Reactive flow in solids

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ABSTRACT

When guest atoms diffuse into a host solid and react, the host may flow inelastically. Often a reaction can stimulate flow in a host too brittle to flow under a mechanical load alone. We formulate a theory of reactive flow in solids by regarding both flow and reaction as nonequilibrium processes, and placing the driving forces for flow and reaction on equal footing. We construct chemomechanical rate-dependent kinetic models without yield strength. In a host under constant stress and chemical potential, flow will persist indefinitely, but reaction will arrest. We also construct chemomechanical yield surface and flow rule by extending the von Mises theory of plasticity. We show that the host under a constant deviatoric stress will flow gradually in response to ramp chemical potential, and will ratchet in response to cyclic chemical potential.

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1. Introduction

Reactive flow in gases has been extensively studied, particularly in the context of combustion, where the chemistry of reaction and the mechanics of flow play distinct roles, incorporated in a broadly applicable theory (Williams, 1985). Reactive flow in liquids, as well as in multi-phase fluid flows, has also received much attention (Oran and Boris, 2005; Prud'homme, 2010). By comparison, the theory of reactive flow in solids is underdeveloped, even though concurrent reaction and flow in solids are commonly observed. For example, chemical reactions in cement cause inelastic deformation (Ulm et al., 2000). As another example, when a metal reacts with oxygen in the environment to form a layer of oxide, much of the new oxide forms at either the metal/oxide interface or the oxide/environment interface, depending on the relative rate of diffusion of metal and oxygen through the oxide; however, new oxide also forms inside the existing oxide, causing the oxide to flow inelastically (Tolpygo and Clarke, 2004; Oh and Thompson, 2011). As a closely related phenomenon, when an aluminum-containing alloy oxidizes, oxygen preferentially reacts with aluminum, driving aluminum atoms to diffuse out and changing the composition of the alloy, so that the alloy flows (Suo et al., 2003; El Kadiri et al., 2008). The phenomenon is analogous to the Kirkendall effect, when different species of atoms mix by diffusion, causing the movements of inert markers in the direction of diffusion (Smigelskas and Kirkendall, 1947), and dimensional changes normal to the direction of diffusion (Balluffi and Alexander, 1952). Even a pure metal develops stress and flow during deposition (Chason et al., 2002) and electromigration (Pharr et al., 2011); one may speak of self-diffusion and self-reaction when atoms interact with defects such as vacancies, dislocations, and grain boundaries (Balluffi and Seigle, 1955; Suo, 2004; Svoboda and Fischer, 2009). Reactive flow may also be significant in metallic glasses (Huang et al., 2002).

The study of reactive flow in solids has recently come into sharp focus as lithium-ion batteries achieve spectacular commercial success. Both electrodes of a lithium-ion battery are hosts of lithium. During charge and discharge, lithium diffuses out of one electrode, migrates across the electrolyte, and then diffuses into the other electrode, while the

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electrodes deform (Benedek and Thackeray, 2002; Huggins, 2009; Zhang, 2011). A high-capacity electrode, silicon, can absorb a large amount of lithium and swell more than three times its initial volume (Beaulieu et al., 2001; Chan et al., 2008; Liu et al., 2011; Yu et al., 2012). The deformation is inelastic: after a cycle of lithiation and delithiation, silicon atoms are rearranged (Zhao et al., 2011a). When a thin film of silicon on a substrate is lithiated and delithiated, the stress in the film exhibits yield strength (Sethuraman et al., 2010; Soni et al., 2011). Atomistic simulation shows that lithium assists the flow of silicon by participating in bond breaking and reforming (Zhao et al., 2011c).

For a small enough piece in a host, the rate of evolution of the piece is limited by reaction and flow, rather than by diffusion within the piece, so that the piece evolves through a sequence of homogeneous states (Fig. 1). Much of the existing theories of reactive flow in solids have assumed that, in each small piece of the host, reaction has reached equilibrium, while flow is a nonequilibrium process (Stephenson, 1988; Zhao et al., 2011b; Bower et al., 2011; Cui et al., 2012). This assumption has been made despite that both reaction and flow in solids involve similar atomic movements. The assumption precludes a powerful coupling between reaction and flow: when local chemical equilibrium has not been reached, the driving force for reaction breaks and forms atomic bonds, enabling the host to flow under a low enough deviatoric stress without fracture.

Here we formulate a theory that regards both flow and reaction as nonequilibrium processes, placing driving forces for flow and reaction on equal footing (Fig. 1). Flow changes the shape of the electrode, preserves its composition and volume, and is driven by the deviatoric stress. By contrast, reaction changes the composition and volume of the electrode, and is driven by a combination of the mean stress and the chemical potential of lithium in the environment. Both flow and reaction are mediated by breaking and forming atomic bonds.

Following a common practice in formulating a field theory, we regard a host as a sum of many small pieces (Fig. 1). Each small piece evolves by flow and reaction through a sequence of homogeneous states. Different pieces communicate through the compatibility of deformation, balance of forces, conservation of the number of guest atoms, and kinetics of diffusion. We will treat infinitesimal deformation in this paper, and will extend the theory to finite deformation elsewhere (Brassart and Suo, 2012). We will devote the body of this paper to the homogeneous states of an individual small piece, and will outline the theory of inhomogeneous states in the host as a whole in Appendix A. The concurrent reaction and flow satisfies a thermodynamic inequality (Section 2). A rheological model is formulated under two assumptions: reaction and flow are both nonequilibrium processes (Section 3), and the inelastic volumetric change of the host is entirely due to the uptake of guest atoms (Section 4). The free energy of the host is taken to be a function of the elastic strain and the concentration of the host atoms (Section 5). Under the constraint of the thermodynamic inequality, we construct kinetic models of reactive flow in solids. For a rate-dependent kinetic model without yield strength, for a host under constant deviatoric stress and chemical potential, flow will persist indefinitely, but reaction will arrest (Sections 6 and 7). For a rate-independent kinetic model with yield strength, a host under a constant deviatoric stress will deform gradually in response to a ramp chemical potential, and will ratchet in response to a cyclic chemical potential (Section 8).

The theory is related to that of reactions in cement (Ulm et al., 2000), of reactions in oxides (Loeffel and Anand, 2011), of poroviscoplasticity in soils (Rice, 1977; Viesca et al., 2008), and of poroviscoelasticity in elastomeric gels (Hu and Suo, 2012). While these theories—and ours—share broad considerations of thermodynamics, kinetics and mechanics, specific rheological behavior can be very different for various classes of materials and types of reactions. For example, under a constant load, a metal can creep indefinitely, while inelastic deformation in elastomeric gels will arrest. A reaction in a condensed phase may be modeled as two distinct processes: insertion of the guest atoms into the host, and reaction between the guest atoms and other species of atoms (de Groot and Mazur, 1984; Loeffel and Anand, 2011). The extent of each process is characterized by a distinct variable. This approach can be applied to the host–guest reaction (Appendix B). In the body of this paper, however, we develop a theory that regards insertion and reaction as one process, and characterize the extent of the process by a single variable: the concentration of the guest atoms in the host. The resulting theory takes a simpler form.
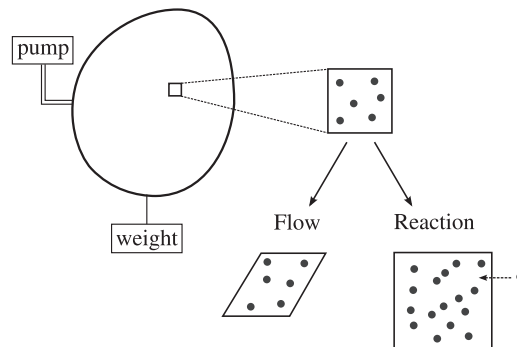
Fig. 1. Guest atoms diffuse into a host and react, while the host flows. The host is a sum of many small pieces. Each small piece evolves through a sequence of homogeneous states by flow and reaction. Different small pieces of the host communicate through the compatibility of deformation, balance of forces, conservation of the number of guest atoms, and kinetics of diffusion of the guest atoms.
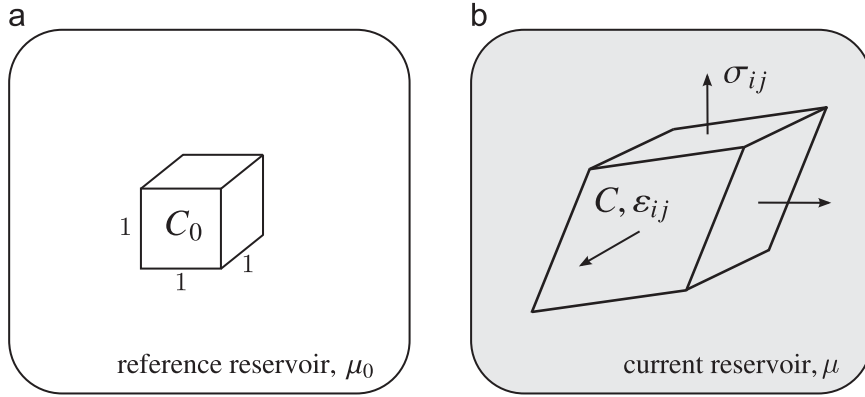
Fig. 2. Subject to mechanical forces and immersed in a reservoir of guest atoms, a host evolves by flow and reaction through a sequence of homogeneous states. (a) In the reference state, subject to no stress and in contact with a reservoir in which the chemical potential of guest atoms is μ_0, the host is a unit cube and contains C_0 number of guest atoms. (b) In the current state, subject to stress σ_{ij} and in contact with a reservoir in which the chemical potential of guest atoms is μ, the host deforms into a parallelepiped of strain ε_{ij} and contains C number of guest atoms.

2. Nonequilibrium thermodynamics of homogeneous states

Consider a setup of a host, a reservoir, a species of guest atoms, and a set of applied forces (Fig. 2). The host and the reservoir may each contain many species of atoms, but can only exchange a single species of atoms: the guest atoms. The host is so small that its rate of evolution is limited by reaction and flow, rather than by diffusion within the host. The host evolves by reaction and flow through a sequence of homogeneous states. In the reference state, the host is a unit cube containing C_0 number of guest atoms and is subject to no applied forces, while the chemical potential of the guest atoms in the reservoir is μ_0. The host and the reservoir equilibrate with each other in the reference state, but not in the current state. In the latter, the host is subject to a state of stress σ_{ij}, while the chemical potential of the guest atoms in the reservoir is μ. The host contains C number of guest atoms, and deforms into the shape of a parallelepiped by a state of strain ε_{ij} relative to the reference state. We restrict our analysis to isothermal processes, and do not list temperature as a variable.

When the host is subject to fixed stresses σ_{ij} and in contact with the reservoir in which the chemical potential of the guest atoms is fixed at μ, one can measure the strain ε_{ij} and the concentration C as a function of time. This experiment can be carried out without knowing any process inside the host. Thus, the strain ε_{ij}, stress σ_{ij}, concentration C, and chemical potential μ are external variables: they can be represented by changes external to the host. The stress can be represented by hanging weights. In the current state, when the host deforms by a small amount $\delta\varepsilon_{ij}$, the potential energy of the weights changes by $-\sigma_{ij}\delta\varepsilon_{ij}$. The chemical potential of the guest atoms in the reservoir can be varied by changing the composition of the reservoir. Associated with the transfer of δC number of guest atoms from the reservoir to the host, the Helmholtz free energy of the reservoir changes by $-(\mu-\mu_0)\delta C$.

These external variables appear in a thermodynamic inequality. Let W be the Helmholtz free energy of the host in the current state minus the Helmholtz free energy of its constituents in the reference state. (The constituents in the reference state consist of the host with C_0 number of guest atoms, as well as $(C-C_0)$ number of guest atoms in the reservoir). The host, the hanging weights and the reservoir together form a composite thermodynamic system. The composite exchanges energy with the rest of the world by heat, but not by work. The composite conserves all species of atoms. The Helmholtz free energy of the composite is the sum of the Helmholtz free energy of the host, the potential energy of the hanging weights, and the Helmholtz free energy of the reservoir. When the composite is in a state of equilibrium, thermodynamics requires that the change of the Helmholtz free energy of the composite should vanish. When the composite is not in a state of equilibrium, however, thermodynamics requires that the change of the Helmholtz free energy of the composite should not increase. These statements are summarized as

$$\delta W - \sigma_{ij}\delta\varepsilon_{ij} - (\mu-\mu_0)\delta C \leq 0. \tag{1}$$

The variation means the value of a quantity at a time minus that at a slightly earlier time. As usual in thermodynamics, this inequality involves the direction of time, but not the duration of time.

3. Reaction and flow are both nonequilibrium processes

To specify a nonequilibrium state of the host, we identify a set of internal variables by describing a rheological model. The total strain of the host, ε_{ij}, is taken to be the sum of an elastic strain ε_{ij}^e and inelastic strain ε_{ij}^i:

$$\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^i. \tag{2}$$

The elastic strain represents distortion of atomic bonds with no rearrangement of atoms. The inelastic strain represents rearrangements of atoms, including both the inelastic flow and the uptake of additional guest atoms. The six components of the inelastic strain are internal variables that characterize dissipative processes in the host.

The Helmholtz free energy of the host is taken to depend only on the elastic strains and the concentration:

$$W = W(\boldsymbol{\varepsilon}^e, C). \tag{3}$$

Thus, the Helmholtz free energy is a function of seven independent variables. We could also make the Helmholtz free energy depend on the inelastic strains ε_{ij}^i to represent, for instance, the effect of a back stress; see a recent review of plasticity theories by Chaboche (2008). Here we adopt (3) as an assumption of the rheological model. According to differential calculus, when the independent variables change by $\delta\varepsilon_{ij}^e$ and δC, the Helmholtz free energy changes by $\delta W = (\partial W/\partial\varepsilon_{ij}^e)\delta\varepsilon_{ij}^e + (\partial W/\partial C)\delta C$.

Under assumptions (2) and (3), the thermodynamic inequality (1) becomes

$$\left[\sigma_{ij} - \frac{\partial W(\boldsymbol{\varepsilon}^e, C)}{\partial\varepsilon_{ij}^e}\right]\delta\varepsilon_{ij}^e + \sigma_{ij}\delta\varepsilon_{ij}^i + \left[\mu - \mu_0 - \frac{\partial W(\boldsymbol{\varepsilon}^e, C)}{\partial C}\right]\delta C \geq 0. \tag{4}$$

The inequality (4) holds for the thirteen independent variations, $\delta\varepsilon_{ij}^e$, $\delta\varepsilon_{ij}^i$ and δC. When the inelastic strain and concentration are held fixed, $\delta\varepsilon_{ij}^i = 0$ and $\delta C = 0$, the host can still deform elastically, $\delta\varepsilon_{ij}^e \neq 0$. Under these conditions, and assuming that the host equilibrates with the applied loads, (4) reduces to an equality for arbitrary small changes $\delta\varepsilon_{ij}^e$, giving that

$$\sigma_{ij} = \frac{\partial W(\boldsymbol{\varepsilon}^e, C)}{\partial\varepsilon_{ij}^e}. \tag{5}$$

This equation is the condition of partial equilibrium with respect to the elastic strain, and results from as yet another assumption of the rheological model. Alternatively, one could consider a stress relaxing in time (Ziegler and Wehrli, 1987). Such behavior would appear in the Kelvin–Voigt model for a viscoelastic material. Here we do not account for this behavior, and will adopt (5).

The thermodynamic inequality (4) now reduces to

$$\sigma_{ij}\delta\varepsilon_{ij}^i + \left[\mu - \mu_0 - \frac{\partial W(\boldsymbol{\varepsilon}^e, C)}{\partial C}\right]\delta C \geq 0. \tag{6}$$

This inequality holds for seven independent variations $\delta\varepsilon_{ij}^i$ and δC that measure the extent of flow and reaction. The inequality also identifies the thermodynamic driving forces: the stress σ_{ij} drives inelastic deformation, and the quantity $\mu - \mu_0 - \partial W(\boldsymbol{\varepsilon}^e, C)/\partial C$ drives reaction. Recall that μ is the chemical potential of the guest atoms in the reservoir in the current state, and μ_0 is the chemical potential of the guest atoms in the reservoir in the reference state, so that $\mu - \mu_0$ represents the chemical load applied on the host associated with the change of the reservoir. The quantity $\partial W(\boldsymbol{\varepsilon}^e, C)/\partial C$ defines the chemical potential of the guest atoms in the host in the current state (Gibbs, 1876, 1878). Consequently, the scalar $\mu - \mu_0 - \partial W(\boldsymbol{\varepsilon}^e, C)/\partial C$ is the unbalanced chemical potential that drives reaction. When $\mu - \mu_0 - \partial W(\boldsymbol{\varepsilon}^e, C)/\partial C > 0$, the chemical potential of the guest atoms in the reservoir exceeds that in the host, motivating the guest atoms to move from the reservoir to the host. When $\mu - \mu_0 - \partial W(\boldsymbol{\varepsilon}^e, C)/\partial C < 0$, the chemical potential of the guest atoms in the reservoir is below that in the host, motivating the guest atoms to move from the host to the reservoir.

4. Inelastic volumetric change of the host is entirely due to the uptake of the guest atoms

In a metal, the volumetric change is caused by elasticity, and inelastic volumetric change is negligible (Bridgman, 1923). We now generalize this observation by assuming that the host flows without inelastic volumetric change when the concentration is fixed. The volumetric strain is ε_{kk} and the deviatoric strain is $e_{ij} = \varepsilon_{ij} - \varepsilon_{kk}\delta_{ij}/3$. Similar definitions hold for elastic and inelastic strains: $e_{ij}^e = \varepsilon_{ij}^e - \varepsilon_{kk}^e\delta_{ij}/3$ and $e_{ij}^i = \varepsilon_{ij}^i - \varepsilon_{kk}^i\delta_{ij}/3$. As a generalization of the classical theory of plasticity, we assume that the inelastic volumetric strain is a function of the concentration of the inserted atoms:

$$\varepsilon_{kk}^i = F(C). \tag{7}$$

Under this assumption, inelastic volumetric strain represents the *insertion* of atoms, and the deviatoric inelastic strains represent the *flow* of atoms. An assumption similar to (7) has been commonly used to describe polymeric gels (Hong et al., 2008; Cai and Suo, 2012). However, the elastic volumetric strain in polymer gels is typically negligible, so that the total volumetric strain is assumed to be a function of the concentration. When the concentration changes by δC, the inelastic volumetric strain changes by $\delta\varepsilon_{kk}^i = \Omega\delta C$, where the slope of the function $\Omega = dF(C)/\partial C$ is the inelastic change in the volume of the host associated with inserting one guest atom.

This assumption (7) places a constraint between the inelastic volume change and the number of atoms in the host. Under the constraint, the thermodynamic inequality (6) becomes

$$s_{ij}\delta e_{ij}^i + \zeta\Omega\delta C \geq 0, \tag{8}$$

where

$$\zeta = \sigma_m + \frac{\mu - \mu_0}{\Omega} - \frac{\partial W(\boldsymbol{\varepsilon}^e, C)}{\Omega \partial C}.$$ (9)

The mean stress is defined by $\sigma_m = \sigma_{kk}/3$ and the deviatoric stress by $s_{ij} = \sigma_{ij} - \sigma_m \delta_{ij}$. Inequality (8) identifies the deviatoric stress as the driving for deviatoric inelastic strain, and $\zeta\Omega$ as the driving force for reaction. The contribution of the mean stress stems from the constraint (7). The pressure-like quantity ζ is known as the osmotic pressure.

The thermodynamic inequality (8) can be interpreted in geometric terms. The six independent components of $(\mathbf{s}, \zeta)$ form a vector in a linear space of six dimensions. In the same space, the six independent components of $(\delta\mathbf{e}^i, \Omega\delta C)$ form another vector. The bilinear form $s_{ij}\delta e_{ij}^i + \zeta\Omega\delta C$ is the inner product of the two vectors. Inequality (8) requires that the angle between the vectors $(\mathbf{s}, \zeta)$ and $(\delta\mathbf{e}^i, \Omega\delta C)$ be acute.

Setting the driving force for reaction to zero, $\zeta = 0$, we recover $\mu = \mu_0 - \Omega\sigma_m + \partial W(\boldsymbol{\varepsilon}^e, C)/\partial C$. That is, the osmosis between the host and the reservoir is balanced by the mean stress in the host. This assumption of the partial equilibrium with respect to insertion is commonly adopted in the literature, for instance in the context of lithium-ion batteries (Zhao et al., 2011b; Bower et al., 2011; Bhandakkar and Johnson, 2012; Cui et al., 2012; Sheldon et al., 2012). The equilibrium chemical potential recovers the well-known expression of Larché and Cahn (1973). Assuming chemical equilibrium unrealistically restricts the power of the reaction to stimulate flow. In the present work, we do not assume chemical equilibrium. Because both inelastic deformation and reaction involve similar atomic rearrangement, to be consistent, in this paper we assume that reaction and inelastic deformation are both nonequilibrium processes.

The thermodynamic inequality (8) is satisfied by prescribing a kinetic model to co-evolve reaction and flow. A general kinetic model assumes that the rates of inelastic deviatoric strain and concentration are functions of the thermodynamic driving forces:

$$\frac{de_{ij}^i}{dt} = f_{ij}(\mathbf{s}, \zeta), \quad \frac{dC}{dt} = g(\mathbf{s}, \zeta).$$ (10)

The kinetic equations must satisfy the inequality (8) for independent variations of the six components of the inelastic strain and the concentration. The assumption (7) provides a constraint, which can also be regarded as a special kinetic equation. The kinetic model couples flow and reaction: both mechanical and chemical driving forces affect the rates of inelastic deviatoric strains and concentration.

The rheological model is pictured with an arrangement of springs and dashpots (Fig. 3). The cartoons illustrate a fundamental difference between flow and reaction: flow is represented by a spring and dashpot in series (the Maxwell model), while reaction is represented by a spring and a dashpot in parallel (the Kelvin model). Assuming a rate-dependent kinetic model with no yield strength, a host under constant stress and chemical potential will flow indefinitely, but reaction will arrest. The chemical load $(\mu - \mu_0)/\Omega + \sigma_m$ is shared by a spring and a dashpot in parallel. The force on the dashpot is the osmotic pressure ζ, and vanishes at equilibrium. The force on the spring is $\partial W(\boldsymbol{\varepsilon}^e, C)/\Omega\partial C$, and is the change in the free energy of the host associated with the uptake of the guest atoms.
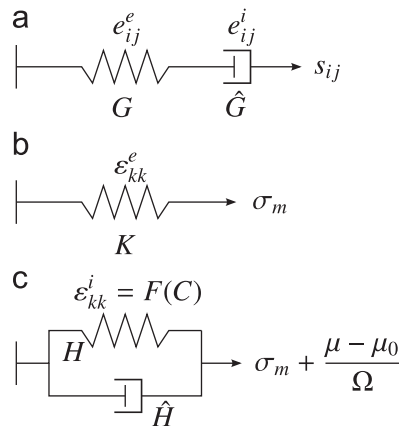
Fig. 3. The rheological model assuming that the inelastic volumetric change of the host is entirely due to the uptake of the guest atoms. (a) The deviatoric strain (flow) is driven by the deviatoric stress, and is represented by a spring and a dashpot in series. (b) The elastic volumetric strain is driven by the mean stress, and is represented by a spring. (c) The inelastic volumetric strain (reaction) is driven by $\sigma_m + (\mu - \mu_0)/\Omega$, and is represented by a spring and a dashpot in parallel. The springs and dashpots are identified with modulus and viscosity of a linear rheological model, but the springs and dashpots can also be nonlinear. Interactions between different types of responses are not represented in these cartoons.

5. Taylor expansions

This section specifies the forms of the functions $F(C)$ and $W(\mathbf{\varepsilon}^e, C)$ assuming that the current state is close to the reference state in that $(C - C_0)$ and ε_{ij}^e are small. Expand (7) into the Taylor series to the leading order, we obtain that

$$\varepsilon_{kk}^i = \Omega(C - C_0), \tag{11}$$

where $\Omega = dF(C)/dC$ is calculated at $C = C_0$.

We next expand the free-energy function $W(\mathbf{\varepsilon}^e, C)$ around the reference state, $\varepsilon_{ij}^e = 0$ and $C = C_0$. Recall that the reference state is a state of equilibrium and that $W(0, C_0) = 0$. Consequently, the leading order terms of the function $W(\mathbf{\varepsilon}^e, C)$ are collectively a quadratic form of ε_{ij}^e and $(C - C_0)$. Here we further assume that the host is isotropic, so that the function $W(\mathbf{\varepsilon}^e, C)$ depends on the elastic strain tensor through its invariants. The only distinct invariants of the elastic strain tensor quadratic in the components are $e_{ij}^e e_{ij}^e$ and $(\varepsilon_{kk}^e)^2$. Consequently, the most general expression for the free-energy function for the linear, isotropic host is the quadratic form

$$W = G e_{ij}^e e_{ij}^e + \frac{1}{2} K (\varepsilon_{kk}^e)^2 + \frac{1}{2} H \Omega^2 (C - C_0)^2 + M \Omega \varepsilon_{kk}^e (C - C_0). \tag{12}$$

Here G is the shear modulus, K the bulk modulus, H the chemical modulus, and M the chemomechanical modulus. While G, K, H are represented by the elastic constants of the springs in the rheological model (Fig. 3), M cannot be so represented. The reference state is taken to be a stable state of equilibrium, so that the quadratic form (12) is positive-definite, requiring $G > 0$, $K > 0$, $H > 0$ and $KH > M^2$. The sign of M is unrestricted.

Inserting the free-energy function (12) into (5), we obtain that

$$s_{ij} = 2G e_{ij}^e, \tag{13}$$

$$\sigma_m = K \varepsilon_{kk}^e + M \Omega (C - C_0). \tag{14}$$

In a linear, isotropic model, the deviatoric stress is independent of the change in the concentration. The shear modulus G relates the deviatoric stress and the deviatoric elastic strain. The bulk modulus K relates the mean stress to the volumetric elastic strain. The chemomechanical modulus M relates the mean stress to the change in the concentration. Eq. (14) indicates that, even during free swelling ($\sigma_m = 0$), a change in the concentration will induce an elastic volumetric strain.

Rearranging (14), we obtain that $\varepsilon_{kk}^e = [\sigma_m - M\Omega(C - C_0)]/K$. The net volumetric strain, $\varepsilon_{kk} = \varepsilon_{kk}^e + \varepsilon_{kk}^i$, is given by

$$\varepsilon_{kk} = \frac{\sigma_m}{K} + \left(1 - \frac{M}{K}\right) \Omega (C - C_0). \tag{15}$$

This equation expresses the total volumetric strain in terms of the mean stress and the change in concentration. A tensile mean stress promotes volumetric expansion. The insertion of guest atoms promotes volumetric expansion if $M < K$, but promotes volumetric contraction if $M > K$. For example, for lithium cobalt oxide, a material commonly used as cathodes in lithium-ion batteries, the insertion of lithium atoms causes the host to contract in volume (Reimers and Dahn, 1992).

Inserting (12) into (9), and using $\varepsilon_{kk}^e = [\sigma_m - M\Omega(C - C_0)/K$, we obtain that

$$\zeta = \left(1 - \frac{M}{K}\right) \sigma_m + \frac{\mu - \mu_0}{\Omega} - \left(H - \frac{M^2}{K}\right) \Omega (C - C_0). \tag{16}$$

This equation expresses the driving force for reaction in terms of the external variables: the mean stress, the chemical potential, and the concentration. The reaction is promoted by an increase in the chemical potential of the guest atoms in the reservoir, but is resisted by an increase of the concentration of the guest atoms in the host. A tensile mean stress promotes the reaction if $M < K$, but resists the reaction if $M > K$. When $M = 0$, within the rheological model (Fig. 3c), $(\mu - \mu_0)/\Omega + \sigma_m$ is equivalent to the net stress applied on the parallel spring and the dashpot, ζ is the stress applied on the dashpot, and $\Omega H(C - C_0)$ the stress applied on the spring.

6. Linear kinetic model

The kinetic model (10) involves six independent functions, each depending on six independent variables. A model of this generality is unlikely to be useful in practice. We now explore more restricted forms of kinetic equations by appealing to the analogy with historically successful examples. We begin with a linear kinetic model. The combination of linearity and isotropy requires that deviatoric and volumetric responses be decoupled

$$\frac{de_{ij}^i}{dt} = \frac{s_{ij}}{2\hat{G}}, \tag{17}$$

$$\frac{\Omega dC}{dt} = \frac{\zeta}{\hat{H}}, \tag{18}$$

where $\hat{G}$ is the shear viscosity, and $\hat{H}$ dictates the rate of reaction. The thermodynamic inequality (8) is satisfied by setting $\hat{G} > 0$ and $\hat{H} > 0$. This linear kinetic model is illustrated with two examples as follows.

6.1. A host subject to a chemical load alone

A unit cube of the host contains C_0 number of guest atoms, and is in equilibrium with a reservoir in which the chemical potential of guest atoms is μ_0. The host is then suddenly put in contact with another reservoir in which the chemical potential of guest atoms is at a higher value μ. In the absence of applied stress, the host absorbs additional guest atoms and swells freely. The swelling is homogeneous and isotropic. In the short-time limit, reaction has not started, and $C(0) = C_0$. In the long-time limit, the reaction arrests, and the driving force for reaction vanishes, $\zeta = 0$ in (16), giving

$$C(\infty) = C_0 + \frac{\mu - \mu_0}{\Omega^2 (H - M^2/K)}. \tag{19}$$

Setting $\sigma_m = 0$ and inserting (16) into (18), we obtain that

$$\frac{dC}{dt} = \frac{1}{\hat{H}} \left[\frac{\mu - \mu_0}{\Omega^2} - \left(H - \frac{M^2}{K} \right)(C - C_0) \right]. \tag{20}$$

Solving this ordinary differential equation, we obtain the evolution of the concentration in time

$$\frac{C(t) - C_0}{C(\infty) - C_0} = 1 - \exp\left(-\frac{HK - M^2}{\hat{H}K} t \right) \tag{21}$$

This solution identifies the relaxation time for the reaction as $\hat{H}K/(HK - M^2)$. In the special case when $M = 0$, the relaxation time reduces to $\hat{H}/H$. Setting $\sigma_m = 0$ in (15), we note that the net strain also approaches the state of equilibrium in a similar way.

When the swelling is constrained by fixed net strains in all directions, the mean stress will evolve along with the concentration towards a constant asymptotic value according to (14) and (18). In the long-time limit, the concentration will in general differ from its free swelling counterpart (19). By contrast, when the constraint is not hydrostatic, the deviatoric and volumetric components of the stress are coupled. Stress will build up initially and then relax to zero. In the long-time limit, the concentration and total volume change coincide with those obtained in the free swelling case.

6.2. A host under mechanical load alone

As a second example, we analyze the commonly performed creep test. This example highlights a fundamental difference between flow and insertion: under a fixed load, the flow will persist, while reaction will arrest. The host is in contact with a reservoir in which the chemical potential of guest atoms is fixed at μ_0. A dead load is suddenly applied to the host, and a state of stress σ_{ij} is fixed subsequently. The elastic deviatoric strain is constant and given by Eq. (13). Integration of the kinetic model (17) in time together with (13) yields

$$e_{ij} = \frac{s_{ij}}{2G} \left(1 + \frac{Gt}{\hat{G}} \right). \tag{22}$$

Under the fixed stress, the inelastic deviatoric strain persists and evolves linearly in time, with a characteristic time $\hat{G}/G$. Observe that this time scale of deviatoric flow differs from that of swelling.

By contrast, the reaction arrests in the long-time limit. Setting $\mu = \mu_0$ and, in chemical equilibrium $\zeta = 0$, we obtain that

$$C(\infty) = C_0 + \frac{K - M}{KH - M^2} \frac{\sigma_m}{\Omega}. \tag{23}$$

Thus, even when the chemical potential of the guest atoms in the reservoir is fixed at μ_0, the applied stress changes the number of guest atoms in the host. Under a tensile mean stress, the host absorbs guest atoms if $M < K$, and desorbs guest atoms if $M > K$. The opposite occurs when the mean stress is compressive. The kinetic model (18) reduces to

$$\frac{dC}{dt} = \frac{1}{\hat{H}} \left[\left(1 - \frac{M}{K} \right) \frac{\sigma_m}{\Omega} - \left(H - \frac{M^2}{K} \right)(C - C_0) \right]. \tag{24}$$

The equation looks similar to (20), and its solution is also of the form (21), with $C(\infty)$ now given by (23).

The net volume change at equilibrium can be directly computed from (15) and (23), giving

$$\varepsilon_{kk}(\infty) = \frac{\sigma_m}{K} \left[1 + \frac{(K - M)^2}{KH - M^2} \right]. \tag{25}$$

In the case where $M = K$, the volume change results only from elasticity, as expected. In both cases $M > K$ and $M < K$, the inelastic volumetric strain is positive under a tensile mean stress.
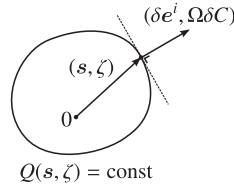
Fig. 4. The six independent components of $(\mathbf{s},\zeta)$ are collectively regarded as a vector in a linear space of six dimensions. In this space, the condition $Q(\mathbf{s},\zeta) = \text{const}$ is a surface, and the six components of $(\delta\mathbf{e}^i, \Omega\delta C)$ also form a vector.

7. Nonlinear rate-dependent kinetic model without yield strength

To construct a family of nonlinear kinetic models, following Rayleigh (1871), we introduce a dissipation function $Q(\mathbf{s},\zeta)$, and postulate that the inelastic strain derives from the dissipation function as

$$\frac{de^i_{ij}}{dt} = \frac{\partial Q(\mathbf{s},\zeta)}{\partial s_{ij}}, \quad \frac{\Omega dC}{dt} = \frac{\partial Q(\mathbf{s},\zeta)}{\partial \zeta}. \tag{26}$$

This kinetic model involves a single scalar as a function of the six independent variables, $Q(\mathbf{s},\zeta)$. Relations (26) may be justified in terms of some macroscopic postulates (e.g., Drucker, 1951) and microscopic models (e.g., Rice, 1971), but other macroscopic postulates and microscopic models can be constructed leading to kinetic models that do not obey (26). Here we take (26) as an assumption of the rheological model, namely, a compromise between flexibility to fit experimental data and convenience to develop a mathematical theory.

The kinetic model (26) is commonly interpreted in geometric terms (Fig. 4). The condition $Q(\mathbf{s},\zeta) = \text{constant}$ is a surface in the six dimensional space, and the partial derivatives $\partial Q(\mathbf{s},\zeta)/\partial s_{ij}$ and $\partial Q(\mathbf{s},\zeta)/\partial \zeta$ are the six components of a vector normal to the surface. Consequently, (26) makes $(\delta\mathbf{e}^i, \Omega\delta C)$ a vector normal to the surface. Thermodynamic inequality (8) requires that the angle between the vector $(\mathbf{s},\zeta)$ and the vector normal to the surface $Q(\mathbf{s},\zeta) = \text{constant}$ be acute. This geometric interpretation helps to visualize the restriction of the thermodynamic inequality imposed on the form the dissipation function $Q(\mathbf{s},\zeta)$. For example, a sufficient (but not necessary) condition for inequality (8) to be satisfied is to choose $Q(\mathbf{s},\zeta)$ to be convex, non-negative and such that $Q(\mathbf{0},0) = 0$.

The dissipation function takes a considerably simpler form for an isotropic material. For an isotropic host, the dissipation function Q depends on the tensor s_{ij} only through its invariants $J_2 = s_{ij}s_{ij}/2$ and $J_3 = s_{ij}s_{jk}s_{ki}/3$, so that

$$Q = Q(J_2, J_3, \zeta). \tag{27}$$

Following von Mises (1928), we further assume that Q does not depend on J_3. Unlike von Mises, we do retain the dependence on ζ to account for reaction. Assuming that small deviation from equilibrium arises independently from the sign of ζ, it follows that Q must be an even function of ζ. Write the dissipation function as

$$Q = Q(J_2, \beta). \tag{28}$$

where $\beta = \zeta^2/2$. The kinetic model (26) becomes

$$\frac{de^i_{ij}}{dt} = \frac{\partial Q(J_2, \beta)}{\partial J_2} s_{ij}, \tag{29}$$

$$\frac{\Omega dC}{dt} = \frac{\partial Q(J_2, \beta)}{\partial \beta} \zeta. \tag{30}$$

This nonlinear kinetic model generalizes the linear kinetic model (17) and (18), with the identification

$$\frac{1}{2\hat{G}} = \frac{\partial Q(J_2, \beta)}{\partial J_2}, \quad \frac{1}{\hat{H}} = \frac{\partial Q(J_2, \beta)}{\partial \beta}. \tag{31}$$

Now both shear and bulk viscosity are functions of the two scalars, $\hat{G}(J_2, \beta)$ and $\hat{H}(J_2, \beta)$. The thermodynamic inequality (8) is satisfied if and only if $\hat{G} > 0$ and $\hat{H} > 0$. This condition is equivalent to requiring that $Q(J_2, \beta)$ be an increasing function with respect to both variables.

As a narrower generalization of the work of von Mises, we may assume that the dissipation function Q depends on $(\mathbf{s},\zeta)$ through a single scalar—a quadratic form of the six-dimensional vector $(\mathbf{s},\zeta)$. For an isotropic host, the most general quadratic form of $(\mathbf{s},\zeta)$ is a linear combination of $s_{ij}s_{ij}$ and ζ^2. Thus, define a scalar measure of the driving forces for flow and reaction

$$\tau_e = \left(\frac{1}{2} s_{ij}s_{ij} + q\zeta^2\right)^{1/2}, \tag{32}$$

where q is a dimensionless constant. When $q = 0$, the scalar τ_e reduces to the equivalent shear stress of von Mises (1913).

We now assume that the dissipation function Q depends on the driving force $(\mathbf{s},\zeta)$ through the scalar τ_e

$$Q = Q(\tau_e). \tag{33}$$

Inserting (33) into (26), we obtain that

$$\frac{de^i_{ij}}{dt} = \frac{s_{ij}}{2\hat{G}(\tau_e)}, \tag{34}$$

$$\frac{\Omega dC}{dt} = \frac{q\zeta}{\hat{G}(\tau_e)}, \tag{35}$$

where $\hat{G}(\tau_e) = \tau_e/(dQ/d\tau_e)$ is the shear viscosity. The thermodynamic inequality (8) is satisfied if $\hat{G}(\tau_e) > 0$ and q is a positive number. This kinetic model couples flow and reaction through τ_e. In particular, a chemical driving force can make deviatoric flow faster if $\hat{G}(\tau_e)$ is a decreasing function, or slower if $\hat{G}(\tau_e)$ is an increasing function. Similarly, a shear stress can accelerate or decelerate the reaction. These two types of behavior correspond to shear-thinning and shear-thickening, respectively, in rheology (Barnes et al., 1989).

This kinetic model is fully determined by two items: the constant q indicates the relative contributions of the chemomechanical stress and the deviatoric stress to the scalar measure of the driving force, and the scalar function $\hat{G}(\tau_e)$ gives the nonlinear viscosity. Both items can be determined experimentally. As an example, suppose we set up an experiment under pure shear stress τ and in chemical equilibrium, $\zeta = 0$, and measure the rate of the inelastic engineering shear strain $\gamma^i(t)$ as a function of the shear stress

$$\frac{d\gamma^i}{dt} = f(\tau). \tag{36}$$

Under this loading condition, $s_{12} = \tau$, $e^i_{12} = \gamma^i/2$, and the scalar measure of the driving force reduces to $\tau_e = \tau$. A comparison between (34) and (36) gives the shear viscosity

$$\hat{G}(\tau_e) = \tau_e/f(\tau_e). \tag{37}$$

This shear viscosity can be inserted into (34) and (35) to obtain the rate of deviatoric inelastic strain rate and concentration. Eq. (35) uses the data determined from the pure-shear test to determine the reaction kinetics, except for the constant q. The constant can be determined by another experiment, for example, free swelling. For a given host–guest system, such a prediction can be validated or falsified by experiments. At this writing, no experiments of this kind are available.

8. Rate-independent kinetic model with yield strength

When a thin film of silicon constrained on a substrate is lithiated, the stress in the plane of the layer is built up to a certain level even when the rate of lithiation is low (Sethuraman et al., 2010). This plastic behavior has also been noted in ab initio atomistic simulation (Zhao et al., 2011c). Here we propose a rate-independent kinetic model of reactive flow by including both the deviatoric stress and the driving force for reaction. We then apply this model to analyze free swelling, stressed swelling, and chemomechanical ratcheting.

8.1. Chemomechanical yield condition and chemomechanical flow rule

As mentioned in Introduction, experimental observations suggest that a reaction may stimulate flow in a host too brittle to flow under mechanical load alone. Here we propose a rate-independent kinetic model by generalizing the von Mises (1913, 1928) theory of plastic potential, which shares similar properties as the Rayleigh dissipation function. Thus, we will still write the plastic potential as $Q(\mathbf{s},\zeta)$. A set of the driving forces $(\mathbf{s},\zeta)$ is a point in the six-dimensional space, and the chemomechanical yield condition is $Q(\mathbf{s},\zeta) = 0$. In general the yield surface may change its shape and its location due to microstructure rearrangements and change in concentration. When the driving forces $(\mathbf{s},\zeta)$ correspond to a point inside the surface, no additional reaction and flow take place, but the host can deform elastically. When the forces reach the yield surface, reaction advances by δC, and the inelastic deviatoric strain changes by δe^i_{ij}. The increments $(\delta e^i_{ij}, \Omega\delta C)$ is also a vector in the six-dimensional space. As an extension of the work of von Mises (1928), we postulate that the vector $(\delta e^i_{ij}, \Omega\delta C)$ is in the direction normal to the yield surface

$$\delta e^i_{ij} = \lambda \frac{\partial Q(\mathbf{s},\zeta)}{\partial s_{ij}}, \quad \Omega\delta C = \lambda \frac{\partial Q(\mathbf{s},\zeta)}{\partial \zeta}. \tag{38}$$

This flow rule is analogous to the time-dependent kinetic model (26). The amplitude of the vector $(\delta e^i_{ij}, \Omega\delta C)$, known as the plastic multiplier λ, is not specified in the rate-independent plastic model; rather, it is determined from the boundary conditions by requiring that the forces cannot leave the yield surface during plastic flow (i.e., the consistency condition).

As a particular example of the plastic potential for an isotropic material, we extend the theory of von Mises (1913) to account for the driving force for reaction by assuming

$$Q = \frac{1}{2} s_{ij} s_{ij} + q\zeta^2 - \tau_Y^2,$$ (39)

where τ_Y is the yield strength under the pure-shear condition. In general, τ_Y varies with concentration and inelastic strains. However, as we assumed small changes in concentration, we will fix the yield strength at its reference value for $C = C_0$. Contrarily to von Mises theory, the yield function (39) depends on the first invariant σ_m through the driving force ζ. Based on similar argument as in the previous section, we assumed the yield function depends on a quadratic form of ζ. Hence, the criterion $Q(\mathbf{s}, \zeta) = 0$ is insensitive to the sign of ζ.

Using (39), the yield condition $Q(\mathbf{s}, \zeta) = 0$ becomes

$$\frac{1}{2} s_{ij} s_{ij} + q\zeta^2 = \tau_Y^2.$$ (40)

The yield strength τ_Y is determined when the host is subject to pure shear condition in the absence of chemical driving force. Under the condition of insertion without stress, the yield condition on the driving force for reaction is deduced from (40) as $\zeta = \zeta_Y \equiv \tau_Y / \sqrt{q}$, where ζ is given by (9) and is computed for vanishing mean stress σ_m. The yield surface is represented by an ellipse in the plane spanned by $(\zeta, \sqrt{s_{ij} s_{ij}/2})$.

Introducing the plastic potential (39) into the flow rule (38), we obtain that

$$\delta e_{ij}^i = \lambda s_{ij}$$ (41)

$$\Omega \delta C = 2q\lambda\zeta$$ (42)

According to (41), inelastic deviatoric strains develop under the condition that shear stresses are applied. Moreover, the ratio of inelastic deviatoric strain increments to the corresponding deviatoric stresses are identical and given by the plastic multiplier. Eq. (41) is similar in form to the classical flow rules of J_2 plasticity (Reuss, 1930). On the other hand, volumetric inelastic strains develop under the condition that chemo-mechanical loading is applied. A positive chemomechanical stress leads to insertion, and a negative one to extraction. Eliminating the multiplier from (41) and (42), we obtain the expression of the inelastic deviatoric strain increment as a function of the shear stress and the increment of concentration

$$\delta e_{ij}^i = \frac{s_{ij}}{2q\zeta} \Omega \delta C.$$ (43)

Relation (43) expresses the constraint introduced by the assumption of normality of the flow rule. Note that Eq. (43) holds under the condition that ζ (and hence δC) is non-zero. The total strain is the sum of the elastic and inelastic strains

$$\delta e_{ij} = \frac{\delta s_{ij}}{2G} + \frac{s_{ij}}{2q\zeta} \Omega \delta C,$$ (44)

$$\delta \varepsilon_{kk} = \frac{\delta \sigma_m}{K} + \left(1 - \frac{M}{K}\right) \Omega \delta C.$$ (45)

8.2. Free swelling

A host is in contact with a reservoir and subject to no stress. Initially, the chemical potential of the guest atoms in the reservoir is set at value of the reference state, $\mu = \mu_0$, and the concentration of the guest atoms in the host is $C = C_0$. Subsequently, the chemical potential of the guest atoms in the reservoir is ramped up. The driving force ζ (9) for reaction under stress-free condition is given by

$$\zeta = \frac{\mu - \mu_0}{\Omega} - \left(H - \frac{M^2}{K}\right) \Omega (C - C_0).$$ (46)

The yield condition is $\zeta = \tau_Y / \sqrt{q}$. As long as the chemical potential has not reached a certain threshold, $\mu - \mu_0 < \Omega \tau_Y / \sqrt{q}$, the host cannot yield, and the concentration remains unchanged. As soon as the yield criterion is reached: $\mu - \mu_0 = \Omega \tau_Y / \sqrt{q}$, the host yields, and the concentration at any subsequent time is determined from the condition that the driving force cannot leave the yield surface, $\zeta = \tau_Y / \sqrt{q}$, so that,

$$C = C_0 + \frac{1}{\Omega(H - M^2/K)} \left(\frac{\mu - \mu_0}{\Omega} - \frac{\tau_Y}{\sqrt{q}}\right)$$ (47)

Eq. (47) indicates that the concentration of the guest atoms in the host increases linearly with the chemical potential. The yield strength reduces the amount of insertion, as compared to the amount of insertion without yield strength (19). In principle, this experiment can be used to measure the value of q by determining the yield condition of the chemical potential.

Note that it is necessary to increase the value of the chemical load as yielding proceeds in order to keep satisfying the yield criterion. This feature differs from classical von Mises perfect plasticity, where a constant state of stress on yield leads to indefinite plastic flow. Here, yield requires an increase in the applied loading, due to the presence of a back stress given by the second term in the right-hand side of expression (46) of the driving force for reaction ζ. The magnitude of the back stress increases with the variation of concentration compared to the reference state.

When swelling is constrained, stress builds up within the host, in turn affecting the condition for further yielding. If the constraint is purely hydrostatic, the resulting mean stress must be accounted for in expression (9) of the driving force for reaction ζ. The evolution of the concentration with the chemical potential remains linear, but the slope is modified, as compared to the free swelling case. The mean stress also evolves linearly with the chemical potential. According to (41), no inelastic deviatoric strain may develop. When the constraint is not hydrostatic, the deviatoric components of the stress affect the yield condition, and cause deviatoric flow.

Contrary to the viscoelastic kinetic model of Sections 6 and 7, plasticity does not allow the stress generated during constrained swelling to relax, even when the chemical load is held constant. Consequently, a constrained body subjected to a given history of chemical load will not reach a homogeneous state. Instead, the field of stress and inelastic deformations will be heterogeneous. In addition, a field of residual stresses and permanent ("plastic") strains will persist within the body if the constraints are subsequently removed. These features are characteristic of plasticity.

8.3. Host under fixed stress and ramp chemical potential

A host is under a fixed state of stress σ_{ij}, and by itself the stress is insufficient to cause yielding. Initially, the chemical potential of the guest atoms in the reservoir is set at value of the reference state, $\mu = \mu_0$, and the concentration of the guest atoms in the host is $C = C_0$. Subsequently, the chemical potential of the guest atoms in the reservoir is ramped up. The effective driving force τ_e is given by

$$\tau_e^2 = \frac{1}{2} s_{ij} s_{ij} + q \left[\left(1 - \frac{M}{K} \right) \sigma_m + \frac{\mu - \mu_0}{\Omega} - \left(H - \frac{M^2}{K} \right) \Omega (C - C_0) \right]^2 \tag{48}$$

The yield condition is $\tau_e = \tau_Y$. Before the chemical potential reaches the yield condition

$$\mu - \mu_0 < \frac{\Omega}{\sqrt{q}} \sqrt{\tau_Y^2 - \frac{1}{2} s_{ij} s_{ij}} - \Omega \left(1 - \frac{M}{K} \right) \sigma_m, \tag{49}$$

the concentration of the guest atoms in the host is unchanged. When the chemical potential exceeds the above value, the concentration increases linearly with the chemical potential, as determined by the yield condition, $\tau_e = \tau_Y$. This can be readily seen by exploiting the consistency condition $\delta \tau_e = 0$ in (48)

$$\delta C = \frac{\delta \mu}{\Omega^2 (H - M^2/K)}. \tag{50}$$

The increment of inelastic deviatoric strain is directly computed from the increment of concentration using relation (43). The only difference with the free swelling case is the value of the chemical load needed to trigger plastic flow. According to (48), the yield condition depends on the applied stress in the following way. Non-vanishing shear components of the stress tensor always promote plasticity by lowering the threshold value of the external chemical potential. In the case where $M < K$, a tensile mean stress promotes yield, while a compressive mean stress hinders yield. On the other hand, the slope of the $\delta \mu / \delta C$ is identical to the free swelling situation.

8.4. Chemomechanical ratcheting

Subject to a cyclic temperature and a fixed force, a metal can undergo accumulative, unidirectional plastic deformation (e.g., Bree, 1967; Huang et al., 2001). Thin-film islands of silicon on a substrate may undergo ratcheting deformation under cyclic lithiation and delithiation (Haftbaradaran and Gao, 2012). We now show that within the theory of reactive flow described in this paper, chemomechanical ratcheting can happen for a host under a constant state of stress, and subject to cyclic change in the chemical potential of the guest atoms in the reservoir. The stress itself is insufficient to cause plastic flow. As the chemical potential is cycled, the host is brought repeatedly to the yield conditions of two types: absorbing guest atoms and exuding guest atoms. In both cases, the inelastic strains are in the same direction as the constant stress—that is, the host undergoes ratcheting plastic deformation. In a model that assumes reaction is in equilibrium, ratcheting will not happen in a homogeneous state under fixed stress. This type of experiments might be used to distinguish the two types of theories.

The phenomenon is readily understood graphically (Fig. 5). Ratcheting will occur if the constant state of stress contains a deviatoric component. For simplicity, assume that the stress tensor admits only one non-vanishing shear component τ. The yield condition is an ellipse on the (τ, ζ) plane. A point inside the ellipse is elastic, and the host neither flows inelastically nor reacts with the guest atoms. For a perfectly plastic host, a point outside the ellipse can never be reached. For a point on the ellipse, the increments in the inelastic engineering shear strain and the concentration form a vector
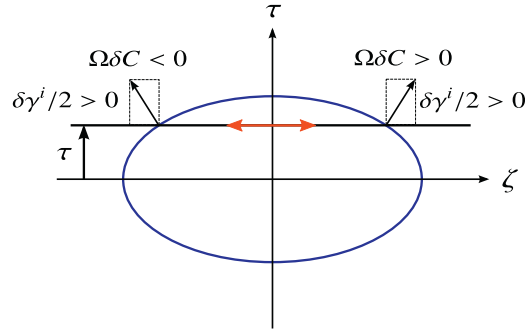
Fig. 5. A host is subject to a constant shear stress and a cyclic chemical potential. The yield condition is represented by an ellipse on the (τ, ζ) plane. At any point on the ellipse, the vector $(\delta\gamma^i/2, \Omega\delta C)$ is normal to the ellipse. As the chemical potential cycles, the host absorbs and desorbs guest atoms, both causing inelastic shear strain in the same direction of the constant shear stress.

$(\delta\gamma^i/2, \Omega\delta C)$ normal to the ellipse. This flow rule has several implications. First, as long as the shear stress is nonzero, an increment in the concentration always gives rise to an increment in the inelastic shear strain. Second, so long as the increment in the concentration per cycle is finite, the increment in the shear strain is also finite. Third, regardless whether the host absorbs or desorbs guest atoms, the increment in the shear strain is always in the same direction as the shear stress. Thus, a cyclic change in the chemical potential causes unidirectional and incremental shear strain. From this graphical interpretation, it is evident that the applied stress need not be constant, so long as the stress is biased toward a direction. Also, the normality of the flow rule is inessential, so long as the reaction and flow is coupled—an increment in concentration will cause an increment in inelastic strain.

This chemomechanical ratcheting is closely analogous to a thin film crawling under thermomechanical loading observed in the microelectronic industry and analyzed before (Huang et al., 2001). This analysis is adapted for chemomechanical ratcheting below. The yield condition is

$$\tau^2 + q\left[\frac{\mu-\mu_0}{\Omega} - \left(H - \frac{M^2}{K}\right)\Omega(C-C_0)\right]^2 = \tau_Y^2. \tag{51}$$

Upon yield, as τ is held constant and μ ramps, the increment of the concentration is

$$\delta C = \frac{\delta\mu}{\Omega^2(H - M^2/K)}. \tag{52}$$

According to the flow rule, the increment of the shear strain is proportional to the increment of the concentration

$$\delta\gamma^i = \frac{\Omega\tau}{q\zeta}\delta C. \tag{53}$$

When the host absorbs guest atoms, $\delta C > 0$ and $\zeta = +\sqrt{(\tau_Y^2 - \tau^2)/q}$. When the host desorbs guest atoms, $\delta C < 0$ and $\zeta = -\sqrt{(\tau_Y^2 - \tau^2)/q}$. In both cases, the increment of the inelastic shear strain is in the same direction as τ, giving rise to chemomechanical ratcheting. We next follow the sequence of events as the chemical potential cycles between μ_0 and μ_1 (Fig. 6).

State A. $\mu_A = \mu_0$: The initial concentration is the reference concentration C_0. The applied shear stress induces an elastic shear strain $\gamma^e = \tau/G$, which remains constant throughout the loading and does not affect insertion and extraction.

Path AB. $\mu_0 < \mu < \mu_B$: The rising chemical potential increases the driving force for insertion, $\zeta = (\mu-\mu_0)/\Omega$, but the yield criterion is not reached, $\tau^2 + q\zeta^2 < \tau_Y^2$, so that the concentration and inelastic shear strain remain unchanged.

State B. $\mu = \mu_B$: The force reaches the critical value for yielding: $\zeta = \sqrt{(\tau_Y^2 - \tau^2)/q} > 0$.

Path BC. $\mu_B < \mu < \mu_1$: Under a positive driving force for reaction, $\zeta = +\sqrt{(\tau_Y^2 - \tau^2)/q}$, Guest atoms are inserted into the host. As the chemical potential ramps up, so does the concentration (52). Meanwhile the inelastic shear strain increases according to (53).

State C. $\mu = \mu_1$: The system reaches the prescribed highest chemical potential.

Path CD. $\mu_1 > \mu > \mu_D$: The dropping chemical potential causes the driving force for reaction to decrease and become negative. The latter is given by: $\zeta = (\mu-\mu_0)/\Omega - (H-M^2/K)\Omega(C_C-C_0)$. However, the yield condition for extraction is not satisfied yet: $\tau^2 + q\zeta^2 < \tau_Y^2$. Therefore, the concentration remains fixed, and no inelastic shear strain develops. As compared to the value of the driving force during the path AB, the driving force now includes the contribution of a back stress which remains constant as long as the yield criterion is not reached.
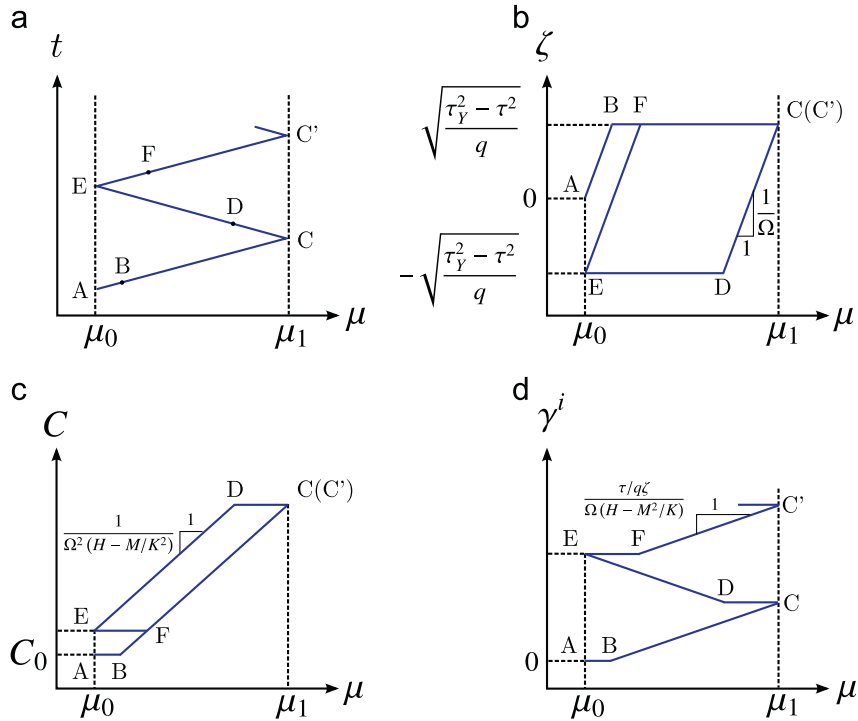
Fig. 6. When a host is subject to a constant shear stress and cyclic chemical potential, the plastic shear strain may ratchet. The chemical potential of the environment changes between μ_0 and μ_1 with time (a). The driving force for reaction varies with the chemical potential (b). During portions of the loading where the yield criterion is satisfied, guest atoms are inserted ($\zeta > 0$) or extracted ($\zeta < 0$) from the host, and the concentration varies linearly with the chemical potential (c). Both insertion and extraction are accompanied with inelastic shear strain in the direction of the applied shear stress (d).
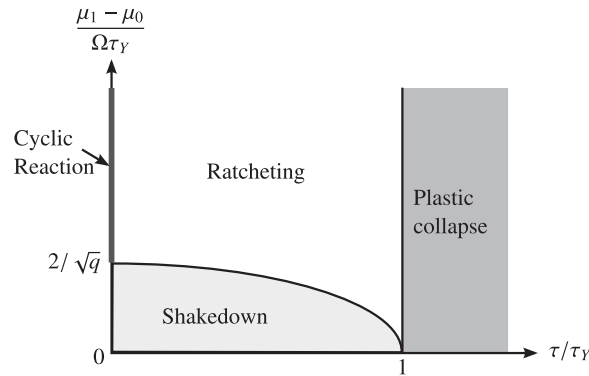
Fig. 7. A host subject to a constant shear stress and cyclic chemical potential exhibits four types of behavior: cyclic reaction, shakedown, ratcheting, and plastic collapse.

State D. $\mu = \mu_D$: The driving force for reaction reaches the yield condition at a negative value, $\zeta = -\sqrt{(\tau_Y^2 - \tau^2)/q}$.

Path DE. $\mu_D > \mu > \mu_0$: Under the negative driving force for reaction, guest atoms are extracted from the host. As the chemical potential ramps down, so does the concentration (52). Meanwhile the inelastic shear strain keeps increasing according to (53).

State E. $\mu = \mu_0$: The system reaches the prescribed lowest chemical potential.

Path EF. $\mu_0 < \mu < \mu_F$: The rising chemical potential causes the driving force to increase, going from negative value to positive value.

State F. $\mu = \mu_F$: The force again reaches the critical value for yielding: $\zeta = +\sqrt{(\tau_Y^2 - \tau^2)/q} > 0$. Due to the back stress, we have $\mu_F > \mu_B$.

Path FC′. $\mu_F < \mu < \mu_1$: Guest atoms are inserted into the host driven by a positive ζ, according to (52). The force remains constant. The inelastic shear strain increases according to (53).

State C′. $\mu = \mu_1$: The chemical potential reaches the prescribed highest point. Starting from state C′, as the chemical potential cycles, the driving force ζ and the concentration cycle around the loop CDEF. The inelastic shear strain, however, *increases* by a definite amount each cycle.

Depending on the value of the shear stress and the range of the chemical potential, the host exhibits four types of behavior: plastic collapse, cyclic reaction, shakedown, and ratcheting (Fig. 7). If $\tau/\tau_Y \geq 1$, the host flows plastically under the shear stress alone without the aid of the chemical load. If $q[(\mu_1-\mu_0)/2\Omega]^2 + \tau^2 < \tau_Y^2$, the host may plastically deform during the first cycle, but cycles elastically afterward (shakedown). Outside the shakedown region, if $\tau = 0$, the change in chemical potential causes cyclic insertion and extraction but no plastic shear strain. If $\tau > 0$ and the range of the chemical potential is above the shakedown condition, the host will ratchet: while the concentration cycles, the plastic shear strain increases by a fixed amount each cycle, given by

$$\Delta\gamma^i = \frac{4\tau}{q(H-M^2/K)}\left[\frac{\sqrt{q}(\mu_1-\mu_0)}{2\Omega\sqrt{\tau_Y^2-\tau^2}}-1\right].\tag{54}$$

9. Concluding remarks

We have formulated a theory of reactive flow in solids by assuming that reaction and flow are both nonequilibrium processes. As an extension of the von Mises theory of plasticity, we have described a chemomechanical yield condition to include both the deviatoric stress and the driving force for reaction. Similarly, the Reuss flow rule is extended to account for concurrent flow and reaction. The resulting theory predicts that the driving force for reaction can lower the stress needed for flow. That is, a reaction can stimulate the flow in a host too brittle to flow under mechanical load alone. The theory further predicts chemomechanical ratcheting. To focus on the essential idea, the body of the paper develops a theory of minimal ingredients, and is devoted to a small piece of the host evolving through homogeneous states. The host as a whole in general evolves in time through a sequence of inhomogeneous states (Appendix A). Stress and chemical potential are then determined by solving the usual equations for mechanical equilibrium and mass conservation for given boundary conditions. A constitutive model for long range diffusion flux is also provided. The general framework for inhomogeneous field encompasses the case of nonequilibrium surface reaction.

Appendix A. Inhomogeneous states

When guest atoms diffuse into a host solid and react, the host can flow inelastically. The three kinetic processes—diffusion, reaction and flow—are concurrent. The host in general evolves in time through a sequence of inhomogeneous fields. Following a common practice in formulating a field theory, we regard the host as a sum of many small pieces (Fig. 1). Each small piece evolves in time by reaction and flow through a sequence of homogeneous states, as studied in the body of the paper. Different small pieces in the host communicate through the compatibility of deformation, balance of forces, conservation of the number of guest atoms, and kinetics of the diffusion. These general principles are independent of the internal degrees of freedom, so that the governing equations for the communication are the same as those in poroelasticity (Biot, 1941). Here we list these equations, and confirm that the theory of concurrent reaction, flow and diffusion satisfies a thermodynamic inequality. This Appendix relies on the body of the paper only through inequality (1).

The host as a whole satisfies a thermodynamic inequality. Name each small piece of the host by its coordinate **x**. At time t, the displacement of the piece is $u_i(\mathbf{x},t)$. The host is subject to a field of body force $B_i(\mathbf{x},t)$ in the volume and a field of surface force $T_i(\mathbf{x},t)$ on part of its boundary, while the rest of the boundary of the host the displacement is prescribed. The applied forces can be represented by a field of weights. The change of the potential energy of the weights per unit time is $-\int B_k \partial u_k/\partial t \, dV - \int T_k \partial u_k/\partial t \, dS$, where the first integral extends over the volume of the host, and the second integral extends over the part of the boundary on which the surface force is applied. Let $J_k(\mathbf{x},t)$ be the field of flux of the guest atoms, namely, $J_k n_k$ is the number of guest atoms crossing a surface element per unit area per unit time, where n_k is the unit vector normal to the element of area. At time t, part of the boundary of the host is in contact with a reservoir in which the chemical potential of the guest atoms is $\bar{\mu}(t)$, while the rest of the boundary does not exchange guest atoms with the reservoir, $J_k n_k = 0$. The change in the Helmholtz free energy of the reservoir per unit time is $\int(\bar{\mu}-\mu_0)J_k n_k \, dS$, where the integral extends

over the part of the boundary in contact with the reservoir. The guest atoms in the host is further subject to a wind force $\mathbf{F}^{wind}$, such that the mechanism applying the wind force changes its potential energy per unit time by $-\int F_k^{wind} J_k dV$. The Helmholtz free energy of the host changes per unit time by $\int (\partial W / \partial t) dV$. The host, reservoir, weights and the mechanism applying the wind force together form a composite thermodynamic system. The composite is isothermal: it exchanges energy with the rest of world by heat, but not by work. The composite conserves all species of atoms. Thermodynamics requires that the Helmholtz free energy of the composite should never increase

$$\int \frac{\partial W}{\partial t} dV - \int B_k \frac{\partial u_k}{\partial t} dV - \int T_k \frac{\partial u_k}{\partial t} dS - \int F_k^{wind} J_k dV + \int (\overline{\mu} - \mu_0) J_k n_k dS \leq 0. \tag{A1}$$

This inequality applies to the host as a whole and generalizes (1).

We next list the equations governing the communication between small pieces in the host. The compatibility of deformation requires that the field of strain be

$$\varepsilon_{ij} = \frac{1}{2} \left[\frac{\partial u_i(\mathbf{x},t)}{\partial x_j} + \frac{\partial u_j(\mathbf{x},t)}{\partial x_i} \right]. \tag{A2}$$

Let $\sigma_{ij}(\mathbf{x},t)$ be the field of stress in the host. The balance of forces requires that

$$\frac{\partial \sigma_{ij}(\mathbf{x},t)}{\partial x_j} + B_i(\mathbf{x},t) = 0 \tag{A3}$$

in the volume of the host, and that

$$\sigma_{ij}(\mathbf{x},t) n_j = T_i(\mathbf{x},t) \tag{A4}$$

on the part of the boundary of the host where the surface force is applied. Let $C(\mathbf{x},t)$ be the field of concentration, namely, the number of guest atoms per unit volume of the host. The conservation of the number of atoms requires that

$$\frac{\partial C(\mathbf{x},t)}{\partial t} + \frac{\partial J_k(\mathbf{x},t)}{\partial x_k} = 0. \tag{A5}$$

For each small piece of the host, the surrounding pieces of the host serve as a reservoir of guest atoms. We may as well regard the host itself as a field of reservoirs. Let $\mu(\mathbf{x},t)$ be the field of the chemical potential of guest atoms in the host. We adopt the usual kinetic model of diffusion:

$$J_k = \frac{CD}{kT} \left[F_k^{wind} - \frac{\partial \mu(\mathbf{x},t)}{\partial x_k} \right], \tag{A6}$$

where D is the diffusivity of the guest atoms in the host, and kT the temperature in the unit of energy.

These equations, along with the divergence theorem, reduce the thermodynamic inequality (A1) to

$$\int \left[\frac{\partial W}{\partial t} - \sigma_{ij} \frac{\partial \varepsilon_{ij}}{\partial t} - (\mu - \mu_0) \frac{\partial C}{\partial t} - \left(F_k^{wind} - \frac{\partial \mu}{\partial x_k} \right) J_k \right] dV + \int (\overline{\mu} - \mu) J_k n_k dS \leq 0. \tag{A7}$$

The integral over the volume is never positive because we have constructed kinetic model of reaction and flow to satisfy (1), and because we have adopted the kinetic model of diffusion (A6). The integral over the surface in (A7) is satisfied by requiring that

$$(\mu - \overline{\mu}) J_k n_k \geq 0. \tag{A8}$$

This inequality is satisfied by a kinetic model of interfacial reaction that relates the flux $J_k n_k$ to the driving force $(\mu - \overline{\mu})$; a classical example is the Butler–Volmer equation in electrochemistry (see e.g. Hamann et al., 1998). Surface reactions within electrode materials have been recently addressed by Zhao et al. (2012) and Pharr et al. (2012) in the context of the reaction of lithium with crystalline silicon.

Appendix B. Insertion and reaction as distinct processes

The theory presented in the paper lumps insertion and reaction as a single process, the extent of which is characterized by the concentration of guest atoms in the host. Alternatively, insertion and reaction can be regarded as two distinct processes (Loeffel and Anand, 2011). The extent of insertion is characterized by the concentration of guest atoms in the host, C. The extent of reaction is characterized by the fraction of the inserted guest atoms that have completed the reaction, ξ. Following a procedure commonly adopted in irreversible thermodynamics (de Groot and Mazur, 1984), insertion may be considered in local equilibrium, while chemical reaction is a nonequilibrium process driven by its conjugate force (called the affinity). This approach is outlined here.

The Helmholtz free energy of the host is taken to be a function of the elastic strain, the concentration of guest atoms, and the extent of reaction:

$$W = W(\mathbf{\varepsilon}^e, C, \xi). \tag{B1}$$

According to differential calculus, when the independent variables change by $\delta\varepsilon^e_{ij}, \delta C$, and $\delta\xi$, the Helmholtz free energy changes by $\delta W = (\partial W/\partial\varepsilon^e_{ij})\delta\varepsilon^e_{ij} + (\partial W/\partial C)\delta C + (\partial W/\partial\xi)\delta\xi$.

In a metal, the volumetric change is caused by elasticity, and the volumetric strain associated with plastic flow is negligible. During insertion and reaction, however, the inelastic volumetric strain is typically much larger than the elastic strain. As a generalization of metal plasticity, we assume that the inelastic volumetric strain is a function of the concentration of the inserted atoms and the extent of reaction:

$$\varepsilon^i_{kk} = F(C, \xi). \tag{B2}$$

According to differential calculus, associated with changes in the two independent variables, the volumetric inelastic strain changes by $\delta\varepsilon^i_{kk} = (\partial F/\partial C)\delta C + (\partial F/\partial\xi)\delta\xi$. The two partial derivatives are readily interpreted: $\Omega = \partial F(C, \xi)/\partial C$ is the change in the volume of the host associated with inserting one guest atom (i.e., the volume of insertion), and $\omega = \partial F(C, \xi)/d\xi$ is a dimensionless measure of the volume of reaction.

Inserting (B1) and (B2) into the thermodynamic inequality (1), we obtain that

$$\left[\sigma_{ij} - \frac{\partial W}{\partial\varepsilon^e_{ij}}\right]\delta\varepsilon^e_{ij} + \left[(\mu - \mu_0) + \Omega\sigma_m - \frac{\partial W}{\partial C}\right]\delta C + s_{ij}\delta e^i_{ij} + \left[\omega\sigma_m - \frac{\partial W}{\partial\xi}\right]\delta\xi \geq 0, \tag{B3}$$

Inequality (B3) holds for independent variations $\delta\varepsilon^e_{ij}, \delta C$ and $\delta\xi$. Within the rheological model in Fig. 3, the elastic strain corresponds to the elongation of the spring and is a non-dissipative process. Consequently, the first part of (B3) vanishes, giving

$$\sigma_{ij} = \frac{\partial W(\boldsymbol{\varepsilon}^e, C, \xi)}{\partial\varepsilon^e_{ij}}. \tag{B4}$$

The second term of (B3) corresponds to the injection of guest atoms from the reservoir to the host. Following de Groot and Mazur (1984), we assume that insertion is in local equilibrium:

$$\mu = \mu_0 + \frac{\partial W(\boldsymbol{\varepsilon}^e, C, \xi)}{\partial C} + \Omega\sigma_m. \tag{B5}$$

With rheological assumptions (B4) and (B5), the thermodynamic inequality (B3) reduces to

$$s_{ij}\delta e^i_{ij} + \chi\delta\xi \geq 0, \tag{B6}$$

with

$$\chi = \omega\sigma_m - \frac{\partial W(\boldsymbol{\varepsilon}^e, C, \xi)}{\partial\xi}. \tag{B7}$$

This expression is the thermodynamic force that drives the reaction. Because the extent of reaction is dimensionless, the driving force for reaction has the same dimension as energy per volume, which is the same as the dimension of stress.

The left-hand side of (B6) is a bilinear form of the changes $(\delta e^i_{ij}, \delta\xi)$ and their associated thermodynamic forces (s_{ij}, χ). The kinetic models should ensure that the bilinear form be positive-definite. The kinetic model may be written as

$$\frac{de^i_{ij}}{dt} = f_{ij}(\mathbf{s}, \chi), \quad \frac{d\xi}{dt} = g(\mathbf{s}, \chi). \tag{B8}$$

The kinetic model has the same structure as discussed in the body of the paper (Sections 6–8). In particular, one can couple reaction and flow by constructing chemomechanical yield surface and flow rule.

References

Balluffi, R.W., Alexander, B.H., 1952. Dimensional changes normal to the direction of diffusion. J. Appl. Phys. 23, 953–956.
Balluffi, R.W., Seigle, L.L., 1955. Effect of grain boundaries upon pore formation and dimensional changes during diffusion. Acta Metall. 3, 170–177.
Barnes, H.A., Hutton, J.F., Walters, K., 1989. An Introduction to Rheology. Elsevier Science.
Bhandakkar, T.K., Johnson, H.T., 2012. Diffusion induced stresses in buckling battery electrodes. J. Mech. Phys. Solids 60, 1103–1121.
Beaulieu, L.Y., Eberman, K.W., Turner, R.L., Krause, L.J., Dahn, J.R., 2001. Colossal reversible volume changes in lithium alloys. Electrochem. Solid-State Lett. 4, A137–A140.
Benedek, R., Thackeray, M.M., 2002. Lithium reactions with intermetallic-compound electrodes. J. Power Sources 110, 406–411.
Biot, M.A., 1941. General theory of three-dimensional consolidation. J. Appl. Phys. 12, 155–164.
Bower, A.F., Guduru, P.R., Sethuraman, V.A., 2011. A finite strain model of stress, diffusion, plastic flow, and electrochemical reactions in a lithium-ion half-cell. J. Mech. Phys. Solids 59, 804–828.
Brassart, L., Suo, Z.G., 2012. Reactive flow in large-deformation electrodes of lithium-ion batteries. Int. J. Appl. Mech. 4, 1250023.
Bree, J., 1967. Elastic–plastic behaviour of thin tubes subjected to internal pressure and intermittent high-heat fluxes with application to fast-nuclear-reactor fuel elements. J. Strain Anal. 2, 226–238.
Bridgman, P.W., 1923. The compressibility of thirty metals as a function of pressure and temperature. Proc. Am. Soc. Arts Sci. 58, 165–242.
Cai, S., Suo, Z.G., 2012. Equations of state for ideal elastomeric gels. Eur. Phys. Lett. 97, 34009.
Chaboche, J.L., 2008. A review of some plasticity and viscoplasticity constitutive theories. Int. J. Plasticity 24, 1642–1693.
Chan, C.K., Peng, H., Liu, G., McIlwrath, K., Zhang, X.F., Huggins, R.A., Cui, Y., 2008. High-performance lithium battery anodes using silicon nanowires. Nat. Nanotechnol. 3, 31–35.
Chason, E., Sheldon, B.W., Freund, L.B., Hearne, J.A., 2002. Origin of compressive residual stress in polycrystalline thin films. Phys. Rev. Lett. 88, 156103.

Cui, Z., Gao, F., Qu, J., 2012. A finite deformation stress-dependent chemical potential and its applications to lithium-ion batteries. J. Mech. Phys. Solids 60, 1280–1295.

de Groot, S.R., Mazur, P., 1984. Non-equilibrium Thermodynamics, 2nd ed. North-Holland.

Drucker, D.C., 1951. A more fundamental approach to plastic stress–strain relations. In: Proceedings of the First U.S. National Congress of Applied Mechanics, pp. 487–491.

El Kadiri, H., Horstemeyer, M.F., Bammann, D.J., 2008. A theory for stress-driven interfacial damage upon cationic-selective oxidation of alloys. J. Mech. Phys. Solids 56, 3392–3415.

Gibbs, J.W., 1876. On the equilibrium of heterogeneous substances. Trans. Conn. Acad. 3, 108–248.

Gibbs, J.W., 1878. On the equilibrium of heterogeneous substances. Trans. Conn. Acad. 3, 343–524.

Haftbaradaran, H., Gao, H.J., 2012. Ratcheting of silicon island electrodes on substrate due to cyclic intercalation. Appl. Phys. Lett. 100, 121907.

Hamann, C.H., Hamnett, A., Vielstich, W., 1998. Electrochemistry. Wiley, New York.

Hong, W., Zhao, X., Zhou, J., Suo, Z.G., 2008. A theory of coupled diffusion and large deformation in polymeric gels. J. Mech. Phys. Solids 56, 1779–1793.

Hu, Y., Suo, Z.G., 2012. Viscoelasticity and poroelasticity in elastomeric gels. Acta Mech. Solida Sinica, 25.

Huang, M., Suo, Z.G., Ma, Q., 2001. Metal film crawling in interconnect structures caused by cyclic temperatures. Acta Mater. 49, 3039–3049.

Huang, R., Suo, Z.G., Prévost, J.H., Nix, W.D., 2002. Inhomogeneous deformation in metallic glasses. J. Mech. Phys. Solids 50, 1011–1027.

Huggins, R.A., 2009. Advanced Batteries. Springer.

Larché, F.C., Cahn, J.W., 1973. A linear theory of thermomechanical equilibrium of solids under stress. Acta Metall. 21, 1051–1063.

Liu, X.H., Zheng, H., Zhong, L., Huang, S., Karki, K., Zhang, L.Q., Liu, Y., Kushima, A., Liang, W.T., Wang, J.W., Cho, J.H., Epstein, E., Dayeh, S.A., Picraux, S.T., Zhu, T., Li, J., Sullivan, J.P., Cumings, J., Wang, C., Mao, S.X., Ye, Z.Z., Zhang, S., Huang, J.Y., 2011. Anisotropic swelling and fracture of silicon nanowires during lithiation. Nano Lett. 11, 3312–3318.

Loeffel, K., Anand, L., 2011. A chemo-thermo-mechanically coupled theory for elastic–viscoplastic deformation, diffusion, and volumetric swelling due to a chemical reaction. Int. J. Plasticity 27, 1409–1431.

Oh, J., Thompson, C.V., 2011. The role of electric field in pore formation during aluminum anodization. Electrochem. Acta 56, 4044–4051.

Oran, E.S., Boris, J.P., 2005. Numerical Simulation of Reactive Flow. Cambridge University Press.

Pharr, M., Zhao, K.J., Suo, Z.G., Ouyang, F.Y., Liu, P., 2011. Concurrent electromigration and creep in lead-free solder. J. Appl. Phys. 110, 083716.

Pharr, M., Zhao, K.J., Wang, X.W., Suo, Z.G., Vlassak, J.J., 2012. Kinetics of initial lithiation of crystalline silicon electrodes of lithium-ion batteries. Nano Lett. 12, 5039–5047.

Prud'homme, R., 2010. Flows of Reactive Fluids. Springer.

Rayleigh, 1871. Some general theorems of vibrations. Proc. London Math. Soc. s1–4, 357–368.

Reimers, J.N., Dahn, J.R., 1992. Electrochemical and in situ X-ray diffraction studies of lithium intercalation in Li_xCoO_2. J. Electrochem. Soc. 139, 2091–2097.

Reuss, A., 1930. Berucksichtigung der elastischen Formanderung in der Plastizitatstheorie. Z. Angew. Math. Mech. 10, 266–274.

Rice, J.R., 1971. Inelastic constitutive relations for solids: an internal variable theory and its application to metal plasticity. J. Mech. Phys. Solids 19, 433–455.

Rice, J.R., 1977. Pore pressure effects in inelastic constitutive formulations for fissured rock masses. In: Proceedings of the 2nd ASCE Engineering Mechanics Specialty Conference, Raleigh, NC, 1977. Advances in Civil Engineering Through Engineering Mechanics, ASCE, New York, NY, pp. 295–297.

Sethuraman, V.A., Chon, M.J., Shimshak, M., Srinivasan, V., Guduru, P.R., 2010. In situ measurements of stress evolution in silicon thin films during electrochemical lithiation and delithiation. J. Power Sources 195, 5062–5066.

Sheldon, B.W., Soni, S.K., Xiao, X., Qi, Y., 2012. Stress contributions to solution thermodynamics in Li–Si alloys. Electrochem. Solid-State Lett. 15, A9–A11.

Smigelskas, A.D., Kirkendall, E.O., 1947. Zinc diffusion in alpha brass. AIME Trans. 171, 130–142.

Soni, S.K., Sheldon, B.W., Xiao, X., Tokranov, A., 2011. Thickness effects on the lithiation of amorphous silicon thin films. Scr. Mater. 64, 307–310.

Stephenson, G.B., 1988. Deformation during interdiffusion. Acta Metall. 36, 2663–2683.

Suo, Z.G., Kubair, D.V., Evans, A.G., Clarke, D.R., Tolpygo, V.K., 2003. Stresses induced in alloys by selective oxidation. Acta Mater. 51, 959–974.

Suo, Z.G., 2004. A continuum theory that couples creep and self-diffusion. J. Appl. Mech. 71, 646–651.

Svoboda, J., Fischer, F.D., 2009. Vacancy-driven stress relaxation in layers. Acta Mater. 57, 4649–4657.

Tolpygo, V.K., Clarke, D.R., 2004. On the rumpling mechanism in nickel-aluminide coatings, Part II: characterization of surface undulations and bond coat swelling. Acta Mater. 52, 5129–5141.

Ulm, F.-J., Coussy, O., Kefei, L., Larive, C., 2000. Thermo-chemo-mechanics of ASR expansion concrete structures. J. Eng. Mech. 126, 233–242.

Viesca, R.C., Templeton, E.L., Rice, J., 2008. J. Geophys. Res. 113, B09307.

von Mises, R., 1913. Mechanik der festen Körper im plastisch-deformablen Zustand. Nachr. Ges. Wiss. Göttingen, Math.–Phys. Klasse 1913, 582–592.

von Mises, R., 1928. Mechanik der plastischen Formanderung von Kristallen. Z. Angew. Math. Mech. 8, 161–185.

Williams, F.A., 1985. Combustion Theory, 2nd ed. The Benjamin/Cummings Publishing Company, Inc., Menlo Park, CA.

Yu, C., Li, X., Ma, T., Rong, J., Zhang, R., Shaffer, J., An, Y., Liu, Q., Wei, B., Jiang, H., 2012. Silicon thin films as anodes for high-performance lithium-ion batteries with effective stress relaxation. Adv. Energy Mater. 2, 68–73.

Zhang, W.-J., 2011. Lithium insertion/extraction mechanism in alloy anodes for lithium-ion batteries. J. Power Sources 196, 877–885.

Zhao, K.J., Pharr, M., Cai, S., Vlassak, J.J., Suo, Z.G., 2011a. Inelastic hosts as electrodes for high-capacity lithium-ion batteries. J. Appl. Phys. 109, 016110.

Zhao, K.J., Pharr, M., Cai, S., Vlassak, J.J., Suo, Z.G., 2011b. Large plastic deformation in high-capacity lithium-ion batteries caused by charge and discharge. J. Am. Ceram. Soc. 94, S226–S235.

Zhao, K.J., Wang, W.L., Gregoire, J., Pharr, M., Suo, Z.G., Vlassak, J.J., Kaxiras, E., 2011c. Lithium-assisted plastic deformation of silicon electrodes in lithium-ion batteries: a first-principles theoretical study. Nano Lett. 11, 2962–2967.

Zhao, K.J., Pharr, M., Wan, Q., Wang, W.L., Kaxiras, E., Vlassak, J.J., Suo, Z.G., 2012. Concurrent reaction and plasticity during initial lithiation of crystalline silicon in lithium-ion batteries. J. Electrochem. Soc. 159, A238.

Ziegler, H., Wehrli, C., 1987. The derivation of constitutive relations from the free energy and the dissipation function. Adv. Appl. Mech. 25, 183–238.