Thermal Physics Semester 1 Hand-in Project

Motivation

This is an exercise in thermodynamic data analysis and interpretation. I set it because physics is, fundamentally, an experimental science, in which the ultimate purpose of all theory is to make sense of experimental observations. So, learning to relate theory to experimental data is a key skill that you should develop irrespective of whether you think you want to be a 'theorist' or 'experimentalist'.

Introduction

The study of phase transitions is a vital part of materials science and technology, because they affect material properties for better or for worse. 'Order-disorder' (OD) transitions are very common: at low temperatures, molecular constituents are ordered in orientation (geometric or magnetic spins) and position. At high enough temperature, they lose one or both kinds of order. The crystalline alloy Cu_3Au undergoes a phase transition at $\approx 680\,\mathrm{K}$. Measuring the heat capacity across this transition has been one main method to help arrive at this conclusion. You will retrace the steps.

Benisek and Dachs (BD) [1] have measured the molar specific heat capacity, c_p, of Cu_3Au as a function of temperature, and analysed their data to obtain the 'excess entropy' across the OD transition. This involves subtracting from the raw data the background heat capacity that has nothing to do with the transition, giving $\Delta c_\mathrm{P}(T)$. Their Δc_P data in the temperature range ($500 \lesssim T \lesssim 720\,\mathrm{K}$) is given in an Excel spreadsheet. (Don't worry about some very small negative values: these are due to slight errors in the background subtraction.)

The proper analysis of this data is somewhat complex, but a useful approximate analysis can be done. Below, I'll guide you on how to do this. Your answer will not be as accurate as the one obtained by BD, but good enough to see what physics may be involved.

I have uploaded BD's paper to LEARN, where in the same folder you will also find the Excel spreadsheet '`Cu3AuData.xlsx`' containing the relevant data set giving columns of T (in K) and $\Delta c_\mathrm{P}(T)$ (in $\mathrm{J\,K^{-1}\,mol^{-1}}$). The necessary theory is covered in my notes, especially Section 11.6.

Practicalities

Your aims are

- to analyse this data and calculate the total molar entropy change across the OD transition in crystalline Cu_3Au,
- to interpret the data in the light of relevant theory, and suggest reasons for any discrepancies,
- write up your results in the style of a brief report.

Your report (suggested length 3-5 pages, I suggest using LaTeX) should

- Review briefly the background theory: how entropy changes can be calculated from heat capacity measurements, and how these are related to mixing.
- Explain how you analyse the heat capacity data given to obtain the entropy change of the OD transition in Cu_3Au, and show appropriate plots.
- Interpret this value in terms of the ideal entropy of mixing, and briefly suggest reasons for the *sign* of this discrepancy, and how further measurements may resolve this.

I will give credit for

- Accuracy of the analysis: is it correct?
- Accuracy of the explanations: again, are they correct?

- Clarity: can the reader easily follow your line of argument from beginning to end?
- Presentation: can plots be easily read and interpreted, etc.

Your final grade will mean:

- A+ = better than can be expected
- A = cannot be expected to do better at this level given knowledge and time constraints
- B = very good but can be improved in places
- C = acceptable but can be improved throughout
- D = poor in places
- E = poor throughout and unacceptable or wrong in places

Do discuss with each other, but do your own analysis and write up: this is not a group project. You will be marked individually.

The steps you need to take

After re-reading Section 11.6 of the notes, download the data spreadsheet, which tabulates the background-subtracted specific molar heat capacity of Cu_3Au **in units of the universal gas constant R**, Δc_P, across its OD transition, Fig. 1. Extract the 'excess entropy' associated with the OD transition, $\Delta s(T)$.

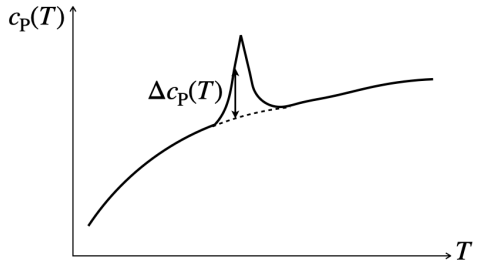

Figure 1: Δc_P = measured c_P minus a suitable baseline. See [1] for the baseline used.

1. Plot $\Delta c_P(T)$ and $\Delta c_P(T)/T$ and check that there is a peak around 680 K in each case.

2. Integrate $\Delta c_P(T)/T$ to obtain the molar entropy change accrued at various values of T across the transition, i.e. $\Delta s(T) = \int_{T_0}^{T} (c_p/T')\mathrm{d}T'$ with T ranging from one side of the peak to the other. In principle $T_0 = 0$; in practice, you only need to choose a value far enough below the peak where the baseline is flat. (Explain your choice in your report!) Integrate the discretised data numerically, e.g., using

$$\int_a^b f(x)\,dx \approx \sum_i f(x_i)\delta x_i, \text{ with } \delta x_i = x_{i+1} - x_i,$$

to approximate the area under a curve as a sum of rectangles of widths $\{\delta x_i\}$. Use any method or software you like, as long as you explain.

3. Write a report ($\approx$ 3 to 5 pages): discuss briefly why measuring entropy changes may be useful in studying the physics of materials; then explain in some detail what you have done to analyse the data; present your calculation of $\Delta s(T)$ and plot the results; finally interpret your findings in terms of the formula for the molar entropy of ideal mixing, Equation (11.12), in my notes (recalling that the data are given in units of R already), and give a physical picture of what may be happening as the temperature rises across the transition region. Propose reason(s) for any discrepancies between your interpretation and the theoretical prediction for ideal mixing, Equation (11.12). If you use insights from DB or elsewhere, quote your sources.

References

[1] A Benisek and E Dachs. The the vibrational and configurational entropy of disordering in Cu_3Au. *Journal of Alloys and Compounds*, 632:585–590, 2015.