Kinetics of Stage Ordering and Stage Transitions

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A model of intercalation is presented which can be used for sophisticated three-dimensional computer simulations of staging kinetics. A realistic microscopic description of the intercalation process and of the stage-3 to stage-2 transition has been obtained for the first time. Stage disorder and three-dimensional effects are shown to be key ingredients of these phenomena. This work makes possible the first critical appraisal of the Daumas-Hérold model, which is shown to be valid for *uniformly* intercalated high- and low-stage crystals, and to provide a useful language for describing the stage transition.

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When a guest species intercalates into a layered host material such as graphite, periodic arrangements of guest and host layers are formed. The period consists of a guest layer followed by n host layers for a stage-n compound. Although the physics and chemistry of staging have attracted a great deal of interest,[1] a definitive understanding of how these remarkable one-dimensionally ordered structures are formed is still lacking. This is also true of the phase transitions in which the stage index n changes. Sophisticated computer simulations of the intercalation kinetics could provide a credible real-space picture of these phenomena (a long-sought objective in this field), and help to resolve a number of difficult and highly controversial issues. These include the question of the validity of the Daumas-Hérold model of staging,[1,2] the possible relationship between stage transitions and stage disorder,[1,3-7] the nature of the "miscibility gaps" observed by Misenheimer and Zabel[3] between successive staged phases, and the relative importance of equilibrium and kinetic effects in the underlying physics. The purpose of this Letter is to report on the first three-dimensional computer "experiments" of this kind.[8]

At normal temperatures, the guest atoms cluster in plane into "islands" because of elastic strains induced in the host.[1,9] This property will be used to formulate a model of intercalation which is physically appealing, and also able to cope with the very large numbers of guest atoms involved in staging phenomena. It will be assumed that there is a smallest energetically allowed island size (~ 10–20 Å) related to the in-plane "healing length" of the deformation induced in the host by an isolated guest atom. The intercalate can then be viewed as being made up of such elementary islands (EI's) interacting via electrostatic and elastic forces. For simplicity the EI's will be restricted to a regular lattice of allowed sites. The model Hamiltonian is $H=\sum_i KN+\frac{1}{2}\sum'_{ij}Nu_{ij}+E_d$. The summations are over the EI's, and N is the number of atoms in the EI (assumed fixed). K is the Helmholtz free energy of an EI per atom, omitting the effects of the bending of host layers and interactions between EI's. The second term is the Safran-Hamann electrostatic interlayer repulsion between EI's.[10] Only EI's separated by a pure c-axis displacement interact and the interaction is strongly screened.[10,11] We will take $u_{ij}=v_0 l^{-\alpha}$ where l is the number of intervening host layers and choose $\alpha=1$.[7,10,11] E_d is the elastic energy associated with the *edges* of the intercalate islands.[9,12] We include only local effects in E_d and treat them very simply. If an EI has a vacant in-plane nearest-neighbor site, then the EI has a *free edge* (FE). For every FE present we include in E_d a positive dislocation energy E_s. If the FE is in a gallery adjacent to the c face, E_s is reduced by a surface factor ϵ. If two EI's in *adjacent* galleries have *adjacent* FE's, then we include in E_d a negative "nesting" energy E_n if the EI's have different in-plane coordinates, and a positive stacking term E_r if they have the same in-plane coordinates.

The Hamiltonian H describes a system with a fixed amount of intercalate. If the same system is instead assumed to be *in equilibrium* with an intercalate reservoir at chemical potential μ, *and* there are few dislocations so that E_d can be neglected, then the transition from stage i to stage $i+1$ occurs at $\mu_{i,i+1}=K-v_0[i(i+1)^{-\alpha}-(i+1)i^{-\alpha}]$. This result was used as a guide in the choice of the reservoir chemical potential used in the computer simulations. Comparing this form for $\mu_{i,i+1}$ with experiment[13] and with domain-wall calculations[9,12] indicates that $-KN \gtrsim v_0 N > E_s$ for typical graphite intercalation compounds.

Consider a crystal with nineteen galleries (i.e., twenty host layers) labeled by z, $1\leq z\leq N_z=19$. Each gallery is represented by a rectangular array of N_x by N_y EI sites. We choose $N_x=60$ (a length $\sim 10^3$ Å), $N_y=20$. Each site has coordinates (x,y,z) with $1\leq x\leq N_x$, etc. Periodic boundary conditions are applied in the y direction. All other surfaces are free. A guest-species reservoir at chemical potential μ_r is placed in contact with the sites at the $x=1$ surface. The movement of EI's between crystal and reservoir and within the crystal is controlled by a Monte Carlo algorithm, with only nearest-neighbor in-plane hop-

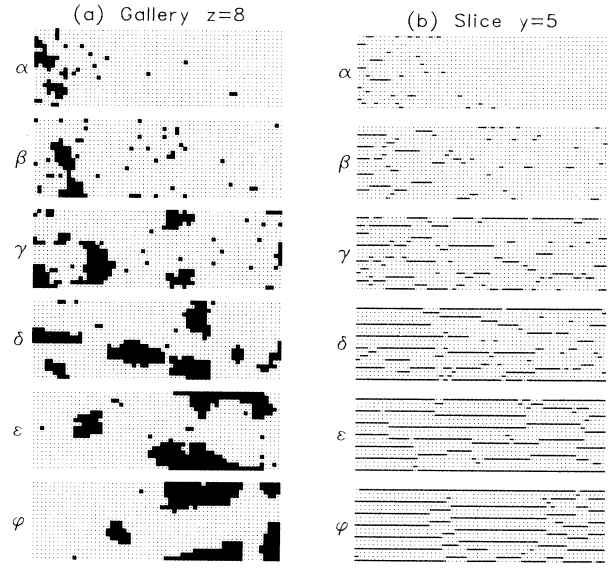

FIG. 1. Growth of stage 3 from pristine host. The sites in row 5 from the bottom in each frame in (a) also appear in row 8 from the bottom in the corresponding frame in (b).

ping allowed. The model parameters used were $KN=-11.5$, $v_0N=10$, $E_s=1$, $E_r=-E_n=\epsilon=0.5$, and $kT=1$, yielding $N\mu_{1,2}=3.5$, $N\mu_{2,3}=-3.1667$, and $N\mu_{3,4}=-5.6667$.

Figure 1 shows the evolution of a typical gallery and out-of-plane slice through the crystal during intercalation of the pristine host to stage 3. Solid squares are EI's, dots are vacant sites, and lines are EI's seen edge on. The reservoir (not shown) is on the left of each frame in this and all other figures in this article. The host layers and c-axis expansion are not depicted for clarity. $N\mu_r$ is set at -4.5, near the center of the stage-3 stability region. Frames α–ϕ are after 2, 10, 80, 300, 1000, and 2505 million EI Monte Carlo steps (MMS), respectively. Frame ν in column i will be denoted (i,ν).

The EI's cluster in plane into assemblies which will henceforth be referred to as "islands." One can follow the history of two islands which form near the surface [frame (a,α)], merge [frames (a,β), (a,γ)] as they migrate into the crystal, and merge again [frames (a,δ), (a,ϵ)] with an island which nucleated directly deep within the crystal [frame (a,γ)] out of the EI "soup." Meanwhile, new islands form at the surface [frames (a,γ), (a,δ)] and also migrate inwards. The migration is driven by the formation and growth of islands at the surface in other galleries [Fig. 1(b)], and by the interlayer repulsion. A well-defined pleated Daumas-Hérold (DH) domain structure[2] forms, but quite late in the process [frames (b,ϵ), (b,ϕ)]. Considerable in-plane restructuring involving island fission

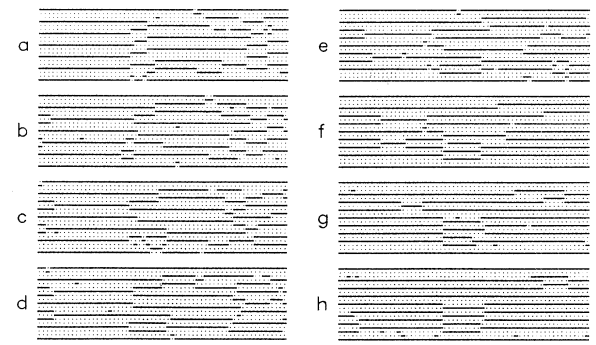

FIG. 2. Stage-3 to stage-2 transition. Slice $y=5$ is shown.

[frame (a,ϕ)] accompanies the final ordering to stage 3. The stage-3 structure achieved after the 2505 MMS (frames ϕ) is still not entirely perfect (the fractions of stage-2, -3, -4, and -5 units are 0.110, 0.757, 0.116, and 0.012, respectively) but intercalation has become extremely slow. The entire surface in contact with the reservoir orders and becomes a single stage-3 DH domain much earlier, at ~ 500 MMS. This may explain why some recent a-face imaging studies yielded nearly perfect structures without any visible domain walls.[14]

Figure 2 shows the same slice through the crystal as Fig. 1(b), but during the stage-3 to stage-2 transition. The stage-3 crystal (Fig. 1, frames ϕ) was intercalated further for 415 MMS at $N\mu_r=-3.8$ followed by 245 MMS at $N\mu_r=-3.1667$ (the stage 3-2 boundary). Intercalation was very slow. f_3 (the fraction of stage 3) changed little, but f_4 decreased and f_2 increased somewhat. The result is shown in Fig. 2(a). The results of further intercalation at $N\mu_r=-2.0$ (just within the stage-2 stability region) to 400, 800, 1200, 2000, and 4020 MMS are shown in Figs. 2(b)–2(f), respectively. The stage transition begins *simultaneously throughout the crystal* in the smallest domains and at domain boundaries, where a disordered mixture of stage-3 and stage-2 units appears. The small disordered domains grow at the expense of the larger predominantly stage-3 domains. As they grow they show greater stage order (becoming predominantly stage 2), in qualitative agreement with theoretical considerations relating domain size and stage disorder.[7] Thus the crystal separates into distinct domains of predominantly stage-3 and predominantly stage-2 units as the transition progresses. This is entirely consistent with the x-ray data of Misenheimer and Zabel, which shows the simultaneous presence in the sample of two such distinct stage-disordered components during the stage transitions,[3] and with earlier related experiments.[1,13,15] By 4020 MMS [Fig. 2(f)] intercalation had become very slow. $N\mu_r$ was then increased to -1.0 for 2040 MMS [Fig. 2(g)] and then to 0.0 (near the center of

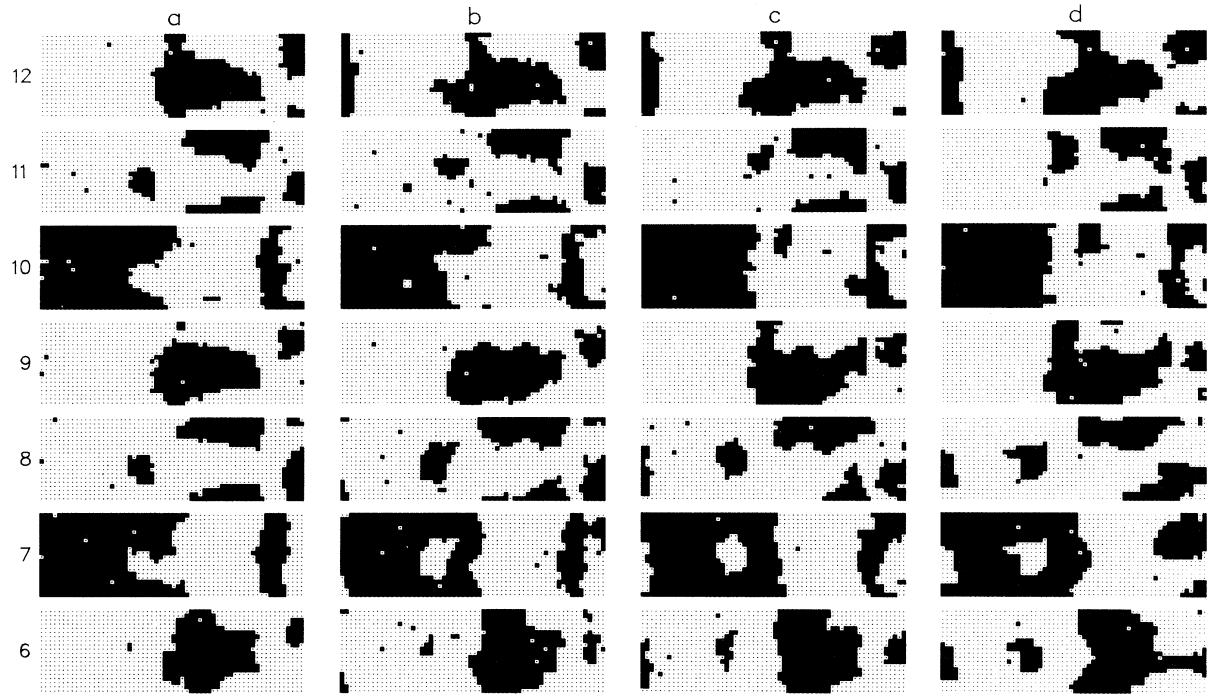

FIG. 3. Evolution of galleries 6–12 during the early part of the stage-3 to stage-2 transition.

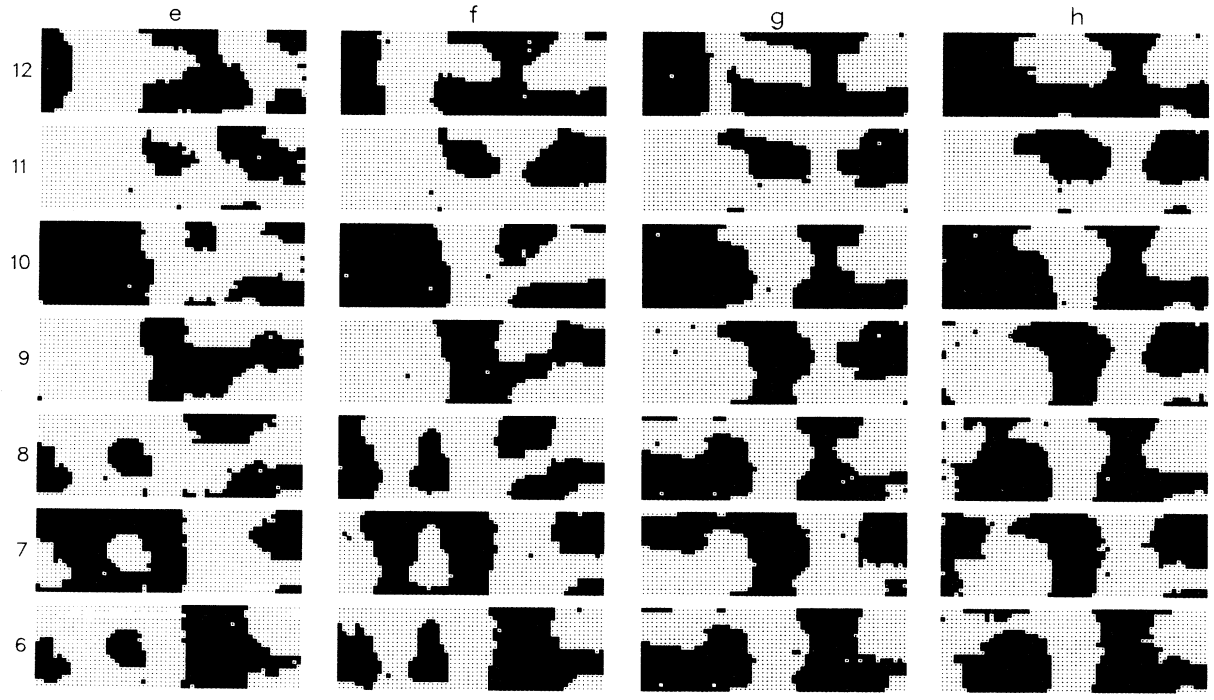

FIG. 4. Evolution of galleries 6–12 during the latter part of the stage-3 to stage-2 transition.

the stage-2 stability region) for a further 1055 MMS [Fig. 2(h)]. The growth and ordering of the stage-2 domains continued. The last structure shown consists of 82% stage-2, 3% stage-1, and 15% stage-3 units, the stage-3 units being mostly near the crystal surfaces.

Figures 3 and 4 present a three-dimensional description of the stage transition. Each column shows galleries 6–12 (as labeled on the left) at a different time. Figures 3(a)–3(d) and 4(e)–4(h) correspond to the same times as Figs. 2(a)–2(h), respectively. Figure 3(a) shows the stage-3 structure. Each sizable island coincides closely with the projection of a DH domain onto the basal plane. Consider the small domain located slightly left of center in the galleries of Fig. 3(a). This domain evolves towards stage 2 as follows. The island in the domain in gallery 11 migrates out of the domain [Figs. 3(a)–3(d)], while the boundary of the largest island in gallery 10 distorts, filling the region of the domain with intercalate, and also making way for the movement of the island in gallery 11 by parting at the upper right. A stage-2 structure calls for an island in the domain in gallery 6. The missing island grows out of EI's [Figs. 3(a)–(d) and 4(e)–4(f)] which migrate individually through the surrounding energetically unfavorable region [see gallery 7, Figs. 3(b)–3(d) and 4(e)–4(f)]. Meanwhile, the domain moves somewhat to the left. Finally, gallery 12 also conforms to the stage-2 structure of the domain by growth and merging of two large islands [Figs. 4(f)–4(h)]. The migration of smaller islands, amoebalike distortion of boundaries of larger ones into and out of small domains, island fission, island growth by capture of EI's which diffuse through energetically unfavorable regions, and, particularly at later times (Fig. 4), the merging of islands as they grow, are basic ingredients of the stage transition. During the stage transition the in-plane dimensions of the DH domains often differ markedly from those of the intercalate islands. The domains change radically in size and shape and are not always precisely defined. Smaller ones appear and disappear. However, the domain concept is clearly very useful in describing the stage transition as well as the highly ordered structures.

The apparent generality of the Daumas-Hérold model is quite remarkable. Figure 5 summarizes the growth of a higher stage from the pristine host. We take $N_x = 75$, $N_y = 30$, $N_z = 37$, $KN = -10$, $v_0 N = 6$, $E_s = 1$, $E_r = -E_n = 0.2$, $\epsilon = 0.5$, $kT = 1.0$, and thus $N\mu_r = -7.55$ (the center of the stage-5 stability region). Figures 5(a) and 5(b) are after 500 and 5160 MMS, respectively. By 5160 MMS, intercalation has become extremely slow, although the structure is still a highly disordered stage 6 ($f_2, \ldots, f_{10} \simeq 0.02, 0.07, 0.13, 0.20, 0.33, 0.14, 0.04, 0.03, 0.01$). However,

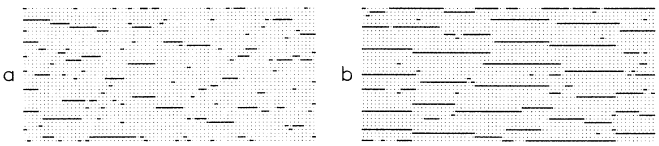

FIG. 5. Higher-stage intercalation. Slice $y = 5$.

this strongly stage-disordered high-stage structure consists almost entirely of well-formed DH domains! This surprising result supports the conjecture[7] that high-stage stage disorder can be treated theoretically within the DH model. A careful comparison of the recently proposed high-stage scaling rules[7] with experiment[4,6] should be very interesting.

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