Chapter 1

Introduction

1.1 Magnetic nanostructures

In 1959, R. P. Feynman stated in a famous programmatic lecture the enormous potential of 'manipulating and controlling things on a small scale' and initiated the investigation of physical objects on the nanometer scale [49].[1] Today, the study of magnetic nanostructures is an active and rapidly advancing area within solid state physics [63]. On the one hand, the investigations are driven by possible technological applications, such as in ultra-high density storage devices, read-heads, sensors, MRAM, etc. where there is generally a great interest in artificially 'engineered' materials on the nanometer scale with 'taylored' magnetic properties. On the other hand, magnetic nanostructures are very interesting from a fundamental physical point of view: Proceeding from magnetic bulk materials towards lower dimensionality to magnetic layers, stripes (wires), dots (islands), and superlattices built of these elements, a variety of new physical phenomena have been discovered whose knowledge and understanding is far from being complete.

Over the past decade, considerable attention has been focused, on the remarkable features of artificially *layered* magnetic films, both experimentally and theoretically. New fascinating phenomena not known from bulk systems were found, such as giant magneto resistance (GMR), oscillatory interlayer exchange coupling, and perpendicular anisotropy [15, 71]. Shortly after its discovery in 1988, GMR was already used in sensors and read heads. One of the most challenging subjects for further research is the exploration of novel magnetic properties arising from *laterally* nanostructered magnetic systems.

The great interest in magnetic nanostructures corresponds to a multitude of experimental techniques for the controlled fabrication of such systems on nonmagnetic substrates, for the structural characterization, and for the exploration of the magnetic properties [63, 179]. Some techniques are self-

[1] The references are numbered in alphabetical order.

organized growth by molecular beam epitaxy (MBE) [22], cluster deposition [19, 14], or chemical synthesis [161, 55]. Even the 'writing' of structures is possible by electron-beam litography [32] or by applying the tip of a scanning tunneling microscope (STM) [45]. Some methods for the structural and magnetic investigation of nanostructured systems are STM, atomic force microscopy (AFM), the magneto optical Kerr effect (MOKE), X-ray magnetic circular dichroism (XMCD), spin scattering electron microscopy with polarization analysis (SEMPA), or spin-polarized scanning tunneling spectroscopy (SP-STS).

Within this context, this thesis presents a theoretical investigation of magnetic properties of laterally nanostructured ultrathin films during their growth. We study nanostructures – ranging from irregular arrays of separated islands in early states of film growth to connected films – which are mainly observed for ultrathin films grown by MBE. Magnetic ensemble properties at finite temperatures in thermodynamic equilibrium as well as in nonequilibrium are examined. In particular, we look at the development of a long-range magnetic ordering of island-type growing films. Furthermore, the magnetic relaxation on a long time scale of the order $\gtrsim 1$ sec due to magnetization reversals ('ageing'), and metastable multi-domain structures are investigated. Special attention is paid to the dependence of the magnetic behavior on the nanomorphology and the relevant magnetic interactions.

In the following, we present an introduction into the subject of this work in greater detail. The leading problems will be discussed and illustrated by experimental results on magnetic ultrathin films. Also, a short overview of the current state of the theory will be presented. It will be shown that previous theoretical studies are partly not sufficient to explain the main experimental results. In this thesis, we present new results on the interdependence of an irregular atomic nanostructure and the magnetic behavior, in particular in thermodynamic nonequilibrium.

1.2 Magnetic ordering and slow relaxation

In the last decade, ultrathin Co films grown pseudomorphically on Cu(001) using MBE evolved into a model system for the investigation and understanding of low-dimensional magnetism. The interplay of structural [95, 137, 33, 48, 114, 125] and magnetic properties [128, 87, 91, 148, 33] of this system has been studied by many groups using different experimental techniques. Sometimes contradictory results concerning the atomic structure and the onset of ferromagnetism at room temperture were reported.

The groups of Kirschner [36, 144, 145, 47] and of Baberschke [155, 17, 133] studied both the atomic structure and the magnetic behavior of Co/Cu(001) in the initial stages of growth. STM results of the surface morphology of this

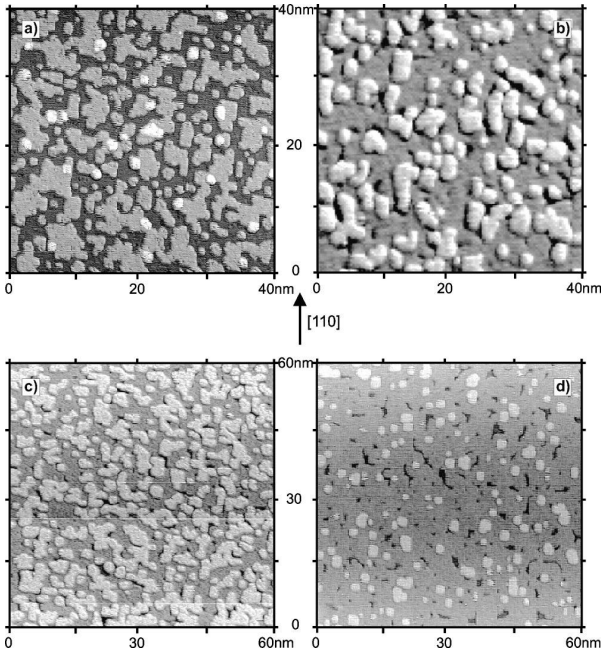

Figure 1.1: Surface morphology of an ultrathin Co/Cu(001) film as observed by STM. Different film coverages during growth are depicted: (a) 0.60 ML, (b) 1.25 ML, (c) 1.45 ML, and (d) 2.03 ML (taken from Ref. [133]).

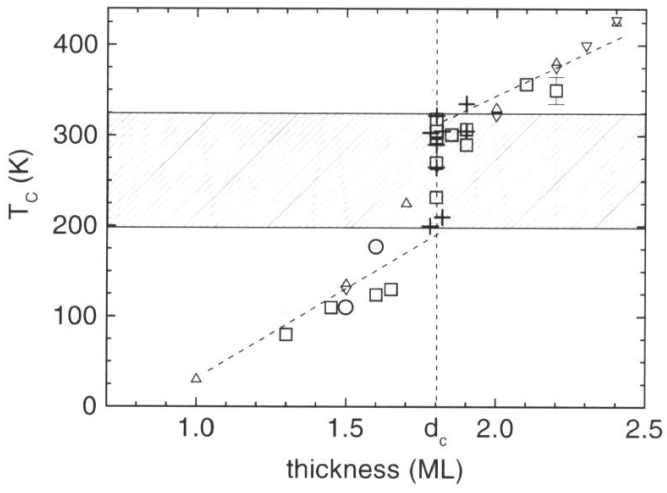

Figure 1.2: Measured thickness (coverage) dependence of the Curie temperature T_C of ultrathin Co/Cu(001) films (taken from Ref. [17]).

system are shown in Fig. 1.1 [133]. Randomly positioned bilayer Co islands are observed at low coverages (Fig. 1.1(a)). Later on, measurements and total energy calculations revealed that there is a considerable admixture of Cu in the first and second addatom layer due to interdiffusion [48, 114, 125]. With further Co deposition, the islands grow together (Fig. 1.1 (b),(c)). The authors report, that in the first layer the magnetic Co islands are separated by nonmagnetic Cu. It is assumed that the Co islands form a connected, percolating magnetic structure at the critical coverage $\Theta_{\mathrm{P}} = 1.7$ ML (monolayers). For coverages $\Theta > 2$ ML ((Fig. 1.1(d)), the system shows a perfect layer-by-layer growth mode.

In the same coverage range, the authors performed temperature-dependent magnetization and susceptibility measurements. The Curie temperature of the long-range magnetic order as a function of the film coverage (thickness) is depicted in Fig. 1.2 [17]. For a connected Co film at 2.5 ML, the exchange coupling results in a high Curie temperature $T_{\mathrm{C}} \approx 450$ K which decreases with decreasing coverage. At the assumed percolation threshold Θ_{P} of the Co system, a strong decrease of T_{C} of about 100 K occurs, see also Schumann *et al.* [148]. Surprisingly, for coverages below Θ_{P}, still a magnetic ordering is observed for temperatures up to ~ 150 K.

Here, the important question arises: Which mechanism causes this strong remanence of an island-type Co film? On the one hand, this could be induced by nonequilibrium *blocking effects* due to anisotropy energy barriers that can impede the magnetic relaxation of noninteracting islands on an extremely long time scale. On the other hand, a finite equilibrium magnetization could originate from a stable *collective order* due to long-range magnetic interactions. Below, we discuss these two limiting cases.

First, we look at the magnetization resulting from *nonequilibrium* effects. At high temperatures, an ensemble of *magnetically isolated* single-domain islands behaves like a superparamagnet. However, for temperatures below the blocking temperature T_{b}, anisotropy energy barriers cause a finite time-dependent magnetization. For Co/Cu(001) films at initial stages of growth, this temperature is estimated to be $T_{\mathrm{b}} \approx 5$ K, following from the Néel-Brown model $k_{\mathrm{B}} T_{\mathrm{b}} = NK/\ln(t_{\mathrm{exp}}\,\Gamma_o)$, and a measurement time $t_{\mathrm{exp}} = 100$ sec [112, 20].[2] This temperature is distinctly lower than the temperatures below which a finite remanence was observed. It should be noted that an island size dispersion sensitively influences the relaxational behavior and T_{b}.

However, a finite film magnetization may also originate from a collectively ordered state in thermal *equilibrium* due to *long-range* inter-island magnetic *interactions*. A long-range magnetic ordering was already measured in rect-

[2] We have inserted the measured in-plane anisotropy $K = 0.01$ meV/atom [60, 91], a typical number of atoms $N = 1000$ per Co island at $\Theta < \Theta_{\mathrm{P}}$ [133], and the attempt frequency $\Gamma_o = 10^9$ sec^{-1} [112, 20], k_{B} is the Boltzmann constant.

angular lattices of separated magnetic nanoparticles and was attributed to the magnetic dipole coupling [31].[3] If a collective magnetic order is induced by such an interaction, the corresponding ordering temperature T_C should be comparable to the average dipole energy per island which, however, is difficult to determine for an irregular system. Assuming two neighboring flat Co islands containing N atoms each, the dipole energy E_{dip} of this island pair is proportional to $\sqrt{N}$. For $N = 1000$, we estimate $E_{dip} \approx 5$ K.[4]

Both simple estimates for the temperatures T_b and T_C are at odds with the experimental observations mentioned above. Hence, improved calculations should take into account the inhomogeneous film structure, characterized by varying island positions, sizes, and shapes. Furthermore, we point out that if the magnetic dipole coupling and the magnetic anisotropy energy have the same strengths, they have to be taken into account at the same time for the calculation of the magnetic behavior. Also, the inter-island exchange coupling has to be considered for coagulated islands. In particular for coverages close to Θ_P, the island coagulation leads to larger effective island sizes N_{eff} at low temperatures and thus to a larger average dipole energy $E_{dip} \propto \sqrt{N_{eff}}$ and higher blocking temperatures $T_b \propto K\, N_{eff}$. Thus, for an irregularly connected island systems, one may expect remanent magnetizations at much higher temperatures than obtained by the simple estimates.

We emphasize that thermal fluctuations must be taken into account for a proper description of the long-range magnetic ordering, since they are very important for 2D systems. This behavior leads to the Mermin-Wagner theorem indicating that there is no finite ordering temperature for an isotropic Heisenberg model with short range interactions [104], in contrast to 3D systems which behave almost mean-field-like, except close to T_C where fluctuations become significant.

The aim of the present work is to understand the equilibrium and nonequilibrium magnetic behavior of an irregular island-type film in the entire coverage range below and above the percolation threshold Θ_P. The main problems are stated the following:

- Does the magnetic dipole interaction lead to a collective magnetic order of an irregular island system for coverages below the percolation threshold Θ_P at finite temperatures? What is the role of the exchange coupling between islands?

[3] In addition, other long-range interactions are possible, such as the indirect exchange (RKKY-) interaction in case of a metallic substrate, and the superexchange for an insulating substrate.

[4] Assume that the distance R between the centers of the island pair is comparable to the diameters, $R \approx D \propto r_o \sqrt{N}$. Then, the point-dipole energy of this island pair is $E_{dip} \approx (N\,\mu_{at})^2/R^3 \approx 0.623\ (\mu_{at}^2/r_o^3)\sqrt{N} \approx 5$ K, where $\mu_{at} = 2.0\,\mu_B$ is the atomic magnetic moment in units of Bohr magnetons measured for 2-ML Co films [155], $r_o = 2.5$ Å the Co interatomic distance [124], and $N = 1000$.

- How does the ordering temperature T_C of the magnetic long-range order depend on the interactions and the coverage?
- How does the magnetic relaxation depend on the magnetic interactions?
- How does the nonequilibrium blocking temperature T_b depend on the interactions and the coverage?
- What mechanism causes the strong remanence of an island-type film below the percolation coverage?

1.3 'As-grown' magnetic domain structure

While the concept of magnetic domains is well established for bulk systems [93, 89, 110], their origin in ultrathin films and nanostructured systems is still not completely understood. In particular, the correlation of the domain structure and the film morphology is a subject of contemporary experimental and theoretical investigations [2, 69, 129]. Generally, in thermodynamic *equilibrium* the subdivision of a ferromagnetic sample into domains can be understood in terms of minimizing its magnetic stray field, resulting from the dipole coupling, at the expence of the exchange energy. The domain size is determined by the balance between exchange and magnetostatic energies, the width of the domain walls results mainly from the balance between exchange energy and magnetocrystalline anisotropy [69].

Allenspach *et al.* observed the interesting and well known magnetic domain structure of a 3-ML Co/Au(111) film in its 'as-grown' state using the SEMPA technique [3], see Fig. 1.3. The image shows irregularly shaped domains with *out-of-plane* magnetizations and lateral sizes of $\sim 1\mu$m. The film growth and the magnetic measurement evolved at room-temperature in a vanishing external magnetic field. Oepen *et al.* detected similar irregular *in-plane* domains for the same system at 6 ML [119]. Between the two coverages a reorientation of the magnetization direction occurs [2]. One important question is: How does the film morphology look like [132, 2]?

The morphology of 3-ML Co/Au(111) films grown at room temperature was examined by Voigtländer *et al.* using STM [170]. The result is depicted in Fig. 1.4. The image shows a *rough* surface consisting of an almost fully connected net of 3D islands with diameters of ~ 10 nm. While some of the Au surface is still uncovered, the 4th and higher layers started to grow on top of the Co islands. Even at 6 ML, a rough morphology resulting from the initial island nucleation pattern has been reported [170, 122, 42].

Consequently, Oepen *et al.* investigated the influence of the surface roughness on the magnetic domain size [154, 73]. For 3-ML Co films grown on *textured* Au surfaces, the authors observed ten times smaller out-of-plane

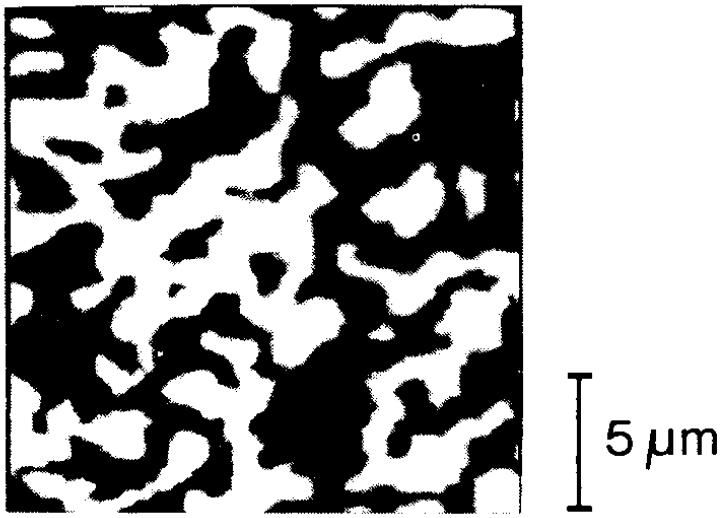

Figure 1.3: 'As-grown' magnetic domain structure of a 3-ML Co/Au(111) film observed by SEMPA showing domains with perpendicular magnetizations (taken from Ref. [3]).

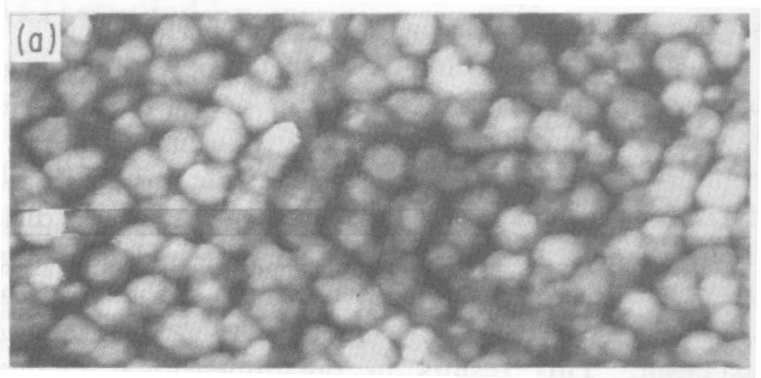

Figure 1.4: Morphology of a 3 ML Co/Au(111) film as observed by STM (160×80 nm^2). A rough film consisting of connected 3D islands is found (taken from Ref. [170]).

domains than for Co grown on Au single crystal as mentioned above. On the other hand, *smooth* 3-ML Co/Au(111) films obtained by an annealing procedure were found in single-domain states with out-of-plane magnetizations [2]. In summary, independent of the direction of the film magnetization, the appearance of small 'as-grown' domains seems to be connected to *rough* surface morphologies. It was observed that the magnetic domains become larger for smoother films. It was suggested that the small 'as-grown' domain structures might be essentially 'frozen-in' during the growth process and represent *metastable* states [2].

The experimental observation of magnetic domains in ultrathin film systems was also of theoretical interest: Calculations of domain structures in thermal *equilibrium* were performed for low temperatures and for perfectly *smooth* 2D systems by minimizing the total magnetic energy. It was shown that for certain strengths of the out-of-plane anisotropy and the temperature, the dipole coupling (magnetostatic energy) leads to stripe domains with perpendicular magnetizations in the vicinity of the reorientation to an in-plane magnetized film [54, 176, 85, 75, 78]. Also, the stability of a checkerboard pattern of out-of-plane domains was reported [34, 85]. In contrast, films with in-plane equilibrium magnetization are calculated to be in the single-domain state. Recently, the equilibrium Monte Carlo (MC) method was used for the investigation of the reorientation transition from perpendicular to in-plane magnetization and the evolution of the corresponding domain structure [70, 165, 166]. Furthermore, the *nonequilibrium* spin configuration during the magnetization reversal of ferromagnetic films with granular structures [88, 115] and of films with monolayer-surface roughness [111] was investigated by means of MC simulations. Recent calculations of the domain structure in periodic inhomogeneous magnetic films revealed metastable chaotic domain patterns [52].

To our knowledge, a realistic inhomogeneous island-type structure of a growing ultrathin film, magnetic states far from thermal equilibrium, and their evolution during film growth have not been considered previously. This thesis examines the following main questions:

- Under which conditions do metastable domain structures occur? How does the domain structure depend on the atomic morphology (roughness) and the lateral nanostructure?
- How does the domain structure develop during film growth? How does the crossover from small single-domain islands ($\sim$ 5 nm) to the large domains of a connected film ($\sim 1\mu$m) happen during film growth?
- What is the role of the magnetic interactions?
- How does the domain structure (domain size, domain roughness) depend on temperature and time?

1.4 Theoretical approach and organization of the thesis

In the present thesis, we investigate by theoretical means irregularly nanostructured film systems during growth and their collective magnetic behavior at finite temperatures in thermodynamical equilibrium and nonequilibrium, taking into account thermal fluctuations. Competing magnetic interactions, large system sizes ($\sim 1\ \mu$m), and long time scales ($\gtrsim 1$ sec) have to be considered. Known analytical methods are not suited for our purposes, since they cannot meet these requirements on equal footing. Also, the numerical solution of the Landau-Lifshitz-Gilbert equation of motion for the time-dependent behavior of interacting island systems can not be applied, since it is restricted to much shorter time scales ($\sim 10^{-9}$ sec) and comparatively small system sizes. Thus, due to the complexity of the problem, we are forced to use MC simulations [10, 59, 13, 92].

The main advantage of the applied MC method is that it allows for an (in principle) *exact* numerical calculation of ensemble properties of interacting many-particle systems in thermodynamical equilibrium. In addition, the stochastic time evolution at large time scales in nonequilibrium can be calculated by the kinetic MC method. Irregular systems with different competing interactions can be treated. The obtained results depend mainly on the assumptions made for the structural and magnetic model. The comparison with experimental observations and analytical theories gives insight into the underlying physical mechanisms, responsible for the observed phenomena. Furthermore, the validity of the model and the corresponding analytical approximations can be tested.

In this thesis, we proceed as follows: In **Chapter 2**, we develop a simple phenomenological growth model resulting in realistic island-type film morphologies. An extended Eden model of island growth is applied resulting in equilibrated island shapes and allowing for the consideration of several magnetic layers. The implementation of the model on a fcc-(001) surface is demonstrated. Examples for resulting nanostructures are presented, in particular a bilayer island growth mode which serves as a model system of this study. In **Chapter 3**, we describe the magnetization reversal of single-domain islands and discuss the relevant magnetic interactions. We deduce a micromagnetic model, treating a nanostructured film as a system of interacting magnetic islands, taking into account a uniaxial single-island magnetic anisotropy, the inter-island dipole coupling and the inter-island exchange interaction. The internal island magnetic order is calculated within a mean-field approach. From the micromagnetic model, rates are deduced for island magnetization reversals due to thermal activation and due to effective magnetic fields resulting from the interactions. As an approximation, we use

a two-state model for the island magnetization directions, including energy barriers for the dynamics. In **Chapter 4**, the flip rates are applied to equilibrium and kinetic MC simulations of the long-range magnetic order and the magnetic relaxation of nanostructured systems. We develop a new cluster MC method which considers correlated island magnetization rotations. This cluster-spin-flip (CSF) algorithm is needed for the treatment of irregularly connected island systems which are in the focus of this study. In **Chapter 5**, our results for the improved relaxation behavior of the CSF method, for the long-range magnetic ordering, the slow magnetic relaxation, and the magnetic domain structure during growth are presented. The dependence of the magnetic properties on the film coverage, the temperature, the time, and the magnetic interactions is discussed in detail. For comparison with the cluster MC results, a simple mean-field theory is used for the calculation of the long-range magnetic order. Finally, a summary and an outlook are given in **Chapter 6**.