

Domain-growth kinetics of herringbone phases

Ole G. Mouritsen

Department of Physical Chemistry, Chemical Institute, Aarhus University, DK-8000 Aarhus C, Denmark

(Received 15 April 1983)

The growth of two-dimensional herringbone phases following quenches from high to low temperatures is analyzed by computer simulation. The herringbone ordering is threefold degenerate and governed by an anisotropic-planar-rotor model on a triangular lattice. The model describes the orientational properties of N_2 on graphite. The growth with time of the average domain radius is shown to be algebraic with a rather low growth exponent $n \simeq 0.25$.

The kinetics of domain growth in systems undergoing crystallization is strongly dependent upon the relation between the number p of thermodynamically degenerate ordered phases and the spatial dimension d of the system. Building on some early ideas proposed by Lifshitz,¹ Safran² has recently advanced a time-dependent Ginzburg-Landau theory which predicts that the domain size at low temperatures equilibrates as a power law for $p < d + 1$ and as a logarithmic function of time for $p \geq d + 1$. In the former case, power-law behavior has indeed been observed in experiments on binary alloys³ ($d = 3, p = 2$) as well as in simulations of simple antiferromagnetic Ising models^{4,5} ($d = 2, p = 2$). In the latter case, the system is subject to frustration and may evolve metastable glasslike states characterized by a distribution of coexisting domains with different types of ordering separated by slowly relaxing domain walls. Such slow relaxation behavior has been reported in experiments on grain growth in polycrystalline metals⁶ ($d = 3, p \rightarrow \infty$) and on the ordering of O on W(110) (Ref. 7) ($d = 2, p = 4$), as well as in various model studies of chemisorbed and physisorbed monolayers⁸⁻¹⁰ ($d = 2, p \geq 3$), of magnetic systems,¹¹ and of Potts models^{12,13} ($d = 2, p \geq 3; d = 3, p \geq 4$).

In this paper I present the results of the first Monte Carlo simulation of the domain-growth kinetics of a specific physisorbed system, N_2 on graphite, using a realistic microscopic interaction Hamiltonian. The Hamiltonian contains not only the correct symmetry of the system but also the appropriate energetics. The computer simulation thus provides experimental information on a system which is difficult to study by conventional experimental techniques since contamination and surface inhomogeneities are likely to influence the kinetics.

At temperatures below 30 K, the registered $(\sqrt{3} \times \sqrt{3})30^\circ$ commensurate phase of N_2 molecules physisorbed on graphite¹⁴ orders orientationally in a (2×1) herringbone structure^{15,16} as shown in Fig. 1. The effective Hamiltonian governing the herringbone ordering can be shown to be that of classical planar quadrupoles on a triangular lattice.^{17,10} The dominant part of this Hamiltonian is the anisotropic-planar-rotor Hamiltonian¹⁰

$$\mathcal{H} = K \sum_{\langle i,j \rangle} \cos(2\phi_i + 2\phi_j - 4\theta_{ij}), \quad K > 0 \quad (1)$$

where ϕ_i is the polar angle of the i th rotor and θ_{ij} is the directional angle of the line joining the centers of the rotors on sites i and j (cf. Fig. 1). The sum is over nearest-neighbor pairs only. The anisotropic-planar-rotor model defined by Eq. (1) has recently been shown to undergo a fluctuation-induced first-order phase transition.¹⁰ There are three equivalent orientations of the herringbone structure and thus six thermodynamically equivalent ground states ($p = 6$). According to the theories by Lifshitz¹ and Safran,² the domain-growth kinetics of the herringbone phases are therefore expected to be slow. This is indeed borne out by the present calculation which at low temperatures, where fluctuations and roughening are unimportant, demonstrates that the growth of the average domain radius is algebraic

$$R(t) = At^n, \quad t \gg 1 \quad (2)$$

with a growth exponent $n \simeq 0.25$ which is considerably smaller than the classical value^{1,2} $n = \frac{1}{2}$ for binary alloys³ and simple antiferromagnetic Ising models.^{4,5} Furthermore, n is found to be independent of details of the local excitation mechanism by which the domain walls relax to equilibrium.

I have calculated the time evolution of the model in Eq. (1) following a quench from $T \simeq \infty$ to $T \simeq 0$ by using standard Monte Carlo sampling. The rotors are arrayed on rectangular-shaped triangular lattices subject to toroidal periodic boundary conditions. To reduce possible boundary effects, the main results are obtained for a very large lattice with 152×152 sites. Also, in the low- t regime some results are reported for a 40×40 lattice. The system of rotors is brought towards the low-temperature states by a single-site Glauber-type excitation mechanism which takes the system from state α to state β with a probability $P_{\alpha\beta} = P_{\alpha\beta}^* \exp[-(E_\beta - E_\alpha)/k_B T]$. The ergodic stochastic matrix P^* basically sets the time scale of the problem $P^* \sim \tau^{-1}$. In order to examine the dependence of the domain growth upon details of the local excitation mechanism, P^* is chosen in two different ways corre-

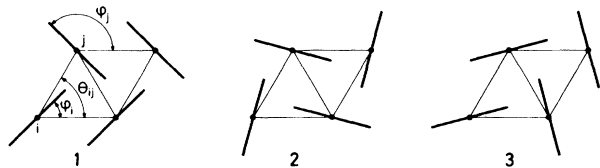


FIG. 1. Unit cells of the three types of herringbone domains on a triangular lattice. The planar rotors represent the interatomic axes of diatomic molecules (e.g., N_2) adsorbed in a commensurate $(\sqrt{3} \times \sqrt{3})30^\circ$ overlay on a hexagonal substrate of graphite. The angles ϕ_i and θ_{ij} enter the Hamiltonian in Eq. (1).

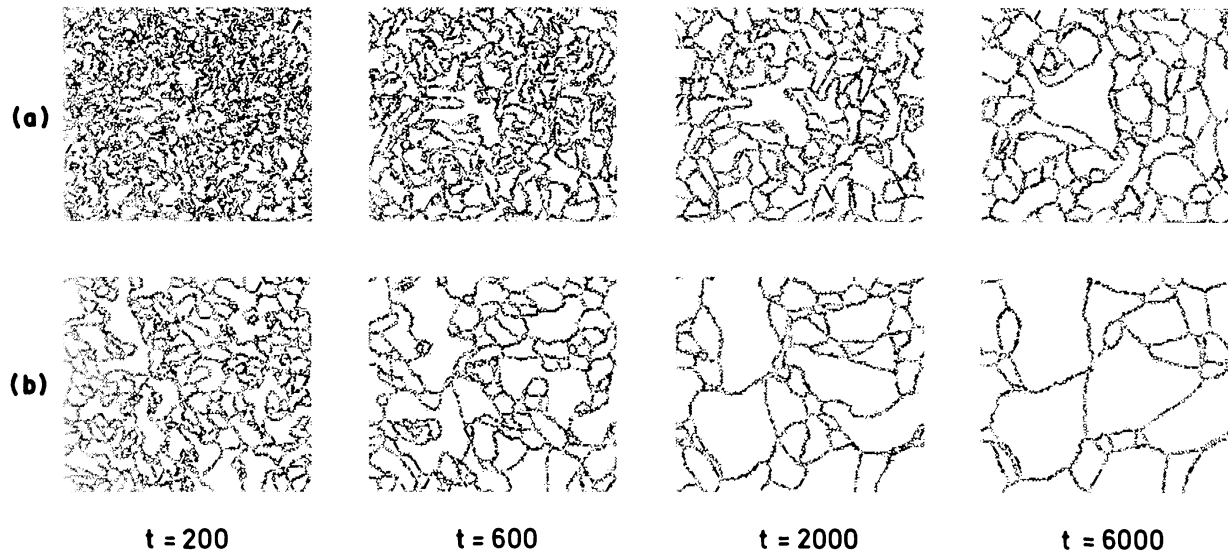


FIG. 2. Snapshots showing the distribution of herringbone domains at various times, t (MCS's/site), following a temperature quench. The system contains 152×152 sites. Only the domain walls are displayed. Panels (a) and (b) correspond to unrestricted and restricted single-site excitation mechanisms, respectively.

sponding to random reorientations (rotational diffusion) of the rotor angle $\phi_i \rightarrow \phi_i + \Delta\phi_i$, without (a) $0 \leq \Delta\phi_i < \pi$ and with (b) $0 \leq \Delta\phi_i \leq \pi/5$ an angular restriction. To provide ensemble values the results are averaged over several quenches corresponding to different initial high-temperature (random) configurations as well as different random number sequences. The time t is measured in units of MCS's/site (Monte Carlo steps per site).

In Fig. 2 snapshots are given of the configurational state of the large system for a series of selected times. For clarity, only the domain walls are displayed. In a lattice model with continuous single-site variables, the walls are soft (in contrast to Ising^{4,5,18} and Potts^{13,19} models) and the extension of the walls is a matter of definition. I have chosen to consider rotors as part of a domain wall if their value of ϕ_i deviates more than $\pi/15$ from the ground-state values of the adjacent ordered domains. The value of this discrimination angle, which only influences the thickness of the wall and not its position, is of marginal importance at low temperatures. However, at higher temperatures and especially near the phase transition, where roughening fluctuations are important,¹⁸⁻²⁰ the criterion for locating the domain walls has to be reconsidered and it may be more convenient to determine the domain sizes via the structure factor. Figure 2 shows that for small t the cluster distribution is very ramified and the shapes of the clusters are irregular. The regularity in shape increases with t . No significant decrease in domain-wall thickness with time is observed for $t \geq 50$. For the range of times studied here, no general form has been found for the internal structure of the walls. Neither do there seem to be any preferred directions of the walls relative to the lattice. However, for the smaller lattice there is some indication of the optimal directions being the three canonical axes of the triangular lattice. The two panels in Fig. 2 show that the excitation mechanism based on a restricted reorientation angle facilitates formation of larger clusters. When two domains of the same type of ordering meet, they coalesce. The coalescence processes occur most frequently

for small t . From visual inspection of snapshots such as those presented in Fig. 2 some general conclusions on domain growth for large t can be drawn: (i) the domains change size by migration of the walls, (ii) the driving force of the migration is the curvature of the walls, and (iii) the points where three domains meet act as pinning centers,^{13,19} the effectiveness of the pinning being commensurate with the similarity of the angles at which the domain walls meet. These observations are in line with results found in classical work on recrystallization phenomena^{21,22} and in model studies of q -state ($q \geq 3$) triangular Potts models.^{13,19}

A quantitative analysis of the domain growth can be carried out by studying the average domain radius $R(t)$ as a function of t . $R(t)$ is calculated from the instantaneous

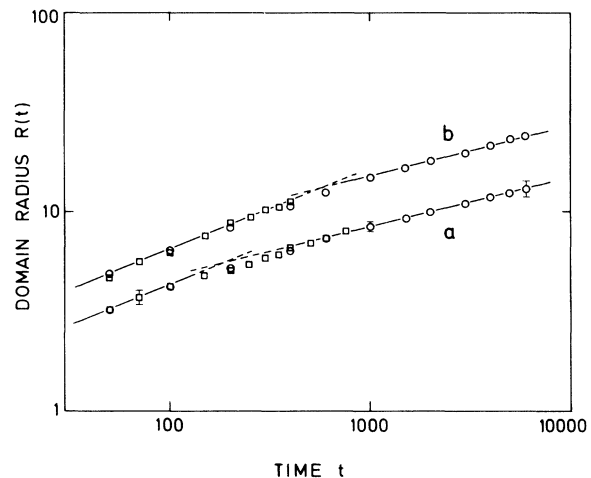


FIG. 3. Average domain radius $R(t)$ as a function of time, t (MCS's/site). Results are shown for two different local excitation mechanisms: (a) unrestricted and (b) restricted reorientation angles. Data are given for systems with 40×40 sites (\square) and 152×152 sites (\circ). Horizontal bars on selected data points indicate typical statistical fluctuations.

domain distribution by defining the radius of a domain as the square root of the number of sites in the domain. Figure 3 shows the results for $R(t)$ in a log-log plot. Data for the smaller lattice are only given for small t where finite-size effects have not yet set in. For both excitation mechanisms a and b there are two time regimes, an initial fast time regime separated from a slower late-time behavior by a crossover region. The position and extension of the crossover region depend on the excitation mechanism. The most important conclusions to be drawn from Fig. 3 are that the growth is algebraic with time in both time regimes and that the associated growth exponents are the same for both excitation mechanisms. In the early regime $n \simeq 0.40$ and in the late regime $n \simeq 0.25$. These results suggest that n is universal and independent of details of the local excitation mechanism. In contrast, the prefactor A in Eq. (2) is a function of the details of the excitation mechanism and its intrinsic characteristic time scale.

The finding in the late-time domain of a nonzero (although small) growth exponent for a system with $p \geq d + 1$ contradicts Safran's theoretical prediction of logarithmic behavior.² However, Safran's theory assumes a continuum and presupposes that the equilibrated domains are ideal six-sided hexagons. The present system is a discrete lattice model, and as Sahni *et al.*¹³ have pointed out, domain-wall defects on a triangular lattice are easily transmitted through the pinning centers leading to a more rapid migration of walls. Also, it is obvious from Fig. 2 that odd-sided irregular domains frequently occur, which again facilitates the overall relaxation of the system.²¹ The late-time exponent $n \simeq 0.25$ determined in the present study is dramatically lower than the classical value^{1,2} $n = \frac{1}{2}$ found for binary alloys³ and Ising models.^{4,5} Moreover, it is smaller than n for any q -state Potts model, $q \geq 3$, for which n decreases from 0.495 for $q = 3$ to 0.41 for $q \rightarrow \infty$.¹³ The much slower kinetics of domain growth found in the present study is probably caused by the continuous nature of the site variable ϕ_i , which makes it pos-

sible for the system to form soft domain walls. The softness of the walls screens the interaction between the different domains and decreases the driving force for the growth. It now seems obvious that the explanation of the presence of a separate early fast time regime is that the high frequency of coalescence processes at low t to some extent outbalances the slow kinetics caused by the screening of the domain-domain interactions. The conclusions drawn in this study about the late-time behavior are, of course, subject to the usual condition in computer simulation studies that the asymptotic region of growth has indeed been attained. For any run of finite length it cannot be excluded that further relaxation will occur and that the cited value of the growth exponent is only an upper bound. The situation thus parallels that of determining critical point exponents (in real as well as computer experiments) over a range of finite reduced temperatures.

In conclusion, I have shown that the domain growth of two-dimensional herringbone phases is algebraic with time and that there are two characteristic time regimes. The growth exponents are independent of the details within the local excitation mechanism (rotational diffusion) in terms of which the relaxation proceeds. The predictions made in this work may, therefore, be tested by measuring the time dependence of the width of the diffraction peaks resulting from diffraction studies, e.g., low-energy electron diffraction,^{7,16} of N_2 on graphite after a temperature quench. Finally, herringbone ordering in liquid crystals²³ may obey a similar growth kinetics. However, since the ordering in smectics is governed by a close-packing condition²⁴ rather than electric quadrupole-quadrupole interactions, the internal structure of the domain walls is expected to be different.

I wish to thank A. John Berlinsky for stimulating discussions. The author was supported by A/S De Danske Spritfabrikkers Jubilaeumslegat during the course of this work.

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