

Structure and Dynamics of Very Thin Films*

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Lattice-dynamics and molecular-dynamics studies of very thin free crystalline films have been carried out, and three effects have been studied in detail: The first is a drastic change in the distribution of vibrational frequencies with respect to the distribution for the bulk. The second is an anomalous increase in the mean-square amplitudes of vibration. The third is an instability in three-layer films with (110) surfaces which leads to a structural transformation in such films.

I. INTRODUCTION

IN this paper we report the results of studies of very thin free crystalline films which have been carried out with the methods of lattice dynamics and molecular dynamics. These methods are described in Secs. II and IV, respectively. The static displacements (changes in the interplanar spacings in a film from the interplanar spacings in an infinite three-dimensional crystal), the vibrational frequencies, and the mean-square amplitudes of vibration were calculated for films of various thicknesses with (100), (111), and (110) orientations. In addition, three effects were studied in detail: The first (described in Sec. II) is a drastic difference between the distribution of vibrational frequencies in a very thin film and the distribution in an infinite three-dimensional crystal. This difference is due primarily to the presence of surface modes. The second effect (described in Sec. III) is an anomalous increase in the mean-square amplitudes of vibration which is associated with the divergence of the mean-square amplitudes in infinite two-dimensional crystals and in infinite films. The third effect (described in Sec. IV) is an instability in three-layer films with a (110) orientation at sufficiently high densities. The instability, which was discovered with lattice dynamics, leads to a structural transformation which was studied with molecular dynamics.

There have been a number of theoretical treatments of the vibrations of particles in thin films,¹⁻³ but these treatments were based on rather simple models and the effects with which this paper is concerned were not investigated. Dickey and Paskin,⁴ however, have used molecular-dynamics techniques to study the frequency distribution of very thin slab-shaped particles. They were primarily interested in obtaining certain moments of the frequency distribution which are of importance in the theory of superconducting transition temperatures. We will consider this same matter in the following paper.⁵ These studies were motivated by the recent

experiments of Strongin *et al.*⁶ on superconducting transition temperatures in structures composed of very thin metallic films.

Besides their relevance to such experiments, theoretical studies of the structure and dynamics of films are of interest in connection with experimental investigations of the structure of films through electron diffraction and possible measurements of the Debye-Waller factor through electron diffraction or the Mössbauer effect.

II. STATIC DISPLACEMENTS AND VIBRATIONAL FREQUENCIES

All the calculations in this paper were carried out for films composed of identical particles arranged in an fcc structure and interacting through a Lennard-Jones (LJ) 12-6 potential

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1)$$

Here ϵ and σ are the LJ potential parameters, and r is the distance between the interacting particles. We regard the LJ potential as a model potential suitable for qualitative studies of monatomic materials in general and for quantitative calculations in the case of the noble-gas solids. Electron-diffraction studies of thin films of the noble-gas solids have, in fact, been carried out.^{7,8}

The first step in performing a lattice-dynamics calculation for thin films is to determine the static displacements, which are slightly different from the displacements in a semi-infinite crystal. The main importance of the static displacements is the change they produce in the force constants near the surface. We define the static displacement δ_m to be the fractional change in the distance between the m th and $(m+1)$ th planes (with $m=1$ for a surface plane) with respect to the distance between planes in the bulk.⁹ In calculating

⁶ M. Strongin, O. F. Kammerer, J. E. Crow, R. D. Parks, D. H. Douglass, Jr., and M. A. Jensen, *Phys. Rev. Letters* **21**, 1320 (1968).

⁷ A. E. Curzon and A. T. Pawlowicz, *Proc. Phys. Soc. (London)* **85**, 375 (1965).

⁸ S. I. Kovalenko and N. N. Bagrov, *Fiz. Tverd. Tela* **9**, 3032 (1967) [English transl.: *Soviet Phys.—Solid State* **9**, 2396 (1968)].

⁹ The static displacements are calculated for a static crystal, but in the approximation that the film expands uniformly they are the same for all densities, since they are defined as *fractional* changes in the interplanar spacings (see Ref. 10).

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¹ A. Corciovei, D. Grecu, and E. Radescu, *Z. Physik* **209**, 134 (1968).

² J. Dlouhá, *Czech. J. Phys.* **B16**, 495 (1966).

³ L. S. Kothari, *Phys. Letters* **24A**, 382 (1967).

⁴ J. M. Dickey and A. Paskin, *Phys. Rev. Letters* **21**, 1441 (1968).

⁵ R. E. Allen and F. W. de Wette, following paper, *Phys. Rev.* **187**, 883 (1969).

the displacements, we assume that each plane is displaced as a whole in the direction perpendicular to the surface. The calculation is performed by minimizing the static energy with respect to the δ_m . (The method of calculation is described in detail in Ref. 10.) Physically, this procedure corresponds to allowing the planes to relax until the force on every atom is equal to zero. The results for the static displacements in films of various thicknesses with (100), (111), and (110) surfaces are given in Table I. It can be seen that the displacements rapidly converge to the values in a semi-infinite crystal as the thickness of the film increases.

After the static displacements have been determined, the vibrational frequencies can be calculated, in the quasiharmonic approximation and with periodic boundary conditions taken within the plane, by numerically solving the eigenvalue equation

$$\sum_{l_3', \beta} D_{\alpha\beta}(l_3 l_3'; q) \xi_\beta(l_3'; q p) = \omega_p^2(q) \xi_\alpha(l_3; q p). \quad (2)$$

In this equation, l_3 and l_3' label planes within the film, α and β stand for x , y , and z , q is a wave vector lying in the first two-dimensional Brillouin zone associated with the planes of the film, $D_{\alpha\beta}(l_3 l_3'; q)$ is an element of the dynamical matrix for the film, $\xi_\alpha(l_3; q p)$ is a component of an eigenvector of the dynamical matrix, and $\omega_p(q)$ is a vibrational frequency; p labels the branches of the function $\omega_p(q)$ and takes on the values $1, 2, \dots, 3N_3$, where N_3 is the number of planes in the film. The method for calculating the vibrational frequencies is described in more detail in Ref. 10.

The calculated frequency distribution functions $f(\omega)$ for the bulk and for films with (100), (111), and (110) surfaces are shown in Fig. 1. The calculation was performed for a density given by $\sigma/a = 1.29724$ (density of a static crystal), where $\sqrt{2}$ is the nearest-neighbor distance. The particle mass is represented by M . The films with (100) and (111) surfaces are three layers thick, and the film with (110) surfaces is five layers thick. In the case of a three-layer film with (110) surfaces, some of the calculated frequencies are imaginary, indicating that such a film is unstable. This matter will be considered in more detail in Sec. IV.

It can be seen in Fig. 1 that the frequency distributions for the films differ greatly from the distribution for the bulk. The primary difference is that, in addition to the usual peaks associated with transverse and longitudinal modes, there is a third peak at $(M\sigma^2/\epsilon)^{1/2}\omega \approx 10$ which is associated with surface modes. The presence of these surface modes causes a large decrease in the average frequency and the higher moments of the frequency distribution, and this decrease is made even larger by a general shift toward lower frequencies on the part of the other modes. In metals this decrease in the frequencies should cause an increase in the strength of the electron-phonon interaction. In superconductors it is believed to cause large increases in the superconducting transition temperature.⁴⁻⁶

¹⁰ R. E. Allen and F. W. de Wette, Phys. Rev. **179**, 873 (1969).

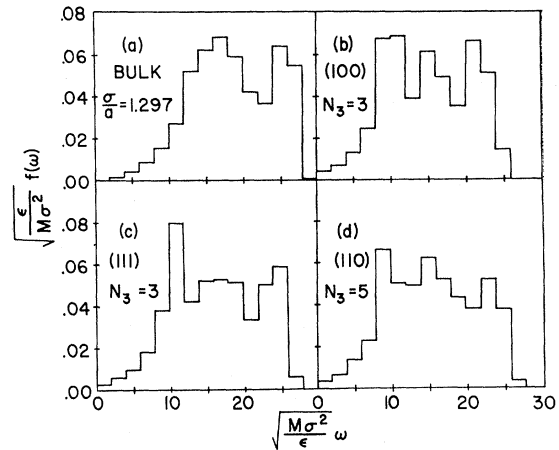


FIG. 1. Frequency distribution at density given by $\sigma/a = 1.29724$ for (a) infinite three-dimensional crystal, (b) three-layer film with (100) surfaces, (c) three-layer film with (111) surfaces and (d) five-layer film with (110) surfaces.

III. MEAN-SQUARE AMPLITUDES OF VIBRATION

The mean-square amplitudes of vibration in films are of interest because they determine the Debye-Waller factor, which can be measured in electron-diffraction experiments.¹¹ We represent the displacement of a particle from its mean position by \mathbf{u} and indicate a thermal average by $\langle \rangle$, so that the mean-square amplitude of vibration in the α direction is $\langle u_\alpha^2 \rangle$, with $\alpha = x, y, \text{ or } z$. In the quasiharmonic approximation, the mean-square amplitudes can be expressed in terms of the eigenvalues and eigenvectors of the dynamical matrix¹⁰:

$$\langle u_\alpha^2(l_3) \rangle = \frac{\hbar}{2NM} \sum_{q,p} |\xi_\alpha(l_3; q p)|^2 \times \frac{\coth[\hbar\omega_p(q)/2k_B T]}{\omega_p(q)}. \quad (3)$$

In Eq. (3), l_3 specifies the plane in which the vibrating

TABLE I. Static displacements δ_m in films N_3 layers thick with (100), (111), and (110) surfaces.

N_3	m	(100)	(111)	(110)
3	1	0.02910	0.01365	0.05832
5	1	0.02610	0.01223	0.03560
	2	0.00703	0.00303	0.01204
7	1	0.02585	0.01210	0.03677
	2	0.00611	0.00258	0.00518
	3	0.00250	0.00107	0.00683
9	1	0.02580	0.01208	0.03676
	2	0.00595	0.00251	0.00532
	3	0.00213	0.00089	0.00438
	4	0.00113	0.00048	0.00248
∞	1	0.02578	0.01207	0.03672
	2	0.00589	0.00248	0.00522
	3	0.00198	0.00081	0.00438
	4	0.00085	0.00035	0.00107

¹¹ See, e.g., A. U. MacRae, Surface Sci. **2**, 522 (1964).

TABLE II. Mean-square amplitudes $\langle u_\alpha^2 \rangle$ and mean-square velocities $\langle v_\alpha^2 \rangle$ at $T=0^\circ\text{K}$ for three-layer films with (100) and (111) surfaces. The ratios of the mean-square amplitudes to the temperature in the high-temperature limit are also given. The density is given by $\sigma/a=1.28$.

	m	$\frac{(M\epsilon)^{1/2}}{\hbar\sigma}\langle u_x^2 \rangle$	$\frac{(M\epsilon)^{1/2}}{\hbar\sigma}\langle u_z^2 \rangle$	$\frac{M^{3/2}\sigma}{\hbar\epsilon^{1/2}}\langle v_x^2 \rangle$	$\frac{M^{3/2}\sigma}{\hbar\epsilon^{1/2}}\langle v_z^2 \rangle$	$\frac{\epsilon}{k_B\sigma^2} \frac{\langle u_x^2 \rangle}{T}$	$\frac{\epsilon}{k_B\sigma^2} \frac{\langle u_z^2 \rangle}{T}$
(100)	1	0.0468	0.0611	6.70	5.03	0.0148	0.0338
	2	0.0403	0.0467	7.64	7.36	0.0117	0.0294
(111)	1	0.0382	0.0597	7.64	5.16	0.0082	0.0278
	2	0.0359	0.0459	8.07	7.53	0.0071	0.0233
Bulk		0.0344	0.0344	8.24	8.24	0.0060	0.0060

atom is located, $\alpha=x, y, \text{ or } z$, N is the number of atoms per plane (or the number of sample points used in the summation over q), k_B is the Boltzmann constant, and T is the temperature. The prime indicates that the three $\omega=0$ modes are to be omitted from the summation. Once Eq. (2) has been solved, the calculation of the mean-square amplitudes with Eq. (3) is straightforward.

In Table II the calculated mean-square amplitudes $\langle u_\alpha^2 \rangle$ at absolute zero and in the high-temperature limit are given for two three-layer films at a density corresponding to $\sigma/a=1.28$ (density of argon at absolute zero). The integer m labels the plane; $m=1$ for a surface plane and $m=2$ for the center plane. The film with (100) surfaces has 800 particles per plane, and the film with (111) surfaces has 625 particles per plane, with periodic boundary conditions taken within the planes. The mean-square velocities, which can be calculated with an equation similar to Eq. (3),¹⁰ are also given for these films at absolute zero.

The main features of the mean-square amplitudes and mean-square velocities, which can be observed in Table II, are well known and easily understood: Near a surface, particles vibrate more freely than they do in the bulk, so that the mean-square amplitudes of

vibration are larger and the mean-square velocities are smaller. The presence of the surface produces an anisotropy in the vibrations, so that $\langle u_x^2 \rangle \neq \langle u_z^2 \rangle$ and $\langle v_x^2 \rangle \neq \langle v_z^2 \rangle$. In the high-temperature limit, $\langle v_\alpha^2 \rangle$ is the same at a surface as in the bulk. However, the ratio $\langle u_\alpha^2 \rangle_{\text{surface}} / \langle u_\alpha^2 \rangle_{\text{bulk}}$ increases with temperature. This last feature is explained in Ref. 10.

It is well known that the mean-square amplitudes in a free film of infinite extent, like those in an infinite two-dimensional crystal, diverge at nonzero temperatures.¹² Although the divergence is rather slow (logarithmic), it can have a sizable effect in films of sufficiently small thickness. In Fig. 2 the mean-square amplitudes in the high-temperature limit for a film three layers thick with (100) surfaces are plotted as functions of the periodicity length $N_1 a$. (The number of particles per plane is $\frac{1}{2} N_1^2$.) It can be seen that the in-plane component $\langle u_x^2 \rangle$ and the normal component $\langle u_z^2 \rangle$ both increase logarithmically with N_1 for $N_1 \gtrsim 30$, but that the normal component increases much more rapidly. In Fig. 3 the mean-square amplitudes for a fixed periodicity length are plotted as functions of the thickness $N_3 a$. It can be seen that $\langle u_\alpha^2 \rangle$ decreases as N_3 increases and asymptotically reaches a fixed value.

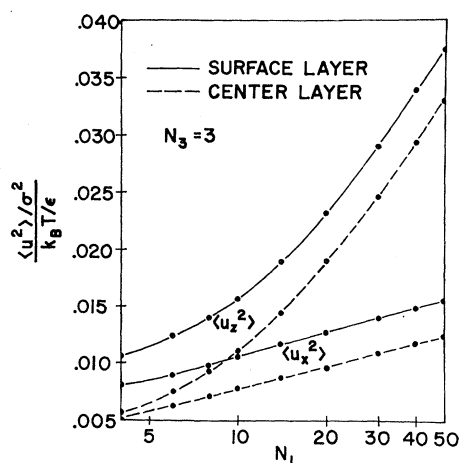


FIG. 2. Mean-square amplitudes $\langle u_\alpha^2 \rangle$ in high-temperature limit for three-layer film with (100) surfaces plotted as functions of the periodicity length $N_1 a$. $\langle u_x^2 \rangle$ corresponds to vibrations parallel to the surface plane and $\langle u_z^2 \rangle$ corresponds to vibrations perpendicular to the plane. N_1 is plotted on a logarithmic scale. The density is given by $\sigma/a=1.28$.

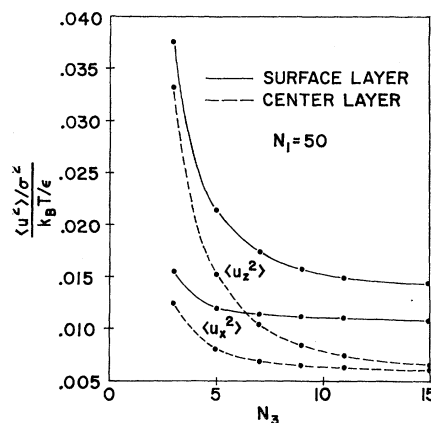


FIG. 3. Mean-square amplitudes $\langle u_\alpha^2 \rangle$ in high-temperature limit for film with (100) surfaces plotted as functions of the thickness $N_3 a$. The periodicity length is given by $N_1=50$ and the density by $\sigma/a=1.28$.

¹² See, e.g., Refs. 2 and 10. This fact was first pointed out to us by Dr. B. J. Alder (private communication).

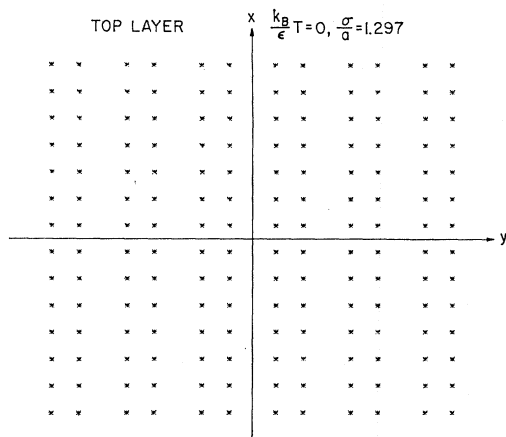


FIG. 4. Top view of uppermost plane of particles in three-layer film with (110) surfaces after structural transformation.

On the basis of the results shown in Figs. 2 and 3, we can make the following statements: (1) The mean-square amplitudes of vibration in a free film are larger than those in the bulk (or in the equivalent plane near the surface of a semi-infinite crystal). (2) For fixed thickness, as the size of the film increases, the mean-square amplitudes increase logarithmically. (3) As the thickness of the film increases (for a fixed number of particles per plane), the mean-square amplitudes decrease. (4) All of these effects are particularly pronounced for vibrations perpendicular to the surface. These effects can be understood by visualizing the film as a membrane which vibrates more freely, particularly in the z direction, as its width and breadth are increased, but becomes stiffer and vibrates less freely as its thickness is increased.

IV. STRUCTURAL STABILITY

In Sec. II it was mentioned that when a lattice-dynamics calculation was performed for a three-layer film with a (110) surface at a density given by $\sigma/a = 1.29724$, some of the frequencies were found to be imaginary, indicating that such a film is unstable.¹³ Further calculations showed that no imaginary frequencies are obtained for a five-layer film at this same density or for a three-layer film with densities given by $\sigma/a \leq 1.25$; imaginary frequencies were obtained, however, for $\sigma/a \geq 1.26$. (For the noble gases, σ/a ranges from about 1.29 for Xe at absolute zero to about 1.22 for Ne at the melting temperature.) The lattice-dynamics calculations indicate, therefore, that very thin films with (100) and (111) surfaces are stable even down to a thickness of three layers, but that a three-layer film with (110) surfaces is unstable at sufficiently high densities ($\sigma/a \geq 1.26$).

¹³ The film is in an equilibrium configuration, in that the force on every atom is zero, but the equilibrium is unstable. A direct calculation of the potential energy before and after the structural transformation described in this section shows that the energy is in fact decreased by the transformation.

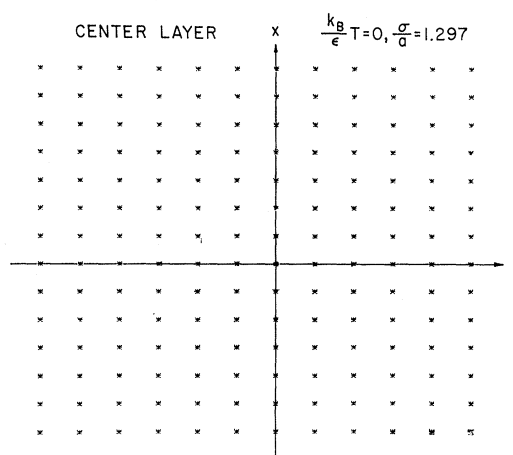


FIG. 5. Top view of center plane of particles after structural transformation. The particles have not been displaced within the plane, so that the top views before and after the transformation are identical.

In order to investigate this instability, we first examined the eigenvectors associated with the imaginary frequencies. It was found that these frequencies correspond to a mode in which the particles in the middle layer are displaced entirely in the z direction (perpendicular to the surface), whereas those in the top and bottom layers are displaced in both the y and z directions.¹⁴

Next we performed a molecular-dynamics computer experiment, using a method which has been described elsewhere.¹⁵ The experiment was performed for 504 particles placed in a three-layer film with an fcc structure and (110) surfaces at a density corresponding

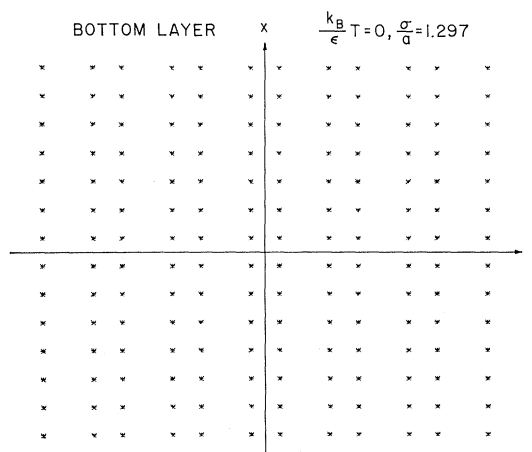


FIG. 6. Top view of lowermost plane of particles after structural transformation.

¹⁴ The x , y , and z axes are taken to point in the [110], [001], and [110] directions, respectively, as shown in Figs. 4 and 7.

¹⁵ R. E. Allen, F. W. de Wette, and A. Rahman, *Phys. Rev.* **179**, 887 (1969). The "background force" described in this paper was omitted in the present calculations, which are for very thin films rather than semi-infinite crystals.

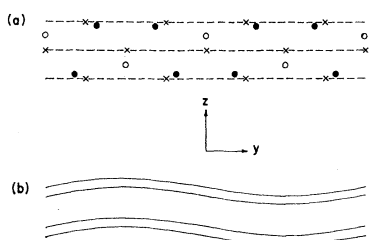


FIG. 7. (a) Schematic side view of film after structural transformation. The positions of the particles before the transformation are indicated by x 's; the positions after the transformation are indicated by solid circles for particles in the outer layers and open circles for particles originally in the center layer. The small "ripple" mentioned in the text is not shown. (b) Schematic side view after transformation, showing the ripple, whose size is exaggerated. The four layers in the film after the transformation (top layer, bottom layer, particles in center layer displaced upward, particles in center layer displaced downward) are represented by the solid lines.

to $\sigma/a=1.29724$. The particles were displaced slightly from their positions in a perfect lattice and then were permitted to move in accordance with classical equations of motion. A damping force proportional to the velocities was imposed to keep the system at a very low temperature. The equation of motion of a particle with damping included is

$$\frac{d^2 \mathbf{s}^l}{d\tau^2} = 24 \sum_{l' \neq l} \left(\frac{1}{s^{ll'}} \right)^8 \left[2 \left(\frac{1}{s^{ll'}} \right)^6 - 1 \right] \mathbf{s}^{ll'} - \gamma \frac{d\mathbf{s}^l}{d\tau}, \quad (4)$$

where γ is the dimensionless damping constant and τ is the dimensionless time defined by

$$\tau = (\epsilon/M\sigma^2)^{1/2} t; \quad (5)$$

$\mathbf{s}^l = \mathbf{r}^l/\sigma$, where \mathbf{r}^l is the position vector of the particle labeled by l , $\mathbf{s}^{ll'} = \mathbf{s}^l - \mathbf{s}^{l'}$, and $s^{ll'} = |\mathbf{s}^{ll'}|$.

When the particles were allowed to move, the system underwent just the kind of structural transformation

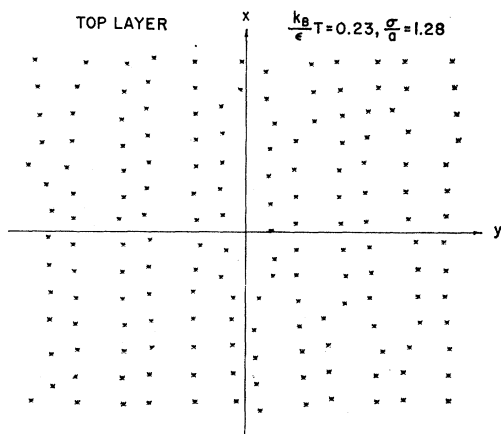


FIG. 8. Top view of uppermost plane of particles after structural transformation at a nonzero temperature ($k_B T/\epsilon=0.23$, or about one-third the melting temperature).

expected on the basis of the lattice-dynamics results; i.e., all the particles were displaced perpendicular to the surface, and those in the outer layers were also displaced parallel to the surface in the y direction. The structure of the film after the transformation is shown in Figs. 4-7.

The transformation involves the coherent displacements of rows of particles (a row being a group of particles lying along a straight line parallel to the x axis); i.e., all the particles in a given row are displaced together. The main features of the transformation are the following: (1) The rows of particles in the center layer are displaced alternately up and down (by an amount equal to 54.6% of the original interplanar spacing of $a/\sqrt{2}$). (2) The rows of particles in the outer layers are displaced alternately to the right and to the left (by an amount equal to 13.5% of the original spacing of $2a$ between rows) in order to "make room" for the particles in the center layer. (3) The particles in the outer layers relax toward the center of the crystal (by an amount equal to 13.4% of the original interplanar spacing). (4) Superimposed upon the larger displacements there is a "ripple" extending throughout the film [see Fig. 7(b)]. This ripple has a wavelength equal to the periodicity length of the crystal and an amplitude equal to about 2% of the original interplanar spacing.

In Fig. 8 the structure of the top layer¹⁶ is shown for another three-layer film with a lower density ($\sigma/a=1.28$) and a higher temperature (about one-third the melting temperature). In this case, the thermal motion of the particles caused the new structure to be imperfect: Some of the particles in a given row were displaced one way and some the other.

The fact that films with (100) and (111) surfaces do not undergo a change of structure can be attributed to the fact that in a (100) or (111) plane a particle is surrounded by four or six nearest neighbors which restrain it from movements within the plane. In a (110) plane, however, this is not the case: A particle has only two nearest neighbors in the plane and is not restrained by particles within its own plane from undergoing displacements in the y direction. It is restrained by particles in the plane below it, but these particles can move aside in correlated displacements, and this is just what happens in the structural transformation described above [see Fig. 7(a)]. It should be mentioned that the periodic boundary conditions undoubtedly play a role in this transformation, in that they constrain the system so that the number of particles per unit length is fixed in the x and the y directions.

¹⁶ The structure shown in Fig. 8 is not stable, of course, and as time passes the system gradually becomes more disordered. The positions of the particles in Fig. 8 are mean positions obtained by averaging over a time $t \sim 10^{-12}$ sec (100 time steps of $\Delta\tau=0.01$ each), whereas those shown in Figs. 4-6 are equilibrium positions in a static crystal.