

Thermodynamic Equilibrium Across a Coherent Interface in a Stressed Crystal

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Abstract

Migrating twin boundaries, boundaries in crystals undergoing displacive phase transformations, coherent precipitates, and coherent exsolution lamellae—all provide examples of coherent interfaces propagating in a stressed crystalline framework. The motion of such boundaries is often reversible or characterized by a sufficiently small hysteresis, so that they can be considered at equilibrium within the stressed solid; the present paper is concerned with the conditions of such equilibrium. It is emphasized, following J. W. Gibbs, that a solid under stress is in equilibrium only if the motion of at least one chemical component (*solid* component) of the solid through the framework is considered an impossible process; other chemical components able to migrate are *fluid* components. After the additional 'constraint of coherency' for the migration of the interface is examined and expressed mathematically, the condition of equilibrium can be established, showing the exact dependence of equilibrium on normal and shear stress along the interface, temperature, and chemical potentials of the fluid components. The general condition is then applied to the following special cases: (1) coherent transformations in which the 'stress-free transformation strain' is much larger than any elastic strain, (2) twinning, and (3) infinitesimal transformation strain. The migration of some low-angle tilt or kink boundaries can be analogous to that of coherent boundaries, and their equilibrium, if reached, is ruled by the same equations. However, growth across most high-angle grain boundaries of a polycrystalline aggregate is not constrained in the same manner; as a consequence it is argued that in presence of a shear stress such boundary cannot be in reversible equilibrium with respect both to growth and to shear.

Introduction

The general problem of thermodynamic equilibrium of stressed solids has concerned many authors because of its possible applications to mineralogy, petrology, geophysics, and materials sciences. The topic has recently been reviewed by Paterson (1973). Gibbs (1906) originally derived the condition of external equilibrium of a stressed solid in contact with a fluid, and introduced the distinction between *solid* and *fluid* components of a solid. These concepts are essential to any study of the thermodynamic equilibrium of a stressed solid and, in particular, to the present work; because their significance is often not fully appreciated, Gibbs' results will be summarized, and the *constraint of solid behavior* defined.

At equilibrium a solid-fluid boundary does not and cannot support any shear stress; there have therefore been attempts to generalize Gibbs' results to boundaries which support shear stresses (see Paterson, 1973). Coherent interfaces are examples of such boundaries; an understanding of their equilibrium has important implications for such problems as twin-boundary migration, precipitation hardening, solid exsolution, and other phase transformations within crystals (or glasses at temperatures sufficiently below their glass transition).

The equilibrium conditions for coherent interfaces derived in this paper are quite general; they do not assume that the transformation strain or the elastic strain are infinitesimal, nor do they assume that the transformation is isochemical. However, the thickness of the interfacial region is neglected and the surface energy is not considered; the applicability of the results depends on the validity of these latter assumptions.

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Constraint of Solid Behavior

Gibbs (1906, pp. 184-218) considered a stressed elastic solid able to dissolve into or crystallize from a fluid. Let the fluid in contact with the solid at one point of its boundary be at a pressure P . External equilibrium is obtained when the solid neither dissolves nor grows spontaneously at its boundary with the fluid. If the solid is of uniform composition and if molar quantities are used, the chemical potential μ of its component in the fluid at pressure P is given by (Gibbs, Eq. 385)

$$\mu = \bar{E} - T\bar{S} + P\bar{V} \quad (1)$$

where \bar{E} , \bar{S} and \bar{V} are respectively molar energy, entropy, and volume of the solid in the equilibrium state considered, and T is the temperature. The significance of this result is better understood when considering, as does Gibbs, the following special case. Three fluid pressures P^1 , P^2 , and P^3 are each applied on two opposite faces of a rectangular parallelepiped of the solid, assumed homogeneous. The solid is then under homogeneous stress, of principal components $-P^1$, $-P^2$ and $-P^3$. The condition of equilibrium with respect to growth or solution becomes for each pair of faces (Gibbs' Eqs. 393-395)

$$\bar{E} - T\bar{S} + P^1\bar{V} = \mu^1$$

$$\bar{E} - T\bar{S} + P^2\bar{V} = \mu^2$$

$$\bar{E} - T\bar{S} + P^3\bar{V} = \mu^3$$

where μ^1 , μ^2 , μ^3 are the values of the chemical potential of the component of the solid in each fluid. If migration of the component of the solid were possible, either through the solid itself or through some external channel, this component would indeed migrate from the fluids at the highest pressures to the fluid at the lowest pressure. Consequently, equilibrium of a non-hydrostatically stressed solid must always be understood to be limited by the constraint that *such migration is not a possible mechanism*. This constraint is called here the *constraint of solid behavior*. We note (Kamb, 1961) that a chemical potential for the component of the solid is not defined within the solid itself.

Gibbs went on to examine (p. 215) the case of a solid which also contains *fluid components* α, β , etc. Recent writers, e.g. Li, Oriani, and Darken (1966) or Paterson (1973), refer to these as *mobile components*. In Gibbs' words, fluid components are such "that there are no passive resistances to the motion of the fluid components except such as vanish

with the velocity of the motion." For these components Gibbs shows that a chemical potential can be defined and is constant throughout the solid and the fluids when the system is in equilibrium. As Gibbs' definition makes clear, a chemical component α is fluid (and therefore a chemical potential μ^α must exist and have a constant value throughout the system at equilibrium) if α can move independently² through the solid, regardless of whether or not the corresponding concentration or concentration variation of α in the solid can be detected.

When a solid contains fluid components, the constraint of solid behavior is that *at least one chemical component of the solid is not free to move through the solid*. Gibbs called such a component a *solid component*.² The very definitions of fluid and solid components imply that there exists a three-dimensional framework which is conserved and with respect to which motion of chemical species may or may not occur, independently of possible translations or deformations of the framework itself.

Recognition of the existence of a solid component and its identification are essential to any consideration of equilibrium of a non-hydrostatically stressed solid. In this work solid behavior is always assumed. In practice, for crystals, this means that mechanisms such as unlimited motion of dislocations or Nabarro-Herring diffusion creep do not occur, or are so slow, compared to boundary migration or diffusion of fluid components, that they can be neglected. We shall also suppose the fluidity of the fluid components to be perfect, "leaving it to be determined by experiment how far and in what cases these suppositions are realized" (Gibbs, 1906, p. 215).

Coherent Transformations and Coherent Interfaces

A coherent transformation in a solid is a phase transformation in which the three-dimensional framework is preserved without rupture. This definition does not exclude the possibility that some

² Not all atomic, ionic, or molecular species which can move may be able to do so independently; there may be relations of dependence between them, such as *site constraints* or *constraints of electroneutrality* (Thompson, 1969). A set of independent fluid components can nevertheless always be defined. Conversely, a *solid component* does not necessarily correspond to any one atomic, ionic, or molecular species unable to diffuse through the lattice of the solid. For example, two substitutional species, α and β , may both be able to diffuse through the lattice but be tied by a site constraint.

atomic rearrangement may occur, allowing some chemical species to change position or migrate. A coherent transformation is therefore not necessarily displacive (Buerger, 1948) although displacive transformations are coherent. In the present paper, attention is concentrated on crystalline solids. Generalization to amorphous chain polymers is possible and may have applications to transition and exsolution phenomena in glasses at low temperatures.

Let us call the two possible states of a crystal 'phase' *a* and 'phase' *b*.³ The transformation of a crystal from phase *a* to phase *b* can be visualized as the sweeping through the crystal of one or more boundaries separating domains of *b* from domains that are still *a*. Such a boundary is a *coherent boundary*, or *coherent interface*. In the presence of such an interface, stresses in *a* and *b* may arise from the very co-existence of the two phases and from the constraint that the two lattices be matched across the interface; stresses may also be imposed at the external boundaries of the crystal.

There are cases where, instead of sweeping through the whole crystal, a coherent interface reaches an equilibrium position. Let us look at a few examples.

Mechanical Twinning

It is only when their state is affected by nonscalar parameters such as electric field, magnetic field, or stress that twins must be considered to be distinct phases, as their molar energies may then differ. Mineralogists are familiar with stress-induced twinning in calcite. Mechanical twinning is found in many other minerals (DeVore, 1970). The migration of Dauphiné twin boundaries in quartz under stress is particularly well documented by Frondel (1945), Thomas and Wooster (1951), and Tullis and Tullis (1972). When non-uniform stresses are applied to the external boundaries of a crystal in which mechanical twinning is possible, the two

twins may coexist within the crystal, separated by coherent twin boundaries. As with other phase transformations, the extent to which equilibrium is actually reached by the migrating twin boundary must be determined in each case and will depend on factors such as time, temperature, and what level of disequilibrium is considered significant. For Dauphiné twinning in quartz, hysteresis appears to vanish at temperatures nearing the α - β transition (Young, 1962). Stress-induced reversible migration of twin boundaries is also observed in metals. Basinsky and Christian (1954a) show how such observed migration can explain the rubber-like elasticity of low-temperature face-centered tetragonal twinned phases in indium-thallium and gold-cadmium alloys.

Isochemical Coherent Transitions

Displacive, semi-reconstructive, and order-disorder transformations (Buerger, 1948) can all be classified as isochemical coherent transformations. A few examples are given by Coe (1970). Well known are the high-low transitions in crystalline phases of silica and in the feldspars, and the transition of calcite I to calcite II at high pressure (Bridgman, 1939). Which, and to what extent, martensitic reactions are coherent transitions is a subject of debate in the metallurgical literature. The W-L-R and B-M crystallographic theories of martensitic transformations (Weschler, Lieberman, and Read, 1953; Bowles and Mackenzie, 1954) in effect assume coherency and have successfully explained many features of these transformations. Yet electron microscopy of Fe-Ni-C alloys reveals that growth of martensite is accompanied by the formation of large numbers of dislocations, and the boundaries have been described as semi-coherent (*e.g.*, see Owen, Schoen, and Srinivasan, 1970). In some systems, however, the reaction shows remarkably little hysteresis: 20°C or less in Au-Cd (Chang and Read, 1951); between 2°C and 4°C in In-Th (Burkart and Read, 1953; Basinsky and Christian, 1954b); it seems accepted that these 'thermoelastic martensites' (Owen *et al.*, 1970) form by truly coherent reactions. The influence of stresses on the temperature at which some of these reactions occur has been explored experimentally: for the α - β transition in quartz (Coe and Paterson, 1969); and for the martensitic reaction in In-Tl (Burkart and Read, 1953) and Fe-Ni alloys (Patel and Cohen, 1953). Wang (1968) has also qualitatively explained the observed smearing out of the calcite I-calcite II transition in limestones

³ The term *phase* is often taken to designate only a state of a substance in which all thermodynamic parameters are uniform throughout. Because stresses, in particular, are not assumed uniform here, the term *phase* simply refers to a portion of the crystal characterized by a unique equation of state and by continuous thermodynamic properties. This broader definition is consistent with usage in the metallurgical or geological (*e.g.*, Wang, 1968) literature. By contrast, 'crystal' designates the framework which is conserved, regardless of which state it is in; such usage is implicit in many studies of displacive or order-disorder transitions.

over a wide range of confining pressure by the inhomogeneous stresses arising in such aggregate. According to Wang and Meltzer (1973), the high absorption of acoustic waves in these limestones over the same range of pressure also indicates an extremely rapid migration of the phase boundaries in response to the alternating stress; their interpretation suggests that calcite I-II boundaries would be very close to their equilibrium positions under static conditions.

Coherent Precipitates

A coherent precipitate is a domain within a crystal which differs from its host by its composition and, in general, by its stress-free lattice dimensions, but yet has retained the continuity of its lattice with the lattice of the host. A non-hydrostatic and often non-uniform stress-field is generally present. To the extent that these stresses are maintained without creep and without the corresponding destruction of the lattice framework, the equilibrium reached implies the existence of a solid component, common to both phases, and of at least one fluid component.

A *fully coherent precipitate* is one which has maintained coherency on all its boundaries with the host. Examples of fully coherent precipitates have been described mostly for metals. The G.P. zones (Guinier-Preston) in Al-Ag, Al-Zn, and Al-Cu alloys, cobalt particles in Cu-Co alloys and γ' in nickel-base alloys are cited by Kelly and Nicholson (1963). A *partially coherent precipitate* is one for which coherency is maintained only along a specific crystallographic orientation. In metals, the Widmanstätten structures of aluminum alloys (Kelly and Nicholson, 1963) are well-known examples.

There is no general review of the nature of the boundaries of exsolution lamellae in oxides and silicates. Fully coherent submicroscopic exsolution lamellae of augite in pigeonite have been observed by transmission electron microscopy in lunar and terrestrial pyroxenes (Christie *et al.*, 1971). The angular relationships between clinopyroxene host and exsolution lamellae reported by Robinson *et al.* (1971) are also often consistent with the assumption of coherency of the boundaries (Robin, 1974b). Champness and Lorimer (1973) observe calcium-rich submicroscopic coherent precipitates in an orthopyroxene from the Stillwater complex, for which they propose the name of G.P. zones, by analogy with metals. Cryptoperthite lamellae in alkali feldspar are also generally coherent (Robin, 1974a).

In summary, known examples of coherent interfaces are many, and more are likely to be found with the increasing use of transmission electron microscopes. It must be emphasized again, however, that whether or not a coherent interface is able to migrate to an equilibrium position must be justified in each case or be explicitly acknowledged as an assumption.

Method

Equilibrium Criterion

Gibbs demonstrated Eq. 1 by using the following *minimum energy criterion*:

“For the equilibrium of any isolated system it is necessary and sufficient that, in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.”

As there have been arguments in the literature regarding the definition and use of energy functions other than internal energy for solids under stress (see Paterson, 1973), we will use the same criterion as Gibbs. As a result, it will be found that one of the conditions of equilibrium is that the temperature be uniform throughout the system. This is, of course a result which could be accepted and bypassed by using the Helmholtz energy. The advantage would be minor, however, and Gibbs' treatment will be followed instead.

Let us then consider a portion of crystal which contains a coherent interface at equilibrium separating phases *a* and *b*. Isolate this volume by a “fixed envelope which is impermeable to matter and to heat, and to which the solid is firmly attached wherever they meet” (Gibbs, 1906, p. 187). We assume that stresses, compositions, energy and entropy densities, etc., although not necessarily uniform, vary continuously within each phase.

States and Coordinate Systems

During a migration of the interface a portion of the lattice changes phase, and the corresponding strain is not necessarily infinitesimal. In order to describe such finite strain one must carefully distinguish between the *identification* of lattice points and their *location*. Identification of points is accomplished by the use of a *reference state* and a *reference coordinate system*; location of these points in the actual coherent *equilibrium state* or in variational departures from the equilibrium state is done by their coordinates in the *equilibrium coordinate system*.

Both coordinate systems are assumed rectangular cartesian and of same handedness.

The coordinates of a point or of a vector in the reference state (noted by a prime) can be regarded mainly as a 'tagging' system. Therefore, the reference state does not have to have any physical reality and can be chosen as is convenient for any particular problem; it must, however, preserve continuity with the actual state. It is sometimes convenient to choose the reference state and its coordinate system to coincide with the equilibrium state and coordinate system; the distinction between identification and position of points must be maintained, however. Physical quantities like energy, entropy, chemical concentrations exist only in an actual state; their densities, however, can be defined with respect to volumes of the lattice equal to unity in the reference state, in which case these densities will also be noted by a primed lower-case letter. Force vectors also only exist in an actual state, and their components are defined in the equilibrium coordinates; in defining stresses or the stress tensor, however, the unit areas used and their orientations are the ones of the lattice in the reference state.

A point in the solid, identified by its reference state coordinates, x_i' , has in the equilibrium state the coordinates x_i ($i = 1, 2, 3$). We can define the quantities

$$x_{i,j} = \frac{\partial x_i}{\partial x_j'} \quad (2)$$

The set of $x_{i,j}$ is a description of the local deformation or *strain* between the reference and the equilibrium states. If the reference state and coordinates are chosen so as to coincide with the equilibrium state and coordinates, then at equilibrium, $x_{i,j} = \delta_{ij}$ (Kronecker's δ).

Fundamental Equation of State

Let us first consider a crystal which does not contain any fluid component. Under conditions where we can neglect body forces, the energy density of the crystal is only a function of the state of strain and of the entropy content. We thus write the fundamental equation of state of each phase as

$$\begin{aligned} e'^a &= e'^a(x_{i,j}^a, s'^a) \\ e'^b &= e'^b(x_{i,j}^b, s'^b) \end{aligned} \quad (3)$$

where e' and s' are respectively energy and entropy densities, or, more precisely, energy and entropy

in the equilibrium state of a small volume of phase which is equal to unity in the reference state. All units of mass, volumes, and areas are chosen small enough so that properties can be considered uniform within them.

In an actual state, the position of a point of the framework may differ from its equilibrium position by a variational amount δx_i , and, consequently, so may the local strain, $\delta x_{i,j}$ (see the virtual deformations of Murnaghan, 1951, p. 44-50). The entropy density may also vary by $\delta s'$, and therefore, from Eq. 3, the internal energy variation is given by

$$\delta e' = \left(\frac{\partial e'}{\partial x_{i,j}} \right) \delta x_{i,j} + \left(\frac{\partial e'}{\partial s'} \right) \delta s'$$

(Einstein's summation convention on repeated subscripts is used in this paper) which we rewrite as

$$\delta e' = \sigma_{ij} \delta x_{i,j} + T \delta s' \quad (4)$$

As Gibbs (1906, p. 186) pointed out, σ_{ij} is the i th component, in the equilibrium coordinates, of the force acting (in the equilibrium state) on a surface element which would be equal to a unit area in the reference state and would be perpendicular to the j axis of the reference coordinate system. (If the reference state coincides with the equilibrium state, or only differs from the equilibrium state by an infinitesimal strain, σ_{ij} is the stress as defined in infinitesimal strain elasticity).

Besides displacements and entropy density changes throughout each phase, there is another possible variation of the system from its equilibrium state: the interface may migrate through the solid, its migration corresponding to a change in phase at the interface and preserving coherency. We need to examine this last variation carefully.

Geometry of a Migrating Coherent Interface

Figure 1a represents portions of phases a and b and a portion of interface *in the equilibrium state*. These portions are chosen small enough for stresses and entropy to be and to remain uniform within each phase and for the variational migration of the interface to be uniform. Figure 1c is the configuration after such a migration. As Figure 1 shows, this migration can be decomposed into the following sequence:

- (1) An imaginary cut is made along the interface.
- (2) Points in a are moved by a distance δx_i^a , points in b are moved by a distance δx_i^b

(Fig. 1b). The relative displacement of b with respect to a is

$$\delta x_i^b - \delta x_i^a = \mathbf{Q}'\mathbf{P}'$$

- (3) A volume of one phase is transformed into a volume of the other phase having the same mass, thereby reestablishing coherency. Points which are not affected by this phase change are not moved (Fig. 1c).

We can make the following remarks:

- (i) The direction of $\mathbf{Q}'\mathbf{P}'$ is imposed by the states of strain of the lattice in a and b and is therefore not an independent parameter subject to variations.
- (ii) The length of $\mathbf{Q}'\mathbf{P}'$ is proportional to the mass transferred from a to b . Let O be the intersection of the direction of $\mathbf{Q}'\mathbf{P}'$ with the new position of the interface (Fig. 1c). We must have $|\overline{OP}'|/|\overline{OQ}'| = \rho^a/\rho^b$, where ρ^a and ρ^b are molar densities of a and b , respectively, in the equilibrium state.

We want to normalize variations to a *unit variation*. Figure 1 represents configurations of the actual state. Let us choose an element of area of interface in the actual state which has an area of unity in the reference state. Let us then consider a particular migration in which *one* mole is transformed from phase a to phase b over this chosen area element; we call \mathbf{v}_i the corresponding particular vector $\mathbf{Q}'\mathbf{P}'$. For an arbitrary migration we have, therefore,

$$\delta x_i^b - \delta x_i^a = \delta g \mathbf{v}_i \quad (5)$$

where δg is the arbitrary parameter, positive or negative; δg is in fact the number of moles transformed from a to b across one unit area of interface in the reference state.

The position at equilibrium of the interface within the lattice can be 'mapped' in the reference state. The variational growth of b at the expense of a (or vice-versa) is mapped in the reference state as a displacement of the interface by a distance $\delta l'$ perpendicular to it. From the definition of \mathbf{v}_i , $\delta l'$, for the same arbitrary migration as in Eq. 5, is given by

$$\delta l' = \delta g / \rho' \quad (6)$$

where ρ' is the molar density of the region swept by the interface in the reference state. The sign con-

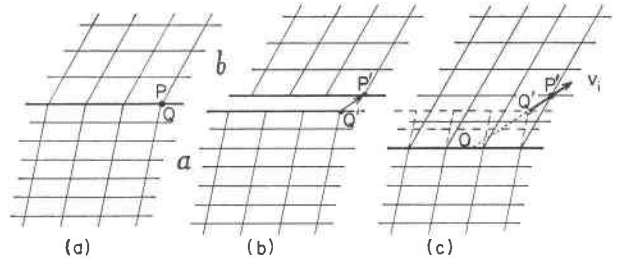


FIG. 1. Migration of a coherent interface in the actual state. Lines have been drawn in a and b to help visualization; they can be interpreted as the traces of two sets of lattice planes preserved in the transformation.

vention on \mathbf{v}_i and δg is such that $\delta l'$ is positive when b grows at the expense of a .

Equations 5 and 6 express completely the constraint of coherency. They show how the growth of each phase and the relative displacements of a and b at a particular point of the interface are functions of only one independent parameter, δg .

In the rest of the paper \mathbf{v}_i is called the *characteristic vector*⁴ of the coherent boundary; in general, if the interface is curved and elastic strains are not uniform within each phase, \mathbf{v}_i is a function of position on the interface.

Conditions of Equilibrium

The total change in energy of the system for an arbitrary variation from the equilibrium state is now stated to be zero or positive. Using Eq. 4, this statement is written

$$\begin{aligned} \delta E = & \int_{V',a} (\sigma_{ij}^a \delta x_{i,j}^a + T \delta s'^a) dV' \\ & + \int_{V',b} (\sigma_{ij}^b \delta x_{i,j}^b + T \delta s'^b) dV' \\ & + \int_{A'} (e'^b - e'^a) \delta l' dA' \geq 0 \quad (7) \end{aligned}$$

where V' and A' are respectively volume and area in the reference state.

⁴ The transformation of the region swept by the interface is an *invariant plane strain* (see Wayman, 1964). In the transformation the length and orientation of any vector parallel to the interface are not affected, and \mathbf{OP}' is transformed into \mathbf{OQ}' (Figure 1). \mathbf{OP}' and \mathbf{OQ}' are colinear and their orientation is therefore that of the only nondegenerate *characteristic vector* (or *eigenvector*) of the transformation; the corresponding eigenvalue is ρ^a/ρ^b .

Not all variations in Eq. 7 are independent, however:

- (1) The total entropy is constrained to remain constant:

$$\int_{V',a} \delta s'^a dV' + \int_{V',b} \delta s'^b dV' + \int_{A'} (s'^b - s'^a) \delta l' dA' = 0. \quad (8)$$

Eqs. 7 and 8 can be satisfied for any arbitrary transfer of entropy only if (Gibbs, 1906, p. 186, Eq. 364)

$$T = \text{constant throughout the system} \quad (9)$$

- (2) Variational displacements, $\delta x_{i,b}$, are continuous throughout the volumes of *a* and *b* and are zero whenever the crystal meets the fixed envelope. Green's divergence theorem gives therefore

$$\int_{V',a} \sigma_{ij}^a \delta x_{i,j}^a dV' = \int_{A'} \sigma_{ij}^a \mathbf{n}'_j{}^a \delta x_i^a dA' - \int_{V',a} \sigma_{ij,i}^a \delta x_i^a dV',$$

and similarly

$$\int_{V',b} \sigma_{ij}^b \delta x_{i,j}^b dV' = \int_{A'} \sigma_{ij}^b \mathbf{n}'_j{}^b \delta x_i^b dA' - \int_{V',b} \sigma_{ij,i}^b \delta x_i^b dV',$$

where $\mathbf{n}'_j{}^a$ and $\mathbf{n}'_j{}^b$ are unit vectors normal to the interface in the reference state, drawn outward from *a* and *b*; clearly $\mathbf{n}'_j{}^a = -\mathbf{n}'_j{}^b$. By using Eq. 5 the sum of the two above integrals can be rewritten as

$$\begin{aligned} & \int_{V',a} \sigma_{ij}^a \delta x_{i,j}^a dV' + \int_{V',b} \sigma_{ij}^b \delta x_{i,j}^b dV' \\ &= - \int_{A'} \sigma_{ij}^a \mathbf{n}'_j{}^a \mathbf{v}_i \delta g dA' \\ &+ \int_{A'} (\sigma_{ij}^a \mathbf{n}'_j{}^a + \sigma_{ij}^b \mathbf{n}'_j{}^b) \delta x_i^b dA' \\ &- \int_{V',a} \sigma_{ij,i}^a \delta x_i^a dV' - \int_{V',b} \sigma_{ij,i}^b \delta x_i^b dV'. \end{aligned} \quad (10)$$

- (3) From Eq. 6, $\delta l'$ is not independent but a function of δg .

Therefore, by inserting Eqs. 6, 8, 9, and 10 into Eq. 7, the total variation of energy of the system is

$$\begin{aligned} \delta E &= - \int_{V',a} \sigma_{ij,i}^a \delta x_i^a dV' - \int_{V',b} \sigma_{ij,i}^b \delta x_i^b dV' \\ &+ \int_{A'} (\sigma_{ij}^a \mathbf{n}'_j{}^a + \sigma_{ij}^b \mathbf{n}'_j{}^b) \delta x_i^b dA' \\ &+ \int_{A'} \left(\frac{e'^b - Ts'^b}{\rho'} - \frac{e'^a - Ts'^a}{\rho'} - \sigma_{ij}^a \mathbf{n}'_j{}^a \mathbf{v}_i \right) \\ &\cdot \delta g dA' \geq 0 \end{aligned} \quad (11)$$

The variational terms in each integral of Eq. 11 are now independent. The equilibrium conditions are therefore obtained by equating the Eulerian of each integral to zero:

- (1) $\sigma_{ij,j} = 0$, throughout *a* and *b*. (12)

This is the usual equation of mechanical equilibrium in the absence of body forces.

- (2) $\sigma_{ij}^a \mathbf{n}'_j{}^a + \sigma_{ij}^b \mathbf{n}'_j{}^b = 0$ on the interface. (13)

Eq. 13 is the condition of mechanical equilibrium on the interface. All components of the stress tensor need not be equal. It is convenient to define T_i , the stress on the interface,

$$T_i = \sigma_{ij}^a \mathbf{n}'_j{}^a = -\sigma_{ij}^b \mathbf{n}'_j{}^b. \quad (14)$$

T_i is the i^{th} component in the equilibrium coordinates of the force on *a* across an element of area of interface equal to unity in the reference state.

- (3) The last condition of equilibrium, and the most important result of this analysis, is

$$\frac{e'^b - Ts'^b}{\rho'} - \frac{e'^a - Ts'^a}{\rho'} - T_i \mathbf{v}_i = 0 \quad (15)$$

on the interface.

If molar energies and entropies are used, as ρ' is a molar density, Eq. 15 becomes

$$(\bar{E}^b - T\bar{S}^b) - (\bar{E}^a - T\bar{S}^a) - T_i \mathbf{v}_i = 0 \quad (16a)$$

or

$$\bar{F}^b - \bar{F}^a - T_i \mathbf{v}_i = 0 \quad (16b)$$

where \bar{F}^a , \bar{F}^b are molar Helmholtz energies. T_i and \mathbf{v}_i are vectors in the equilibrium coordinates, and can be resolved into components normal and tangential to the interface at that point:

$$\mathbf{v}_i = \epsilon \mathbf{n}_i + \gamma_i,$$

$$T_i = -P \mathbf{n}_i + \tau_i,$$

where \mathbf{n}_i is a unit vector normal to the interface outward from *a* in the equilibrium state. Then

$$\mathbf{T}_i \mathbf{v}_i = -P\epsilon + \gamma_i \tau_i.$$

If the reference state is chosen to coincide with the actual coherent equilibrium state, the definition of \mathbf{v}_i makes

$$\epsilon = \bar{V}^b - \bar{V}^a$$

where \bar{V}^a , \bar{V}^b are molar volumes in the equilibrium state. Then the equilibrium condition becomes

$$(\bar{E}^b - T\bar{S}^b + P\bar{V}^b) - (\bar{E}^a - T\bar{S}^a + P\bar{V}^a) - \gamma_i \tau_i = 0 \quad (16c)$$

where, it is recalled, $-P$ and τ_i are respectively the normal stress and the components of the tangential stress on a across the interface.

In spite of their familiar look, the expressions in parentheses should not be confused with the expression of \bar{G} , or μ , defined for phases under hydrostatic pressure: (i) P is only one component of a nonhydrostatic stress tensor; (ii) equality of the two parentheses does not ensure equilibrium, unless $\gamma_i \tau_i = 0$; (iii) in the most general case of equilibrium, when the interface is curved and stresses within each phase are not uniform (e.g., coherent boundaries within grains of a stressed polycrystalline aggregate), the terms in parentheses do not maintain a constant value along the interface.

Existence of Fluid Components

In developing Eq. 16 it was assumed that there was no fluid component in the solid. As noted earlier, Gibbs (1906, p. 215-218) points out that a chemical potential can be defined in the solid for each fluid component by (Gibbs' Eq. 467)

$$\delta e' = \sigma_{ij} \delta x_{i,j} + T \delta s' + \sum_{\alpha} \mu^{\alpha} \delta \rho'^{\alpha} \quad (17)$$

and demonstrates that μ^{α} is constant throughout the system at equilibrium; ρ'^{α} is the molar density of α , that is, the number of moles of component α in the equilibrium state in a volume of solid equal to unity in the reference state. The demonstration is in fact formally identical to the demonstration that the temperature is uniform. It is sufficient to treat ρ'^{α} like s' , and μ_{α} like T in Eqs. 4, 7, 8, and 9. The final equilibrium equation therefore becomes

$$(\bar{E}^b - T\bar{S}^b - \sum_{\alpha} \mu^{\alpha} X^{b,\alpha}) - (\bar{E}^a - T\bar{S}^a - \sum_{\alpha} \mu^{\alpha} X^{a,\alpha}) - \mathbf{T}_i \mathbf{v}_i = 0 \quad (18a)$$

where $X^{a,\alpha}$, $X^{b,\alpha}$ are ratios of the molar density of

fluid component α to the molar density of the solid component in a and b respectively. Only independent fluid components are included in the summation.

If the reference state is chosen to coincide with the equilibrium state (or if it only differs from the equilibrium state by an infinitesimal strain), and \mathbf{T}_i and \mathbf{v}_i are decomposed into normal and tangential components, Eq. 18a becomes

$$(\bar{E}^b - T\bar{S}^b + P\bar{V}^b - \sum_{\alpha} \mu^{\alpha} X^{b,\alpha}) - (\bar{E}^a - T\bar{S}^a + P\bar{V}^a - \sum_{\alpha} \mu^{\alpha} X^{a,\alpha}) - \gamma_i \tau_i = 0 \quad (18b)$$

In the most general case, only temperature, T , and chemical potentials of the fluid components, μ^{α} , have a constant value throughout a volume at equilibrium.

Case of Finite Transformation Strain

Let us consider here a situation in which the stress-free transformation strain is finite and much larger than any elastic strain of either phase. In practice such a transition is not coherent unless a composition plane exists over which the two phases can be matched with stresses which do not exceed the strength of the mineral. Let us therefore assume that we are dealing with a coherent interface along such a plane, at equilibrium at a temperature T . The characteristic vector of the transformation across this plane is chiefly determined by the stress-free transformation strain.

We first restrict our discussion to a solid with no fluid component. At the temperature T , a and b would also be in equilibrium if both were under a hydrostatic pressure P^e . If $\bar{F}^{a,e}$, $\bar{F}^{b,e}$, $\bar{V}^{a,e}$, $\bar{V}^{b,e}$ are the molar Helmholtz energies and molar volumes at P^e and T , this equilibrium is described by the equation of hydrostatic equilibrium

$$(\bar{F}^{b,e} - \bar{F}^{a,e}) + P^e(\bar{V}^{b,e} - \bar{V}^{a,e}) = 0 \quad (19)$$

When a and b are at equilibrium across the coherent interface under stress, the equilibrium condition (Eq. 16c) is

$$(\bar{F}^{b,e} - \bar{F}^{a,e}) + (\Delta\bar{F}^b - \Delta\bar{F}^a) + P(\bar{V}^{b,e} - \bar{V}^{a,e}) + P(\Delta\bar{V}^b - \Delta\bar{V}^a) - \gamma\tau = 0 \quad (20)$$

where $\Delta\bar{F}^a$, $\Delta\bar{F}^b$, $\Delta\bar{V}^a$ and $\Delta\bar{V}^b$ are molar strain energies and volume changes when going from hydrostatic pressure P^e to the coherent situation; γ is the absolute value of the tangential component, γ_i , of the characteristic vector, and τ is the resolved shear stress in the

direction of γ_i (hence $\gamma_i \tau_i = \gamma \tau$). Because the transformation strain is much larger than the elastic strains, as soon as τ is of the same order of magnitude as the stresses required to maintain coherency the term $\gamma \tau$ is much larger than the elastic strain energy terms $\Delta \bar{F}^a$, $\Delta \bar{F}^b$, and also than $P \Delta \bar{V}^a$, $P \Delta \bar{V}^b$; *a fortiori*, the differences $(\Delta \bar{F}^b - \Delta \bar{F}^a)$ and $P(\Delta \bar{V}^b - \Delta \bar{V}^a)$ are negligible compared to $\gamma \tau$. Consequently, subtracting Eq. 19 from Eq. 20, the equilibrium condition reduces to

$$(P - P^e) \Delta \bar{V} - \gamma \tau = 0, \quad (21)$$

where $\Delta \bar{V}$ is now the molar volume difference

$$\Delta \bar{V} = \bar{V}^{b,e} - \bar{V}^{a,e} \simeq \bar{V}^b - \bar{V}^a.$$

By combining Eq. 19 with Eq. 16b instead of Eq. 16c, Eq. 21 can also be written

$$T_i v_i = -P^e \Delta \bar{V}.$$

Eq. 21 can be differentiated with respect to T and gives

$$\left(\frac{dP}{dT} - \frac{\Delta \bar{S}}{\Delta \bar{V}} \right) \Delta \bar{V} - \gamma \frac{d\tau}{dT} = 0 \quad (22)$$

(using the Clausius-Clapeyron equation for dP^e/dT , and neglecting $d\gamma/dT$). Therefore the following relations must be satisfied for the maintenance of equilibrium:

$$\text{at constant } \tau: \left(\frac{\delta P}{\delta T} \right)_{\tau, \text{equil.}} = \frac{\Delta \bar{S}}{\Delta \bar{V}} = \frac{dP^e}{dT}, \quad (23)$$

$$\text{at constant } P: \left(\frac{\delta \tau}{\delta T} \right)_{P, \text{equil.}} = -\frac{\Delta \bar{S}}{\gamma}. \quad (24)$$

Patel and Cohen (1953) combined Eqs. 23 and 24 to explain the effects of hydrostatic compression, uniaxial compression, and uniaxial tension on the martensitic reaction in iron-nickel and iron-nickel-carbon alloys.

Finite Strain with Fluid Components

Coherent transformations characterized by large finite strains may also involve fluid components. A possible case, for example, is the ortho (*Pbca*) to clino (*P2₁/c*) transition in the pyroxene quadrilateral; formation of shear-induced lamellae of clinopyroxene in orthopyroxene is reported by several authors (*e.g.*, Coe and Müller, 1973) and, at temperatures where cation diffusion is sufficiently rapid, such clinopyroxene lamellae could become richer than the host in Fe and Ca, becoming in ef-

fect shear-induced pigeonite lamellae (Robin, 1974c).

An analogous argument leads to an equilibrium condition similar to Eq. 20):

$$\begin{aligned} (\bar{F}^{b,e} + P \bar{V}^{b,e}) - (\bar{F}^{a,e} + P \bar{V}^{a,e}) - \gamma \tau \\ = \sum_{\alpha} \mu^{\alpha} (X^{b,\alpha} - X^{a,\alpha}) \end{aligned} \quad (25)$$

Case of Finite Simple Shear and No Fluid Component

In this case $\bar{V}^a = \bar{V}^b = \bar{V}$, and (see Fig. 2)

$$\gamma = \bar{V} \tan \psi. \quad (26)$$

Eq. 16b becomes

$$\bar{F}^b - \bar{F}^a - \bar{V} \tau \tan \psi = 0 \quad (27)$$

Eq. 24 becomes

$$\left(\frac{\delta T}{\delta \tau} \right)_{P, \text{equil.}} = \frac{\bar{V} \tan \psi}{\Delta \bar{S}}. \quad (28)$$

Eqs. 27 and 28 are identical to the results of Coe (1970), except for a different sign convention on $\Delta \bar{S}$.

Finite Strain Twinning

Twins are at equilibrium with each other under any hydrostatic pressure, and in particular when the hydrostatic pressure is equal to the normal component of stress P . If the stress-free transformation strain (a finite simple shear) satisfies the assumptions of this section, the equilibrium condition (Eq. 21) becomes

$$\gamma \tau \simeq 0$$

or

$$\tau \simeq 0 \quad (29)$$

In its equilibrium position, such a twin boundary does not support any resolved shear stress. This does not mean that other shear stress components are zero. The finite resolved shear stress which is often required to move a twin boundary is thus a measure of the disequilibrium ($\gamma \tau$ is a molar energy) that the boundary can support before migrating.

Infinitesimal Transformation Strain

If the transformation strain is very small, the reference state can be chosen such that the strain of the lattice with respect to the reference state is infinitesimal in any actual state of the system. The characteristic vector of the transformation is (see Appendix)

$$\mathbf{v}_i = \bar{V}[2(\mathbf{e}_{ij}^b - \mathbf{e}_{ij}^a)\mathbf{n}_i^a - (\mathbf{e}_{kk}^b - \mathbf{e}_{kk}^a)\mathbf{n}_i^a]$$

or

$$\mathbf{v}_i = \bar{V}(2 \Delta \mathbf{e}_{ij}\mathbf{n}_i^a - \Delta \mathbf{e}_{kk}\mathbf{n}_i^a) \quad (30)$$

where $\mathbf{e}_{ij}^a, \mathbf{e}_{ij}^b$ are the symmetric strain tensors with respect to the reference state, and $\Delta \mathbf{e}_{ij}$ is therefore the total transformation strain across the interface.

The scalar product $\mathbf{T}_i \mathbf{v}_i$ may be expressed as

$$\mathbf{T}_i \mathbf{v}_i = \bar{V}(2\tau_i \Delta \mathbf{e}_{ij}\mathbf{n}_i^a + P \Delta \mathbf{e}_{kk}) \quad (31a)$$

If the coordinate system is such that its 1-axis is perpendicular to the interface at the point under consideration,

$$\Delta \mathbf{e}_{22} = \Delta \mathbf{e}_{33} = \Delta \mathbf{e}_{23} = 0, \Delta \mathbf{e}_{kk} = \Delta \mathbf{e}_{11},$$

$$v_1 = \bar{V} \Delta \mathbf{e}_{11}, v_2 = 2 \bar{V} \Delta \mathbf{e}_{12}, v_3 = 2 \bar{V} \Delta \mathbf{e}_{13}$$

$$T_1 = \sigma_{11}^a = \sigma_{11}^b = \sigma_{11}, T_2 = \sigma_{12}^a = \sigma_{12}^b = \sigma_{12},$$

$$T_3 = \sigma_{13}^a = \sigma_{13}^b = \sigma_{13}$$

and therefore

$$\mathbf{T}_i \mathbf{v}_i = \bar{V}(\sigma_{11} \Delta \mathbf{e}_{11} + 2\sigma_{12} \Delta \mathbf{e}_{12} + 2\sigma_{13} \Delta \mathbf{e}_{13}), \quad (31b)$$

or, in matrix notation,

$$\mathbf{T}_i \mathbf{v}_i = \bar{V}(\sigma_1 \Delta \mathbf{e}_1 + \sigma_2 \Delta \mathbf{e}_2 + \sigma_3 \Delta \mathbf{e}_3) \quad (31c)$$

We recognize the decomposition $-P\epsilon + \gamma_i \tau_i$ obtained previously. The equilibrium condition follows immediately by inserting Eq. 31 into Eqs. 16 or 18.

Previous Results and Discussion

In spite of their many possible applications, only a few attempts to obtain results analogous to the ones presented here can be found in the literature. The works of Patel and Cohen (1953) and of Coe (1970), for finite transformation strain and no fluid component, have already been mentioned. Oriani (1966) considered the equilibrium of a coherent spherical precipitate of an isotropic phase β in an isotropic matrix α , the stress-free transformation strain being itself infinitesimal and isotropic. Because of the symmetry of the situation, pressure is hydrostatic and uniform in β , and the characteristic vector of the transformation is everywhere normal to the interface. Oriani's problem is thus not different from that of finding the equilibrium between a solid matrix α and a spherical inclusion of fluid β which can dissolve the solid. McLellan (1970) and Paterson (1973) give the condition of equilibrium of a coherent interface, when the strain is infinitesimal and there are no fluid components, as

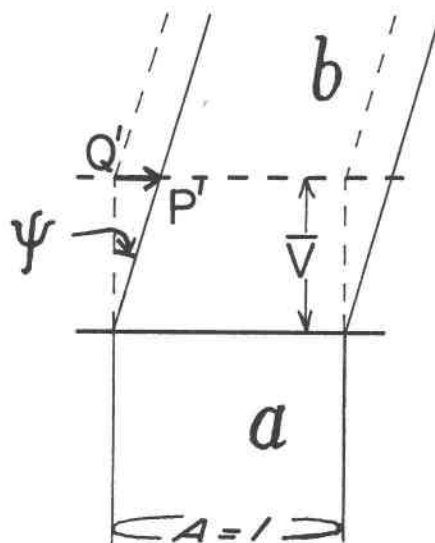


FIG. 2. Characteristic vector, for finite simple shear. The vector \mathbf{v}_i has only a tangential component, of modulus γ . The transformation is more easily characterized by its shear angle ψ . When a molar volume \bar{V} changes phase across a unit area of interface, $|Q'P'| = \gamma = \bar{V} \tan \psi$; hence Eq. 26.

$$\mathbf{F}^b - \mathbf{F}^a - \bar{V} \sigma_{ij} \Delta \mathbf{e}_{ij} = 0. \quad (32)$$

Although Eq. 32 appears to ignore the fact that the stresses are in general not equal on both sides of the interface, the last term does reduce to Eq. 31 when the proper coherency conditions for $\Delta \mathbf{e}_{ij}$ are taken into account. Fletcher (1973) also reached the proper equilibrium condition for infinitesimal strain.

Kamb (1959) and Paterson (1973) give the following equilibrium equation for a 'grain boundary' supporting a shear stress:

$$(\mathbf{E}^b - T\bar{S}^b + P\bar{V}^b) - (\mathbf{E}^a - T\bar{S}^a + P\bar{V}^a) = 0 \quad (33)$$

where P is, as before, the normal component of stress on the interface.

Although Kamb (1959) does not detail his derivation, the only stated assumptions are that "there is no slippage at the interface and . . . the shear stress is continuous across the interface . . .," conditions which are fulfilled by a coherent interface. There is also no assumption which would exclude a coherent boundary in Paterson's derivation. The discrepancy between Eqs. 33 and 16 therefore requires examination.

The very notion of *equilibrium with respect to a possible grain growth* requires that such grain growth be reversible. That is, if the state of the

system is altered by a small variational growth of, say, phase b , at the expense of a , the reverse variation must bring the system to its original state. In particular, in presence of a shear stress, points of one phase must have recovered their original position with respect to points of the other phase. If this requirement were not met, the sum of the two variations would amount to a slip; slip then being a possible mechanism, equilibrium would require no shear component of stress along the interface. On the contrary, when the above requirement of reversibility is met, it can be verified that any variational migration of the boundary must occur in a way similar to that described in Figure 1, and can therefore be described by a characteristic vector \mathbf{v}_i .

At this point it is important to recognize that the migration of an interface, as in Figures 1 or 2, is indeed not restricted to coherent interfaces. We may, for example, consider a row of parallel edge-dislocations oriented as in Figure 3. When conditions are such that these dislocations cannot climb and do not move independently from one another, this boundary migrates like the coherent boundaries of Figures 1 or 2. Growth of kink bands constitutes another possible example.

Therefore, in order to obtain Eq. 33, Kamb (1959) and Paterson (1973) had to implicitly assume that for a grain boundary supporting a shear stress the characteristic vector \mathbf{v}_i was perpendicular to the interface (and therefore $\gamma_i = 0$ in Eq. 16). This is particularly clear in Paterson's derivation, in which an imaginary, inert, and permeable matrix

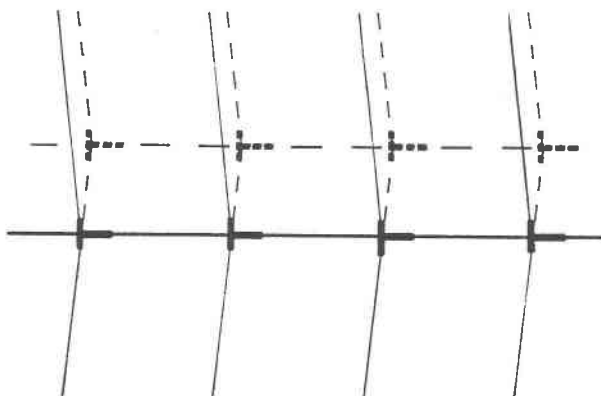


FIG. 3. Wall of gliding edge dislocations. The full lines are traces of glide planes. Simultaneous gliding of the dislocations results in a shear deformation of the framework, essentially similar to the interface migrations presented in Figures 1 and 2.

applies the stress to the solid. To calculate the change in potential energy of the matrix for a variational growth of the crystal, Paterson assumes that points of the matrix are moved along a direction perpendicular to the interface to meet the new surface of the crystal. If contact between the solid and the matrix is assumed to be reestablished by moving points of the matrix along some different direction, a different value for the change in potential energy results; yet, there is no *a priori* reason to choose between these two assumptions.

Kamb (1959) and Paterson (1973) sought to apply Eq. 33 to the grain boundaries in polycrystalline aggregates. However, contrary to the subgrain or the kink boundaries envisaged above, random high-angle grain boundaries generally have no mechanism which could constrain their migration in presence of a shear stress to be reversible in the same manner. Indeed, because of the generally complete disruption of the lattices along the boundary, the position of the a lattice has no way of influencing (or of being influenced by) the position of the b lattice. It is possible to conceive equilibrium with respect to growth while at the same time the boundary is sliding irreversibly. In reality, however, sliding along the boundary is likely to occur much faster than any phase growth across it; growth, or equilibrium with respect to it, would therefore obtain when the grain boundary no longer supports any shear stress, in which case Gibbs' equilibrium condition applies.

Except for theories of preferred orientations, Gibbs equilibrium condition has so far not been used in mineralogical problems. By contrast, equilibrium conditions for coherent interfaces have found applications in various problems of phase changes in the solid state (Patel and Cohen, 1953; Coe, 1970; Robin, 1974a,c) and are likely to find more as the microscopic study of interfaces develops.

Appendix

The infinitesimal strain with respect to the reference state can be characterized by the symmetric strain tensors

$$\begin{aligned} \mathbf{e}_{ij}^b &= \frac{1}{2}(x_{i,j}^b + x_{j,i}^b) - \delta_{ij} \\ \mathbf{e}_{ij}^a &= \frac{1}{2}(x_{i,j}^a + x_{j,i}^a) - \delta_{ij} \end{aligned} \quad (\text{A1})$$

The characteristic vector is

$$\mathbf{v}_i = \bar{V}(x_{i,j}^b - x_{i,j}^a)\mathbf{n}_j^a$$

or, using Eq. A1,

$$\mathbf{v}_i = \bar{V}[2(\mathbf{e}_{ij}^b - \mathbf{e}_{ij}^a)\mathbf{n}_j^a - (x_{i,j}^b - x_{i,j}^a)\mathbf{n}_j^a] \quad (\text{A2})$$

The fact that the transformation strain leaves the plane of the interface invariant is expressed by

$$(x_{j,i}^b - x_{j,i}^a) \mathbf{t}_i = 0 \quad (\text{A3})$$

where \mathbf{t}_i is any vector tangent to the interface at the point under consideration. Also, the molar volume change is

$$\mathbf{v}_i \mathbf{n}_i^a = \bar{V}(\mathbf{e}_{ii}^b - \mathbf{e}_{ii}^a) \quad (\text{A4})$$

The term $(x_{j,i}^b - x_{j,i}^a) \mathbf{n}_j^a = k_i$ of Eq. A2 can be evaluated. From Eq. A3, $k_i \mathbf{t}_i = 0$. Also

$$\begin{aligned} k_i \mathbf{n}_i^a &= (x_{j,i}^b - x_{j,i}^a) \mathbf{n}_j^a \mathbf{n}_i^a = \frac{1}{\bar{V}} \mathbf{v}_i \mathbf{n}_i^a, \\ &= \mathbf{e}_{ji}^b - \mathbf{e}_{ji}^a, \text{ from Eq. A4.} \end{aligned}$$

Therefore k_i is normal to the interface and equal to

$$k_i = (\mathbf{e}_{kk}^b - \mathbf{e}_{kk}^a) \mathbf{n}_i^a$$

Inserting into Eq. A2, we obtain finally

$$\mathbf{v}_i = \bar{V} [2(\mathbf{e}_{ij}^b - \mathbf{e}_{ij}^a) \mathbf{n}_j^a - (\mathbf{e}_{kk}^b - \mathbf{e}_{kk}^a) \mathbf{n}_i^a] \quad (\text{A5}) = (30)$$

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