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Temperature dependence of the heat capacity of copper

Richard Leven
richard.leven@udo.edu

Max Koch
max.koch@udo.edu

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TU Dortmund – Faculty for Physics

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1 Motivation

The main goal of this experiment is to determine the Debye temperature of copper. For this, a copper proof is first cooled down to liquid nitrogen temperatures, after which it is slowly heated up. The necessary heat energy for the heating process is measured.

2 Theory

This part of the lab protocol will discuss the theory behind the heat capacity of condensed matter. The different models of heat capacity will be shown and their motivation and usage will be described.

2.1 Classical model

Heat capacity

$$C = \frac{\Delta Q}{\Delta T} \tag{1}$$

is described as the amount of heat energy ΔQ that is needed to heat a probe by the temperature ΔT. With the first law of thermodynamics, it is then possible to describe the amount of heat ΔQ in a more accurate way. The first law of thermodynamics states

$$\mathrm{d}Q = \mathrm{d}U + p\mathrm{V}$$

the infinitesimal amount of heat $\mathrm{d}Q$ equals the inner energy $\mathrm{d}U$ added by the work done by the system or on the system. Now two different heat capacities derive from the equation (1) depending on the circumstances. If the probe is heated up while its volume stays the same $\mathrm{d}V = 0$ the heat capacity will be

$$C_\mathrm{V} = \frac{\mathrm{d}U}{\mathrm{d}T} \tag{2}$$

which is easy to calculate, but hard to measure. If the probe is heated up by constant pressure the calculations will be hard but it is easier to measure the heat capacity as the heat expansion or contraction does not matter. To calculate the heat capacity at constant pressure c_p from the heat capacity of a constant volume c_v the formula

$$c_\mathrm{p} - c_\mathrm{v} = TVB\alpha_\mathrm{V}^2 \tag{3}$$

can be used. It contains the bulk module

$$\frac{1}{B} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

and the compression module

$$\alpha_v = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p .$$

2.2 Dulong-Petit

As already mentioned the easiest way to calculate the heat capacity of a probe is to assume a constant volume. By doing so just the inner energy needs to be derived by the temperature T. In the classical model the inner energy

$$U = \frac{f}{2} N k_{\mathrm{B}} T$$

with f being the degrees of freedom, N the number of atoms, k_{B} the Boltzman constant and T the temperature. The classical model assumes that the heat capacity is given by the amount of oscillating atoms N inside the probe. Because the atoms can oscillate into three directions, they have $f = 6$ degrees of freedom. This means the heat capacity at constant volume can be written as

$$c_{\mathrm{v}} = \frac{\mathrm{d}U}{\mathrm{d}T} = 3 N k_{\mathrm{B}}$$

which further simplifies to the law of Dulong-Petit

$$c_{\mathrm{v,mol}} = 3R \tag{4}$$

if we plug in the Avogadro constant $N_{\mathrm{A}} = N$ for the number of atoms and write $R = N_{\mathrm{A}} k_{\mathrm{B}}$, with R being the gas constant. The law of Dulong-Petit is a good approximation for some metals at high temperatures above $T = 300\,\mathrm{K}$. However, it loses its accuracy for lower temperature at which the influence of quantum effects can not be neglected anymore.

2.3 Einstein model

As already mentioned the classical model breaks apart at low temperatures. This is due to the impossibility of lattice oscillations, which are called phonons, to take any energy level. Similar to the harmonic oscillator, phonons can just take on discrete energy

$$E_n = (n + \frac{1}{2}) \hbar \omega$$

with n being a natural number called the occupation number, ω being its eigenfrequency and $\hbar$ being the reduced Planck constant. As their energy $\hbar\omega >> k_{\mathrm{B}} T$ becomes bigger than the energy given by the temperature they can not promote to a different energy level. This behavior is illustrated in figure 1. Because of the quantized nature of phonon energy the average inner energy $< U >$ becomes

$$< U >= U_{\mathrm{eq}} + 3 N \hbar \omega (\frac{1}{2} + < n >) \tag{5}$$

where U_{eq} is the inner energy in equilibrium. One model that takes the quantum effects into account is the Einstein model. In this model, all the phonon modes are given the same possible eigenfrequency ω_{E}. This assumption suits optical phonons, acoustic

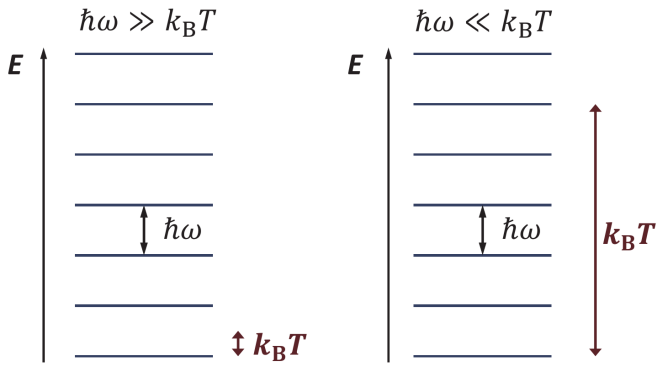


Figure 1: The picture illustrates the impossibility of a phonon to absorb heat energy as the temperature lowers beneath the possible energy that the phonon can take on.

phonons however, do not show this behavior. With this assumption the average inner energy

$$< U >= 3N\hbar\omega_{\mathrm{E}} \left(\frac{1}{2} + \frac{1}{\mathrm{e}^{\hbar\omega_{\mathrm{E}}/k_{\mathrm{B}}T} - 1} \right)$$

can be calculated by equation (5). The heat capacity in the Einstein model is now calculate by equation (2). The substitution

$$\Theta_{\mathrm{E}} = \frac{\hbar\omega_{\mathrm{E}}}{k_{\mathrm{B}}}$$

finally gives the heat capacity at constant volume

$$c_v^{\mathrm{E}} = 3Nk_{\mathrm{B}} \left(\frac{\Theta_{\mathrm{E}}}{T} \right)^2 \frac{\mathrm{e}^{\Theta_{\mathrm{E}}/T}}{\left[\mathrm{e}^{\Theta_{\mathrm{E}}/T} - 1 \right]^2}$$

in the Einstein model. At low temperatures $T << \Theta_{\mathrm{E}}$ the heat capacity becomes

$$c_v^{\mathrm{E}} = 3Nk_{\mathrm{B}} \left(\frac{\Theta_{\mathrm{E}}}{T} \right)^2 \mathrm{e}^{-\Theta_{\mathrm{E}}/T}$$

this result however, does not fit to measurements at low temperatures. Experiments show that the heat capacity should have a T^3 depends at low temperatures. The reason is that the einstein model does not model acoustic phonons, which are the main actors for heat capacity in condensed matter. For this, a new model is needed.

2.4 Debye model

The Debye model makes the following assumptions. First of all the possible phonon modes follow a linear dispersion as so

$$\omega_{\mathrm{i}} = v_{\mathrm{i}} q$$

with v_i being the velocity of sound in the medium and q being the absolute value of the wave vector $\vec{q}$. It should be mentioned that this assumption fits well for the dispersion behavior of acoustic phonons. Secondly the sum over all wave vectors $\vec{q}$ in the first Brillouin-Zone becomes an integral over a sphere with the same volume as the first Brillouin-Zone. The radius of this sphere is the Debye-wavevector

$$q_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3}$$

with which the debye temperature

$$\Theta_\mathrm{D} = \frac{\hbar v_s q_D}{k_\mathrm{B}}$$

can be defined. With one more substitution $x := \hbar v_s q / k_\mathrm{B} T$ the heat capacity in the Debye model can be expressed as

$$c_v^\mathrm{D} = 9 N k_\mathrm{B} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3 \int_0^{\Theta_\mathrm{D}/T} \frac{x^4 \mathrm{e}^x \mathrm{d}x}{(\mathrm{e}^x - 1)^2} \,.$$

As the goal is to find a good approximation of the heat capacity at lower temperature the heat capacity for temperature $T << \Theta_\mathrm{D}$ is looked at. The result is the expression

$$c_v^\mathrm{D} = \frac{12\pi^4}{5} N k_\mathrm{B} \left(\frac{T}{\Theta_\mathrm{D}}\right)^3$$

which shows the desired T^3 depends at lower temperatures.

The difference in the behavior at lower temperatures between the Einstein model and the Debye model can be seen in figure 2. Moreover, the T^3 and e^{-T} are well distinguishable as the exponential falls to zero way faster.

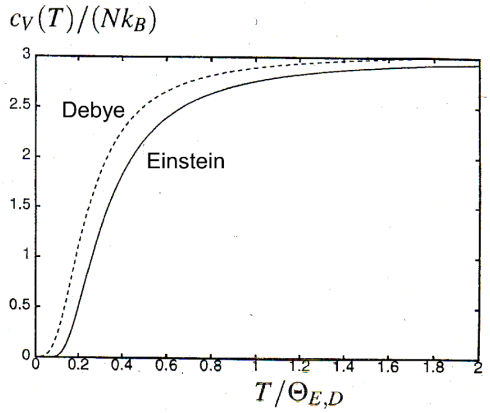


Figure 2: The heat capacity in the Einstein and the Debye model is plotted against the temperature. As the Einstein model contains a e^{-T} depends in temperature it falls way faster.

3 Setup and execution

The first part of this section will describe the setup, the later the execution of the experiment.

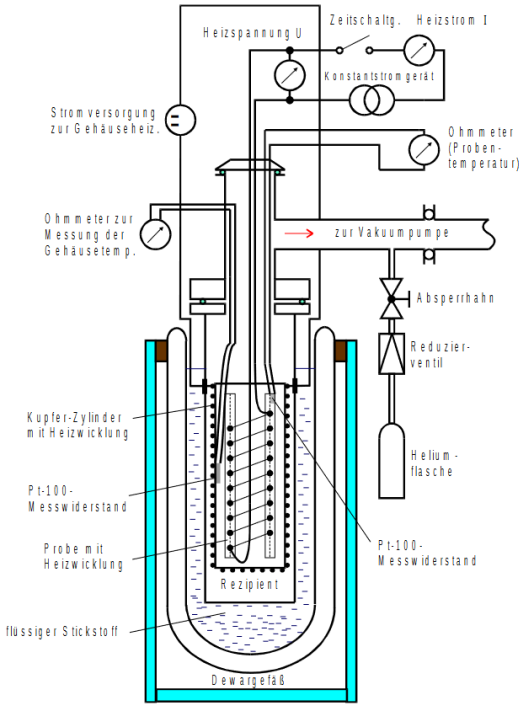
3.1 Setup

A diagram of the setup is shown in figure 3a, the actual experimental setup is shown in figure 3b. The main interest of this experiment is to measure the heat capacity at low temperatures two main things are needed

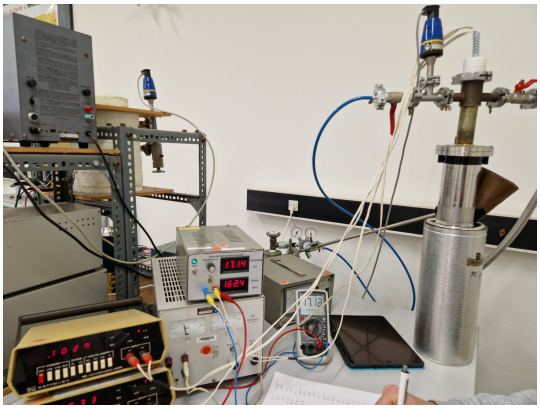
1. Low temperatures
2. Good heat isolation.

To achieve low temperatures, advantage is taken of a Dewar vessel, which is filled with liquid nitrogen. The Dewar vessel contains a recipient in which the copper probe is contained. Through the recipient, the second thing that is needed can be achieved as a vacuum can be pumped inside the recipient. Besides that, the recipient is connected to a helium container. This gives a high heat conduction to cool down the probe to liquid nitrogen temperatures. On the other hand through the vacuum that is pumped afterwards a good heat isolation is achieved, the heat isolation is additionally aided by a heat shield which is located inside the recipient.
The probe is located inside the recipient and surrounded by the heat shield. Inside the heat shield and the probe are a wire to control and measure the temperature of both. The temperature of the probe and heat shield is measured by a platinum 100 resistor.

As already mentioned the heat shield and the probe contain two separate wires. Both of them have a voltage source to accurately apply a heating current. Both voltage sources



(a) Schematic of the experimental setup. [**anleitung**]



(b) The actual experimental setup while the measurements are taken.

Figure 3

are connected to a volt meter, so that the heat power that is put into the copper can later be determined. A stopwatch is used to monitor the time.

3.2 Execution

At first the copper probe needs to be cooled down. To do so the Dewar vessel is filled with liquid nitrogen and the recipient is flooded with helium. The resistance of both the heat shield and the probe is constantly monitored while waiting for the probe to cool down to liquid nitrogen temperatures. After the probe and the heat shield reach the desired temperature, the helium bottle is disconnected from the recipient. Moreover, a vacuum pump is connected to the recipient to pump a vacuum inside the probe chamber. After some time the vacuum inside the recipient is sufficient to start the actual measurement. Now the voltage source of the probe heater and the heat shield are turned on, the stopwatch is turned on, the resistance of the platinum 100 at both the heat shield and the probe is written down as well as the applied voltage and current at the probe heater. Now every minute a new measurement of the heat shield and probe resistance is taken, the corresponding time and applied heat voltage and current is written down. This process is repeated until the probe reaches room temperature levels.

4 Evaluation

All calculations and graphs were calculated using the *python* package *uncertainties*[4]. The captured data values for resistance, current and voltage have been assigned the uncertainties:

- R[Ω] $\pm$ 0.1
- I[A] $\pm$ 0.0001
- U[V] $\pm$ 0.01

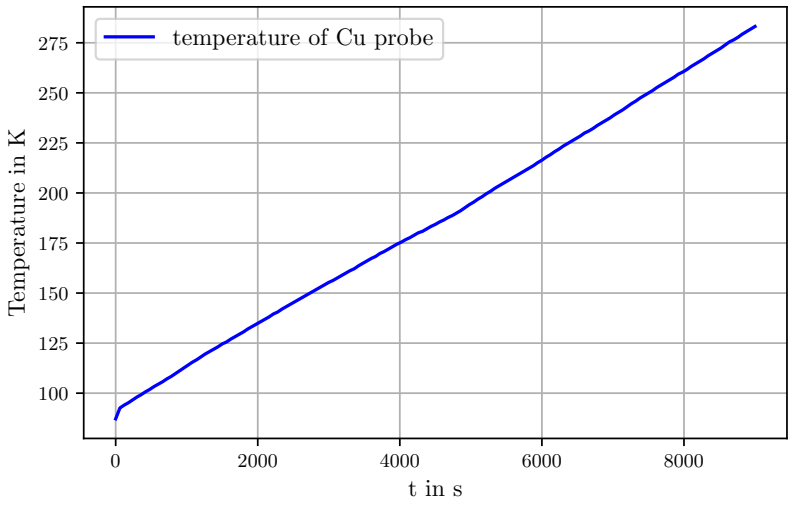
4.1 Molar heat capacity at constant pressure

During the execution of the experiment only resistances of the probe and shield and the current and voltage of the probe were monitored, see Table 1. To calculate the molar heat capacity those values need to be transformed into temperature and energy. With that the heat capacity can be calculated via Equation 2.

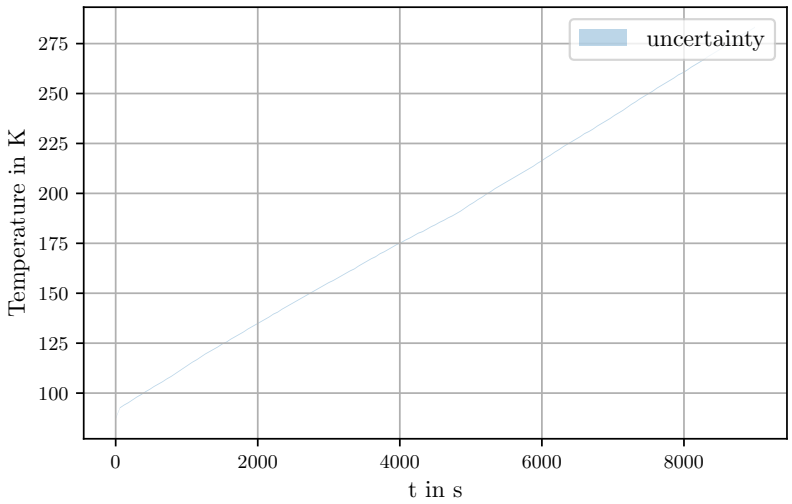
To calculate the temperature of the copper probe, the following formula was provided in source[3].

$$T = 0.00134R^2 + 2.296R - 243.02 \tag{6}$$

It gives the current temperature in C°, so in order to use it in calculations it needs to be transformed into units of Kelvin, by adding 273.15.
The resulting temperature and its uncertainty is displayed in Figure 4.



(a)



(b)

Figure 4: a)The rise in temperature as time increases is linear and spans an interval between 87 K and 283 K. b)This graph shows the total area of uncertainty of the temperature graph in a). It is shown separately because the area is smaller than the temperature's line width.

To use Equation 2, the energy E of the system must be calculated first, which is

$$E = \Delta t \cdot P = \Delta t \cdot U \cdot I \tag{7}$$

With the energy, the molar heat capacity at constant pressure follows Equation 8.

$$C_P = \frac{E}{\Delta T} \cdot \frac{M}{m} \tag{8}$$

The additional term $^M/_m$ is included as the molar part, where M is the molar mass of copper and m the mass of the copper probe. ΔT is the change in temperature. The copper probe weighs 342 g and the molar mass of copper is $M = 63{,}546\,\mathrm{g/mol}$[1]

Using Equation 8 the resulting heat capacity C_P averages to around 23,75 J/Kmol after approximately 200 K, as seen in Figure 5.

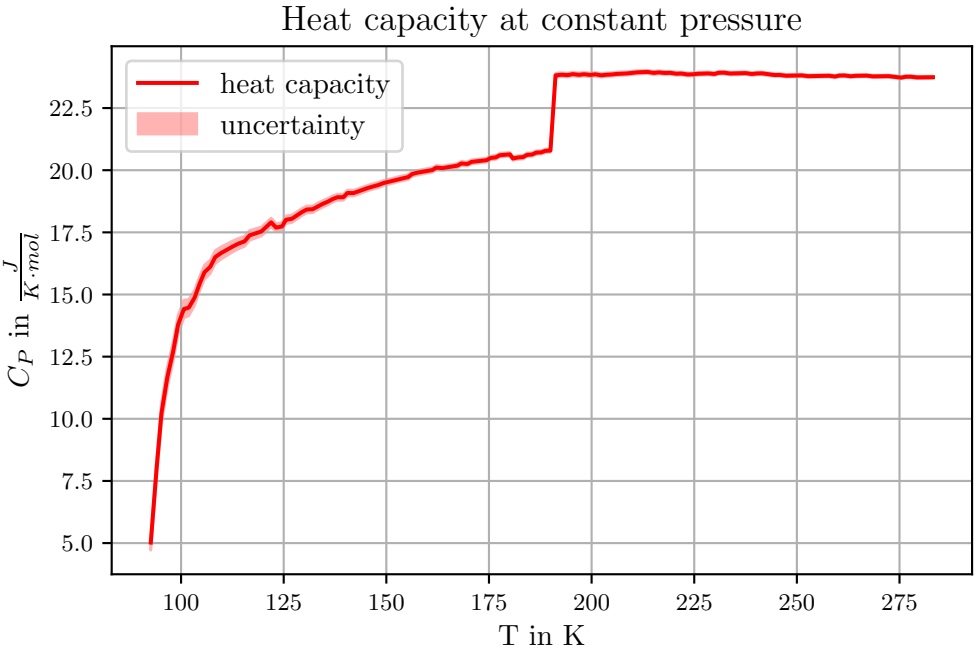


Figure 5: The molar heat capacity at constant pressure is displayed together with its uncertainty.

4.2 Molar heat capacity at constant volume

As it is experimentally considerably easier to have a setup operate at a constant pressure, rather than constant volume, the molar heat capacity at constant volume can be calculated with a correction term based on the properties of copper. The correction term states:

$$C_V = C_P - 9\alpha^2 \kappa V_0 T \tag{9}$$

Besides the temperature T, the other factors are the compression module $\kappa = 137{,}8\,\mathrm{GPa}$[1], the molar volume $V_0 = 7.11 \cdot 10^{-6}\ \mathrm{m^3/mol}$[1] and the thermal expansion coefficient α. The thermal expansion coefficient is described as linear in source [3] and a table with

24 values is provided. Given that there are 150 measurements in Table 1, 24 values is not enough to assign a thermal expansion coefficient to every entry. Therefore a fit was performed on the 24 given values based on a natural logarithmic function.
The resulting fit function is

$$f(T) = 3.46524982 \cdot \ln(T - 56.0189805) - 2.29906327 \tag{10}$$

Figure 6 shows the fitted function in comparison to the initial curve composed of 24 values.

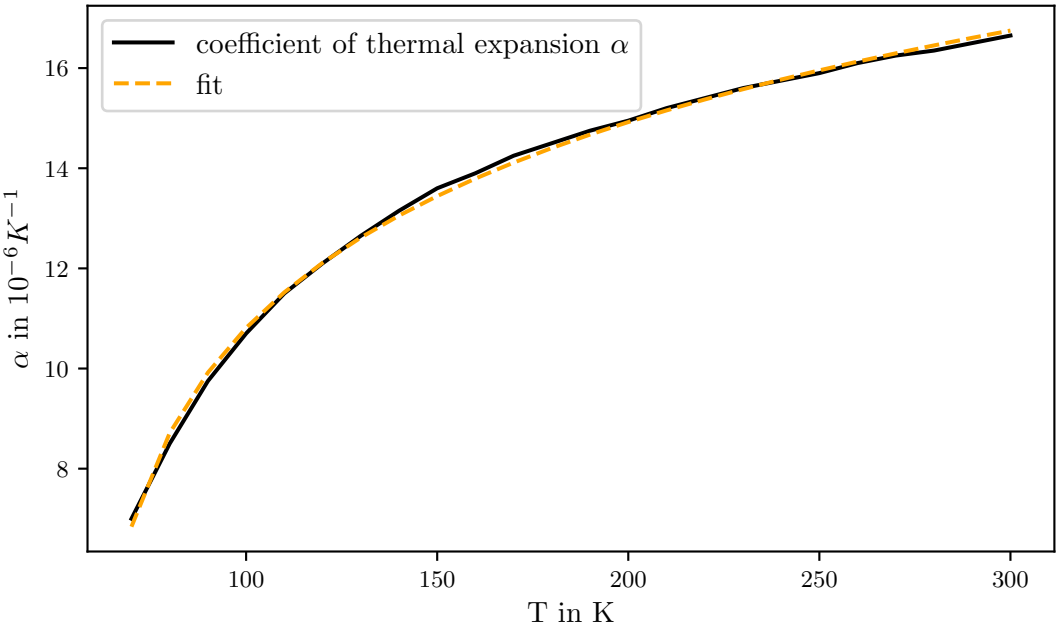


Figure 6: This graph shows the thermal expansion coefficient given in source [3] for a temperature range of 70 K to 300 K, in comparison to the fitted function.

With the compression module κ, the molar volume V_0 and the thermal expansion coefficient known, the molar heat capacity at constant volume is calculated and shown in Figure 7.

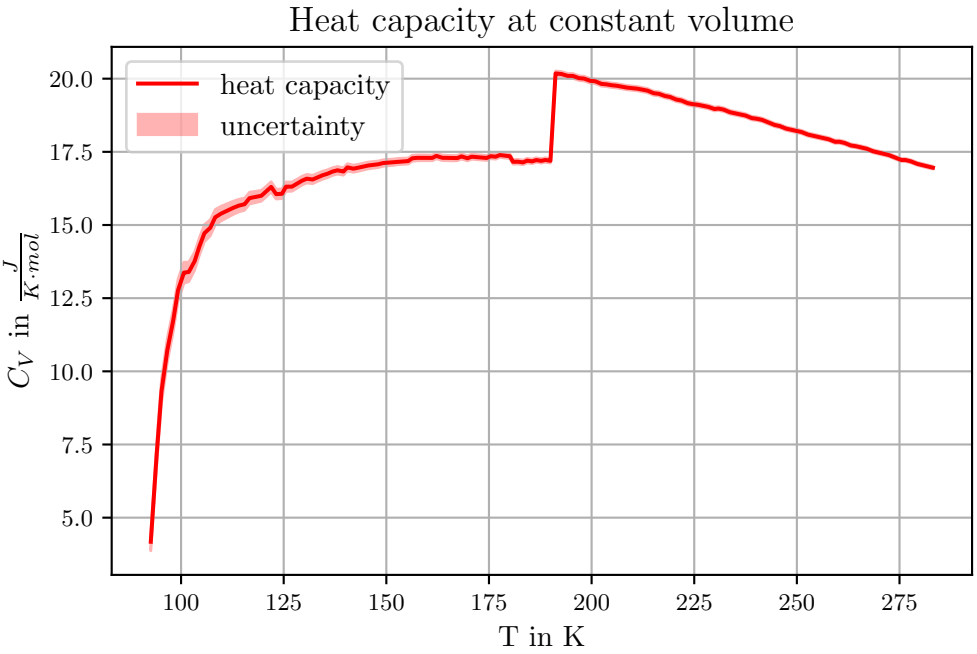


Figure 7: This graph shows the molar heat capacity at constant volume as well as its uncertainty against the temperature of the probe.

4.3 Debye temperature

The Debye number $\frac{\theta_D}{T}$ is proportional to the molar volume heat capacity as seen in subsection 2.4. The table in source [3] provides a method of comparison by looking up the value of C_V and assining it to a Debye number with an accuracy of 0.1. In this manner the Debye number has been determined and shown visually in Figure 8.

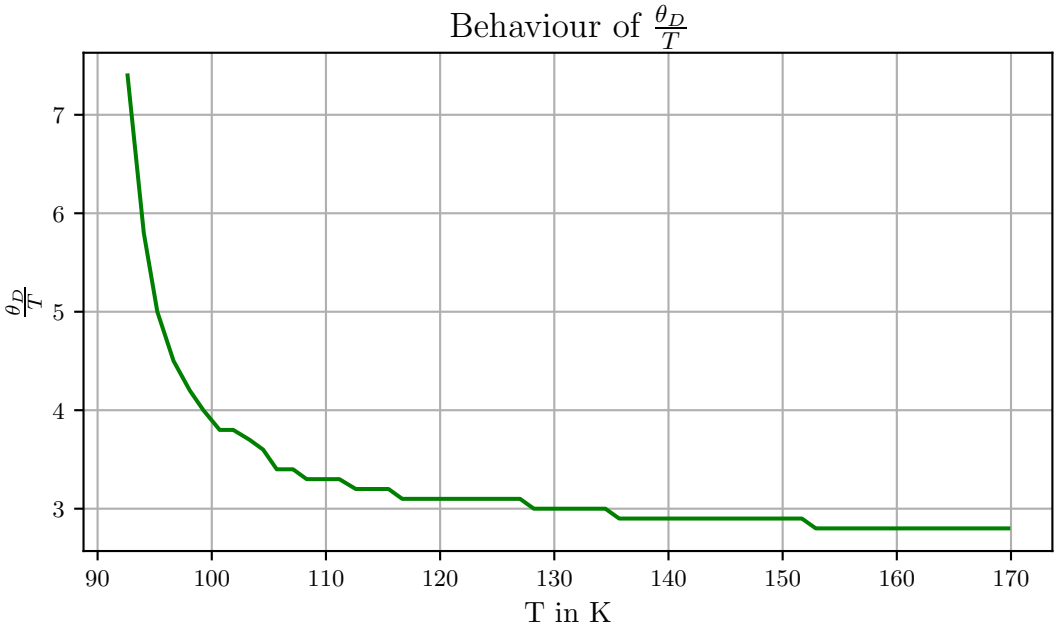


Figure 8: This graph shows the Debye number at rising temperature in steps of 0.1.

The average Debye temperature from $T = 87\text{K} - 170\text{K}$ is $\theta_D \approx 415.425\text{K}$. The average Debye temperature close to $T = 170\text{K}$ is $\theta_D \approx 443.113\text{K}$.

4.3.1 Theoretical approach

The Debye temperature can be calculated using the function

$$\theta_D = \frac{\hbar\omega_D}{k_B} \tag{11}$$

where k_B in the Boltzmann constant and ω_D is the Debye frequency.
The Debye frequency is dependent on the velocities of a transversal wave v_{trans} and a longitudinal wave v_{long} of copper. Equation 12 shows the calculation formula for the frequency.

$$\omega_D^3 = 18\pi^2 \frac{N_A}{V_0} \left(\frac{1}{v_{long}^3} + \frac{2}{v_{trans}^3} \right)^{-1} \tag{12}$$

N_A is the Avogadro constant and the velocities are given as $v_{trans} = 2260\,\text{m/s}$ and $v_{long} = 4700\,\text{m/s}$[3].

The resulting theoretical Debye frequency is $\omega_D \approx 43.493 \cdot 10^{12}1/\text{s}$ and the Debye temperature $\theta_D \approx 332.208\text{K}$.

5 Discussion

The average Debye temperature has been calculated to be $\theta_D \approx 415.425$K. The literature value $\theta_D = 345$K implies a divergence of around 16,95 %. The theoretically calculated value differs from measurement and literature, being $\theta_D \approx 332.208$K. Compared to measurement its 20,03 % smaller.
This concludes that the measured average value was influenced by exterior factors. Those could have been a weak vacuum in the probe chamber or a malfunction of the corresponding pressure gauge. Additionally the discrepancy between shield temperature and probe temperature has been kept at an average of 1,89 K, instead of the recommended 7 to 11 K.
There are noticeable jumps in Figure 5 and Figure 7 at around 180 K, which influenced the outcome of θ_D. They were caused by increasing the voltage in order to speed up the heating process to save experimentation time. As the errors of the measurements were relatively small, see for example Figure 4, the outcome is not strongly dependent on that. It is noteworthy that due to the Debye number being determined only in steps of 0.1 an additional increase in difference between theory and experiment is to be expected.

To sum up the molar heat capacity of copper was measured to be approximately $22.5\frac{J}{Kmol}$ with C_V being slightly less as expected. That is a difference of 9,99 % to the literature value of $C = 25\frac{J}{Kmol}$[2]. The Debye temperature difference lies at around 17 % to 20 % depending on theoretical or literature value.

Table 1: Measured data

Δt in s	shield resistance in Ω	probe resistance in Ω	voltage in V	current in A
0	23,5	24,5	15,87	0,1532
60	24,2	26,8	16	0,1531
120	24,9	27,4	16,08	0,1533
180	25,3	27,9	16,03	0,1535
240	25,8	28,5	16,12	0,1537
300	26,4	29,1	16,14	0,1539
360	27	29,6	16,16	0,154
420	27,6	30,2	16,18	0,1542
480	28,3	30,7	15,82	0,1507
540	29	31,3	15,84	0,1509
600	29,8	31,8	15,86	0,1510
660	30,6	32,3	15,87	0,1511
720	31,4	32,9	15,88	0,1512
780	32,2	33,4	15,9	0,1513
840	33,0	34,0	15,91	0,1514
900	33,9	34,6	15,92	0,1514
960	34,6	35,2	15,93	0,1515
1020	35,5	35,8	15,94	0,1516
1080	36,1	36,4	15,94	0,1516
1140	36,4	36,9	15,95	0,1517
1200	36,5	37,5	15,96	0,1517
1260	36,8	38,1	15,97	0,1518
1320	37,2	38,6	15,97	0,1518
1380	37,7	39,1	15,98	0,1519
1440	38,4	39,6	15,82	0,1503
1500	39,1	40,2	15,83	0,1504
1560	39,7	40,6	15,84	0,1505
1620	40,3	41,2	15,85	0,1506
1680	40,9	41,7	15,86	0,1506
1740	41,4	42,2	15,87	0,1507
1800	41,9	42,7	15,87	0,1507
1860	42,5	43,3	15,88	0,1507
1920	43,0	43,8	15,88	0,1508
1980	43,5	44,3	15,89	0,1508
2040	44,0	44,8	15,89	0,1508
2100	44,6	45,3	15,90	0,1509
2160	45,1	45,8	15,90	0,1509
2220	45,6	46,4	15,91	0,1509
2280	46,2	46,8	15,91	0,1510
2340	46,7	47,4	15,92	0,1510
2400	47,2	47,9	15,92	0,1510
2460	47,8	48,4	15,92	0,1511
2520	48,3	48,9	15,93	0,1511
2580	48,8	49,4	15,93	0,1511
2640	49,2	49,9	15,93	0,1511
2700	49,7	50,4	15,94	0,1512
2760	50,2	50,9	15,94	0,1512
2820	50,7	51,4	15,94	0,1512
2880	51,1	51,9	15,95	0,1512
2940	51,6	52,4	15,95	0,1512
3000	52,0	52,9	15,95	0,1512
3060	52,6	53,3	15,95	0,1513
3120	53,1	53,8	15,96	0,1513
3180	53,7	54,3	15,96	0,1513
3240	54,2	54,8	15,96	0,1513
3300	54,7	55,3	15,96	0,1513
3360	55,3	55,7	15,96	0,1513
3420	55,8	56,3	15,97	0,1513
3480	56,4	56,8	15,97	0,1513
3540	57,0	57,3	15,97	0,1513
3600	57,5	57,8	15,97	0,1514
3660	58,0	58,2	15,97	0,1514
3720	58,5	58,8	15,98	0,1514
3780	59,0	59,2	15,98	0,1514
3840	59,3	59,7	15,98	0,1514
3900	59,7	60,2	15,98	0,1514
3960	59,9	60,7	15,98	0,1514
4020	60,3	61,1	15,99	0,1514
4080	60,7	61,6	15,99	0,1514
4140	61,0	62,0	15,99	0,1515
4200	61,3	62,5	15,99	0,1515
4260	61,8	63,0	15,99	0,1515
4320	62,2	63,3	15,88	0,1504
4380	62,7	63,8	15,89	0,1505
4440	63,1	64,3	15,89	0,1505
4500	63,7	64,7	15,90	0,1506
4560	64,3	65,2	15,90	0,1506
4620	64,9	65,6	15,91	0,1506
4680	65,5	66,1	15,91	0,1506
4740	66,2	66,5	15,91	0,1506
4800	67,0	67,0	15,91	0,1506
4860	67,7	67,5	17,02	0,1612
4920	68,4	68,1	17,05	0,1614
4980	69,2	68,7	17,06	0,1615
5040	69,7	69,2	17,07	0,1616
5100	70,2	69,8	17,07	0,1617
5160	70,6	70,3	17,08	0,1617
5220	70,9	70,9	17,08	0,1618
5280	71,1	71,4	17,09	0,1618
5340	71,3	72,0	17,09	0,1618
5400	71,6	72,5	17,09	0,1619
5460	71,9	73,0	17,09	0,1619
5520	72,2	73,5	17,10	0,1619
5580	72,7	74,0	17,10	0,1619
5640	73,2	74,5	17,10	0,1619
5700	73,8	75,0	17,10	0,1620
5760	74,5	75,5	17,11	0,1620
5820	75,4	76,0	17,11	0,1620
5880	76,4	76,5	17,11	0,1620
5940	77,3	77,1	17,11	0,1620
6000	78,2	77,6	17,11	0,1621
6060	79,0	78,2	17,12	0,1621
6120	79,6	78,7	17,12	0,1621
6180	80,1	79,3	17,12	0,1621
6240	80,5	79,8	17,12	0,1621
6300	80,8	80,4	17,12	0,1621
6360	81,1	80,9	17,12	0,1621
6420	81,5	81,4	17,12	0,1622
6480	81,7	81,9	17,12	0,1622
6540	82,0	82,4	17,12	0,1622
6600	82,5	83,0	17,13	0,1622
6660	83,1	83,4	17,13	0,1622
6720	83,7	83,9	17,13	0,1622
6780	84,4	84,5	17,13	0,1622
6840	85,3	85,0	17,13	0,1622
6900	85,9	85,5	17,13	0,1622
6960	86,6	86,0	17,13	0,1622
7020	87,3	86,6	17,13	0,1622
7080	87,9	87,1	17,13	0,1623
7140	88,6	87,6	17,13	0,1623
7200	89,0	88,2	17,13	0,1623
7260	89,6	88,8	17,13	0,1623
7320	90,0	89,3	17,13	0,1623
7380	90,6	89,9	17,13	0,1623
7440	91,0	90,4	17,13	0,1623
7500	91,5	90,9	17,13	0,1623
7560	91,9	91,4	17,13	0,1623
7620	92,5	92,0	17,13	0,1623
7680	92,8	92,5	17,13	0,1623
7740	93,3	93,0	17,13	0,1623
7800	93,8	93,5	17,13	0,1623
7860	94,3	94,0	17,13	0,1623
7920	94,8	94,6	17,13	0,1623
7980	95,3	95,0	17,13	0,1623
8040	95,8	95,5	17,13	0,1623
8100	96,4	96,1	17,13	0,1623
8160	97,0	96,6	17,13	0,1624
8220	97,6	97,1	17,13	0,1624
8280	98,2	97,6	17,13	0,1624
8340	98,7	98,2	17,13	0,1624
8400	99,2	98,7	17,13	0,1624
8460	99,7	99,2	17,13	0,1624
8520	100,3	99,7	17,13	0,1624
8580	100,9	100,3	17,13	0,1624
8640	101,4	100,9	17,13	0,1624
8700	102,0	101,3	17,13	0,1624
8760	102,4	101,8	17,13	0,1624
8820	102,8	102,4	17,13	0,1624
8880	103,3	102,9	17,13	0,1624
8940	103,8	103,4	17,13	0,1624
9000	104,2	103,9	17,13	0,1624

References

[1] *chemie.de/kupfer*. Last visited 01.12.2022. URL: https://www.chemie.de/lexikon/Kupfer.html.

[2] *chemie.de/waermekapazitaet*. Last visited 01.12.2022. URL: https://www.chemie.de/lexikon/Molare_W%C3%A4rmekapazit%C3%A4t.html.

[3] TU Dortmund. *Temperaturabhängigkeit der Molwärme von Festkörpern*. Versuchsanleitung. 2018.

[4] Eric O. Lebigot. *Uncertainties: a Python package for calculations with uncertainties*. Version 2.4.6.1. URL: http://pythonhosted.org/uncertainties/.