CpFit program

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Chapter 1

Thermodynamic Model

CpFit program is designed for approximation of experimental heat capacities and heat contents using third generation CALPHAD models. This class of models allows to approximate experimental data in the entire temperature range including the low-temperature interval. It uses approach has been developed by Voronin and Kutsenok [1] and extended by Bigdeli et al. [2] All thermodynamic functions (e.g. heat capacity, entropy and enthalpy) are represented as sums of Einstein functions terms with optional polynomial part:

$$C_p(T) = \sum_{i=1}^{m} \alpha_i C_{\mathrm{E}} \left(\frac{\theta_i}{T}\right) + R \sum_{i=1}^{p} a_i \left(\frac{T}{T_0}\right)^{n_i} ; \ \frac{C_{\mathrm{E}}(x)}{R} = \frac{3x^2 e^x}{(e^x - 1)^2} \tag{1.1}$$

$$S(T) - S(0) = \sum_{i=1}^{m} \alpha_i S_{\mathrm{E}} \left(\frac{\theta_i}{T}\right) + R \sum_{i=1}^{p} \frac{a_i}{n_i} \left(\frac{T}{T_0}\right)^{n_i} ; \ \frac{S_{\mathrm{E}}(x)}{R} = 3\left[\frac{x}{e^x - 1} - \ln\left(1 - e^{-x}\right)\right] \tag{1.2}$$

$$H(T) - H(0) = \sum_{i=1}^{m} \alpha_i \left[U_{\mathrm{E}} \left(\frac{\theta_i}{T}\right) - U_0\right] + R \sum_{i=1}^{p} \frac{a_i T}{n+1} \left(\frac{T}{T_0}\right)^{n_i} ; \ \frac{U_{\mathrm{E}}(x) - U_0}{RT} = \frac{3x}{e^x - 1} \tag{1.3}$$

where α_i, θ_i and a_i are adjustable model parameters, $T_0 = 298.15$ K. The adjustable parameters can be estimated from experimental data using least squares method. An exact universal gas constant value $R = 8.314462618\ \mathrm{J} \cdot (\mathrm{mol} \cdot \mathrm{K})^{-1}$ from CODATA 2018 is used in the CpFit program. In eqs. 1.1, 1.2 and 1.3 α_i and a_i values are dimensionless and θ_i values are expressed in K.

The thermodynamic model of heat capacity based on Einstein functions allows to approximate $C_p(T)$, $S(T) - S(0)$ and $H(T) - H(0)$ in a wide temperature range using a unified set of parameters. Also unlike polynomial models it can give a physically correct extrapolation to a wider temperature range.

Implementation of this model in CpFit hides all analytical expressions and technical details and allow to use it as an ordinary statistical package for a nonlinear regression.

Chapter 2

Optimization Procedure

2.1 Theory

In CpFit program α_i and θ_i parameters are found by the least squares method using the next sum of squares χ^2:

$$\chi^2(\beta) = \sum_{i-1}^{n} W_i^2 \left[Y_i^{\text{calc}}(\beta) - Y_i^{\text{exp}} \right]^2 \tag{2.1}$$

where $Y_i = c_p(T_i)$ or $Y_i = H(T_{2,i}) - H(T_{1,i})$, $W_i = \omega_i$ for the case of absolute deviation or $W_i = \omega_i \left(Y_i^{\text{exp}}\right)^{-1}$ for the case of relative deviation where ω_i are user-defined statistical weights (default values are $\omega_i = 1$) and β is generalized notation for the α_i and θ_i model parameters. To minimize χ^2 value Levenberg-Marquardt algorithm implementation from `levmar` library [3] are used.

Standard deviations of the α_i and θ_i parameters are calculated using the next formula:

$$s_\beta^2 = \hat{\sigma}^2 \text{diag}\left[\left(J^\top J \right)^{-1} \right];\ J_{ij} = \frac{\partial Y_i^{\text{calc}}}{\partial \beta_j};\ \hat{\sigma}^2 = \frac{\chi^2}{n - 2m} \tag{2.2}$$

where J is Jacobian, n is number of experimental points, m is number of terms (and $2m$ is number of parameters respectively), $\hat{\sigma}^2$ is the model standard error. Parameters confidence intervals can be estimated as:

$$\Delta\beta = s_\beta \cdot t_{p,f};\ f = n - 2m \tag{2.3}$$

where $t_{p,f}$ is t-distribution two-sided quantile with probability p (CpFit uses $p = 0.95$ for 95 % confidence intervals), $f = n - 2m$ is number of freedom degrees. Usually $t_{\alpha,f} \approx 2 \div 3$.

CpFit also can estimate standard deviations of thermodynamic functions that can be used to estimate their confidence intervals (don't mix with prediction intervals!) using the next formula:

$$s_Y(T) = \sqrt{J_x^\top C J_x} = \hat{\sigma} \sqrt{J_x^\top \left(J^\top J \right)^{-1} J_x} \tag{2.4}$$

where C is covariance matrix, $J_x = J_x(T)$ is column vector that has the next layout:

$$J_x(T) = \begin{pmatrix} \frac{\partial Y(T)}{\partial \beta_1} \\ \vdots \\ \frac{\partial Y(T)}{\partial \beta_{2m}} \end{pmatrix} \tag{2.5}$$

Confidence intervals of $Y(T)$ thermodynamic functions (i.e. c_p and $H(T) - H(T_0)$ at the point (T) can be calculated using the next relationship similar to eq 2.3:

$$\Delta Y = s_Y \cdot t_{p,f};\ f = n - 2m \tag{2.6}$$

If heat capacity dependence has anomalies that cannot be described by Einstein-Planck functions sum it is possible to add extra terms, i.e. use the next formula for $C_p(T)$:

$$C_p(T, \vec{\alpha}, \vec{\theta}, \vec{b}_1, \ldots, \vec{b}_k) = C_p^{\mathrm{BL}}(T, \vec{\alpha}, \vec{\theta}) + \sum_{i=1}^{k} C_{p,i}^{\mathrm{ex}}(T, \vec{b}_i) \tag{2.7}$$

where C_p^{BL} is Einstein-Planck function sum ("baseline" term), C_p^{ex} is arbitrary terms ("extra" terms) and $\vec{b}_i$ is vector with optimized model parameters for i-th extra term. A list of extra terms supported by CpFit program is given in Chapter 4.2. The next algorithm is used to optimize model parameters:

1. Optimize $\vec{\alpha}$ and $\vec{\theta}$ parameters by minimizing eq. 2.1 using only data outside C_p anomalies.

   Note: in the current version of CpFit program experimental enthalpies are not excluded at all.

2. Optimize $\vec{b}_i$ values for each extra term separately using the next objective function:

$$\chi^{\mathrm{ex}}\left(\vec{b}_i\right) = \sum_j \left(W_j^{(i)}\right)^2 \left[Y_j^{(i)} - Y_j^{(i),\mathrm{BL}} - Y_j^{(i),\mathrm{ex}}\left(\vec{b}_i\right)\right]^2 \tag{2.8}$$

2.2 Practical Tips

The goal of the optimization process is to minimize the model standard error $\hat{\sigma}^2$. However during increasing the number of parameters there is a risk to obtain an ill-conditioned task and not reliable values set. To avoid it you can follow the next tips:

1. Begin the optimization for 2–3 terms (or 4–6 parameters) and gradually increase it using previous results as initial approximations

2. Avoid statistically not significant coefficients (i.e. the conditions $\alpha_i \geq \Delta\alpha_i \approx 2s_{\alpha_i}$ and $\theta_i \geq \Delta\theta_i \approx 2s_{\theta_i}$ should be satisfied). CpFit program will automatically highlight in red statistically not significant coefficients (see Figure 4.2).

3. Both α_i and θ_i must be positive numbers (automatically controlled by the CpFit optimization engine).

You can also use evaluations procedures with automatic selection of terms number (see Chapter 4.2). They use iterative addition of new terms and control of statistical significance of them using t-criterion. However they sometimes can give number of terms less than can be obtained by manual selection of initial approximations.

If you optimize heat capacity and enthalpy data together always remember that their orders of magnitude are different, i.e. $\frac{\Delta H}{c_p} \approx 10^3$. In this case either relative deviations or adequate statistical weights must be used. In the case of $\omega_i = 1$ for all data and absolute deviations c_p data will not be optimized correctly.

Chapter 3

File Formats

3.1 Experimental data file format

Input data can be supplied in human readable text files with `.dat` or `.txt` extension. A description of the format is present in Table 3.1.

The main features of the format are:

- .dat file is an ordinary ASCII text file
- Dot (and only dot) is used as a decimal separator
- Both DOS/Windows and UNIX line endings are supported
- Numbers are separated by either spaces or tabs (one or multiple)
- Empty lines and comments in the data set are ignored without warning

It currently supports two kind of data: heat capacities $C_p(T)$ and enthalpies/heat content $H(T_2) - H(T_1)$.

3.2 Model parameters file format

Files with model parameters can be either exported from the Results Window or imported to the Main Window. That files have `.csv` format, semicolon `;` is used as a separator and dot `.` is used as a decimal point sign. An example of the `.csv` file with model parameters is given below:

```
alpha;dalpha;salpha;theta;dtheta;stheta
14.0168725905787;0.914895;0.457827;3583.8945135367;151.031;75.5782
6.26905917915019;0.401292;0.200813;1393.30718925711;88.5056;44.2895
7.3042223855265;0.350348;0.175319;688.948063566627;41.8236;20.9292
5.69813172425687;0.238324;0.119261;306.421049769356;20.2346;10.1257
2.86883301382133;0.329537;0.164905;145.550553624711;12.1593;6.0847
0.289410000831521;0.171896;0.0860195;66.9793881821218;12.0881;6.04905
```

The first row contains columns description and can contain the next values:

- `alpha` — α_i model parameter, dimensionless.

Table 3.1: .dat file format used by CpFit

Line number	**Example**	**String content**

1–3	`Heat capacity (ScF3)`
	`Temperature`
	`Cp`
		Arbitrary text information

4	`539`	Number of dots
5	`0`	Reserved and should be equal to zero (intended to be a number of dots to be ignored at the end of file but it is not used now)

6–k	`303.35 82.806`
	`302.98 82.421  0  1`
	`303.01 82.417  1  0.85`
	`303.01 82.417  1  0.85 Rom15`
		Heat capacity experimental data. Either T–C_p lines or T-C_p–rf–ω–Data series lines where ω are statistical weights from eq 2.1 and rf is "use relative deviation" flag (can be either 0 or 1).
		If ω or rf are omitted their default values will be used for this line ($\omega = 1$ and $rf = 0$). Data series name can be omitted.

6–k	`H 298.15 940 46534 1 1 Aga03`	Enthalpy experimental data. Kept as T_1–T_2–ΔH–rf–ω–Data series lines where $\Delta H = H(T_2) - H(T_1)$. rf, ω and Data series names can be omitted. Format is similar to C_p data format.
6–k	`# Some comment`	Comment (will be ignored by CpFit). Note: comments won't be saved by CpFit if "Save as" option is used.
6–k	`X 265 310 DEFAULT 293.91 |` `1 1e-005 0.5`	Extra (excess) heat capacity term. Kept as `X`–T_min–T_max–Term name–Constant parameters—`|`—Optimized parameters (initial values).
6–k	`AL 3.012 1.022`	Initial approximation for α parameters.
6–k	`TH 1023.2 3.02e2`	Initial approximation for θ parameters.
6–k	`PO 0.079517 1 0.31421 4`	n values and initial approximation for a parameters for the polynomial part.

- `dalpha` — $\Delta\alpha_i$, 95 % confidence interval (using two-sided t-distribution quantile) for the model parameter α_i.
- `salpha` — $s(\alpha_i)$ standard deviation for the model parameter α_i.
- `theta` — θ_i model parameter, K.
- `dtheta` — $\Delta\theta_i$, 95 % confidence interval (using two-sided t-distribution quantile) for the model parameter θ_i.
- `stheta` — $s(\theta_i)$, standard deviation for the model parameter θ_i.

Export from the Results Window (see Figure 4.2) gives all six columns. Import to the Main Window uses only two columns `alpha` and `theta`.

3.3 Examples

Several examples of `.dat` files with heat capacity and heat content are supplied with CpFit program. They contain real experimental data:

- `natrolite.dat` — natrolite $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ [4]. Contains no extra terms.
- `K_natrolite.dat` — potassium-substituted natrolite $K_{1.86}Na_{0.01}Ca_{0.04}Mg_{0.01}\,[Al_{1.96}Si_{3.04}O_{10}] \cdot 2.33H_2O$ [5]. Contains one extra term that describes one lambda-transition.
- `Tl_natrolte.dat` — thallium-substituted natrolite $Tl_{1.87}Na_{0.05}Mg_{0.03}\,[Al_{1.98}Si_{3.04}O_{10}] \cdot 2.72H_2O$ [6]. Contains one extra term that describes two partially overlapping phase transitions.
- `ThO2.dat` — thorium dioxide ThO_2 [7, 8, 9, 10, 11, 12, 13]. Contains one extra term that describes one (pre-melting) lambda-transition.
- `UO2.dat` — uranium dioxide UO_2. Contains one extra term that describes two lambda-transitions. [14, 15, 16, 17, 18, 19, 20, 21].

`K_natrolite.dat` and `Tl_natrolite.dat` contain only heat capacity data, other `.dat` files — both heat capacity and heat content data.

3.4 Custom extra terms file format

Custom extra terms are written in Lua 5.3 language in text files with `.lua` extension. Recompilation of CpFit is not required for their usage. Each file is Lua script that can contain only one extra term. The term is returned in the form of table (array) by `return` statement. An example of the script:

```
-- Custom excess heat capacity term for CpFit
-- Cp(T)/R = CpE(T)/R + a*T + b*T^2 model implementation
-- Chase M.W. et al. // Calphad Vol. 19, NO. 4, pp. 437-447, 1995
return {
```

```
  type = 'EPPOLY',
  description = 'Einstein + poly',
  formula = 'C_p/R=3x^2e^x/(e^x-1)^2+aT+bT^2; x=TH/T',
  cpfunc = function(T, lsqparam, fixparam, Tmin, Tmax)
    local theta = lsqparam[1]
    local a, b = lsqparam[2], lsqparam[3]
    local x = theta / T
    local ex = math.exp(x)
    local cp = 0
    if x < 300 then
      cp = R * (3*x^2 * ex / (ex - 1) ^ 2 + a*T + b*T^2);
    else
      cp = R * (3*x^2 / ex + a*T + b*T^2);
    end
    return cp
  end,
  lsqparam = {100, 0, 0},
  lsqparam_names = {'theta', 'a', 'b'},
  lsqparam_lb = {0,   -1e5, -1e5},
  lsqparam_ub = {1e5,  1e5,  1e5},
  fixparam = {},
  fixparam_names = {}
  Tmin = 0.0,
  Tmax = 3000.0
}
```

The next fields in the table are required:

- `type` — term type name. Must be a string. Will be used in `.dat` files as term type identifier.
- `description` — term short description (will be shown in CpFit GUI). Must be a string.
- `formula` — formula that will be shown in CpFit GUI. Must be a string. Simplified subset of LaTeX formatting is supported (`_` for subscripts and `^` for superscripts; no brackets support). Greek letters and other mathematical symbols must be written in UTF-8, LaTeX formatting is not supported for them.
- `cpfunc` — function that calculates heat capacity value. It has five inputs and one output, i.e. `function(T, lsqparam, fixparam, Tmin, Tmax)`. The function must return C_p numeric value in $\mathrm{J} \cdot (\mathrm{mol} \cdot \mathrm{K})^{-1}$.
  - `T` — temperature, K (numeric value)
  - `lsqparam`, `fixparam` — tables with current values of model parameters that are filled with numeric values. Their size is consistent to the default values given in the script (see below).
  - `Tmin`, `Tmax` — current values of $T_{\min}$ and $T_{\max}$ parameters. They are numeric values.
- `lsqparam` — default initial approximation for LSQ optimized parameters.

- `lsqparam_lb`, `lsqparam_ub` — lower and upper boundaries for LSQ optimized parameters.
- `lsqparam_names` — LSQ optimized parameters names.
- `fixparam` — default values for fixed parameters.
- `fixparam_names` — fixed parameters names.
- `Tmin`, `Tmax` — default value for minimal and maximal temperatures, K.

There are several predefined constants and functions:

- `R` — universal gas constant
- `CAL` — number of joules in calorie (4.184)
- `CpDebye` — `CpDebye(T, theta)` function, implementation of Debye heat capacity model:

$$\frac{C_p^{\mathrm{D}}\left(T_D, T\right)}{R} = 9\left(\frac{T}{T_{\mathrm{D}}}\right)^3 \int_0^{\frac{T_{\mathrm{D}}}{T}} \frac{x^4 e^x}{\left(e^x - 1\right)^2}\, dx \tag{3.1}$$

Chapter 4

User interface

4.1 Installation

CpFit program has the next system requirements:

- Microsoft Windows XP/Vista/7/8/8.1/10 (32-bit or 64-bit)
- 256 Mb of RAM
- 5 Mb of free disk space
- SVGA with 1024x768 resolution or higher

The program doesn't require any installation. You can just unpack an archive with the program and begin the work.

If you want to make the program from the source code (that is not required) you will need:

- CMake 3.0 or higher.
- GCC C++ compiler 4.5.2 or higher and MinGW environment.
- levmar 2.6 or higher.
- Lua 5.3.x.
- wxWidgets 3.0.2 or higher.
- Doxygen and MathJax are not required but highly recommended (to generate documentation about the source code).

More detailed information about compilation and linking is given in the source code.

4.2 Main window

Main window (see Figure 4.1) allows to load, save and edit experimental data and manage the parameters optimization process.

A menu of the main window contains the next items:

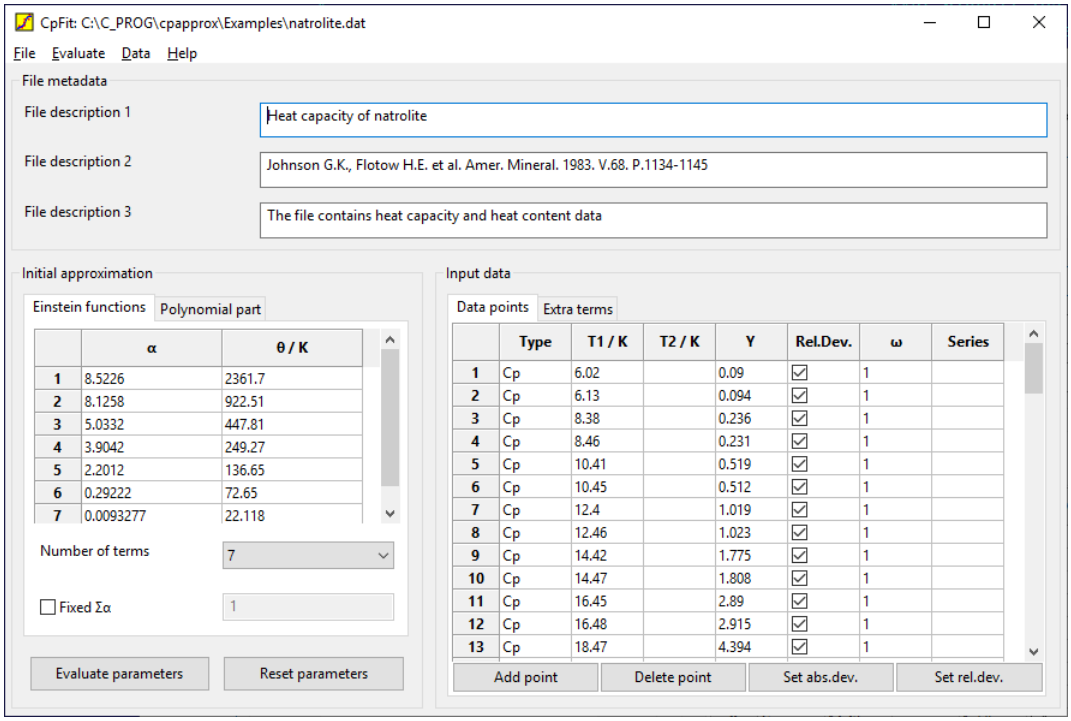

Figure 4.1: CpFit program main window

- **File** — Contains operations for loading and saving experimental data from and to files.
  - **New** — Clear all data in the window.
  - **Open** — Open `.dat` file with C_p data.
  - **Save as** — Save current data set into `.dat` file.
  - **Load parameters** — Loads parameters (i.e. initial approximation) from `.csv` file and puts them into an initial approximation table.
  - **Load custom extra term** — Loads custom user-defined extra terms from `.lua` file (must be written in Lua 5.3 language)
  - **Exit** — Close the main window and exit from the program.
- **Evaluate** — Different variants of the model parameters evaluation.
  - **Parameters values** — Evaluate only values, number of terms is fixed (similar to "evaluate parameters" button).
  - **Parameters set (don't use init.approx.)** — Evaluation of both number of terms and parameters values without using of an initial approximation given by a user.
  - **Parameters set: extra terms only** — Evaluate only extra terms parameters , use base line parameters $\vec{\alpha}$ and $\vec{\theta}$ from the initial approximation as constants.
  - **Parameters set (use init.approx.)** — Evaluation of both number of terms and parameters values with using of an initial approximation given by a user.

- **Evaluate without optimization** — Creates results window with parameters given as initial approximation by a user but doesn't run any optimization process. Can be used without any experimental data. If experimental data are given the program will evaluate deviations and parameters confidence intervals.

- **Data** — Operations with experimental data
  - **Sort data** — Sort data points by temperature and by data series identifier.

- **Help** — Contains information about the program.
  - **About** — Show the window with a brief information about the program.

All evaluation methods that evaluate number of terms use the next algorithm:

1. Set initial approximation. CpFit can use either user-defined initial approximation (see Figure 4.1) or set it automatically. In the case of automatic selection one term with $\alpha_1 = 0.1$, $\theta_1 = 1$ will be used.

2. Run optimization for a given initial approximation and test an obtained set of parameters for statistical significance (using t-test with two-sided 95 % confidence intervals, see eq. 2.3).

3. If all parameters are statistically significant — add new term with $\alpha_i = 10^{-3}$ and $\theta = 1$ and go to the Step 2. If some parameters are statistically not significant — take the previous result of optimization and return it.

Such algorithm allows to obtain reasonable results in most cases. However in some cases it can give less model terms than possible and manual setting of an initial approximation consisting from several terms may be beneficial.

The main window contains three areas: file metadata area, initial approximation area and input data area.

File metadata area contains three arbitrary text strings that are used to describe a content of the data set. It is recommended to use the first line for data series description and leave default values in the second and in the third line.

Initial approximation area contains tools for setting initial values of model parameters and number of terms in eq 1.1, 1.2 and 1.3. It contains two tabs: "Einstein functions" for $\vec{\alpha}$ and $\vec{\theta}$ parameters and "Polynomial part" for $\vec{a}$ and n parameters. Number of polynomial terms and n_i values should be set manually by a user and won't be changed during the optimization procedure.

- "Einstein functions" tab elements:
  - *Table* — This table contains values for the weighted Einstein-Planck functions sum. Each row corresponds to the model term, "α" and "θ / K" columns correspond to α_i and θ_i parameters respectively. Note that the content of this table can be modified by results window by means of transferring results into initial approximation area.
  - *Number of terms* combo box — Use this combo box to select a desired number of terms (Einstein functions).
  - *Fixed* $\sum\alpha$ check box and text field are used to enable or disable $\sum_i \alpha_i = N_{\text{atoms}}$ constraints. The constraint is disabled (and check box is unchecked) by default.

- "Polynomial part" tab elements:
  - *Table* — This table contains values for the model parameters. Each row correspond to the model term, "`a`" and "`n`" columns correspond to a_i and n_i parameters in the polynomial part respectively. Note that the content of this table can be modified by results window (by means of transferring results into initial approximation area).
  - *Number of terms* combo box — Use this combo box to select a desired number of terms in the polynomial.
- *Evaluate parameters* button — Runs a proces of the parameters optimization. Results window will be opened.
- *Reset parameters* button — Sets each α_i and each θ_i value in the table to 10^{-6} and 1 respectively.

Input data area contains the data set and extra terms that will be used for model parameters optimization. It consists of two tabs: *Data points* tab and *Extra terms* tab.

Data points tab allows to view and edit all experimental points. It contains the next elements:

- *Table* — Contains the used data set and contains seven columns:
  - `Type` — data type (either heat capacity `Cp` or enthalpy `H`). Selected by combo box.
  - `T1 / K` — temperature in K. It is either T for $C_p(T)$ (heat capacity) or T_1 for $H(T_2) - H(T_1)$ (enthalpy) data.
  - `T2 / K` — temperature in K. It is T_2 for $H(T_2) - H(T_1)$ (enthalpy) data. In the case of heat capacity data it is ignored and uneditable.
  - `Y` is for C_p in $\mathrm{J} \cdot \mathrm{mol} \cdot \mathrm{K}^{-1}$.
  - `Rel.dev.` — absolute/relative deviation selection
  - ω — statistical weights ω_i from eq 2.1.
  - `Series` — data series ID that is used for markers and legends at 2D plots.
- *Add point* button — Adds a new point into the table.
- *Delete point* button — Removes selected rows from the table.
- *Set abs.dev.* button — Sets all deviations for all points as absolute (i.e. unselects all checkboxes in the third row)
- *Set rel.dev.* button — Sets all deviations for all points as relative (i.e. selects all checkboxes in the third row)

Extra terms tab allows to modify extra terms in the heat capacity model that cannot be described by Einstein-Planck functions sum. It contains the next controls:

- *Terms* combo box — allows to select the current term.
- *Add* button — adds a new term.

- *Delete* button — removes the current term.
- *Fix.param.* table — contains fixed parameters c_i that are not changed during extra terms parameters optimization.
- *LSQ param.* table — contains varied parameters b_i that are optimized by the least squares method.
- *Term type* combo box — select the type of the current term. The possible options are:
  - `Default` (named as `DEFAULT` in `.dat` files) — default term for description of lambda-transition, i.e.:

$$\frac{C_p^{\text{ex}}}{R} = b_1 \exp\left[b_2\left(b_3\Delta T - |\Delta T|\right)\right];\ \Delta T = T - T_{\text{tr}};\ T_{\text{tr}} = c_1 \tag{4.1}$$

  - `Two terms` (named as `TWOTERMS` in `.dat` files) — sum of two terms for description of two partially overlapping lambda-transitions.

$$\frac{C_p^{\text{ex}}}{R} = \sum_{i=1}^{2} d_1^{(i)} \exp\left[d_2^{(i)}\left(d_3^{(i)}(\Delta T)_i - |(\Delta T)_i|\right)\right];\ (\Delta T)_i = T - T_{\text{tr},i};\ T_{\text{tr},i} = c_i \tag{4.2}$$

$$d_i^{(j)} = b_{i+3(j-1)} \tag{4.3}$$

  - `Left exp.` (named as `LEFTEXP` in `.dat` files) — exponential function for description of the left side of a peak.

$$\frac{C_p^{\text{ex}}}{R} = b_1 \exp\left[b_2\left(T - T_{\max}\right)\right] \tag{4.4}$$

  - `Right exp.` (named as `RIGHTEXP` in `.dat` files) — exponential function for description of the left side of a peak.

$$\frac{C_p^{\text{ex}}}{R} = b_1 \exp\left[-b_2\left(T - T_{\min}\right)\right] \tag{4.5}$$

  - `Left exp.2` (named as `LEFTEXP2` in `.dat` files) — exponential function for description of the left side of a peak (sum of the two terms).

$$\frac{C_p^{\text{ex}}}{R} = b_1 \exp\left[b_2\left(T - T_{\max}\right)\right] + b_3 \exp\left[b_4\left(T - T_{\max}\right)\right] \tag{4.6}$$

  - `Right exp.2` (named as `RIGHTEXP2` in `.dat` files) — exponential function for description of the left side of a peak (sum of the two terms).

$$\frac{C_p^{\text{ex}}}{R} = b_1 \exp\left[-b_2\left(T - T_{\min}\right)\right] + b_3 \exp\left[-b_4\left(T - T_{\min}\right)\right] \tag{4.7}$$

  - `Skewed` (named as `SKEWED` in `.dat` files) — function based on Gauss bell curve but with possibility of asymmetry.

$$\frac{C_p^{\text{ex}}}{R} = \frac{b_1 e^{-x^2}}{1 + e^{-b_2 x}};\ x = \frac{T - b_3}{b_4} \tag{4.8}$$

  - `Empty` (named as `EMPTY` in `.dat` files) — function that is always equal to 0. Useful for just excluding heat capacity anomalies without their approximation.
  - Custom terms written in Lua. See Chapter 3.4 for details.

4.3 Results window

Results window (see Figure 4.2) contains an optimized set of parameters. It allows to create reports, draw 2D plots and different tables using the optimized parameters.

A menu of the main window contains the next items:

- **File** — File input-output (exporting parameters to files)
  - **Save as CSV** — Exports optimized baseline parameters into `.csv` file readable by MS Excel and another programs.
  - **Save as HTML** — Exports optimized parameters and model errors into `.html` file that can be considered as a report suitable for printing.
- **Plots** — Creation of plots (thermodynamic functions, absolute deviations, relative deviations). Every new plot will be opened in a separate window.
  - **Cp function** — Plots for the $C_p(T)$ function.
  - **Cp/T function** — Plots for the $C_p(T)/T$ function.
  - **H function** — Plots for the $H(T) - H_0$ function. The next graphs are supported:
    - **H plot** — Plots $H_T - H_0$ function without experimental points.
    - **Absolute residuals** — Plots absolute residuals for all experimental points.
    - **Relative residuals** — Plots relative residuals for all experimental points.
    - **H(T)-H(T0) plot** — Plots a figure with both theoretical $H_T - H_{T_0}$ function and experimental data. Two forms are possible: $H_T - H_{T_0}$ function and $(H_T - H_{T_0}) / (T - T_0)$ function.
  - **S function** — Plots for the $S(T)$ function.
- **Tables** — Creation of tables with thermodynamic data in separate windows. All tables can be exported into `.csv` files.
  - **Thermodynamic functions** — Customizable table with tabulated thermodynamic functions values (and their confidence intervals). $C_p(T)$, $H(T) - H(0)$ and $S(T)$ functions are supported.
  - **Residuals** — Table with absolute and relative residuals for experimental points.
    - **Cp residuals** — residuals for $C_p(T)$ experimental points.
    - **H residuals** — residuals for $H(T_2) - H(T_1)$ experimental points.
- **Evaluate** — Evaluates some extra properties and values useful for management of optimization procedure.
  - **Low-T S correction** — Allows to evaluate deviation of isobaric heat capacity $C_p(T)$ from Debye function at low temperatures. Such estimation can be used for correction of entropy values.

Results window contains two areas: model parameters area and Cp model errors area.

Model parameters area contains the optimized parameters of the model. It contains two tabs: base line tab and extra terms tab:

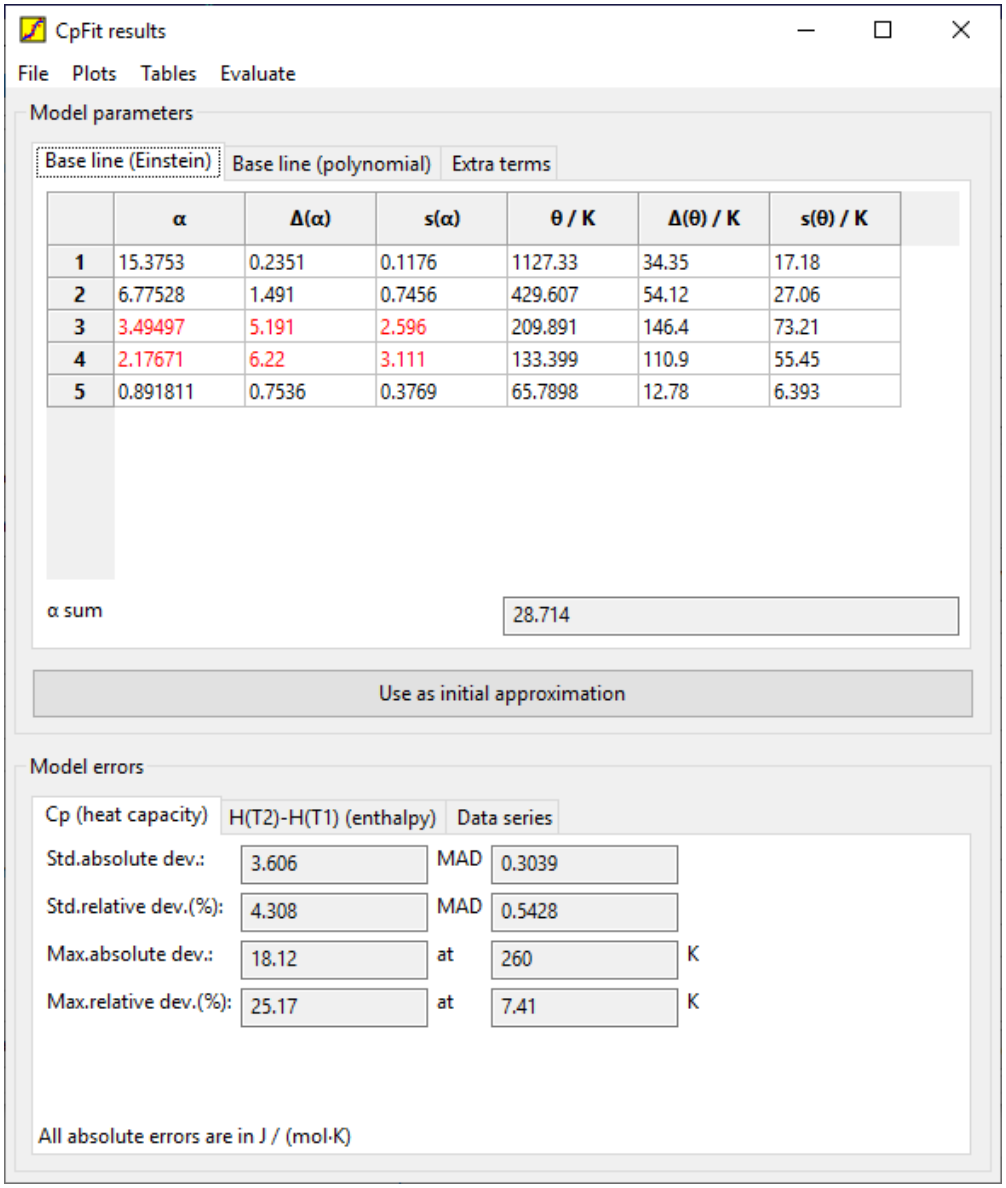

Figure 4.2: CpFit results window

- **Base line (Einstein)** tab contains α_i and θ_i parameters with their standard errors ($s(\alpha)$ and $s(\theta)$) and 95 % confidence intervals ($\Delta\alpha$ and $\Delta\theta$) calculated using eq 2.2 and eq 2.3 respectively. Statistically not significant terms are automatically highlighted in red colour. Each row correspond to one model term.
- **Base line (polynomial)** tab contains a_i and n parameters for the polynomial part. For a_i their standard errors and 95 % confidence intervals are given too.
- **Extra terms** tab contains results of extra terms optimization. They are presented in the form of text report.

Model errors area contains information about accuracy of the optimized parameters data set present in the window. There are three tabs:

- **Cp (heat capacity)** — heat capacity data approximation uncertainties for all data series including points inside anomalies.
- **H(T2)-H(T1) (enthalpy)** — heat content data approximation uncertainties for all data series including points inside anomalies.
- **Data series** — data series approximation uncertainties. It is possible to see these uncertainties for each data series and for each data type separately. Separate consideration of data inside and outside anomalies is also supported.

for heat capacities and for enthalpies respectively. Note that all deviations are calculated without taking statistical weights ω_i from 2.1 into account (however they were used during the optimization).

4.3.1 Debye function

Evaluate — Low-T S correction menu item of *Results window* uses Debye model. In Debye model heat capacity is approximated by means of the next formula:

$$\frac{C_p^{\mathrm{D}}(T)}{3NRT} = 4D\left(\frac{T_{\mathrm{D}}}{T}\right) - \frac{3\frac{T_{\mathrm{D}}}{T}}{\exp\left(\frac{T_{\mathrm{D}}}{T}\right) - 1} \tag{4.9}$$

where N is the number of atoms in the compound, T_{D} is Debye temperature, $D(x)$ is Debye function:

$$D(x) = \frac{3}{x^3}\int_0^x \frac{y^3}{e^y - 1}\,dy \tag{4.10}$$

The next algorithm of entropy correction calculation is used:

- Get the lowest trusted point T_0 and $C_p(T_0)$ at the curve (i.e. Einstein-Plank model). T_0 is manually set by user and usually is 5–30 K. The user also must give N (number of atoms) value.

- Calculate Debye model parameters. Two options are available. The first one is evaluate only T_{D} value by solving $C_p^{\mathrm{D}}(T_0) = C_p(T_0)$ equation and use N value given by a user. The second one is evaluate both T_{D} and N (i.e. treat it as "effective" number of atoms) by solving the next system of equations:

$$\begin{cases} C_p^{\mathrm{D}}\left(T_0, T_{\mathrm{D}}, N\right) & = C_p(T_0) \\ \left.\frac{\partial C_p^{\mathrm{D}}(T, T_{\mathrm{D}}, N)}{\partial T}\right|_{T_0} & = \left.\frac{\partial C_p(T)}{\partial T}\right|_{T_0} \end{cases} \tag{4.11}$$

- Calculate $S^{\mathrm{D}}(T_0)$ value using eq. 4.9. It is also possible to add virtual points to the input data to improve Einstein-Planck function sum behaviour at low temperatures.

4.4 Plots

CpFit 2-dimensional plot is a resizable window that can show experimental data points, analytical functions obtained by a nonlinear regression or both of them. They can also contain plots with absolute or relative deviations. Use results window to build new plots.

A menu of any 2D plot window in the CpFit program contains the next items:

- **File** — Export of the plot into graphic files.
  - **Save as** — Export into `.png` file with screen resolution.
- **Edit** — Figure customization and clipboard operations.
  - **Copy** — Copy the plot into Clipboard (in a vector format similar to Windows Metafile)
  - **Legend** — Enable/disable legend.
  - **Log scale for X** — Enable/disable logarithmic scale for axis X (usually for temperature T).
  - **Grid** — Enable/disable grid.

In the case of the $C_p(T)/T$ function plot extra dashed lines of different color that correspond to the function terms (see eq 1.1) are shown. A color of the line codes the term number (see Table 4.1).

You can also zoom in/zoom out plots using mouse wheel scrolling and drag-n-drop technique to navigate inside a zoomed plot.

Plots with experimental points can contain legend (it is enabled by default). It is formed by the next steps:

1. Read all data series IDs from the input `.dat` file and find unique values. Sort these values by alphabet.
2. Assign marker (i.e. color and form of dots) for each unique value obtained in the previous step.
3. Draw legend for data series that are present at the plot.

Table 4.1: Terms colors in the $C_p(T)/T$ function plots.

Term number	Color
1	Black
2	Blue
3	Green
4	Cyan
5	Red
6	Magenta
7	Brown
8	Gray

4.5 Tables

Two kinds of tables can be constructed by CpFit: tables with tabulated thermodynamic values and tables with comparison of calculated and experimental values. Both of them can be exported into `.csv` file format (readable by Microsoft Excel).

4.5.1 Tabulated thermodynamic functions

This kind of table contains tabulated values for $C_p(T)$, $H(T) - H(0)$ and $S(T)$ thermodynamic functions. Every new table contains rows for default T values for $T = 10 \div 1000$ K and always contains a 298.15 K row. However a user can add or delete any rows with any step.

A menu of the tabulated thermodynamic functions table window contains the next items:

- **File** — File input-output (exporting table to files).
  - **Save as** — Export into `.csv` file.
- **Edit** — A customization of the table.
  - **Reset the table** — Removes all rows from the table.
  - **Add T range to the table** — Adds new rows for requested temperature range with requested step.

    When a user adds a new T range a special dialog shown in Figure 4.3 is opened. The user can set Tmin (minimal temperature), Tmax (maximal temperature) and Tstep (a step between new points). After the addition a table of tabulated values will be automatically sorted by the temperature.
  - **Errors estimation** — Allows to select the mode used for estimation of errors for tabulated S, H and C_p values.
    - **Standard deviation** — calculate standard deviations.
    - **95 % confidence interval** — calculate confidence intervals (95 % confidence intervals using two-sided t-distribution quantiles).

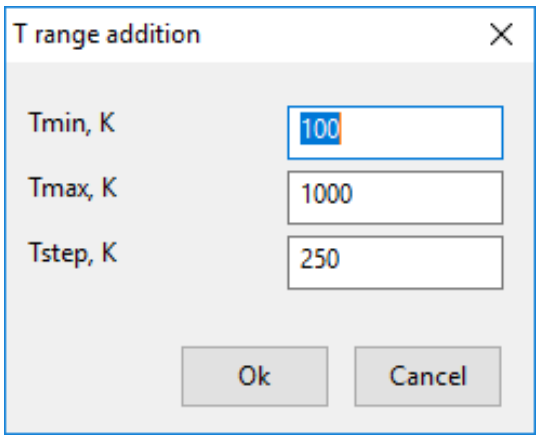

Figure 4.3: T range addition dialog

4.5.2 Calculated vs experimental

A menu of the residuals table window contains the next items:

- **File** — File input-output (exporting table to files).
  - **Save as** — Export into `.csv` file.

Chapter 5

Changelog

- 07 November 2020 — CpFit 0.9
  - Automatic (and optional) exclusion of experimental points with $\omega = 0$, i.e. zero statistical weights.
  - Extra markers for data series.
  - HTML reports were extended by reports about individual data series.
  - Low-temperature C_p–T, C_p/T–T^2 and C_p/T^3–T^2 plots for analysis of asymptotic behaviour of models.
  - New examples of input files including `diamond.txt` and `graphite.txt` with experimental data for diamond and graphite. These files also include the C_p models by Bigdeli et al. [2] that include polynomial parts.
  - Scripts for CMake.
  - Semi-logarithmic scale for plots. It is useful for visualization of low-temperature regions.
  - Support of entropies as experimental points (may be applied if e.g. $S_2 98.15°$ was estimated by other methods).
  - Support of polynomial term in the baseline C_p model.
  - Support of the $\sum_i \alpha_i = N_{\text{atoms}}$ condition (it is optional).
  - The universal gas constant CODATA 2014 value was replaced to the CODATA 2018 exact value.
  - Visualization of α–θ scatter plot as approximation of the phonon density state function.
  - Bugfix: sorting of experimental data now doesn't discard changes in data made by a user.
- 31 December 2018 — CpFit 0.8
  - Support of custom extra terms written in Lua. Examples of such scripts were added (see `eq_debpoly.lua`, `eq_eppoly.lua`, `natrolite_eppoly.dat`).
  - Editing of LSQ parameters lower and upper boundaries was added.
  - New "empty" extra term with zero value (useful for exclusion of anomalies).
  - Sorting of experimental points.

  - Uncertainties for data series inside and outside anomalies.
  - Improved procedure of Debye function based extrapolation. Generation of virtual points.
  - Improved source code documentation.
  - Bugfix: improved calculation of confidence intervals for C_p and S values (around 5%).
  - Bugfix: fixed number of points field in `K_natrolite.dat` (has no influence on the results of optimization).

- 25 December 2017 — CpFit 0.7
  - Four new extra terms were added
  - Now data files can have either `.dat` or `.txt` extension.
  - More informative message about exceeding the maximum number of iteration (the program now recommends to use another initial approximation)
  - Support of α_i and θ_i storage (i.e. initial approximations for them) was added into data files.
  - Some bugfixes

- 03 November 2017 — CpFit 0.6
  - Extra (excess) heat capacity terms support was added. Currently it is designed for description of lambda-transitions.
  - `UO2.dat`, `K_natrolite.dat`, `Tl_natrolite.dat` examples were added. They contain experimental data for UO_2, K-substituted natrolite and Tl-substituted natrolite respectively.
  - `ThO2_shifted15.dat` was added. It contains altered high-temperature C_p data to improve description of high-temperature heat content.
  - Heat content data were added to `natrolite.dat` data file.
  - Extra data were addded to data file `ThO2.dat`.
  - Calories support in `.dat` files was added.
  - Heat content plots with experimental points were added. Two kind of plots are supported: $H_T - H_{T_0}$ plots and $(H_T - H_{T_0})/(T - T_0)$ plots where T_0 is set by a user.
  - Export of plots to `.wmf` and `.m` (MATLAB scripts) files was added.
  - Some bugfixes.

- 30 August 2017 — CpFit 0.5
  - Enthalpies ($H(T_2) - H(T_1)$ heat content) experimental data approximation support was added.
  - Support multiple data series with different markers was implemented.
  - Support of comments (ignored by CpFit) in `.dat` files was added.
  - Grid and legend management (possibility to enable or disable them) were added in 2D plots.

  - `ThO2.dat` example was added. It contains heat capacity and heat content (enthalpies differences) data for ThO_2. It also an example of data series names in the file.
  - Some bugfixes

- 05 July 2017 — CpFit 0.4
  - Errors in columns name (`s(H-H0)` and `s(S-S0)` names mismatch) in `.csv` files containing exported tables of thermodynamic functions was fixed.
  - Some typos in the manual were fixed
  - Bibliographic references were added to examples (`natrolite.dat`), (`ScF3.dat`).
  - Low-temperature entropy correction (by means of Debye function) was added.

- 21 December 2016 — CpFit 0.3
  - Automatic search of model terms number was added.
  - t-test for model coefficients (for statistical significance) was added.
  - Negative values of the model cannot be obtained during an optimization now.
  - Confidence intervals for parameters and tabulated values (using two-sided 95 % quantile of t-distribution).
  - Improved export of tabulated values.
  - Zooming for 2D plots.
  - Loading of model parameters from `.csv` files.
  - Estimation of confidence intervals for user-supplied parameters.

- 31 October 2016 — CpFit 0.2 — First public version

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Chapter 6

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End of Terms and Conditions

Appendix: How to Apply These Terms to Your New Programs

If you develop a new program, and you want it to be of the greatest possible use to the public, the best way to achieve this is to make it free software which everyone can redistribute and change under these terms.

To do so, attach the following notices to the program. It is safest to attach them to the start of each source file to most effectively convey the exclusion of warranty; and each file should have at least the "copyright" line and a pointer to where the full notice is found.

> one line to give the program's name and a brief idea of what it does.
> Copyright (C) yyyy name of author
>
> This program is free software; you can redistribute it and/or modify it under the terms of the GNU General Public License as published by the Free Software Foundation; either version 2 of the License, or (at your option) any later version.
>
> This program is distributed in the hope that it will be useful, but WITHOUT ANY WARRANTY; without even the implied warranty of MERCHANTABILITY or FITNESS FOR A PARTICULAR PURPOSE. See the GNU General Public License for more details.
>
> You should have received a copy of the GNU General Public License along with this program; if not, write to the Free Software Foundation, Inc., 51 Franklin Street, Fifth Floor, Boston, MA 02110-1301, USA.

Also add information on how to contact you by electronic and paper mail.

If the program is interactive, make it output a short notice like this when it starts in an interactive mode:

> Gnomovision version 69, Copyright (C) yyyy name of author
> Gnomovision comes with ABSOLUTELY NO WARRANTY; for details type 'show w'.
> This is free software, and you are welcome to redistribute it under certain conditions;
> type 'show c' for details.

The hypothetical commands `show w` and `show c` should show the appropriate parts of the General Public License. Of course, the commands you use may be called something other than `show w` and `show c`; they could even be mouse-clicks or menu items—whatever suits your program.

You should also get your employer (if you work as a programmer) or your school, if any, to sign a "copyright disclaimer" for the program, if necessary. Here is a sample; alter the names:

> Yoyodyne, Inc., hereby disclaims all copyright interest in the program
> 'Gnomovision' (which makes passes at compilers) written by James Hacker.
>
> signature of Ty Coon, 1 April 1989
> Ty Coon, President of Vice

This General Public License does not permit incorporating your program into proprietary programs. If your program is a subroutine library, you may consider it more useful to permit linking proprietary applications with the library. If this is what you want to do, use the GNU Library General Public License instead of this License.