at all other points of \( \mathcal{T} \). This confirms the D-optimality of the obtained design (5.14) for the SRE model (5.8). The design \( \xi_D^* \) is a
Design space: $T, \{K\}$

Figure 5.3: Checking $D$-optimality of the design (5.14) using the general equivalence theorem (5.7).

A minimally supported design, since the number of support points of $\xi\_D^*$ is equal to the number of model parameters.

The locally optimal design $\xi\_D^*$ suggests to put $1/5$ of the observations at each of the temperatures $159.93, 593.31, 1034.87, 1476.43$ and $1800$ Kelvin. The first support point $T_1 = 159.93$ corresponds to low temperatures. Usually low temperature measurements are performed to define physical parameters such as the Debye $\theta_D$ and Einstein $\theta_E$ temperatures which are correlated with each other by a well-known relationship $\theta_E \approx 0.714\theta_D$ obtained by Chen and Sundman (2001). More on the experimental determination of $\theta_D$ for pure Cr can be found, for example, in Anderson (1937), Estermann et al. (1952) and Wolcott (1955). The collected experimental values of $\theta_D$ and $\theta_E$ for pure Cr together with the corresponding temperature regions used in experimental studies are reported in Table 4.1.

The next three support points $T_2 = 593.31, T_3 = 1034.87$ and $T_4 = 1476.43$ are very close to the values of $\hat{\tau} - \hat{\gamma}, \hat{\tau}$ and $\hat{\tau} + \hat{\gamma}$ which define the end of first linear function, the middle of quadratic bent transition and the beginning of the second linear regime respectively.

The last support point of the design (5.14) is equal to the value of the upper bound of $T$ defined in (5.11). We also performed a benchmark study and changed the upper bound of the design space (5.13) from the fixed temperature $T_f = 1800$ to the melting point $T_m = 2130$. This revealed that the optimal design has the tendency to always include the upper bound of the design space as a support point. Moreover, such changes did not affect any other support point and the resulting design is also $D$-optimal according to the general equivalence theorem (5.7).
5.2.3 Alternative locally $D$-optimal design for pure Cr

Since locally optimal designs are not parameter robust, we construct a locally $D$-optimal design $\xi_{D,2}^*$ for the SRE model with an alternative set of initial parameter values. The SR model (4.19) has been proposed in two formulations - with the Debye (4.12) and Einstein (4.13) functions for the modeling of phonon vibrations. Both models have been fitted to the collected heat capacity data of pure Cr and the estimated model parameters are reported in Table 4.2. Taking into account that $\theta_E \approx 0.714 \theta_D$, we can assume that

$$\hat{\theta}_E^{(2)} = 0.714 \cdot \hat{\theta}_D, \quad \hat{\beta}_1^{(2)} = \hat{\beta}_{1,D}, \quad \hat{\beta}_2^{(2)} = \hat{\beta}_{2,D}, \quad \hat{\tau}^{(2)} = \hat{\tau}_D, \quad \hat{\gamma}^{(2)} = \hat{\gamma}_D,$$

(5.15)

where $(\hat{\theta}_D, \hat{\beta}_{1,D}, \hat{\beta}_{2,D}, \hat{\tau}_D, \hat{\gamma}_D)^T$ is the vector of the least-squares estimates of the SR model parameters with the Debye function. Then using the alternative initial values

$$\hat{\theta}_E^{(2)} = 352.14, \quad \hat{\beta}_1^{(2)} = 5.456 \cdot 10^{-3}, \quad \hat{\beta}_2^{(2)} = 1.942 \cdot 10^{-2}, \quad \hat{\tau}^{(2)} = 1072, \quad \hat{\gamma}^{(2)} = 372.6,$$

(5.16)

we calculated the alternative locally $D$-optimal design $\xi_{D,2}^*$ given by

$$\xi_{D,2}^* = \left\{ \begin{array}{cccccc}
163.57 & 699.39 & 1072 & 1444.61 & 1800 \\
0.2 & 0.2 & 0.2 & 0.2 & 0.2
\end{array} \right\}. $$

(5.17)

To compare $\xi_{D}^*$ (5.14) and $\xi_{D,2}^*$ (5.17), the support points of both designs have been normalized by the $T_f = 1800$ value. The resulting normalized designs are presented in Table 5.1.

<table>
<thead>
<tr>
<th>Initial parameter values</th>
<th>normalized locally $D$-optimal design</th>
</tr>
</thead>
</table>
| $\hat{\theta} = (356.40, 4.780 \cdot 10^{-3}, 2.010 \cdot 10^{-2}, 1035, 441.5$) | $\xi_{D}^* = \left\{ \begin{array}{cccc}
0.09 & 0.33 & 0.57 & 0.82 \\
0.2 & 0.2 & 0.2 & 0.2
\end{array} \right\}$ |
| $\hat{\theta}^{(2)} = (352.14, 5.456 \cdot 10^{-3}, 1.942 \cdot 10^{-2}, 1072, 372.6$) | $\xi_{D,2}^* = \left\{ \begin{array}{cccc}
0.09 & 0.39 & 0.6 & 0.8 \\
0.2 & 0.2 & 0.2 & 0.2
\end{array} \right\}$ |

Table 5.1: Sensitivity analysis of locally $D$-optimal design for pure Cr

The results in Table 5.1 show that there are no significant changes in the locations of the support points of the two designs $\xi_{D}^*$ and $\xi_{D,2}^*$. In particular, for both designs we obtain the same position of the support points, which is $T_1^{(2)}$ at low temperature, $T_2^{(2)}$ near the end of the first linear regime $\hat{\tau}^{(2)} - \hat{\gamma}^{(2)}$, $T_3^{(2)}$ close to the middle of the bent transition $\hat{\tau}^{(2)}$, $T_4^{(2)}$ near the beginning of the second linear regime and $T_5^{(2)}$ exactly at the fixed final temperature $T_f$.

5.2.4 Comparison of designs

Usually, almost every experimental study begins with an overview of previous works and a collection of already published experimental data relevant to the research subject. In this
Chapter 5

Section, we are interested in obtaining practical recommendations on the data collection process of the heat capacity data in order to estimate the parameters of SRE model with high precision. To reach this goal, several alternative designs are generated based on the previously constructed locally $D$-optimal design (5.14) and their influence on the precision of SRE parameter estimates are compared via simulation.

First, we consider the properties of the collected experimental data on $C_P(T)$ of pure Cr that have been used to obtain the SRE parameter estimates (5.12) via least-squares method. These data are given by the current design $\xi_{\text{cur}}$. The design $\xi_{\text{cur}}$ is presented in Figure 5.2 and it contains 444 observations in total where 390 are distinct values. The measurements cover the temperature range $1.8 \leq T \leq 1800$ Kelvin. To the best of our knowledge there are no experiments on the heat capacity of pure Cr out of this range. The data represented in the $\xi_{\text{cur}}$ design have been collected without any application of the optimal design theory. The main goal of this data collection process was to find as much data as possible to cover the entire temperature range from 0K to the melting point of pure Cr.

The constructed locally $D$-optimal design (5.14) places $1/5$ of the total observations at the each support points $T_1 = 159.93$, $T_2 = 593.31$, $T_3 = 1034.87$, $T_4 = 1476.43$ and $T_5 = 1800$. Suppose we perform 445 measurements on the heat capacity of pure Cr, that is, just one experiment more than the total number of experimental points in the current design $\xi_{\text{cur}}$. Then an exact locally $D$-optimal design corresponding to $\xi^*_D$ (5.14) will contain 89 observations at each of the support points of $\xi^*_D$. According to these recommendations we can perform an experimental study to obtain this exact design and compare it to $\xi_{\text{cur}}$. However, since our goal is to collect experimental data from the available literature, it would be rather difficult to find so many measurements performed exactly at these 5 support points. Therefore, in order to make our results applicable to the data collection processes we slightly modify the recommendations of the locally $D$-optimal design $\xi^*_D$ (5.14).

Assume that the support points $T_i, i = 1,...,5$ corresponding to (5.14) are replaced by their non-empty neighborhoods $U_\delta(T_i) : |T_i - T| \leq \delta$ for some fixed size $\delta > 0$. Also define $\delta = 106.5$ and consider all $T_j, j = 1,...,444$ from $\xi_{\text{cur}}$ belonging to the neighborhoods $U_\delta=106.5(T_i), i = 1,...,5$. Then the following design

$$\xi^\text{exp}_D = \begin{pmatrix} U_\delta(159.93) & U_\delta(593.31) & U_\delta(1034.87) & U_\delta(1476.43) & U_\delta(1800) \\ 98 & 10 & 27 & 10 & 3 \end{pmatrix}, \quad (5.18)$$

is obtained by counting the number of $T_j, j = 1,...,444$ in each neighborhood. The design (5.18) is shown in Figure 5.4a and it contains 148 observations that correspond to $1/3$ of the observations for the design $\xi_{\text{cur}}$.

Note that the design $\xi^\text{exp}_D$ does not contain the equal proportion of observations in each neighborhood as it is recommended in (5.14). Therefore, an alternative exact design with equal number of repeated measurements in each neighborhood $U_\delta(T_i), i = 1,...,5$ has been considered. The simulated data have been generated from the SRE model (5.8) with the
parameters (5.12) and additive normally distributed random errors. Then we obtain
\[
\xi_{D}^{\text{sim}} = \begin{bmatrix}
U_{6}(159.93) & U_{6}(593.31) & U_{6}(1034.87) & U_{6}(1476.43) & U_{6}(1800)
\end{bmatrix}^{T}.
\] (5.19)

The design \( \xi_{D}^{\text{sim}} \) contains 150 observations and it is presented in figure 5.4b.

Figure 5.4: Generated designs based on (5.14) for the data collection process.

To make the alternative designs, \( \xi_{D}^{\text{sim}} \) and \( \xi_{D}^{\exp} \), comparable with \( \xi_{\text{cur}} \) we construct a design \( \xi_{1/3} \) which contains all points \( \{T_{i} : i = 3j - 2, j = 1, \ldots, 444\} \) from \( \xi_{\text{cur}} \). This means that \( \xi_{1/3} \) includes every third observation of the collected heat capacity data. The properties of all considered designs \( \xi_{\text{cur}}, \xi_{D}^{\text{sim}}, \xi_{D}^{\exp} \) and \( \xi_{1/3} \), are summarized in Table 5.2.

<table>
<thead>
<tr>
<th>Design</th>
<th>n</th>
<th>Description</th>
<th>Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current design, ( \xi_{\text{cur}} )</td>
<td>444</td>
<td>( {T_{j}}, j = 1, \ldots, 444 )</td>
<td>original experiments</td>
</tr>
<tr>
<td>Alternative design, ( \xi_{D}^{\exp} ) (5.18)</td>
<td>148</td>
<td>( {U_{6=106.5}(T_{i})}, ) where ( T_{i}, i = 1, \ldots, 5 ) are support points of (5.14)</td>
<td>original experiments</td>
</tr>
<tr>
<td>Simulated design, ( \xi_{D}^{\text{sim}} ) (5.19)</td>
<td>150</td>
<td>( {U_{6=106.5}(T_{i})}, ) where ( T_{i}, i = 1, \ldots, 5 ) are support points of (5.14)</td>
<td>generated points with (5.8)</td>
</tr>
<tr>
<td>Reduced design, ( \xi_{1/3} )</td>
<td>148</td>
<td>( {T_{i} : i = 3j - 2, j = 1, \ldots, 148} ) every third observation of ( \xi_{\text{cur}} )</td>
<td>original experiments</td>
</tr>
</tbody>
</table>

Table 5.2: Designs used in simulation studies

Similar to the calculations performed with the current design \( \xi_{\text{cur}} \), the least-squares estimates of the SRE model parameters (5.8) are obtained using the alternative designs, \( \xi_{D}^{\exp} \).
\( \xi^\text{sim} \), \( \xi^{1/3} \) and their values are reported in Table 5.3. The calculations have been performed using the R-package \textit{nls2} [Grothendieck (2013)].

| Design   | \( n \) | Parameter | Value   | Std.Error, \( SE \) | \( t \)-value | \( \text{Pr}(>|t|) \) |
|----------|---------|-----------|---------|---------------------|---------------|---------------------|
| \( \xi^\text{car} \) | 444     | \( \theta_E \) | 356.4   | 3.20                | 111.46        | < 2 \cdot 10^{-16} |
|          |         | \( \beta_1 \)  | 4.76 \cdot 10^{-3} | 0.259 \cdot 10^{-3} | 18.45         | < 2 \cdot 10^{-16} |
|          |         | \( \beta_2 \)  | 2.01 \cdot 10^{-2} | 0.213 \cdot 10^{-2} | 9.42          | < 2 \cdot 10^{-16} |
|          |         | \( \tau \)     | 1035    | 55.5                | 18.65         | < 2 \cdot 10^{-16} |
|          |         | \( \gamma \)    | 441.5   | 80.96               | 5.45          | 8.24 \cdot 10^{-8}  |
| \( \xi^\text{exp} \) | 148     | \( \theta_E \) | 356.8   | 3.35                | 106.52        | < 2 \cdot 10^{-16} |
|          |         | \( \beta_1 \)  | 4.94 \cdot 10^{-3} | 0.439 \cdot 10^{-3} | 11.347        | < 2 \cdot 10^{-16} |
|          |         | \( \beta_2 \)  | 1.77 \cdot 10^{-2} | 0.203 \cdot 10^{-2} | 8.706         | < 6.95 \cdot 10^{-15} |
|          |         | \( \tau \)     | 971.7   | 66.85               | 14.535        | < 2 \cdot 10^{-16} |
|          |         | \( \gamma \)    | 307.1   | 124.2               | 2.473         | 0.0146             |
| \( \xi^\text{sim} \) | 150     | \( \theta_E \) | 354.9   | 6.12                | 58.002        | < 2 \cdot 10^{-16} |
|          |         | \( \beta_1 \)  | 4.51 \cdot 10^{-3} | 0.380 \cdot 10^{-3} | 11.869        | < 2 \cdot 10^{-16} |
|          |         | \( \beta_2 \)  | 2.11 \cdot 10^{-2} | 0.102 \cdot 10^{-2} | 20.681        | < 2 \cdot 10^{-16} |
|          |         | \( \tau \)     | 1037    | 33.03               | 31.383        | < 2 \cdot 10^{-16} |
|          |         | \( \gamma \)    | 431.4   | 65.94               | 6.542         | 7.02 \cdot 10^{-5}  |
| \( \xi^{1/3} \) | 148     | \( \theta_E \) | 355.3   | 5.86                | 60.612        | < 2 \cdot 10^{-16} |
|          |         | \( \beta_1 \)  | 4.64 \cdot 10^{-3} | 0.489 \cdot 10^{-3} | 9.487         | < 2 \cdot 10^{-16} |
|          |         | \( \beta_2 \)  | 1.81 \cdot 10^{-2} | 0.423 \cdot 10^{-2} | 4.283         | < 3.37 \cdot 10^{-5} |
|          |         | \( \tau \)     | 998.8   | 123.8               | 8.067         | < 2.65 \cdot 10^{-13} |
|          |         | \( \gamma \)    | 458.6   | 172.9               | 2.652         | 0.00891            |

Table 5.3: The \textit{nls2}-output for the fits based on \( \xi^\text{car} \), \( \xi^\text{exp} \), \( \xi^\text{sim} \) and \( \xi^{1/3} \) designs.

Note that the designs \( \xi^\text{exp} \), \( \xi^\text{sim} \) and \( \xi^{1/3} \) resulting estimates of the SRE model parameters close to the ones of \( \xi^\text{car} \) but using 1/3 of the observations and thus less time for the data collection is required. Now these three alternatives to the current design \( \xi^\text{car} \) are compared with each other in order to identify the most appropriate one. To perform the evaluation of the alternative designs, the accuracy of the parameters estimates is analyzed by comparing the values of standard errors \( SE \) reported in Table 5.3 with each other. The goal of this analysis is check whether the designs \( \xi^\text{exp} \), \( \xi^\text{sim} \) which are constructed based on the modified recommendations of the locally \( D \)-optimal design \( \xi^\text{opt} \) (5.14) result in an improvement of the parameter estimates, that is, whether there is a reduction of the corresponding standard errors in comparison to the design \( \xi^{1/3} \). Such a technique is widely used for the evaluation of several alternative optimal designs in industrial applications.

Using on the standard error values of the parameter estimates given in Table 5.3, we calculate for each parameter estimate the ratio of standard error based on design \( \xi^{1/3} \) over the standard error based on each of the design \( \xi^\text{exp} \) and \( \xi^\text{sim} \) designs and the results are reported.
in Table 5.4. This ratio can be interpreted as a reduction factor of the standard errors by using $\xi_{D}^{exp}$ or $\xi_{D}^{sim}$, if its value greater than 1. If this factor is equal to 1, it means that no changes in the standard errors of the parameter estimates is observed. A value less than 1 denotes that the accuracy of parameter estimates will be reduced if the design $\xi_{D}^{exp}$ or $\xi_{D}^{sim}$ used instead of $\xi^{1/3}$.

<table>
<thead>
<tr>
<th></th>
<th>$\theta_E$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\tau$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SE^{1/3}$</td>
<td>1.75</td>
<td>1.12</td>
<td>2.08</td>
<td>1.85</td>
<td>1.39</td>
</tr>
<tr>
<td>$SE^{exp}$</td>
<td>0.96</td>
<td>1.29</td>
<td>4.14</td>
<td>3.75</td>
<td>3.75</td>
</tr>
<tr>
<td>$SE^{sim}$</td>
<td>0.96</td>
<td>1.29</td>
<td>4.14</td>
<td>3.75</td>
<td>3.75</td>
</tr>
</tbody>
</table>

Table 5.4: Reduction factors of $SE$.

Note that the application of the $\xi_{D}^{exp}$ design for the estimation of the SRE model parameters in comparison to the $\xi^{1/3}$ design significantly reduces the $SE$ values of all model parameters by the factors presented in Table 5.4. A similar reduction of the standard errors is also observed for the $\xi_{D}^{sim}$ design, except for the parameter $\theta_E$, where this factor is equal to 0.96. At the same time the accuracy of other SRE model parameters is significantly improved: by a factor of 4.14 for the parameter $\beta_2$ and by a factor of 3.75 for the parameters $\tau$ and $\gamma$. The fits of the segmented heat capacity model (5.8) based on data from the alternative designs $\xi_{D}^{sim}$ and $\xi_{D}^{exp}$ are shown in Figures 5.5a and 5.5b respectively.

![Figure 5.5](image)

**Figure 5.5:** Fitted SRE model with $\xi_{D}^{exp}$ and $\xi_{D}^{sim}$ designs.

During the simulation study we have encountered some difficulties in the estimation of the parameters of the segmented heat capacity model (5.8) when the design $\xi^{1/3}$ is used. In particular, several computational procedures available in the R-package nls2 have failed to
find a solution of the nonlinear least-squares problem. This can be interpreted as some kind of computational inefficiency of the design $\xi^{1/3}$, which has been generated without taking into account the modified recommendation of the locally $D$-optimal design $\xi^*_D$.

The alternative designs $\xi_{D}^{exp}, \xi_{D}^{sim}$ based on the modified recommendation of the locally $D$-optimal design $\xi^*_D$ showed a significant improvement of the accuracy of the parameter estimates. Taking into account that usually measurements are performed for some finite and fixed temperature range and not for the entire temperature range as $[0, T_m]$, we recommend to set up the size of the neighborhoods corresponding to the support points, to be equal to any values between 100 and 200$K$. Such temperature ranges are typical for experimental studies of the heat capacity and other thermodynamic quantities that are usually reported together.
A novel physically-based model for the description of the thermodynamic properties from 0K up to the melting point has been proposed in this thesis and its properties have been investigated from different perspectives. The proposed modeling approach is based on the fitting of the heat capacities by a physically-sounded segmented model which allows us to consider different physical contributions to the heat capacity that can be activated in low and high temperatures. The thermodynamic properties of pure Cr, Al and Fe have been modeled by a segmented regression model and the proposed method provides a very good description of experimental data at low and high temperatures. Especially, significant improvement of the description of experimental data has been achieved in the low temperature range, which was an issue for the existing models. The obtained estimates of the model parameters have been successfully validated from physical points of view with respect to the relevant thermodynamic properties. Moreover, the new segmented model has been compared with the already existing physically-based formulations and it has been demonstrated that for all selected pure elements, the proposed model is most appropriate for the description of the heat capacity data with respect to several statistical criteria, which measure the quality of a fitted model to experimental data.

Additionally to this practical issue, the asymptotic theory for the key component of the segmented heat capacity model, the bent-cable model, is developed. In particular, the consistency and asymptotic normality of the nonlinear least-squares estimator is proved under non-standard assumptions on the error distribution. Based on the established asymptotic theory for the bent-cable model and application results, optimal designs for the segmented regression model are constructed. A set of recommendations is given regarding how heat capacity measurements should be collected from different literature sources in order to
estimate the parameters of the segmented heat capacity model as accurately as possible. The optimization problem has been considered in terms of the approximate optimal design theory and locally $D$-optimal designs have been determined. Since the most comprehensive study has been performed to pure Cr, this element has been selected for the simulation study, to demonstrate the advantages of optimal design theory with respect to misspecification of the parameters.

The modeling concept presented in this thesis has an important practical application for the accurate description of existing materials and robust designs of new materials. The proposed segmented model, supported by the developed asymptotic theory and the practical recommendations for the data collection process based on the application of optimal design theory, can be used as a basis for the development of a new generation of thermodynamic databases. These databases should be based on the physically-sounded models and take into account the available theoretical and experimental data. The presented segmented model is satisfying all these requirements and can be considered as a candidate model to establish a standard for the description of the temperature dependency of the Gibbs energy.

Such an investigation of the practical engineering problem can be considered as a general strategy for the robust modeling of thermo-physical properties and development of a new generation of CALPHAD databases. Moreover, this modeling strategy reduces the time required for traditional thermodynamic assessment of complex multicomponent alloys and increases a predictive capability of the thermodynamic databases. The established modeling approach presented in this work has been successfully extended to other pure elements such as Ge, Ir, Mo, Nb, Re, W, Ni [Roslyakova et al. (2016c)], Nb-Mo, Mo-Ta, Ta-Nb binary and Mo-Nb-Ta ternary systems [Roslyakova et al. (2016b)].


Selbständigkeitserklärung

Ich erkläre, dass ich meine Dissertation ”Modeling thermodynamical properties by segmented non-linear regression” selbstständig verfasst habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe, sowie Zitate kenntlich gemacht habe.

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