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Evolving material structures of small feature sizes

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Abstract

Modern electronic and photonic devices are solid structures of small feature sizes. During fabrication and use, diffusive processes can relocate matter, so that the structures evolve over time. A film may break into droplets, and a conducting line may grow cavities. Stress and electric current have long been understood as forces that drive the changes. Evidence has accumulated that, while important, these forces are insufficient to account for diverse experimental phenomena, suggesting forces of other physical origins also operate. In a structure, collective actions of atoms, electrons, and photons contribute to the free energy. When the structure changes its configuration, the free energy also changes. The free energy change defines a thermodynamic force which, in its turn, drives the configurational change of the structure. This article illustrates the concepts with specific phenomena. Emphasis is placed on physical descriptions of forces of diverse origins, including elasticity, electrostatics, capillarity, electric current, composition gradient, photon dispersion, and electron confinement. The effects of some of these forces are particularly significant in structures of small feature sizes, say, between a few to hundreds of nanometers. Insights into these forces are increasingly valuable as devices miniaturize. This area of research holds great promises for solid mechanics innovation. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A solid structure, such as a film on a substrate, is not a peaceful object. Inside it atoms jiggle all the time. Most atoms vibrate around their equilibrium positions with amplitudes smaller than the atomic spacing. Occasionally, an atom moves so violently that it jumps into a different equilibrium position. If such jumps are random, with equal probability for all atoms in all directions, their collective effects will average out: no change will be perceived at gross length and time scales. If the jumps are not completely random, perceptible changes will occur. For example, the film on the substrate may break into many droplets. A particular jump is more likely than other jumps if it lowers the free energy of the structure.

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The central idea is this. The free energy depends on the configuration of the structure. When the configuration changes, so does the free energy. This change in free energy defines a thermodynamic force which, in its turn, motivates the configuration change of the structure. The change is effected by a diffusive process, requiring less time in a structure with a smaller feature size, held at a higher temperature.

Study of evolving structures goes back decades. Impetus for recent work comes from two broad trends: the ever smaller structures, and the ever faster computers. The feature size in integrated circuits is now about a tenth of a micron-meter; nanostructures are being developed for photonic networks. Computers allow us to synthesize models from decades of experience to simulate realistic processes. Over centuries solid mechanics discipline has advanced by studying large structures like bridges, ships, airplanes, nuclear reactors, and tectonic plates. The study of small structures will once again extend the boundaries of understanding of our discipline. We now have effective tools to analyze large structures. Can we develop similarly effective tools for evolving small structures? This article integrates aspects of this expanding field. In the following three sections, we first give examples of structural evolution, then discuss self-assembled nanostructures and configurational forces of less familiar origins, and finally consider the main challenges in developing simulation tools.

2. Examples of structural evolution

This section uses examples to illustrate basic concepts. Our descriptions here will be entirely conceptual; a mathematical account of these examples and others can be found in Suo (1997). The first example, crack growth and healing, illustrates the use of free energy and configurational force. We then look at a pore changing shape as matter diffuses on the pore surface, driven by elastic field and electric current. This example leads to a discussion of energy landscape and kinetic law. The annealing of a polycrystalline film provides an example of multiple kinetic processes: the final configuration is selected by competing kinetic processes, as well as by competing forces. The last example, domain patterns in a ferroelectric crystal, shows the need to understand coupled electrical and mechanical fields.

2.1. Growing crack and healing crack

After the atomic nature of matter was confirmed by the beginning of the twentieth century, it became useful to link macroscopic phenomena to atomic processes. In 1920 the British engineer A.A. Griffith looked at one such macroscopic phenomenon: fracture of glass. The main puzzle had been that glass usually breaks under an applied stress much below the atomic bond strength. He suggested that a piece of glass is never perfect: small cracks pre-exist on its surface. The applied stress is amplified many times, via an elastic field, at the tip of such a crack. It is this intense stress at the crack tip that breaks atomic bonds.

This picture is easy to understand, but difficult to quantify. The atomic behavior at the crack tip is highly nonlinear, and differs in details for different materials. Griffith took a less direct approach. An atom at the surface of a solid has a bonding environment different from that of an atom in the solid, so that the free energy per atom at the surface is higher than that in the solid. The excess defines the surface energy, which he measured for glass by a clever experiment. He then applied thermodynamics to a sample with a pre-existing crack, subject to an external load. For the present purpose, suppose that, after a certain amount of displacement, the loading grips are held fixed. The free energy of the system is the sum of the elastic energy in the bulk of the sample, and the surface energy in the faces of the crack. When the crack advances, the stress in the sample is partially relieved, so that the elastic energy is reduced. At the same time, the advancing crack creates more surface area, so that the surface energy increases. Thermodynamics dictates that the process go in the direction that reduces the total free energy. If the decrease in elastic energy prevails, the crack grows. If the increase in surface energy prevails, the crack heals. The nonlinear zone, localized around the crack tip, remains invariant at the crack advances. Consequently, the presence of the nonlinearity dose not affect the energy accounting. The Griffith approach circumvents the nonlinear crack tip behavior by invoking one quantity: the surface energy per unit area. The science of fracture was thus born. See Lawn (1993) for later developments.

Scientific study of the reverse process — crack healing — also has a long history and many applications (Yu and Suo, 1998). When two glass slides are placed in contact, they adhere. The contact has long been used in making optical instruments. The same process has in recent years led to novel optoelectronic devices by directly bonding dissimilar semiconductor wafers. Occasionally adhesion can be a nuisance. For example, parts in a micromachine may stick unintentionally, causing malfunction.

The reduction in the elastic energy associated with an increment in the crack area defines a thermodynamic force, known as the elastic energy release rate. Eshelby (1970) generalized the idea to any variation of configuration, be it the motion of a crack front, a surface, or a dislocation. A further generalization, to be explored in this article, is to include free energies due to various physical origins. The variation of the free energy associated with a variation of the configuration defines a configurational force. This is a central, unifying idea. The remainder of the article refines this idea in various ways

2.2. Shape change of a pore

A small piece of a crystal can sustain a large stress without fracture or plastic flow. At an elevated temperature, atoms can diffuse on the crystal surface, changing the shape of the crystal over time. Consider, for example, a crystalline fiber containing a small spherical pore. Pull the fiber in tension, keep the loading grips fixed, and hold the fiber at an elevated temperature. The fiber remains elastic. However, atoms diffuse on the pore surface, so that the pore changes shape over time, keeping its volume fixed. The free energy consists of the surface energy of the pore and the elastic energy stored in the fiber. They compete to shape the pore. The surface energy favors a rounded pore, for a sphere has the smallest surface area among solid figures of an equal volume. The elastic energy favors a pore elongated in the direction normal to the tensile load, for it reduces the elastic energy stored in the fiber. If the surface energy prevails, the pore reaches an equilibrium shape close to an ellipsoid, and no further change occurs. If the tensile load prevails, the pore keeps changing shape, and develops a nose running in the direction normal to the loading axis. Once a sharp crack tip forms, the rate of crack extension is not limited by mass diffusion on the pore surface, but by the bond breaking process at the crack tip. While this kind of crack nucleation process has been discussed for decades (Hillig and Charles, 1964; Asaro and Tiller, 1972), detailed models have appeared only recently (Chiu and Gao, 1993; Yang and Srolovitz, 1993), and its practical significance still remains to be established (Wang and Suo, 1997).

Both phenomena — crack growth and pore shape change — involve surface and elastic energy. Yet their models differ in one important aspect. Griffith modeled a crack as a slit, so that the thermodynamic system has only one degree of freedom: the length of the slit. The length either increases or decreases to reduce the free energy. Once the free energy as a function of the crack length is known, one can decide whether a given crack will grow or heal. To describe the pore shape change, however, requires many degrees of freedom. Countless ways of shape change would each reduce the free energy. A spherical pore can evolve to an ellipsoid, or a slit, or numerous other shapes. Consequently, free energy by itself cannot select a sequence of shapes.

To evolve the pore shape, the model must have another ingredient: a kinetic law that describes the rate of atomic relocation. In a continuum theory, a configurational force is defined as the amount of free energy reduction associated with a unit volume of matter moving a unit distance on the surface. This definition gives a *local* quantity, the diffusion driving force, at every point on the pore surface. A kinetic law is then prescribed which requires that the mass flux is proportional to this driving force. This model evolves the pore shape as follows. Starting from an initial shape, one computes surface energy and solves the elasticity problem. Both the surface and the elastic energy contribute to the diffusion driving force. According to the kinetic law the driving force causes the mass flux, which, following mass conservation, gives the velocity of the surface. The velocity updates the pore shape for a time step. Repeat the whole procedure for many time steps.

This way of combining the free energy and a kinetic law has a long tradition (Herring, 1951). It results in nonlinear partial differential equations (Mullins, 1957) or variational statements (Needleman and Rice, 1980; Suo, 1997).

2.3. Electromigration in interconnects

On a silicon chip, interconnects transport electrons among transistors. These interconnects are aluminum lines, often of submicron width. Silicon dioxide fills the space in between to provide electrical insulation and structural support. The whole structure is a metal network embedded in an oxide matrix. The interconnects are subject to conditions unprecedented for bulk aluminum. The chips are fabricated in many temperature cycles. Thermal expansion mismatch induces large stresses in the interconnects. Plastic flow in aluminum is limited because the small dimension confines dislocation movements, and because the matrix oxide imposes a triaxial constraint. When a circuit is in use, the interconnects carry huge electric current densities, orders of magnitude higher than those in house wiring. The moving electrons impart momenta to atoms, motivating atoms to diffuse in the direction of electron flow. This process is known as electromigration. As a consequence of these brute forces acting in a small dimension, voids nucleate, grow, and sever the interconnects. The failure mechanism is a major roadblock for further miniaturization of integrated circuits.

Microscopes have revealed complex void dynamics in interconnects (Marieb et al., 1995). A void may nucleate at a junction of a grain boundary and an aluminum-oxide interface. The void may enlarge, migrate, penetrate grain boundaries, and change shape. Several voids may get trapped at a location and coalesce into a single void, which some time later may break into smaller voids. One intriguing behavior has captured much attention in recent years. A void sometimes takes the shape of a slit, lying inside a single grain, severing the metal line. Observation of Kraft et al. (1993) revealed that a void is initially rounded; it moves, grows, and then changes shape to become a slit. The present understanding assumes that a void changes shape by surface diffusion, driven by surface energy and electric current (Suo et al., 1994). As stated before, the surface energy favors a rounded void. Now the electron flow also motivates atoms to diffuse on the surface. A rounded void is unstable when the electric current density is too high (Zhang et al., 1999).

2.4. Evolving structure as a dynamical system

There has been an explosive activity to apply the mathematics of nonlinear dynamics in many fields. An evolving structure is a dynamical system (Yang and Suo, 1996). Describe the configuration of the structure with a set of generalized coordinates. For example, a sample containing a crack is described with one generalized coordinate: the crack length. A sample containing a pore has to be described with an infinite number of generalized coordinates. In numerical simulation, however, we use a finite subset of the generalized coordinates. The free energy of the structure is a function of the generalized coordinates. Imagine a multi-dimensional space with the free energy as the vertical axis, and the generalized coordinates as the horizontal axes. In this space the free energy function is a hypersurface, called the energy landscape. A point on the landscape represents in general a nonequilibrium state of the structure; the bottom of a valley is an equilibrium state. A curve on the landscape represents an evolution path of the structure.

Thermodynamics requires that the system evolve to reduce the free energy. Consequently, an evolution path is a descending curve on the landscape. Starting from any point other than a valley bottom on the landscape, infinite descending curves exist. Thermodynamics by itself cannot select an the evolution path. Nor can thermodynamics select one valley as a final equilibrium state among several valleys. The evolution path is set by thermodynamics and kinetics acting together. At a point on the landscape, the slopes of the landscape represent the generalized forces. For a given time step, the kinetic law allows one to compute the increments of the generalized coordinates, which give the direction and magnitude of the incremental motion on the landscape. The evolution path is thus determined incrementally.

This global, geometric picture does not add any new information to the problem, but does give some intuitive feel. If the energy landscape contains several valleys, which one will be reached by the system as the final equilibrium state will also depend on kinetics. In all the above examples, forces of different origins compete to select morphology. When the magnitude of forces change, the shape of the energy landscape changes. Each of the above phenomena is described by a single kinetic process: bond breaking for crack growth, and diffusion for pore shape change. When a phenomenon has multiple kinetic processes, a change in their relative rate, without changing the energy landscape, may shift the structure from moving to one valley to another. In the language of nonlinear dynamics, we say that the change of kinetic parameters alters the basin of attraction. It is, after all, a common practice to obtain a desired microstructure by manipulating kinetics via time and temperature control. An example follows.

2.5. Annealing polycrystalline film

When gold atoms are deposited on a surface of a sodium chloride crystal at room temperature, a polycrystalline gold film forms. The grain size is small compared to the film thickness. Two neighboring grains meet at a grain boundary, where atoms are poorly packed compared to the atoms inside the lattice of the grains. Consequently, the free energy per atom at the grain boundary is higher than that in the grains. The excess defines the grain boundary energy. When the system is held at an elevated temperature, to reduce the free energy, the total area of all grain boundaries must reduce. The film accomplishes this by grain boundary migration. Atoms vibrate perpetually as a result of thermal energy. At a grain boundary, occasionally an atom jumps so violently that it detaches from one grain, and attaches to the other grain. If the grain boundary is flat, such jumps occur in both directions with equal probability. If the grain boundary is curved, one grain being convex and the other concave, the probability of a jump from the convex grain to the concave grain is higher than the reverse jump. This bias tends to flatten the grain boundary and thereby reduce its area. At a gross scale, one perceives the migration of the grain boundary.

In a continuum description, the total free energy of a polycrystal is the excess energy over all grain boundary area. The configurational force for grain boundary migration is the free energy reduction associated with a unit area moving a unit distance. A kinetic law is prescribed which requires that the migration velocity of a grain boundary be proportional to the configurational force.

After some time, the gold grain sizes become comparable to the film thickness. Further evolution is affected by two other kinds of surfaces: the film-air interface and the film-substrate interface. The two interfaces have their own excess free energies. For each grain, the two interfacial energies depend on the orientation of the grain relative to the substrate. Consequently, the sum of the two interfacial energies of one grain may be lower than its neighbors. To reduce the total free energy, the grain boundaries migrate to allow this grain to grow at the expense of its neighbors. After some time, the in-plane size of the survival grains can be much larger than the film thickness (Thompson, 1993).

Yet another outcome may occur during the annealing. Gold atoms can diffuse on the film surface. The film surface can change shape to reduce the area of grain boundaries. Along a junction between the film surface and a grain boundary, atoms leave the junction and diffuse to the top of grains on either side. A groove develops along the junction, deepening and widening over time. The film eventually breaks into droplets (Srolovitz and Safran, 1986).

The two kinds of motion compete to select the final morphology. If grain boundary migration is fast, the annealing results in a large-grained, continuous film. If surface diffusion is fast, the annealing results in droplets. The two processes interact dynamically. To select the final morphology, one must simulate the two processes simultaneously (Sun and Suo, 1997).

2.6. *Ferroelectric domain patterns*

Barium titanate is a prototype of ferroelectric crystals. At room temperature, the crystal has a unit cell slightly distorted from a cube, with a titanium ion off the center by a small distance, taking one of the six equivalent positions in the cell: up, down, back, front, left or right. That is, the crystal has a tetragonal unit cell and an electric dipole moment; the cell has six variants of polar directions. A single crystal sample often contains all six variants, each occupying some regions, known as domains. Two neighboring domains are separated by a domain wall. The free energy now includes elastic, dielectric and piezoelectric contributions, in addition to domain wall energy. To lower the free energy, the domains have to arrange into some pattern. Subject to a stress or an electric field, some domains grow at the expense of others, and the pattern changes. A domain wall moves as atoms detach from one domain and attach to the other. This process can be modeled in a way analogous to grain growth (Loge and Suo, 1996). Domain wall motion underlie all phenomena of polarization and deformation, such as poling, creep, aging, and fatigue. Linking the wall motion to these macroscopic phenomena is an active research field.

Commercial uses of ferroelectrics have mostly been in the form of bulk ceramics (Uchino, 1997; Campbell, 1998). In the last decade, intense research has been motivated by the potential of integrating ferroelectrics onto silicon chips. Examples include high-permittivity capacitors in dynamic random-access memories, bi-stable media in nonvolatile random-access memories, or piezoelectric motors and sensors in micromachines (Ramesh, 1997). This activity has brought fundamentals of ferroelectricity into forefront (Suo, 1998). For example, the domain pattern of a ferroelectric film is affected by the constraint of the substrate, which in turn affects ferroelectric action. Pattern changes driven by forces of various physical origins pose a new class of solid mechanics problems.

3. Self-assembly and long-range forces

3.1. *Self-assembled nanostructures*

Techniques now exist to fabricate multilayer films of sharply defined composition and thickness. These structures are modulated only in the thickness direction. More complex structures have in recent years raised great interest. Small semiconductor particles can achieve three dimensional quantum confinement and lead to superior lasers (Zunger, 1998). A dielectric matrix containing a regular lattice of voids can give rise to photonic band gap (Lin et al., 1998). A main challenge has been to produce the nanostructures economically.

Nanostructures can sometimes self-assemble themselves. For example, both germanium and silicon have a crystal structure like diamond, but their lattice constants differ by about 4%. When a germanium film grows on a thick silicon substrate, cube on cube, the germanium film strains to match the silicon lattice. The elastic energy stored in the film can be reduced if the film breaks into droplets. The shape change is effected by atomic diffusion on the film surface, driven by the elastic energy variation (Freund, 1999; Gao and Nix, 1999). In many material systems, it has been found that the droplets can self-organize into a periodic lattice (Springholz et al., 1998).

The key to self-assembly is configurational forces acting over the scale comparable to the feature size of the nanostructure. Such forces are therefore much longer ranging than atomic bond length. Although we are mainly interested in solid structures, it is instructive to first look at a family of well studied systems: colloids. A colloid consists of small solid particles suspended in a liquid (Russel et al., 1989). The particles are in ceaseless Brownian motion. If two particles come too close to each other, the van der Waals attraction can join them. The thermal energy is insufficient to break them apart. Subsequently, more and more particles adhere together to form flocs.

To prevent a colloid from flocculation, some long-range force must act to repel approaching particles. Electrical double layer can mediate such a repulsion. The surface of a solid particle in a liquid electrolyte is charged. In the electrolyte, ions of the opposite sign (counterions) are attracted to the particle surface. Entropy, on the other hand, tends to spread the counterions throughout the electrolyte. A compromise dictates that the counterions in the electrolyte form a cloud around the particle. When two particles approach each other, their counterion clouds overlap, leading to a repulsion that prevents them from joining.

Both van der Waals attraction and electrical repulsion act over a distance larger than atomic bond length. Such long-range forces can lead to self-assembled structures. In a liquid electrolyte, monosized solid particles can organize into a lattice, i.e., a colloidal crystal (Grier, 1998). In solids, elasticity and electrostatics mediate long-range forces, as we have seen before. By comparison, other long-range forces have received little attention. They can be just as potent in controlling the morphology of solid nanostructures. In what follows we discuss several likely candidates. Substantial work is required to establish the roles of these forces in solid structures.

3.2. Photon dispersion

About a century ago the German physicist Max Planck discovered a way to calculate the energy of electromagnetic oscillations. He was trying to understand the radiation from a blackbody, e.g., a hole on a large cavity with conducting walls. The Maxwell equations determine the electromagnetic oscillation modes in the cavity. Each mode has an amplitude pattern and a frequency ω. Planck postulated that the energy in the mode can only take the form $n\hbar\omega$, where $\hbar$ is a constant to fit experimental data, and n is zero or a positive integer, called the number of photons in the mode. Planck then used the statistical mechanics to calculate the energy in the cavity.

The procedure was later extended to structures other than a large cavity with conducting walls. A structure is made of several media, e.g., a film, a substrate and the air. The electromagnetic oscillations need not be confined in any particular part of the structure. However, because the dielectric properties are different for various constituent media, the electromagnetic field can still form standing waves, governed by the Maxwell equations. Upon obtaining the frequencies for all the modes, one can follow the statistical mechanics procedure to compute the energy. When the configuration of the structure changes, the oscillation frequencies and the free energy also change. This leads to a configurational force, known as the dispersion force or van der Waals force (Mahanty and Ninham, 1976). For example, for a film of thickness D on a semi-infinite substrate, the energy per film area is A/D^2. The constant A can be calculated from the data of dielectric response functions of the substrate and the film.

The dispersion force has so far been considered in systems that can change configuration by rigid body motion or fluid flow. As discussed above, the dispersion force causes solid particles to attract one another. The same force has manifested itself in several surprising phenomena involving liquid films. For example, a film of a suitable liquid can lie stably above another liquid of a lower density (Kwon et al., 1982). In this case, the dispersion force tends to thicken the film, counteracting the gravity. The dispersion force can also cause destabilize a liquid film, giving rise to intriguing patterns when the film begins to uncover the substrate (Herminghaus et al., 1998).

Due to its ubiquitous origin, the dispersion force exists in any system of media. In a solid structure, the force can drive mass diffusion, causing morphological changes over time. The dispersion force is responsible for the bonding of van der Waals solids, which are much weaker than covalent, ionic, or metallic solids. This may give an impression that the dispersion force is too weak to drive morphological changes in most solids. The impression is misguided. It is a small deviation from the cohesive energy, such as elastic energy, rather than the cohesive energy itself, that drives morphological changes. Consequently, when considering morphological changes, one should compare the photon energy to elastic energy, instead of cohesive energy. Indeed, Suo and Zhang (1998) have shown that the magnitude of the dispersion force is comparable to that of elasticity in thin solid films, and can either stabilize or destabilize the films.

3.3. Electrical double layer

We have discussed the role of electrical double layers in preventing solid particles in an electrolyte from flocculation. A counterpart in solid state is an electrical double layer formed at a semiconductor surface or a semiconductor-metal interface. For many technological and scientific reasons, nano-sized metallic dots are grown on semiconductor substrates. A dot can move on a substrate by means of atomic diffusion on the surfaces of the dot. An isolated dot, far away from all other dots, moves in a way like the Brownian motion of a particle in a liquid, albeit with a longer time scale. In a recent experiment with Cu dots on TiO_2 substrates (Bonnell et al., 1998), it was found that the copper dots tended to move very close to one another. Some areas on the substrate surface were covered with densely packed dots, and other areas with virtually no dots at all. Despite their large collective surface area, the densely packed dots did not coalesce, but maintained small distances from one another.

These observations call for an attractive force between two dots when they are far apart, and a repulsive force when they are close. The following interpretation is plausible. When the dots are far apart, they attract one another by the van der Waals force. When the dots are close together, they repel one another by a force which is understood as follows. The interface between a metal and a semiconductor is usually charged. In the semiconductor, a cloud of charge with a sign opposite to the interfacial charge forms. Thus, underneath a metallic dot, there is such a charge cloud inside the semiconductor. When the dot moves, the charge cloud moves with it. When two dots approach each other, their accompanying charge clouds overlap, leading to a repulsive force that prevent the dots to coalesce. This possibility is exciting because the repulsive force may help to self-assemble a lattice of dots, much like colloidal crystals.

The existence of electric double layers at interfaces between dissimilar solids is well established in the semiconductor literature (Sze, 1981). The double layers form the basis of *p–n* junctions and metal-semiconductor contacts. The attention in the past, however, has been focused on their electrical properties. Their role in structural evolution has yet to be established. In a liquid electrolyte, ions of both signs are mobile. By contrast, in a semiconductor, say *n*-doped, electrons are mobile, but positive ions are not. This difference must be taken into consideration in developing a theory of electrical double layer forces in solids (Suo and Yang, 1998).

3.4. Electron confinement

It has been known for many years that, when Ag atoms are deposited on a GaAs substrate at room temperature, Ag droplets from. That is, Ag does not wet GaAs. Recently Smith et al. (1996) discovered a different behavior. They grew a Ag film on a GaAs substrate at a low temperature. Because Ag atoms have low mobility at the low temperature, the film covered the substrate, but was rough. Upon warming to room temperature, Ag becomes a flat, single crystal film. A recent theory suggests that electrons confined in the metal film can mediate a force to flatten the film (Zhang et al., 1998). The energy levels of the conduction electrons in a piece of metal are determined by modeling the metal as a box, and solving the Schrödinger equation for one electron confined in the box. In the ground state, electrons fill the energy levels from bottom up, two electrons per level. When the box is small, the energy levels depend on the size and shape of the box. The gaps between the energy levels are larger for the film than the bulk. If ions in the film and in the bulk are taken to have identical free energy, the difference in electronic energy results in an excess free energy of the film relative to the bulk. Furthermore, Suo and Zhang (1998) have shown that, for thin metallic films, the effect of electron confinement is surprisingly strong compared to elastic stress, and can stabilize films up to several hundreds of monolayers.

3.5. Strain-dependent surface energy

As discussed before, the bonding environment of an atom on a surface differs from that in the bulk, so that the free energy per atom on the surface exceeds that in the bulk. This excess is the origin of the surface energy. For a solid, an applied stress can induce an elastic strain, perturbing the bonding environment of atoms both on the surface and in the bulk. Consequently, the surface energy depends on the state of the elastic strain. The idea is quantified as follows.

Consider two identical semi-infinite bodies, both under an elastic strain ϵ parallel to the surfaces. Use an infinite body under the same strain as a reference state. Due to the presence of the surfaces, the free energy stored in the two semi-infinite bodies differs from that in the infinite body. The excess free energy per unit area of the surfaces defines the surface energy, γ. We adopt the Lagrangian definition by using the area of an unstrained solid (Cammarata, 1994). The surface energy is a function of the elastic strain, $\gamma(\epsilon)$. For a small strain one can truncate the Taylor series to the first order term: $\gamma(\epsilon)=\gamma_0+f\epsilon$. The two coefficients have clear physical significance: γ_0 is the surface energy of the unstrained solid, and f is the force per length built in the surface and is called the surface stress. It is straightforward to generalize to a multiaxial strain state, so that the surface stress is a second order tensor.

Because the surface strain has to be compatible with the strain in the body, the surface stress can induce an elastic field inside the solid, and contributes to the free energy of a structure. For a solid sphere, the surface stress induces inside the sphere a triaxial stress. The surface stress also induces a biaxial stress in a thin free standing sheet. On some crystal surfaces, the surface stress tensor is anisotropic, leading to surface domain patterns (Ibach, 1997).

3.6. Composition-dependent surface energy and surface stress

When a sub-monolayer quantity of Ag is deposited on a Pt substrate, a two-dimensional alloy forms (Röder et al., 1993). At an elevated temperature, diffusion of Ag is rapid within the topmost layer, but negligible in the bulk of the substrate. Consequently, a mixture of Ag and Pt forms the topmost layer, to which all Ag atoms are confined. Islands of Ag about 1 nm in size form in the Pt matrix. The phenomenon is an analog of spinodal decomposition in bulk alloys (Cahn, 1961). The thermodynamics of the two-dimensional alloy can be described by the surface energy γ_0 as a function of the Ag concentration C. If the function $\gamma_0(C)$is convex down, the chemical driving force tends to maintain the uniform distribution. If the function is convex up, the chemical driving force tends to motivate spinodal decomposition.

The superficial alloy, however, is not strictly two-dimensional; rather, it couples with the substrate. We next examine the effect of the surface stress (Suo and Lu, 1999). The surface energy is a function of both the concentration and the surface strain, $\gamma(C,\epsilon)$. The leading terms of its Taylor expansion in strain are expressed as $\gamma(C,\epsilon)=\gamma_0(C)+f(C)\epsilon$. Consequently, the surface stress, $f(C)$, is a function of the concentration. When Ag atoms are uniformly distributed in the topmost layer, the surface stress is uniform, and the bulk of the substrate is stress-free. When the Ag concentration is nonuniform, the nonuniform surface stress induces a strain field. This strain field, in its turn, reduces the total surface energy, but adds elastic energy to the substrate. The net effect is that the composition-dependent surface stress always provides a driving force for spinodal decomposition. This effect is particularly strong for short wavelength perturbations. To prevent short-wavelength decomposition, one may add the free energy contribution due to the concentration gradient.

A multi-component semiconductor epitaxial film often has an uneven composition within the plane of the film (Guyer and Voorhees, 1998). The phenomenon is of scientific interest and technological importance, as it is a basis for making novel devices.

4. Simulation tools

This article focuses on the physical description of phenomenology, but would be inappropriate without mentioning the efforts to develop computer codes to simulate evolving structures. Today general-purpose finite element codes exist to analyze stress fields in complex materials and structures. However, no such a tool exists, similarly accommodating and robust, to simulate evolving structures. Several groups are developing the finite element method for evolving structures (Cocks and Gill, 1996; Huang et al., 1998; Socrate and Parks, 1993; Sun and Suo, 1997; Zhang et al., 1998a). It is premature to compare this method critically with other methods being developed outside the solid mechanics community. However, the main challenges to any candidate general-purpose code are known. The code should be able to describe sharp surfaces and interfaces. It should allow large geometric changes, e.g., faceting, crack tip emergence, and grain elimination. It should handle both short and long range forces. The latter usually requires solving boundary value problems repeatedly as the structure evolves. It should incorporate multiple kinetic processes, e.g., diffusion along various paths, creep, and grain boundary migration. Furthermore, its relation with molecular dynamics simulation tools should be clarified. The task is formidable. If the history of developing general-purpose codes for large structures offers any perspective, the task will be done, most likely by a persistent, collective effort.

5. Concluding remarks

Small scale structural evolution in materials is driven by forces of various physical origins, effected by diffusive mass transport mechanisms. The final morphology is selected by a dynamical process, rather than an equilibrium condition. The complexity calls for theoretical simulations to map out diverse evolution paths and identify regulatory parameters. A unifying framework is based on the ideas of configurational forces and kinetic laws. Within this framework, diverse phenomena can be understood, and general-purpose simulation tools can be developed. As we explore behaviors of nanostructures, forces of less familiar origins will manifest themselves. They assemble the ‘self-assembled’ structures. The study of evolving small structures will position the solid mechanics discipline at the frontier of a field of great intellectual challenge and technological value. The field is wide open.

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