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Diffusion of particles in anisotropic systems and its role in the crystal layers self-organization

Particle diffusion over crystal surfaces and inside its structure is an important process deciding about the character and the rate of the crystal growth. In solid state diffusion occurs via thermally activated jumps from one energy minimum to another. The energy landscape in which that process takes place can be very complex. It is not an easy task to calculate diffusion coefficient for particles in such conditions. On the other hand, knowledge of diffusion coefficient, its anisotropy and exact paths along which particles move is very important for the understanding and the control of layer by layer growth process.

The PhD thesis includes calculations of diffusion coefficient in concrete systems using variational method. It is shown that this method is very effective in the case of quite complex energy landscapes, for single particles as well as for clusters. Surface or bulk diffusion of particles in crystals are often anisotropic, which can be related to the anisotropy of the crystal lattice itself or due to some external bias, which distinguishes one of the directions. The direction of the crystal growth is distinguished due to the presence of the surface and due to the temperature gradient. It is analyzed how the anisotropy of the diffusion influences the character of the structures obtained during the growth. The structures found in the kinetic Monte Carlo calculations are compared with experimental ones for PbTe/CdTe immiscible materials.

The thesis consists of seven chapters. Chapter 1 is the introduction, Chapter 2 describes the concept of diffusion and the variational approach to calculating diffusion coefficients in a given energy landscape, in Chapters from 3 to 6 diffusion coefficients for different systems are calculated by means of that approach and, finally, Chapter 7 describes a microscopic model of the immiscible crystals growth.

First, diffusion coefficients for various systems are calculated by means of the variational method. That method had been previously effectively used for solving various problems of surface diffusion. In the thesis it is for the first time applied to real systems, namely a Ga adatom at GaAs(001) surface in two different reconstructions and a Cu monomer and dimer at Cu(111) and Ag(111) surfaces. The necessary data on the energetic landscape of those systems were found in the literature. Then, the variational approach is used to analyze collective diffusion at surfaces with complex energetic landscapes. A few types of lattices of different geometry are analyzed and for some of them the diffusion was found to be anisotropic. The main direction of the diffusion depends on the specific values of the jump rates. The same approach is used to calculate diffusion coefficients for interacting particles in a model consisting of energetic minima of two different depth arranged alternately in rows. The particles interact along the rows. The equilibrium occupancy probabilities are calculated by means of the transfer-matrix method. The interaction has a significant influence on the character and the rate of the diffusion.

In the last part of the thesis a microscopic model of immiscible crystals growth is proposed. That study is motivated by the experiment on PbTe/CdTe multilayer growth conducted at the Institute of Physics. It was found that depending on the growth temperature structures of different character can be obtained. The intended layered character is preserved only at low temperatures, during growth at slightly higher temperatures vertical columns are observed instead and at even higher temperatures both components are completely separated from each other. The proposed model takes into account three dynamical processes: adsorption, surface diffusion and bulk diffusion. Additionally, the bulk diffusion is biased due to the distinguished direction of the crystal growth. The Monte Carlo simulations based on that model reproduce all the structures observed in the experiment.

Both parts of the thesis: calculations of diffusion coefficient and the model which is based on the diffusion process make up the schema for the systematic analysis of crystal growth process. It is shown in examples how to calculate diffusion coefficient in complex situation, including diffusion of clusters and interactions between particles. The model built up for PbTe/CdTe system of immiscible compounds illustrates consequences of the anisotropy in the diffusion process.

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