2.2.1 Semiadiabatic heat pulse method

The most intuitive approach to the heat capacity $C_p = \frac{\partial U}{\partial T}$ is the adiabatic supply of heat ΔQ to the system while monitoring the temperature change ΔT. The ratio is the heat capacity of the system. In a real experiment adiabatic conditions can only be approximated. Because of that one speaks of the semiadiabatic heat pulse method. The basic set-up for measurements at low temperatures includes a platform, where the thermometer, the heater and the sample is installed. It is depicted schematically in Figure 1. For the electric connections and setting up the platform one uses wires or fibers with a low thermal conduction to increase the thermal resistance R_1. However, it should not become to high, since it is the only connection over which the sample platform is cooled. On the other hand, the thermal resistance R_2 between the platform and the sample is to be minimized. R_2 becomes noticeable in an internal relaxation time τ_2, that concerns the temperatures of the single components on the platform.

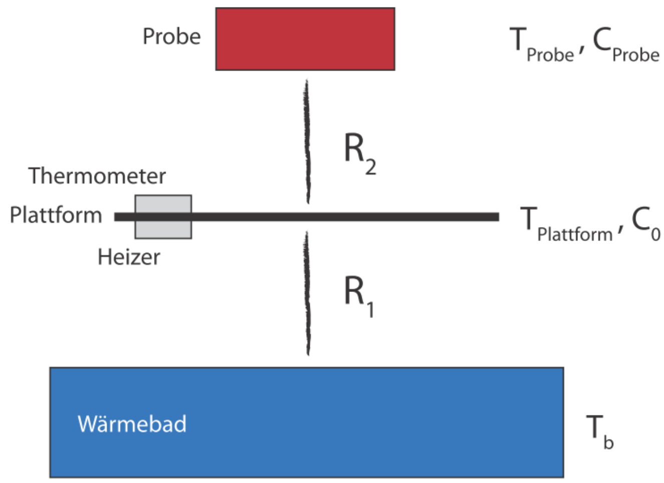

Figure 1: Schematic view of the set-up for measuring the heat capacity at low temperatures. The reservoir temperature T_b is kept as constant as possible. The thermometer measures the temperature of the platform, which has a good thermal contact to the sample over the thermal resistance R_2. The measured heat capacity is $C = C_0 + C_{\text{sample}}$.

In the ideal case ($R_1 \to \infty$ and $R_2 \to 0$) an adiabatic heat supply ΔQ leads to a change in temperature ΔT. In a non-adiabatic case thermal energy is already lost during the heating process to the environment. Moreover, after the heat pulse there is a fast relaxation in temperature because of the internal relaxation processes, that (in the most cases) eventually changes into a slower relaxation. The typical behaviour is shown in Figure 2 (red curve). The external relaxation against the heat reservoir with the time constant τ_1 is superimposed with an internal relaxation τ_2 directly after the heater is switched off. Now, the temperature measured straight after the heating pulse does correspond to the ideal adiabatic ΔT. But it is possible to extrapolate the measured temperature profile and calculate the value ΔT for an ideal adiabatic heating curve. We consider the thermal balance of the sample platform and the environment and obtain for the heat supplied by the heater:

$$Q_{\text{heat}} = \frac{1}{R_1} \int_0^\infty (T(t) - T_0)\, dt$$

Here $T(t)$ is the time dependence of the sample temperature and T_0 the base temperature before the heating pulse. The result is independent of internal relaxation processes, so that the supplied heat can always be obtained by multiplying the area under the curve $T(t)$ with $K_1 = \frac{1}{R_1}$. The formula is also valid for a virtual curve $T_{\text{id}}(t)$ without internal relaxation, but with an external relaxation over the thermal resistance R_1 and an assumed instantaneous heat pulse at t_{id}. Then:

$$T_{\text{id}}(t) - T_0 \propto e^{\frac{-t}{\tau}} \text{ with } \tau = R_1(C_0 + C_{\text{sample}})$$

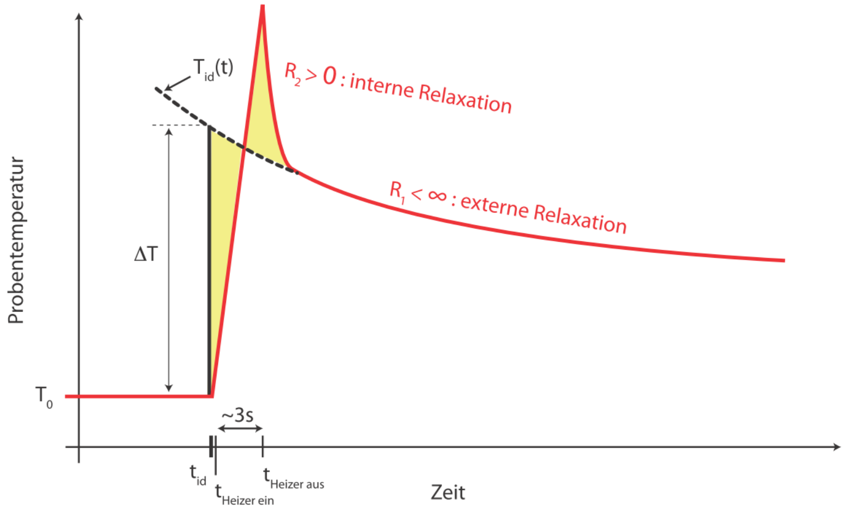

Figure 2: Heat pulse technique – Interpretation of the measurement curve using the area adjustment method. By enhancing the external relaxation backwards to a virtual time t_{id} the internal relaxation processes can be considered.

The function can be adjusted to the real temperature behaviour for $t \gg \tau_2$, i.e. when internal relaxation processes do not play a role any more. The time t_{id} follows from the requirement that the invested energy is the same:

$$Q_{\text{heat, real}} = Q_{\text{heat, ideal}} \Leftrightarrow \int_0^{\infty} (T(t) - T_0)\, dt = \int_{t_{\mathrm{id}}}^{\infty} (T_{\mathrm{id}}(t) - T_0)\, dt$$

This equation for t_{id} holds, if the yellow shaded areas in Figure 2 are equal. For the ideal height of the heating pulse we now obtain

$$\Delta T = T_{\mathrm{exp}}(t_{\mathrm{id}}) - T_0 \ .$$

Finally, with the thermal resistance of the heater R, the heating time t and the heater current I, the heat capacity follows from:

$$C_p = \frac{\Delta Q}{\Delta T} = \frac{RI^2 \cdot t}{T_{\mathrm{exp}}(t_{\mathrm{id}}) - T_0}$$

2.2.2 Relaxation method

The relaxation method is based on the coupling of the sample to the heat reservoir and monitoring the sample temperature as a function of time. For each measuring point the following procedure is followed:

- Wait for the sample temperature T_0 to stabilize
- Increase the heating power by ΔP at the time t
- Observe the exponential development of a temperature gradient ΔT between the sample and the environment
- Reset the heating power at the time t_2
- Observe the exponential relaxation back to T_0

The exponential behaviour of the sample temperature after the increase and decrease of the heating power is determined by the heat capacity and the thermal conductance K_1 with respect to the heat reservoir. The theoretical description becomes easier for $R_2 \to 0$, i.e. for a vanishing internal relaxation time in the ensemble of sample and platform[1]. You have then $T = T_{\text{sample}} = T_{\text{platform}}$ and a mutual heat capacity $C = C_0 + C_{\text{sample}}$. The temperature behaviour follows from the first law of thermodynamics.

$$\Delta Q = C\, dT$$

ΔQ is the amount of heat that is supplied by the heater and discharged over the finite thermal resistance R_1.

$$\Delta Q = \Delta Q_{\text{heat}} + \Delta Q_{R_1}$$

The resistance R_1 (or the conductance $K_1 = 1/R_1$), that corresponds to the thermal coupling to the heat reservoir, is for example a wire that connects the platform with the environment. By applying the law of diffusion ($\vec{j} = -\kappa \vec{\nabla} T$) and the continuity equation ($\dot{\rho} = -div\, \vec{j}$) we obtain for an one-dimensional conduction of heat in the thermodynamic equilibrium ($\dot{\rho} = 0$)

$$\frac{\dot{Q}_{R_1}}{A} = \kappa(T) \frac{dT}{dx} \ ,$$

where $\dot{Q}_{R_1}$ is the amount of heat per time that flows through the wire with the cross section A. κ is the temperature-dependent thermal conductivity. Integration over the thermal conductance coefficient $K(T) \equiv A \cdot \kappa(T)/l$ yields

$$\dot{Q}_{R_1} = -\int_{T_b}^{T} K(T)\, dT \ .$$

Here, T_b and T are the temperatures at the beginning and at the end of the wire with the temperature gradient. If the change of the sample temperature T caused by the heating is small in comparison to the base temperature T_b, it is possible to integrate over the constant averaged value $\bar{K}_1$ and we get

$$\dot{Q}_{R_1} = -\bar{K}_1 (T - T_b) \ .$$

Using a constant heating power ΔP, one can now write down a differential equation for the thermal behaviour. For reasons that become obvious later, we use T_0 instead of T_b in the following.

$$C\, dT = \Delta P\, dt - \bar{K}_1 (T - T_0)\, dT$$

The solution is an exponential curve with the general form:

$$T(t) - T_0 = \partial T(t) = \frac{\Delta P}{\bar{K}_1} + \left(\partial T(t_0) - \frac{\Delta P}{\bar{K}_1} \right) e^{-\bar{K}_1/C(t-t_0)}$$

For the turn-on procedure with $\Delta P > 0$, times $t > t_1$ and the relaxation time $\tau \equiv C/\bar{K}_1$ the temperature curve corresponds to that of a capacitor.

$$T_{\text{heat}}(t) = T_0 + \underbrace{\frac{\Delta P}{\bar{K}_1}}_{\equiv \Delta T} (1 - e^{-(t-t_1)/\tau})$$

The value of $\bar{K}_1$ is initially not known, but can be derived from the heating curve. After a long heating period a temperature gradient $\frac{\Delta P}{\bar{K}_1} = \Delta T$ is established:

$$T_{\text{heat}}(t \to \infty) = T_0 + \frac{\Delta P}{\bar{K}_1}$$

[1] From the experimental point of view a minimized internal relaxation time is desirabel. It is possible to consider these processes in the analysis, but you rarely obtain more information than by just ignoring the measuring points that are affected by the internal relaxation.

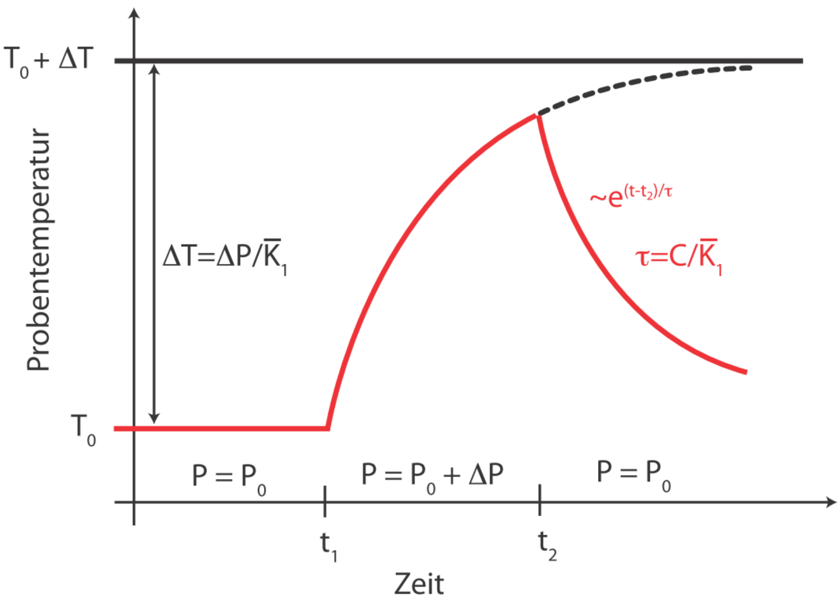

Figure 3: Relaxation technique – The red curve shows the typical course of a warm-up and cool-down curve depending on the heating power. The dashed line represents the extrapolated warm-up curve, approaching the limit $T_0 + \Delta T$. The thermal conductance to the environment can then be derived from the equation $\Delta T = \Delta P/\bar{K}_1$.

The power ΔP and the stabilized base temperature T_0 are known, so that $\bar{K}_1$ can be calculated. However, in practice it is not possible to heat infinitely long. But ΔT can be determined by extrapolation of the heating curve to long time scales. The typical course of a warm-up and cool-down curve is shown in Figure 3, as well as a schematical representation of the extrapolation towards long time scales. Fitting of T_{relax} to the cool-down curve yields a value for the relaxation time $\tau = C/\bar{K}_1$. Thus, for each measured temperature value the relaxation method delivers the relaxation time and the thermal conductance coefficient, and consequently the heat capacity

$$C = \tau \cdot \bar{K}_1 \ .$$