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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. The methods you will use are described in the accompanying .pdf (`H2a_auxiliary.pdf`). Of particular note is the part on the Ising model and the binary alloy problem.

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. Determine the energy U of the alloy at temperatures $400, 600$, and $1000\,\mathrm{K}$. 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.

   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 for each sublattice, containing the nearest neighbours of all atoms in that sublattice. Periodic boundary conditions can be built into these matrices.

   Perform calculations at $400, 600$, and $1000\,\mathrm{K}$. 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 can be generated by swapping the positions of two atoms, followed by applying the Metropolis algorithm to decide whether the change should be accepted or rejected (see appendix). For each independent calculation, perform $N_{\mathrm{tot}} = N_{\mathrm{eq}} + N$ 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}. To obtain accurate numbers when evaluating the average properties, use at least $N = 10^6$. (4p)

3. Determine U, C, P, and the short range order r as a function of temperature. Calculations should be performed within the temperature range of 300 to $1000\,\mathrm{K}$. Note that the number of required equilibration steps N_{eq} depends on temperature and the initial state of the system. 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, $C(T) = \frac{1}{k_B T^2}\left(\langle E^2 \rangle - \langle E \rangle^2\right)$. To obtain a correct estimate of the error determine the statistical inefficiency s for U, C, P, and r, using both the correlation method and block averaging. Compare the

results from the Monte Carlo simulation with the mean field solution. Discuss similarities and differences. (8p)

Appendix

Metropolis Algorithm

1. Start with an initial state x.
2. For each iteration:
   (a) Propose a new state x' swapping two atoms.
   (b) Calculate the probability ratio:
   $$\alpha = \frac{p(x')}{p(x)} = \frac{\exp(-E(x')/k_BT)}{\exp(-E(x)/k_BT)} = \exp\left(-\frac{\Delta E}{k_BT}\right)$$
   where $\Delta E = E(x') - E(x)$ is the energy difference between the states.
   (c) The acceptance criterion for the new state x' is based on the following cases:
   - If $\alpha \geq 1$, accept the new state x'.
   - If $\alpha < 1$, generate a random number $u \in [0, 1]$. Accept x' if $u < \alpha$; otherwise, reject x'.

   (d) If accepted, set $x = x'$. Otherwise, keep the current state x.
3. Repeat the process until the system reaches equilibrium or the desired number of iterations is completed.

Hint: Proposing to swap two atoms of the same type will result in no change between the current and proposed state, i.e., $x = x'$. To improve the acceptance rate of the algorithm, it is recommended to avoid such proposals.

References

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