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A family of herringbone patterns in thin films

Xi Chen [a,*], John W. Hutchinson [b]

[a] Department of Civil Engineering and Engineering Mechanics, Columbia University, 500 West 120th Street, New York, NY 10027, USA
[b] Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA

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Abstract

Upon cooling, a thin metal film deposited on compliant elastomer substrate undergoes equi-biaxial compression and begins to buckle at a critical stress. As further cooling occurs, a highly ordered herringbone pattern self-assembles. The preference for the herringbone pattern over other potential modes is demonstrated based on minimum energy arguments. Control of the pre-buckling in-plane stress components may be one way to influence the pattern formation, possibly giving rise to a family of unbalanced herringbone modes that links one-dimensional modes with the balanced herringbone mode.
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1. Introduction

Self-assembly involving thin films has important applications in microfabrication. Recent studies [1,2] have shown that a thin film on an elastomer substrate can form highly ordered patterns with distinctive features simply by elastic buckling. If such mechanical means can be exploited for pattern formation, they may provide useful alternatives to chemical routes to self-assembly.

Due to the large thermal expansion mismatch, a thin metal film vapor deposited on a thick compliant elastomer substrate undergoes equi-biaxial compression when the system is cooled. The film buckles into periodic structures with distinctive features when the temperature variance exceeds a critical number. The buckling patterns can be manipulated by creating non-planar substrate topography prior to deposition [1,2]. In this case, the self-assembled structure in thin film conforms to the pre-buckling stress pattern induced by the underlying substrate profile. An intriguing phenomenon happens when the substrate is not pre-patterned. As shown in Fig. 1, for a system where a 50 nm Au film is vapor deposited on a flat thick PDMS substrate, the highly ordered *herringbone mode* arises when the temperature is lowered well below the temperature at the onset of buckling [1,2]. Here, the crest-to-crest separation, or the buckle wavelength is about 30 μm, and the distance between jogs in the herringbone mode is about 100 μm. The change in direction of the crest at each jog is approximately 90°. The amplitude of the waves is on the order of one micron when the temperature drop is 100 °C. Thus, although the amplitude is large compared to the film thickness, the mode is shallow in the sense that the slopes of the pattern are small. The herringbone buckle pattern diminishes when the temperature is re-elevated to the deposition temperature and the film remains attached with the substrate. This indicates that the phenomenon is elastic with no delamination. The strains associated with the buckling mode are also small, and both the film and the substrate materials are within their respective linear elastic ranges.

When the substrate is initially flat, the herringbone buckle pattern appears to be the preferred buckling mode when the system has been cooled well below the onset of buckling. It is very different from any mode obtained from the classical linear bifurcation analysis discussed below. The emergence of the herringbone mode is due to the highly non-linear nature of the system as the temperature drops well below critical. Compared with other competing classical buckling modes, such as the *one-dimensional mode* and the *checkerboard mode* sketched in Fig. 1, the herringbone mode has the

* Corresponding author. Tel.: +1-212-854-3787; fax: +1-212-854-6267.
E-mail address: xichen@civil.columbia.edu (X. Chen).

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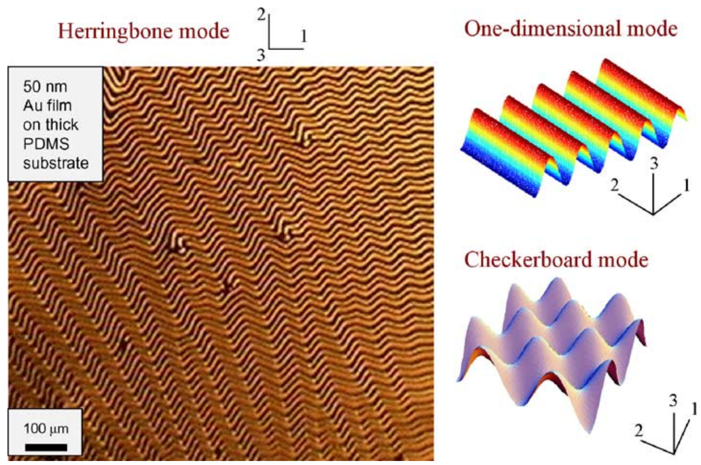

Fig. 1. On the left, the herringbone buckling pattern of a 50 nm gold film on a thick flat elastomer (PDMS) substrate [1,2]. The wavelength of the pattern across the crests is approximately 30 μm while the distance between jogs of the herringbone mode is approximately 100 μm. On the right, the sketch of the competing one-dimensional and checkerboard buckling modes.

ability to reduce the overall in-plane stress in the film in all directions *and* its near-inextensionality induces only very little stretching energy. Apart from the immediate vicinity of the jogs, the mode has zero Gaussian curvature and thus avoids the high energy cost of stretching in a thin film. As will be shown later, these two characteristics ensure the herringbone mode to be the minimum energy configuration among its competitors (cf. Fig. 1). Most of the analysis leading to the results in this paper is taken from an earlier paper [3]. The present paper emphasizes features that might be used to provide some control of the pattern assembly process and provides speculation as to an entire family of unbalanced herringbone modes that provide a continuous transition from one-dimensional modes to the regular herring bone mode seen in Fig. 1.

The Young's modulus, Poisson's ratio and coefficient of thermal expansion of the film are denoted by E, v, and α, respectively. The corresponding substrate properties are E_s, v_s and α_s. All numerical results in this study are presented for Au film deposited on PDMS substrate, where $v = 1/3$, $v_s = 0.48$, $\alpha/\alpha_s = 1/20$ and $\overline{E}_s/\overline{E} = 4100$ with $\overline{E} = E/(1-v^2)$ and $\overline{E}_s = E_s/(1-v_s^2)$. The film thickness is t. The substrate is taken to be infinitely thick.

2. Linearized stability analysis of a compressed film on an elastic substrate

We begin by considering the case where the pre-buckling stress is not equi-biaxial. Suppose the pre-stress in the x_1-direction is $-\sigma_{11}^0$ and that in the x_2-direction is $-\sigma_{22}^0$ with $\sigma_{12}^0 = 0$. For an isotropic film on an isotropic substrate subject to a temperature drop ΔT, the pre-buckling stress state is equi-biaxial compression with

$$\sigma_{11}^0 = \sigma_{22}^0 \equiv \sigma_0 = [E/(1-v)]\Delta\alpha\Delta T \tag{1}$$

where $\Delta\alpha = \alpha_s - \alpha$. However, if the substrate is constrained in one-direction and not the other or if the film/substrate system is bent about one-direction, σ_{11}^0 and σ_{22}^0 may differ. The film is represented as an infinite elastic thin plate satisfying von Karman plate theory [4]. When linearized about the uniform pre-buckling state, the classical buckling equation is

$$D\nabla^4 w + \sigma_{11}^0 w_{,11} + \sigma_{22}^0 w_{,22} = -p \tag{2}$$

Here, ∇^4 is the bi-harmonic operator, $D = Et^3/[12(1-v^2)]$ is the bending stiffness of the plate, w is its displacement perpendicular to the plane, (x_1, x_2), p is the stress component acting perpendicular to the plate exerted on it by the deformed substrate. If the tangential traction exerted by the substrate is ignored, (1) admits doubly-periodic solutions of the form

$$w = \hat{w}\cos(k_1 x_1)\cos(k_2 x_2),$$
$$p = \hat{p}\cos(k_1 x_1)\cos(k_2 x_2) \tag{3}$$

where from a three-dimensional elasticity analysis of the substrate, $\hat{w} = 2\hat{p}/(\overline{E}_s k)$ with $k = \sqrt{k_1^2 + k_2^2}$ and $\overline{E}_s = E_s/(1-v_s^2)$. A solution where one of the wave numbers, k_1 or k_2, is zero is called a one-dimensional mode and the case where $k_1 = k_2$ is called the checkerboard mode. The eigenvalue equation, $\sigma_{11}^0 k_1^2 + \sigma_{22}^0 k_2^2 = Dk^4 + \overline{E}_s k/2$, governs the critical stress and critical wave numbers.

If the two pre-buckling stress components are unequal then it is readily shown that the eigenvalue equation predicts a critical mode that is always one-dimensional with crests lying perpendicular to the direction of maximum compression. For example, if $\sigma_{11}^0 > \sigma_{22}^0$, then the critical mode for the onset of buckling has

$$\sigma_{11}^0 = \sigma_0^{\mathrm{C}} \equiv \frac{\overline{E}}{4}\left(3\frac{\overline{E}_{\mathrm{s}}}{\overline{E}}\right)^{2/3} \quad \text{and}$$

$$k_1 t = k^{\mathrm{C}} t \equiv \left(3\frac{\overline{E}_{\mathrm{s}}}{\overline{E}}\right)^{1/3} \quad (k_2 = 0) \tag{4}$$

This is the well-known wrinkling mode for buckling of a thin film or plate on a compliant substrate [5].

It is less known that an entire family of critical modes is possible when the pre-buckling stress equi-biaxial [3]. The critical stress is still given by (4), but now any mode whose wave numbers satisfy $\sqrt{k_1^2 + k_2^2}t = k^{\mathrm{C}}t = (3\overline{E}_{\mathrm{s}}/\overline{E})^{1/3}$ is possible. This family includes the one-dimensional mode (in any direction) and the checkerboard mode ($k_1 = k_2 = k^{\mathrm{C}}/\sqrt{2}$). Other mode forms result from combinations of the critical modes, although the herringbone mode is not one of them. An example that can be formed by a combination of critical modes is a mode with three-fold symmetry whose nodal lines coincide with a pattern of regular hexagons covering the plane.

3. Non-linear post-buckling energy for equi-biaxial compression

In this section we consider the case of equi-biaxial compressive pre-stresses. The herringbone mode is not critical at the onset of buckling. To gain insight into its preferred existence as the system is cooled well below the onset, we have computed the energy of the film/substrate system for this mode and compared it with the energy for two competing modes; the one-dimensional mode and the checkerboard mode. The full non-linear problem for the one-dimensional mode can be solved in closed form, but solution of the other two modes requires a three-dimensional finite element analysis [3,6]. In each of these two cases, the basic periodic cell of the mode is identified and meshed. Within the cell, the film is represented by 1000 three-dimensional eight-node, quadratic thin shell elements (with 5° of freedom at each node and with reduced integration) that account for finite rotations of the middle surface. The stresses and strains within the plate are linearly related. The substrate is meshed with 20-node quadratic block elements with reduced integration. The constitutive relation of the substrate is also taken to be linear isotropic elasticity, but the geometry is updated. Non-linear strain-displacement behavior of the substrate has essentially no influence on the results of interest. The substrate is taken to be very deep (depth d) compared to mode wavelength, and the boundary conditions along its bottom surface are zero normal displacement and zero tangential tractions. The calculations are carried out within the framework of quasi-static deformation and kinetic effects in the polymer substrate are ignored. In the case of

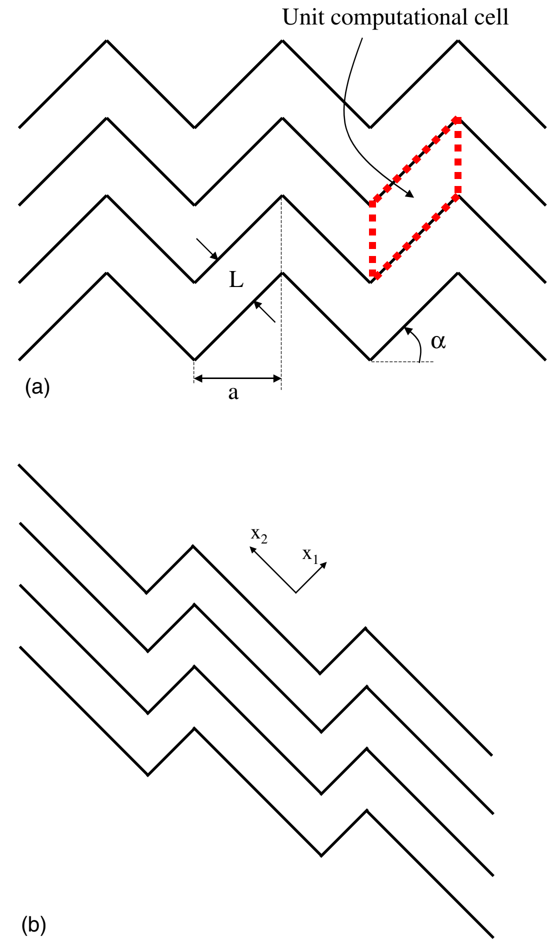

Fig. 2. (a) Periodic cell of the regular herringbone mode (or the transitional herringbone mode with $\alpha < 45°$ and the direction of maximum compression in the vertical direction). (b) A schematic view of the unbalanced herringbone mode.

the herringbone mode (Fig. 2a), the parameters of the cell geometry were treated as variables, i.e. L/t, the cell aspect ratio (a/L) and the angle between crests at the jog, α. The energy in the buckled state was computed as a function of these variables and the minimum was determined.

The energy per unit area of the system in the unbuckled state is $U_0 = (1-\nu)\sigma_0^2 t/E$. For the one-dimensional mode the energy per unit area in the buckled state, U, is given by

$$\frac{U}{U_0} = \frac{1+\nu}{2}\left[\left(\frac{\sigma_0^{\mathrm{C}}}{\sigma_0}\right)^2 + \frac{(1-\nu)}{(1+\nu)}\right] + (1-\nu)\frac{\sigma_0^{\mathrm{C}}}{\sigma_0}\left(1 - \frac{\sigma_0^{\mathrm{C}}}{\sigma_0}\right) \tag{5}$$

with amplitude $\hat{w}/t = \sqrt{\sigma_0/\sigma_0^{\mathrm{C}} - 1}$. These results apply to the critical wave number ($k_1 = k^{\mathrm{C}}, k_2 = 0$), but the energy for one-dimensional modes is minimum, or nearly minimum, at this wave number even at temperatures well below the onset of buckling. The normalized

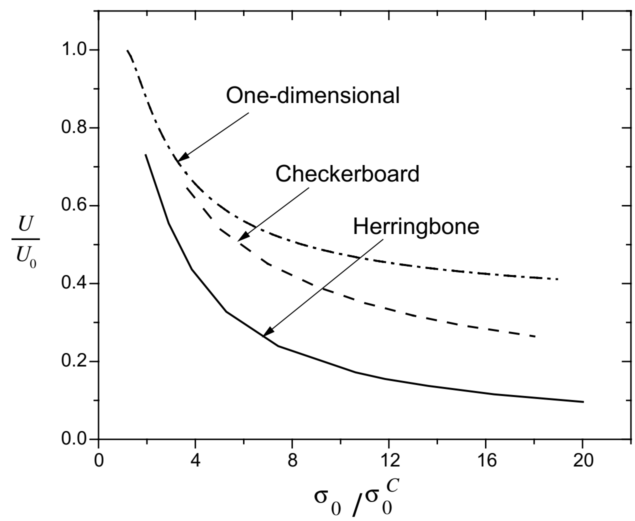

Fig. 3. Ratio of average elastic energy per unit area in the film/substrate system in the buckled state to that in the unbuckled state, U/U_0, as a function of σ_0/σ_0^C for the three modes considered. The wavelengths correspond to the critical at the onset of buckling. For the herringbone mode, $a = 2L$ and $\alpha = 45°$.

energy is shown in Fig. 3. Also plotted in Fig. 3 is the computed normalized energy for the checkerboard mode and the herringbone mode. For the checkerboard mode, the wave numbers determining the periodicity are those of the onset mode in the previous section. For the herringbone mode, the distance between crests leading to minimum energy is essentially identical to that found for the one-dimensional mode. The minimum is only weakly dependent on a/L-the results shown in Fig. 2 were computed with $a/L = 2$ but almost identical results are obtained for a/L in range from about 1.5 to 4. The minimum is attained for jogs that are at right angles and the results in Fig. 3 were computed with $\alpha = 45°$.

The results of Fig. 3 show that at σ_0/σ_0^C well above unity, the energy of the herringbone mode is distinctly lower than that of the other two modes. The reason for this, as mentioned in the introduction, is the herringbone mode is the only one of the three modes that relaxes the in-plane stress in all directions without incurring significant stretch energy. Only in the immediate vicinity of the jogs is significant stretch induced. The one-dimensional mode lowers the pre-stress only in one-direction. The checkerboard mode lowers the stress in all directions, but it produces significant stretch energy accompanying the bending. Similarly, a mode with nodal lines coincident with a hexagon pattern covering the plane would relax stress in all directions but would also induce significant stretching. The features of the herringbone pattern seen in Fig. 1 are in accord with the parameters of the theoretical herringbone mode associated with the minimum energy. The jog angle is approximately a right angle, and the variation in distance between jogs seen in Fig. 1 is consistent with the fact that the energy depends only weakly on this distance over a fairly large range.

4. Factors controlling self-assembly of herringbone patterns

The process by which the herringbone pattern forms as the system is cooled below the critical temperature has not been observed—the pattern seen in Fig. 1 is observed under the microscope when the specimen is at room temperature [1,2]. As discussed above, the herringbone mode is not expected to emerge at temperatures just below critical since it is not among the bifurcation buckling modes of the classical theory. One suspects that it slowly emerges from some combination of the classical modes as the temperature is lowered. Does it form spontaneously across wide regions of the film, or does it form locally, at an edge for example, and then spread across wide regions? We do not yet know.

Assembly can be influenced by the creation of nonplanar surface features on the substrate, although this leads to patterns other than the herringbone [1,2]. An alternative process for influencing the herringbone pattern might exploit control of the two in-plane prebuckling stresses in the film, σ_{11}^0 and σ_{22}^0. These components can be controlled by various forms of substrate constraint, e.g. constraint during cooling or by bending after cooling. If $\sigma_{11}^0 > \sigma_{22}^0$, the classical mode is a one-dimensional mode aligned perpendicular to the one-direction. As the system is cooled below critical the one-dimensional mode will be preferred, but at some point, depending on $\sigma_{22}^0/\sigma_{11}^0$, we speculate that some other herringbone-like mode should become energetically favorable. This assertion can be inferred from Fig. 3. At temperatures well below critical, there is a wide separation between the energy associated with the one-dimensional mode and the herringbone mode. By continuity, one expects the existence of a mode similar to the herringbone mode when $\sigma_{22}^0/\sigma_{11}^0$ is not much smaller than unity.

We speculate that for $0 < \sigma_{22}^0/\sigma_{11}^0 < 1$, there exist other modes of herringbone character such a *transitional herringbone mode* with $0 < \alpha < 45°$ (now with one-direction aligned in the vertical direction in Fig. 1), or an *unbalanced herringbone mode* with the major branch of crests aligned perpendicular to the one-direction and the minor branch aligned perpendicular to the two-direction (Fig. 2b). Based on the findings for the equi-biaxial mode, the crest-to-crest distance is expected to be the same for either of these modes. For the transitional mode, the inclination of the crests to the direction of maximum compression, α, permits accommodation of the differing pre-stresses in the two-directions. Similarly, the larger distance between the jogs for crests perpendicular to the maximum compression direction in the unbalanced mode relaxes more stress in that direction. Either feature would accommodate the different pre-stresses in the two-directions. Another attractive feature of both families of modes is that they provide a continuous transition between the one-dimensional mode and the "regular" herringbone mode associated with equi-biaxial stressing. For the transitional mode, this occurs as α varies from 0° to 45°, while for the unbalanced mode it occurs as the ratio of length the minor branch to that of the major branch varies from 0 to 1.

If the buckling process is strictly elastic, it might be possible to observe continuous changes in the unbalanced herringbone mode as $\sigma_{22}^0/\sigma_{11}^0$ is varied. Such a variation occurs naturally near an edge (or elevation step) of the compliant substrate where the pre-stress component in the film in the direction perpendicular to the edge is relaxed. At an edge or step, there is a transition region where the pre-stress varies from uniaxial at the edge to equi-biaxial in the interior well away from the edge over a distance set by shear lag in the substrate. In such regions one does indeed see clear evidence of a transition from a distinct one-dimensional mode, through what appears to be best described by the transitional herringbone mode, to the regular herringbone mode in the interior well away from the edge or step [1–3].

In summary, there appears to be scope for exploring and perhaps utilizing the film pre-stresses to generate a family of highly regular patterns ranging from one-dimensional modes to the balanced herringbone mode.

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