Binary alloy

David Fitzek and Fabian Mikulasch

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Introduction

In this work we will take a look at an Ising-model like model of a binary alloy of copper and zinc atoms. We will see how different properties of this alloy depend on the temperature of the system, which determines the mobility of the particles.

Problem 1

The analytical solution for the critical temperature where the phase transition occurs can be computed as

$$T_c = \frac{2\Delta E}{k_b} = \frac{2(E_{cucu} + E_{znzn} - 2E_{cuzn})}{k_b} = 905.153K \tag{1}$$

To find the equilibrium structure we computed the minimum of F (free energy) with respect to the order parameter P via bisection method. Figure 0.0.2 shows that the order parameter decreases continuously until reaching T_c. Increasing the temperature increases the energy of each atom (see figure 0.0.2 middle) and increases the likelihood of changing the position. This results in a decrease of order and thus a diminishing P. The energy increases with increasing temperature. The heat capacity is computed using a finite difference approximation. The heat capacity peaks as expected at T_c. The energy doesn't change after passing the critical temperature. The atoms that were in the beginning perfectly ordered (P=1) are now randomly located (P=0). A completely random order of atoms converges to a certain energy (see figure 0.0.2 middle) and stays constant. The heat capacity C is defined as $\frac{\partial U}{\partial T}$, thus the heat capacity is zero for a constant energy, which is the case after passing T_c. We computed this quantity via a finite difference approximation of the derivative.

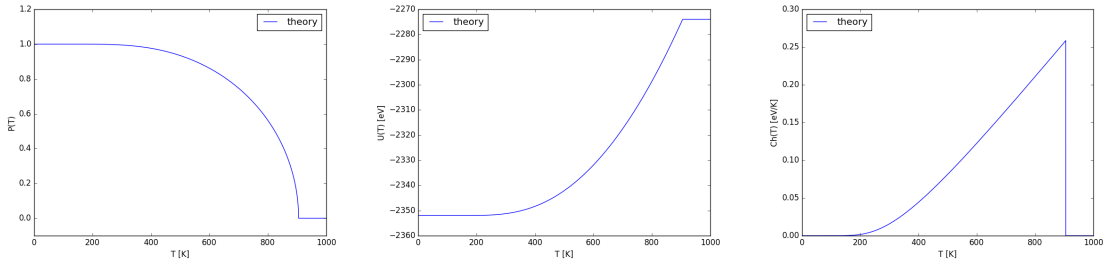

Figure 0.0.1: The graphs show the order parameter P (left), the energy U (middle) and the heat capacity C (right) as a function of temperature. The phase transition is visible in all the graphs at around $900K$.

Problem 2

For this problem we implemented the model and found the time evolution by using a monte carlo simulation. The first step is to create the structure of the two lattices. With $n = 10$, the side length

of the cube of atoms, the types of the atoms are stored in a vector of length n^3. As we chose the indices to increase by n when moving down one row in the cube and by n^2 when moving down one level, we can easily find the neighbors in the other lattice by adding 1, n and n^2 to the index of the current atom (including modulo operations for the periodic boundary conditions) (figure 0.0.2).

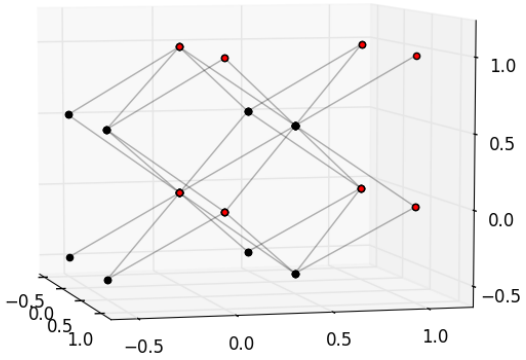

Figure 0.0.2: Section of the resulting two lattices created in the simulation. Nearest neighbors are interacting (periodic boundary conditions have been omitted).

Once the structure is established we can perform the monte carlo simulation for different temperatures, where the temperature determines the probability of two atoms switching places. From the resulting dynamics we can estimate the properties we computed in task 1 and also the local order parameter r.

Before we average to get the measurements, we have to let the system converge to avoid having measurement errors due to the initial transient. We chose the initial condition of the two lattices to be perfectly ordered, as we found that the convergence to order takes more steps. To find an adequate number of equilibration steps we averaged the evolution of the energy $U(t)$ for 20 runs for different temperatures (figure 0.0.3). We (conservatively) chose to use 300,000 steps for initialization.

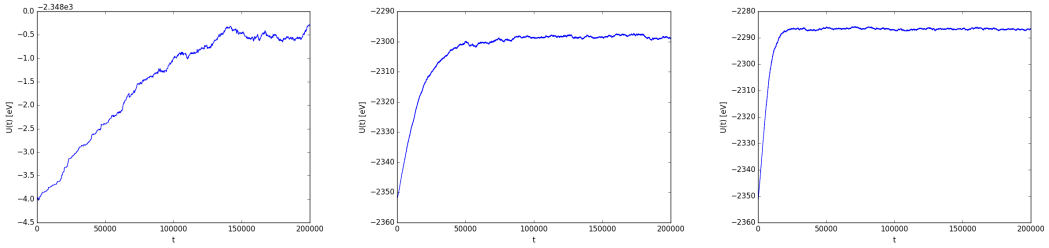

Figure 0.0.3: Averaged evolution of energy $U(t)$ for 20 runs for (left to right) 400K, 750K and 900K.

After converging to equilibrium we can measure U, P and r by looking at the distribution of atoms on the two lattices and their nearest neighbors. We then determine a point estimate for a certain temperature T of these quantities by averaging over $2 \cdot 10^6$ timesteps. In order to calculate the heat capacity of the system we use the fluctuations of the energy $U(t)$ where $C(T) = \frac{1}{k_B T^2}(\langle E^2 \rangle - \langle E \rangle^2)$. The statistical errors of the estimates can be found by measuring the correlation length of the fluctuations and using them to estimate the variance of statistically independent values of the measures. We did this for two approaches, the box-averaging method (figure 0.0.4) and the direct use of the correlation length (figure 0.0.5). Both give very similar results.

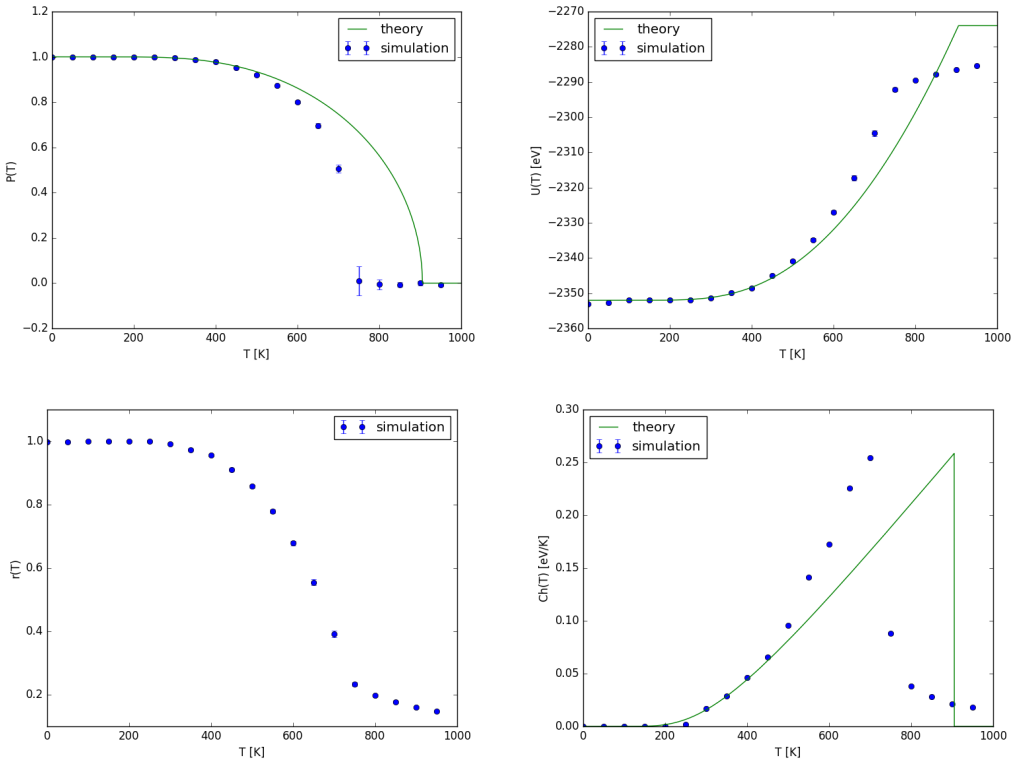

Figure 0.0.4: Results for different temperatures for (from top left to bottom right) $P(T)$, $U(T)$, $r(T)$ and $C(T)$. Error bars give the standard deviation of the measures calculated with the box averaging method. After looking at the results of the averages with different block-sizes, we decided to average over sizes of 100,000 to 200,000. Very similar results for the correlation length method validate this approach.

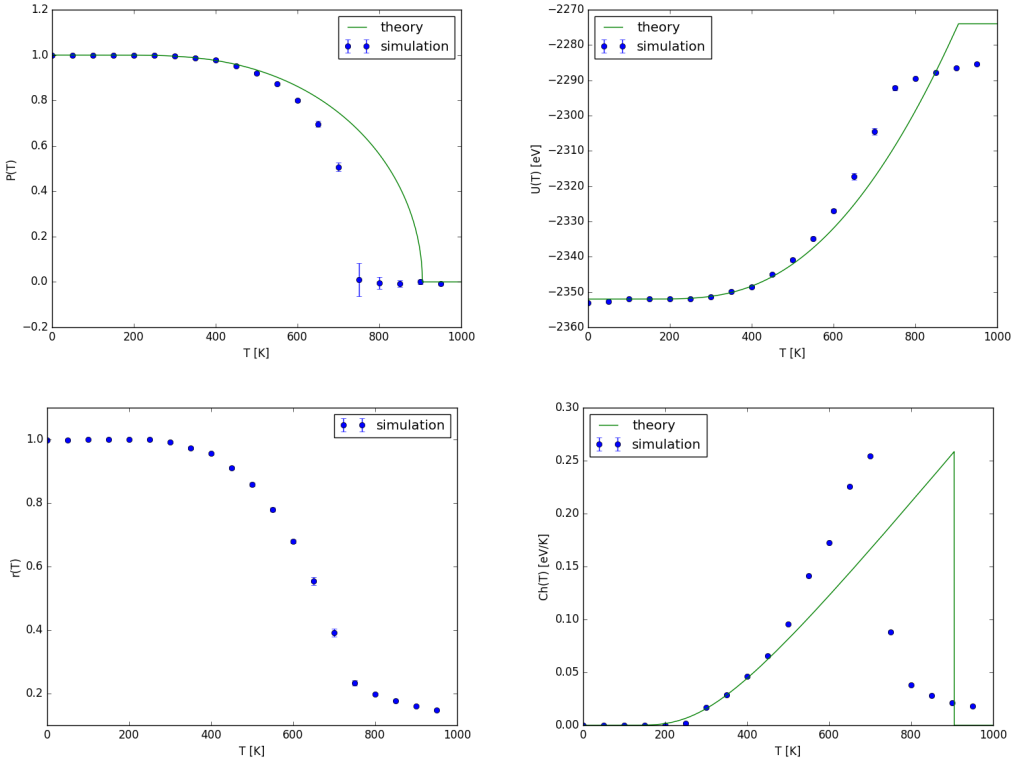

Figure 0.0.5: Results for different temperatures for (from top left to bottom right) $P(T)$, $U(T)$, $r(T)$ and $C(T)$. Error bars give the standard deviation of the measures calculated with correlation length method. We used a binary search approach, in order to keep computation time low.

It is easy to see that close to the critical point the error is the biggest. This is to be expected, as here the correlation length diverges and fluctuations are large. Because of the number of steps we used for the averaging the size of the error is very small for most of the measurements and results seem to be fairly accurate.

Another thing we immediately notice when looking at the graphs is that simulation and mean field theory give different results. For small temperatures until about 400K they are in good agreement, for bigger temperatures however the theory doesn't seem to be able to capture the dynamics well. Qualitatively they predict the changes (especially for P, not so well for U and C) but the critical point is shifted to higher temperatures in comparison.

The order parameter P drops down to zero at about 750K, approximately 150K earlier than the theory predicts. The energy, instead of reaching a plateau as in the theory, continues to rise very slowly after the critical point. This can also be seen in the heat capacity, which is proportional to the derivative U in respect to temperature, as it does not drop to zero but instead seems to converge to a value bigger than zero.

Furthermore we notize that, instead of having the 'hard' transitions of the mean field theory, the measured values appear to change smoothly also during the phase transition. Most of the disagreements can be explained by two crucial differences of the mean field theory to the model. First of all the model is finite, whereas the theory assumes an infinite lattice so the fluctuations average out. Secondly because of the mean field approximation local fluctuations, which should become important at close to the critical point, are not captured.

References

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[3] Tipler, P.A. and Mosca, G. *Physics for Scientists and Engineers*, Physics for Scientists and Engineers: Standard, W. H. Freeman, 2007