PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1980 **295**, 151-163
doi: 10.1098/rsta.1980.0096

Phil. Trans. R. Soc. Lond. A **295**, 151–163 (1980) [151]
Printed in Great Britain

Adsorption-induced losses in interfacial cohesion

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A model for interfacial cohesion is developed which describes the loss in the strength of an interface owing to the segregation and adsorption of impurities on it. Distinctions are made between interface separations that occur too rapidly for any significant redistribution of adsorbing matter to take place, which are suggested conform to many actual fracture processes, and separations that are slow enough to allow full adsorption equilibrium. Expressions for the total work of complete decohesion are presented for both cases. The results are applied to well known model adsorption isotherms and some experimental data for grain boundary adsorption of phosphorus in iron are analysed with respect to the losses in intergranular cohesion.

1. INTRODUCTION

The recent and past literature has provided many examples of environmentally induced or assisted fractures in the form of 'hydrogen embrittlement', 'temper' or solute embrittlement, and a variety of forms of stress corrosion cracking. Although in some cases the environment serves mainly to accelerate the 'normal' process of fracture, it happens, and especially in higher strength materials, that a change in fracture mode from a ductile hole initiation, growth and coalescence sequence to more brittle-like processes such as transgranular or intergranular cleavage is induced. Since the beginning stages of most fracture processes in metals, whether they be ductile or brittle, involve separations (or decohesion) along interfaces of one sort or another, it is of immediate importance to understand to what extent an environment might facilitate such events. Indeed, once having begun a relatively sharp crack, for instance with a temper or hydrogen embrittled condition at an interface between a second phase and a ductile matrix or a grain boundary, there remains the important question of whether or not the crack stays sharp in growth along the interface or through the grain matrix leading to a brittle fracture, or blunts to a void. The parameters of importance in analysing the fracture initiation process and which also enter into the ductile–brittle decision for crack growth are the cohesive properties γ, the work to separate the interface, and σ_c, the maximum force required to fully separate a unit area of interface (Rice & Thomson 1974). This paper is concerned with an analysis of interfacial cohesion with specific attention paid to the effects of the environment in altering these cohesive properties. In what follows we shall examine cohesion losses caused by interfacial adsorption of the constituents of the environment.

The plan is to further develop a thermodynamic description for separating interfaces begun by Rice (1976). This approach is particularly attractive for applications in adsorption induced brittle fracture since it explicitly acknowledges the fact that interfacial cohesion is affected (usually lowered) by the segregation of solute impurities to interfaces and that the degree of segregation is determined in large part by the kinetics of transport. Explicitly, we may note that changes in interfacial chemistry may occur either before or during the fracture process.

If the segregant is hydrogen, for example, it may derive from an external environment such as a gas phase or from an aqueous corrosive medium. On the other hand, hydrogen may be already present in the lattice owing to pre-exposure to a gas or through cathodic charging; in solute or temper embrittlement, the segregating impurities are already dissolved in the matrix and adsorb (not necessarily in an equilibrium fashion) on the interfaces before fracture. In addition, since most interstitial impurities such as those involved in the temper embrittlement process and hydrogen embrittlement have positive partial volumes, there is the tendency for solute migration to regions of high triaxial tension, e.g. out ahead of notches or partly opened cracks. Thus, in describing environmental influences on cohesion through adsorption, there must be a way to distinguish between those cases with rapid kinetics where during the actual loading and separation process further adsorption (or desorption) takes place and the cases of the other extreme where slow kinetics preclude any significant redistribution of matter. Rice's model naturally accounts for these diverse possibilities and, as I shall demonstrate, it leads to rather different results for the work of separation in the extremes of slow (equilibrium) and rapid (limited mass redistribution) fractures.

In the next section I treat the thermodynamics of a separating interface including the effects of multicomponent adsorption. This leads (§2.5) to expressions for the work of separation under conditions that correspond to slow, i.e. equilibrium conditions (equations (25) and (30)), and to fast separation which corresponds to a fracture process that takes place at essentially fixed interfacial composition (equations (33) and (34)). The work for slow separation is shown to be naturally less than that for fast separation and in §3 the results are given explicit form for some common and useful model adsorption isotherms. Finally, some experimental data for polycrystalline iron with dilute concentrations of phosphorus are analysed in §3.2 with respect to the adsorption induced loss in intergranular cohesion. The next several subsections outline the approach and provide preliminary derivations and definitions.

2. THERMODYNAMICS OF THE SEPARATING INTERFACE

2.1. *Cohesion and interfacial strength*

We begin with a general interface, which is undergoing a process of decohesion caused by the applied stress, σ, as shown in figure 1. The interface is taken to be planar, to ignore the effects of its curvature, and infinitely extended, but is otherwise quite arbitrary in that it may separate two identical grains as a grain or subgrain boundary, or a second phase and a grain matrix. These boundaries are, of course, very complex in structure; they may be heavily dislocated and are quite inhomogeneous in composition because of adsorption. Now presumably for such a general interface there exists a force–displacement relation, dependent on its composition and structure, that describes its strength during separation, such as that shown in figure 2. This relation, however, is uniquely determined only when a definite prescription is given for allowing the progress of the various relaxation processes that will occur during separation. For example, it is necessary to determine the degree to which mass, of all species present in the interface and its immediate surroundings, can redistribute within the interfacial region or between this region and outlying sites in the bulk matrix or external phases. In addition, it is necessary to keep track of any phase transitions that may occur with adsorption since the interface properties depend on structure as well as on the amount of impurity present. Alternatively speaking, it is necessary to determine first what variables the σ versus δ relation

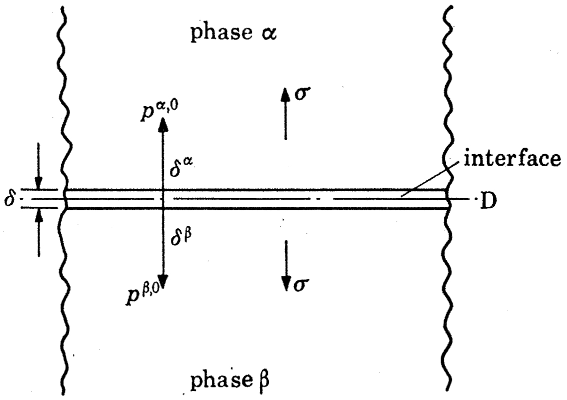

FIGURE 1. A planar interface, located along the dividing surface D, which separates two homogeneous bulk phases α and β. δ is the displacement across the interface caused by the uniform normal stress, σ.

depends on. For the present purposes we will develop the simplifying model for which σ *depends only upon the composition of the interface and the interface displacement*, δ. Then if Γ_i is the composition of the ith species in the interface and δ is the interface displacement, where both quantities are to be described more precisely in the following subsections, then

$$\sigma = \sigma(\delta, \Gamma). \tag{1}$$

A constitutive law of the above type implies at the very least local relaxations of the atoms in the interface such that the amount of each component fully determines the interface properties. This is an important constraint which will be re-emphasized in § 2.5. However, it is certain that (1) will not be completely representative of a large number of actual fracture situations since when an internal interface separates, even with no substantial change in its composition, the impurities require time to relax locally from their initial positions within the interface to their new equilibrium configuration in the free surfaces. As will be made clear in § 2.5, (1) also implies that the interface is in internal equilibrium even when equilibrium with the outlying bulk phases is not established. Thus we shall require that the chemical potential of an adsorbed species on each of two newly formed free surfaces formed upon interface separation be equal.

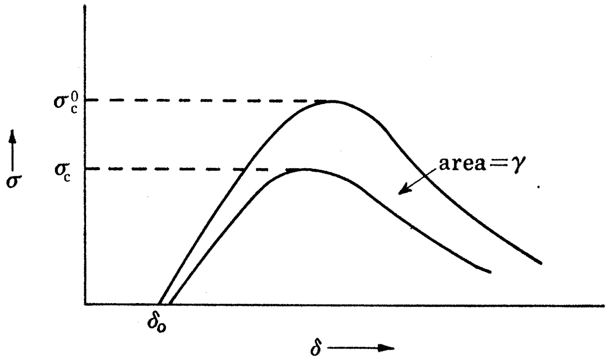

FIGURE 2. Stress–displacement relation for a separating interface. The upper curve is for a 'pure' or 'clean' surface and the lower for a segregated one. σ_c is the cohesive stress and γ, the work of separation, is equal to the area beneath the σ–δ curve. δ_0 is the normal displacement corresponding to $\sigma = 0$.

Finally, we note from the figure that σ_c is the theoretical cohesive stress of the interface, or the maximum force per unit area required to pull the two homogeneous phases apart. σ_c^0 belongs to the 'clean' interface and σ_c to the segregated. Evidently the area beneath the curves is γ, the total isothermal work to form the *two* free surfaces from the initial interface, and that this work is less for the segregated interface than for the clean. Our primary goal now is to calculate γ and relate its value to the degree of interface and surface adsorption.

2.2. *Gibbs relations for the interface and bulk phases*

For the interface we write in accordance with Gibbs's (1961) approach to capillary for the change in surface internal energy

$$\mathrm{d}u = T\mathrm{d}s + \sigma\mathrm{d}\delta + \sum_{i=1}^{n} \mu_i \mathrm{d}\Gamma_i. \tag{2}$$

In (2) we have specialized to a unit area of planar interface so that the 'superficial' quantities of entropy s, of compositions Γ_i of the n constituents composing the interface, and of internal energy u are defined by a choice of a dividing surface called D. The surface tension γ, that is the reversible work required to separate such an interface isothermally, is given by the net work done by σ, or in differential form by

$$\mathrm{d}\gamma = \sigma\mathrm{d}\delta = \mathrm{d}(u - Ts) - \sum_{i=1}^{n} \mu_i \mathrm{d}\Gamma_i. \tag{3}$$

The Gibbs procedure has well known limitations, some of which will become evident in the next subsections. In particular, it is clear that all the excess quantities depend upon the arbitrary choice for D, yet as I shall show, the final expression for γ, at least under equilibrium conditions, does not have any such arbitrary dependence.

For the bulk phases consider next a channel of homogeneous phase α (or β) located on one side of the interface (i.e. D) as shown in figure 1. Let its cross sectional area be unity and call its entropy $S^{\alpha(\beta)}$, its energy $U^{\alpha(\beta)}$, and the number of atoms (or molecules or moles) of the ith constituent within it, $N^{\alpha(\beta)}$. Then if $\delta^{\alpha(\beta)}$ marks out the displacement of an arbitrary point out in the homogeneous phase, then for the change in U^α up to δ^α we have

$$\mathrm{d}U^\alpha = T\mathrm{d}S^\alpha + \sigma^\alpha \mathrm{d}\delta^\alpha + \sum_{i=1}^{n} \mu_i^\alpha \mathrm{d}N_i^\alpha, \tag{4a}$$

and in U^β

$$\mathrm{d}U^\beta = T\mathrm{d}S^\beta + \sigma^\beta \mathrm{d}\delta^\beta + \sum_{i=1}^{n} \mu_i^\beta \mathrm{d}N^\beta. \tag{4b}$$

If we now integrate these equations and divide through by $\delta^{\alpha(\beta)}$ we find that

$$\sigma^\alpha = u^\alpha - Ts^\alpha - \sum_{i=1}^{n} \mu_i^\alpha c_i^\alpha \tag{5a}$$

and

$$\sigma^\beta = u^\beta - Ts^\beta - \sum_{i=1}^{n} \mu_i^\beta c_i^\beta. \tag{5b}$$

The relations (4) and (5) are a set of Gibbs relations for the bulk phases which will be used shortly.

2.3. *Excess thermodynamic quantities*

As is known from the original formulation of the model by Gibbs, the excess thermodynamic quantities depend upon the particular choice of the dividing surface, D. On the other hand,

γ, at least for surfaces at equilibrium, does not have such a dependence. In this section the excess quantities are defined more precisely and the lack of a dependence of γ on D is explored.

2.3.1. *Excess entropy, energy and free energy*

If we define $s^{\alpha}(s^{\beta})$ and $u^{\alpha}(u^{\beta})$ as the specific entropies and energies of the bulk phases on either side of the interface and S and U as the actual entropy and energy of a channel of unit cross section cutting through the interface, extending into each bulk phase a distance δ^{α} (and δ^{β}), then the excess quantities are defined by the equations

$$s = S - \delta^{\alpha}s^{\alpha} - \delta^{\beta}s^{\beta} \tag{6a}$$

and

$$u = U - \delta^{\alpha}u^{\alpha} - \delta^{\beta}u^{\beta}. \tag{6b}$$

Once D is chosen, the two homogeneous phases are presumed to be uniformly extended up to the dividing surface with the excess in each quantity ascribed wholly to the interface. The surface free energy is then defined in terms of these excesses as

$$f = u - Ts. \tag{7}$$

2.3.2. *Excess surface compositions*

Again we assume that the two bulk phases are uniformly extended up to the dividing plane D. Their compositions are respectively c_i^{α} and c_i^{β}. If the actual quantity of component i in the channel is N_i, then the excess in i is

$$\Gamma_i = N_i - \delta^{\alpha}c_i^{\alpha} - \delta^{\beta}c_i^{\beta}. \tag{8}$$

2.3.3. *Excess surface displacement*

The excess displacement, δ, also depends upon the choice of D. Consider the displacement of two points P^{α} and P^{β}, each located far enough from the interface as measured from D to be considered in a region of homogeneous phase. When the stress σ is applied, the relative change in their separation is δ_{a} where

$$\delta_{\mathrm{a}} = [P^{\alpha} - P^{\beta}] - [P^{\alpha} - P^{\beta}]_{\sigma=0}. \tag{9}$$

The surface excess δ is now defined by the difference between δ_{a} and the displacement, δ_{h}, that would result if the two homogeneous phases were uniform up to D and were acted on by σ, i.e.

$$\delta = \delta_{\mathrm{a}} - \delta_{\mathrm{h}}. \tag{10}$$

It is also possible to prescribe other choices for δ by redefining δ_{h} as the net displacement from P^{α} and P^{β} to arbitrary points located on either side of the interface. For example, it is possible to describe the separation of two adjacent *atomic* planes by locating these arbitrary points one on each of the planes. This latter scheme would be useful in carrying out a process of separation of a perfect lattice to form two free surfaces; in this case δ, if defined as an excess, would identically vanish.

In terms of the homogeneous strains in the two bulk phases, δ_{h} is given by

$$\delta_{\mathrm{h}} = P^{\alpha}\epsilon^{\alpha} + P^{\beta}\epsilon^{\beta}, \tag{11}$$

and since

$$\delta = \delta_{\mathrm{a}} - \delta_{\mathrm{h}},$$

δ also clearly depends on the choice for D.

2.3.4. *Dependence of γ on* D

The surface tension, γ, is defined for a particular choice for D as

$$\gamma = f - \sum_{i=1}^{n} \Gamma_i \mu_i, \tag{12}$$

as can be seen by an integration of (3). For a dividing plane located a distance λ toward the α phase, u, s, f and Γ_i receive the respective increments

$$\lambda(u^\alpha - u^\beta), \quad \lambda(s^\alpha - s^\beta), \quad \lambda[u^\alpha - u^\beta - T(s^\alpha - s^\beta)] \quad \text{and} \quad \lambda(c_i^\alpha - c_i^\beta).$$

Thus, by this relocation of D, γ in (12) receives the increment

$$\lambda(u^\alpha - u^\beta) - T\lambda(s^\alpha - s^\beta) - \lambda \sum_{i=1}^{n} \mu_i (c_i^\alpha - c_i^\beta). \tag{13}$$

Now, if we express μ_i as $\mu_i^{\alpha(\beta)} + [\mu_i - \mu^{\alpha(\beta)}]$, the change in γ becomes, by using (5),

$$\lambda\left\{(\sigma^\alpha - \alpha^\beta) + \sum_{i=1}^{n} (A_i^\alpha c_i^\alpha - A_i^\beta c_i^\beta)\right\}, \tag{14}$$

where

$$A_i^{\alpha(\beta)} = -(\mu_i - \mu_i^{\alpha(\beta)}). \tag{15}$$

Mechanical equilibrium requires that $\sigma^\alpha = \sigma^\beta$ and so (14) becomes

$$\lambda \sum_{i=1}^{n} (A_i^\alpha c_i^\alpha - A_i^\beta c_i^\beta). \tag{16}$$

If full equilibrium between the bulk phases and the interface is established, $\mu_i^\alpha = \mu_i = \mu_i^\beta$, $A_i^\alpha = A_i^\beta = 0$ and γ is *independent* of D. According to our model, though, if α and β are *identical* phases, $c_i^\alpha = c_i^\beta$ and if α and β were initially in equilibrium, $A_i^\alpha = A_i^\beta$: once again, γ is independent of D. Of course in this latter case, all the excess quantities are themselves also independent of the choice for dividing surface. For other situations we must conclude that γ cannot be made independent of D and so it is prudent to rephrase the expression for it as follows in §2.5.

2.4. *Some useful thermodynamic relations*

The Helmholtz free energy, f, and the surface tension, γ, have already been defined as

$$f = u - Ts \tag{17}$$

and

$$\gamma = f - \sum_{i=1}^{n} \mu_i \Gamma_i. \tag{18}$$

To complete our derivations it is now useful to introduce the Legendre transform on the conjugate variables σ, δ as

$$g = f - \sigma\delta = u - Ts - \sigma\delta. \tag{19}$$

Differential forms of these quantities follow as

$$\mathrm{d}f = -s\,\mathrm{d}T + \sigma\,\mathrm{d}\delta + \sum_{i=1}^{n} \mu_i\,\mathrm{d}\Gamma_i, \tag{20}$$

$$\mathrm{d}\gamma = -s\,\mathrm{d}T + \sigma\,\mathrm{d}\delta - \sum_{i=1}^{n} \Gamma_i\,\mathrm{d}\mu_i \tag{21}$$

and

$$\mathrm{d}g = -s\,\mathrm{d}T - \delta\,\mathrm{d}\sigma - \sum_{i=1}^{n} \mu_i\,\mathrm{d}\Gamma_i. \tag{22}$$

From (20)–(22) we obtain the useful reciprocal relations

$$(\partial\sigma/\partial\Gamma_i)_\delta = (\partial\mu_i/\partial\delta)_{\Gamma_i}, \tag{23a}$$

$$-(\partial\delta/\partial\Gamma_i)_\sigma = (\partial\mu_i/\partial\sigma)_{\Gamma_i} \tag{23b}$$

and

$$(\partial\sigma/\partial\mu_i)_\delta = -(\partial\Gamma_i/\partial\delta)_{\mu_i}. \tag{23c}$$

2.5. *Interfacial cohesion*

2.5.1. ‘*Slow*’ *or equilibrium separation*

The interfacial cohesion can be computed from (3). We shall consider first the process whereby the interface is separated slowly enough for equilibrium to be established at each stage of the process between the interfacial region and the bulk phases. Since equilibrium demands equality of the chemical potentials of each component in the bulk phases and the interface, we may designate this process, as did Rice, ‘separation at constant μ’. The equation of state for the interface can now be expressed in the form

$$\sigma = \bar{\sigma}(\delta, \mu),$$

where $\bar{\sigma}(\delta_0(\mu), \mu) = 0$ defines the unstressed displacement of the interface, $\delta_0(\mu)$. From (3), the total work of separation is given as

$$\bar{\gamma}(\mu) = \int_{\delta_0(\mu)}^{\infty} \bar{\sigma}(\delta, \mu)\, \mathrm{d}\delta, \tag{24}$$

which when integrated yields

$$\bar{\gamma}(\mu) = \bar{f}_\infty(\mu) - \bar{f}_0(\mu) - \sum_{i=1}^{n} \mu_i[\Gamma_{i,\infty}(\mu) - \Gamma_{i,0}(\mu)]. \tag{25}$$

In (25) it must be remembered that f_∞ is the Helmholtz free energy of the *two* newly formed surfaces and similarly $\Gamma_{i,\infty}$ are the adsorption excesses for these two free surfaces. $\bar{\gamma}$ can be re-written in the form

$$\bar{\gamma} = \{f_\infty^{(1)} + f_\infty^{(2)}\} - \sum_{i=1}^{n} \mu_i[\Gamma_{i,\infty}^{(1)} + \Gamma_{i,\infty}^{(2)}] - \left\{\bar{f}_0(\mu) - \sum_{i=1}^{n} \mu_i \Gamma_{i,0}\right\}, \tag{26}$$

or

$$\bar{\gamma} = \gamma_\infty^{(1)} + \gamma_\infty^{(2)} - \gamma_0, \tag{27}$$

where the superscripts 1 and 2 denote each of the two new surfaces. When the two bulk phases are identical, (27) may be written as

$$\bar{\gamma} = 2\gamma_\infty - \gamma_0. \tag{28}$$

Equation (28) is the usually employed definition of cohesion which the foregoing derivation has shown represents the work of separation *only* under these equilibrium conditions. The adsorption isotherm can be formed by differentiating (24) as follows:

$$\frac{\partial\bar{\gamma}}{\partial\mu_i} = \int_{\bar{\delta}_0(\mu)}^{\infty} \left(\frac{\partial\bar{\sigma}}{\partial\mu_i}\right)_\delta \mathrm{d}\delta. \tag{29}$$

Equation (29) can be integrated by substituting (23c) for the integrand to yield

$$\partial\bar{\gamma}/\partial\mu_i = -[\Gamma_{i,\infty} - \Gamma_{i,0}]. \tag{30}$$

As is typically done, (30) may be used to estimate the changes in $\bar{\gamma}$ with varying μ under equilibrium conditions. For this purpose, we note that there are two Gibbs–Duhem type relations that hold in the bulk phases, namely

$$\mathrm{d}\sigma^a + s^a\,\mathrm{d}T + \sum_{i=1}^{n} c_i^a\,\mathrm{d}\mu_i = 0 \tag{31a}$$

and
$$d\sigma^{\beta}+s^{\beta}dT+\sum_{i=1}^{n}c_{i}^{\beta}d\mu_{i} = 0, \tag{31b}$$

and that these may be used to eliminate one of the $d\mu_i$ so that those remaining are truly independent. This procedure is standard (Defay *et al.* 1966) and for brevity is not carried through here.

2.5.2. '*Fast*' *or non-equilibrium separations*

Now although (28) has often been used to estimate cohesion for actual fracture processes, it must be realized that the implied conditions of equilibrium are rarely met in practice. For example, the kinetics of adsorption may be diffusion limited and since solid state diffusivities are, at temperatures near to 25 °C, in the range 10^{-9} to 10^{-14} cm^2/s, which is very limited if any matter redistribution will occur except perhaps in the *immediate* vicinity of the fracture site. In terms of an actual size scale, if we take quasi-static separation times as being on the order of 10^{-3} s, then the word 'immediate' can be interpreted as several atomic spacings. Thus during a typically rapid fracture process we expect only local relaxation involving atomic movements so that the interfacial region has the same concentrations before and after separation. This is analogous to what Rice had called 'separation at constant composition'. Here we recall, however, our constitutive assumption that although the interface separates at fixed composition, the atoms within it relax to their equilibrium states.

To calculate the work of separation at constant composition, we must first identify the dividing plane such as that shown in figure 1. Having chosen D, all the excess quantities are defined. We may now write

$$\sigma d\delta = d(u-Ts)-\sum_{i=1}^{n}\mu_{i}d\Gamma_{i}, \tag{32}$$

where μ_i are the chemical potentials for the interface. In writing (32), we have assumed that the interface is always self equilibrating so that the potentials are constant within it although they are not generally equal to those of bulk phases. Then since $d\Gamma_i = 0$, the separation work is

$$\hat{\gamma} = f_{\infty}(\Gamma)-f_{0}(\Gamma). \tag{33}$$

The quantities f_∞ and f_0 $(\Gamma)$are the Helmholtz free energies of the *two* newly formed surfaces and the initial interface respectively; both quantities depend upon the choice of dividing surface. After separation, it seems only reasonable to define the dividing surface for each free surface as the original plane of separation.

An adsorption isotherm follows by differentiating (3) with respect to Γ_i to yield

$$\frac{d\hat{\gamma}}{d\Gamma_i} = \int_{\delta_0(\Gamma_i)}^{\infty}\left(\frac{d\sigma}{\partial\Gamma_i}\right)d\delta = \mu_{i\infty}(\Gamma)-\mu_{i,0}(\Gamma). \tag{34}$$

Here $\mu_{i,\infty}(\Gamma)$ is the chemical potential of *each* newly formed free surface and $\mu_{i,0}(\Gamma)$ is the chemical potential of the initial interface. We note again that a *single* $\mu_{i,\infty}(\Gamma)$ is sufficient to describe the free surfaces, implying that these two surfaces equilibrate each other.

2.5.3. *Difference between 'slow' and 'fast' separation*

I shall follow for the moment the procedure used by Rice to determine the difference between $\hat{\gamma}(\Gamma)$ and $\bar{\gamma}(\mu)$. Consider an initially unstressed interface which has come to equilibrium with the bulk phases. In this case we can equate the interfacial Helmholtz free energy, $f_0(\mu)$ with the quantity $f_0(\Gamma)$; the isotherm $\Gamma_{i,0} = \Gamma_{i,0}(\mu)$ also applies. Then

$$\hat{\gamma}(\Gamma)-\overline{\gamma}(\mu) = f_\infty(\Gamma)-f_\infty(\mu)+\sum_{i=1}^{n}\mu_i[\Gamma_{i,\infty}(\mu)-\Gamma_{i,0}], \tag{35}$$

and since $f_\infty(\mu) = f_\infty[\Gamma_\infty(\mu_i)]$, we may write that

$$\hat{\gamma}-\overline{\gamma} = -\sum_{i=1}^{n}\int_{\Gamma_{i,0}}^{\Gamma_{i,\infty}(\mu)}\frac{\mathrm{d}f_\infty(\Gamma)}{\mathrm{d}\Gamma_i}\,\mathrm{d}\Gamma_i+\sum_{i=1}^{n}[\Gamma_{i,\infty}(\mu)-\Gamma_{i,0}]. \tag{36}$$

But $\mu_{i\infty}(\Gamma) = \partial f_\infty(\Gamma)/\partial\Gamma_i$, and so

$$\begin{aligned}\hat{\gamma}(\Gamma)-\overline{\gamma}(\mu) &= -\sum_{i=1}^{n}\int_{\Gamma_{i,0}}^{\Gamma_{i,\infty(\mu)}}\mu_{i,\infty}(\Gamma)\,\mathrm{d}\Gamma_i+\sum_{i=1}^{n}\mu_i[\Gamma_{i,\infty}+\Gamma_{i,0}]\\ &= \sum_{i=1}^{n}\int_{\Gamma_{i,0}}^{\Gamma_{i,\infty(\mu)}}(\mu_i-\mu_{i,\infty})\,\mathrm{d}\Gamma_i. \end{aligned}\tag{37}$$

A somewhat heuristic procedure can be used to arrive at essentially the same result. We define cohesion by the quantity γ, where γ is given by

$$\gamma = \gamma_\infty-\gamma_0. \tag{38}$$

The quantity γ_∞ is the work required to create a unit area of *two* free surfaces, whereas γ_0 is similarly defined for the initial internal interface. Now γ_∞ differs from $\overline{\gamma}_\infty$ because of the non-equilibrium state of adsorption and we can determine the difference in $\gamma_\infty-\overline{\gamma}_\infty$ by computing the work required to alter reversibly the adsorption excess from its equilibrium extent to the actual level. If we envision that this hypothetical desorption takes place from the surfaces to the bulk phases (which are at the potentials μ_i) then this work is given as

$$\delta W_\infty = -\sum_{i=1}^{n}\int_{\Gamma_{i,\infty(\mu)}}^{\Gamma_{i,\infty}}[\mu_i-\mu_{i,\infty}(\Gamma_\infty)]\,\mathrm{d}\Gamma_{i,\infty}; \tag{39}$$

this being so since the amount of mass transported, N_i, is given by

$$N_i = \Gamma_{i,\infty}(\mu)-\Gamma_{i,\infty}, \tag{40}$$

and hence

$$\mathrm{d}(\delta W_\infty) = -\sum_{i=1}^{n}[\mu_i-\mu_{i,\infty}(\Gamma_\infty)]\,\mathrm{d}\Gamma_{i,\infty}. \tag{41}$$

For the initial interface we may calculate the difference between γ_0 and $\overline{\gamma}_0$ similarly and obtain

$$\delta W_0 = -\sum_{i=1}^{n}\int_{\Gamma_{i,0(\mu)}}^{\Gamma_{i,0}}[\mu_i-\mu_{i,0}(\Gamma_0)]\,\mathrm{d}\Gamma_{i,0}. \tag{42}$$

Then, according to our definition (37),

$$\hat{\gamma}-\overline{\gamma} = \delta W_\infty-\delta W_0. \tag{43}$$

When the initial interface is at equilibrium, i.e. $\mu_i = \mu_{i,0}$ and $\delta W_0 \equiv 0$, (43) and (37) are identical.

The main results of our derivations are embodied in the relations (25) and (30) for the work of slow or equilibrium separation and in (33) and (34) for fast separation. In the next section I apply these formulae to some specific model cases.

3. Some specific applications

Considerable progress can be made in applying the results of § 2.5 by assuming that adsorption is adequately described by simple and well known isotherms. We treat in detail one of these below where for simplicity only a single adsorbing species is considered.

3.1. *Ideal localized Langmuir adsorption*

The chemical potential for a locally adsorbing species has the general form

$$\mu_s(\Gamma) = kT \ln\{\Gamma/(\beta-\Gamma)\,q\}. \tag{44}$$

Here the excess Γ is simply defined as the amount of material adsorbed per unit area of surface into sites whose areal density is β; q is the single site partition function and k is the Boltzmann constant. With $\Gamma(\mu)$ again referring to an equilibrium coverage, (44) can be rewritten as

$$\mu_s(\Gamma) = \mu + kT \ln\left\{\left(\frac{\Gamma}{\beta-\Gamma}\right)\left(\frac{\Gamma(\mu)}{\beta-\Gamma(\mu)}\right)^{-1}\right\}, \tag{45}$$

with the one proviso that if applied to the *two* free surfaces, Γ and $\Gamma(\mu)$ must be replaced by $\frac{1}{2}\Gamma_\infty$ and $\frac{1}{2}\Gamma_\infty(\mu)$. Hence, we find that

$$\Gamma_\infty(\mu) - \Gamma_0(\mu) = \left(\frac{2q_\infty\beta_\infty}{1+q_\infty\,\mathrm{e}^{\mu/kT}} - \frac{q_0\beta_0}{1+q_0\,\mathrm{e}^{\mu/kT}}\right)\mathrm{e}^{\mu/kT}, \tag{46}$$

and if the initial interface is at equilibrium,

$$\mu_\infty(\Gamma_\infty) - \mu_0(\Gamma) = kT \ln\left\{\left(\frac{\Gamma_\infty}{\beta_\infty-\frac{1}{2}\Gamma_\infty}\right)\left(\frac{\Gamma_\infty(\mu)}{\beta_\infty-\frac{1}{2}\Gamma_\infty(\mu)}\right)^{-1}\right\}. \tag{47}$$

Then, δW_∞ is found to be

$$\delta W_\infty = -kT\left[\ln\left(\frac{\Gamma_\infty(\mu)}{\beta_\infty-\frac{1}{2}\Gamma_\infty(\mu)}\right)^{-1} + \int_{\Gamma_0(\mu)}^{\Gamma_\infty(\mu)} \ln\left(\frac{\Gamma_\infty}{\beta_\infty-\frac{1}{2}\Gamma_\infty}\right)\mathrm{d}\Gamma_\infty\right], \tag{48}$$

or after integration,

$$\begin{aligned}\delta W_\infty = {} & -kT[2\beta_\infty \ln(\beta_\infty-\tfrac{1}{2}\Gamma_\infty(\mu)) - 2(\beta_\infty-\tfrac{1}{2}\Gamma_0(\mu))\ln(\beta_\infty-\tfrac{1}{2}\Gamma_0(\mu)) \\ & +\Gamma_0(\mu)\ln(\Gamma_\infty(\mu)/\Gamma_0(\mu)) - \Gamma_0(\mu)\ln(\beta_\infty-\tfrac{1}{2}\Gamma_\infty(\mu))].\end{aligned} \tag{49}$$

An interesting limit of (49) is the case where $\Gamma_0(\mu) = 0$. Then if θ_∞ ($\equiv \frac{1}{2}\Gamma_\infty/\beta_\infty$) is the fractional coverage on a free surface, we find that δW_∞ is given by

$$\begin{aligned}\delta W_\infty(\Gamma_0(\mu)=0) &= 2kT\beta_\infty \ln(\beta_\infty-\tfrac{1}{2}\Gamma_\infty(\mu)) - 2\beta_\infty \ln\beta_\infty \\ &= -2kT\beta_\infty \ln(1-\theta_\infty).\end{aligned} \tag{50}$$

The right hand side of (50) is exactly twice the negative of the reduction in free energy for Langmuir adsorption onto a unit area substrate as should be expected from the definition of δW_∞. That is, δW_∞ is in this case just the work required to desorb reversibly an equilibrium amount of adsorption.

The adsorption isotherm, (44), can be rewritten as

$$\Gamma = q\beta\,\mathrm{e}^{\mu/kT}/(1+q\,\mathrm{e}^{\mu/kT}), \tag{51}$$

and upon integrating (30) we find that

$$\bar{\gamma} - \gamma_0 = -2kT\beta_\infty \ln(1+q_\infty\,\mathrm{e}^{\mu/kT}) + kT\beta_0 \ln(1+q_0\,\mathrm{e}^{\mu/kT}). \tag{52}$$

If adsorption is from a relatively dilute solid solution where the bulk chemical potentials have the form $\mu = \mu^0 + kT\ln x$, then (52) becomes

$$\bar{\gamma} - \gamma_0 = -2kT\beta_\infty \ln\{1+q_\infty\,\mathrm{e}^{\mu^0/kT}x\} + kT\beta_0 \ln\{1+q_0\,\mathrm{e}^{\mu^0/kT}x\}. \tag{53}$$

Furthermore, upon integrating (34) we obtain, for the reduction in the work of 'fast' fracture,

$$\hat{\gamma}-\gamma_0 = kT\left\{\Gamma_0 \ln\,(q_0/q_\infty)+\beta_0 \ln\left(\frac{\beta_0}{\beta_0-\Gamma_0}\right)-2\beta_\infty \ln\left(\frac{2\beta_\infty}{2\beta_\infty-\Gamma_0}\right)+\Gamma_0 \ln\left(\frac{\beta_0-\Gamma_0}{2\beta_\infty-\Gamma_0}\right)\right\}, \qquad (54)$$

with Γ_0 being given by

$$\Gamma_0 = q_0\beta_0 \mathrm{e}^{\mu^0/kT}x/(1+q_0\,\mathrm{e}^{\mu^0/kT}x). \qquad (55)$$

3.2. *The system* Fe (δ)–P

The data collected by Hondros (1965) and summarized by Hondros & McLean (1968) and by Hondros & Seah (1977) for the adsorption of P, from a dilute solid solution, onto the free surfaces and grain boundaries of iron suggest that the Langmuir model may be applicable. Actually, the data have been previously analysed with the use of the McLean isotherm (McLean 1957), which has the same form as (44) or (51), i.e. the McLean isotherm has the form

$$\theta = x\,\mathrm{e}^{Q/RT}/(1+x\,\mathrm{e}^{Q/RT}), \qquad (56)$$

where θ is the fractional coverage (the surface concentration) and Q is the heat of adsorption. What is then required are values for the quantities $q_\infty \mathrm{e}^{\mu^0/kT}$, $q_0 \mathrm{e}^{\mu^0/kT}$, β_∞, β_0, and the ratio q_0/q_∞ that appear in (53) and (54).

From Hondros's data for free surfaces, $Q \approx 101$ kJ/mol for the average surface at a temperature of 1450 °C; $q_\infty \mathrm{e}^{\mu^0/kT}$ is then found to be approximately 1204. From the suggestion of Hondros & Seah, $q_0 \mathrm{e}^{\mu^0/kT}$ is found to be 750, although we must note that a lower value is deduced from Hondros's estimate of $Q \approx 67$ kJ/mol for average grain boundaries; q_0/q_∞ is then 0.625. Finally, β_∞ and β_0 are estimated from Hondros's reported saturation coverages as 1.4×10^{15} sites/cm^2 and 6.5×10^{14} sites/cm^2 respectively. If γ is expressed in units of ergs per square centimetre (1 erg $= 10^{-7}$ J), $\bar{\gamma}$ is given by

$$\tfrac{1}{240}(\bar{\gamma}-\gamma_0) = -2.8 \ln\{1+1204x\}+0.65 \ln\{1+750x\}, \qquad (57)$$

with a similarly following set of equations for $\hat{\gamma}$. In (57), x, the lattice atom fraction of P, is taken as a variable instead of μ. The reductions in γ are shown in figure 3 along with a curve constructed directly from Hondros's (1965) experimentally measured surface tensions. The approximate agreement between the computed curve for $\bar{\gamma}$ (equation (57)) and the experimental curve provides some confidence for using these model isotherms. In fact, we may note that if we had accepted the value of $Q \approx 67$ kJ/mol for grain boundary adsorption, we would find that $q_0 \mathrm{e}^{\mu^0/kT} = 109$ and that the computed curve for $\bar{\gamma}$ is essentially coincident with Hondros's (1965) experimental data. However, for now we shall take the more recent suggestion of Hondros & Seah (1977) mentioned above. The relation between $\hat{\gamma}$ and x is also shown in figure 3 and it is seen that the reduction in cohesion is much less than when equilibrium conditions prevail. Nevertheless, the reduction is significant and when we realize that the concentrations shown in the figure are representative of those involved in phosphorus temper embrittlement of steels (McMahon 1968), we are led to suspect that the loss in cohesion of the grain boundaries in iron need not be very large to cause brittle behaviour – at least if simple adsorption induced cohesion losses are responsible for the boundary's brittle response. Of course, if we were to except the value of 109 for $q_0 \mathrm{e}^{\mu^0/kT}$, the reduction in $\hat{\gamma}$ would be slightly greater than is shown in figure 3. Evidently, the experimental data require a more careful scrutiny.

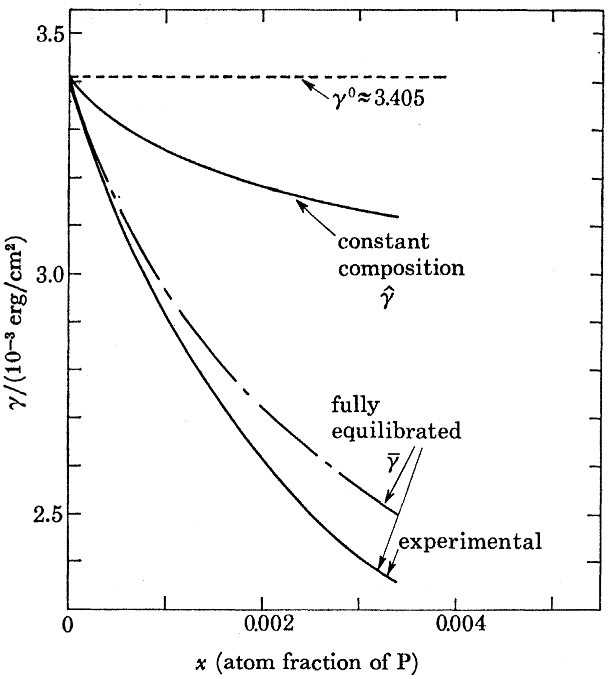

FIGURE 3. Adsorption induced loss in intergranular cohesion in iron with dilute concentrations of phorphorus at 1450 °C; x is the atom fraction of P in the Fe matrix. The experimental curve is from Hondros (1965).

4. DISCUSSION AND CONCLUSIONS

A thermodynamic analysis for adsorption induced cohesion loss has been presented and applied. The derivations follow closely the original procedure adopted by Rice (1976) in that the interface displacement, δ, defined in §2.3.3, and its conjugate force, σ, have been included as independent variables in the expression for the interface energy. Specifically, in (1) for the differential du the work term $\sigma\,\mathrm{d}\delta$ was included. Our model explicitly accounts for the work of separation (decohesion) under equilibrium conditions where adsorptions are allowed to proceed to completion (equations (25)–(30)) and under conditions where the separating interface is not equilibrated with the bulk environment with respect to adsorption (equations (33) and (34)). The model is accurate only with the assumption that the Γ, the interface compositions, are the only variables which influence the σ–δ relation. In applying the results of §2.5 in §3, we have already presumed that the chemical potentials $\mu_{i,0}$ and $\mu_{i,\infty}$ are those that are derived from *equilibrium* statistical thermodynamic models and, of course, the numerical values of the important quantities were estimated from what are meant to be equilibrium adsorption data. Clearly there will be many cases where this will not be an adequate idealization, especially when the adsorbates have severely limited mobility. It is possible, in principle, to extend the heuristic procedures of §2.5.3 to include, for example, the work to shift a given *quantity* of adsorbate from its equilibrium state on a free surface to non-equilibrium sites in which it may have been 'trapped' during a 'fast' separation. Such calculations would undoubtedly require very accurate atomic models for this sort of adsorption and would be difficult to do with confidence. For many cases, however, and in particular for the case of mobile adsorbates like hydrogen, the present model should be quite useful for estimating cohesion losses.

The present model should be extended to include other model isotherms and include the possibility of lateral interactions which lead to phase transitions. In addition the problem of non-equilibrium separations, so important to interpreting actual brittle fractures, certainly requires further study. For example, it would be of considerable interest to find ways to estimate cohesion and adsorption induced losses in cohesion without employing the constitutive assumptions phrased in (1).

Finally, we note that the frequently adopted procedure of using the relation (28) with its implied assumption of equilibrium to estimate boundary cohesion can lead to serious error. The example of grain boundary adsorption of phosphorus in iron presented in §3.2 (see also figure 3) makes this clear since in an actual temper induced intergranular fracture process in iron containing phosphorus, at least at lower temperatures, phosphorus diffusion is expected to be extremely slow. This means that the actual work of separation should correspond better with that evaluated at 'constant composition' rather than with the work computed at 'constant μ'. As the calculations have shown, the difference between these two estimates of cohesion can be substantial.

The author gratefully acknowledges the very helpful discussions with J. R. Rice on topics relating to interface cohesion. Support from the Energy Research and Development Administration through contract E(11-1)3084 is also much appreciated.

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