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Molecular-dynamics simulation of thin-film growth and relaxation

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ABSTRACT

We simulate the growth of a thin film in two dimensions with a computer implementation of the molecular dynamics (MD) method. The system consists of a krypton substrate maintained at a temperature of about 10 degrees Kelvin, toward which argon atoms are periodically directed (with a velocity corresponding to 120 degrees Kelvin). The resulting argon film follows the (horizontal) spacing of the krypton lattice until the thickness of the film approaches an average thickness of about 10 monolayers. As deposition proceeds, the configuration of the film changes to incorporate an edge misfit dislocation at the film-substrate interface; this relieves the interfacial stress.

We also apply the MD method to study the relaxation of thin-film structures predicted by a hard-disk growth model. We consider two variations of the growth model; the first is similar to that described by Henderson et al.,[6] the second is a variation which incorporates the effect of surface diffusion. The voids in the relatively open microstructure predicted by the Henderson model are very effective in relieving interfacial stress. The numerous lattice defects (grain boundaries, dislocations, and vacancies) in the denser microstructure predicted by the second type of hard-disk model result in a film with high stress.

1. INTRODUCTION

Several authors have applied the molecular-dynamics (MD) method to the study of thin-film growth.[1-4] In these references, it is important to distinguish between fully dynamical MD simulations and MD simulations in which further approximations have been made. In a fully dynamical MD simulation, often referred to as a *full* MD simulation, the classical equations of motion are solved iteratively for the system without further approximation. The only stochastic element in such a simulation is the random introduction of new (evaporant) atoms into the system at suitable intervals.

Various techniques have been applied to reduce the computational intensity of the MD calculation. The approximations in such simulations made possible computations of larger systems over longer time periods than fully dynamical simulations. Examples of this nonstandard type of molecular dynamics simulation are the simulations of Leamy, Gilmer, and Dirks[1] and those of Gilmer and Grabow.[2]

In previous full MD simulations, it was assumed that the substrate and film particles were of the same type,[3] that is, fully dynamical MD thin-film growth simulations to date have been limited to the case of auto-epitaxy. Here we simulate a system film in which the substrate atoms differ from the deposited film atoms, employing a full MD simulation technique. The study is limited to two dimensions, and the particles interact through a Lennard-Jones potential. In our growth study, the system consisted of a substrate of krypton atoms, toward which argon atoms were periodically directed. The lattice mismatch for this case is approximately 7%. We recorded the deposition by video taping a sequence of frames of the simulation cell on a computer screen. For presentation in this work, a sequence of the frames is plotted.

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We also used the MD method to calculate properties of thin-film structures predicted by a hard-disk-aggregation growth model. We concentrated on the property of stress and performed simulations on several different structures. The film stresses of two such structures were calculated with a MD simulation; one structure was that predicted by the Henderson model, and the other was predicted by a Henderson-like model that included surface adatom mobility.

2. MD SIMULATION OF FILM GROWTH

2.1. The system

We composed our system of particles interacting through a Lennard-Jones (L-J) potential:

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1}$$

The simulation performed in this work consisted of 360 atoms of Ar deposited on a substrate of 150 atoms of Kr.

The L-J parameters of the film and substrate particles were taken to be in the ratio of those of argon to krypton. Though far from practical thin film materials, these elements do interact primarily through van der Waals interactions, and their Lennard-Jones parameters are well known. The Lennard-Jones parameters for the Ar-Ar interaction were chosen as the reference parameters, and the Ar mass for the reference mass. The parameters for the Kr-Ar interaction were estimated by the following formulas:

$$\sigma_{Ar\text{-}Kr} = \frac{\sigma_{Ar} + \sigma_{Kr}}{2} \tag{2}$$

$$\epsilon_{Ar\text{-}Kr} = \sqrt{\epsilon_{Ar} \epsilon_{Kr}} \tag{3}$$

The values of the L-J parameters for argon and krypton are:

	σ (Å)	ϵ (Joules)
Ar	3.40 Å	1.67×10^{-21} Joule (.0104 eV)
Kr	3.65 Å	2.25×10^{-21} Joule (.0140 eV)

The thin film growth version of the model was nominally operated in the canonical (N, V, T) ensemble. The simulation cell dimensions were kept constant; the number of particles was only changed when a new evaporant atom was added to the simulation. A periodic boundary condition along the substrate length was employed.

The substrate consisted of two fixed rows of atoms followed by three rows of moving atoms. The velocities of the moving atoms were reset every other MD time step to correspond to the desired substrate temperature. The three rows of moving atoms were maintained at a temperature of $T = .08\ \epsilon/k$ ($T \cong 10°K$). The range of particle interaction was truncated between 3rd and 4th neighbors at a distance of $r_i = 2.7\ \sigma$.

The natural time unit in our MD implementation was:

$$t_0 = \left(\frac{\sigma}{2} \right) \sqrt{\frac{m_{Ar}}{\epsilon}}, \tag{4}$$

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and we chose a time step of $\Delta t = .01\ t_0$. With argon as the reference particle, this corresponds to $\Delta t \cong 10^{-14}$ seconds. Evaporant atoms were introduced at the distance r_i above the highest particle in the film, and with a random horizontal position. Atoms were added into the simulation every 500 time steps, and were given velocities corresponding to a temperature of $T = 1.0\ \epsilon/k$ ($T \cong 120°K$).

2.2. Results and discussion

2.2.1. Film growth

A single simulation lasting 210,000 MD time steps was run, with the parameters described above. A summary of the simulation is in the following table.

Time Step	Event
0-10,000	Substrate allowed to equilibrate
10,001-190,000	Ar atoms introduced every 500 steps
190,001-200,000	System allowed to settle
200,001-210,000	Calculation of film properties

A sequence of plots of the positions of the particles is given in Fig. 1.

In the early stage of deposition, the Argon film follows the atomic spacing of the Krypton substrate. When the film approaches an average thickness of approximately 10 monolayers, the configuration of the film changes to incorporate a single edge misfit dislocation at the film-substrate interface (Fig. 2). The misfit dislocation forms by a crystal slippage parallel to one of the three principal directions of the argon triangular lattice. The atom slip appears to be initiated at the film surface and to propagate toward the film-substrate interface. Two Burgers circuits superposed onto (a) a region of good match between the film and substrate, and (b) the misfit dislocation illustrate the drastic atomic relaxation that occurred at the interface. A misfit dislocation is defined by the continuity of corresponding lattice planes and directions across the interface. As the two crystal lattices adjoining the interface are incommensurate, lattice continuity across the boundary generates long-range strain fields which can be represented in terms of an array of interfacial dislocation. In the particular case of argon on a krypton substrate, such misfit dislocations should form approximately every 14 to 15 atoms along the interface to fully accommodate the 7% mismatch between the film and the substrate. Therefore, the substrate length of 30 atoms should lead to the formation of two dislocations instead of a single one.

The compatibility between the predicted dislocation spacing and the substrate length suggests that the artificial periodic boundary condition is not directly responsible for the formation of a single dislocation. However, it appears that there is a large void at the borders of the simulation cell. The small thickness of the film in that region (~4 atomic layers) may accommodate the mismatch more easily thus preventing the formation of the second dislocation.

It is worth noting that the temperature of the film surface at the end of the deposition part of this simulation was found to be higher than the substrate temperature by about a factor of two. This nonuniform temperature distribution was due to the short time between the introduction of successive evaporant atoms. However, the system was allowed to settle without further deposition for 20,000 integration time steps. After this period the temperature attained a uniform distribution.

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2.2.2. Stress calculation

The stress parallel to the film can be calculated from the virial theorem[5]

$$\sigma = \frac{1}{V}\left\{\sum_i m_i v_i^{x^2} - \sum_{j>1}^{N}\sum_{i}^{N-1} \frac{1}{r_{ij}} \frac{\partial \phi(r_{ij})}{\partial r_{ij}} r_{ij}^{x^2}\right\} \tag{5}$$

where

V = the volume of the film

m_i = mass of particle i

v_i^x = the xth component (along the film) of velocity vector of particle i

$\phi(r)$ = the pair potential is in the potential between particles i and j

r_{ij}^x = xth component of $\vec{r}_{ij}$ as $\vec{r}_i - \vec{r}_j$.

The stress was calculated over the film particles only; this was accomplished by including only film type particles in the $\sum_i m_i v_i v_i$ term, and including elements of the $\sum_i \sum_{j>1} \left[\frac{1}{r_{ij}}\right]\left[\frac{\partial \phi}{\partial r_{ij}}\right] r_{ij} r_{ij}$ term only if at least one of the particles (i or j) was a film particle. The volume was taken as the volume of the film (actually this was an area in two dimensions).

The stress of the final configuration was calculated during the last 10000 time steps. The stress is tensile as expected (negative in sign) and the value is about three times greater than for a reference film of argon atoms in a perfect lattice on an argon substrate (the reference system consisted of 600 atoms on a substrate containing two rows of 40 fixed argon atoms). The value of stress for both systems are reported in units of ϵ/σ^2 in the following table.

System	Stress Value
Ar film grown on Kr substrate	-.2530 ϵ/σ^2
Reference Ar film	-.0886 ϵ/σ^2

The stress of the reference film is essentially caused by the energy of the free surface. The large value of the deposited film stress results from the partially relaxed nature of the deposited film structure as well as the dislocation stress field. The formation of a single misfit dislocation only partially relaxes the film-substrate mismatch. The attractive van der Waals forces between those pairs of argon atoms forced by the substrate to be at nonequilibrium interatomic spacings will strongly contribute to the tensile stress. Furthermore, the residual long range stress field associated with the edge dislocation will superpose onto the film stress. At this point both contributions cannot be separated.

3. THIN FILM RELAXATION

Here we describe the use of the MD method to study the relaxation of thin-film structures by a hard-disk growth model. We consider two variations of the growth model; the first is similar to that described by Henderson et al.,[6] and the second is a variation which incorporates the effect of surface diffusion.[7] The Henderson-type model (type 1) generated structures having a density of 0.6 relative to a two-dimensional hexagonal close-packed structure. The model incorporating surface

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diffusion (type 2) generated a structure with a relative density of 0.8; the average surface diffusion length was 3.4 atom diameters.

The same MD model described in part one was used for relaxing the hard-disk films (except that new particles were no longer periodically introduced). The time step was chosen to be $\Delta t = .002\ t_0$, and the simulations were run for 10000 time steps. The particles were given velocities corresponding to the desired temperature. The structures were judged stable or not only by visual inspection of "before" and "after" plots of particle positions.

The substrate consisted of two fixed rows of 40 atoms each; this ensured that a film atom lying on top of the substrate had nearest, second-nearest, and third-nearest neighbors in the substrate. The substrate and film atoms were again chosen to have relative L-J parameters corresponding to those of krypton and argon. Figs. 3(a) and 4(a) show the morphology of films produced with the hard-disk growth model for type 1 and type 2, respectively. The former possesses a columnar structure with a large number of voids; the structure of most columns is crystalline while patches of the film are very disordered. The latter film is more dense with only a few voids; it exhibits regions of crystallinity as well as regions of relatively high disorder.

Simulations lasting 12,000 integration time steps have been run to observe the relaxation of the films. Interestingly these structures were stable only at relatively low temperatures; they tended to settle "down" towards the substrate, and form crystallites. The lowest temperature simulations were run at $T = .01\ \epsilon/k$ ($T \cong 1.2°K$), and even these simulations displayed restructuring. Figs. 3(b) and 4(b) represent the relaxed structures of films 3(a) and 4(a). In both cases, some relaxation has occurred. The disordered regions in both films have recovered their crystallinity. The general morphology of the films is, however, retained.

The relaxed type 2 film contains a variety of structural defects such as dislocations: one misfit dislocation at the film-substrate interface indicated as (a), and lattice dislocations such as the one marked (b), a point defect in the form of vacant sites (c) and a high angle grain boundary (d).

In all simulations, the systems were allowed to equilibrate for 2000 time steps, then the stress was calculated over the next 10000 time steps. The average values were obtained, the volumes of the films estimated, and the stress values corrected. A summary of the results is given in the following table. (This table includes the stress of the reference Ar film described in the first section.)

System	Stress Value
Reference Ar film	$-.0886\ \epsilon/\sigma^2$
Columnar film	$-.0860\ \epsilon/\sigma^2$
Dense polycrystalline film	$-.2448\ \epsilon/\sigma^2$

In all cases, the stress is tensile. The columnar type 1 film produces little stress as could be expected from a disjointed structure. The large number of voids in this structure can be viewed as effective relaxation sites for stress.

It is worthy to note that the stress produced by the type 2 film is comparable in magnitude to the stress associated with the film grown with the MD simulation of Section 2. This stress can be thought of as the superposition of two contributions; the stress resulting from internal sources such as the structural defects, and film stress resulting from the film-substrate mismatch. At this stage the contributions from both sources cannot be separated quantitatively. The radial normal stress due to a vacancy is short range.[8] Therefore, these local point sources of dilatation are not anticipated to contribute significantly to the overall film stress.

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Grain boundaries do not produce long-range stress fields.[8] Thus, the single high angle grain boundary (d) present in the film will not add to the film stress. The stress field around an edge dislocation is long-range[8] and may supply most of the measured field stress.

4. CONCLUSION

A full molecular dynamic simulation of thin-film growth was carried out in which the substrate and film-particle L-J parameters were different. Stress was calculated and found to be tensile. Unfortunately, it was possible to run only one growth simulation, so comparison of stress values in films with various evaporant energies or lattice mismatches was not possible.

Since the energy of the evaporant was on the order of the bond energy, ϵ, in a sense the simulation we performed more nearly simulated the sputtering process than a thermal-evaporation process. This curiosity results from the nature of the Lennard-Jones interaction; the ratio of the "bond" energy ϵ (the L-J well depth) to the melting temperature is much larger for the L-J interaction than for more commonly observed interactions. To simulate thermal evaporation, Müller[9] has used evaporant energies corresponding to temperatures of less than 1/10 of the L-J melting point.

The stress of structures predicted by a hard-disk aggregation simulation was determined using molecular dynamics. The structures were not stable under a Lennard-Jones interaction, and relaxed into a more close-packed structure, even at a temperature as low as 0.01 ϵ/k ($t \simeq 1.2°K$). At temperatures this low, the stress of the structures might as well be made by using only the potential energy term in the virial theorem, neglecting the contribution of the particle velocities.

Every MD relaxation of a hard-disk simulation exhibited tensile stress. The dense polycrystalline film with a network of structural defects of Section 3 and the MD grown film of Section 2 had the greatest stress. These films exhibited similar tensile stress values; both films contained a single misfit dislocation.

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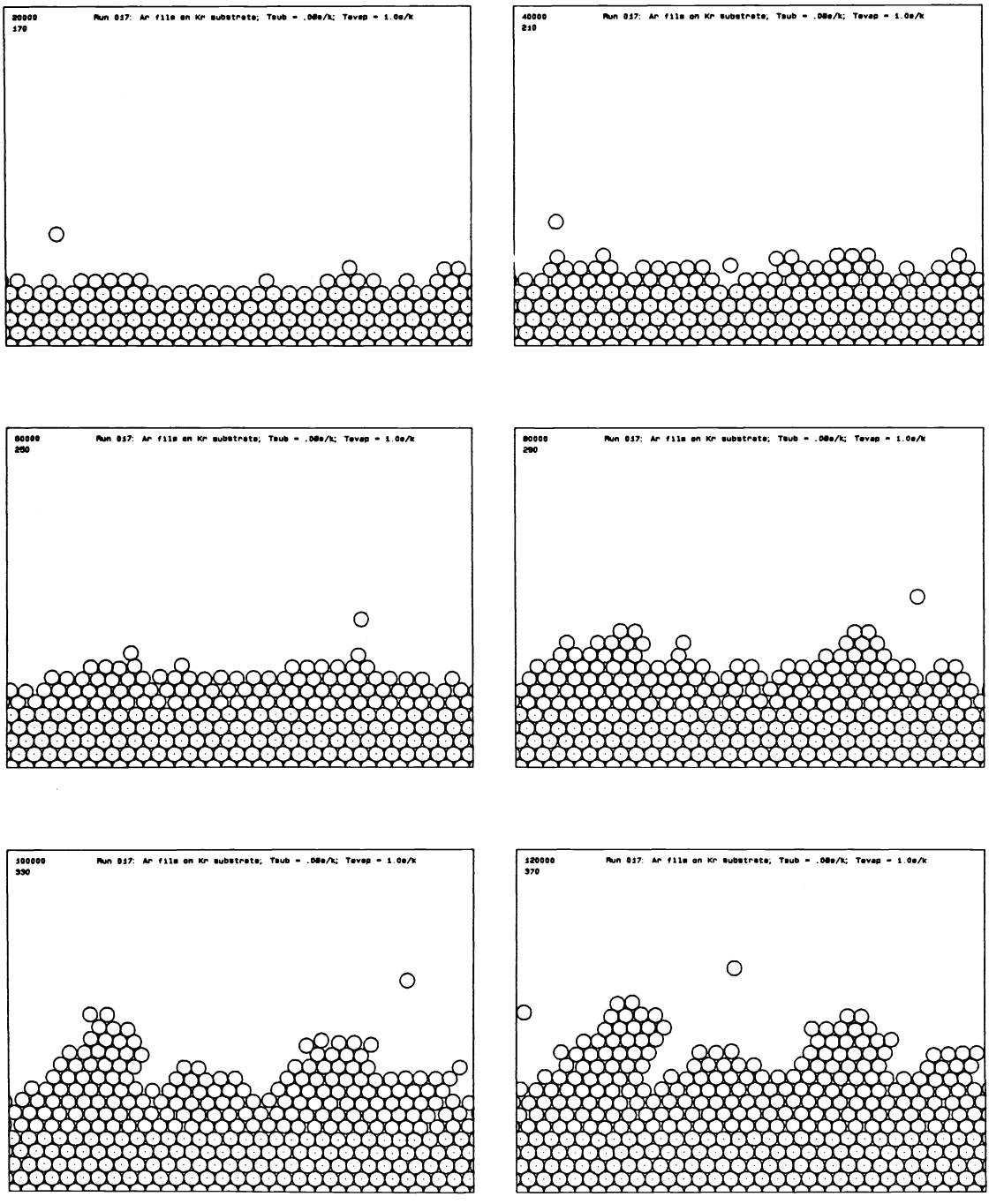

Fig. 1. Sequence of plots of MD simulation of Ar film growth on Kr substrate.

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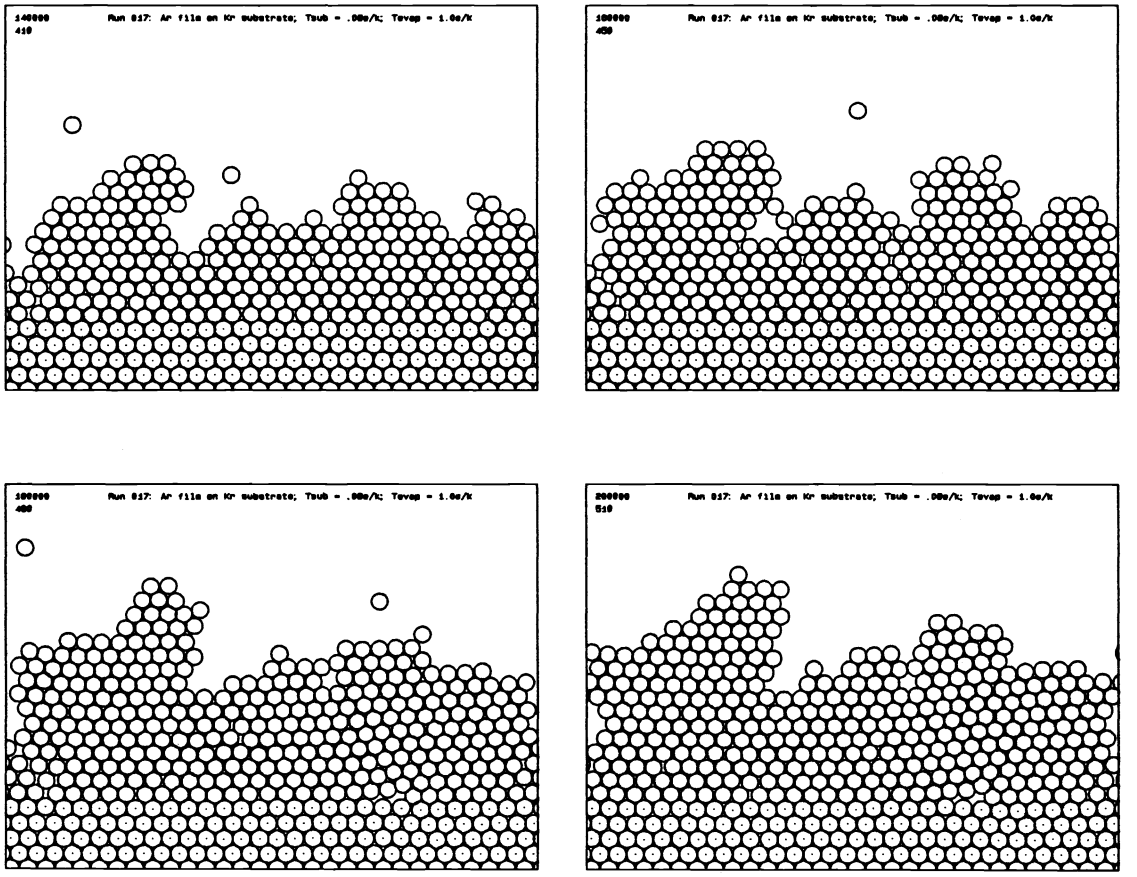

Fig. 1. Sequence of plots of MD simulation of Ar film growth on Kr substrate (continued).

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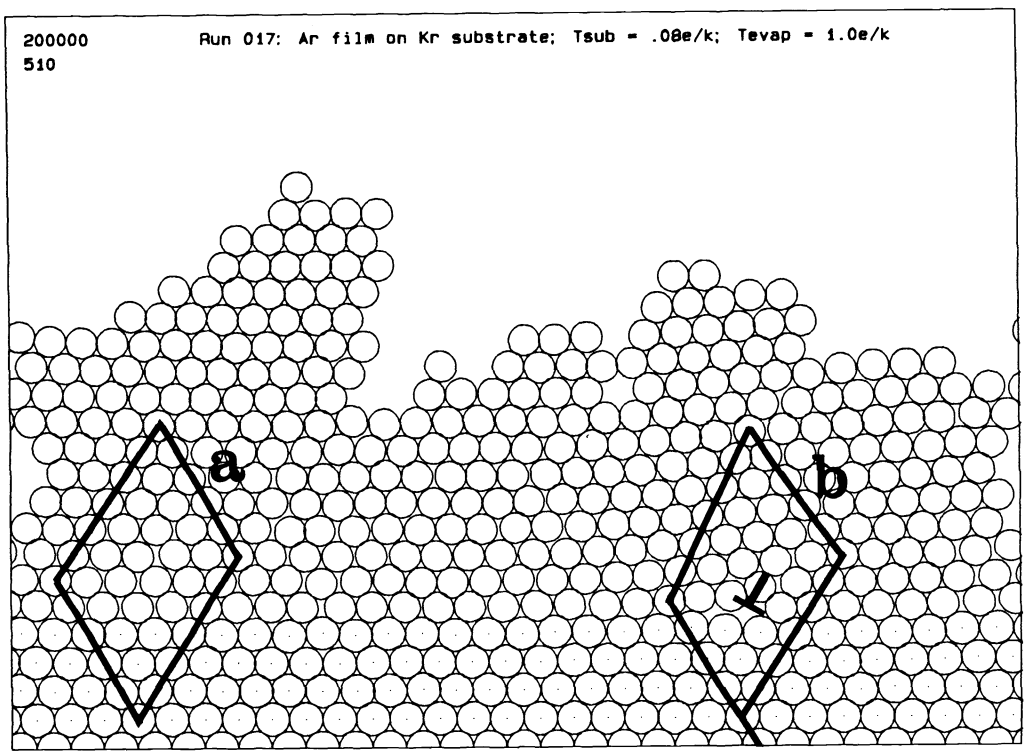

Fig. 2. Final structure of Ar film on Kr substrate. A closed reference Burger's circuit has been drawn in the region "a" showing good match between film and substrate. Another Burger's circuit, "b," which fails to close is drawn around the misfit dislocation (indicated as "⊥"). Note the open nature of the Ar lattice in region "a."

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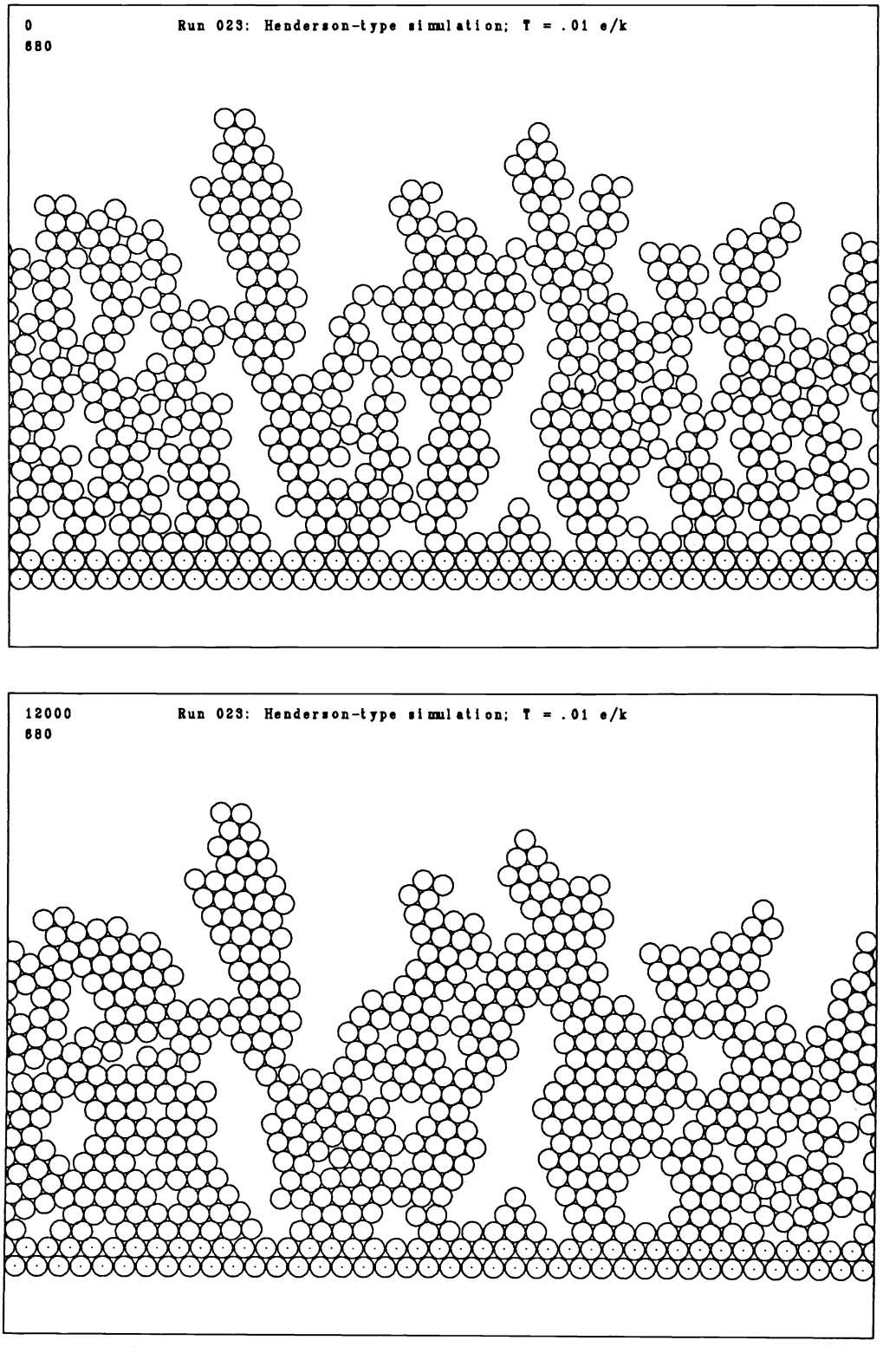

(a)

(b)

Fig. 3. (a) Type 1 columnar film produced by hard-disk model.
(b) The same film after a molecular dynamics relaxation.

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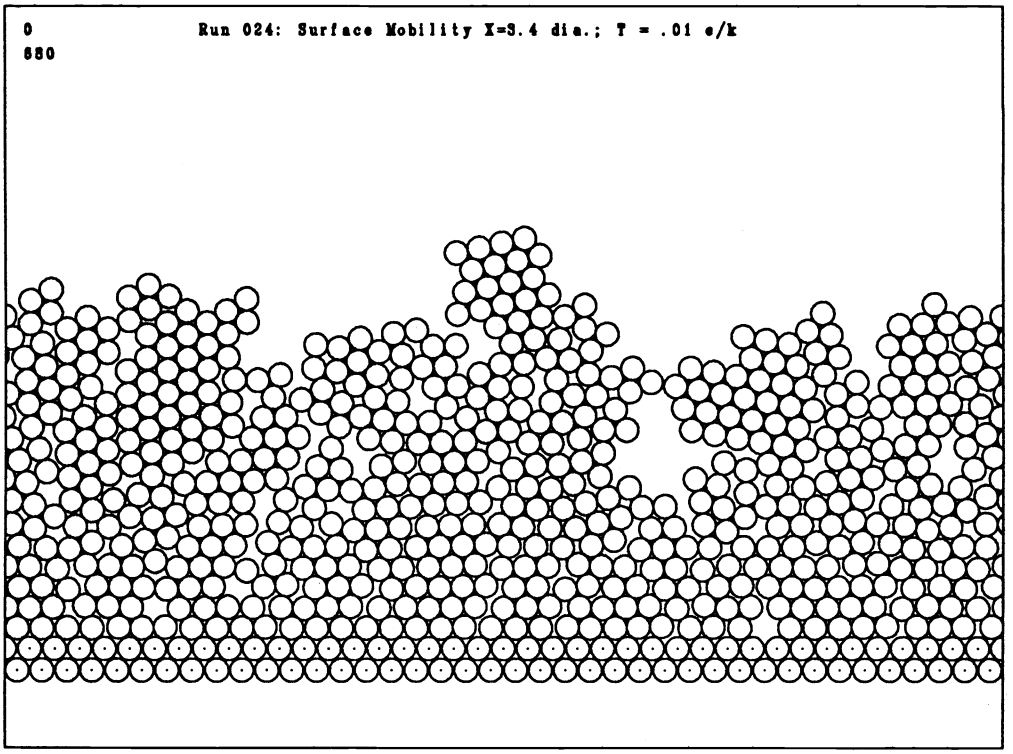
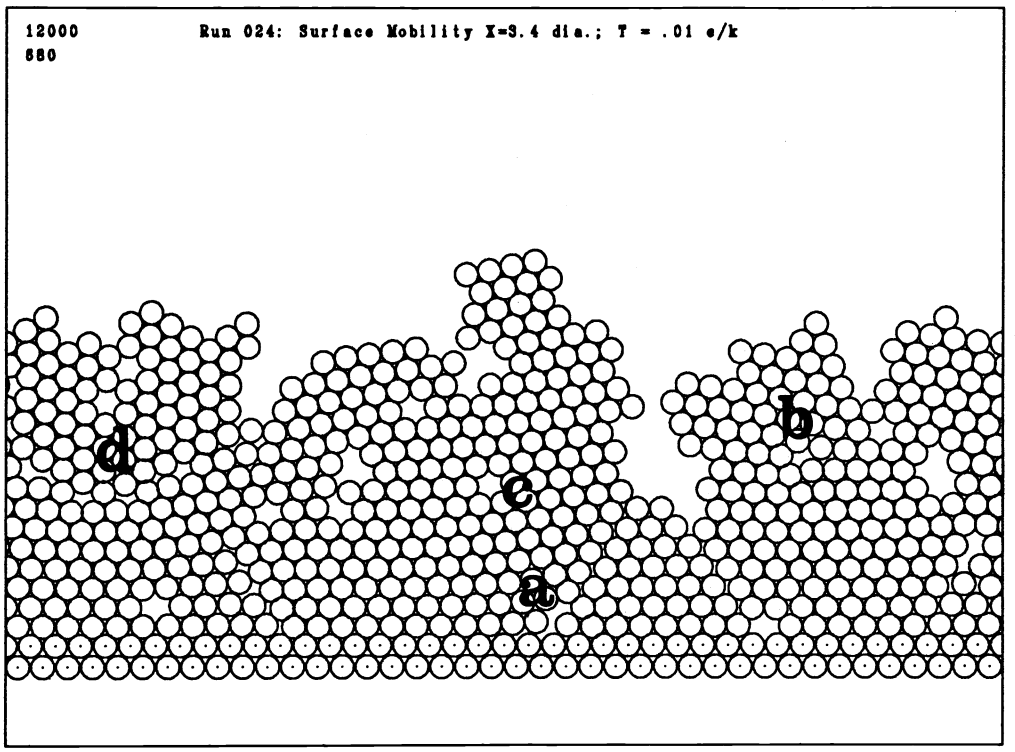


(a)



(b)

Fig. 4. (a) Type 2 dense film obtained by a hard-disk growth model with surface diffusion. (b) The molecular dynamics relaxed structure.

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