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H2a Binary Alloy

In this exercise you are asked to determine a few properties of a binary alloy model. You will use the Metropolis algorithm to find accurate estimations of short and long range order, energy, and specific heat.

Model

Consider an alloy of N atoms of type A and N atoms of type B. The atoms are located at the sites of a bcc lattice. In the perfectly ordered structure, all A atoms sit on the corner point and all B atoms sit on the middle point of the unit cell (or vice versa). The bcc lattice may be considered as two interpenetrating sc sublattices, a and b. In the ordered structure, all nearest neighbors of an A atom are B atoms.

To quantify the concept of order, we define a long range order P through

$$\text{Number of } A \text{ atoms on the } a \text{ sublattice} = \frac{1}{2}(1+P)N. \tag{1}$$

For perfect order, $P = \pm 1$, and for no order, $P = 0$. We also define a short range order r by

$$r = \frac{1}{4N}(q - 4N) \tag{2}$$

where q is the number of nearest neighbor bonds that are AB bonds.

In this model, the energy is given by the bond energies of AA, AB, and BB nearest neighbor pairs. The total energy of the alloy is

$$E = N_{AA}E_{AA} + N_{BB}E_{BB} + N_{AB}E_{AB}, \tag{3}$$

where N_{ij} is the number of nearest neighbor ij bonds, and E_{ij} is the energy of an ij bond.

Application

An example of an AB alloy is the CuZn system. For $Cu_{0.5}Zn_{0.5}$ the transition temperature between the ordered bcc structure (β' phase) and the disordered bcc structure (β phase) takes place at approximately 468 °C [1]. To model this system, we have to make proper choices of the bond energies. Reasonable values are $E_{\mathrm{CuCu}} = -436\,\mathrm{meV}$, $E_{\mathrm{ZnZn}} = -113\,\mathrm{meV}$, and $E_{\mathrm{CuZn}} = -294\,\mathrm{meV}$.

Task

1. Use the mean field approximation as given in the lecture notes for the free energy to obtain the temperature dependence for the long range order parameter $P(T)$. This has to be done numerically. Plot your

result. What is the value for the transition temperature T_c (which can be derived analytically)? Determine and plot also the temperature dependences for the energy $U(T)$ and heat capacity $C(T)$. Comment on the behavior near the phase transition. What happens for $U(T)$ and $C(T)$ for $T > T_c$? (4p)

2. Implement a Monte Carlo program using the Metropolis algorithm that simulates the binary alloy system. Use a 3D bcc structure with periodic boundary conditions. A reasonable system size is $10 \times 10 \times 10$ unit cells. Determine U, C, P, and the short range order r as a function of temperature.

   In this problem, the atomic sites do not move during the execution. Therefore, it is convenient to define the structure before making any simulation step. In the bcc structure each atom has 8 nearest neighbors, so one suggestion is to construct a neighbor list consisting of two constant $8 \times N$ matrices, which take care of the periodic boundary conditions.

   Perform calculations at several different temperatures. The initial state of the system may be chosen to be perfectly ordered ($T = 0$, cold start) or random ($T = \infty$, warm start). A new configuration of the system may be given by interchanging the position of two atoms. Be sure to count all trial steps in the Metropolis algorithm. For each independent calculation, perform $N_{\text{tot}} = N_{\text{eq}} + N$ steps, where the first N_{eq} steps are used to equilibrate the system and are not used in evaluating average properties. Study the evolution of the energy and see where it reaches stationarity to determine a good choice of N_{eq}. Note that the choice of N_{eq} depends on temperature and the initial state of the system.

   To obtain accurate numbers, you have to use at least $N = 10^6$. To obtain a correct estimate of the error determine the statistical inefficiency s, using both the correlation method and block averaging. When calculating the heat capacity, you can either use a finite difference approximation of $C(T) = dU(T)/dT$, or use the variance in the energy, $C(T) = \frac{1}{k_B T^2}\left(\langle E^2 \rangle - \langle E \rangle^2\right)$. Compare the results from the Monte Carlo simulation with the mean field solution. Discuss similarities and differences. (12p)

References

[1] C Kittel, *Introduction to Solid State Physics*, (Wiley).