

GLOBAL VIEW OF MICROSTRUCTURAL EVOLUTION: ENERGETICS, KINETICS AND DYNAMICAL SYSTEMS

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ABSTRACT: An evolving material structure is in a non-equilibrium state, with free energy expressed by the generalized coordinates. A global approach leads to robust computations for the generalized thermodynamic forces. Those forces drive various kinetic processes, causing dissipation at spots, along curves, surfaces and interfaces, and within volumetric regions. The actual evolution path, and therefore the final equilibrium state, is determined by the energetics and kinetics. A virtual work principle links the free energy landscape and the kinetic processes, and assigns a viscous environment to every point on the landscape. The approach leads to a dynamical system that governs the evolution of generalized coordinates. The microstructural evolution is globally characterized by a basin map in the coordinate space; and by a diversity map and a variety map in the parameter space. The control of basin boundaries raises the issue of energetic and kinetic bifurcations. The variation of basin boundaries under different sets of controlling parameters provides an analytical way to plot the diversity maps of structural evolution.

KEY WORDS: microstructural evolution, energetics, kinetics, dynamic system

1 INTRODUCTION

In this paper we describe a framework for the global approach to microstructural evolution, applicable to a wide range of thermodynamic forces and kinetic processes. The principle of virtual work plays a central role in connecting the global energetic forces and the kinetics. An evolution process is modeled by a dynamic system for the generalized coordinates. The computations on the energetic forces are robust and insensitive to the local details of material structures. Qualitative features on terminating microstructures and manufacture control will be revealed.

This approach has been illustrated through diversified case studies: such as on diffusion-controlled evolution of closed thermodynamic systems^[1]; evolution of a diffusive void in an elastic solid^[2]; void shape instability^[3]; wrinkling of oxide scales on high temperature

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alloys^[4]; ferroelectric domain evolution^[5]; and capillary instability^[6]. The above-mentioned works came as a departure from the local approach of chemical potential modeling originated from the work of Herring^[7], who extended the chemical potential of Gibbs to non-equilibrium structures.

Global view has long been held among scientists. A non-equilibrium structure is described by a set of generalized coordinates. Kinetics, though proceeds locally, can be transcribed approximately onto the free energy landscape. That approach has been used in modeling non-equilibrium problems, including diffusion^[8], creep void growth^[9], creep crack growth^[10], superplasticity^[11] and powder sintering^[12]. These authors formulated variational principles by assembling local quantities such as chemical potentials and relating them to the boundary conditions. A global version of the above mentioned approach will be formulated here in the framework of virtual work principle (which may lead to a variational principle) for a wide range of non-equilibrium material structures.

2 ENERGETICS IN GENERALIZED COORDINATES

The structure evolution toward an equilibrium state is driven by the change of free energy, denoted by G in this paper. The free energy consists of an internal energy G_0 (the energy of the material system in its reference frame) and a potential energy imposed to the material system by its mechanical and electrical fields:

$$G = G_0 + U - W \quad (1)$$

The internal energy G_0 comes from the bulk of the material, the surface of the material and the interfaces among different components, phases and domains:

$$G_0 = \sum_{\alpha} \Gamma_{\alpha} V_{\alpha} + \gamma_s A_s + \gamma_b A_b \quad (2)$$

where Γ_{α} is the specific chemical energy for the α -th phase, V_{α} the volume of the same phase, γ_s the specific surface tension, and A_s the surface area. The last term in (2) denotes the interface energy formed by interfacial tension γ_b times the interface area A_b , which should be replaced by a summation when interfaces of different types are involved. The internal energy relates to the global quantities, such as volumes and areas, of the material system.

On the other hand, one has to solve the mechanical and electrostatic fields under a prescribed material structure to obtain the potential energy. The potential energy is expressed as the field energy U stored in the material system minus the work supply W to the system. If only mechanical field is of interest, one has

$$U = \int_V \left(\int_0^{\varepsilon_{ij} - \varepsilon_{ij}^p} \sigma_{ij} d\varepsilon_{ij} \right) dV \quad W = \int_{S_t} t_i u_i dS \quad (3)$$

where S_t denotes the surface on which traction t_i is prescribed. We emphasize in (3) that the inelastic strain ε_{ij}^p only dissipates, and does not store energy. For the case of mechanical

field coupled with the electric field, an expression of U can be found from Yang and Suo^[13]. Since (3) only involves integration, the evaluations of potential energy are computational robust and insensitive to the local variation of microstructures.

The global feature of the total free energy suggests a characterization in a global sense, by a set of independent global structural variables. We describe the microstructure with n degrees of freedom, with $q = \{q_1, \dots, q_n\}$ as the generalized coordinates, and $\dot{q} = \{\dot{q}_1, \dots, \dot{q}_n\}$ as the generalized velocities. Quantities that do not change during evolution are called *control parameters*. These parameters control the structural evolution in a material system.

The function $G(q_1, \dots, q_n)$ describes a surface in the space spanned by G, q_1, \dots, q_n . The state of the microstructure is a point on the surface, and an evolution path a descending curve on the surface. We call the surface formed by G and coordinates a free energy landscape. The free energy landscape also depends on a set of non-evolving parameters, denoted by g . The parameter set g contains certain material parameters (such as the surface tension, interface tension and chemical energies of various phases) and loading parameters (such as remote stresses, external electric field, and ambient temperature). Some of the parameters in g , especially those from the second group, are controllable during a microstructural evolution. The free energy landscape in the generalized coordinate space is completely defined by q and g . We restrict the free energy landscape to be single-valued at any generalized coordinates. This restriction eliminates cliffs and foldings in a free energy landscape.

The energetic forces, f_1, \dots, f_n , conjugating to the generalized coordinates are the differential coefficients of the free energy

$$f_i = -\partial G / \partial q_i \quad (4)$$

At a given point on the energy surface, the forces are the slopes of the tangent plane contacting the surface at the point. The negative sign in (4) refers to the sense that these forces release the total free energy. If the external loads vary much slower than the microstructural evolution, then the free energy G depends on time only through the coordinates, the energy variation is

$$\delta G = \sum_{i=1}^n \frac{\partial G}{\partial q_i} \delta q_i = - \sum_{i=1}^n f_i \delta q_i \quad (5)$$

3 KINETICS OF MICROSTRUCTURAL EVOLUTION

The energetics alone neither determines the descending path, nor selects the final state of a microstructural evolution. The actual evolution path, and therefore the final equilibrium state, is determined by the energetics and kinetics. The kinetics of microstructural evolution can have different geometric characteristics. A structural evolution could be movements of points, such as discrete spots or point defects, drifting in a matrix. It could associate with the movement of curves, such as the motion of a dislocation line or a crack front. Microstructural evolution frequently connects to kinetics along surfaces. The examples include surface diffusion, interface or grain boundary diffusion, vapor condensation, grain growth, island formation, electromigration, sintering, surface reaction, and so on. Various transformation

processes, such as martensitic transformation, polarization switch, domain formation, recrystallization, progress by the movements of phase boundaries, domain boundaries and grain boundaries, and consequently belong to the surface kinetics. Finally, a class of microstructural evolutions involve kinetics in volumetric regions, such as lattice diffusion, viscous flow, as well as dislocations and cracks drag by diffused dissipation zones.

All kinetic processes induce dissipation. The total dissipated work, δW_D , is generated by kinetics of all kinds:

$$\delta W_D = \sum_{\alpha=1}^{m_P} p_P^{(\alpha)} \delta I_P^{(\alpha)} + \sum_{\alpha=1}^{m_L} \int_{L_\alpha} p_L^{(\alpha)} \delta I_L^{(\alpha)} dL + \sum_{\alpha=1}^{m_S} \int_{S_\alpha} p_S^{(\alpha)} \delta I_S^{(\alpha)} dS + \sum_{\alpha=1}^{m_V} \int_{V_\alpha} p_V^{(\alpha)} \delta I_V^{(\alpha)} dV \quad (6)$$

We use subscripts P, L, S, V to label the quantities associated with point, line, surface and volume kinetics. The superscript (α) marks the different mechanisms of dissipation. There are m_P kinetics mechanisms at different spots, m_L mechanisms along curves of different types, m_S mechanisms along various surfaces and interfaces, and m_V mechanisms within volumetric regions. The total number of different kinetic mechanisms is $m = m_P + m_L + m_S + m_V$. Follow the notation of Biot^[8], we denote I_P, I_L, I_S and I_V as the amounts of material flow across each spot, unit arc length, unit surface area and unit volume, respectively. Symbols p_P, p_L, p_S and p_V denote the conjugate dissipative forces induced by the variations of I_P, I_L, I_S and I_V . We emphasize that Eq.(6) only states the definition of dissipative forces, not the kinetic laws. The kinetic laws characterize the relationship between the dissipative forces and the material flows, the latter are represented by both the current material structure (including various material flow amounts) and the material fluxes

$$J_P = \dot{I}_P \quad J_L = \dot{I}_L \quad J_S = \dot{I}_S \quad J_V = \dot{I}_V \quad (7)$$

The control parameters in the kinetic processes are the mobility and viscosity parameters. The mobility parameters control the relations between the dissipative forces and the material fluxes when the irreversible material flows take place near material spots, along curves and along surfaces and interfaces. As results, the spots translate; the dislocation lines and crack fronts advance; and the grain boundaries, surface morphologies and cavity surfaces evolve. The viscosity parameters control the relations between the dissipative forces and viscous flow (or lattice diffusion) in volumetric regions. The mobility and viscosity parameters will be denoted in the following by a parameter set d .

We now describe the multiple kinetics in the setting of generalized coordinates. The fluxes are linear to the generalized velocities:

$$J^{(\alpha)} = \sum_{i=1}^n N_i^{(\alpha)}(q) \dot{q}_i \quad (8)$$

The shape functions, $N_i^{(\alpha)}$, $\alpha = 1, \dots, m$, depend on the coordinates but not on the velocities. Similar shape functions interpolate the variations of the material flow amounts and the variations of the generalized coordinates.

Substituting (8) and (7) into (6), one has

$$\delta W_D = \sum_{i=1}^n P_i \delta q_i \quad (9)$$

where the generalized dissipative forces are

$$P_i = \sum_{\alpha=1}^{m_P} p_P^{(\alpha)} N_i^{(\alpha)} + \sum_{\alpha=1}^{m_L} \int_{L_\alpha} p_L^{(\alpha)} N_i^{(m_P+\alpha)} dL + \sum_{\alpha=1}^{m_S} \int_{S_\alpha} p_S^{(\alpha)} N_i^{(m_P+m_L+\alpha)} dS + \sum_{\alpha=1}^{m_V} \int_{V_\alpha} p_V^{(\alpha)} N_i^{(m_P+m_L+m_S+\alpha)} dV \quad (10)$$

Throughout this work, we assume

$$\lim_{\dot{q} \rightarrow 0} P_i(q, \dot{q}; d) = 0 \quad i = 1, \dots, n \quad (11)$$

which excludes the possibility of a non-zero threshold force to cause an infinitesimal dissipation flux.

For the special case of linear kinetics, the generalized dissipative forces assume the following form^[6]

$$P_i = H_{ij}(q; d) \dot{q}_j \quad (12)$$

where the viscosity matrix H_{ij} is given by

$$H_{ij} = \sum_{\alpha=1}^{m_P} \frac{1}{M_P^{(\alpha)}} N_i^{(\alpha)} N_j^{(\alpha)} + \sum_{\alpha=1}^{m_L} \int_{L_\alpha} \frac{1}{M_L^{(\alpha)}} N_i^{(m_P+\alpha)} N_j^{(m_P+\alpha)} dL + \sum_{\alpha=1}^{m_S} \int_{S_\alpha} \frac{1}{M_S^{(\alpha)}} N_i^{(m_P+m_L+\alpha)} N_j^{(m_P+m_L+\alpha)} dS + \sum_{\alpha=1}^{m_V} \int_{V_\alpha} \frac{1}{M_V^{(\alpha)}} N_i^{(m_P+m_L+m_S+\alpha)} N_j^{(m_P+m_L+m_S+\alpha)} dV \quad (13)$$

Quantities M_P, M_L, M_S, M_V denote the mobilities of the respective kinetic processes.

4 PRINCIPLE OF VIRTUAL WORK

Constraints on motion are often imposed by mass conservation. There are infinitely many flux and velocity distributions that conserve mass. We call a motion that conserves mass a *virtual motion*. A virtual motion needs not obey the kinetic laws. The *actual motion* both conserves mass and obeys the kinetic laws.

If a non-equilibrium thermodynamic process is described by the generalized coordinates and proceeded at the generalized velocities. The Lagrangian of the system is denoted by

$$L = G + T \quad (14)$$

where the kinetic energy is defined by

$$T = \frac{1}{2} \int_V \rho \dot{u}_i \dot{u}_i dV = \frac{1}{2} \sum_{i,j=1}^n m_{ij}(q) \dot{q}_i \dot{q}_j \quad (15)$$

where ρ denotes density and m_{ij} denotes the generalized mass matrix. Under any virtual motions, the generalized dissipative forces are defined by the energy released from the Lagrangian, namely

$$\delta L + \sum_{i=1}^n P_i \delta q_i = 0 \quad (16)$$

The first term is the virtual change of Lagrangian, and the remaining terms are the virtual dissipative works. The equation says that, for any virtual motion, the decrease in the Lagrangian balances the induced dissipation. Following its usage in mechanics, we call (16) the *principle of virtual work*. Note that we exclude any dissipation term associated with the motion that does not conserve mass. Substituting (5), (14) and (15) into the above principle, one obtains the following Euler equation:

$$\frac{d}{dt} (m_{ij} \dot{q}_j) + P_i = f_i + \frac{\partial T}{\partial q_i} \quad (17)$$

Many microstructural evolution processes are either slow or spontaneous, so that the inertial force term can be omitted. In quasistatic processes, (17) is reduced to

$$P_i = f_i \quad (18)$$

where P_i is given by (10) and f_i by (5). At a given location of the free energy landscape, the right hand side of (18) provides the energetic driving force for microstructural evolution, while its left hand side assigns a viscous environment. The equation furnishes a dynamic system to govern the evolution. The quasistatic reduction (18) is true for diffusive microstructural evolutions. For non-diffusive kinetics, such as phase transformation or polarization switching, the complete version of (17) should be used. The derivations to follow are confined to quasistatic processes.

If a total dissipation D exists, and can be expressed by dissipation potentials for all kinetic processes, namely

$$D = \sum_{\alpha=1}^m \int_0^{J^{(\alpha)}} p^{(\alpha)}(J) dJ \quad (19)$$

then the principle of virtual work implies a variational principle. Let $J^{(1)}, \dots, J^{(m)}$ be the *actual fluxes* that both conserve mass and obey the kinetic laws (19). From (5), the rate of total free energy depends linearly on the fluxes. Then one can write $\dot{G} = \dot{G}(J^{(1)}, \dots, J^{(m)})$. Introduce a rate potential

$$\Pi = \dot{G} + D = \Pi(J^{(1)}, \dots, J^{(m)}) \quad (20)$$

which refers to the difference between the energy dissipated by the system and the energy released from the system. For a virtual variation of material fluxes, $\delta J^{(1)}, \dots, \delta J^{(m)}$, we explore the consequences for the stationary condition of Π . This condition, coupled with the linear representation of material fluxes by generalized velocities, Eq. (8), leads to

$$\frac{\partial \Pi}{\partial \dot{q}_i} = 0 \quad (21)$$

Substituting (20) into (21) and making use of (5), we arrive at the following dynamic system for microstructural evolution

$$\frac{\partial D}{\partial \dot{q}_i} = -\frac{\partial G}{\partial q_i} \quad (22)$$

We notice that (18) is equivalent to (22) if dissipation potentials exist.

The second variation of Π with respect to the virtual motion is

$$\delta^2 \Pi = \sum_{i,j=1}^n \frac{\partial^2 D}{\partial \dot{q}_i \partial \dot{q}_j} \delta \dot{q}_i \delta \dot{q}_j = \sum_{i,j=1}^n \frac{\partial P_i}{\partial \dot{q}_j} \delta \dot{q}_i \delta \dot{q}_j \equiv \sum_{i,j=1}^n H_{ij} \delta \dot{q}_i \delta \dot{q}_j \quad (23)$$

It is an easy matter to confirm that the actual motion minimizes the functional, provided that the viscosity matrix H_{ij} is positive definite. The definition in (23) indicates the symmetry of H_{ij} . When H_{ij} is positive definite, the actual motion is unique. The uniqueness of the solution might be lost if H_{ij} is no longer positive definite.

At a point on the energy landscape, the energetic force vector points to the direction of the steepest descent and, according to (22), the velocity vector points to a different direction, unless the viscosity matrix happens to be isotropic. Consequently, the evolution path does not usually follow the trajectory of the steepest descent. The second law of thermodynamics requires monotonic increase of total dissipation during a non-equilibrium microstructural evolution

$$\sum_{i=1}^n \frac{\partial D}{\partial \dot{q}_i} \dot{q}_i = \sum_{i=1}^n P_i \dot{q}_i > 0 \quad (24)$$

For nonlinear kinetics, the second law of thermodynamics does not require the positive definiteness of the viscosity matrix. Some kinetic processes do involve non-positive definite viscosity matrix. For a dislocation dragging by Cottrell atmosphere, the drag force first increases with dislocation velocity, reaches its maximum value at a critical velocity, and then declines as the dislocation accelerates to break away from the solute atmosphere.

Combining (24) with (22), one has

$$\sum_{i=1}^n \frac{\partial G}{\partial q_i} \dot{q}_i = \dot{G} < 0 \quad (25)$$

For a quasistatic non-equilibrium thermodynamic process under constant temperature and constant external loading, the total free energy is strictly decreasing. One geometric explanation of (25) is: the second law of thermodynamics requires that the velocity and the energetic force vector make an acute angle. This requirement has powerful consequences in the subsequent derivations on the dynamical system.

5 DYNAMICAL SYSTEM FOR STRUCTURAL EVOLUTION

the viscosity matrix H_{ij} is positive definite, the actual material motion is unique and (22) is invertable. The inversion of (22) with respect to the generalized velocities leads to a dynamic system of canonical form:

$$\dot{q}_i = v_i(q; p) \quad (26)$$

where $p = \{g, d\}$ is the set of all control parameters. Its integration starts from an initial material structure $q_i(t_0)$.

For the case of linear kinetics, the dissipative forces link to generalized velocities linearly by (12), with the viscosity matrix given by (13) and independent of velocities. From the second law of thermodynamics, the symmetric viscosity matrix H_{ij} is positive-definite and consequently invertible. Upon inversion, the evolution equation under linear kinetics law is

$$\dot{q}_i = - \sum_{j=1}^n H_{ij}^{-1}(q; d) \frac{\partial}{\partial q_j} G(q; g) \quad (27)$$

Equation (26) or (27) is a set of autonomous ordinary differential equations for the generalized coordinates, incorporating the information from both energetics and kinetics.

6 ATTRACTORS OF MICROSTRUCTURAL EVOLUTION

In the research of microstructural evolutions, the interest is focused on the evolution destiny, rather than the transients to approach it. A destiny can be described mathematically as the positive limit sets of the dynamical system (26) or (27). Namely, to what states the microstructure would approach as the time t tends to positive infinity.

The positive limit sets of a dynamical system are called the attractors. Known attractors in dynamical systems are sinks, limit cycles, and strange attractors. On the basis of the second law of thermodynamics and the single-value requirement for the free energy landscape, we are able to rule out the limit cycles and strange attractors for quasi-static microstructural evolution under fixed loads and ambient temperature.

A sink must be a critical point. The set of critical points refers to the q values (denoted by q^c) such that $\dot{q}_1, \dots, \dot{q}_n$ vanish. From Eq.(26) and the restriction (11), one concludes that the number and the locations of the critical points only rely on the energy landscape, and irrelevant to the dissipation processes. They are given by

$$\frac{\partial}{\partial q_j} G(q^c; g) = 0 \quad (28)$$

Those critical points appear as peaks, valleys, and saddles of the free energy landscape. At different sets of control parameters g , the number and the locations of the critical points may change.

At any critical point q^c , the phase flow in its neighborhood is determined by the Jacobian matrix. We first discuss the simple case of linear kinetics. Denote $\Delta q_i = q_i - q_i^c$, then the linearized evolution equations for Δq_i are governed by

$$\frac{d}{dt} \Delta q_i = \sum_{j=1}^n L_{ij}(q^c; p) \Delta q_j \quad (29)$$

The Jacobian matrix in (29) is defined by

$$L_{ij} = - \sum_{k=1}^n H_{ik}^{-1}(q^c; d) \frac{\partial^2}{\partial q_k \partial q_j} G(q^c; g) \quad (30)$$

Accordingly, kinetic processes would effect the quantitative values of the Jacobian matrix of a critical point.

It is interesting at this point to examine the structure of Jacobian matrix at a critical point q^c . The $-\frac{\partial^2 G}{\partial q_i \partial q_j}$ factor on the right hand side of (30) represents a negative curvature tensor of the free energy landscape. Since H_{ij} is positive definite, (30) would predict a sink, a source or a saddle if q^c is a valley, a peak, or a saddle of the energy landscape. The incorporation of H_{ik}^{-1} factor in (30), however, has two effects: scaling and twisting. The determinant of the viscosity matrix modulates the evolution speed toward the critical point, the larger the $\sqrt[3]{\det H}$, the slower the trajectories flow into or out of the critical point. The uni-modular part of the viscosity matrix twists the direction of flow trajectories, leading to interesting issues like kinetic bifurcation.

For the case of nonlinear kinetics, a linearized equation of the form (29) can also be obtained under the restriction (11). The H_{ik}^{-1} matrix, however, either vanishes when the dissipative forces fall below the linear relationships with the material fluxes, or becomes unbounded when the dissipative forces surge above the linear relationships with the material fluxes. The evolution in the neighborhood of q^c would be infinitely slow in the former case, and infinitely fast in the latter case.

The eigenvalues of the Jacobian matrix defines the nature of the critical point. Those eigenvalues λ are solved by

$$\det \{L_{ij} - \lambda I_{ij}\} = 0 \quad (31)$$

where I_{ij} is the identity matrix in the n -dimensional space of generalized coordinates. The Jacobian matrix has n eigenvalues. They can either be real, or form complex-conjugates. Parallel to the argument to rule out a periodic orbit, one can exclude the possibility of a pair of purely imaginary eigenvalues. Thus neither a center, nor a Hopf bifurcation in the center manifold, exists in quasistatic microstructural evolutions. All eigenvalues are classified into three groups: (1) the eigenvalues of positive real parts, leading to an unstable manifold; (2) the eigenvalues of negative real parts, leading to a stable manifold; and (3) the eigenvalue zero, leading to a center manifold. The first two classes are termed hyperbolic eigenvalues. A non-hyperbolic eigenvalue (namely the eigenvalue zero) leads to energetic bifurcation. In the absence of eigenvalue zero, a critical point is a source if all eigenvalues have positive real parts, a sink if all eigenvalues have negative real parts, a saddle if eigenvalues have mixed signs.

The destinies of microstructural evolutions are characterized by the attractors. If the viscosity matrix is positive definite, the judgment for the sinks only relies on the free energy landscape.

Each attractor has an *attracting basin* under a prescribed set of control parameters. That attracting basin embodies all initial states in the q -space which have the same destiny. Though the attractors are identified by the free energy landscape, the respective attracting basins emerge as an interplay between energetics and kinetics.

Let $\{q_{(1)}^a, \dots, q_{(N)}^a\}$ denote the coordinates of attractors, and N is the total number of the attractors, termed the *variety* of terminating material structures. In a finite domain

of generalized coordinates, the structural variety is given by the sinks in that domain. For the case of an infinite domain, one may find the extra-sinks at infinity through a Poincaré transformation. Within individual attracting basins, the ground levels of free energy at the attractors are

$$G_{(l)} = G(q_{(l)}^a) \quad (32)$$

The attractors with lower ground free energies are favored if large perturbations by dynamic excitation are allowed. We discuss two issues: (1) how to construct a *basin map* in the phase space so that various attracting basins are separated by basin boundaries; and (2) in each attracting basin, how long to evolve an initial state to the terminating material structure.

For graphical convenience, we restrict the discussion for the first issue to the two dimensional case. Each sink has a basin such that any initial state located within the basin would eventually evolve to that sink. The boundaries among various basins are the ridges (not necessarily to be lines), or separatrices of the dynamical system. The basin map around a sink is composed by boundary segments that connect the nearby sources (peaks) to the adjacent saddles, and that connect one saddle to a nearby saddle. Any segment of the basin boundaries is the evolution path from a source or the most convex path of a saddle to the most concave path of a nearby saddle. The latter case of saddle connection is unstable and may lead to bifurcations. For the integration stability of the separatrices, it is easier to obtain the basin boundaries if one starts from the most concave path of a saddle point and integrates backward. When proceeding in this way, the backward integration path would converge to the desired basin boundary even though the initial data is slightly inaccurate.

We next describe how to initiate the backward integration. For the two dimensional case, the determinant of the Jacobian matrix is negative near a saddle point. Among the two eigenvalues of that point, one is positive and the other is negative. The negative eigenvalue is

$$\lambda_- = -L_m - \sqrt{L_m^2 - \det \mathbf{L}} \quad L_m = \frac{1}{2}(L_{11} + L_{22}) \quad (33)$$

The associated eigenvector is

$$\mathbf{P}_- = \frac{1}{\sqrt{L_{12}^2 + (\lambda_- - L_{11})^2}} \begin{Bmatrix} L_{12} \\ \lambda_- - L_{11} \end{Bmatrix} \quad (34)$$

The backward integration can be started from an initial state slightly off the saddle point in the direction of \mathbf{P}_- .

We now address the second issue concerning the evolution time under a general n -dimensional case. For the case of nonlinear kinetics, the descending time from an initial state q_i^0 to its attractor q_i^a can be found from (26) as

$$t = \int_{q^0}^{q^a} \sum_{i=1}^n \frac{\partial G}{\partial q_i} dq_i / \sum_{k=1}^n v_k \frac{\partial G}{\partial q_k} \quad (35)$$

For the case of linear kinetics, (35) is reduced to

$$t = - \int_{q^0}^{q^a} \sum_{i=1}^n \frac{\partial G}{\partial q_i} dq_i / \sum_{k=1}^n \sum_{j=1}^n H_{jk}^{-1} \frac{\partial G}{\partial q_j} \frac{\partial G}{\partial q_k} \quad (36)$$

Influences on the evolution time now become transparent. The steeper the downward slope, the faster the structure evolves in a material; the more slippery in the downward steepest descend direction, the faster the structure evolves; and vice versa. Equations (35) and (36) put the time-keeping role of kinetics in a quantitative perspective.

The characteristic time for a trajectory to approach the attractor is inversely proportional to the trace of the Jacobian matrix. For linear kinetics, this characteristic time is

$$t_c = \frac{1}{n} \sum_{k=1}^n \sum_{j=1}^n H_{jk}(q^c; d) \left(\frac{\partial^2 G(q^c; g)}{\partial q_j \partial q_k} \right)^{-1} \quad (37)$$

7 DIVERSITY MAPS

Consider a prescribed initial state q^0 in the phase space q . We examine various processes starting from the same raw state q^0 under different sets of control parameters. As shown in Fig.1(a), the basin boundary $\partial B(p)$ at a set of control parameter p is on the right of q^0 . The structural evolution would end up at an attractor q_{left}^a located on the left side of the basin boundary. At a different set of controlling parameters p^* , the basin boundary $\partial B(p^*)$ may move to the left side of q^0 , and for this case the structural evolution would approach another attractor q_{right}^a located on the right side of the basin boundary, as shown in Fig.1(b). We observe that the variation of the control parameters p may cause a shift on the terminating material structures.

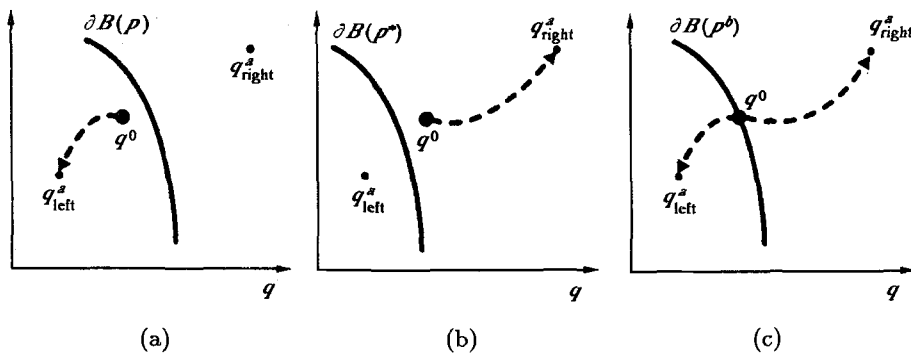


Fig.1 Shifting of basin boundaries. (a) basin boundary $\partial B(p)$ locates on the right of the initial state; (b) basin boundary $\partial B(p^*)$ locates on the left of the initial state; (c) basin boundary $\partial B(p^b)$ just passes the initial state, a destiny bifurcation occurs.

Under a specific set of the control parameters p^b , the basin boundary $\partial B(p^b)$ passes q^0 , as shown in Fig.1(c). This p^b set describes a *destiny bifurcation*. In actual microstructural evolution processes, if the destiny bifurcation is manipulated by changing g , such as by applying loads, we call it an energetically controlled destiny bifurcation; if the destiny bifurcation is achieved by changing d , such as by varying mobility, we call it a kinetically controlled destiny bifurcation, or simply kinetic bifurcation. An interesting example of kinetic bifurcation is examined in detail by Sun et al.^[6] for the structural evolution of a row

of grains.

The above considerations lead us to use the control parameters as coordinates to construct a *parameter space*, in which each point represents a set of parameters. All parameter sets p^b for destiny bifurcation form surfaces in the parameter space. Then parameter space is divided into different regions, called parameter regions, separating by those surfaces. Any parameter set in one parameter region leads to the same terminating material structure. The adjacent parameter regions lead to different terminating structures. Disjoined parameter regions may or may not have the same terminating structure.

Under a fixed raw state of a material system, the diversity map contains a complete knowledge on the evolution control to achieve a desired equilibrium structure. The actual control of the structural evolution can be exercised by varying both energetic and kinetic parameters.

The determination of the diversity map is one of the ultimate goals to link the processing with material structures. A diversity map reserves global information of the structure, as demonstrated by Sun et al.^[6]. This feature may simplify the actual calculation of a diversity map. Modeling details of a structural evolution process only affect the exact position of the boundary. Given the uncertainties in the experimental data of the parameters, a simple model that yields an approximate boundary is often adequate.

The variety of terminating material structures, N , depends on the control parameters, and is irrelevant to the initial states. A *variety map* in the parameter space can also be constructed, as illustrated in Fig.2. We mark the varieties in various parameter regions in Fig.2. The boundaries separating different regions in the variety map correspond to the parameter sets at which a variety bifurcation occurs. There are two types of bounding curves in a variety map, as shown in solid and dashed curves in Fig.2. The solid curves refer to a variety change, which controls the parameter set to move from one side of the solid curve

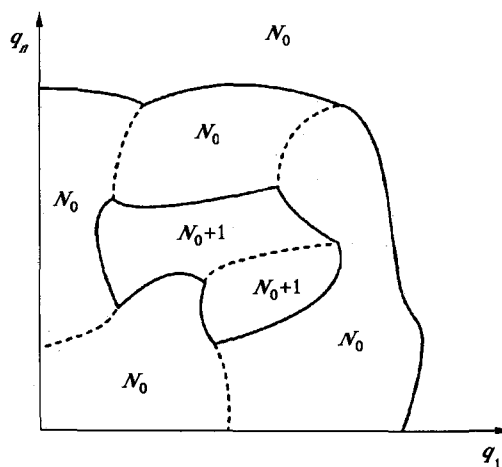


Fig.2 Variety map in the space of energetic parameters. The solid curves denote supercritical or subcritical bifurcations with variety change; the dashed curves denote transcritical bifurcations that reserve the variety but switch the terminating material structures.

to the other side. If the variety increases by one, we call it a supercritical bifurcation; if the variety decreases by one, we call it a subcritical bifurcation. The dashed curves in Fig.2 refer to the case that variety is unchanged across the curve, but the terminating material structures switch. Such a situation relates to a transcritical bifurcation. The structural variety is not influenced by kinetics, provided that the viscosity matrix is positive definite. Thus, the variety bifurcation is energetic in nature. A variety map should be drawn in the subspace g of the parameter space, as exercised in Fig.2.

8 CONCLUDING REMARKS

In this paper, we have described a global vision for structural evolution. One may describe an evolving structure with any number of generalized coordinates, global or local, depending on one's purpose. The free energy is represented by a landscape in the space spanned by the free energy and the generalized coordinates. A point on the landscape represents a (non-equilibrium) state, and the slopes of the tangent plane contacting the point represent the generalized forces. This formulation works for kinetics of many types. Its geometric characterization contains the kinetic processes occurring at discrete spots, along curves or surfaces, and within volumetric regions. It covers linear kinetics and the monotonic nonlinear kinetics, in which the viscosity matrix is positive definite. The principle of virtual work assigns a viscous environment to any points of the landscape. A dynamical system emerges to govern the evolution of the generalized coordinates.

For a quasi-static process under constant loads and ambient temperature, the attractors and bifurcation of the attractors assume a simple picture. There are only sinks, no periodic attractors, no strange attractors, no chaos. The only variety bifurcations are those associated with the eigenvalue zero. The studies on basin map, diversity map and variety map would provide basic understandings for the individual microstructural evolution processes. This global view will lead to robust computational scheme to simulate diverse phenomena in microstructural evolutions.

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