On the effect of elastic distortions on the kinetics of diffusion-induced phase transformations

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Abstract

We derive the evolution equation for a sharp concentric interface in a two-phase elastic solid of spherical shape. The solid is immersed in a reservoir of interstitial species whose diffusion triggers phase transformation. We find that mismatch strain accelerates phase–tranformation processes that initiate at the center of the specimen, and slows down those that begin at the boundary.

Keywords: diffusion-induced stress, phase transformation.

1. Introduction

Consider a body undergoing phase and compositional changes due to the diffusion of one ore more chemical species. If different phases coexist, and if the interfaces that separate different phases are *coherent*, then transformation-induced strain may give rise to a non-vanishing stress field that has profound effects on phase equilibria and phase-transformation kinetics [1, 2].

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Schwarz and Kachaturyan [3] examined a two-phase solid solvent in contact with a reservoir providing solute interstitial atoms. They showed that transformation-induced strain renders the coexistence of different phases impossible at equilibrium and is responsible for the hysteresis loop observed in a isothermal cyclic process where the chemical potential of the reservoir is changed to induce adsorption and desorption of atoms. A typical plot of reservoir chemical potential versus solute content is shown in Fig. 1. At low

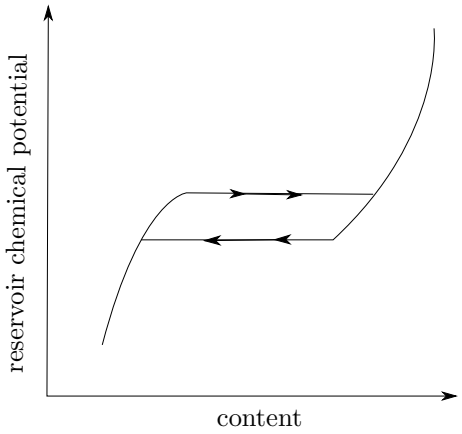

Figure 1: The hysteresis loop. On the horizontal axis we have the solute content. On the vertical axis, the chemical potential of the reservoir

chemical potential, the solid is in the α *phase*, characterized by low content of atoms. As chemical potential increases, the solute dissolves in the solid, until a solubility limit is reached. Then, adsorption of further atoms takes place at constant chemical potential, while the high-content β *phase* starts to form, until the solid is completely transformed. At that point, further addition of atoms requires an increase of chemical potential. If, subsequently, the chemical potential of the reservoir is lowered, desorption of atoms from the specimen takes place, but the reverse transformation takes place at a lower chemical potential.

We capture this phenomenology through a simple model where diffusion of interstitial atoms takes place in a spherical body $\mathscr{B}$ partitioned in two time-dependent regions $\mathscr{B}_\alpha(t)$ and $\mathscr{B}_\beta(t)$, each associated to a particular phase, separated by an evolving *coherent sharp interface* $\mathscr{S}(t)$, which we assume to be concentric, as depicted in Fig. 1. Our working tool is the theory of species diffusion coupled with linear elasticity for a two-phase solid

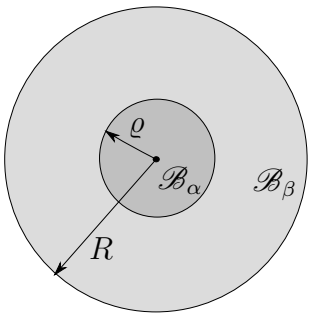

Figure 2: The spherical body $\mathscr{B}$ partitioned into two phases by a concentric sharp interface. The inner core of radius ϱ is occupied by the phase α, while the outer region $\mathscr{B}_\beta$ is occupied by the β phase.

proposed in [4] and further developed in [5]. The theory in question describes three interdependent phenomena taking place in the body:

- deformation,
- diffusion of a chemical species,
- phase transformation,

with the latter being associated to the motion of the interface $\mathscr{S}(t)$. In the theory in question, the independent variables in the constitutive equations are:

- the *linear strain* $\mathbf{E} = \mathrm{sym}\nabla\mathbf{u}$,
- the *chemical potential* μ.

In particular, the *grand canonical potential* ω is determined by chemical potential and strain through a constitutive prescription that involves a *constitutive mapping* $\widehat{\omega}_\phi$ for the individual phases $\phi = \alpha, \beta$:[1]

$$\omega = \widehat{\omega}_\phi(\mu, \mathbf{E}). \tag{1}$$

[1]When writing constitutive equations governing a field, the index ϕ equals α or β according the whether the field is evaluated in the region occupied by the α or by the β phase.

In this theory, the concentration c of the mobile species and the stress $\mathbf{S}$ are dependent variables delivered by the following constitutive equations:

$$c = -\frac{\partial \widehat{\omega}_\phi(\mu, \mathbf{E})}{\partial \mu}, \qquad \mathbf{S} = \frac{\partial \widehat{\omega}_\phi(\mu, \mathbf{E})}{\partial \mathbf{E}}. \tag{2}$$

Each of the constitutive mappings $\widehat{\omega}_\phi$ that deliver the grand canonical potential in the two phases is the sum of two terms, separately dependent on μ and $\mathbf{E}$, with the dependence on μ being linear (see [5, Eq. 3.57]):

$$\widehat{\omega}_\phi(\mu, \mathbf{E}) = -c_\phi(\mu - \mu_{\rm eq}) + \widehat{W}_\phi(\mathbf{E}). \tag{3}$$

The theory is appropriate to describe processes wherein the interplay between deformation, diffusion, and interface motion involves small strains and small deviations of the chemical potential from a *reference value* $\mu_{\rm eq}$. As we shall see, $\mu_{\rm eq}$ is the chemical potential at which the two phases would be in equilibrium if phase transformation was accompanied by no mechanical effects.

An immediate consequence of (2) and (3) is that concentration is constant within each phase, namely,

$$c(x,t) = \begin{cases} c_\alpha & \text{if } x \in \mathscr{B}_\alpha(t), \\ c_\beta & \text{if } x \in \mathscr{B}_\beta(t), \end{cases} \tag{4}$$

a circumstance that is encountered when *interface motion is slow compared to diffusion*, and that greatly simplifies the mathematical treatment of the problem. Indeed, thanks to (4), we have that

- $\dot{c} = 0$ in the *bulk region* $\mathscr{B}_\alpha(t) \cup \mathscr{B}_\beta(t)$, that is, away from the interface.

Thus, away from the interface, the standard balance law for the mobile species, namely

$$\dot{c} + \mathrm{div}\mathbf{h} = 0 \tag{5}$$

reduces to:

$$\mathrm{div}\mathbf{h} = 0. \tag{6}$$

In particular, if the flux of diffusant is assumed to be proportional to the gradient of chemical potential through a constant mobility for each phase,[2]

$$\mathbf{h} = -m_\phi \nabla \mu, \tag{7}$$

[2]If the diffusing species is an interstitial, the mobility of each phase is proportional to concentration. Thus, $m_\phi = c_\phi \bar{m}_\phi$ with $\bar{m}_\phi$ a constant that depends on the particular phase $\phi = \alpha, \beta$. Such explicit dependence does not play any role as long as (4) holds true.

then chemical potential is harmonic in the bulk:

$$\Delta\mu = 0. \tag{8}$$

The aforementioned equations are supplemented by:

1) the *coherency condition* for the displacement field $\mathbf{u}$ and the condition of *local equilibrium* for μ, respectively,

$$[\![\mathbf{u}]\!] = 0, \qquad \text{and} \qquad [\![\mu]\!] = 0, \tag{9}$$

both enforced at the interface $\mathscr{S}(t)$;

2) the force balance in the bulk $\mathscr{B}_\alpha(t) \cup \mathscr{B}_\beta(t)$, the continuity of the normal traction at the interface $\mathscr{S}(t)$, and the condition of null traction on the boundary $\partial\mathscr{B}$:[3]

$$\mathrm{div}\mathbf{S} = \mathbf{0}, \qquad [\![\mathbf{S}]\!]\mathbf{n} = \mathbf{0} \qquad \mathbf{S}|_{\partial\mathscr{B}}\mathbf{n} = \mathbf{0}; \tag{10}$$

3) the standard Maxwell condition at the interface:[4]

$$[\![\omega - \partial_{\mathbf{n}}\mathbf{u}\cdot\mathbf{S}\mathbf{n}]\!] = 0. \tag{11}$$

4) the requirement that, at the boundary $\partial\mathscr{B}$, chemical potential equals that of the reservoir:

$$\mu|_{\partial\mathscr{B}} = \mu_R. \tag{12}$$

The resulting system can be solved to determine the chemical-potential field $\mu(\cdot, t)$ at time t. With this information, the localization of (5) at the interface:

$$[\![c]\!]V = [\![\mathbf{h}]\!]\cdot\mathbf{n} \tag{13}$$

delivers V, *the radial velocity of the interface*, and hence restitutes an evolution equation for $\mathscr{S}(t)$, which is the main contribution of the present paper. The equation in question, which we anticipate here, has the form:

$$M(\varrho/R)V = \mu_{\mathrm{eq}} - \mu_R + \widehat{\mu}_{\mathrm{el}}(\varrho/R) \tag{14}$$

[3]In writing the third of (10) we are neglecting the pressure that the invironment exerts on the body.

[4]We remark that the Maxwell condition (11) may be interpreted as a balance statement localized at the interface $\mathbf{n}\cdot[\![\mathbf{C}]\!]\mathbf{n} = 0$, involving the *configurational stress* $\mathbf{C} = \omega\mathbf{I} - \nabla\mathbf{u}^T\mathbf{S}$ (see [6]). If one adopts this point of view, then implicit in (11) is the assumption that the interface be dissipationless and structureless. This assumption may well be relaxed, as in [7], where surface energy and dissipation are ascribed to the interface.

where

$$M(y) = \frac{(c_\beta - c_\alpha)R}{m_\beta}(1-y)y, \qquad 0 \le y \le 1 \tag{15}$$

is interpreted as the *interface mobility* and $\widehat{\mu}_{\rm el}(\varrho/R)$, defined in (75) is the *elastic chemical potential*, which depends on the position of the interface and is proportional to ϵ_0^2, the square of the elastic misfit ϵ_0 between the two phases (see (26) and (27)).

From the mathematical standpoint, the problem we consider in this paper is similar to those studied by Vooheers and collaborators in their investigations on the role played by elastic effects on the growth kinetics of a coherent precipitate from a solid solution. See for instance [8, 9], the review [1], and also [10].

In these investigation they consider that the precipitate grows in an infinite matrix, whose composition at infinity (the *far-field* composition) is prescribed. At variance with the approach adopted in the present paper, they take concentration as independent variable in their constitutive prescriptions. In particular, chemical potential appears in the position of a dependent variable, related to concentration through the standard relation:

$$\mu = \widehat{\mu}_\phi(c), \qquad \phi = \alpha, \beta. \tag{16}$$

In order to make the problem tractable with simple analytical tools, several approximations are in order. First of all, (16) is approximated through its linearization:

$$\widehat{\mu}_\phi(c) \simeq \mu_{\rm eq} + \widehat{\mu}'(c_{{\rm eq},\phi})(c - c_{{\rm eq},\phi}), \tag{17}$$

about a reference state in which each phase $\phi = \alpha, \beta$ is characterized by a given composition $c_{{\rm eq},\phi}$, which corresponds to an ideal situation when the two phases are in equilibrium, at a common chemical potential $\mu_{\rm eq}$, without elastic and surface effects. [5]

A consequence of the above-mentioned approximation is that the mass-balance equation in the bulk yields the standard, linear diffusion equation for concentration (provided that mobility is independent on concentration). If, in addition, one assumes (as we also do) that diffusion is fast in comparison

[5] It is argued in [4] (see also [5]) that a problem with the linearization (17) is that it pollutes the thermodynamic structure of the system. This is the motivation for the different path taken in [4] — a path we follow in the present paper — based on taking μ as independent variable and on stipulating (3).

with the interface motion, then the diffusion equation reduces to the Laplace equation for concentration.

The boundary conditions for the Laplace equation are the far-field concentration and the interfacial concentration, the latter obtained by combining (17) with the Gibbs-Thompson condition, which in that context plays the same role as (11), taking also into account interfacial energy.

With the aforementioned approximations, and with the assumption that the precipitate is spherical, a kinetic equation for the rate of growth of a spherical inclusion of radius ρ in an infinite elastically isotropic matrix is obtained (see equations (75) to (77) of [1]). This result can be obtained from the result of our paper by assuming that R goes to infinity (i.e., by letting the body $\mathscr{B}$ have infinite size), neglecting capilarity effects, and relating μ_R with the far-field concentration.

2. Setting the stage

We consider the spherical body $\mathscr{B} = \{\mathbf{x} : |\mathbf{x}| \leq R\}$. At each time t the body is partitioned in two phases $\mathscr{B}_\alpha(t)$ and $\mathscr{B}_\beta(t)$, separated by a *concentric* sharp interface $\mathscr{S}(t)$:

$$\mathscr{S}(t) = \{\mathbf{x} : |\mathbf{x}| = \varrho(t)\}, \tag{18}$$

with the inner core occupied by the α phase and the outer region by the β phase:

$$\mathscr{B}_\alpha(t) = \{\mathbf{x} : 0 \leq |\mathbf{x}| < \varrho(t)\}, \qquad \mathscr{B}_\beta(t) = \{\mathbf{x} : \varrho(t) < |\mathbf{x}| < R\}. \tag{19}$$

Accordinaly, at the typical point $\mathbf{y}$ of $\mathscr{S}(t)$, the outward unit normal and the normal velocity fields are given by:

$$\mathbf{n}_t(\mathbf{y}) = \mathbf{e}(\mathbf{y}), \quad V_t(\mathbf{y}) = \dot{\varrho}(t), \tag{20}$$

where

$$\mathbf{e}(\mathbf{x}) = \frac{\mathbf{x}}{|\mathbf{x}|} \tag{21}$$

is the radial unit vector field.

Having our geometry set up, our next step is to establish the constitutive prescription for the stress $\mathbf{S}$. In view of (2) and (3), we have

$$\mathbf{S} = \widehat{\mathbf{S}}_\phi(\mathbf{E}) = \widehat{W}'_\phi(\mathbf{E}). \tag{22}$$

and choice of the *strain-energy mapping* $\widehat{W}_\phi$ is in order. With a view towards making such a choice, we take as a *reference state* for measuring strain the body in a stress-free state at uniform phase α and uniform concentration $c_{0,\alpha}$. According to *Vegard's law*, the stress-free state in the same phase, at concentration c_ϕ, depends linearly on the difference $c_\alpha - c_{0,\alpha}$. The simplest choice is that the stress-free strain be purely dilatational:

$$\mathbf{E}_\alpha = (c_\phi - c_{0,\alpha})e_\alpha \mathbf{I}, \tag{23}$$

for some suitable constant e_α. By its turn, the stress-free strain in the β phase can be thought as the sum of two contributions: a term representing the homogeneous strain due to a homogeneous change in concentration from a reference concentration $c_{0,\beta}$; a term accounting for the transformation between the reference state for measuring strain and the natural state for the β phase at com- position $c_{0,\beta}$. Again, the simplest choice is that all these contributions be purely *dilatational*:

$$\mathbf{E}_\beta = ((c_\beta - c_{0,\beta})e_\beta + e_T)\mathbf{I}, \tag{24}$$

where e_β and e_T are suitable constants. Notice that the transformation strain is purely dilatational, and represented by e_T.

We restrict attention to isotropic response and we select:[6]

$$W = \widehat{W}_\phi(\mathbf{E}) = G|\mathbf{E} - \mathbf{E}_\phi|^2 + \frac{\lambda}{2}|\mathrm{tr}(\mathbf{E} - \mathbf{E}_\phi)|^2, \qquad \phi = \alpha, \beta, \tag{25}$$

where $\mathbf{E}_\alpha$ and $\mathbf{E}_\beta$ are the *stress-free strains* of, respectively, the stress-free strains of the α and β phase. Accordingly, the constititive equation delivering the stress becomes:

$$\mathbf{S} = \widehat{\mathbf{S}}_\phi(\mathbf{E}) = 2G(\mathbf{E} - \mathbf{E}_\phi) + \lambda \mathrm{tr}(\mathbf{E} - \mathbf{E}_\phi)\mathbf{I}. \tag{26}$$

Now, on setting $\epsilon_\alpha = (c_\phi - c_{0,\alpha})e_\alpha$ and $\epsilon_\beta = (c_\beta - c_{0,\beta})e_\beta + e_T$, we can write:

$$\mathbf{E}_\phi = \epsilon_\phi \mathbf{I}, \tag{27}$$

[6]Given that the mechanical effects of phase tranformation are essentially those engendered by elastic misfit, we assume for simplicity that the stiffness in either phase is the same. This approximation delivers fairly accurate results in many situations, such as for instance the hydriding process of a metallic particle [11].

so that $\mathbf{E}_0 = \epsilon_0 I$ with

$$\epsilon_0 = \epsilon_\beta - \epsilon_\alpha \tag{28}$$

represents the *misfit strain* between the two phases. Then, on introducing the *bulk modulus*:

$$K = \frac{2}{3}G + \lambda, \tag{29}$$

we can rewrite (26) as:

$$\widehat{\mathbf{S}}_\phi(\mathbf{E}) = 2G\mathbf{E} + (\lambda(\mathrm{tr}\mathbf{E}) - 3K\epsilon_\phi)\mathbf{I}. \tag{30}$$

3. Computation of stress, strain, and chemical potential

In this section we turn our attention to determining stress, strain and chemical potential. As we shall see, these fields can be computed knowing only the current position of the interface. Accordingly, we restrict attention to a fixed time t, and we let $\varrho = \varrho(t)$ be the distance of the interface from the center of the sphere at that particular time. We anticipate that displacement field and chemical potential are radially symmetric and we write:

$$\mathbf{u}(\mathbf{x}) = \bar{u}(r)\mathbf{e}, \qquad \mu(\mathbf{x}) = \bar{\mu}(r), \qquad \text{where} \qquad r = |\mathbf{x}|. \tag{31}$$

For typographical convenience, we drop overbars in what follows.

Our plan is the following: by appealing to the balance equations in the bulk $(10)_1$ and the constitutive equation (30), we shall first derive a general representation formula for the displacement, which depends on three constants. We shall then choose these constants consistent with:

- the coherency condition $(9)_1$;
- the traction condition $(10)_3$;
- the continuity of the traction at the interface $(10)_2$.

In our second step, we shall determine a representation formla for the chemical-potential field, which we recall is harmonic in the bulk because of the balance equation (6) and the constitutive equation (26). Again, the representation formula will contain three constants that we shall select by exploiting, in the order:

- the condition of local equilibrium $(9)_2$;

- the prescription of chemical potential at the boundary (12);
- the Maxwell condition (11).

As we shall see, it is through the latter that chemical potential, strain, and stress interact.

3.1. Step 1: displacement, strain and stress

On recalling (21), it is easy to see from $(31)_1$ that $\nabla\mathbf{u}$ is symmetric and hence equal to the infinitesimal strain tensor $\mathbf{E}$:

$$\nabla\mathbf{u} = u'\mathbf{e}\otimes\mathbf{e} + \frac{u}{r}(\mathbf{I}-\mathbf{e}\otimes\mathbf{e}) = \mathrm{sym}\nabla\mathbf{u} = \mathbf{E}. \tag{32}$$

Then, the constitutive equation (32) yields:

$$\mathbf{S} = \sigma_r\mathbf{e}\otimes\mathbf{e} + \sigma_\theta(\mathbf{I}-\mathbf{e}\otimes\mathbf{e}), \tag{33}$$

where

$$\sigma_r(r) = \lambda(u'(r)+2\frac{u(r)}{r}) + 2Gu'(r) - \begin{cases} 3K\epsilon_\alpha & \text{if } 0<r<\varrho, \\ 3K\epsilon_\beta & \text{if } \varrho<r<R, \end{cases} \tag{34}$$

is the *radial stress* and

$$\sigma_\theta(r) = \lambda(u'(r)+2\frac{u(r)}{r}) + 2G\frac{u(r)}{r} - \begin{cases} 3K\epsilon_\alpha & \text{if } 0<r<\varrho, \\ 3K\epsilon_\beta & \text{if } \varrho<r<R, \end{cases} \tag{35}$$

is the *hoop stress*. By substituting (33) into the balance equation $(10)_1$ we obtain:

$$0 = \mathrm{div}\mathbf{S} = \big(\sigma_r' + 2(\sigma_r-\sigma_\theta)/r\big)\mathbf{e}, \tag{36}$$

which hold in $(0,\varrho)$ and (ϱ,R). A further substitution of (34)–(22) into (36) yields the differential equation

$$\left(\frac{(r^2u)'}{r^2}\right)' = 0, \tag{37}$$

which is integrated on the intervals $(0,\varrho)$ and (ϱ,R):

$$u(r) = \begin{cases} C_1^\alpha r, & \text{for } 0<r<\varrho, \\ C_1^\beta r + \dfrac{C_2^\beta}{r^2}, & \text{for } \varrho<r<R, \end{cases} \tag{38}$$

with C_i^ϕ suitable constants. From (38) and (34)–(35) we obtain:

$$\sigma_r(r) = \sigma_\theta(r) = 3K(C_1^\alpha - \varepsilon_\alpha) \text{ for } 0 < r < \varrho, \tag{39}$$

and

$$\left.\begin{aligned} \sigma_r(r) &= 3K(C_1^\beta - \varepsilon_\beta) - 4G\tfrac{C_2^\beta}{r^3} \\ \sigma_\theta(r) &= 3K(C_1^\beta - \varepsilon_\beta) + 2G\tfrac{C_2^\beta}{r^3} \end{aligned}\right\} \text{ for } \varrho < r < R. \tag{40}$$

In view of $(31)_1$, the coherency condition $(9)_1$ reduces to the requirement that

$$[\![u]\!] = 0, \tag{41}$$

namely, that $u(r)$ be continuous at $r = \varrho$. In turn, by (38), this requirement yields:

$$C_1^\beta - C_1^\alpha + \frac{C_2^\beta}{\varrho^3} = 0. \tag{42}$$

Likewise, the continuity of the normal traction at the interface, expressed by $(10)_2$, becomes

$$[\![\sigma_r]\!] = 0, \tag{43}$$

whence, by (39) and (40),

$$3K(C_1^\beta - C_1^\alpha - \epsilon_0) - 4G\frac{C_2^\beta}{\varrho^3} = 0. \tag{44}$$

Finally, the null-traction condition at the boundary $(10)_3$ yields $\sigma_r(R) = 0$, whence, by (40),

$$3K(C_1^\beta - \epsilon_\beta) - 4G\frac{C_2^\beta}{R^3} = 0. \tag{45}$$

Now, on using (42) and (44), we find $-C_2^\beta/\varrho^3 = C_1^\beta - C_1^\alpha = \frac{4G}{3K}C_2^\beta/\varrho^3 + \epsilon_0$, whence:

$$C_2^\beta = -\frac{K}{2G+\lambda}\epsilon_0\varrho^3. \tag{46}$$

The above equation, combined with (45) restitutes:

$$C_1^\beta = \epsilon_\beta - \frac{4G}{3(2G+\lambda)}\frac{\varrho^3}{R^3}\epsilon_0. \tag{47}$$

Finally, by making use of (42) and (46)–(47), we find

$$C_1^\alpha = \epsilon_\beta - \frac{\epsilon_0}{(2G+\lambda)}\left(K + \frac{4G}{3}\frac{\varrho^3}{R^3}\right). \tag{48}$$

3.2. Step 2: chemical potential

We now turn our attention to the radial profile $\mu(r)$ of chemical potential. We recall (*cf.* (8)) that chemical potential is harmonic away from the interface. Accordingly, the function $\mu(r)$ satisfies the following differential equation:

$$(r\mu')' = 0 \tag{49}$$

in $(0, \varrho) \cup (\varrho, R)$, whose most general non-singular solution has the form:

$$\mu(r) = \begin{cases} D_1^\alpha, & \text{for } 0 < r < \varrho, \\ D_1^\beta + \dfrac{D_2^\beta}{r}, & \text{for } \varrho < r < R, \end{cases} \tag{50}$$

with arbitrary constants D_1^α, D_1^β, and D_2^β. We select the values of these constants by imposing the following conditions:

- the continuity of μ at the interface, which follows from the condition of local equilibrium $(9)_2$, that we rewrite for the Reader's convenience:

$$[\![\mu]\!] = 0; \tag{51}$$

- the prescription of chemical potential at the boundary, as stipulated in (12), which becomes:

$$v(R) = \mu_R; \tag{52}$$

- the Maxwell condition (11) at the interface.

From (51) and (52) we have, respectively,

$$D_1^\alpha = D_1^\beta + \frac{D_2^\beta}{\varrho}, \tag{53}$$

and

$$D_1^\beta + \frac{D_2^\beta}{R} = \mu_R. \tag{54}$$

In particular, the value attained by chemical potential at the interface is:

$$\mu_\varrho := \mu(\rho) = D_1^\alpha. \tag{55}$$

On combining (53) with (54), we get $D_2^\beta \left(\frac{1}{\varrho} - \frac{1}{R}\right) - \mu_\rho = -\mu_R$, whence

$$D_2^\beta = (\mu_\varrho - \mu_R)\,\frac{\varrho R}{R-\varrho}, \tag{56}$$

and thence, again by using (54),

$$D_1^\beta = \mu_R - \frac{D_2^\beta}{R} = \left(1 - \frac{\varrho}{R-\varrho}\right)\mu_R - \frac{\varrho}{R-\varrho}\mu_\rho. \tag{57}$$

From (50) and (55)–(57) we can express the chemical-potential profile in terms of μ_ϱ:

$$\mu(r) = \begin{cases} \mu_\rho & \text{for } 0 < r \le \varrho, \\ \mu_R - \dfrac{\rho(\mu_R - \mu_\rho)}{R-\rho}\left(\dfrac{R}{r} - 1\right) & \text{for } \rho < r < R, \end{cases} \tag{58}$$

Our next step consists in computing the chemical potential at the interface by making use of the Maxwell condition (11). To this aim, we notice that, by (1), (3), (4), (25), and (26), the grand canonical potential may be written as:

$$\omega = -c(\mu - \mu_{\rm eq}) + \frac{1}{2}\mathbf{S}\cdot(\mathbf{E} - \mathbf{E}_\phi). \tag{59}$$

In view of $(31)_1$, (32), (33), (51), and (59), we can rewrite (11) as:

$$[\![c(\mu - \mu_{\rm eq})]\!] = [\![\frac{1}{2}(\sigma_r(u' - \epsilon_\phi) + 2\sigma_\theta(u/r - \epsilon_\phi)) - u'\sigma_r]\!], \tag{60}$$

that is,

$$[\![c(\mu - \mu_{\rm eq})]\!] = \frac{1}{2}[\![-\sigma_r u' + 2\sigma_\theta(u/r) - (\sigma_r + 2\sigma_\theta)\epsilon_\phi]\!]. \tag{61}$$

The right-hand side of (61) can be further manipulated by making use of the identity

$$[\![ab]\!] = [\![a]\!]\langle b\rangle + \langle a\rangle[\![b]\!], \tag{62}$$

where, given a smooth field a defined in the bulk, we denote by $\langle a\rangle$ the average of the limit values attained by a at either side of the interface.[7]

[7] Namely, $\langle a\rangle = \frac{a(\varrho+) - a(\varrho-)}{2}$.

Indeed, on recalling that μ, σ_r and u do not jump at the interface, and that $[\![\epsilon_\phi]\!] = \epsilon_0$ is the mismatch strain, we can rewrite (62) as:

$$[\![c]\!](\mu_\rho - \mu_{\rm eq}) = -\frac{1}{2}\sigma_r(\varrho)([\![u']\!] + \epsilon_0) + [\![\sigma_\theta]\!](u(\varrho)/\varrho - \langle\!\langle\epsilon_\theta\rangle\!\rangle) - \langle\!\langle\sigma_\theta\rangle\!\rangle\epsilon_0. \quad (63)$$

We now examine the individual *addenda* on the right-hand side of (63). On using (39), along with the continuity of σ_r, and on taking (48) into account, we immediately find that:

$$-\frac{1}{2}\sigma_r(\varrho) = -\frac{3}{2}K(C_1^\alpha - \epsilon_0) = -\Big(1 - \frac{\varrho^3}{R^3}\Big)\frac{2GK\epsilon_0}{2G+\lambda}. \quad (64)$$

Next, we note that, by (43) and (34), we have $0 = [\![\sigma_r]\!] = (2G+\lambda)[\![u']\!] - 3K\epsilon_0$, whence

$$[\![u']\!] + \epsilon_0 = \left(\frac{3K}{2G+\lambda} + 1\right)\epsilon_0 = 4\frac{G+\lambda}{2G+\lambda}\epsilon_0. \quad (65)$$

By the same token, thanks to (35), we have $[\![\sigma_\theta]\!] = \lambda[\![u']\!] - 3K\epsilon_0$, and therefore

$$[\![\sigma_\theta]\!] = -3\frac{2GK\epsilon_0}{2G+\lambda}. \quad (66)$$

Furthermore, on using (40), (46) and (47), a slightly involved calculation leads to:

$$\langle\!\langle\sigma_\theta\rangle\!\rangle = \frac{1}{2}\Big(1 - 4\frac{\varrho^3}{R^3}\Big)\frac{2GK\epsilon_0}{2G+\lambda}. \quad (67)$$

Eventually, from (38) and (48), we have

$$\begin{aligned} u(\varrho)/\varrho - \langle\!\langle\epsilon_\phi\rangle\!\rangle &= C_1^\alpha - \frac{\epsilon_\alpha + \epsilon_\beta}{2} \\ &= \frac{\epsilon_0}{2} - \frac{\epsilon_0}{(2G+\lambda)}\left(K + \frac{4G}{3}\frac{\varrho^3}{R^3}\right) \\ &= \frac{1}{6(2G+\lambda)}\left(2G - 3\lambda - 8G\frac{\varrho^3}{R^3}\right)\epsilon_0. \end{aligned} \quad (68)$$

By putting (63)–(68) together, we obtain:

$$[\![c]\!](\mu_\rho - \mu_{\rm eq}) = -\frac{1}{2}\sigma_r(\varrho)([\![u']\!] + \epsilon_0) + [\![\sigma_\theta]\!](u/r - \langle\!\langle\epsilon_\theta\rangle\!\rangle) - \langle\!\langle\sigma_\theta\rangle\!\rangle\epsilon_0 \quad (69)$$

$$= -4\frac{G+\lambda}{2G+\lambda}\Big(1 - \frac{\varrho^3}{R^3}\Big)\frac{2GK\epsilon_0^2}{2G+\lambda} \quad (70)$$

$$-\frac{1}{2(2G+\lambda)}\left(2G-3\lambda-8G\frac{\varrho^3}{R^3}\right)\frac{2GK\epsilon_0^2}{2G+\lambda} \tag{71}$$

$$-\frac{1}{2}\Big(1-2\frac{\varrho^3}{R^3}\Big)\frac{2GK\epsilon_0^2}{2G+\lambda}, \tag{72}$$

whence

$$[\![c]\!](\mu_\rho-\mu_{\rm eq})=-3\left(1-2\frac{\varrho^3}{R^3}\right)\frac{2GK\epsilon_0^2}{2G+\lambda}, \tag{73}$$

and thence, as announced, the value of chemical potential at the interface:

$$\mu_\rho=\mu_{\rm eq}+\widehat{\mu}_{\rm el}\left(\varrho/R\right), \tag{74}$$

where

$$\widehat{\mu}_{\rm el}(y)=\mu_{\rm el}(2y^3-1)\quad\text{with}\quad\mu_{\rm el}=\frac{2G}{2G+\lambda}\frac{3K\epsilon_0^2}{c_\beta-c_\alpha}. \tag{75}$$

This result is in accordance with the notion of $\mu_{\rm eq}$ as the equilibrium value of chemical potential at the interface in the absence of elastic misfit between the two phases.

4. The evolution equation of the interface

Having determined the instantaneous values of displacement and chemical potential that correspond to a prescribed distance ϱ of the interface from the center of the body, it remains for us to enforce the continuity equation that follows from (13), namely, the localization at the interface of the balance of diffusant. From (7) and $(31)_2$ we find

$$\mathbf{h}=h\mathbf{e}\quad\text{with}\quad h=-m_\phi\mu', \tag{76}$$

and hence, by taking the scalar product of both sides of (13) with $\mathbf{e}$, we obtain:

$$[\![c]\!]V=-[\![m_\phi\mu']\!]. \tag{77}$$

We now invoke the representation formula (58), which yields the chemical-potential profile. The formula in question entails:

$$\mu'(r)=\begin{cases}0 & \text{for } 0<r<\varrho,\\ \dfrac{\mu_R-\mu_\rho}{R-\rho}\dfrac{\rho R}{r^2} & \text{for } \rho<r<R.\end{cases} \tag{78}$$

As a consequence of (78), we have:

$$-[\![m_\phi \mu']\!] = -m_\beta(\mu_R - \mu_\rho)\frac{R}{R-\rho}\frac{1}{\varrho} = -\frac{m_\beta}{q\left(\frac{\varrho}{R}\right)}\frac{\mu_R - \mu_\rho}{R}, \tag{79a}$$

with

$$q(y) = (1-y)\,y, \tag{79b}$$

whence

$$q\left(\frac{\varrho}{R}\right)\frac{(c_\beta - c_\alpha)}{m_\beta}RV = \mu_\rho - \mu_R. \tag{80}$$

The combination of (80) with (74) restitutes the sought-for evolution equation (14) we anticipated in the Introduction, and that we are going to scritinize in the next section.

5. The transition time

As a first step, we shall provide (14) with a form that makes it more suitable for the ensuing calculations. To this aim, we define:

$$y = \varrho/R, \tag{81}$$

and we introduce the *characteristic time*:

$$\tau = \frac{c_\beta - c_\alpha}{m_\beta \mu_{\rm eq}}R^2, \tag{82}$$

along with the parameters:

$$a = \frac{\mu_R}{\mu_{\rm eq}}, \qquad b = \frac{\mu_{\rm el}}{\mu_{\rm eq}}, \tag{83}$$

where we recall that $\mu_{\rm el}$, the constant introduced in (75), takes into account the elastic misfit. With (81)–(83), we can write (14) as:

$$\tau y(1-y)\dot{y} = 1 - a + b(2y^3 - 1). \tag{84}$$

5.1. The $\beta \to \alpha$ transformation

We look for increasing solutions of (84) satisfying the *initial condition*:

$$y(0) = 0. \tag{85}$$

Any such solution describes the nucleation of the α phase at the center of a specimen initially in the β phase, and the propagation of the phase front towards the boundary. We refer to this process as the $\beta \to \alpha$ *transformation*.

We observe that no such solution exists if $1 - a \leq b$. Indeed, if $1 - a < b$ then the right-hand side of (84) is strictly negative in a neighborhood of $y = 0$, which forbids increasing solutions. If, instead $1 - a = b$, then (84) becomes:

$$\tau y(1 - y)\dot{y} = 2by^3. \tag{86}$$

The differential equation (86) with the initial condition (85) admits only the constant solution. On account of these facts, we see that a necessary condition for the $\beta \to \alpha$ transformation to take place is:

$$1 - a > b. \tag{87}$$

Condition (87) entails that the function

$$T_\alpha(y) = \tau \int_0^y \frac{z(1 - z)}{1 - a + b(z^3 - 1)} \mathrm{d}z \tag{88}$$

is well defined, strictly increasing with respect to y, and hence invertible. Thus, for each $t \in [0, T_\alpha(1)]$ the equation

$$T_\alpha(y) = t \tag{89}$$

has a unique solution $Y_\alpha(t)$. The function $Y_\alpha(t)$ obtained in this fashion is strictly increasing and, as can easily be checked, is a solution of the Cauchy problem (84)–(85).

The function $T_\alpha(y)$ can be computed in closed form. The resulting expression is however quite lengthy and in our opinion it does not provide special insight. This function represents the time needed for the phase-transition front to reach the position y starting from $y = 0$. Its value at $y = 1$ is of special interest, since it represents the time required for the entire transformation to take place — for short, the *transformation time*.

In order to better appreciate how elastic energy affects transformation time, it is useful to introduce the parameter

$$\kappa = \frac{b}{1-a}.$$

Then, (88) implies

$$T_\alpha(1) = \frac{\tau}{1-a} f(\kappa), \tag{90}$$

where

$$f(\kappa) = \int_0^1 \frac{z(1-z)}{1+\kappa(2z^3-1)} \mathrm{d}z.$$

Keeping in mind that $\kappa = 0$ describes the absence of elastic effects, we obtain from (88) the following result:

- the ratio between the total transition time with and without elastic effects is given by $f(\kappa)/f(0)$.

Since b is positive, we see from (87) that κ is in the interval $[0, 1)$ for the case we are considering. By looking at the plot of f for $\kappa \in [0, 1)$ drawn in Figure 2 we reckon that

- an increase of elastic misfit slows down the transition from the β to the α phase.

5.2. The $\alpha \to \beta$ transformation

In Fig. 5.1, the graph of $f(\kappa)$ for $\kappa < 0$ is relevant when studying the process in which the β phase nucleates at the boundary of a body initially in the α phase, and the phase front propagates towards the interior of the body. To this effect, we seek decreasing solutions of (84) such that

$$y(0) = 1. \tag{91}$$

Considerations analogous to those made before lead us to assume:

$$a - 1 \geq b. \tag{92}$$

Arguing as before, we define the strictly-decreasing function:

$$T_\beta(y) = \tau \int_y^1 \frac{y(1-y)}{a-1-b(2y^3-1)} \mathrm{d}y, \tag{93}$$

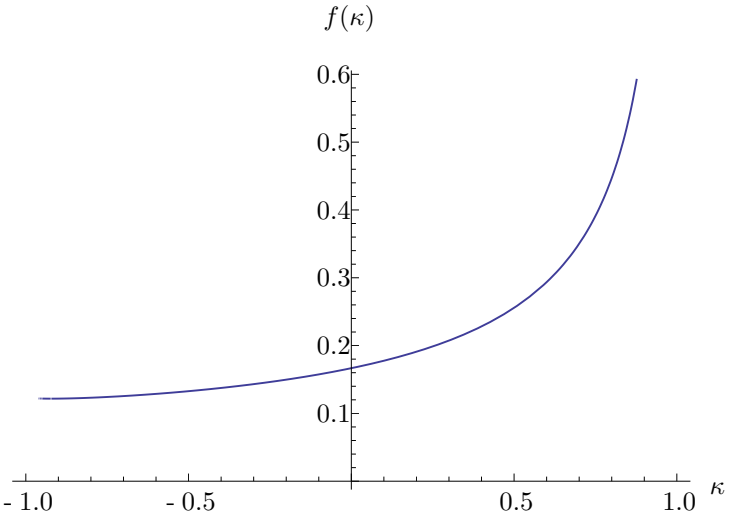

Figure 3: Plot of $f(\kappa)$. Positive values of κ yield the transition time for the $\beta \to \alpha$ transformation. Negative values of κ yield the transformation time for the $\alpha \to \beta$ transformation. Remarkably, elastic misfit slows down the $\beta \to \alpha$ transformation and speeds up the $\alpha \to \beta$ transformation.

whose inverse on $[0, T_\beta(1)]$ we denote by $Y_\beta(t)$. Again, it is immediate to check that $Y_\beta(t)$ is a solution of the Cauchy problem (84)–(91). The total transition time is:

$$T_\beta(1) = \frac{\tau}{a-1} f(\kappa), \tag{94}$$

where now $-1 \leq \kappa \leq 0$. In this case, and increase of the elastic misfit yields a decrease of κ and in turn, as is apparent from Figure 2, a reduction of the trasition time. Taking also the previous discussion into account, we can draw the following conclusion:

- lattice misfit accelerates the transformation from the α to the β phase.

5.3. Hysteresis

In order for (87) or (92) to hold, the chemical potential of the reservoir must satisfy, respectively, $\mu_R < \mu_{\rm eq}(1-b)$ or $\mu_R > \mu_{\rm eq}(1+b)$. We therefore interpret

$$\mu_R^{\beta\to\alpha} = \mu_{\rm eq}(1-b) = \mu_{\rm eq} - \mu_{\rm el}$$

and

$$\mu_R^{\alpha\to\beta} = \mu_{\text{eq}}(1+b) = \mu_{\text{eq}} + \mu_{\text{el}}$$

as the chemical potentials that must be imposed at the boundary to trigger, respectively, the $\beta \to \alpha$ or the $\alpha \to \beta$ transformation. Hysteretic behavior is the main consequence of this fact: suppose that the chemical potential imposed on the boundary is not constant, but (slowly) oscillates within a range containing $\mu_R^{\alpha\to\beta}$ and $\mu_R^{\beta\to\alpha}$. Then, the path of y versus μ_R would define the hysteresis loop shown in Figure 3. The width of this loop depends only on the elastic misfit and on the elastic moduli of the material. We therefore conclude that:

- the height of the hysteresis loop is $2\mu_{\text{el}}$

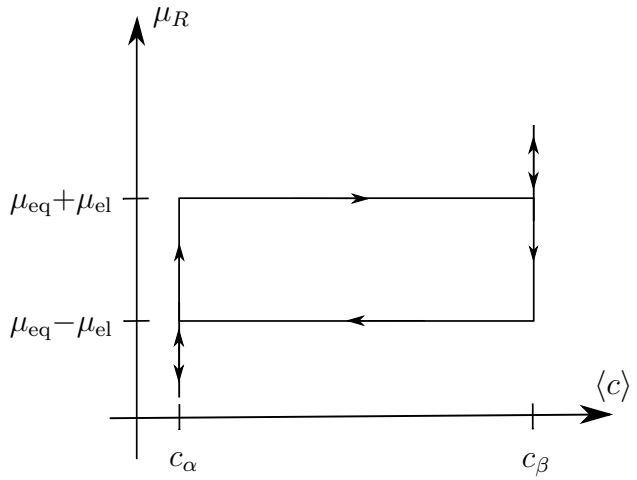

Figure 4: Plot of chemical potential of the reservoid μ_R vs. average concentration $\langle c\rangle = \frac{1}{|\mathscr{B}|}\int_{\mathscr{B}} c\mathrm{d}v$ during a loading-unloading stage. The amplitude of the hysteresis loop is $2\mu_{\text{el}}$.

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