Projektarbeit

Measurement of the Specific Heat Capacity at Low Temperatures

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by

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Abstract

In Solid-state physics measurement of the heat capacity at low temperatures is important for various different aspects like heavy fermions or superconducters. During the scope of this thesis the implementation of a heat pulse calorimeter was investigated. Control of the calorimeter as well as the processing of its recorded data were integrated into the existing set-up of the dilution fridge using the programming language python. The calorimeter including the method of measurement then were tested at room temperature and also measurements at low temperatures were conducted.

Zusammenfassung

Die Messung der spezifischen Wärme bei tiefen Temperaturen ist wichtig für viele festkörperphysikalische Anwendungen wie z.B. schwere Fermionen oder Supraleiter. Im Rahmen dieser Arbeit wurde die Bestimmung der spezifischen Wärme mittels des Heizpulsverfahren untersucht. Für die Steuerung und Auswertung des Kalorimeters wurde ein Pythonprogramm entwickelt welches in das bestehende Mess- und Steuerungssystem des Mischungskryostaten eingebunden wurde. Zum testen des Programms und der Messmethode wurden Messungen bei Raumtemperatur und bei sehr tiefen Temperaturen durchgeführt.

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1 Introduction

Specific heat capacity is a physical property of mass which describes the temperature rise dT due to energy input dQ. A change in temperature also results in a change of pressure and volume. Therefore the specific heat is measured either at constant pressure or constant temperature:

$$c_p = \left(\frac{dQ}{dT}\right)_p \qquad\qquad c_v = \left(\frac{dQ}{dT}\right)_v$$

For a solid body the free electrons of the eletron gas and the phonons contribute mostly to the specific heat capacity which has the following temperature dependency:

$$c(T) = \gamma T + \beta T^3 \tag{1}$$

The contribution of the free electrons, described by the Drude-Sommerfeld model, is linear in the temperature T. The impact of phonons on the heat capacity can be described with a cubic term, which is described by the Einstein model or the Debye model.

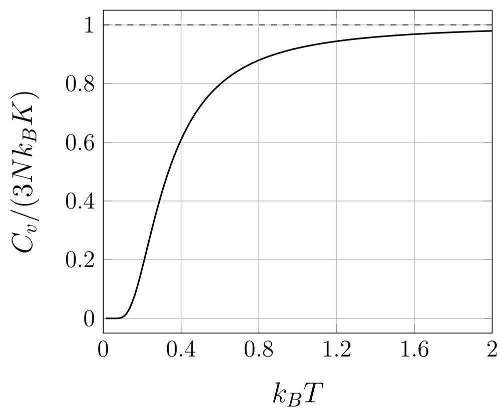


Figure 1: Heat capacity according to the Einstein model.

According to the equipartition theorem, the average energy of a classical harmonic oscillator is k_BT. If there are N atoms in a solid, there will be 3N harmonic vibrations and the average energy is given by $U = 3Nk_BT$. The heat capacity is therefore $c = \frac{dU}{dT} = 3Nk_B$. This is known as the Dulong-Petit law which states that at high temperatures the heat capacity is constant. With temperature decreasing, the heat capacity also decreases and is proportional to T^3 at low temperatures.

At low temperatures the contribution of the electrons is much higher than that of the phonons because lattice vibration is decreasing at lower temperatures. On the other hand, at high temperatures the contribution of the electrons can be neglected because it is smaller than the lattice heat capacity as can be seen from Eq. (1).

1.1 Heat Capacity Measurement

Measurement of the heat capacity can be done using the heat pulse method. This set-up is shown in Fig. 2. The sample of which the heat capacity should be determined is embedded in grease on a sample platform. Underneath the sample platform a heater and thermometer are mounted to measure the energy input into the platform and its temperature. Thermometer and heater are connected with wires to a heat bath with constant temperature T_0. To reduce radiation from the sample a radiation shield is placed atop and the whole set-up is evacuated to reduce heat conduction through convection. Therefore the heat flow is governed by the connection of the wires which connect the sample platform and the heat bath electrically and thermally. The wires also act as a mechanical support for the sample platform. Ideally the measurement

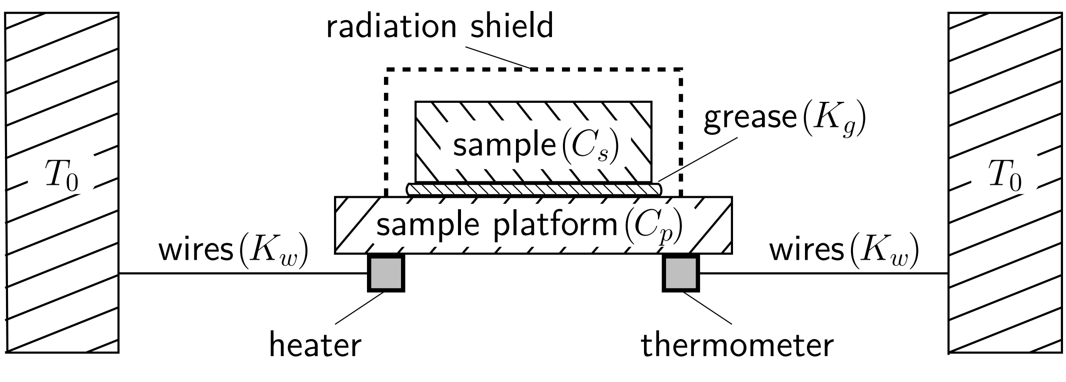


Figure 2: Overview of the heat pulse method set-up.

is done adiabatically, which means that the energy from the heater is only deposited into the sample and there is no heat flowing from the sample into the environment. To ensure that the energy is mainly flowing into the sample, the thermal conductivity of the wires K_w should be small compared to the thermal conductivity of the grease K_g. With this assumptions, this calorimeter can be classified as quasi-adiabatic.

A typical response curve from a heat pulse calorimeter is illustrated in Fig. 3. Starting at a temperature T_0 the heater is turned on and delivers a constant power P_0 until it is shut down at a time t_0. Hence it is called a heat pulse calorimeter. By fitting the measured data to a mathematical model describing

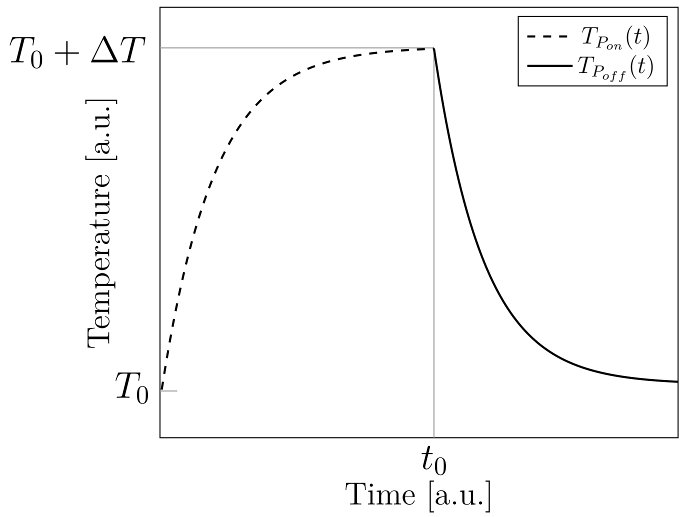


Figure 3: Example temperature response curve from a heat pulse calorimeter. During heating-up the temperature rises exponentially from T_0 to $T_0 + \Delta T$. For $t > t_0$ the heater is turned off and the temperature decreases. The parts of the curve are called $T_{P_{on}}$ and $T_{P_{off}}$, respectively.

the calorimeter presented in Fig. 2 the specific heat can be determined. The heat capacity in the measured temperature interval ($t \in [T_0, T_0 + \Delta T]$) should not change much. Therefore, this method fails if there occurs a phase transition in this interval.

1.2 Two-tau Model

The equations describing the calorimeter presented in the previous section are given by [1]

$$P(t) = C_p \frac{dT_p(t)}{dt} + K_w\Big(T_p(t) - T_0\Big) + K_g\Big(T_p(t) - T_s(t)\Big) \tag{2}$$

and

$$C_s \frac{dT_s(t)}{dt} = K_g\Big(T_p(t) - T_s(t)\Big). \tag{3}$$

This so called two-tau model describes the heat flow through the wires between heat bath and sample platform, and the heat flow through the grease between the sample and the sample platform. The thermal conductivity of the grease K_g and the wires K_w are given in units of $\frac{W}{K}$ and the the heat capacities of the sample C_s and the sample platform C_p are given in units of $\frac{J}{K}$. Since the thermometer is firmly attached to the underside of the sample platform we can only measure the temperature of the sample platform. To eliminate the temperature of the sample $T_s(t)$, we therefore substitute Eq. (2) into Eq. (3) and recieve a second order differential equation only dependent of the temperature of the platform $T_p(t)$. The solutions of Eqs. (2) and (3) are derived in Appendix A.2, and are given by

$$T_{P_{on}}(t) = \frac{P_0}{2\beta K_w}\left(\frac{e^{-t/\tau_1}}{\tau_2} - \frac{e^{-t/\tau_2}}{\tau_1}\right) + \frac{P_0 + K_w T_0}{K_w}, \qquad 0 \leq t \leq t_0 \tag{4}$$

$$T_{P_{off}}(t) = \frac{P_0}{4\beta K_w}\left[2 - \frac{1}{\beta}\left(\frac{e^{-t_0/\tau_2}}{\tau_1} - \frac{e^{-t_0/\tau_1}}{\tau_2}\right)\right]\left[\frac{e^{(t_0-t)/\tau_2}}{\tau_1} - \frac{e^{(t_0-t)/\tau_1}}{\tau_2}\right] + T_0, \qquad t > t_0 \tag{5}$$

with

$$\tau_1 = \frac{1}{(\alpha+\beta)}, \qquad \tau_2 = \frac{1}{(\alpha-\beta)}, \qquad \alpha = \frac{K_w}{2C_p} + \frac{K_g}{2C_s} + \frac{K_g}{2C_p},$$

$$\beta = \frac{\sqrt{(C_s K_w + C_p K_g + C_s K_g)^2 - 4C_p C_s K_g K_w}}{2C_p C_s}.$$

Solutions for the parameters τ_1 and τ_2 given above are in agreement with [2].

1.3 Simple Model

If the thermal conductivity of the grease K_g is very high compared to the thermal conductivity of the wires K_w, Eqs. (2) and (3) can be simplified and the result is the so called simple model which is given by

$$P(t) = C_{tot}\frac{dT(t)}{dt} + K_w\big(T(t) - T_0\big). \tag{6}$$

Here C_{tot} is the total heat capacity of the calorimeter (sample, platform,...). The solution of the simple model is

$$T(t) = \begin{cases} \dfrac{P_0\tau}{C_{tot}}\left(1 - e^{-t/\tau}\right) + T_0 & 0 \leq t \leq t_0 \\ \dfrac{P_0\tau}{C_{tot}}\left(1 - e^{-t/\tau}\right)e^{-(t-t_0)/\tau} + T_0 & t > t_0 \end{cases} \tag{7}$$

with the time coefficient

$$\tau = \frac{C_{tot}}{K_w}.$$

1.4 Time Coefficients

The parameters τ obtained from the simple model and the two-tau model are given in units of time and hence called time constants or time coefficients. They quantify how fast the temperature rises during heating up and how fast it decreases during cooling down of the calorimeter. The simple model has only one time constant τ which describes how fast the temperature changes: During the period of $1\,\tau$ the temperature increases or decreases by about 63 % from the starting value whether the heater is turned on or off. Similarly, the time coefficients obtained from the two-tau model represent the rate of incline or decline of temperature as can be seen in Fig. 4.

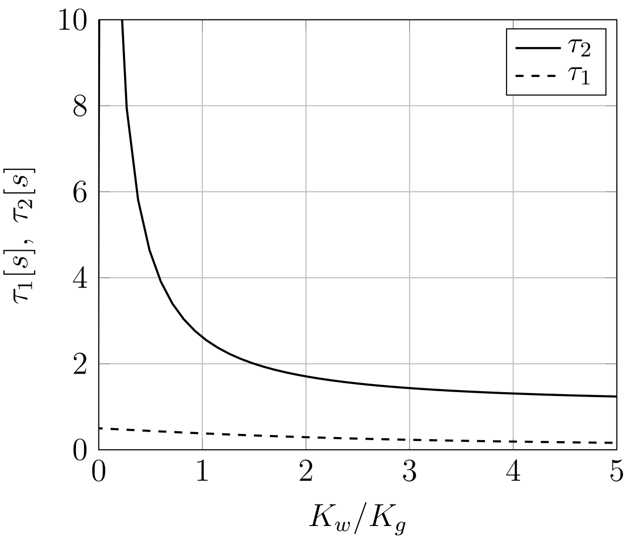


Figure 4: Time coefficients τ_1 and τ_2 as a function of the ratio K_w/K_g with the parameters $K_g = C_p = C_s$ set to a fixed value of one. The smaller the ratio K_w/K_g, the larger τ_2 gets compared to τ_1. Since the thermal conductivity is proportional to the heat flow, τ_1 corresponds to the temperature flow between sample and platform, and τ_2 to the temperature flow between sample platform and temperature bath.

Ideally τ_2 should be much greater than τ_1 because we want the energy from the heater flowing into the sample and not into the temperature bath. The transition from the two-tau model to the simple model can also be seen from

Fig. 4: The smaller K_w/K_g gets, the more τ_1 is negligible compared to τ_2. Further discussion of the time coefficients with regard to measurements is given in Sec. 2.2.

2 Measurements

Several steps are required to obtain the heat capacity of a sample. First the puck (the sample platform without sample or grease) must be calibrated. Starting at the lowest temperature a heat pulse increases the temperature of the platform to a set temperature (this usually means an increase of one or two percent). During heating-up the thermometer records the temperature over time and the result is a temperature response curve like the one shown in Fig. 3. This data is then fitted with the solutions of the simple model (Eq. (7)) where $\mathtt{P_0}$ and $\mathtt{T_0}$ are known parameters and the other ones, i.e., $\mathtt{K_w}$, and $\mathtt{C_{tot}}$ are unknown and determined by the least squares fit. If this is a valid measurement, the temperature at which a measurement starts is increased and another measurement follows subsequently until the desired temperature range has been sweeped. Since the measurement is done without a sample and without grease, the total heat capacity $\mathtt{C_{tot}}$ obtained by the fit of the simple model is the heat capacity of the platform $\mathtt{C_p}$ which includes the heat capacity of the thermometer and the heater. This calibration of the puck only needs to be done once unless the puck is changed.

To obtain the highest accuracy a complete measurement sweep with grease needs to be done additionally. All measurements are fitted with the simple model and the resulting parameter $\mathtt{C_{tot}}$ from the fit is the sum of the heat capacity of the platform and the grease. If a known quantitiy of grease is applied and the heat capacity of the grease is known, this step may be skipped. The result $\mathtt{C_{add}}$ of the so called “addenda measurement” is the heat capacity of the calorimeter without the sample and with grease.

Finally, sample measurements are performed. Here, the simple model and the two-tau model are fitted to the temperature response curve with fixed $\mathtt{T_0}$ and $\mathtt{P_0}$. The parameters $\mathtt{K_w}$ and $\mathtt{C_{add}}$ are taken from the calibration and addenda measurements. During the fit of the two-tau model, $\mathtt{C_{add}}$ is set to $\mathtt{C_p}$ and the values $\mathtt{K_g}$ and $\mathtt{C_s}$ are obtained through the fit. While fitting the simple model only $\mathtt{K_w}$ is used to obtain $\mathtt{C_{tot}}$. Since $\mathtt{C_{tot}} = \mathtt{C_{add}} + \mathtt{C_s}$ the heat capactity of the sample can be determined from fitting the simple model. Now the model with the better fitting parameters (sum of the residuals of the fit) provides the estimate value of $\mathtt{C_s}$. From the fit of the two-tau model, the sample coupling in percent can be obtained:

$$100 \times \frac{\mathtt{K_g}}{\mathtt{K_g} + \mathtt{K_w}}$$

It describes how well the sample is thermally connected to the sample platform.

A value of 100 % is equivalent to perfect coupling and 0 % means that there is no heat flowing from the sample to the platform and vice versa. In case of perfect coupling the two-tau model cannot be applied and its fit therefore fails to converge. Figure 5 shows the flow chart of a possible implementation as described above.

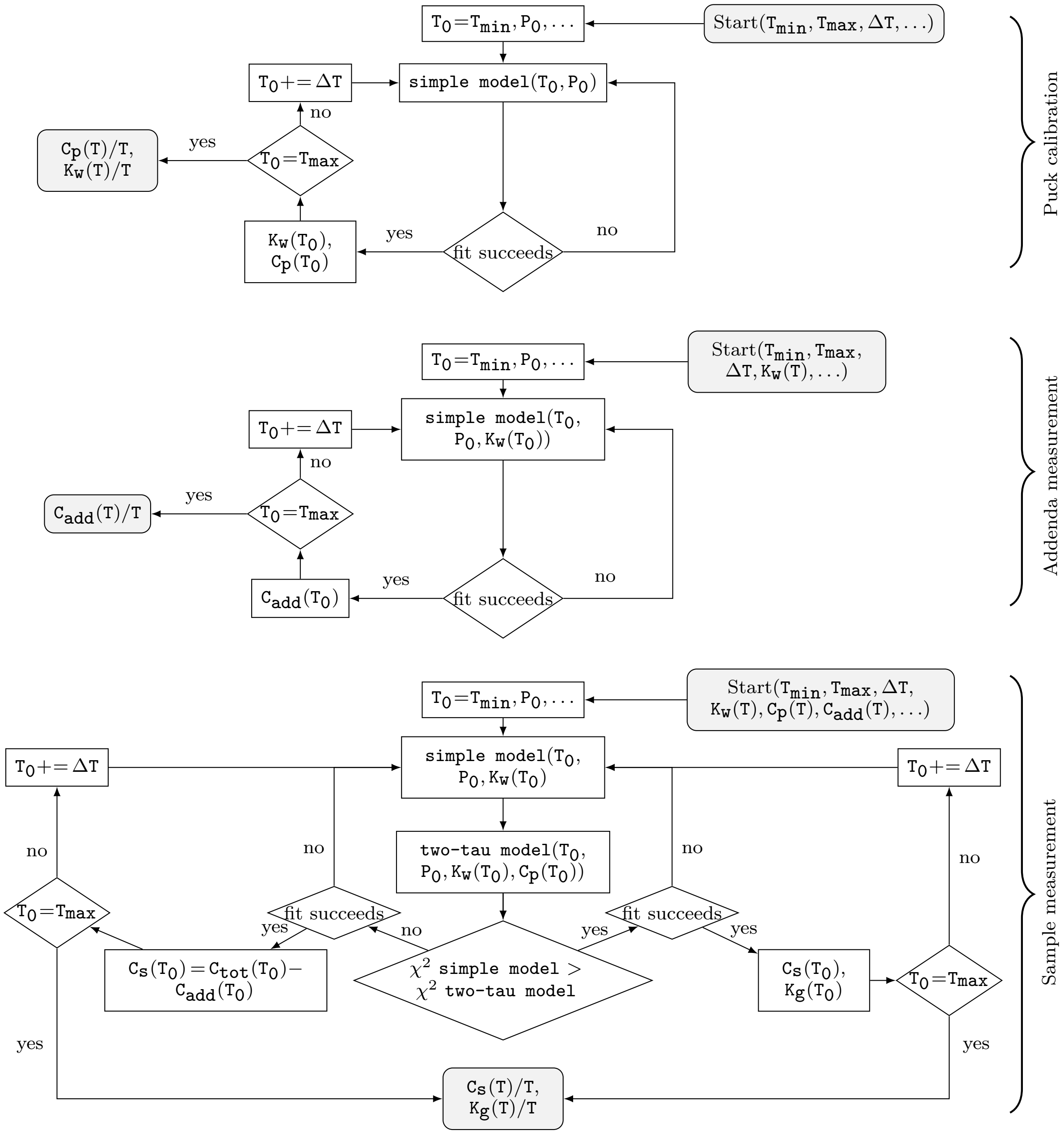


Figure 5: Flow chart of a complete heat capacity measurement cycle as described in the section above.

2.1 Data Fitting

Fitting of the data is the most crucial part of the measurement and should be therefore discussed briefly here. Communication with the instruments as well as storing and processing of the data is done using a python program. The general layout of the measurement set-up is presented and discussed in Sec. 2.2.

The fit is performed using the function `leastsq` from the package `scipy.optimize` which takes a function to minimize, initial parameter guesses, the data to fit and some optional arguments as parameter values. For example, the function used to fit $T_{P_{on}}$ of the two-tau model is given by

```
def f(x, K_g, C_s):
    p3 = P_0/K_w+T_0
    alpha = K_w/(2*C_p)+K_g/(2*C_s)+K_g/(2*C_p)
    beta = np.sqrt((C_s*K_w+K_g*C_p+C_s*K_g)**2/(4*C_s**2*C_p**2)- \
        (K_g*K_w)/(C_s*C_p))
    return (P_0/(2*K_w*beta))*((alpha-beta)*np.exp(-x*(alpha+beta))- \
        (alpha+beta)*np.exp(-x*(alpha-beta)))+p3
```

It is important in which form the parameters are expressed, which are passed to the fit function. The fit fails to converge more often if the expression of beta above is expanded like in Eq. (14). The guess of the initial parameters is also very important since the fit is using a greedy algorithm and runs into the nearest local minimum. More information concerning the initial parameters and its impact on the fit is given in Sec. 2.2.2. The initial parameters are stored in the array `pstart` and passed to the function which performs the fit.

```
pstart = [1.0, 0.25]
```

With this information the fit is called through

```
fitparameter, cov, infodict, mesg, ier = scipy.optimize.leastsq(f, \
     pstart, args = (datax, datay), full_output = 1, epsfcn = 0.0001)
```

The two numpy arrays `datax` and `datay` contain the time and temperature values, respectively.

2.2 Room-temperature Set-up

The final experimental set-up is placed in a dilution refrigerator to measure the heat capacity at very low temperatures. Changing samples or any manipulation of the set-up is very time-consuming due to the long heat-up and cool-down times of the dilution refrigerator. Therefore room-temperature measurements with the set-up shown in Fig. 6 were conducted to test the data acquisition and the fit of the data.

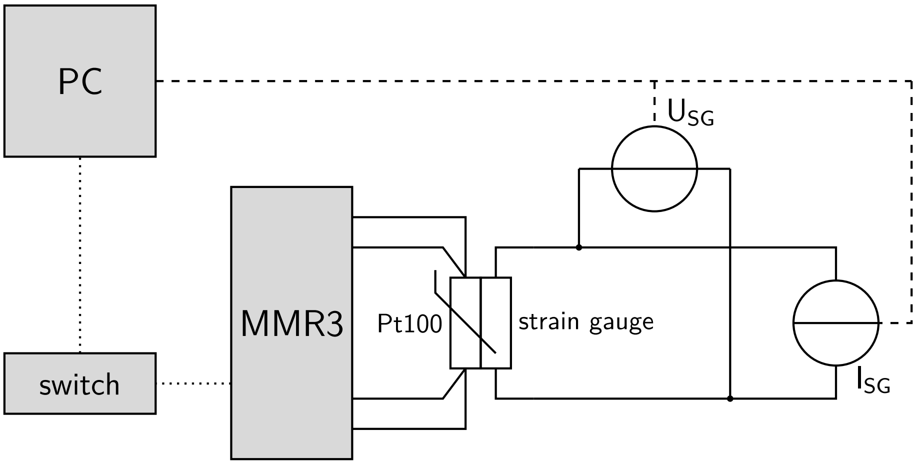


Figure 6: Overview of the measurement set-up at room temperature. A strain gauge with a resistance of 350 Ω was used as a heater which was firmly connected to a Pt100 for temperature recording. The heating power was set by a current source (I_{SG}) with a voltmeter attached to measure the voltage drop across the heating resistor (U_{SG}). The temperature was read by the Pt100 using a MMR3 bridge connected by a 4-point probes method. Solid lines represent current-carrying wires. Dashed (IEEE-488) and dotted (RJ45, RS-232) lines connected the measuring instruments to the Computer (PC).

Measurements were conducted with the set-up described above but due to its simplicity compared to the set-up shown in Fig. 2, all results discussed below should be interpreted with caution. In addition, without vacuum and temperature control (heat bath) the measurements at room temperature were not performed adiabatically.

2.2.1 Simple Model

The temperature response curves are recorded and processed by a python program. Addressing the instruments is done using the existing socket server framework which is used for measurement and monitoring of the dilution refrigerator. Results of measurements with the high-temperature set-up are shown in Fig. 7.

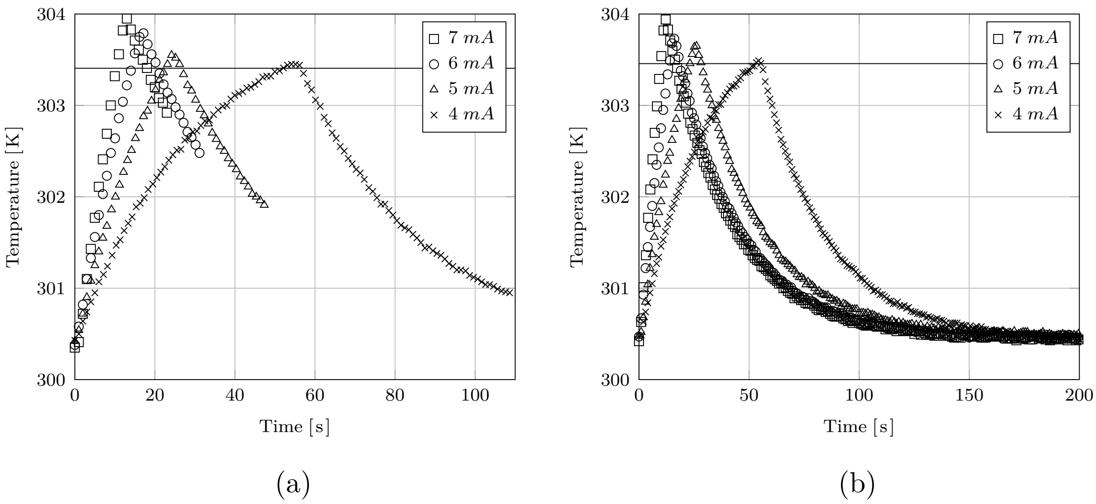


Figure 7: High-temperature measurements with the horizontal line representing the temperature at which the heater is turned off. Measurements were made between 4 and 7 mA in 0.5 mA steps but for better visibility only every second measurement is shown. For every measurement the baseline temperature T_0 was set to around 300.4 K before the heat pulse arrived and the threshold for turning the heater off was set to an increase of 1 %. While in (a) the number of measuring points for heating-up and cooling-down were set the same, in (b) a total of 200 measuring point were recorded.

Without external temperature control, i.e., T_0 set to ambient temperature and the increase of $\Delta T = 1\,\%$, the measurements done presented in the Figure above represent the maxium range of measurements possible. Due to possible damage to the heater, no measurements with currents higher than 7 mA were conducted. On the other hand, using heating currents below 4 mA resulted in the temperature never exceeding the set 1 % limit due to heat leaks. To determine the impact of the heating current on the resulting fit parameters, all measurements described above were fitted using the simple model.

Table 1: Results from the fit of the simple model to the temperature response curves presented in Fig. 7a. To perform the fit, every temperature response curve was split between heating-up and cooling-down, representing every odd and even numbered row. Every single measurement is divided by a dashed line. The first column gives the heating current and the next three columns list the values obtained from of the fit. The last two columns specify the calculated time coefficients τ, with t_{meas} being the time of the associated measurement in seconds. See the text for details.

Current [A]	K_w $[W/K]$	C_{tot} $[J/K]$	$\sqrt{\chi^2/\nu}$	τ $[s]$	t_{meas}/τ
0.0070	-0.00257	0.07148	0.1199	-27.813	-0.43
0.0070	0.00266	0.04132	0.0495	15.533	0.71
0.0065	-0.00052	0.06241	0.0917	-120.019	-0.12
0.0065	0.00242	0.04082	0.0417	16.867	0.77
0.0060	0.00095	0.05209	0.0384	54.831	0.29
0.0060	0.00223	0.04006	0.0383	17.964	0.83
0.0055	0.00096	0.05351	0.0543	55.739	0.34
0.0055	0.00206	0.04040	0.0332	19.611	0.93
0.0050	0.00135	0.04932	0.0207	36.533	0.66
0.0050	0.00187	0.04086	0.0299	21.850	1.06
0.0045	0.00150	0.04705	0.0177	31.366	1.06
0.0045	0.00171	0.04130	0.0331	24.152	1.33
0.0040	0.00153	0.04688	0.0167	30.640	1.80
0.0040	0.00157	0.04338	0.0200	27.630	1.94

To fit the simple model against the measurements, P_0[1] and T_0 were treated as constants and the other two parameters (K_w and C_{tot}) were determined from the fit. The fourth column of Table 1 represents the reduced chi square obtained from the fit with χ^2 being the sum of the squared residuals and ν the degree of freedom, i.e., the difference between the number of measuring points and fit parameters. Using $\tau = C_{tot}/K_w$, the time coefficient for each measurement is calculated. The last column in Table 1 lists the time t_{meas} a measurement took in seconds divided by τ. The initial parameter values for every fit to start with were set to $K_w = 0.005$ and $C_{tot} = 0.05$.

Every fit yields two values which corresponds to the heater being turned on or off. Since we want to determine the heat capacity from a temperature response curve, a great difference would raise the question which value is the correct

[1]The heating power was calculated using the set current and resistance of the heater using $P = I^2R$.

one. The difference in K_w and C_{tot} obtained from a single measurement is proportional to the current of the heater, i.e., the smaller the current the lower the difference. The two time coefficients τ from a single measurement share the same trend, as can be seen from Table 1. The developing of the values K_w and C_{tot} over the series of measurements is nonlinear and interleaved. For example the values for K_w in Table 1 are converging to approximately 0.0015 but depending on the current source being turned on or off the values converge from below or above, respectively. The parameters and its difference are presented in Fig. 8.

To determine the impact of the length of a measurement on the fit parameters, measurements with a fixed amount of 200 measuring points were conducted. For that purpose, all settings were set the same way as before but measurement and recording of the temperature was stopped at a total amount of 200 measuring points.

Table 2: Results from the fit of the simple model to the temperature response curves presented in Fig. 7b. During these measurements the cool-down time was extended. The parameters used are the same as in Table 1, in which description further information is given.

Current [A]	K_w [W/K]	C_{tot} [J/K]	$\sqrt{\chi^2/\nu}$	τ [s]	t_{meas}/τ
0.0070	0.00039	0.05300	0.0516	135.8974	0.08
0.0070	0.00246	0.05011	0.1185	20.3699	9.27
0.0065	0.00076	0.05139	0.0386	67.6184	0.19
0.0065	0.00227	0.04833	0.1064	21.2907	8.78
0.0060	0.00147	0.04623	0.0193	31.4490	0.48
0.0060	0.00213	0.04680	0.0940	21.9718	8.42
0.0055	0.00110	0.05067	0.0332	46.0636	0.42
0.0055	0.00199	0.04710	0.0827	23.6683	7.63
0.0050	0.00126	0.05005	0.0356	39.7222	0.63
0.0050	0.00181	0.04581	0.0745	25.3094	6.91
0.0045	0.00143	0.04777	0.0302	33.4056	0.99
0.0045	0.00168	0.04568	0.0676	27.1905	6.14
0.0040	0.00151	0.04627	0.0199	30.6424	1.77
0.0040	0.00156	0.04480	0.0291	28.7179	5.07

The temperature response curves from these measurements are presented in Fig. 7b and the results of the data fits are shown in Table 2. The fit parameters from this series of measurements are nearly identical to the one before where the number of measuring points during heating-up and cooling-down were set equally. The amount of measuring points per τ is obviously greater during cooling-down for the latter described series of measurements. In the figures below the parameters K_w and C_{tot} obtained from the fit from both series of measurements and their relative difference is presented.

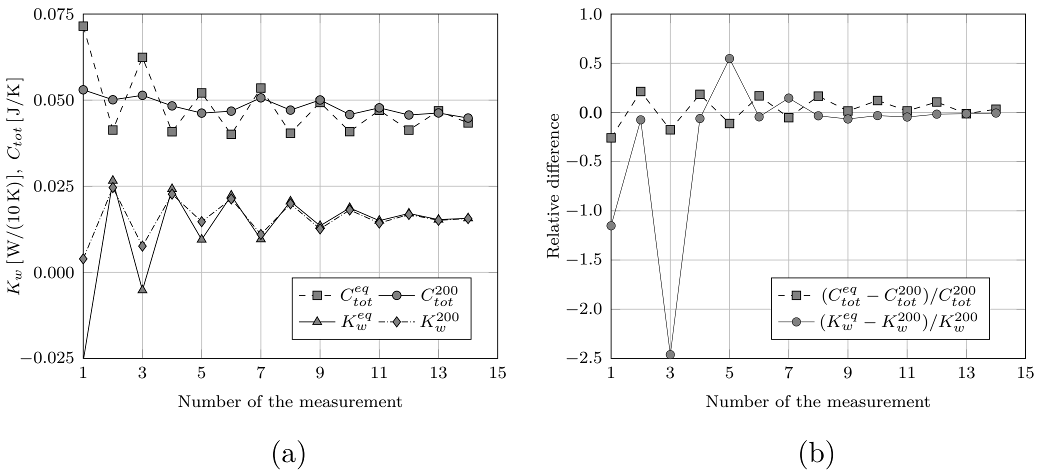
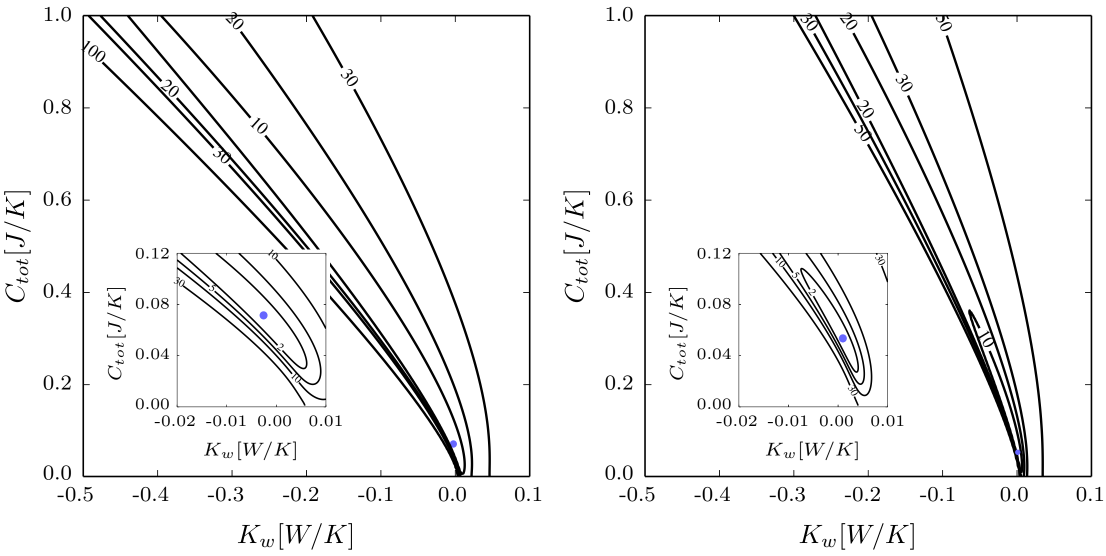


Figure 8: (a) Visual presentation of K_w and C_{tot} from Tables 1 and 2. The upper index indicates the origin of the data (eq . . . Table 1, 200 . . . Table 2) and the x-axis represents the number of measurement, i.e., the row of the table. Please note the different scale of K_w and C_{tot}. (b) shows the relative difference between K_w and C_{tot} of Tables 1 and 2, respectively.

As mentioned earlier, both fit parameters K_w and C_{tot} converge in an interleaving way, as can be seen from Fig. 8a. Every single measurement yields two sets of parameters for the part where the heater is turned on and off. Unless there is a phase transition during the measurement these two sets of parameters should be equal. The longer a measurement takes, the smaller this difference gets, as can be seen from Fig. 8a.

The measurement time per τ serves as a performance metric on the quality of the fit parameters. One complete measurement, i.e., heating-up and cooling-down of the calorimeter done in $2\,\tau$ seconds seems to be optimal. If a measurement takes much longer than $2\,\tau$ seconds there is no additional gain since the parameters K_w and C_{tot} do not change beyond that time, as can be seen from Fig. 8b.

Fitting the data is the most important part of a measurement and will therefore be discussed briefly. As mentioned earlier in Sec. 2.1, the fit uses a greedy algorithm and depending on the initial values it propagates to the nearest minimum which is shown in Fig. 9.



(a) (b)

Figure 9: Contour map of the χ^2 distribution the fit is minimizing. Every pair of numbers in the coordinate system represent a starting point for a fit. Starting from this point the fit then propagates towards the nearest minimum. The values of K_w and C_{tot} corresponding to this found minimum are the results of the fit. Both plots are generated from the heat-up data presented in Fig. 7a with a heating current of (a) 7 mA and (b) 5.5 mA. The insets show a zoom of the χ^2 distribution with its minimum, which is given by the blue dot.

As can be seen from the figures above, each of the plots has only one single minimum which is the pair of return values from the fit. Since this is the global minimum, the fit converges reliably against the same value for a vast range of initial parameters.

2.2.2 Two-tau Model

Despite the limitations of the room-temperature set-up, the fit of the two-tau model was investigated. Similarly to the the simple model before, the contour plots of the χ^2 distribution for the two-tau model were created and are presented in Fig. 10. During a measurement, the fit of the two-tau model takes K_w and C_p from the calibration (see Sec. 1). Since it is not possible to perform a calibration with the high-temperature set-up, the average values of the parameters K_w and C_{tot} obtained from the fit against the simple model were used as input parameters for the fit of the two-tau model. The value of C_{tot} was reduced by an arbitrary percentage of 25 %. This should simulate the fact that C_{tot} from the simple model is the addenda value C_{add}, which should smaller than the heat capacity during the measurements with sample and grease.

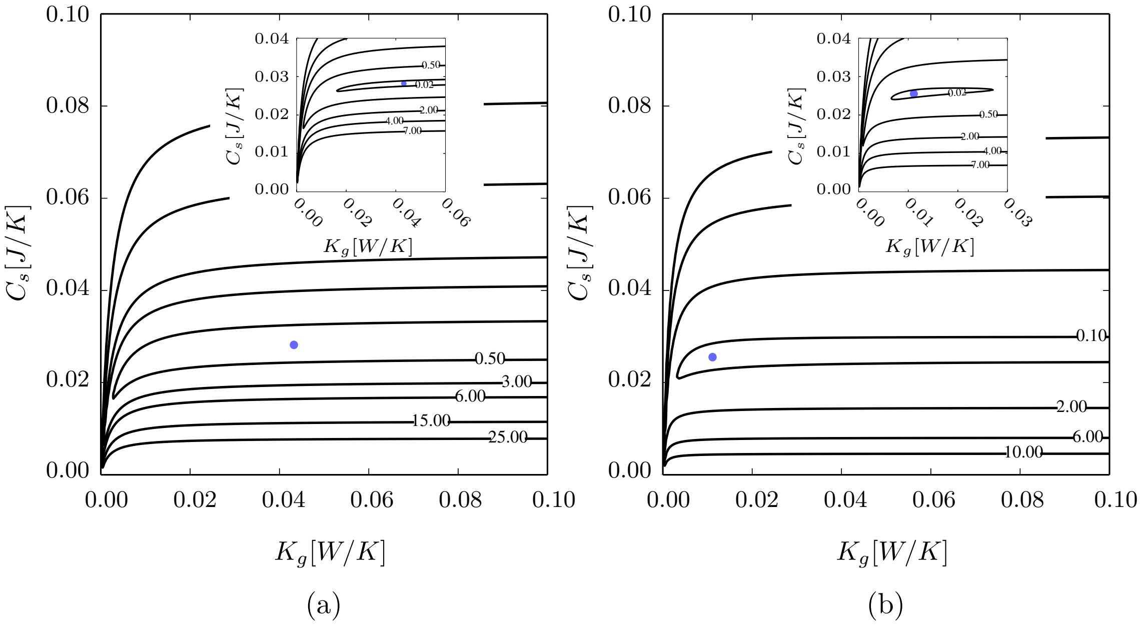


Figure 10: Contour plot of the χ^2 distribution for (a) heating-up and (b) cooling-down of the two-tau model using the measurement with a heater current of 4.5 mA presented in Fig. 7a. For details, see the text and image description of Fig. 9.

The χ^2 distribution of the two-tau model converges against a single global minimum like the fit of the simple model, as can be seen from Fig. 10. The RMS error for the heat-up data is 0.0124 and the resulting fit parameters are $K_g = 0.0432 \pm 0.0070\, W/K$ and $C_s = 0.0282 \pm 0.00021\, J/K$. For the cool-down data, the two-tau fit yields a RMS error of 0.0176 and the resulting fit parameters are $K_g = 0.0111 \pm 0.0013\,W/K$ and $C_s = 0.0255 \pm 0.0003\,J/K$. The time coefficients are $\tau_1 = 0.24\,s$ and $\tau_2 = 29.83\,s$ for the heat-up data and the fit of the cool-down data yields the time coefficients $\tau_1 = 0.14\,s$ and $\tau_2 = 77.0\,s$. Using these parameters, the best approximation of the two-tau fit is presented in Fig. 11.

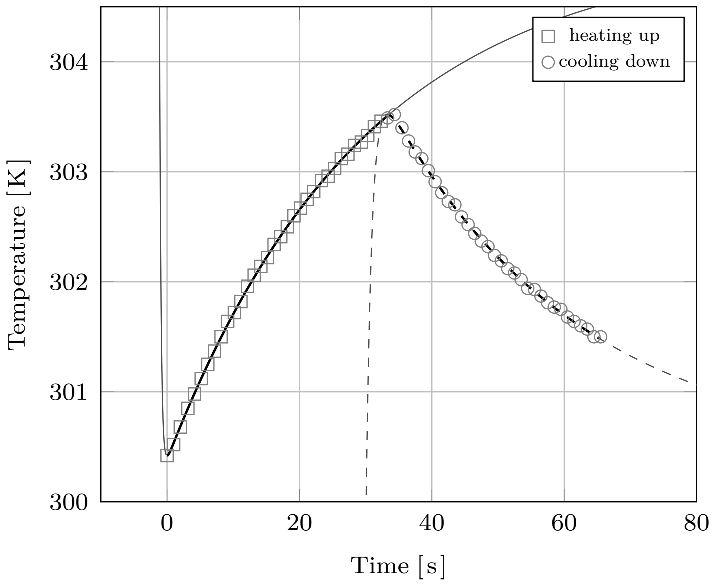
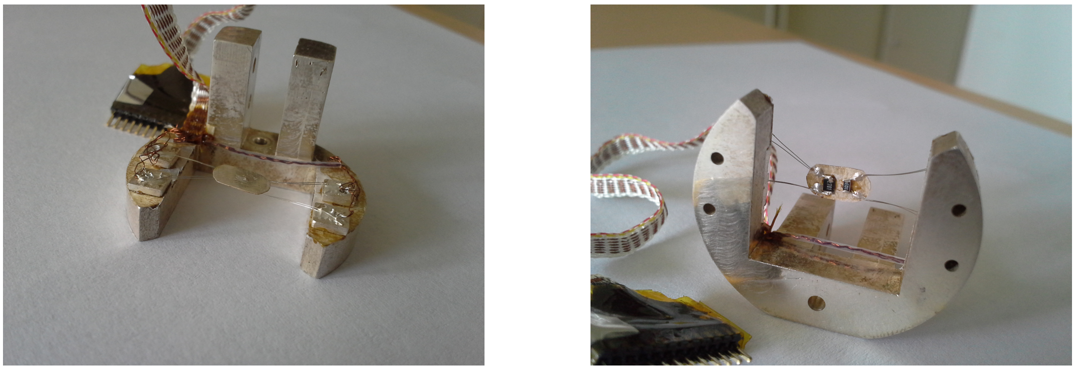


Figure 11: Measured temperature response curve and the corresponding fit of the two-tau model. The fit represents the best approximation of the two-tau model to the measured data with the initial parameters C_p and K_w as can be seen from Fig. 10. Please note the minimum of the fit for the heat-up data at the beginning of the measurement and the maximum for the cool-down data when the heater was turned off. These extrema occur because of the initial and continuity conditions used to derive the model (see Sec. A.2 for more information). Therefore the fit can only be used to approximate the measurements for times greater than the extremum ($t > 0$ for heating up and $t > t_0$ for cooling down).

The parameters from both fits of the two-tau model are prone to small variations in C_{tot}, i.e., small changes in the above mentioned arbitrary chosen 25 % of C_{tot} result in a big change of the values obtained from the two-tau fit. Additionally the quality and amount of the data available is very limited (no calibration, limited ΔT) and the nonadiabatic set-up generates noise due to the strong temperature coupling with the environment. Therefore, the fit of the two-tau model can only be tested properly using a low-temperature set-up, i.e., a sample measurement.

2.3 Low-temperature Set-up

As mentioned earlier in Sec. 2.2, the measurements at low temperatures are done using a dilution fridge to measure temperatures up to approximately 50 mK. The sample holder used for these measurements is shown in Fig. 12.



(a) (b)

Figure 12: Sample holder for the low-temperature measurements. The top side (a) where the grease and sample is placed on a platform made of silver, and the bottom side (b) with the heater (thin film metal resistor 10 kΩ) and thermometer (RuO2 2.7 kΩ). Please note the four wires (Pt0.9Ir0.1) connecting thermometer and heater each to utilize the 4-point probes method.

The sample holder was designed to be expandable, which means that additional measurement units can be placed on top of the sample holder. This allows to perform multiple measurements at once with different samples simultaneously to save time.

2.3.1 Measuring Program

Figure 5 provides a good overview of the measurement process, but some aspects are presented in a simplified way, like the success of a fit. Hence, we will present a more detailed description of the program. At its start various initial parameters are set: $\mathtt{T}_{\mathtt{min}}$ and $\mathtt{T}_{\mathtt{max}}$ define the temperature sweep range of the series of measurements. This sweep range is divided into `measpts` linear or logarithmic intervals, which are stored in an array. Each value in this array represents a starting temperature $\mathtt{T}_{\mathtt{start}}$ for a measurement. The temperature of the sample is set to $\mathtt{T_{start}}$ and a heat pulse is applied until the temperature rises to `tempPercentInc` percent of the heat bath, i.e., $\mathtt{T_{start}}$. The maximum allowed current the heater can be set to is definded by `maxCrt`. For the first measurement, the initial fit parameters as well as the heatercurrent `setcurrent` are set manually and the program adapts these values for subsequently measurements. A measurement and its involved parameters are presented in Fig. 13.

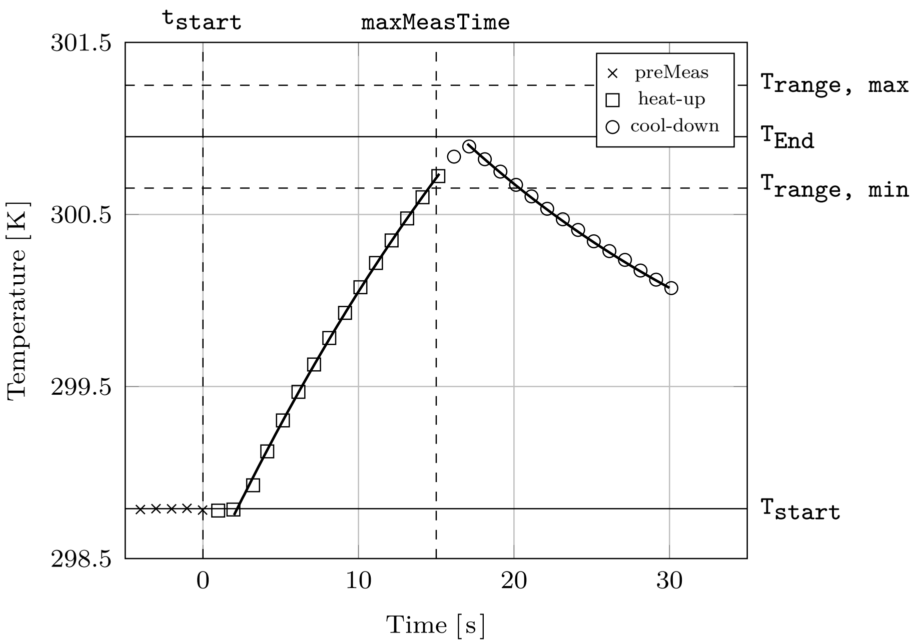


Figure 13: Measured temperature response curve including all the important parameters and the resulting fit of the simple model. Five measuring points are recorded to visualize the change in temperature prior to the heat pulse. At t=$\mathtt{t_{start}}$ the heater is switched on until the temperature or time surpasses $\mathtt{T_{end}}$ or `maxMeasTime`, respectively.

The function which performs the measurement yields the time and temperature values, as well as the measurement at which the current source was shut down. Recording of a single point takes almost exactly one second, which results in a delayed response in the temperature response curve, as can be seen from Fig. 13. Hence, the first point of both the heat-up data and the cool-down data are not used for the fit.

Figure 14 shows the flow chart of the program to measure the specific heat capacity. After initialization, the temperature is set to $\mathtt{T_{start}}$ and the measurement starts when the temperature has settled, i.e., when the slope of the linear fit of the last 10 temperature measuring points falls under a certain threshold. The first measuring point after the current source was turned off is taken as the maximum temperature $\mathtt{T}_{\mathtt{max}}$ (see Fig. 13). For a sample measurement, the addenda is read by evaluation through a cubic spline. The dashed lines in Fig. 14 represent these two different measurements. Despite the implementation of the addenda and sample measurement in two different programs, both are presented in the same flow chart because of their major similarities.

During an addenda measurement, the thermal conductivity of the wires is calculated using $\mathtt{K}_{\mathtt{W}} = \mathtt{P}_{\mathtt{0}}/(\mathtt{T}_{\infty} - \mathtt{T}_{\mathtt{start}})$ with $\mathtt{T}_{\infty}$ being the value of the fit to the heat-up data as $\mathtt{T}$ approaches infinity. Then it is determined, whether $\mathtt{T}_{\mathtt{max}}$ reached the desired temperature range ($t \in [\mathtt{T}_{\mathtt{range,\ min}} : \mathtt{T}_{\mathtt{range,\ max}}]$). If this is true, the heater current was set properly and the time parameters are used to verify the success of the fit. A failure of the fit is indicated either by a negative time parameter of the heat-up data or the ratio of the time parameters between heating-up and cooling-down being either too large or too small. With only the fit failing, the current of the heater is not changed and the measurement will be repeated up to three times. If $\mathtt{T}_{\mathtt{max}}$ does not reach the desired temperature range, the current of the heater is adjusted using

$$\mathtt{setcurrentNew} = \sqrt{\frac{\mathtt{tempPercentInc}}{100} \cdot \frac{\mathtt{T}_{\mathtt{start}}}{\mathtt{T}_{\mathtt{start}} - \mathtt{T}_{\mathtt{max}}}} \cdot \mathtt{setcurrent},$$

which will increase the current if $\mathtt{T}_{\mathtt{max}}$ is smaller than $\mathtt{T}_{\mathtt{end}}$ and decrease the current if $\mathtt{T}_{\mathtt{max}}$ is greater than $\mathtt{T}_{\mathtt{end}}$. One change of the current is limited to the factor of two, which means the new set current is limited to two times or half of the old value. With a valid measurement and a valid fit, the corresponding values are written to a file and `maxMeasTime` is set to two times the time parameter of the fit against the heat-up data. Similar to the current, the parameter `maxMeasTime` can vary at maximum by the factor of two. The resulting values from the fit are used as initial parameters for the next measurement.

To summarize, starting from set initial parameters the program performs a measurement and fits the measured data. The current is changed until the maximum of the temperature response curve $\mathtt{T}_{\mathtt{max}}$ resides in the desired range, which yields a valid measurement. In the event of an incorrect fit, the measurement is repeated up to three times before it is skipped. If both, measurement and its fit succeed the values are written to a file and these parameters are used for the next measurement.

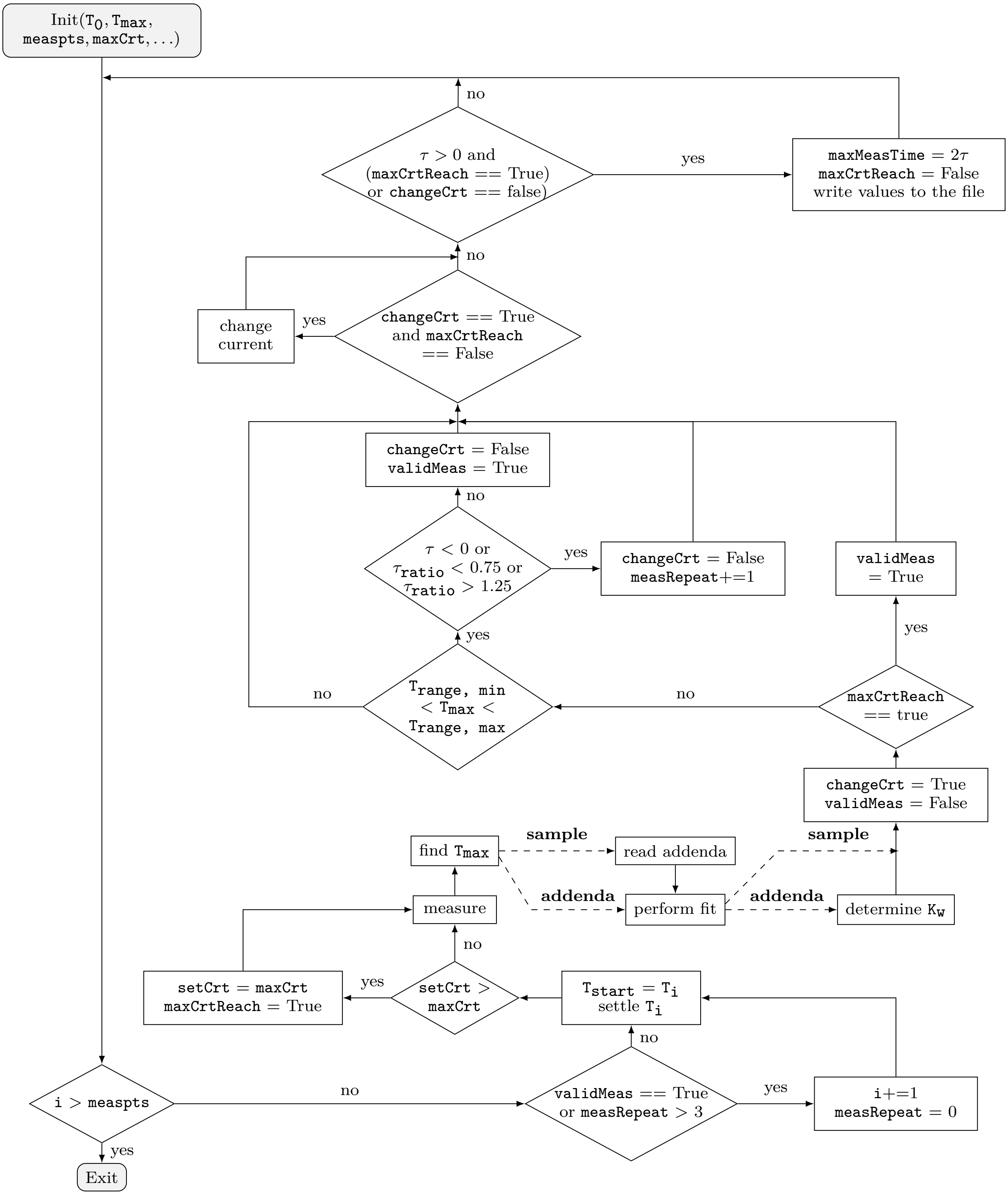


Figure 14: Flow chart of the calibration and sample measurement. For details please see text.

2.3.2 Measurements

In this Section, measurements performed with the program described in the previous Section will be presented. Figure 15 shows an addenda measurement.

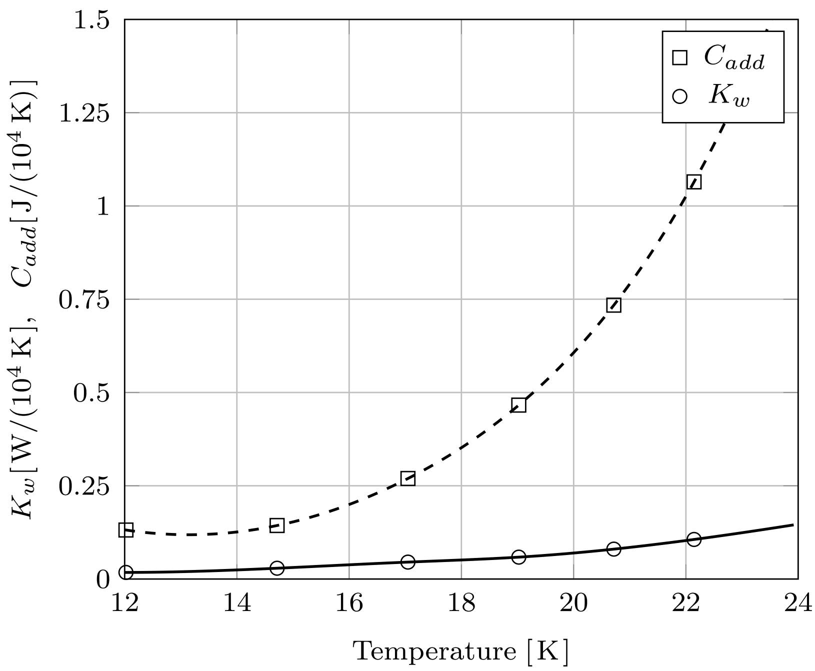


Figure 15: Addenda measurement (sample holder without grease and sample) at low temperatures with the corresponding spline interpolation. While C_{add} is the heat capacity of the platform, wires, heater and thermometer, K_w represents the thermal conductivity of the wires. Please note the low temperature dependency of K_w.

3 Conclusions

The two-tau model, which is being used for the measurement of the heat capacity, has been derived. A python program was written to control measurements and process the recieved temperature response curves. Measurements with a room-temperature set-up have been conducted to test this program. These measurements have shown that it is possible to apply the two-tau method to the data from the room-temperature set-up. These measurements show that one single measurement should be done in 2τ seconds (see Sec. 2.2.1).

Appendix

A Derivation of the Time Coefficients

A.1 Simple Model

The differential equation for the simple model is given by Eq. (6), which can be rewritten as follows:

$$C_{tot}\,\frac{dT(t)}{dt} + K_w T(t) = P(t) + K_w T_0 \tag{8}$$

with the homogeneous part of the equation:

$$C_{tot}\,\dot{T}(t) + K_w T(t) = 0. \tag{9}$$

Equation (9) is solved by separation of variables and integrating both sides.

$$\frac{\dot{T}(t)}{T(t)} = -\frac{K_w}{C_{tot}}$$

$$\int \frac{\dot{T}(t)}{T(t)} dt = -\int \frac{K_w}{C_{tot}} dt$$

$$ln(T(t)) = -\frac{K_w}{C_{tot}}\,t + C$$

$$y_h(t) = C'\;e^{-t(K_w/C_{tot})} = C'\;e^{-t/\tau} \tag{10}$$

Since the inhomogeneity in Eq. (8) is a constant, we guess a constant particular solution $y_p(t) = D$. Substitution of $y_p(t)$ and its derivative into Eq. (8) gives

$$K_w D = P_0 + K_w T_0$$

and therefore the particular solution is given by

$$y_p(t) = \frac{P_0}{K_w} + T_0.$$

The general solution for $T_{P_{on}}(t)$, i.e., $P(t) = P_0$ is

$$T_{P_{on}}(t) = \underbrace{C' \, e^{-t/\tau}}_{y_h(t)} + \underbrace{\frac{P_0}{K_w} + T_0}_{y_p(t)} .$$

With the initial condition $T_{P_{on}}(0) = T_0$ the constant C' can be determined:

$$T_{P_{on}}(0) = C' + \frac{P_0}{K_w} + T_0 = T_0,$$

and thus the solution to the initial-value problem during heating-up is

$$T_{P_{on}}(t) = \underbrace{-\frac{P_0}{K_w}}_{C'} e^{-t/\tau} + \frac{P_0}{K_w} + T_0 = \frac{P_0 \tau}{C_{tot}} \left(1 - e^{-t/\tau}\right) + T_0.$$

For $t > t_0$, the heater is turned off and therefore $P(t)$ is zero in Eq. (8). The inhomogeneous part is solved similarly to $T_{P_{on}}(t)$. We assume that the particular solution is a constant $y_p(t) = E$. Substitution of $y_p(t)$ and $\dot{y}_p(t)$ into Eq. (8) gives

$$K_w E = K_w T_0,$$

and the general solution is

$$T_{P_{off}}(t) = \underbrace{C' \, e^{-t/\tau}}_{y_h(t)} + \underbrace{T_0}_{y_p(t)} .$$

Continuity of $T_{P_{off}}(t)$ and $T_{P_{off}}(t)$ at $t = t_0$ yields:

$$\underbrace{\frac{P_0 \tau}{C_{tot}} \left(1 - e^{-t_0/\tau}\right) + T_0}_{T_{P_{on}}(t_0)} = \underbrace{C' e^{-t_0/\tau} + T_0}_{T_{P_{off}}(t_0)}$$

$$C' = \frac{P_0 \tau}{C_{tot}} \left(1 - e^{-t_0/\tau}\right) e^{t_0/\tau}.$$

With the constant C', one can write $T_{P_{off}}(t)$ as follows:

$$T_{P_{off}}(t) = \underbrace{\frac{P_0 \tau}{C_{tot}} \left(1 - e^{-t_0/\tau}\right) e^{t_0/\tau}}_{C'} e^{-t/\tau} + T_0 = \frac{P_0 \tau}{C_{tot}} \left(1 - e^{-t_0/\tau}\right) e^{(t_0 - t)/\tau} + T_0.$$

A.2 Two-tau Model

Since the thermometer is firmly attached to the sample platform there is no way to measure the temperature of the sample directly. The idea is to eliminate the temperature of the sample $T_s(t)$ in Eq. (3) using Eq. (2). Solving Eq. (2) for $T_s(t)$ and differentiate it yields:

$$T_s(t) = \frac{C_p}{K_g}\dot{T}_p(t) - \frac{P(t)}{K_g} + \frac{K_w}{K_g}T_p(t) - \frac{K_w}{K_g}T_0 + T_p(t), \tag{11}$$

and

$$\dot{T}_s(t) = \frac{C_p}{K_g}\ddot{T}_p(t) - \frac{\dot{P}(t)}{K_g} + \frac{K_w}{K_g}\dot{T}_p(t) + \dot{T}_p(t). \tag{12}$$

By substituting Eq. (11) and Eq. (12) into Eq. (3) we get a second order differential equation which is only dependent of T_p:

$$\ddot{T}_p(t)+\frac{K_g}{C_pC_s}\left(\frac{C_sK_w}{K_g}+C_p+C_s\right)\dot{T}_p(t)+\frac{K_gK_w}{C_pC_s}T_p(t) = \frac{K_g}{C_pC_s}\Big(P(t)+K_wT_0\Big). \tag{13}$$

With the assumption that the solution will be in the form of $T(t) = Ae^{-\lambda t}$ we plug it into Eq. (13) and obtain the characteristic polynomial

$$\lambda^2 - \left(\frac{C_sK_w + C_pK_g + C_sK_g}{C_pC_s}\right)\lambda + \frac{K_gK_w}{C_pC_s} = 0$$

with the solutions

$$\lambda_{1,2} = \underbrace{\frac{C_sK_w + C_pK_g + C_sK_g}{2C_pC_s}}_{\alpha} \pm \underbrace{\sqrt{\frac{(C_sK_w + C_pK_g + C_sK_g)^2}{4{C_p}^2{C_s}^2} - \frac{K_gK_w}{C_pC_s}}}_{\beta}.$$

Using the abbreviations

$$\tau_1 = \frac{1}{(\alpha+\beta)}, \qquad \tau_2 = \frac{1}{(\alpha-\beta)}, \qquad \alpha = \frac{K_w}{2C_p} + \frac{K_g}{2C_s} + \frac{K_g}{2C_p},$$

and

$$\beta = \frac{\sqrt{{C_s}^2K_w+2{C_s}^2K_gK_w+2C_pC_s{K_g}^2+{C_p}^2{K_g}^2+{C_s}^2{K_g}^2-2C_pC_sK_gK_w}}{2C_pC_s} \tag{14}$$

the homogeneous solution of Eq. (13) can be written as follows:

$$y_{hom}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}. \tag{15}$$

The inhomogeneous part of Eq. (13) is solved similarly to the one of the simple model. For the domain $0 \leq \text{t} \leq t_0$ where $P(t) = P_0$ we obtain the general solution

$$T_{P_{on}}(t) = \underbrace{A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}}_{y_h(t)} + \underbrace{\frac{P_0 + K_w T_0}{K_w}}_{y_p(t)}. \tag{16}$$

With the initial conditions $T_{P_{on}}(0) = T_0$ and $\dot{T}_{P_{on}}(0) = 0$ the coefficients A_1 and A_2 are

$$A_1 = \frac{P_0}{K_w}\left(\frac{\tau_1}{\tau_2 - \tau_1}\right) = \frac{P_0}{K_w}\left(\frac{1}{2\beta\tau_2}\right)$$

and

$$A_2 = -\frac{P_0}{K_w}\left(\frac{\tau_2}{\tau_2 - \tau_1}\right) = -\frac{P_0}{K_w}\left(\frac{1}{2\beta\tau_1}\right).$$

Inserting A_1 and A_2 into Eq. (16) gives

$$T_{P_{on}}(t) = \frac{P_0}{2\beta K_w}\left(\frac{e^{-t/\tau_1}}{\tau_2} - \frac{e^{-t/\tau_2}}{\tau_1}\right) + \frac{P_0 + K_w T_0}{K_w}. \qquad 0 \leq t \leq t_0$$

In the domain $t > t_0$ the heater is turned off ($P(t) = 0$) and the general solution for Eq. (13) is

$$T_{P_{off}}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + T_0. \tag{17}$$

With the conditions $T_{P_{on}}(t_0) = T_{P_{off}}(t_0)$ and $\dot{T}_{P_{on}}(0) = -\dot{T}_{P_{off}}(t_0)$, one can determine the coefficients

$$A_1 = -\frac{P_0}{4\beta^2 K_w \tau_2}\left(\frac{e^{-t_o/\tau_1}}{\tau_2} - \frac{e^{-t_o/\tau_2}}{\tau_1} + 2\beta\right)e^{t_0/\tau_1}$$

and

$$A_2 = \frac{P_0}{4\beta^2 K_w \tau_1}\left(\frac{e^{-t_o/\tau_1}}{\tau_2} - \frac{e^{-t_o/\tau_2}}{\tau_1} + 2\beta\right)e^{t_0/\tau_2}.$$

Inserting A_1 and A_2 into Eq. (17) gives after some manipulation

$$T_{P_{off}}(t) = \frac{P_0}{4\beta K_w}\left[2 - \frac{1}{\beta}\left(\frac{e^{-t_0/\tau_2}}{\tau_1} - \frac{e^{-t_0/\tau_1}}{\tau_2}\right)\right]\left[\frac{e^{(t_0-t)/\tau_2}}{\tau_1} - \frac{e^{(t_0-t)/\tau_1}}{\tau_2}\right] + T_0. \qquad t > t_0$$

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[2] Hwang *et al.*, Rev. Sci. Instrum. **68**, 94 - 101 (1997)