USING PRINCIPLE OF VIRTUAL MOTION AND GALERKIN APPROXIMATION TO ANALYZE SURFACE DIFFUSION

B. SUN *, Z. SUO * and A.C.F. COCKS **
*Mechanical and Environmental Engineering Department, Materials Department, University of California, Santa Barbara, CA 93111
**Engineering Department, Cambridge University, Cambridge CB2 1PZ, UK

ABSTRACT

This paper outlines the use of the Principle of Virtual Motion and the Galerkin approximation to analyze surface diffusion phenomena. Various ideas are illustrated with an analysis of the evolution of a fiber of bamboo-like grain structure.

INTRODUCTION

An approach to analyzing surface diffusion, as developed by Herring [1] and Mullins [2], relates the chemical potential to the curvature of the surface, and assumes that the mass flux is proportional to the chemical potential gradient. Together with mass conservation, these ideas lead to a nonlinear partial differential equation that govern the motion of the surface. The equation can only be solved analytically for a few situations. In addition, because the equation contains high-order differentiation, numerical solution has been difficult.

An alternative, more global view regards the surface evolution as a means to release the free energy of the entire structure. The shape of the structure is described, approximately, with a set of generalized coordinates. The free energy of the structure is a function of the generalized coordinates. Picture this function as the *landscape* in a space with the generalized coordinates spanning and the free energy erecting. A point on the energy landscape represents a nonequilibrium state in general, and the bottom of a valley represents an equilibrium state. Thermodynamics requires that an evolution path be a curve on the landscape, descending from the initial state to the bottom of a valley. By itself, thermodynamics cannot determine the evolution path or final state, because there are many descending curves on the energy landscape. Kinetic information is required to determine the evolution path.

Kinetics, such as atomic diffusion, proceeds locally. How can one transcribe such local information onto the energy landscape? The Principle of Virtual Motion assigns a viscosity matrix to every point on the landscape. The principle has been used to simulate diverse structural evolution phenomena in recent years; see [3,4] for literature review. This paper outlines the approach in the context of surface diffusion. The use of the Principle of Virtual Motion to analyze dissipative structures goes back to Lord Rayleigh. His book *The Theory of Sound* [5] can still be read profitably today.

PRINCIPLE OF VIRTUAL MOTION

Kinematics and Mass Conservation

We outline the ideas by surface diffusion in two-dimension, where a surface is represented by a curve. Let r be the position vector of a point on the surface, ξ the number of atoms added to unit area of the surface, and I the number of atoms flowing across unit length on the surface. Use the superimposed dot to indicate the partial derivative with respect to time, and denote $\dot{\xi}$ and $\dot{I}$ as the growth rate and atomic flux, respectively. A geometric consideration shows that

$$\dot{\xi} = n \cdot \dot{r} / \Omega. \tag{1}$$

Here n is the unit vector normal to the surface, and Ω the volume per atom. Mass conservation requires that the growth rate relate to the flux divergence:

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$$\dot{\xi} = -\partial \dot{l} / \partial s. \tag{2}$$

The derivative is with respect to the arc length s.

Imagine that the surface undergoes a small virtual motion, δr, which may be of different amount at different positions on the surface. Associated with this virtual motion, $\delta\xi$ atoms add to unit area of the surface, and δl atoms cross unit length on the surface. They obey the similar relations as above, namely

$$\delta\xi = n \cdot \delta r / \Omega, \tag{3}$$

and

$$\delta\xi = -\partial(\delta l) / \partial s. \tag{4}$$

<u>Energetics and Forces</u>

Denote the free energy of the structure by G. In the present problem, the free energy is the surface tension integrated over the entire surface area. Let the change of the free energy associated with the virtual motion by δG. Define the driving force for diffusion, F, as the free energy decrease associated with an atom moving unit distance. That is,

$$\int F\delta l ds = -\delta G. \tag{5}$$

The integral extends over the surface. One can confirm that the driving force so defined relates to the chemical potential gradient [3], consistent with that of Herring [1]. In the present approach, however, this local relation will *not* be used.

If the structure has a triple point, the free energy also varies when the triple point moves. Equation (5) requires that the driving force associated with the triple point motion vanish. This is equivalent to the local equilibrium assumption that the dihedral angles take the equilibrium values at all time [3]. Our approach need not enforce the equilibrium dihedral angles; rather, the equilibrium angles come out as a part of the solution, although in our numerical example the angles take some time to reach equilibrium due to low order of approximation.

<u>Kinetics</u>

We adopt a kinetic law that the flux is proportional to the force:

$$\dot{l} = MF. \tag{6}$$

This equation defines the atomic mobility on the surface, M. The mobility is related to the self-diffusivity on the surface, and is usually measured experimentally by its consequences, such as surface grooving.

GALERKIN APPROXIMATION

We use (5) to define the thermodynamic force at every point on the surface, then use this force to specify a kinetic relation, (6). The result is a local kinetic relation in that the flux at a point only depends on the force at this point. By no means such a relation is universally correct. Neither (5) nor (6) is a law of nature—they are just one way to specify a kinetic relation without violating thermodynamics. This said, however, the use of thermodynamic force to specify local kinetic laws has been pervasive in science. In what follows, we will refer to (5) as the Principle of Virtual Motion. This does not elevate the equation to a fundamental principle of the nature, but is simply a

less wordy way to refer to "the equation that defines the thermodynamic force associated with the virtual mass displacement".

A combination of the principle of virtual motion (5) and the kinetic law (6) gives

$$\int \frac{\dot{I}}{M} \delta I ds = -\delta G.$$ (7)

The *actual* flux distribution, $\dot{I}$, is selected to satisfy (7) for *all* virtual motions. To approximate, one may select a distribution of the flux to satisfy (7) for *some* virtual motions, or for a family of virtual motions. Obviously, the larger the family, the more accurate the flux. This is the basic idea of the Galerkin approximation, as detailed below.

Describe the surface with n degrees of freedom, writing $q_1, ...q_n$ for the generalized coordinates, and $\dot{q}_1,...\dot{q}_n$ for the generalized velocities. The virtual mass displacement is linear in the change of the generalized coordinates,

$$\delta I = \sum_i N_i \delta q_i.$$ (8)

The shape functions N_i are determined by the kinematic relations (3) and (4). Similarly, the flux is linear in the generalized velocities,

$$\dot{I} = \sum_i N_i \dot{q}_i.$$ (9)

The free energy is a function of the coordinates. The generalized forces, $f_1, ..f_n$, are the differential coefficients of the free energy, namely

$$-\delta G = f_1 \delta q_1 + f_2 \delta q_2 +...$$ (10)

At a given point on the energy surface, the forces are the slopes of the tangent plane contacting the surface at the point.

Equation (7) becomes

$$\sum_{i,j} H_{ij} \dot{q}_j \delta q_i = \sum_i f_i \delta q_i$$ (11)

with coefficients H_{ij} given by

$$H_{ij} = \int \frac{N_i N_j}{M} ds.$$ (12)

They do not depend on the generalized velocities, and form a symmetric, positive-definite matrix, which we call the viscosity matrix.

Equation (11) is valid for arbitrary virtual changes δq_i, so that

$$\sum_j H_{ij} \dot{q}_j = f_i.$$ (13)

The significance of H as a viscosity matrix now becomes evident: H_{ij} is the resistant force in the q_i direction when the state moves at unit velocity in q_j direction. Equation (13) is a set of linear algebraic equations for the generalized velocities. Once solved, they update the generalized coordinates for a small time step. The process is repeated for many steps to evolve the structure.

A ROW OF GRAINS

As an illustration, we analyze the evolution of a fiber of bamboo-like grain structure [3]. Some changes should be made to take care of the axisymmetry. The fiber consists of a row of identical grains, initially cylindrical in shape and connected at their ends, of length L_0 and diameter D_0 (Fig. 1a). The grains change shape by atomic diffusion on the surface and on the grain-boundary, under the action of the free energy of the surface and the grain-boundary. The grains are assumed to remain identical to one another (Fig. 1b). They will evolve to either one of two equilibrium structures: the isolated spheres (Fig. 1c), or connected disks of truncated spheres (Fig. 1d).

Following Miller and Lange [6], we approximate the shape of a nonequilibrium grain by a barrel formed by rotating a circular arc about a prescribed axis. The geometry is fully specified by three lengths: the arc radius R, the grain length L, and the grain-boundary diameter D. The volume of each grain is conserved during evolution, which places a constraint on possible values for the three lengths. Consequently, within the approximation, the structure has only two degrees of freedom, which we chose to be the grain length L, and the dihedral angle, Ψ.

Quantities that do not change during evolution are the *control parameters*. The present problem has three dimensionless control parameters: the initial grain aspect ratio L_0/D_0, the ratio of the grain-boundary tension to the surface tension γ_b/γ_s, and the ratio of the mobility on the grain-boundary to that on the surface M_b / M_s. In equilibrium, the dihedral angle, Ψ, reaches a value, Ψ_e, determined by $\gamma_b / \gamma_s = 2\cos(\Psi_e / 2)$. We will use Ψ_e to indicate the ratio of the surface and the grain-boundary tensions.
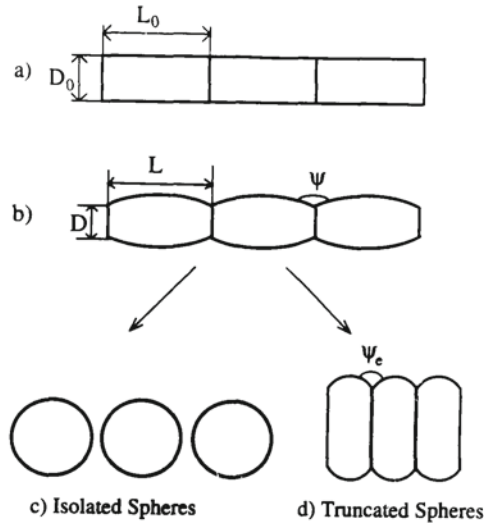

Fig. 1 A bamboo-like fiber may evolve to one of two equilibrium states.

Energy Landscape

Denote the area of the surface of a grain by A_s, and the area of a grain-boundary by A_b. The free energy per grain is $G = \gamma_s A_s + \gamma_b A_b$. For a given set of control parameters, the energy function is a surface in the space spanned by the free energy and the two generalized coordinates. Figure 2 shows the energy landscape for $L_0/D_0 = 2.5$ and $\Psi_e = 150°$. A point on the surface

represents a state, generally a nonequilibrium state. The upper left corner of the surface terminates when the grains pinch off. Indicated on the landscape are the three special states: the initial cylinders, the isolated spheres, and the truncated spheres. From the initial state of cylinders, the landscape descends steeply towards the minimum energy state of the truncated spheres. The landscape, however, does contain descending paths from the state of cylinders to the state of isolated spheres. Energy landscape alone does not determine the evolution path.
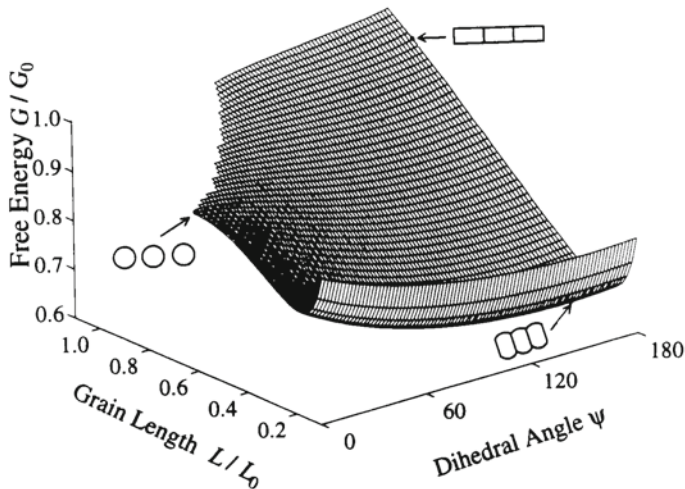
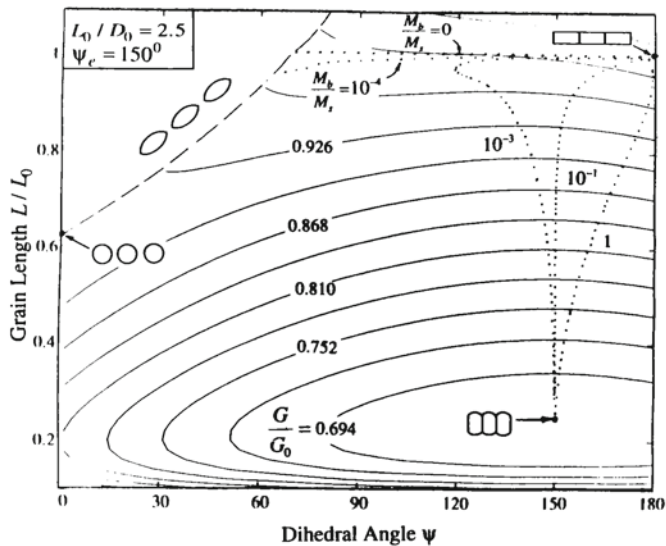Fig. 2. Free energy as a function of grain length and dihedral angle.
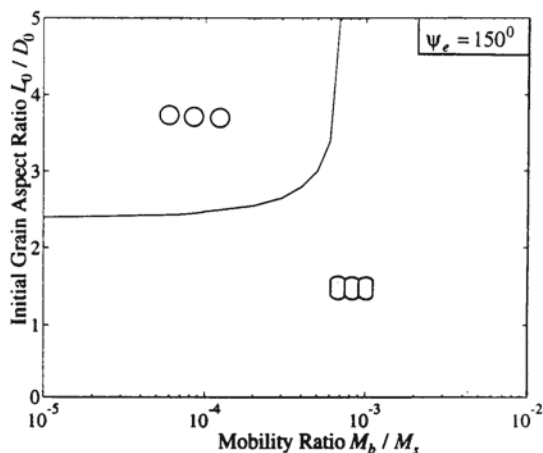

Fig. 3 Evolution Path.

Fig. 4 A diversity map.

Evolution Path

The Galerkin approximation leads to two ordinary differential equations for L and Ψ. The numerical results are plotted in Fig. 3. The solid lines are the energy contours. After the grains pinch off, they spheroidize with only one degree of freedom, Ψ, as represented by the dashed line at the upper left corner. The dotted lines are the evolution paths for various mobility ratios, M_b/M_s. When the grain-boundary mobility is vanishingly small, $M_b/M_s = 0$, the grain length remains constant while the surface grooves; the grains pinch off and spheroidize, approaching a row of isolated spheres. Increasing the mobility ratio to $M_b/M_s = 10^{-3}$ allows the grains to shrink to the state of truncated spheres. Consequently, everything else being fixed, a critical grain-boundary mobility exists, above which the grains shrink to the lowest energy state, the truncated spheres. The evolution path depends on both energetics and kinetics.

Simulations with various values of the control parameters allow us to draw a map in Fig. 4. A point on the map represents a pair of parameters, L_0/D_0 and M_b/M_s. A boundary divides the plane into two regions. A parameter pair in one region makes the grains evolve to isolated spheres, and a parameter pair in the other region makes the grains evolve to truncated spheres.

ACKNOWLEDGMENTS

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