Sharp interface model of creep deformation in crystalline solids

Y. Mishin,[1] G. B. McFadden,[2] R. F. Sekerka,[3] and W. J. Boettinger[4]

[1]*Department of Physics and Astronomy, MSN 3F3, George Mason University, Fairfax, Virginia 22030, USA*

[2]*Information Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

[3]*Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA*

[4]*Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

We present a rigorous irreversible thermodynamics treatment of creep deformation of solid materials with interfaces described as geometric surfaces capable of vacancy generation and absorption and moving under the influence of local thermodynamic forces. The free energy dissipation rate derived in this work permits clear identification of thermodynamic driving forces for all stages of the creep process and formulation of kinetic equations of creep deformation and microstructure evolution. The theory incorporates capillary effects and reveals the different roles played by the interface free energy and interface stress. To describe the interaction of grain boundaries with stresses, we classify grain boundaries into coherent, incoherent and semicoherent, depending on their mechanical response to the stress. To prepare for future applications, we specialize the general equations to a particular case of a linear-elastic solid with a small concentration of vacancies. The proposed theory creates a thermodynamic framework for addressing more complex cases, such as creep in multicomponent alloys and cross-effects among vacancy generation/absorption and grain boundary motion and sliding.

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I. INTRODUCTION

At high temperatures and under sustained mechanical loads below the yield strength, many crystalline materials undergo a slow, time-dependent plastic deformation called creep. A typical mode of creep deformation involves diffusion of vacancies between sources and sinks located at grain boundaries or free surfaces [1–6]. The rate at which the vacancies are created and/or annihilated at these interfaces depends on the nature of the interfaces and the local state of stress. During creep deformation, free surfaces can migrate producing macroscopic shape changes of the material. Grain boundaries can also migrate, altering the material's microstructure and affecting its physical and mechanical properties [7].

In a recent paper [8], a theory of creep deformation of polycrystalline materials was proposed based on gradient thermodynamics with phase field variables describing grain boundaries and other interfaces. A continuous distribution of vacancy sinks and sources was assumed, but they could be localized in interface regions by appropriate coupling between the kinetic coefficient of vacancy generation/annihilation and gradients of phase fields. The advantage of this approach is that it incorporates the lattice site generation and annihilation, plastic deformation, and grain boundary motion within a unified thermodynamic framework. However, implementation of this approach requires highly complicated numerical simulations and relies on a large database of material parameters representing bulk and interface thermodynamics as well as various kinetic coefficients. To complement that approach, it is desirable to develop a less detailed but more efficient model of creep deformation in which the interfaces are represented by geometric surfaces capable of vacancy generation and annihilation and moving under the influence of local thermodynamic forces. This task requires the development of a nonequilibrium thermodynamic framework capable of predicting the rates of vacancy generation by interfaces, lattice deformation, and interface motion in a self-consistent manner. It is the goal of this paper to create this thermodynamic framework focusing on a single-component solid with vacancies as a model material. The proposed theory will be referred to as the sharp-interface model of creep.

After introducing a thermodynamic model of a deformable lattice with vacancies in Sec. II, we analyze the time evolution of an isolated crystalline grain subject to a given set of mechanical stresses applied at its surface (Sec. III). The analysis includes capillary forces with a clear distinction drawn between the surface free energy and surface stress. Kinetic equations are derived from the free energy dissipation rate and describe vacancy diffusion inside the grain coupled with vacancy generation and annihilation at the surface and concomitant surface migration. Next, we address a more complicated case of two grains separated by a curved grain boundary (Sec. IV). Here, we introduce three types of grain boundary: coherent, incoherent, and semicoherent, depending on the ability of the boundary to support static shear stresses. For coherent boundaries, our model incorporates the shear coupling effect [9]. It is shown that shear-coupling affects the grain boundary motion and ultimately the creep deformation rate. Semicoherent boundaries constitute an intermediate case when coupled motion coexists with grain boundary sliding. Again, a full set of kinetic equations is derived from an expression for the free energy dissipation rate. Along with applied and internal stresses, we include capillary forces associated with the excess grain boundary free energy and its surface stress. In Sec. V we specialize the theory to a particular case of a linear-elastic anisotropic solid with a small concentration of vacancies. Finally, in Sec. VI we summarize the results and discuss future work.

II. THERMODYNAMICS OF DEFORMABLE LATTICE

Consider an *elastically* deformed single-component single-crystalline solid. As customary in continuum mechanics, deformation of the solid is described by a time-dependent

mapping $\mathbf{x} = \mathbf{x}(\mathbf{x}',t)$ of reference points $\mathbf{x}'$ to deformed points $\mathbf{x}$, where t is time [10]. To simplify the analysis, the reference state is taken to be spatially uniform with respect to all physical properties. The solid may contain vacancies but there are no vacancy sinks or sources inside the lattice, except possibly at its boundary.

The following fundamental equation is postulated to describe thermodynamic properties of the solid:

$$f_s = f_s(T,\mathbf{F},c). \tag{1}$$

Here f_s is the Helmholtz free energy per site,[1]

$$\mathbf{F} \equiv \left(\frac{\partial \mathbf{x}}{\partial \mathbf{x}'}\right)_t \equiv \mathbf{x}\overleftarrow{\nabla}', \tag{2}$$

is the deformation gradient tensor [10], T is temperature, and c is the fraction of lattice sites that are filled by atoms. The crystalline structure is assumed to have a Bravais lattice, i.e., a primitive lattice with a single-site basis (non-Bravais structures would require dealing with sites that are not equivalent and additional variables to describe internal strains of the unit cell). Thus, $(1 - c)$ is the fraction of vacant sites.

In all processes considered below, the material is assumed to remain in thermal equilibrium. Thus temperature T is considered constant and uniform throughout the system. Accordingly, the equations appearing below do not contain temperature gradients or time derivatives of T, and in most equations T is not displayed as a variable.

Variations of f_s are described by the standard relation [11]:

$$\delta f_s = M\delta c + \Omega'\mathbf{P} \cdot\cdot \delta\mathbf{F}, \tag{3}$$

where

$$M \equiv \left(\frac{\partial f_s}{\partial c}\right)_{T,\mathbf{F}} \tag{4}$$

is the diffusion potential [12–14] of atoms relative to vacancies, Ω' is the reference volume per lattice site, and $\mathbf{P}$ is the first Piola-Kirchhoff stress tensor. The latter is related to the true (Cauchy) stress tensor $\boldsymbol{\sigma}$ by [10]

$$\mathbf{P} = G\mathbf{F}^{-1} \cdot \boldsymbol{\sigma}, \tag{5}$$

where $G = \det \mathbf{F}$ is the Jacobian of the deformation gradient. The Cauchy stress $\boldsymbol{\sigma}$ tensor is symmetric according to angular-momentum balance in the absence of body couples [10].

III. EVOLUTION OF AN ISOLATED GRAIN

We first consider time evolution of a single-crystalline region (grain) subject to mechanical stresses and under a given initial distribution of vacancies. Before formulating the

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[1] We follow the convention [10] that the dot between vectors or tensors (e.g., $\mathbf{a} \cdot \mathbf{b}$) denotes their inner product (contraction) while juxtaposition (e.g, $\mathbf{ab}$) their outer (dyadic) product. Two dots denote the double contractions $\mathbf{a} \cdot\cdot \mathbf{b} = \mathrm{Tr}(\mathbf{a} \cdot \mathbf{b})$ and $\mathbf{a} : \mathbf{b} = \mathbf{a} \cdot \mathbf{b}^{\mathbf{T}}$, where $\mathbf{a}$ and $\mathbf{b}$ are second-rank tensors and superscript T denotes transposition. The differentiation operator ∇ is treated as a vector. We use the notation $\mathbf{a}\overleftarrow{\nabla}$ to show that ∇ operates on the vector or tensor $\mathbf{a}$ appearing on its left.

general evolution equations of the grain, we will consider two particular cases, referred to as Case 1 and Case 2.

A. Case 1: No site creation

Consider a lattice region $\mathcal{R}$ obtained by deformation of a given reference region $\mathcal{R}'$ and thus containing a *fixed* number of lattice sites. We assume that there is no exchange of atoms between the grain and the environment, so that the total number of atoms in the grain is fixed. The grain can be thought of as embedded in a chemically inert medium whose only role is to exert mechanical stresses $\boldsymbol{\sigma}_{\mathrm{ext}}$ along its boundary $\partial\mathcal{R}$. In turn, this medium is enclosed in a rigid box equilibrated with a thermostat and incapable of performing any work at the walls.

The total free energy of the system is

$$\Phi_1 = \int_{\mathcal{R}'}\frac{f_s}{\Omega'}dv' + \int_{\partial\mathcal{R}}\gamma\, dA + \Phi_m. \tag{6}$$

The first term is the free energy stored inside the grain, which is computed by integration over the volume of the reference region $\mathcal{R}'$, where dv' is the increment of the reference volume. The second integral is taken over the deformed surface of the grain and represents the total surface free energy, dA being an increment of the surface area and γ the reversible work needed to create a unit area of the surface. The latter is called the surface free energy. Finally, Φ_m represents the free energy of the surrounding medium.

We will adopt a treatment of surface thermodynamics in which the fundamental equation of the surface has the form,

$$\gamma = \gamma(T,\varphi). \tag{7}$$

In this equation,

$$\varphi = \frac{dA}{dA'}, \tag{8}$$

where dA' is the area of a surface element in the reference state and dA is the area of the same surface element in the elastically deformed state. Thus φ is a measure of elastic surface deformation at a given location at the surface. The use of Eq. (7) implies that the surface free energy is independent of the surface orientation, and thus isotropic. Namely, it depends only on the elastic change in the surface area regardless of the directions in which the area was stretched or compressed to produce the given area change.

Consider a time-dependent process accompanied by changes in the elastic deformation of the grain and variations in its local composition c. These changes create a lattice velocity field,

$$\mathbf{v}_L(\mathbf{x}',t) = \left(\frac{\partial \mathbf{x}}{\partial t}\right)_{\mathbf{x}'}, \tag{9}$$

which can be expressed as a function of deformed coordinates, $\mathbf{v}_L(\mathbf{x},t)$. The rate of free energy change per site seen by an observer moving with the lattice is

$$\begin{aligned}
\frac{d^L f_s}{dt} &= M\frac{d^L c}{dt} + \Omega'\mathbf{P} \cdot\cdot \frac{d^L\mathbf{F}}{dt}\\
&= -MG\Omega'\nabla \cdot \mathbf{J}_L + \Omega'\mathbf{P} \cdot\cdot \mathbf{v}_L\overleftarrow{\nabla}', \tag{10}
\end{aligned}$$

where the lattice material time derivative d^L/dt is defined by

$$\frac{d^L}{dt} \equiv \left(\frac{\partial}{\partial t}\right)_{\mathbf{x}'} = \left(\frac{\partial}{\partial t}\right)_{\mathbf{x}} + \mathbf{v}_L\cdot\nabla, \tag{11}$$

and $\mathbf{J}_L$ is the diffusion flux of atoms relative to the moving lattice. In the second line of Eq. (10) we used the relations,

$$\frac{d^L\mathbf{F}}{dt} = \mathbf{v}_L\overleftarrow{\nabla'}, \tag{12}$$

and

$$\frac{d^L c}{dt} = -G\Omega'\nabla\cdot\mathbf{J}_L. \tag{13}$$

Equation (12) is an identity readily obtainable by combining the definitions (2) and (9).[2] To prove Eq. (13), we use the atomic balance relation,

$$\frac{d^L}{dt}\left(\frac{c}{\Omega}\right) = -\frac{c}{\Omega}\nabla\cdot\mathbf{v}_L - \nabla\cdot\mathbf{J}_L, \tag{14}$$

combined with the Jacobi identity [10],

$$\frac{d^L}{dt}\left(\frac{1}{\Omega}\right) = -\frac{1}{\Omega}\nabla\cdot\mathbf{v}_L, \tag{15}$$

where $\Omega = G\Omega'$ is the deformed volume per site and thus c/Ω is the number density of atoms per unit volume in the deformed state.

Applying the identity,

$$\nabla'\cdot(\mathbf{P}\cdot\mathbf{v}_L) = (\nabla'\cdot\mathbf{P})\cdot\mathbf{v}_L + \mathbf{P}\cdot\cdot(\mathbf{v}_L\overleftarrow{\nabla'}), \tag{16}$$

Eq. (10) can be rewritten as

$$\frac{d^L f_s}{dt} = -MG\Omega'\nabla\cdot\mathbf{J}_L + \Omega'\nabla'\cdot(\mathbf{P}\cdot\mathbf{v}_L) - \Omega'(\nabla'\cdot\mathbf{P})\cdot\mathbf{v}_L. \tag{17}$$

The rate of free energy change of the entire system (i.e., the grain, its surface, and the surrounding medium) is obtained as the time derivative of Eq. (6):

$$\dot{\Phi}_1 = \int_{\mathcal{R}'}\frac{d^L f_s}{dt}\frac{dv'}{\Omega'} + \int_{\partial\mathcal{R}}\gamma\,d\dot{A} + \int_{\partial\mathcal{R}}\dot{\gamma}\,dA$$
$$- \int_{\partial\mathcal{R}}\mathbf{n}\cdot\boldsymbol{\sigma}_{\text{ext}}\cdot\mathbf{v}_L\,dA, \tag{18}$$

where $\mathbf{n}$ is a unit normal to the surface pointing outside the grain, $d\dot{A}$ is the rate of area change of the surface element dA, and $\dot{\gamma}$ is the rate of change of the surface free energy γ. The first integral is the rate of free energy change inside the grain. The next two integrals represent the rate of work expended on elastic deformation of the surface. The last integral is the rate of mechanical work performed by the surrounding medium on the grain, the negative of which gives the rate $\dot{\Phi}_m$ of free energy change of the medium.

Equation (18) will now be transformed to a form that is more suitable for the analysis of creep deformation. We start

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[2]Indeed, $\frac{d^L\mathbf{F}}{dt} = (\frac{\partial\mathbf{F}}{\partial t})_{\mathbf{x}'} = (\frac{\partial}{\partial t}(\frac{\partial\mathbf{x}}{\partial\mathbf{x}'})_t)_{\mathbf{x}'} = (\frac{\partial}{\partial\mathbf{x}'}(\frac{\partial\mathbf{x}}{\partial t})_{\mathbf{x}'})_t = (\frac{\partial}{\partial\mathbf{x}'}\mathbf{v}_L)_t = \mathbf{v}_L\overleftarrow{\nabla'}$.

with the first integral by inserting $d^L f_s/dt$ from Eq. (17). The integral of the first term in Eq. (17) is

$$-\int_{\mathcal{R}'}MG\nabla\cdot\mathbf{J}_L\,dv' = -\int_{\mathcal{R}}M\nabla\cdot\mathbf{J}_L\,dv$$
$$= -\int_{\mathcal{R}}\nabla\cdot(M\mathbf{J}_L)\,dv + \int_{\mathcal{R}}\mathbf{J}_L\cdot\nabla M\,dv$$
$$= -\int_{\partial\mathcal{R}}M\mathbf{n}\cdot\mathbf{J}_L\,dA + \int_{\mathcal{R}}\mathbf{J}_L\cdot\nabla M\,dv, \tag{19}$$

where $G\,dv' = dv$ (increment of deformed volume). At the last step we applied the divergence theorem. For the integral of the second term in Eq. (17) we again use the divergence theorem to convert it to a surface integral in the reference state and then in the deformed state,

$$\int_{\mathcal{R}'}\nabla'\cdot(\mathbf{P}\cdot\mathbf{v}_L)\,dv' = \int_{\partial\mathcal{R}'}\mathbf{n}'\cdot(\mathbf{P}\cdot\mathbf{v}_L)\,dA' = \int_{\partial\mathcal{R}}\mathbf{n}\cdot\boldsymbol{\sigma}\cdot\mathbf{v}_L\,dA, \tag{20}$$

where $\mathbf{n}'$ is the normal to the boundary $\partial\mathcal{R}'$ of the reference region. At the last step we applied Nanson's formula [10] $\mathbf{n}'dA' = G^{-1}\mathbf{n}\cdot\mathbf{F}\,dA$ and Eq. (5) for $\mathbf{P}$. Finally, the integral of the third term in Eq. (17) is

$$-\int_{\mathcal{R}'}(\nabla'\cdot\mathbf{P})\cdot\mathbf{v}_L\,dv' = -\int_{\mathcal{R}}G^{-1}(\nabla'\cdot\mathbf{P})\cdot\mathbf{v}_L\,dv. \tag{21}$$

Combining the three terms,

$$\int_{\mathcal{R}'}\frac{d^L f_s}{dt}\frac{dv'}{\Omega'} = \int_{\mathcal{R}}(\mathbf{J}_L\cdot\nabla M - G^{-1}(\nabla'\cdot\mathbf{P})\cdot\mathbf{v}_L)\,dv$$
$$- \int_{\partial\mathcal{R}}M\mathbf{n}\cdot\mathbf{J}_L\,dA + \int_{\partial\mathcal{R}}\mathbf{n}\cdot\boldsymbol{\sigma}\cdot\mathbf{v}_L\,dA. \tag{22}$$

We now turn to the surface integrals in Eq. (18). Recall that $d\dot{A}$ is the rate of area change of a surface element obtained by elastic deformation of a given reference surface element dA'. The volume swept by this surface element per unit time during the elastic deformation is $d\dot{v} = \mathbf{n}\cdot\mathbf{v}_L\,dA$. Introducing the total surface curvature $k \equiv d\dot{A}/d\dot{v}$, we have $d\dot{A} = k\mathbf{n}\cdot\mathbf{v}_L\,dA$. Thus the two surface integrals can be combined together to give

$$\int_{\partial\mathcal{R}}\gamma\,d\dot{A} + \int_{\partial\mathcal{R}}\dot{\gamma}\,dA = \int_{\partial\mathcal{R}}\left(\gamma + \dot{\gamma}\frac{dA}{d\dot{A}}\right)d\dot{A}$$
$$\equiv \int_{\partial\mathcal{R}}k\tau\mathbf{n}\cdot\mathbf{v}_L\,dA, \tag{23}$$

where τ is defined by

$$\tau \equiv \gamma + \dot{\gamma}\frac{dA}{d\dot{A}}. \tag{24}$$

Applying Eqs. (7) and (8) and the obvious relations $\dot{\varphi} = d\dot{A}/dA'$ and $\dot{\gamma} = (\partial\gamma/\partial\varphi)\dot{\varphi}$, we have

$$\tau \equiv \gamma + \varphi\frac{\partial\gamma}{\partial\varphi} = \gamma + A\frac{\partial\gamma}{\partial A}, \tag{25}$$

showing that τ has the meaning of isotropic surface stress. The obtained expression for τ is consistent with the Shuttleworth equation for the surface stress tensor [15].

Combining the above equations we finally obtain the rate of total free energy dissipation for Case 1:

$$
\dot{\Phi}_1 = \int_{\mathcal{R}} (\mathbf{J}_L \cdot \nabla M - G^{-1}(\nabla' \cdot \mathbf{P}) \cdot \mathbf{v}_L) dv
$$
$$
- \int_{\partial \mathcal{R}} M \mathbf{n} \cdot \mathbf{J}_L dA + \int_{\partial \mathcal{R}} \mathbf{n} \cdot (k\tau \mathbf{I} + \boldsymbol{\sigma} - \boldsymbol{\sigma}_{\text{ext}}) \cdot \mathbf{v}_L dA,
$$
$$(26)$$

where $\mathbf{I}$ is the rank two identity tensor. Note that the appearance in this equation of the lattice diffusion flux $\mathbf{n} \cdot \mathbf{J}_L$ normal to the surface does not contradict the conservation of atoms in the system. As will be discussed later, this flux need not be zero in the presence of surface diffusion.

B. Case 2: Pure site creation

Now suppose that the grain $\mathcal{R}$ expands by generation of new lattice sites at its surface without changing the physical state of the material. This process is similar to surface growth and can be described as expansion of the reference region $\mathcal{R}'$ by the motion of its boundary $\partial \mathcal{R}'$ with velocities $\mathbf{v}'_s$ at a fixed composition field $c(\mathbf{x}')$ and fixed deformation mapping $\mathbf{x}(\mathbf{x}')$. In this process, the deformed region expands by the motion of its surface with the velocities,

$$
\mathbf{v}_s = \mathbf{F} \cdot \mathbf{v}'_s,
$$
$$(27)$$

incorporating new sites with the same composition and state of deformation as the old.

Under certain surface growth mechanisms it can be possible to uniquely identify the local growth velocities $\mathbf{v}_s$. In such cases, the reference velocities $\mathbf{v}'_s$ can be back-calculated from Eq. (27) to match the actual growth velocities dictated by the adopted growth mechanism. In the absence of a surface growth model, the choice of the reference velocity field $\mathbf{v}'_s$ is not unique: Different choices can produce physically the same evolution of the growing surface. A natural choice, which will be assumed here as default, is to align the reference velocities $\mathbf{v}'_s$ parallel to the reference normal $\mathbf{n}'$. Note that in this case, the actual growth velocities $\mathbf{v}_s$ need not be parallel to the physical normal $\mathbf{n}$.

The rate of change of the total free energy of the system (the grain, its surface, and the medium) is

$$
\dot{\Phi}_2 = \int_{\partial \mathcal{R}} f_s \mathbf{n} \cdot \mathbf{v}_s \frac{dA}{\Omega} + \int_{\partial \mathcal{R}} k\gamma \mathbf{n} \cdot \mathbf{v}_s dA - \int_{\partial \mathcal{R}} \mathbf{n} \cdot \boldsymbol{\sigma}_{\text{ext}} \cdot \mathbf{v}_s dA.
$$
$$(28)$$

The first term is the rate of free energy change due to the incorporation of the new lattice regions. The second term is the rate of work expended on creation of new surface area with the rate $d\dot{A}_s = k \mathbf{n} \cdot \mathbf{v}_s dA$. Note that an integral with $\dot{\gamma}$ similar to one of the terms in Eq. (18) does not appear in Eq. (28). Indeed, according to Eq. (7) γ is a function of temperature and the elastic surface deformation φ, both of which remain constant in the process described here. Finally, the last term in Eq. (28) is the rate of work done on the region by the surrounding medium.

C. General variation of state with site generation

We are now ready to address the general case in which the surface of the grain moves by both site generation as in Case 2 and due to variations in the composition and strain fields as in Case 1. The total velocity $\mathbf{v}_b$ of the surface is obtained as the time derivative of the deformation map $\mathbf{x} = \mathbf{x}(\mathbf{x}',t)$,

$$
\mathbf{v}_b = \frac{d\mathbf{x}}{dt} = \left(\frac{\partial \mathbf{x}}{\partial t} \right)_{\mathbf{x}'} + \left(\frac{\partial \mathbf{x}}{\partial \mathbf{x}'} \right)_t \frac{d\mathbf{x}'}{dt} = \mathbf{v}_L + \mathbf{F} \cdot \mathbf{v}'_s = \mathbf{v}_L + \mathbf{v}_s.
$$
$$(29)$$

The total free energy change of the system is $\dot{\Phi} = \dot{\Phi}_1 + \dot{\Phi}_2$ and is obtained by adding Eqs. (26) and (28),

$$
\dot{\Phi} = \int_{\mathcal{R}} (\mathbf{J}_L \cdot \nabla M - G^{-1}(\nabla' \cdot \mathbf{P}) \cdot \mathbf{v}_L) dv
$$
$$
- \int_{\partial \mathcal{R}} M \mathbf{n} \cdot \mathbf{J}_L dA + \int_{\partial \mathcal{R}} \mathbf{n} \cdot (k\tau \mathbf{I} + \boldsymbol{\sigma} - \boldsymbol{\sigma}_{\text{ext}}) \cdot \mathbf{v}_L dA
$$
$$
+ \int_{\partial \mathcal{R}} \mathbf{n} \cdot \left(\left(\frac{f_s}{\Omega} + k\gamma \right) \mathbf{I} - \boldsymbol{\sigma}_{\text{ext}} \right) \cdot (\mathbf{v}_b - \mathbf{v}_L) dA. \quad (30)
$$

It should be noted that Eq. (30) does not take into account the conservation of atoms in the system. To formulate this conservation, we introduce the quantity,

$$
\nu \equiv \frac{c}{\Omega} \mathbf{n} \cdot (\mathbf{v}_b - \mathbf{v}_L) - \mathbf{n} \cdot \mathbf{J}_L,
$$
$$(31)$$

which generally represents the flux of atoms measured relative to the moving surface and considered positive if atoms are added to the grain. For a surface in contact with an inert medium, such atoms can only be supplied by surface diffusion. Thus, the conservation of atoms can be expressed by the relation,

$$
\nu = -\nabla_b \cdot \mathbf{J}_b,
$$
$$(32)$$

where $\mathbf{J}_b$ is a two-dimensional diffusion flux at the surface (number of atoms crossing a unit length at the surface per unit time) taken with respect to the surface layer of atoms. The surface divergence $-\nabla_b \cdot \mathbf{J}_b$ is the rate of supply of atoms by diffusion along the surface.

We will now incorporate the atom conservation condition (32) by eliminating the surface integral of $M \mathbf{n} \cdot \mathbf{J}_L$ from the free energy dissipation rate (30), which becomes

$$
\dot{\Phi} = \int_{\mathcal{R}} (\mathbf{J}_L \cdot \nabla M - G^{-1}(\nabla' \cdot \mathbf{P}) \cdot \mathbf{v}_L) dv
$$
$$
+ \int_{\partial \mathcal{R}} \mathbf{n} \cdot (k\tau \mathbf{I} + \boldsymbol{\sigma} - \boldsymbol{\sigma}_{\text{ext}}) \cdot \mathbf{v}_L dA - \int_{\partial \mathcal{R}} M \nabla_b \cdot \mathbf{J}_b dA
$$
$$
+ \int_{\partial \mathcal{R}} \mathbf{n} \cdot \left(\left(\frac{f_s - Mc}{\Omega} + k\gamma \right) \mathbf{I} - \boldsymbol{\sigma}_{\text{ext}} \right) \cdot (\mathbf{v}_b - \mathbf{v}_L) dA.
$$
$$(33)$$

The integral with $\nabla_b \cdot \mathbf{J}_b$ can be further transformed by using the identity,

$$
M \nabla_b \cdot \mathbf{J}_b = \nabla_b \cdot (M \mathbf{J}_b) - \mathbf{J}_b \cdot \nabla_b M,
$$
$$(34)$$

to give

$$\dot{\Phi} = \int_{\mathcal{R}} (\mathbf{J}_L \cdot \nabla M - G^{-1}(\nabla' \cdot \mathbf{P}) \cdot \mathbf{v}_L) dv$$
$$+ \int_{\partial\mathcal{R}} \mathbf{n} \cdot (k\tau \mathbf{I} + \boldsymbol{\sigma} - \boldsymbol{\sigma}_{\text{ext}}) \cdot \mathbf{v}_L dA + \int_{\partial\mathcal{R}} \mathbf{J}_b \cdot \nabla_b M dA$$
$$+ \int_{\partial\mathcal{R}} \mathbf{n} \cdot \left(\left(\frac{f_s - Mc}{\Omega} + k\gamma \right) \mathbf{I} - \boldsymbol{\sigma}_{\text{ext}} \right) \cdot (\mathbf{v}_b - \mathbf{v}_L) dA$$
$$+ \int_{\partial\mathcal{R}} \nabla_b \cdot (M\mathbf{J}_b) dA. \tag{35}$$

The integral in the last line is computed by applying the surface divergence theorem,

$$\int_{\partial\mathcal{R}} \nabla_b \cdot (M\mathbf{J}_b) dA = \int_{\mathcal{L}} \mathbf{e} \cdot (M_b \mathbf{J}_b) dl = 0, \tag{36}$$

where $\mathbf{e}$ is a unit vector tangential to the boundary and normal to the contour $\mathcal{L}$ bounding the surface. This integral obviously vanishes for an isolated grain. The final expression for the rate of free energy dissipation becomes

$$\dot{\Phi} = \int_{\mathcal{R}} (\mathbf{J}_L \cdot \nabla M - G^{-1}(\nabla' \cdot \mathbf{P}) \cdot \mathbf{v}_L) dv$$
$$+ \int_{\partial\mathcal{R}} \mathbf{n} \cdot (k\tau \mathbf{I} + \boldsymbol{\sigma} - \boldsymbol{\sigma}_{\text{ext}}) \cdot \mathbf{v}_L dA + \int_{\partial\mathcal{R}} \mathbf{J}_b \cdot \nabla_b M dA$$
$$+ \int_{\partial\mathcal{R}} \mathbf{n} \cdot \left(\left(\frac{f_s - Mc}{\Omega} + k\gamma \right) \mathbf{I} - \boldsymbol{\sigma}_{\text{ext}} \right) \cdot (\mathbf{v}_b - \mathbf{v}_L) dA. \tag{37}$$

As a test of Eq. (37), we will apply it to determine the conditions of equilibrium in the system. To this end, the quantities $\mathbf{v}_L$, $(\mathbf{v}_b - \mathbf{v}_L)$, $\mathbf{J}_L$, and $\mathbf{J}_b$ are treated as virtual variations occurring per unit time. Accordingly, the coefficients before these variations inside the grain $\mathcal{R}$ and at its surface $\partial\mathcal{R}$ must be zero. This leads to the following equilibrium conditions:

$$\nabla' \cdot \mathbf{P} = \mathbf{0} \quad \text{Mechanical equilibrium inside } \mathcal{R}, \tag{38}$$

$$M = \text{const} \quad \text{Chemical equilibrium inside } \mathcal{R}, \tag{39}$$

$$\mathbf{n} \cdot \boldsymbol{\sigma}_{\text{ext}} - \mathbf{n} \cdot \boldsymbol{\sigma} = k\tau \mathbf{n} \quad \text{Mechanical equilibrium at the surface } \partial\mathcal{R}, \tag{40}$$

$$M = \text{const} \quad \text{Chemical equilibrium at the surface } \partial\mathcal{R}, \tag{41}$$

$$(f_s - Mc + \Omega k\gamma)\mathbf{n} = \Omega \mathbf{n} \cdot \boldsymbol{\sigma}_{\text{ext}} \quad \text{Site generation equilibrium at the surface } \partial\mathcal{R}. \tag{42}$$

The latter relation shows that the surface traction vector $\mathbf{n} \cdot \boldsymbol{\sigma}_{\text{ext}}$ must be normal to the boundary and equal in magnitude to $f_s - Mc + \Omega k\gamma$. This condition can be rewritten in the form,

$$f_s - Mc + \Omega k\gamma = \Omega \mathbf{n} \cdot \boldsymbol{\sigma}_{\text{ext}} \cdot \mathbf{n}, \tag{43}$$

or

$$f_s - Mc + \Omega k(\gamma - \tau) = \Omega \mathbf{n} \cdot \boldsymbol{\sigma} \cdot \mathbf{n}. \tag{44}$$

Combining Eqs. (40) and (42) we conclude that the traction vector $\mathbf{n} \cdot \boldsymbol{\sigma}$ is also normal to the surface.

Next, we apply Eq. (37) to relatively slow processes in which mechanical equilibrium is maintained both inside the grain and at the surface. Accordingly, Eqs. (38) and (40) are assumed to be satisfied at all times. Then Eq. (37) simplifies to

$$\dot{\Phi} = \int_{\mathcal{R}} \mathbf{J}_L \cdot \nabla M dv + \int_{\partial\mathcal{R}} \mathbf{J}_b \cdot \nabla_b M dA$$
$$+ \int_{\partial\mathcal{R}} \mathbf{n} \cdot \left(\left(\frac{f_s - Mc}{\Omega} + k\gamma \right) \mathbf{I} - \boldsymbol{\sigma}_{\text{ext}} \right) \cdot (\mathbf{v}_b - \mathbf{v}_L) dA. \tag{45}$$

Note that this equation is invariant under Galilean transformations because the fluxes $\mathbf{J}_L$ and $\mathbf{J}_b$ are defined relative to the lattice and the surface layer, respectively, and $(\mathbf{v}_b - \mathbf{v}_L)$ is the surface velocity relative to the lattice.

Using Eq. (45) and neglecting kinetic cross-effects, we can formulate the following phenomenological kinetic relations. The equation,

$$\mathbf{J}_L = -L\nabla M, \tag{46}$$

describes diffusion inside the lattice, $L > 0$ being the kinetic coefficient of lattice diffusion. This equation assumes that the diffusivity of the lattice is isotropic. Likewise, diffusion along the surface follows the equation,

$$\mathbf{J}_b = -L_b \nabla_b M, \tag{47}$$

where the kinetic coefficient $L_b > 0$ characterizes surface diffusion and is generally different from L (even in dimensions). Surface diffusion is also considered isotropic. Finally, the rate $\dot{s}$ of site generation at the surface (number of sites per unit area per unit time) can be described by the phenomenological equation,

$$\dot{s} = \frac{1}{\Omega} \mathbf{n} \cdot (\mathbf{v}_b - \mathbf{v}_L) = -K_s (f_s - Mc + \Omega k\gamma - \Omega \mathbf{n} \cdot \boldsymbol{\sigma}_{\text{ext}} \cdot \mathbf{n}), \tag{48}$$

$K_s > 0$ being the kinetic coefficient related to the site generation process.

The right-hand side of Eq. (48) identifies the thermodynamic driving force for site generation by the surface. For a stress-free plane surface, the driving force is simply the grand potential per lattice site $(f_s - Mc)$. The surface curvature and applied stress $\boldsymbol{\sigma}_{\text{ext}}$ contribute to the driving force, affecting

the site generation process and thus the shape change of the material.

IV. EVOLUTION OF A BICRYSTAL

A. Calculation of the free energy dissipation

Moving to the next level of complexity, we now consider a bicrystal composed of two grains, labeled α and β, enclosed in a rigid box. The grains fill the entire volume of the box without voids. The boundary $\mathcal{S}$ between the grains can either terminate at the walls of the box or form a closed surface bounding grain α. In either case, one or both of the grains are in contact with the walls of the box. We assume that the contact planes between the grains and the walls satisfy a no-slip condition eliminating any mechanical work done on such planes. There is no transfer of atoms through or generation of sites at the walls of the box. These assumptions are made in order to focus the attention on processes occurring inside the grains and at the grain boundary $\mathcal{S}$. The role of the wall conditions is only to ensure that the box and the grains form a closed thermodynamic system equilibrated with a thermostat, with all mechanical work performed only inside the grains and at the grain boundary.

Evolution of this system can be described by treating the grains as growing or shrinking lattice regions, $\mathcal{R}_\alpha$ and $\mathcal{R}_\beta$, as in Sec. III. The total rate of free energy change includes a volume part, $\dot{\Phi}_\alpha + \dot{\Phi}_\beta$, and a grain boundary contribution $\dot{\Phi}_b$. For the volume parts, $\dot{\Phi}_\alpha$ and $\dot{\Phi}_\beta$, we use the previously derived Eq. (30) in which we omit the terms involving the external stress $\boldsymbol{\sigma}_{\text{ext}}$ as well as the interface free energy and interface stress:

$$\dot{\Phi}_\alpha = \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv$$

$$- \int_{\mathcal{S}} M_\alpha \mathbf{n}^\alpha \cdot \mathbf{J}_L^\alpha dA + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot \boldsymbol{\sigma}_\alpha \cdot \mathbf{v}_L^\alpha dA$$

$$+ \int_{\mathcal{S}} \frac{f_s^\alpha}{\Omega_\alpha} \mathbf{n}^\alpha \cdot \left(\mathbf{v}_b^\alpha - \mathbf{v}_L^\alpha \right) dA, \quad (49)$$

$$\dot{\Phi}_\beta = \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv$$

$$- \int_{\mathcal{S}} M_\beta \mathbf{n}^\beta \cdot \mathbf{J}_L^\beta dA + \int_{\mathcal{S}} \mathbf{n}^\beta \cdot \boldsymbol{\sigma}_\beta \cdot \mathbf{v}_L^\beta dA$$

$$+ \int_{\mathcal{S}} \frac{f_s^\beta}{\Omega_\beta} \mathbf{n}^\beta \cdot \left(\mathbf{v}_b^\beta - \mathbf{v}_L^\beta \right) dA. \quad (50)$$

All quantities appearing in these equations have the same meaning as in Sec. III, with the labels α and β referring to the grains. We did not yet impose any contact conditions between the grains, which at this point can be thought of as separated by a gap. Thus $\mathbf{n}^\alpha$ is a unit normal to the surface of grain α pointing outside of this grain, and $\mathbf{n}^\beta$ is a unit normal to the surface of grain β pointing outside of that grain. Similarly, $\mathbf{v}_b^\alpha$ is the surface velocity of grain α and $\mathbf{v}_b^\beta$ the surface velocity of grain β.

We now impose the condition that the two grains stay in contact. The contact condition is expressed by the equations,

$$\mathbf{n}^\alpha \cdot \mathbf{v}_b^\alpha = \mathbf{n}^\alpha \cdot \mathbf{v}_b^\beta, \quad (51)$$

and

$$\mathbf{n}^\beta = -\mathbf{n}^\alpha. \quad (52)$$

As will be discussed later, these conditions do not preclude grain boundary sliding.

The boundary part of the free energy rate has the form similar to Eq. (23):

$$\dot{\Phi}_b = \int_{\mathcal{S}} \gamma d\dot{A} + \int_{\mathcal{S}} \dot{\gamma} dA, \quad (53)$$

where γ is the grain boundary free energy. The rate of change of the boundary area can be computed from the kinematic description of grain α,

$$d\dot{A} = k_\alpha \mathbf{n}^\alpha \cdot \mathbf{v}_b^\alpha dA, \quad (54)$$

or from the kinematic description of grain β,

$$d\dot{A} = k_\beta \mathbf{n}^\beta \cdot \mathbf{v}_b^\beta dA. \quad (55)$$

These two equations give the same result for $d\dot{A}$ due to the contact conditions (51) and (52) and the relation $k_\beta = -k_\alpha$ between the two descriptions of the same boundary curvature.

Further calculations require a postulated fundamental equation of interface thermodynamics. We will adopt the following fundamental equation:

$$\gamma = \gamma(T, \varphi_\alpha, \varphi_\beta), \quad (56)$$

where $\varphi_\alpha = (dA/dA')_\alpha$ and $\varphi_\beta = (dA/dA')_\beta$ describe elastic deformations of the two lattices in contact with the boundary. Note that γ is postulated to depend only on the areal deformations and not be affected by other components of the elastic deformation. Furthermore, γ is not affected by possible relative sliding of the two grains. While kinematic descriptions based on more complex fundamental equations have been proposed [16], we focus the attention of this simple case to make the model more tractable.

Using the fundamental equation (56) in conjunction with the easily derivable relations $\dot{\varphi}_\alpha = (d\dot{A}/dA')_\alpha = \varphi_\alpha k_\alpha \mathbf{n}^\alpha \cdot \mathbf{v}_L^\alpha$ and $\dot{\varphi}_\beta = (d\dot{A}/dA')_\beta = \varphi_\beta k_\beta \mathbf{n}^\beta \cdot \mathbf{v}_L^\beta$, we obtain

$$\dot{\gamma} = k_\alpha \mathbf{n}^\alpha \cdot \left(\varphi_\alpha \frac{\partial \gamma}{\partial \varphi_\alpha} \mathbf{v}_L^\alpha + \varphi_\beta \frac{\partial \gamma}{\partial \varphi_\beta} \mathbf{v}_L^\beta \right), \quad (57)$$

where we took into account that $k_\alpha \mathbf{n}^\alpha = k_\beta \mathbf{n}^\beta$. Putting Eqs. (53) to (57) together, the rate of free energy change associated with the grain boundary becomes

$$\dot{\Phi}_b = \int_{\mathcal{S}} k_\alpha \mathbf{n}^\alpha \cdot \left(\gamma \mathbf{v}_b^\alpha + \varphi_\alpha \frac{\partial \gamma}{\partial \varphi_\alpha} \mathbf{v}_L^\alpha + \varphi_\beta \frac{\partial \gamma}{\partial \varphi_\beta} \mathbf{v}_L^\beta \right) dA. \quad (58)$$

We next impose the condition of conservation of atoms in the system. The number of atoms added to grain α at the grain boundary (per unit area per unit time) is

$$\nu_\alpha = \frac{c_\alpha}{\Omega_\alpha} \mathbf{n}^\alpha \cdot \left(\mathbf{v}_b^\alpha - \mathbf{v}_L^\alpha \right) - \mathbf{n}^\alpha \cdot \mathbf{J}_L^\alpha, \quad (59)$$

with a similar number for grain β:

$$\nu_\beta = \frac{c_\beta}{\Omega_\beta} \mathbf{n}^\beta \cdot \left(\mathbf{v}_b^\beta - \mathbf{v}_L^\beta \right) - \mathbf{n}^\beta \cdot \mathbf{J}_L^\beta. \quad (60)$$

If there were no grain boundary diffusion, the conservation of atoms would dictate $\nu_\alpha + \nu_\beta = 0$. In the presence of

grain boundary diffusion, the conservation of atoms can be expressed by

$$v_\alpha + v_\beta = -\nabla_b \cdot \mathbf{J}_b, \tag{61}$$

where $\mathbf{J}_b$ is a two-dimensional diffusion flux (number of atoms crossing a unit boundary length per unit time) relative to the boundary layer, and $\nabla_b \cdot \mathbf{J}_b$ is the surface divergence of this flux. The conservation relation (61) must hold at every point of the boundary.

To incorporate the conservation of atoms in the free dissipation, we use Eqs. (59) and (60) to eliminate the surface integrals of $M_\alpha \mathbf{n}^\alpha \cdot \mathbf{J}_L^\alpha$ and $M_\beta \mathbf{n}^\beta \cdot \mathbf{J}_L^\beta$ from Eqs. (49) and (50), respectively. This gives

$$\dot{\Phi}_\alpha = \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv$$
$$+ \int_{\mathcal{S}} v_\alpha M_\alpha dA + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot \boldsymbol{\sigma}_\alpha \cdot \mathbf{v}_L^\alpha dA$$
$$+ \int_{\mathcal{S}} \left(\frac{f_s^\alpha - M_\alpha c_\alpha}{\Omega_\alpha} \right) \mathbf{n}^\alpha \cdot (\mathbf{v}_b^\alpha - \mathbf{v}_L^\alpha) dA, \tag{62}$$

$$\dot{\Phi}_\beta = \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv$$
$$+ \int_{\mathcal{S}} v_\beta M_\beta dA + \int_{\mathcal{S}} \mathbf{n}^\beta \cdot \boldsymbol{\sigma}_\beta \cdot \mathbf{v}_L^\beta dA$$
$$+ \int_{\mathcal{S}} \left(\frac{f_s^\beta - M_\beta c_\beta}{\Omega_\beta} \right) \mathbf{n}^\beta \cdot (\mathbf{v}_b^\beta - \mathbf{v}_L^\beta) dA. \tag{63}$$

Finally, adding together the free energy dissipations in the grains and at the grain boundary we obtain the following expression for the total free energy dissipation rate:

$$\dot{\Phi} = \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv$$
$$+ \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv$$
$$+ \int_{\mathcal{S}} (v_\alpha M_\alpha + v_\beta M_\beta) dA + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot \left(\boldsymbol{\sigma}_\alpha \cdot \mathbf{v}_L^\alpha - \boldsymbol{\sigma}_\beta \cdot \mathbf{v}_L^\beta \right) dA$$
$$+ \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot \left(\omega^\alpha (\mathbf{v}_b^\alpha - \mathbf{v}_L^\alpha) - \omega^\beta (\mathbf{v}_b^\alpha - \mathbf{v}_L^\beta) \right) dA$$
$$+ \int_{\mathcal{S}} k_\alpha \mathbf{n}^\alpha \cdot \left(\gamma \mathbf{v}_b^\alpha + \varphi_\alpha \frac{\partial \gamma}{\partial \varphi_\alpha} \mathbf{v}_L^\alpha + \varphi_\beta \frac{\partial \gamma}{\partial \varphi_\beta} \mathbf{v}_L^\beta \right) dA, \tag{64}$$

where

$$\omega_\alpha \equiv \frac{f_s^\alpha - M_\alpha c_\alpha}{\Omega_\alpha} \tag{65}$$

and

$$\omega_\beta \equiv \frac{f_s^\beta - M_\beta c_\beta}{\Omega_\beta} \tag{66}$$

are grand potentials per unit volume inside the grains. Note that we replaced $\mathbf{n}^\alpha \cdot \mathbf{v}_b^\beta$ by $\mathbf{n}^\alpha \cdot \mathbf{v}_b^\alpha$ using Eq. (51).

The subsequent calculations can be simplified by adopting the following notations [16]. For a vector or tensor field $\mathbf{A}(\mathbf{x})$, let $\mathbf{A}_\alpha$ and $\mathbf{A}_\beta$ denote the limits of this field when approaching

the grain boundary from each grain at the same location. Then

$$[\mathbf{A}] \equiv \mathbf{A}_\alpha - \mathbf{A}_\beta \tag{67}$$

is the jump of $\mathbf{A}$ across the boundary while

$$\langle \mathbf{A} \rangle \equiv \frac{\mathbf{A}_\alpha + \mathbf{A}_\beta}{2} \tag{68}$$

is the average boundary value of $\mathbf{A}$. It can be expected that driving forces acting on the grain boundary arise from jumps of thermodynamic properties across the boundary or gradients of average values of thermodynamic properties along the boundary.

Furthermore, we decompose the lattice velocity jump $[\mathbf{v}_L]$ into a normal and parallel components,

$$[\mathbf{v}_L] = [\mathbf{v}_L]_\perp + [\mathbf{v}_L]_{||}, \tag{69}$$

and similarly decompose the average lattice velocity,

$$\langle \mathbf{v}_L \rangle = \langle \mathbf{v}_L \rangle_\perp + \langle \mathbf{v}_L \rangle_{||}, \tag{70}$$

the average traction vector $\mathbf{s} \equiv \mathbf{n}^\alpha \cdot \boldsymbol{\sigma}$ at the boundary,

$$\mathbf{n}^\alpha \cdot \langle \boldsymbol{\sigma} \rangle = \langle \mathbf{s} \rangle_\perp + \langle \mathbf{s} \rangle_{||}, \tag{71}$$

and the jump of the traction vector,

$$\mathbf{n}^\alpha \cdot [\boldsymbol{\sigma}] = [\mathbf{s}]_\perp + [\mathbf{s}]_{||}. \tag{72}$$

The following identities are helpful during mathematical manipulations with jumps and averages:

$$[\mathbf{A} \cdot \mathbf{B}] = \langle \mathbf{A} \rangle \cdot [\mathbf{B}] + [\mathbf{A}] \cdot \langle \mathbf{B} \rangle, \tag{73}$$

$$\langle \mathbf{A} \cdot \mathbf{B} \rangle = \langle \mathbf{A} \rangle \cdot \langle \mathbf{B} \rangle + \frac{1}{4}[\mathbf{A}] \cdot [\mathbf{B}], \tag{74}$$

where $\mathbf{B}(\mathbf{x})$ is another vector or tensor field of the same rank as $\mathbf{A}(\mathbf{x})$. Similar relations obviously hold for scalar fields.

Going through a chain of mathematical transformations described in Appendix, the final form of the free energy dissipation rate becomes

$$\dot{\Phi} = \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv \tag{75}$$

$$+ \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv \tag{76}$$

$$+ \int_{\mathcal{S}} \mathbf{J}_b \cdot \nabla_b \langle M \rangle dA - \int_{\mathcal{S}} J_n [M] dA \tag{77}$$

$$+ \int_{\mathcal{S}} ([\mathbf{s}]_\perp + k_\alpha \tau \mathbf{n}^\alpha) \cdot \langle \mathbf{v}_L \rangle_\perp dA \tag{78}$$

$$+ \int_{\mathcal{S}} [\mathbf{s}]_{||} \cdot \langle \mathbf{v}_L \rangle_{||} dA \tag{79}$$

$$- \int_{\mathcal{S}} \left(\left(\langle \omega \rangle - \frac{1}{2} k_\alpha \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] \right) \mathbf{n}^\alpha - \langle \mathbf{s} \rangle_\perp \right) \cdot [\mathbf{v}_L]_\perp dA, \tag{80}$$

$$+ \int_{\mathcal{S}} \langle \mathbf{s} \rangle_{||} \cdot [\mathbf{v}_L]_{||} dA \tag{81}$$

$$+ \int_{\mathcal{S}} ([\omega] + k_\alpha \gamma) \mathbf{n}^\alpha \cdot \langle \mathbf{v}_b - \mathbf{v}_L \rangle dA, \tag{82}$$

where

$$\tau \equiv \gamma + \varphi_\alpha \frac{\partial \gamma}{\partial \varphi_\alpha} + \varphi_\beta \frac{\partial \gamma}{\partial \varphi_\beta} \qquad (83)$$

has the meaning of the surface stress of the grain boundary. In Eq. (77), we introduced the normal flux of atoms leaving grain α across the grain boundary and entering grain β:

$$J_n = \frac{(v_\beta - v_\alpha)}{2} = -\frac{1}{2}[v]. \qquad (84)$$

B. Classification of grain boundaries by mechanical response

Applications of the obtained Eqs. (75)–(82) depend on whether the velocity jumps and velocity averages at the grain boundary can vary independently or are subject to constraints arising, for example, from a particular grain boundary structure or mechanism of motion. Three types of grain boundaries will be distinguished in this work, depending on the existence and nature of such constraints.

(i) Suppose all velocity jumps and averages appearing in Eqs. (78)–(82) are completely independent of one another. As will be shown below, the boundary then responds to applied shear stresses by sliding. In equilibrium, the parallel (shear) component of the traction vector $\mathbf{s} = \mathbf{n}^\alpha \cdot \boldsymbol{\sigma}$ must be zero,

$$\mathbf{s}_{||}^\alpha = \mathbf{s}_{||}^\beta = \mathbf{0}. \qquad (85)$$

Following Larché and Cahn [13,14], we classify such grain boundaries as *incoherent* interfaces.

(ii) As will be discussed later,

$$v_{\mathrm{GB}} \equiv \mathbf{n}^\alpha \cdot \langle \mathbf{v}_b - \mathbf{v}_L \rangle = \mathbf{n}^\alpha \cdot \mathbf{v}_b^\alpha - \frac{1}{2}\mathbf{n}^\alpha \cdot (\mathbf{v}_L^\alpha + \mathbf{v}_L^\beta) \qquad (86)$$

has the meaning of the velocity of GB migration relative to the lattices of the two grains. This velocity is positive if grain α grows at the expense of grain β and negative otherwise. For some grain boundaries, v_{GB} is coupled to relative translations of the grains represented by the parallel velocity jump $[\mathbf{v}_L]_{||}$. Suppose the grain translations occur parallel to a particular direction $\mathbf{t}$ (unit vector) tangential to the boundary. The coupling effect [9,17] is characterized by the linear relation,

$$[\mathbf{v}_L]_{||} \cdot \mathbf{t} = \beta v_{\mathrm{GB}}, \qquad (87)$$

where the coupling factor β depends on crystallographic characteristics of the grain boundary and other factors [9]. The sign of the coupling factor β defines the direction of GB motion for the same jump in parallel velocity. To simplify further analysis, suppose the grain translations always occur in the direction parallel to the shear traction $\langle \mathbf{s} \rangle_{||}$ applied to the boundary: $\mathbf{t}||\langle \mathbf{s} \rangle_{||}$. Then, due to the constraint imposed by Eq. (87), Eqs. (81) and (82) can be combined into one integral,

$$\int_{\mathcal{S}} ([\omega] + k_\alpha \gamma + \beta \langle \mathbf{s} \rangle_{||} \cdot \mathbf{t}) v_{\mathrm{GB}} dA. \qquad (88)$$

As will be shown later, such boundaries can be equilibrated in the presence of applied shear stresses. They can be referred to as *coherent* interfaces [13,14,18].

(iii) There can be an intermediate case when the boundary responds to applied shears by both coupling and sliding. As before, we assume for simplicity that the grain translations

occur parallel to the direction of $\langle \mathbf{s} \rangle_{||}$. The respective constraint on the velocities can be written as [17,19]

$$[\mathbf{v}_L]_{||} \cdot \mathbf{t} = \beta v_{\mathrm{GB}} + w, \qquad (89)$$

where w is the sliding velocity. A grain boundary obeying this constraint can be called *semicoherent*. In this case, Eq. (81) becomes

$$\int_{\mathcal{S}} (\langle \mathbf{s} \rangle_{||} \cdot \mathbf{t}) w \, dA, \qquad (90)$$

whereas the last line of Eq. (82) is given by the same Eq. (88).

Several classifications of solid-solid interfaces can be found in the literature [20]. The classification outlined above is based on different mechanical responses to applied shear stresses, namely, pure sliding, coupled motion, and a mixture of both. Interfaces are often classified as incoherent, coherent, and semicoherent according to their structure, a semicoherent interface being composed of a network of misfit dislocations. These three interface structures often display mechanical responses corresponding to the three cases (i)–(iii) introduced above, which justifies our terminology.

The assumption that the relative grain translations accompanying coupled motion and sliding always occur parallel to $\langle \mathbf{s} \rangle_{||}$ is consistent with our treatment of the grain boundary as isotropic. A generalization of Eqs. (88)–(90) to anisotropic cases is straightforward but is beyond the present work.

C. Equilibrium conditions

Before formulating dynamic equations, we will first apply the obtained free energy dissipation rate, Eqs. (75)–(82), to find the conditions of thermodynamic equilibrium in the system. This will be achieved by requiring that the coefficients multiplying all independent velocities and fluxes be zero.

Equations (75) and (76) require that the diffusion potentials be spatially uniform inside the grains. In addition, the grains must satisfy the internal mechanical equilibrium conditions $\nabla' \cdot \mathbf{P}_\alpha = \mathbf{0}$ and $\nabla' \cdot \mathbf{P}_\beta = \mathbf{0}$, respectively. Equation (77) states that there must be no jump of the diffusion potential across the boundary, $[M] = 0$, and that the average value of the diffusion potential, $\langle M \rangle$, must be uniform along the grain boundary. In other words, M must be uniform throughout the entire two-grain system. Equations (78) and (79) give the conditions of mechanical equilibrium at the grain boundary, namely, the parallel component of the traction vector must be continuous across the boundary,

$$[\mathbf{s}]_{||} = \mathbf{0}, \qquad (91)$$

while the normal component undergoes a nonzero jump equal to $-k_\alpha \tau$,

$$[\mathbf{s}]_\perp + k_\alpha \tau \mathbf{n}^\alpha = \mathbf{0}. \qquad (92)$$

For a plane boundary, $k_\alpha = 0$ and this equation gives $[\mathbf{s}]_\perp = \mathbf{0}$; the traction vector $\mathbf{s}$ is continuous across the boundary. According to Eq. (80), the average boundary value of ω must satisfy the relation,

$$\langle \omega \rangle = \frac{1}{2} k_\alpha \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] + \mathbf{n}^\alpha \cdot \langle \mathbf{s} \rangle_\perp. \qquad (93)$$

As will be discussed later, this is the condition of equilibrium with respect to site generation at the grain boundary.

The remaining equilibrium conditions depend on the type of the boundary. For an incoherent boundary, Eq. (81) gives $\langle \mathbf{s} \rangle_{||} = \mathbf{0}$, which in combination with the already established condition $[\mathbf{s}]_{||} = \mathbf{0}$ leads to the conclusion that the parallel component of the traction vector must be zero [see Eq. (85)]. Thus the traction vector is normal to the incoherent boundary. The remaining condition (82) states that ω undergoes a jump equal to $-k_\alpha \gamma$,

$$[\omega] + k_\alpha \gamma = 0. \qquad (94)$$

This equation expresses the absence of driving forces for grain boundary migration (see below). In the particular case of a plane grain boundary, the traction vector is continuous across the boundary, $[\mathbf{s}]_\perp = \mathbf{0}$ [see Eq. (92)]. The grand potential density is also continuous and, by Eq. (93), has the boundary value,

$$\omega = \mathbf{n}^\alpha \cdot \mathbf{s}_\perp \quad \text{(plane grain boundary)}. \qquad (95)$$

Now turn to a coherent interface. Recall that in this case, Eqs. (81) and (82) merge into one integral (88). We can no longer conclude that the parallel component of the traction vector must be zero. Although it is still continuous across the boundary, it can remain finite at equilibrium. In other words, a coherent grain boundary is capable of supporting a static shear stress parallel to its plane [13,14,18]. The condition preventing grain boundary migration now reads

$$[\omega] + k_\alpha \gamma + \beta \langle \mathbf{s} \rangle_{||} \cdot \mathbf{t} = 0. \qquad (96)$$

Note that the grand potential density is now discontinuous even across a plane grain boundary ($k_\alpha = 0$). The magnitude of the jump $[\omega]$ can vary along the boundary due to variations in both $\langle \mathbf{s} \rangle_{||} \cdot \mathbf{t}$ and β.

Finally, for a semicoherent boundary, Eq. (81) is replaced by Eq. (90), which leads to a zero parallel component of the traction vector similar to the incoherent case. As a result, Eqs. (94) and (95) remain valid. Thus, all equilibrium conditions are exactly the same as for an incoherent boundary. Both types of boundary are capable of sliding under shear and thus can be only equilibrated in the absence of shear stresses. Their dynamics properties, however, are different as will be discussed below.

D. Phenomenological equations of time evolution

The free energy dissipation rate given by Eqs. (75)–(82) allows us to formulate a set of phenomenological equations for the evolution of the system. In the context of creep deformation, it is reasonable to assume that the interiors of the grains maintain mechanical equilibrium at all times. These equilibrium conditions only involve elastic deformation of the material and can be readily maintained during slow processes such as creep. Likewise, we can assume that the mechanical equilibrium conditions at the grain boundary, Eqs. (91) and (92), are also satisfied at all times. In addition, we will neglect all cross-effects between different thermodynamic driving forces and generalized fluxes. Taking these assumptions into

account, the free energy dissipation rate becomes

$$\dot{\Phi} = \int_{\mathcal{R}_\alpha} \mathbf{J}_L^\alpha \cdot \nabla M_\alpha dv + \int_{\mathcal{R}_\beta} \mathbf{J}_L^\beta \cdot \nabla M_\beta dv \qquad (97)$$

$$+ \int_{\mathcal{S}} \mathbf{J}_b \cdot \nabla_b \langle M \rangle dA - \int_{\mathcal{S}} J_n [M] dA \qquad (98)$$

$$- \int_{\mathcal{S}} \left(\left(\langle \omega \rangle - \frac{1}{2} k_\alpha \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] \right) \mathbf{n}^\alpha - \langle \mathbf{s} \rangle_\perp \right) \cdot [\mathbf{v}_L]_\perp dA, \qquad (99)$$

$$+ \int_{\mathcal{S}} \langle \mathbf{s} \rangle_{||} \cdot [\mathbf{v}_L]_{||} dA \qquad (100)$$

$$+ \int_{\mathcal{S}} ([\omega] + k_\alpha \gamma) v_{\text{GB}} dA, \qquad (101)$$

with v_{GB} defined by Eq. (86).

From Eq. (97), diffusion inside the grains is described by the equations,

$$\mathbf{J}_L^\alpha = -L_\alpha \nabla M_\alpha, \qquad (102)$$

and

$$\mathbf{J}_L^\beta = -L_\beta \nabla M_\beta, \qquad (103)$$

$L_\alpha > 0$ and $L_\beta > 0$ being diffusion kinetic coefficients. The remaining equations describe grain boundary kinetics. For diffusion of atoms across the grain boundary we obtain

$$J_n = -L_t (M_\beta - M_\alpha), \qquad (104)$$

where $L_t > 0$ is the kinetic coefficient for trans-boundary diffusion. Diffusion of atoms along the grain boundary is described by the equation,

$$\mathbf{J}_b = -L_p \nabla_b \langle M \rangle, \qquad (105)$$

$L_p > 0$ being the kinetic coefficient of lateral grain boundary diffusion.

Suppose the grain boundary is incoherent. Then $[\mathbf{v}_L]_\perp$, $[\mathbf{v}_L]_{||}$ and v_{GB} can be treated as three independent variables representing generalized fluxes. The normal velocity jump $[\mathbf{v}_L]_\perp$ characterizes the rate of separation of the two lattices in the direction normal to the boundary. This separation is a measure of the site generation at the boundary. Based on Eq. (99), the site generation kinetics can be described by the equation,

$$\mathbf{n}^\alpha \cdot [\mathbf{v}_L]_\perp = R \left(\langle \omega \rangle - \frac{1}{2} k_\alpha \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] - \mathbf{n}^\alpha \cdot \langle \mathbf{s} \rangle_\perp \right), \qquad (106)$$

$R > 0$ being the kinetic coefficient of site generation. Thus, the driving force for site generation depends on the average value of ω at the boundary, the boundary curvature, and the average normal component of the traction vector. For a plane grain boundary, the traction vector is continuous across the boundary and Eq. (106) becomes

$$\mathbf{n}^\alpha \cdot [\mathbf{v}_L]_\perp = R(\langle \omega \rangle - \mathbf{n}^\alpha \cdot \mathbf{s}_\perp) \quad \text{(plane grain boundary)}. \qquad (107)$$

The parallel velocity jump $[\mathbf{v}_L]_{||}$ represents grain boundary sliding which, according to Eq. (100), is driven by the shear component of the traction vector $\langle \mathbf{s} \rangle_{||}$. As in Sec. IV C, we assume that $[\mathbf{v}_L]_{||}$ is parallel to $\langle \mathbf{s} \rangle_{||}$, leading to the sliding law,

$$[\mathbf{v}_L]_{||} = -K_s \langle \mathbf{s} \rangle_{||}, \qquad (108)$$

where $K_s > 0$ is the sliding coefficient.

Turning to Eq. (101), recall that the velocity v_{GB} defined by Eq. (86) represents the grain boundary motion relative to the lattices of the two grains. Indeed, if the lattice velocities are equal, $\mathbf{v}_L^\alpha = \mathbf{v}_L^\beta \equiv \mathbf{v}_L$, then Eq. (86) gives $v_{\mathrm{GB}} = \mathbf{n}^\alpha \cdot (\mathbf{v}_b^\alpha - \mathbf{v}_L)$, which is indeed the grain boundary velocity relative to the common velocity of the grains. Note that according to Eq. (106), the total rate of site generation is then zero, which is consistent with the notion that lattice sites disappear in front of the moving grain boundary and reappear in its wake. This is the case of pure grain boundary migration without net generation of lattice sites. On the other hand, suppose the lattices of the grains are pushed away from the grain boundary in opposite directions with equal speeds, i.e., $\mathbf{n}^\alpha \cdot (\mathbf{v}_b^\alpha - \mathbf{v}_L^\alpha) = -\mathbf{n}^\alpha \cdot (\mathbf{v}_b^\beta - \mathbf{v}_L^\beta)$. Thus the rate of site generation is the same on either side of the boundary. This process is not associated with grain boundary migration as commonly understood. And indeed, in this case Eq. (86) yields the expected result $v_{\mathrm{GB}} = 0$. We can now formulate the phenomenological equation of grain boundary migration in the form,

$$v_{\mathrm{GB}} = -L_{\mathrm{GB}}([\omega] + k_\alpha \gamma), \qquad (109)$$

where the kinetic coefficient L_{GB} characterizes grain boundary mobility. In particular, the motion of a plane incoherent grain boundary is driven by the jump of the grand potential density $[\omega]$.

These phenomenological laws have been derived for an incoherent grain boundary. For a coherent boundary, $[\mathbf{v}_L]_\parallel$ and v_{GB} are coupled by Eq. (87). As a result, Eqs. (100) and (101) merge into one Eq. (88). Sliding disappears and the law of grain boundary migration becomes

$$v_{\mathrm{GB}} = -L_{\mathrm{GB}}([\omega] + k_\alpha \gamma + \beta \langle \mathbf{s} \rangle_\parallel \cdot \mathbf{t}). \qquad (110)$$

The third term in the right-hand side is the "coupling driving force" responsible for the effect of stress-induced grain boundary migration [7,9,17]. Namely, a shear stress applied parallel to a coherent grain boundary causes its motion in the normal direction.

A semicoherent grain boundary supports both coupling and sliding. We have three independent flux variables, as in the incoherent case, but the lattice velocity jump $[\mathbf{v}_L]_\parallel$ is now decomposed into coupling and sliding components according to Eq. (89) [9,17,19]. The boundary migration law in Eq. (110) remains valid but the sliding law is formulated in terms of the sliding velocity w,

$$w = -K_s \langle \mathbf{s} \rangle_\parallel \cdot \mathbf{t}. \qquad (111)$$

The obtained grain boundary migration and sliding laws, Eqs. (110) and (111), are consistent with the equations derived previously for the shrinkage and rotation of an embedded cylindrical grain [17,19] with the following modifications: (i) for the cylindrical grain analysis [17,19] included an additional driving force arising from the change in the boundary free energy γ as a result of grain rotation, which is disregarded in the present treatment; (ii) the "volume free energy" term [17,19] has now been identified as the jump of the grand potential density $[\omega]$; (iii) our theory includes site generation at the grain boundary, which was not part of any previous models.

V. SPECIFIC MODEL OF STRESSED SOLID

A. Bulk thermodynamics

We will now consider a particular model of the solid in which the elastic deformation is treated in the small-strain approximation. As the reference state for the small-strain tensor $\boldsymbol{\varepsilon}$ we choose the stress-free solid without vacancies ($c = 1$). It should be noted that this reference state changes with temperature due to thermal expansion. However, all calculations discussed below are conducted at a fixed temperature.

We postulate that the stress-free deformation $\boldsymbol{\varepsilon}^0$ produced by vacancies is isotropic and given by

$$\boldsymbol{\varepsilon}^0 = \frac{\Delta \Omega_v}{3\Omega'}(1 - c)\mathbf{I}. \qquad (112)$$

Here and everywhere below, the superscript 0 refers to the stress-free state. The quantity $\Delta \Omega_v < 0$ is the vacancy relaxation volume, i.e., the change in equilibrium volume of the solid when an atom is replaced by a vacancy under zero stress conditions. In the present model, $\Delta \Omega_v$ is treated as a function of temperature only and thus remains fixed. The total lattice strain $\boldsymbol{\varepsilon}$ is composed of the stress-free strain $\boldsymbol{\varepsilon}^0$ and an elastic component obeying Hooke's law of linear elasticity:

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^0 + \mathbf{S} : \boldsymbol{\sigma}. \qquad (113)$$

Here, $\mathbf{S}$ is the tensor of isothermal elastic compliances considered to be a function of temperature only (and thus fixed). Note that the volume of the deformed lattice per site equals

$$\Omega = \Omega'[1 + \mathrm{Tr}(\boldsymbol{\varepsilon})] = \Omega'\left[1 + \frac{\Delta\Omega_v}{\Omega'}(1 - c) + \mathrm{Tr}(\mathbf{S} : \boldsymbol{\sigma})\right]. \qquad (114)$$

The Helmholtz free energy per site has the functional form similar to Eq. (1),

$$f_s = f_s(T, \boldsymbol{\varepsilon}, c), \qquad (115)$$

with the differential form,

$$df_s = M dc + \Omega' \boldsymbol{\sigma} : d\boldsymbol{\varepsilon}, \quad T = \mathrm{const}, \qquad (116)$$

where

$$M \equiv \left(\frac{\partial f_s}{\partial c}\right)_{T,\boldsymbol{\varepsilon}} \qquad (117)$$

is the diffusion potential of atoms relative to vacancies.

For the stress-free state, the free energy $f_s^0(T, c) \equiv f_s(T, \boldsymbol{\varepsilon}^0, c)$ is postulated in the form,

$$f_s^0(T, c) = \overline{f} + \overline{M}c + kT[c \ln c + (1 - c)\ln(1 - c)], \qquad (118)$$

where $\overline{f}$ and $\overline{M}$ are functions of temperature only (and thus constant) and k is Boltzmann's constant. This free energy form corresponds to the ideal solution model [21]. The free energy of a stressed state is obtained by integrating f_s with respect to stress at fixed values of c and T:

$$f_s = f_s^0 + \int_0^{\boldsymbol{\sigma}} \left(\frac{\partial f_s}{\partial \boldsymbol{\varepsilon}}\right)_{T,c} : \left(\frac{\partial \boldsymbol{\varepsilon}}{\partial \boldsymbol{\sigma}}\right)_{T,c} : d\boldsymbol{\sigma}$$

$$= f_s^0 + \int_0^{\boldsymbol{\sigma}} \Omega' \boldsymbol{\sigma} : \mathbf{S} : d\boldsymbol{\sigma}, \qquad (119)$$

where we used Eqs. (113) and (116). Performing the integration,

$$f_s = \overline{f} + \overline{M}c + kT[c \ln c + (1-c)\ln(1-c)] + \frac{\Omega'}{2}\boldsymbol{\sigma} : \mathbf{S} : \boldsymbol{\sigma}. \tag{120}$$

As expected, the stress effect on f_s is quadratic in stress.

We next determine the effect of stress on the diffusion potential M. For the stress-free state we use Eq. (118) to obtain

$$M^0 = \left(\frac{\partial f_s^0}{\partial c}\right)_T = \overline{M} + kT \ln \frac{c}{1-c}. \tag{121}$$

The stress effect on M is found by the standard manipulation involving the Legendre transformation of Eq. (116) [11–14],

$$d(f_s - \Omega'\boldsymbol{\sigma} : \boldsymbol{\varepsilon}) = -\Omega'\boldsymbol{\varepsilon} : d\boldsymbol{\sigma} + M dc, \quad T = \text{const}, \tag{122}$$

and the Maxwell relation,

$$\left(\frac{\partial M}{\partial \boldsymbol{\sigma}}\right)_{T,c} = -\Omega'\left(\frac{\partial \boldsymbol{\varepsilon}}{\partial c}\right)_{T,\boldsymbol{\sigma}}. \tag{123}$$

Integration of this relation gives

$$M = M^0 + \int_0^{\boldsymbol{\sigma}} \left(\frac{\partial M}{\partial \boldsymbol{\sigma}}\right)_{T,c} : d\boldsymbol{\sigma}$$

$$= M^0 - \Omega' \int_0^{\boldsymbol{\sigma}} \left(\frac{\partial \boldsymbol{\varepsilon}}{\partial c}\right)_{T,\boldsymbol{\sigma}} : d\boldsymbol{\sigma}. \tag{124}$$

Using Eqs. (112) and (113) for $\boldsymbol{\varepsilon}$, the integrand equals

$$\left(\frac{\partial \boldsymbol{\varepsilon}}{\partial c}\right)_{T,\boldsymbol{\sigma}} = \left(\frac{\partial \boldsymbol{\varepsilon}^0}{\partial c}\right)_T = -\frac{\Delta\Omega_v}{3\Omega'}\mathbf{I}, \tag{125}$$

which immediately gives

$$M = M^0 + \frac{\Delta\Omega_v}{3}\mathbf{I} : \boldsymbol{\sigma} = M^0 + \Delta\Omega_v \sigma_h, \tag{126}$$

where

$$\sigma_h = \frac{1}{3}\text{Tr}(\boldsymbol{\sigma}) \tag{127}$$

is the hydrostatic part of the stress tensor. Thus the diffusion potential is

$$M = \overline{M} + kT \ln \frac{c}{1-c} + \Delta\Omega_v \sigma_h, \tag{128}$$

showing that the stress effect on M is linear in σ_h. Combining Eqs. (120) and (128), the grand potential per site equals

$$\omega_s = f_s - Mc = \overline{f} + kT \ln(1-c) - \Delta\Omega_v c\sigma_h$$
$$+ \frac{\Omega'}{2}\boldsymbol{\sigma} : \mathbf{S} : \boldsymbol{\sigma}. \tag{129}$$

Equations (128) and (129) can be further rearranged as follows. Equation (95) shows that for a plane stress-free grain boundary, the condition of thermodynamic equilibrium dictates $\omega_s = 0$. This condition is satisfied at a particular composition denoted c^*, for which Eq. (129) gives

$$\overline{f} + kT \ln(1-c^*) = 0. \tag{130}$$

For brevity, c^* will be referred to as the "equilibrium vacancy concentration." The latter depends only on temperature and

is treated here as a material constant. Using Eq. (128), the respective equilibrium diffusion potential is

$$M^* = \overline{M} + kT \ln \frac{c^*}{1-c^*}. \tag{131}$$

Utilizing these relations, Eqs. (128) and (129) can be rewritten as

$$\omega_s = kT \ln \frac{1-c}{1-c^*} - \Delta\Omega_v c\sigma_h + \frac{\Omega'}{2}\boldsymbol{\sigma} : \mathbf{S} : \boldsymbol{\sigma}, \tag{132}$$

$$M = M^* + kT \ln \frac{c(1-c^*)}{c^*(1-c)} + \Delta\Omega_v \sigma_h. \tag{133}$$

The obtained expressions for ω_s and M are exact within the adopted model of the solid. We will now make certain approximations.

Given that the vacancy concentration $c_v \equiv (1-c)$ is very small in most solids, it can be neglected in comparison with all terms of order unity. In particular, Eqs. (132) and (133) can be approximated by

$$\omega_s = kT \ln \frac{c_v}{c_v^*} - \Delta\Omega_v \sigma_h + \frac{\Omega'}{2}\boldsymbol{\sigma} : \mathbf{S} : \boldsymbol{\sigma}, \tag{134}$$

$$M = M^* - kT \ln \frac{c_v}{c_v^*} + \Delta\Omega_v \sigma_h. \tag{135}$$

Furthermore, the term $\Delta\Omega_v c_v/\Omega'$ appearing in Eq. (114) is $\ll 1$ and can be neglected, giving

$$\Omega \approx \Omega'[1 + \text{Tr}(\mathbf{S} : \boldsymbol{\sigma})]. \tag{136}$$

This is equivalent to neglecting the stress-free strain caused by the vacancies. In this approximation, the site volume is only affected by the elastic strain.

In most applications, the stress effect on thermodynamics is captured accurately enough by keeping only terms linear in stress and neglecting higher order terms. In this approximation,

$$\frac{1}{\Omega} \approx \frac{1}{\Omega'}[1 - \text{Tr}(\mathbf{S} : \boldsymbol{\sigma})], \tag{137}$$

and the grand potential per unit volume can be approximated by

$$\omega = \frac{\omega_s}{\Omega} \approx \frac{kT}{\Omega'} \ln \frac{c_v}{c_v^*} - \frac{kT}{\Omega'}\left(\frac{\Delta\Omega_v \sigma_h}{kT} + \text{Tr}(\mathbf{S} : \boldsymbol{\sigma}) \ln \frac{c_v}{c_v^*}\right). \tag{138}$$

The second term in the right-hand side of Eq. (138) is often neglected. This is equivalent to disregarding the vacancy relaxation volume $\Delta\Omega_v$ and assuming that the stress is small enough to neglect elastic dilatation $\text{Tr}(\mathbf{S} : \boldsymbol{\sigma})$. It is in this approximation that the equilibrium condition of plane grain boundary expressed by Eq. (95) takes the form,

$$kT \ln \frac{c_v}{c_v^*} = \Omega' \mathbf{n}^\alpha \cdot \mathbf{s}_\perp. \tag{139}$$

This equation reproduces the frequently used Herring's relation for the effect of stresses on the vacancy concentration near boundaries in solids [2,22]. Insertion of ω from Eq. (138) into Eq. (95) gives a more accurate equation for this effect. This equation shows that the equilibrium vacancy concentration near a boundary is affected by not only the normal stress $\mathbf{n}^\alpha \cdot \mathbf{s}_\perp$ but also lateral stresses parallel to the interface.

B. Diffusion kinetics

Diffusion kinetics inside the grains are governed by the phenomenological relations (102) and (103) between the diffusion flux relative to the lattice and the gradient of the diffusion potential. Using Eq. (128) for M,

$$\mathbf{J}_L = -L\nabla M = -\frac{LkT}{c(1-c)}\nabla c - L\Delta\Omega_v\nabla\sigma_h. \quad (140)$$

For diffusion in a uniform stress-free lattice we have

$$\mathbf{J}_L^0 = -\frac{LkT\Omega}{c(1-c)}\nabla\frac{c}{\Omega}. \quad (141)$$

The coefficient before the gradient of the atomic density c/Ω can be identified with the diffusion coefficient of atoms. Assuming the vacancy mechanism of diffusion, this diffusion coefficient is proportional to the vacancy concentration c_v and can therefore be written as Dc_v/c_v^*, where D is the diffusion coefficient in the stress-free solid with the equilibrium vacancy concentration c_v^*. Thus, the kinetic coefficient L can be found from the condition,

$$\frac{LkT\Omega}{c(1-c)} = D\frac{c_v}{c_v^*}, \quad (142)$$

where D is treated as a material constant. Inserting this L in Eq. (140) and expressing the composition in terms of the vacancy concentration c_v, the flux equation becomes

$$\mathbf{J}_L = D\frac{c_v}{\Omega c_v^*}\nabla c_v - D\frac{\Delta\Omega_v c_v^2}{\Omega kT c_v^*}\nabla\sigma_h. \quad (143)$$

In the second term we approximated $c(1-c) \approx c_v$.

The continuity equation (13) can be rewritten in terms of the vacancy concentration,

$$\frac{\partial c_v}{\partial t} = -\mathbf{v}_L\cdot\nabla c_v + \Omega\nabla\cdot\mathbf{J}_L. \quad (144)$$

Inserting $\mathbf{J}_L$ from Eq. (143) and keeping only first-order terms in stress,

$$\frac{\partial c_v}{\partial t} = \frac{D}{c_v^*}c_v\nabla^2 c_v + \frac{D}{c_v^*}(\nabla c_v)^2 - \mathbf{v}_L\cdot\nabla c_v$$
$$- \frac{D\Delta\Omega_v}{kT c_v^*}c_v^2\nabla^2\sigma_h - \frac{2D\Delta\Omega_v}{kT c_v^*}c_v\nabla\sigma_h\cdot\nabla c_v$$
$$+ D\frac{c_v}{c_v^*}\nabla c_v\cdot\nabla\text{Tr}(\mathbf{S}:\boldsymbol{\sigma}), \quad (145)$$

where we applied Eq. (136) for the stressed site volume Ω. In Eq. (145), all stress-free terms have been collected in the first line, while the second line contains the terms linear in stress or its derivatives.

VI. DISCUSSION AND CONCLUSIONS

Previous sharp-interface descriptions of creep deformation [1–4] relied on numerous rough approximations and *ad hoc* assumptions regarding the vacancy generation and absorption process and the associated interface motion that causes the shape deformation. In this work, we presented a rigorous irreversible thermodynamic description of creep deformation treating the interfaces as geometric surfaces capable of vacancy generation and absorption. The central result is the free energy

dissipation rate given by Eq. (37) for an open surface and by Eqs. (75)–(82) for a grain boundary. The dissipation rate enables us to identify clearly the thermodynamic forces for vacancy generation and absorption at the interface, interface migration, and vacancy diffusion along the interface and inside the grains. In addition, and in contrast to previous theories, our equations naturally incorporate mechanical processes at interfaces, such as grain boundary sliding and shear-coupled motion. These processes are part of the overall creep deformation process and can impact the deformation rate and the microstructure evolution during the creep.

To treat the grain boundary processes mentioned above, we have introduced a classification of grain boundaries into three categories according to their mechanical response to applied shear stresses. The concepts of coherent and incoherent interfaces has been known before [13,14,18], although not in the context of creep deformation and without considering the lattice site generation at the interface. We find that a complete description of creep requires the introduction of semicoherent interfaces, in which the shear-coupled motion can coexist with sliding. Formally, the coherent and incoherent interfaces can be obtained as limiting cases of a semicoherent interface when the sliding coefficient $K_s \to 0$ and when $K_s \to \infty$ and $\beta \to 0$, respectively. However, in view of their practical significance, the coherent and incoherent interfaces should be kept as separate categories.

It should be emphasized that the equations obtained for the dissipation rate fully incorporate capillary effects, which can be especially important in nanoscale creep phenomena. Care has been taken to separate the interface free energy and interface stress, which are two related but physically and numerically different interface properties [15,23,24]. The equations derived here clearly display their separate roles in the creep process.

The free energy dissipation rate derived in this work has the structure of thermodynamic driving forces multiplied by generalized fluxes or rates of different processes. This enables us to derive phenomenological kinetic equations employing the Onsager formalism of irreversible thermodynamics [25–27]. In this paper, we have formulated a set of kinetic equations assuming constant kinetic coefficients and neglecting cross-effects. Numerical solution of these equations enables a description of the creep deformation kinetics and microstructure evolution in the material. To prepare for future applications, the model has been specialized to a linear-elastic solid material with a small vacancy concentration. Work is under way to apply this model to creep deformation in relatively simple structures, such as a spherical nanoparticle with an oversaturated vacancy concentration and a bi-crystal subject to applied stresses and containing nonequilibrium vacancies (to be published).

The present version of the theory is based on several simplifying assumptions that can be lifted in the future. Although we restricted the analysis to a single-component material, the equations can be readily generalized to a multicomponent solid solution containing both vacancies and interstitials. The interface coupling and sliding relations can be reformulated for anisotropic cases. In particular, the theory could include the multiplicity coupling modes and switching between them during the grain boundary motion [9]. The phenomenological

kinetic equations can include cross-effects between different driving forces and fluxes. The incorporation of such effects may reveal new interesting phenomena, such as the possible effect of grain boundary motion and sliding on the vacancy generation and absorption processes, as well as the reciprocal process: the effect of vacancy generation and absorption on the coupling factor and sliding resistance of grain boundaries. Finally, the present version of the theory assumes that the sinks and sources of vacancies are located only at interfaces. The theory does not consider the role of sinks and sources inside the grains, such as climbing dislocations. A generalization of the theory to include such bulk sinks and sources could be the subject of future work.

APPENDIX: DERIVATION OF EQS. (75)–(82)

In this Appendix we derive the free energy dissipation rate given by Eqs. (75)–(82). The starting point is Eq. (64) derived in the main text. Using the notations (67) and (68) for grain boundary jumps and averages, Eq. (64) can be rewritten as

$$
\begin{aligned}
\dot{\Phi} = & \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv \\
& + \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv \\
& + \int_{\mathcal{S}} 2\langle \nu M \rangle dA + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot [\boldsymbol{\sigma} \cdot \mathbf{v}_L] dA \\
& + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot [\omega(\mathbf{v}_b - \mathbf{v}_L)] dA \\
& + \int_{\mathcal{S}} k_\alpha \mathbf{n}^\alpha \cdot \left(\gamma \mathbf{v}_b^\alpha + 2 \left\langle \varphi \frac{\partial \gamma}{\partial \varphi} \mathbf{v}_L \right\rangle \right) dA.
\end{aligned}
\tag{A1}
$$

Decomposing the jumps and averages according to Eqs. (73) and (74),

$$
\begin{aligned}
\dot{\Phi} = & \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv \\
& + \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv \\
& + \int_{\mathcal{S}} 2 \left(\langle \nu \rangle \langle M \rangle + \frac{1}{4} [\nu][M] \right) dA \\
& + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot (\langle \boldsymbol{\sigma} \rangle \cdot [\mathbf{v}_L] + [\boldsymbol{\sigma}] \cdot \langle \mathbf{v}_L \rangle) dA \\
& + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot ([\omega] \langle \mathbf{v}_b - \mathbf{v}_L \rangle + \langle \omega \rangle [\mathbf{v}_b - \mathbf{v}_L]) dA \\
& + \int_{\mathcal{S}} k_\alpha \mathbf{n}^\alpha \cdot \left(\gamma \mathbf{v}_b^\alpha + 2 \left\langle \varphi \frac{\partial \gamma}{\partial \varphi} \right\rangle \langle \mathbf{v}_L \rangle + \frac{1}{2} \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] [\mathbf{v}_L] \right) dA.
\end{aligned}
\tag{A2}
$$

The product $\langle \nu \rangle \langle M \rangle$ appearing in the second line of Eq. (A2) can be transformed using Eq. (61) rewritten as $2\langle \nu \rangle = -\nabla_b \cdot \mathbf{J}_b$:

$$
\langle \nu \rangle \langle M \rangle = -\tfrac{1}{2} \langle M \rangle \nabla_b \cdot \mathbf{J}_b = -\tfrac{1}{2} \nabla_b \cdot (\langle M \rangle \mathbf{J}_b) + \tfrac{1}{2} \mathbf{J}_b \cdot \nabla_b \langle M \rangle.
\tag{A3}
$$

The surface integral of $\langle \nu \rangle \langle M \rangle$ is computed using the surface divergence theorem,

$$
\int_{\mathcal{S}} \langle \nu \rangle \langle M \rangle dA = \frac{1}{2} \int_{\mathcal{S}} \mathbf{J}_b \cdot \nabla_b \langle M \rangle dA - \frac{1}{2} \int_{\mathcal{L}} \langle M \rangle \mathbf{e} \cdot \mathbf{J}_b dl,
\tag{A4}
$$

where $\mathbf{e}$ is a unit vector parallel to the boundary $\mathcal{S}$ and normal to the contour $\mathcal{L}$ bounding $\mathcal{S}$. The line integral is zero by our supposition that the boundary $\mathcal{S}$ is either closed or terminates at the walls where $\mathbf{J}_b = \mathbf{0}$. The second line of Eq. (A2) finally becomes

$$
\int_{\mathcal{S}} \mathbf{J}_b \cdot \nabla_b \langle M \rangle dA - \int_{\mathcal{S}} J_n [M] dA,
\tag{A5}
$$

where the normal diffusion flux J_n is given by Eq. (84). Taking into account that $\mathbf{n}^\alpha \cdot [\mathbf{v}_b - \mathbf{v}_L] = -\mathbf{n}^\alpha \cdot [\mathbf{v}_L]$ and $\mathbf{n}^\alpha \cdot \mathbf{v}_b^\alpha = \mathbf{n}^\alpha \cdot \langle \mathbf{v}_b - \mathbf{v}_L \rangle + \mathbf{n}^\alpha \cdot \langle \mathbf{v}_L \rangle$, Eq. (A2) becomes

$$
\begin{aligned}
\dot{\Phi} = & \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv \\
& + \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv \\
& + \int_{\mathcal{S}} \mathbf{J}_b \cdot \nabla_b \langle M \rangle dA - \int_{\mathcal{S}} J_n [M] dA \\
& + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot (\langle \boldsymbol{\sigma} \rangle \cdot [\mathbf{v}_L] + [\boldsymbol{\sigma}] \cdot \langle \mathbf{v}_L \rangle) dA \\
& + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot ([\omega] \langle \mathbf{v}_b - \mathbf{v}_L \rangle - \langle \omega \rangle [\mathbf{v}_L]) dA \\
& + \int_{\mathcal{S}} k_\alpha \mathbf{n}^\alpha \cdot \left(\gamma \langle \mathbf{v}_b - \mathbf{v}_L \rangle + \left(\gamma + 2 \left\langle \varphi \frac{\partial \gamma}{\partial \varphi} \right\rangle \right) \langle \mathbf{v}_L \rangle \right. \\
& \left. + \frac{1}{2} \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] [\mathbf{v}_L] \right) dA.
\end{aligned}
\tag{A6}
$$

At the next step, we group the terms with $\langle \mathbf{v}_L \rangle$, $[\mathbf{v}_L]$, and $\langle \mathbf{v}_b - \mathbf{v}_L \rangle$ into separate lines:

$$
\begin{aligned}
\dot{\Phi} = & \int_{\mathcal{R}_\alpha} \left(\mathbf{J}_L^\alpha \cdot \nabla M_\alpha - G_\alpha^{-1}(\nabla' \cdot \mathbf{P}_\alpha) \cdot \mathbf{v}_L^\alpha \right) dv \\
& + \int_{\mathcal{R}_\beta} \left(\mathbf{J}_L^\beta \cdot \nabla M_\beta - G_\beta^{-1}(\nabla' \cdot \mathbf{P}_\beta) \cdot \mathbf{v}_L^\beta \right) dv \\
& + \int_{\mathcal{S}} \mathbf{J}_b \cdot \nabla_b \langle M \rangle dA - \int_{\mathcal{S}} J_n [M] dA \\
& + \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot ([\boldsymbol{\sigma}] + k_\alpha \tau \mathbf{I}) \cdot \langle \mathbf{v}_L \rangle dA \\
& - \int_{\mathcal{S}} \mathbf{n}^\alpha \cdot \left(\left(\langle \omega \rangle - \frac{1}{2} k_\alpha \left[\varphi \frac{\partial \gamma}{\partial \varphi} \right] \right) \mathbf{I} - \langle \boldsymbol{\sigma} \rangle \right) \cdot [\mathbf{v}_L] dA, \\
& + \int_{\mathcal{S}} ([\omega] + k_\alpha \gamma) \mathbf{n}^\alpha \cdot \langle \mathbf{v}_b - \mathbf{v}_L \rangle dA.
\end{aligned}
\tag{A7}
$$

Decomposing the lattice velocity $\mathbf{v}_L$ and boundary traction vector $\mathbf{s} \equiv \mathbf{n}^\alpha \cdot \boldsymbol{\sigma}$ into parallel and normal components according to Eqs. (69)–(72), we finally obtain the free energy dissipation rate given by Eqs. (75)–(82).

[1] F. R. Nabarro, in *Report of a Conference on Strength of Solids* (The Physical Society, London, 1948), pp. 75–90.

[2] C. J. Herring, J. Appl. Phys. **21**, 437 (1950).

[3] R. L. Coble, J. Appl. Phys. **34**, 1679 (1963).

[4] F. A. Mohamed and Y. Li, Mater. Sci. Eng. A **298**, 1 (2001).

[5] J. Svoboda, F. D. Fischer, and P. Fratzl, Acta Mater. **54**, 3043 (2006).

[6] J. Svoboda and F. D. Fischer, Acta Mater. **59**, 1212 (2011).

[7] Y. Mishin, M. Asta, and J. Li, Acta Mater. **58**, 1117 (2010).

[8] Y. Mishin, J. A. Warren, R. F. Sekerka, and W. J. Boettinger, Phys. Rev. B **88**, 184303 (2013).

[9] J. W. Cahn, Y. Mishin, and A. Suzuki, Acta Mater. **54**, 4953 (2006).

[10] L. E. Malvern, *Introduction to the Mechanics of a Continuous Medium* (Prentice-Hall, Upper Saddle River, 1969).

[11] P. W. Voorhees and W. C. Johnson, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen, Vol. 59 (Elsevier Academic Press, San Diego, 2004), pp. 2–201.

[12] F. Larché and J. W. Cahn, Acta Metall. **21**, 1051 (1973).

[13] F. C. Larché and J. W. Cahn, Acta Metall. **26**, 1579 (1978).

[14] F. C. Larché and J. W. Cahn, Acta Metall. **33**, 331 (1985).

[15] R. Shuttleworth, Proc. Phys. Soc. A **63**, 444 (1950).

[16] M. E. Gurtin, J. Weissmüller, and F. Larché, Philos. Mag. A **78**, 1093 (1998).

[17] J. W. Cahn and J. E. Taylor, Acta Mater. **52**, 4887 (2004).

[18] T. Frolov and Y. Mishin, Phys. Rev. B **85**, 224106 (2012).

[19] Z. T. Trautt and Y. Mishin, Acta Mater. **60**, 2407 (2012).

[20] A. P. Sutton and R. W. Balluffi, *Interfaces in Crystalline Materials* (Clarendon Press, Oxford, 1995).

[21] L. A. Girifalco, *Statistical Mechanics of Solids* (Oxford University Press, Oxford, 2000).

[22] C. Herring, in *The Physics of Powder Metallurgy*, edited by R. Gomer and C. S. Smith (McGraw-Hill, New York, 1949).

[23] J. W. Gibbs, *The Collected Works of J. W. Gibbs*, Vol. 1 (Yale University Press, New Haven, 1948).

[24] J. W. Cahn, in *Interface Segregation*, edited by W. C. Johnson and J. M. Blackely (American Society of Metals, Metals Park, 1979), Chapter 1, pp. 3–23.

[25] L. Onsager, Phys. Rev. **37**, 405 (1931).

[26] L. Onsager, Phys. Rev. **38**, 2265 (1931).

[27] S. R. De Groot and P. Mazur, *Non-equilibrium Thermodynamics* (Dover, New York, 1984).