MONTE CARLO MODELLING OF CRYSTAL GROWTH

Introduction

Crystal growth from solution occurs when molecules or atoms move from solution to attach to the growing crystal. This process is impossible to model directly, using deterministic methods, because of the large number of atoms and interactions involved. However statistical techniques, such as Monte Carlo modelling, can provide a lot of information. When a growth unit (atom or group of atoms) hits the crystal surface the probability of it sticking to the surface will depend on the interaction energy with the surface. The interaction energy will be a function of the number of neighbours, or bonds. Thus if it hits a flat defect free surface there is a low probability of sticking and if it lands on a step or kink on the surface it will have a high sticking probability, due to the high number of neighbours at these sites. The effects of supersaturation, temperature and surface diffusion can all be included in this type of model.

The Model

In a simple model of crystal growth the surface can be represented by a square grid of cells on which growth units are deposited or removed at random positions, at a rate determined by the conditions. The height of the surface at cell i (h_i) is the total number of growth units added to that cell minus the total number removed. For a flat surface h_i is the same everywhere. At each Monte Carlo step a site is selected at random. A growth unit is added to the site with a probability proportional to $W^+ = \exp(\Delta\mu/k_BT)$. Here $\Delta\mu$ is the difference between the chemical potential of the solution and the surface, T is the temperature and k_B is Boltzmann's constant. The unit comes off the surface with a probability proportional to $W^- = \exp(-((n-c/2)E_b/k_BT))$. Here n is the number of neighbours, c is the coordination number ($c = 4$ for a square lattice) and E_b represents the energy of the bonds to neighbouring units. $W^-_{\max}$ is defined as the case when $n = 0$ (no neighbours). Periodic boundary conditions are used: this means the cell at one edge of the lattice is assumed to be a neighbour of the cell at the opposite edge.

Thus the structure of the program is as follows:

1. Select a site at random (using a random number generator)
2. Count the number of neighbours for that site (n)
3. Compute $W^- = \exp(-(n - c/2)E_b/k_BT)$
4. Do one of the following with the corresponding probability:
   (a) Add a growth unit: $h_i \to h_i + 1$: probability $P^+ = W^+/\left(W^+ + W^-_{\max}\right)$
   (b) Subtract a growth unit: $h_i \to h_i - 1$: probability $P^- = W^-/\left(W^+ + W^-_{\max}\right)$
   (c) Do nothing $h_i \to h_i$: probability $1 - P^+ - P^-$.

Which event to choose can be determined by selecting a random number N_r between 0 and 1. If N_r lies between 0 and P^+ then add a growth unit. If N_r lies between P^+ and $P^+ + P^-$ then subtract a unit and if it is greater than $P^+ + P^-$ then leave the surface unchanged.

0.1 The Project

Once the program is working there are a number of computer experiments that may be carried out. The growth rate (the rate of change $\langle s \rangle$, of the mean value of s) depends on both the temperature and the chemical potential (related to the supersaturation). The surface roughness (defined as $\langle s^2 \rangle - \langle s \rangle^2$) will also vary with temperature, and, under some circumstances, the surface may undergo a roughening transition where the surface roughness increases sharply with temperature. The effect of the initial surface structure may also be studied. Real surfaces have defects, in the form of vacancies, adatoms and steps, and these have a strong effect on the rate of crystal growth. It is also interesting to consider the difference between a square lattice and a hexagonal lattice.

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