

ON THE THERMODYNAMICS OF
ADSORPTION AT INTERFACES AS IT INFLUENCES DECOHESION

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ABSTRACT

Earlier computations on the work of separation of boundaries with adsorbed solute atmospheres are reconsidered in terms of reversible work cycles. Special attention is given to two limiting cases. These are the separation of a material interface under fully equilibrated conditions, for which the chemical potential of the adsorbed solute remains constant, and separation under constrained conditions for which the surface excess solute concentration remains constant (i.e., the same on the two newly created free surfaces as present initially on the unstressed interface). The results are consistent with the limiting cases treated before and include the extension to more general cases of solute interactions, including multi-component systems. The work terms are conveniently represented on diagrams of chemical potential versus surface excess solute concentration. A general separation process is then represented as a path in this diagram which begins on the adsorption isotherm for the unstressed interface and ends on the adsorption isotherm for the pair of newly created surfaces.

1. Introduction

There are a number of embrittlement phenomena, such as temper embrittlement and hydrogen embrittlement in which solute absorption at a grain boundary or other interface is thought to degrade its cohesion and lead to intergranular separation. A limiting case, tractable for thermodynamic analysis, occurs when the separation is ideally brittle and involves no plastic flow. The analysis is also applicable to the situation first considered by Thomson¹ where plastic flow occurs but where dislocations screen the crack tip from the remote stress field and the local crack tip region separates as in the limiting case.

Seah² first considered the differences between two types of boundary separation as influenced by solute adsorption: (i) quasi-equilibrium separation with the chemical potential of solute maintained uniform throughout the system and, (ii) "rapid" separation in such a manner that the excess amount of solute initially residing in the boundary remains attached to the created free surfaces with no solute exchange taking place with bulk phases.

However, Rice³ presented an analysis of the work terms in the two limits for the grain boundary case which suggests that details of Seah's² analysis require modification. In particular, the Rice analysis disagrees with Seah's conclusion that adsorption has no effect on the work of separation in the fixed composition (rapid) limit, although both agree that the effect of adsorption on the work in this limit is less than for separation at the fixed potential (slow) limit. The problem has also been considered by Asaro⁴ and by Hirth⁵, Asaro extending Rice's³ work to interphase interfaces and Hirth discussing a number of irreversible phenomena which can

cause deviations in work from that predicted for the limiting case.

In this presentation, we first discuss various mechanisms of interface separation, together with the appropriate variables giving the work term. Rice's³ analytical result, expressed in terms of Helmholtz free energies related to stress displacement variables for an interface separating uniformly, is given in terms of a reversible work cycle in chemical potential-composition space. An alternate reversible work cycle is then presented for surface energy area variables. Finally, the results are extended to several cases of interface separation other than the two previously treated.

2. Modes of Separation

There are various modes of separation of an interface, amenable to calculation of surface energies for a hypothetical reversible path, three of which are illustrated in Fig. 1. These produce different stress (or local force) displacement curves as shown in Fig. 2. However, the surface energy, equal to the integral of the stress displacement curve from an unstressed equilibrium separation δ_0 to infinity, is the same for all three paths (assuming that all three correspond to one of the limiting composition states discussed above). Mode a in Fig. 1 corresponds to clamping the two bulk phases rigidly and separating the boundary region, the path used by Rice³, Asaro⁴, and, in an atomic calculation, by Zaremba⁶. The initial slope of the σ - δ curve for case a, determined for the anharmonic case by a weighted average of phonon frequencies⁶, is larger than the elastic constant corresponding to the tensile extension of the bicrystal in case b. For case c, a crack is supposed to propagate

reversibly along the boundary. A given atom pair being separated undergoes a stress-displacement excursion which differs from the other cases because of the varying compliance to the left and surrounding the crack tip, although initially it would coincide with case b .

For reversible separation, the work performed by the external device applying the stress σ equals the free energy change in creating the surface. In all cases the work term performed by the external device, i.e., the negative of the work done by the system, in this reversible separation is

$$w = \int_{\delta_0}^{\infty} \sigma d\delta \quad . \quad (1)$$

(For a crack, case c , this is the "energy release" \mathcal{E} in extending the crack).

3. Thermodynamic Relations for Systems with Boundaries

Before considering the analysis of interfacial separation we review briefly the thermodynamics of systems having one or more planar boundaries. These may consist of grain or phase boundaries or of free surfaces. For reversible alterations of state of a system, the combined statement of the first and second laws is

$$dU = TdS + dw_{rev} \quad , \quad (2)$$

where dw_{rev} is the reversible work*. This may be written, for example, in an isothermal system under uniform pressure P , capable of receiving matter

* In order to connect to the fracture mechanics concept of work done on the system appearing at least in part as surface energy, the sign of work terms are defined opposite to the conventional chemical thermodynamics usage.

dn_i of all its k constituents ($i=1,2,\dots,k$) from appropriate matter reservoirs with chemical potentials (Gibbs free energy per mole) μ_i , and capable of changing areas dA_α ($\alpha=1,2,\dots,\beta$) of its β interfaces under surface tensions γ_α ,

$$dw_{\text{rev}} = -PdV + \mu_i dn_i + \gamma_\alpha dA_\alpha + dw \quad (3)$$

where V is volume of the system and dw represents the work of any external devices on changes in the system not already accounted for by the terms listed. The alterations of boundary areas A_α that we shall consider will be such that a change in A_α will always be considered to take place by adding atom sites to a surface rather than by the elastic stretching of bonds at existing sites. In this case the distinction between the surface "tension" (i.e., surface stress) and the surface "energy" can be disregarded and the terms γ_α are consistently interpreted as surface energies, which we shall henceforth call them. In the absence of device work

$$dU = TdS - PdV + \mu_i dn_i + \gamma_\alpha dA_\alpha \quad (4)$$

The system as it exists in any hydrostatically pressurized equilibrium state of temperature T , pressure P , potentials μ_i of the constituents and surface energies γ_α can be regarded as having been created by adding matter to a system of initially vanishingly small size, under conditions for which these intensive variables are held fixed, so that by integration

$$U = TS - PV + \sum_i \mu_i n_i + \sum_\alpha \gamma_\alpha A_\alpha \quad (5)$$

and differentiation now yields the Gibbs-Duhem relation

$$0 = -SdT + VdP - \sum_i n_i d\mu_i - \sum_\alpha A_\alpha d\gamma_\alpha \quad (6)$$

With the neglect of surface terms for the moment, with j phases present, Eq. (6) applies for each so that there are $k+2$ variables (the μ_i , P and T) and j constraints, giving the phase rule $\mathcal{F} = k-j+2$ where \mathcal{F} is the variance of the system. With surface terms considered, β added variables are present but Eq. (6) also applies (in terms of surface excess quantities) to each of the β interfaces so that the phase rule remains unchanged.

The applications which we consider are to isothermal processes, and in terms of the Helmholtz free energy $F = U - TS$,

$$dF = dw_{\text{rev}} = -SdT - PdV + \sum_i \mu_i dn_i + \sum_\alpha \gamma_\alpha dA_\alpha + dw \quad (7)$$

Thus dF represents isothermal reversible work dw_{rev} and the device reversible work dw can be equated to dF when V , n_i and A_α are fixed. Other potentials for which changes can be equated to device work under appropriate conditions are the Gibbs free energy $G = F + PV$, and $\Omega = F - \sum_i \mu_i n_i$, $\Lambda = F + PV - \sum_i \mu_i n_i$. In terms of these

$$dG = VdP - SdT + \sum_i \mu_i dn_i + \sum_\alpha \gamma_\alpha dA_\alpha + dw \quad (8)$$

$$d\Omega = -PdV - SdT - \sum_i n_i d\mu_i + \sum_\alpha \gamma_\alpha dA_\alpha + dw \quad (9)$$

$$dA = VdP - SdT - \sum_i n_i d\mu_i + (\sum_i \mu_i dn_i - \sum_i n_i d\mu_i) + \sum_\alpha \gamma_\alpha dA_\alpha + dw \quad (10)$$

The extensive quantities F , V , n_i can be divided into bulk quantities and surface excess quantities $(F)_\alpha$, $(V)_\alpha$, $(n_i)_\alpha$ associated with each of the β boundaries, or into the surface excess quantities $[F]_\alpha = f_\alpha$, $[V]_\alpha$, $[n_i]_\alpha = \Gamma_{i\alpha}$ normalized to unit area of boundary. This can be done in the Gibbs sense⁷ of the total extensive quantity minus its amount residing in hypothetical bulk phases that are uniform up to a mathematical dividing surface, or in the Guggenheim sense⁸ of excesses over the average bulk amount in a boundary zone of finite but small thickness.

For any particular boundary of surface energy γ and area A , Eqs. (4,5,6) take the form

$$d(F) = -Pd(V) - (S)dT + \sum_i \mu_i d(n_i) + \gamma dA \quad (11)$$

$$(F) = -P(V) + \sum_i \mu_i (n_i) + \gamma A \quad (12)$$

$$0 = -(S)dT + (V)dP - \sum_i (n_i)d\mu_i - A d\gamma \quad (13)$$

The last two equations show that

$$f = -P[V] + \sum_i \mu_i \Gamma_i + \gamma \quad (14)$$

and that

$$d\gamma = d(f+P[V]-\sum_i u_i \Gamma_i) = -[S]dT + [V]dP - \Gamma_i du_i \quad (15)$$

For an isothermal system, we note that when the dividing surface can be chosen so that $[V] = 0$, or when the term $[V]dP$ can be disregarded (see below), this last expression becomes the Gibbs adsorption equation

$$\gamma = \gamma^* - \int_{\mu_j^*}^{\mu_j} \Gamma_i du_i \quad (16)$$

As noted by Cahn⁹, however, Eq. (15) cannot be directly applied without taking into account the number of bulk phases and the phase rule. For example, with two components and two phases, two variables are fixed once the two free variables temperature T and μ_2 are fixed, so that under isothermal conditions Eq. (15) would assume the form

$$d\gamma = [V](\partial P/\partial \mu_2)_T d\mu_2 - \Gamma_1 (\partial \mu_1/\partial \mu_2)_T d\mu_2 - \Gamma_2 d\mu_2 \quad (17)$$

This result is equivalent to Eq. (21) of Cahn⁹ and indicates that μ_1 and P are automatically fixed once T and μ_2 are fixed. Thus it is not meaningful, for example, to consider variations of γ with P for constant T and μ_2 . Hence, if the Gibbs adsorption equation is written as $d\gamma = -\Gamma d\mu$, where $\mu = \mu_2$, the precise meaning to be given to Γ must be consistent with the coefficient of $d\mu_2$ in (17), at least if the surface is not to be regarded as being constrained from equilibrium with the adjoining bulk phases.

Also of interest are the surface excess free energies $(G) = Ag$,
 $(\Omega) = A\omega$, $(\Lambda) = A\lambda$, inter-related by

$$\begin{aligned} g &= f + P[V] = \omega + P[V] + \mu_i \Gamma_i \\ &= \lambda + \mu_i \Gamma_i = \gamma + \mu_i \Gamma_i \end{aligned} \quad (18)$$

We note that the potentials g , f , ω , and λ are dependent on choice of dividing surface^{7,9} since Γ_i and $[V]$ are so dependent.*

Equations (4-6) and (11-17) refer to alterations of equilibrium states brought about by variations of the quantities P , μ_i and T (with T fixed for eqs. (16) and (17)). In the following applications we are concerned with processes involving device work to separate a grain boundary into a pair of free surfaces. Consider a closed system consisting initially of a solid containing a grain boundary and surrounding vapor, all within a chamber fitted with a piston to supply a pressure P . If the grain boundary is separated into free surfaces by device work under constant pressure P , in such a manner that μ_i remains uniform among all parts of the system which exchange mass with one another,

$$dw_{\text{rev}} = -PdV + dw \quad (19)$$

and

$$\Delta F = -P\Delta V + w \text{ , or } \Delta G = \Delta F + P\Delta V = w \text{ .} \quad (20)$$

Here the Δ 's denote changes in state and w is the necessary device work.

* However, as shown subsequently, changes in these quantities can be identified with changes in thermodynamic state functions, and thus are unique.

But ΔG is independent of path and can equally be calculated by the reversible work of the surface energy terms in progressively diminishing grain boundary area A_b and increasing free surface area A_s under constant pressure, so that

$$\begin{aligned} dw_{\text{rev}} &= -PdV + \gamma_s dA_s + \gamma_b dA_b \\ &= -PdV + (\gamma_s - \gamma_b/2) dA_s \end{aligned} \quad (21)$$

since $\frac{1}{2} A_s + A_b = \text{constant} = A_0$ (the initial grain boundary area). Hence

$$\Delta F = -P\Delta V + (2\gamma_s - \gamma_b)A_0 \quad \text{or} \quad \Delta G = \Delta F + P\Delta V = (2\gamma_s - \gamma_b)A_0, \quad (22)$$

so that for a unit area A_0 the device work is

$$w = 2\gamma_s - \gamma_b \quad (23)$$

This result applies directly for the one limiting case of fully equilibrated separation at constant potentials. As shown in Section 5, it represents only one portion of the total device work associated with separation under constrained equilibrium conditions of no exchange of matter with bulk phases.

In the application to the separation processes of Fig. 1, in order to avoid carrying the factor 2 throughout, we set $\gamma = \gamma_b$ and $\Gamma = \Gamma_b$ for the initial boundary, whereas for the pair of free surfaces created by separation, $\gamma = 2\gamma_s$ and $\Gamma = 2\Gamma_s$ where, as is conventional,

γ_s and Γ_s pertain to a single free surface. Moreover, we consider the above thermodynamic relations to apply for three classes of systems. One is the totally equilibrated system. A second is a constrained equilibrium situation where the surface is constrained not to equilibrate with one or more of the bulk phases with which it is in contact. As a physical example essentially corresponding to such a situation, we can imagine a gas (oxygen) equilibrated with a metal (copper) at low temperature where local equilibrium with the vapor is rapidly attained but where equilibrium with the bulk is a slow diffusion controlled process. The third situation is one where partial equilibration of a surface species has occurred so that its chemical potential is intermediate between an initial value and the value equilibrated with the bulk phase. This situation has been considered by Defay and Prigogine¹⁰, who describe the departure of the chemical potentials from the equilibrated values in terms of so-called cross chemical potentials. In connection with these applications, there are obvious questions of relaxation times for degrees of equilibration which are beyond the scope of the present work. Some of these considerations as well as some irreversible effects, are presented elsewhere.⁵

4. Analysis in Terms of Stress-Separation Distance Variables

Before applying the formalism of the last section, based on classical approaches to processes of surface creation in terms of surface energy-area variables, we digress to explain the formulation by Rice³ in terms of stress-separation distance variables. Rice treated the surface itself as

an independent thermodynamic system, decoupled from the adjoining bulk phases, and having a state characterized by T , the separation δ (as in Fig. 1a, with $\delta=\delta_0$ corresponding to a coherent, unstressed grain interface and $\delta=\infty$ to a pair of fully separated surfaces), and the surface concentration Γ of an adsorbed species, writing (for T constant) the Gibbs relation

$$df = dw_{\text{rev}} = \sigma d\delta + \mu d\Gamma \quad (24)$$

where σ is the stress tending to open the interface and μ is the equilibrating potential corresponding to Γ and the opening separation δ .

At first sight this approach is not obviously reconcilable with a theory based on rigorously defined surface excess quantities for a surface in equilibrium (full or constrained) with adjoining bulk phases. For example, in the initial and final states Eq. (24) reduces to $df = \mu d\Gamma$ since $\sigma=0$, and this may be contrasted with Eq. (15) which shows that in general for either such state

$$df = -Pd[V] + \mu_1 d\Gamma_1 + \mu d\Gamma \quad (25)$$

(here $\mu=\mu_2$, $\Gamma=\Gamma_2$ and a binary system in which 1 denotes the major constituent of the bulk solid phases is being considered). Moreover, it cannot be expected that a dividing surface can be chosen so that $\Gamma_1 = 0$ and $[V] = 0$, specifically both before and after separation. It is, however, possible to interpret Rice's formulation as corresponding to a choice of dividing surface for which $\Gamma_1 = 0$, with neglect of the $-Pd[V]$ work term,

which is expected to be negligible in typical circumstances compared to the $\sigma\delta$ work term, since the cohesive strength will generally be very much greater than P . In fact, Rice's formulation tacitly assumed that $P=0$, that is, that no stress acted on the interface before and after separation. We will show in the next section that the principal results of Rice's formulation can be duplicated exactly by reference to appropriate cycles analyzed in terms of surface energy-area variables. Nevertheless, this formulation, in which thermodynamic properties are ascribed to partially separated interfaces ($\delta_0 < \delta < \infty$) would seem to have great utility for discussing kinetic processes during actual separations, which will in general correspond to neither of the limiting cases that we treat.

We consider the boundary separation process shown in Fig. 3a and represented in μ, Γ space in Fig. 4. The system is imagined to be initially in complete equilibrium, A, (for which $\mu=\mu_0$ and $\Gamma=\Gamma_0$) and to be separated reversibly at constant T in one of two ways. One is path I (A to B, Fig. 3a), separation at constant μ . The other is path III (A to C, Fig. 3a), separation in such a manner that the excess amount residing on the created unit areas of free surface equals the amount initially residing on the boundary, i.e.,

$$2\Gamma_s^C = \Gamma_b^A = \Gamma_0. \quad (26)$$

Schematically, the system is shown as blocked from access to a matter reservoir in Fig. 3 for path III, but open to it for path I. For path III, constrained equilibrium is assumed in which there is no exchange between surface and bulk phases but in which the solute is imagined to distribute

evenly between the two created surfaces and to equilibrate to a surface state which would be in equilibrium with a reduced chemical potential μ_C . In this case the μ coordinate in Fig. 4 corresponds to μ for the progressively separating interface, and this value of μ differs from μ in the bulk phase as noted in Fig. 3a. The arrows in Fig. 3a represent the reversible work $\sigma d\delta$ performed by the external device in separating the interface.

For path III the reversible work \bar{w} is given by setting $\Gamma = \Gamma_0$ (constant), and hence Eq. (24) integrates to

$$\bar{w} = \int_{\delta_0}^{\infty} \sigma(\delta, \Gamma_0) d\delta = f(\infty, \Gamma_0) - f(\delta_0, \Gamma_0) = 2f_s^C - f_b^A \quad (27)$$

Here the notations $\sigma(\delta, \Gamma)$, $f(\delta, \Gamma)$ indicate the dependence on state variables δ, Γ ; $f(\delta_0, \Gamma_0) = f_b^A$ (the boundary free energy in state A); $f(\infty, \Gamma_0) = 2f_s^C$ (the free energy of the pair of free surfaces in state C). Since $f = \gamma + \mu\Gamma$, Eq. (18), when the $P[V]$ terms are neglected, becomes

$$\bar{w} = 2\gamma_s^C - \gamma_b^A + \Gamma_0(\mu_C - \mu_0) \quad (28)$$

For path I, Rice³ introduced the Legendre transform $w = f - \mu\Gamma$ (see Eq. 18), so that (24) becomes

$$dw = d(f - \mu\Gamma) = \sigma d\delta - \Gamma d\mu \quad (29)$$

Note further that because of the neglect of the $P[V]$ term, $w=\gamma$ and hence the reversible work \hat{w} of separation with $\mu = \mu_0$ (constant) is

$$\hat{w} = \int_{\delta_0}^{\infty} \sigma(\delta, \mu_0) d\delta = \gamma(\infty, \mu_0) - \gamma(\delta_0, \mu_0) = 2\gamma_s^B - \gamma_b^A \quad (30)$$

where now the notations $\sigma(\delta, \mu)$, $\gamma(\delta, \mu)$ denote a dependence on the state variables δ, μ .

Comparing this last result with Eq. (28), the differences in works for the two paths is

$$\begin{aligned} \hat{w} - \bar{w} &= 2\gamma_s^B - 2\gamma_s^C - \Gamma_0(\mu_C - \mu_0) \\ &= \int_{\mu_0}^{\mu_C} \Gamma(\mu) d\mu - \Gamma_0(\mu_C - \mu_0) = \int_{\mu_0}^{\mu_C} [\Gamma(\mu) - \Gamma_0] d\mu \\ &= - \int_{\Gamma_0}^{\Gamma^B} [\mu(\Gamma) - \mu_0] d\Gamma \quad (31) \end{aligned}$$

Here, in the second step we have used the Gibbs adsorption relation, Eq. (16), in the form $d\gamma = -\Gamma d\mu$, and have integrated by parts to put the final expression in the form given by Rice³; the term Γ stands for $2\Gamma_s$ and $\Gamma(\mu) [=2\Gamma_s(\mu)]$ denotes the adsorption isotherm for the pair of separated surfaces, whereas $\mu(\Gamma)$ represents the same isotherm in inverted form.

As remarked, Rice's formulation tacitly assumed that $P=0$ before and after separation. This is not consistent with the concept of a surface layer being in equilibrium with a bulk phase, say in the form of a vapor or

other fluid adjoining a solid surface. The approach can be modified by defining σ as the stress acting in addition to the pressure, so that $\sigma-P$ is the total tensile stress on the interface and writing

$$df = dw_{rev} = -Pd[V] + \sigma d\delta + \mu d\Gamma \quad (32)$$

in place of Eq. (24). This mode of writing the reversible work expression envisions that a bulk fluid phase of pressure P may be assumed to fill the opening gap at some separation $\delta=\delta^*$ before σ has fallen to zero; $[V]=\delta$ for $\delta < \delta^*$, so that the work expression is consistently $(\sigma-P)d[V]$, but the work of P and σ decouple once the bulk phase emerges in the gap. Equation (32) reduces exactly to (25) in the cases of the coherent grain boundary and fully separated surfaces, under pressure P , if the interface is chosen so that $\Gamma_1=0$. Further, based on (32) as a starting point the foregoing analysis applies for separations at constant P , without approximations involving the neglect of the $P[V]$ term, if f is replaced by $g(=f+P[V])$ in Eqs. (27) and (29) and ω by $\omega+P[V] = \gamma$ in Eq. (29). Equations (28) and (30), and hence (31), are then exact.

We observe now, and will apply in section 6, the observation that for isothermal processes consisting of the opening or rejoining of interfaces at constant P , possibly accompanied by adsorption or desorption, the reversible work term $dw'_{rev} = dg[=d(f+P[V])]$, which incorporates the $-Pd[V]$ work term in the usual way for constant pressure systems, consists of the device work $dw(=\sigma d\delta)$ and the work $\mu d\Gamma$ of matter addition:

$$dw'_{rev} = dg = d(f+P[V]) = \sigma d\delta + \mu d\Gamma = dw + \mu d\Gamma .$$

Hence if we consider a process which separates the interface, the total reversible work $\Delta w_{\text{rev}}^i = \Delta g$ is independent of path (say, in δ, Γ space) and depends only on the initial and final states. But the separate terms $\Delta w = \int \sigma d\delta$ and $\int \mu d\Gamma$ are path dependent. That is, the work of separation, Δw , is not a state function in general but depends on the path followed during separation. It will prove convenient to represent these paths in μ, Γ space as in Fig. 4 and Fig. 6, to follow.

For any cycle which restores the initial state of the system

$\oint dg = 0$, and hence Eq. (33) requires that

$$\oint dw \equiv \oint \sigma d\delta = - \oint \mu d\Gamma . \quad (34)$$

5. Analysis in Terms of Surface Energy-Area Variables

We show here that working within the classical framework of surface energy-area variables (section 3), for surfaces in equilibrium (full or constrained) with adjoining bulk phases, one can construct reversible work cycles which identically reproduce the results of Eqs. (28), (30) and (31). This provides an alternate derivation of Rice's results and provides a fuller understanding of essential assumptions in a more realistic setting than for the somewhat nonphysical example illustrated in Fig. 3a. The separation processes considered are shown in Figs. 3b to d, and the separated surfaces are always assumed to be equilibrated with the vapor phase.

For the process in Fig. 3b, the surfaces are also equilibrated with the bulk phase. However, for processes in Fig. 3c and 3d, as for that of Fig. 3a, the surfaces are constrained not to equilibrate with the bulk solid phase.

For simplicity we treat the case where component 1 has essentially zero concentration in the vapor phase. A concrete example would be adsorption of oxygen on a separating copper interface. Then, fixing T and P , μ_1 and μ_2 are fixed by the phase rule. However, both paths I and III can be accomplished at constant P since transport of component 2 between vapor and surface does not change the vapor composition (or μ_2). Thus, the appropriate reversible work cycles at constant P and T can be performed in terms of the familiar Gibbs free energy. [For the more general case where components 1 and 2 both appear in the fluid (vapor or liquid) phase, a reversible work calculation can still be performed in terms of the Λ function. In this case, P and T are again fixed, fixing μ_1 and μ_2 according to the phase rule. However, the system of Fig. 3 is attached by a membrane, semipermeable to component 1, to a matter reservoir at chemical potential μ_1 . Then transport of component 2 between surface and vapor can still be accomplished while maintaining constant μ_1 and μ_2 by means of more flow of component 1.]

Separation at constant chemical potential is represented by the process in Fig. 3b. The process is isothermal and, since bulk equilibrium with the vapor phase is maintained, also occurs at constant pressure. The system is also closed so n_i is constant and the appropriate reversible work term for this process is provided by ΔG as analyzed in Eqs. (19) to (23) and hence for unit area we have from Eq. (23):

$$\hat{w} = \Delta G = 2\gamma_s^B - 2\gamma_b^A \quad (35)$$

As illustrated in Fig. 3b, PdV work is performed by the weight sustaining the pressure P_0 , but this work does not contribute to the reversible work which must be performed by the external device in the process.

For process III, the actual separation is represented by the passage from steps A' to C in Fig. 3c. The bulk phase and interface are supposed to have been pre-equilibrated, A, at constant chemical potential μ_0 but now to be initially in a "low temperature" environment, A', of chemical potential μ_C . Separation at constant pressure P_C then proceeds with external work performed as indicated by the arrows. For this process at constant P , T , and n_i , the appropriate reversible work term is again G . However, ΔG cannot be calculated directly for this process in which there is a discontinuous change in chemical potential accompanying the rapid separation. Instead, since ΔG is path independent, the process A'-C in Fig. 3c can be replaced by the hypothetical reversible path in Fig. 3d with the sequence: (i) Compress the vapor from P_C to P_0 . As shown by the arrow, device work is required to compress the system and can be envisioned as reversibly adding the small weight to the system as shown: as in the previous case, however, PdV work done by the initial large weight in the compression does not contribute to the needed device work. With n_C moles of vapor present and $v(P)$ the molar volume of the vapor, the device work is

$$n_C \int_{P_C}^{P_0} v dP = n_C (\mu_0 - \mu_C) \quad (36)$$

since $dp = v dP$. (ii) The boundary is removed, D, at constant chemical

potential μ_o with work $-\gamma_b^A$. The number of moles in the vapor increases by Γ_o in this step. (iii) The vapor phase is expanded, E, to P_C with device work

$$(n_C + \Gamma_o) \int_{P_o}^{P_C} v dP = (n_C + \Gamma_o) (\mu_C - \mu_o) . \quad (37)$$

(iv) New surfaces are created at chemical potential μ_C with work $2\gamma_s^C$. Thus, the total reversible work is

$$\bar{w} = \Delta G = \Delta g = 2\gamma_s^C - \gamma_b^A + \Gamma_o (\mu_C - \mu_o) . \quad (38)$$

Thus, the results for \hat{w} and \bar{w} are identical to Eqs. (28) and (30)

Another perspective of the problem is presented in Fig. 5, where μ and Γ for matter on the surfaces are given as in Fig. 4, but where an additional axis, the chemical potential in the vapor phase, μ_v , is added. It is apparent that states A and A' differ with respect to reversible work. Since the net reversible work for the closed cycle is zero, the cycle in Fig. 5 shows that

$$w_I + w_{II} - w_{III} + w_{IV} = \hat{w} - \bar{w} + w_{II} + w_{IV} = 0 \quad (39)$$

or

$$\hat{w} - \bar{w} = -(w_{II} + w_{IV}) . \quad (40)$$

The work for path IV is the expansion work of Eq. (36). The work in path II

is that of expanding from P_0 to P_C with the moles in the vapor varying from $n_C - \Delta n$ to n_C . But Δn is just the amount $\Gamma - \Gamma_0$, since the moles appearing on the surface as absorbate have disappeared from the vapor. Thus,

$$-(w_{II} + w_{IV}) = -\int_{\mu_C}^{\mu_0} n_C d\mu - \int_{\mu_0}^{\mu_C} [n_C - (\Gamma - \Gamma_0)] d\mu \quad (41)$$

Together, Eqs. (40) and (41) again give the result of Eq. (31). Note that the integral giving the difference in work terms $\hat{w} - \bar{w}$ is represented by the simple cyclic integral $\oint \Gamma d\mu$ in Fig. 4, despite the fact that the actual cycle, Fig. 5, is more complex.

We are now in a position to review Seah's² analysis of separation at constant Γ . He correctly remarks that $2\Gamma_s^C = \Gamma_b^A = \Gamma_0$ for such a process. But he assumes that the appropriate device work term in this case is $\bar{w} = 2\gamma_s^C - \gamma_b^A$. Instead, the correct result, Eq. (28), differs from what Seah assumed by the term $\Gamma_0 (\mu_C - \mu_0)$. Thus, Seah's evaluation of \bar{w} is equivalent to ignoring the Γ_0 term in (28) or (31). In particular, his demonstration for the dilute concentration case that \bar{w} is independent of Γ_0 is not supported by the present analysis. The key differences with the work of Seah are revealed in Figs. 3c and 3d. While no VdP or $\Gamma d\mu$ work is obvious in Fig. 3c, the reversible cycle of Fig. 3d shows that in addition to the surface work terms considered by Seah, the external device must perform VdP work in the "fast, low temperature" process. Alternatively, in terms of Fig. 5, if one simply computed the net reversible work for path II in Fig. 5, restoring the moles μ_C back to the original state,

one would reproduce Seah's result. Only when path IV is included in the analysis is Eq. (31) obtained.

For the closed cycle of (40), if one substitutes Eqs. (35), (38) and (41) for the various work terms, one obtains

$$2\gamma_s^o - 2\gamma_s^c = - \int_{\mu_c}^{\mu_o} \Gamma d\mu \quad (42)$$

in agreement with the Gibbs relation (16). The Gibbs adsorption relation (42) and the analogous relation for changes of γ_b can be combined with the previous expressions for \hat{w} and \bar{w} to give Rice's³ equations

$$\begin{aligned} \hat{w} &= (w)_{\Gamma=0} - \int_{-\infty}^{\mu} [2\Gamma_s(\mu) - \Gamma_b(\mu)] d\mu \\ \bar{w} &= (w)_{\Gamma=0} - \int_0^{\Gamma} [\mu_b(\Gamma) - \mu_s(\Gamma/2)] d\Gamma \end{aligned} \quad (43)$$

where $(w)_{\Gamma=0} = (2\gamma_s - \gamma_b)_{\Gamma=0} = (2g_s - g_b)_{\Gamma=0}$ pertains to separation in the absence of the solute, and where $\Gamma_s = \Gamma_s(\mu)$ and $\Gamma_b = \Gamma_b(\mu)$, or $\mu = \mu_s(\Gamma_s)$ and $\mu = \mu_b(\Gamma_b)$, represent adsorption isotherms for the free surface and unstressed grain boundary, respectively. Rice³ derived these equations as consequences of reciprocity relations based on Eq. (24). For example, the latter follows by writing $(\partial\sigma/\partial\Gamma)_\delta = (\partial\mu/\partial\delta)_\Gamma$ and integrating first from $\delta_o(\Gamma)$ to ∞ on δ , and then from 0 to Γ on Γ .

In application of the expressions derived for \bar{w} to practical cases of separation at fixed composition, it is well to remember that there is a tacit assumption of local equilibrium within the adsorbed layer during separation. This implies some atomic mobility over distances comparable to

the layer thickness, and such mobility requirements may not always be met for fracture on practical time scales. An unresolved question is, then, that of by how much the work of separation at a completely "frozen" composition differs from \bar{w} .

6. General Separation Paths and Work Cycles

We have considered two special separation paths: constant $\Gamma(w=\bar{w})$, and constant $\mu(w=\bar{w})$. More generally, and with reference to Fig. 6, we can regard separation as a transition from a state Γ_0, μ_0 along the adsorption isotherm for the coherent, unstressed interface to a state Γ_F, μ_F along the isotherm for free surface adsorption and can determine a general work term w . With the assumption that there is local equilibrium within the adsorbed layer during separation, the separation process can be represented as a path in Γ, μ space as shown.

The actual details of the path are governed by the kinetics of matter transport by diffusion to the separating interface. The details differ for the different modes of separation illustrated in Fig. 1, and in the crack case there is the possibility of transport from the surrounding environment. Nevertheless, stressing the grain boundary generally should tend to lower the potential there and induce a flow of matter to the separating interface. Hence, the typical case is $d\mu < 0$ and $d\Gamma > 0$ during separation, as for the path OF shown in Fig. 6.

We show here that our principal results can be obtained in a concise way by application of the cycle result of Eq. (34), which follows directly from the expression for dg in Eq. (33). Noting that $\oint \mu d\Gamma = - \oint \Gamma d\mu$ for any cycle, Eq. (34) may be rewritten as

$$\oint dw = \oint \Gamma d\mu \quad . \quad (44)$$

For example, application of this expression to the path OCBO in Fig. 6 (i.e., separate at constant $\Gamma (= \Gamma_0)$ on OC, adsorb onto the free surfaces to restore μ to μ_0 on CB, close the surfaces at constant $\mu (= \mu_0)$ on BO) leads to

$$\tilde{w}_{OC} - \hat{w}_{OB} = \oint_{OCBO} \Gamma d\mu = + \int_{\mu_C}^{\mu_0} [\Gamma(\mu) - \Gamma_0] d\mu \quad (45)$$

which gives Eq. (31), where $\Gamma(\mu) [= 2\Gamma_s(\mu)]$ is the equation of the adsorption isotherm CB. The integral is just the area OCBO, and hence $\tilde{w} > \hat{w}$.

Let w_{OF} be the work on path OF in Fig. 6. Then Eq. (44) shows that

$$\tilde{w}_{OC} - w_{OF} = \oint_{OCFO} \Gamma d\mu \quad (46)$$

$$w_{OF} - \hat{w}_{OB} = \oint_{OFBO} \Gamma d\mu$$

Both integrals correspond to areas (the first to OCFO and the second to OFBO) in the μ, Γ plane, and since these are both positive for locations of state F between B and C, we conclude that

$$\tilde{w}_{OC} > w_{OF} > \hat{w}_{OB} \quad (47)$$

Thus the two limiting cases of separation at constant Γ and at constant μ have works which bracket that in the typical process where $d\mu < 0$ and $d\Gamma > 0$ during separation. Further, the fact that the integrals in Eq. (46)

can be interpreted as areas shows clearly that w_{OF} is necessarily path dependent, and not determined solely by the initial and final states.

Finally, we observe that as $\mu \rightarrow -\infty$, $\Gamma_s \rightarrow 0$ and $\Gamma_b \rightarrow 0$, i.e., both adsorption isotherms approach the μ axis in this limit. In the limit without adsorption,

$$\bar{w} = \hat{w} = (w)_{\Gamma=0} \quad \text{where} \quad (w)_{\Gamma=0} = (2g_s - g_b)_{\Gamma=0} = (2\gamma_s - \gamma_b)_{\Gamma=0} \quad . \quad (48)$$

Now consider the cycle consisting of separating the interface at μ_0 (OB in Fig. 6) with work \hat{w} , desorbing the free surfaces along the isotherm to $\mu = -\infty$, rejoining the surfaces to a grain boundary at $\mu = -\infty$, with work $-(w)_{\Gamma=0}$, and adsorbing along the grain boundary isotherm to potential μ_0 . In this case Eq. (44) gives

$$\hat{w} - (w)_{\Gamma=0} = - \int_{-\infty}^{\mu_0} [2\Gamma_s(\mu) - \Gamma_b(\mu)] d\mu \quad (49)$$

which is Rice's³ equation for the effect of adsorption on the work of separation at constant μ , alternately re-derived here as Eq. (43). The complementary equation, for separation at constant Γ , is readily derived by consideration of a similar cycle that starts along OC and is

$$\bar{w} - (w)_{\Gamma=0} = - \int_0^{\Gamma} [\mu_b(\Gamma) - \mu_s(\Gamma/2)] d\Gamma \quad . \quad (50)$$

7. Three-Component System

In the temper embrittlement case there is evidence for coupled solute effects of a three-component type with two dilute solute concentrations. The preceding analysis can be extended to the three-component case as illustrated in Fig. 7. As shown there, it is now necessary to retain subscripts to distinguish the dilute components 2 and 3.

Proceeding as before, we find for step I, separation at constant chemical potential

$$\hat{w} = 2\gamma_s^B - \gamma_b^A \quad (51)$$

In order to compute the reversible work terms for step II, the process is separated into two stages, a change of μ_2 at constant μ_3 followed by a change of μ_3 at constant μ_2 giving

$$\Delta w = \hat{w} - \tilde{w} = - \int_{\mu_2}^{\mu_2^C} (\Gamma_2 - \Gamma_2^0)_{\mu_3} d\mu_2 - \int_{\mu_3}^{\mu_3^C} (\Gamma_3 - \Gamma_3^0)_{\mu_2} d\mu_3 \quad (52)$$

From Eqs. (51) to (52), the result for the "rapid" separation stage I is then

$$\begin{aligned} \tilde{w} &= 2\gamma_s^C - \gamma_b - \int_{\mu_2}^{\mu_2^C} \Gamma_2^0 d\mu_2 - \int_{\mu_3}^{\mu_3^C} \Gamma_3^0 d\mu_3 \\ &= \hat{w} + \int_{\mu_2}^{\mu_2^C} (\Gamma_2 - \Gamma_2^0)_{\mu_3} d\mu_2 + \int_{\mu_3}^{\mu_3^C} (\Gamma_3 - \Gamma_3^0)_{\mu_2} d\mu_3 \quad (53) \end{aligned}$$

By analogy with the cases treated for the binary case in the preceding section, and with the above expressions as a guide, equivalent expressions can be developed for the three-component case. Indeed, Asaro⁴ has extended the Rice formulation to multi-component adsorption in a manner consistent with the above result.

8. Summary

A reversible work analysis in terms of surface energy-area variables reproduces Rice's³ result for the work of separation of interfaces at constant chemical potential of the components or at constant excess solute concentration at the interface. The work terms can be conveniently represented on graphs of solute potential versus concentration. In terms of these developments, one can express the work of separation for arbitrary paths of excess solute chemical potential versus excess solute concentration for binary or for multi-component systems.

These results provide a basis for determining the work of separation from data on solute adsorption⁴ obtained either from experiment or by statistical thermodynamical prediction. The resulting alterations of the work of separation may be decisive for the question of brittle versus ductile response of a grain boundary³, and should also be relevant to the kinetics of crack growth in cases of solute embrittlement, at least for cases in which the crack tip remains atomistically sharp, even if screened by dislocation fields¹. The extent to which the assumptions of the model apply to separation at low temperature remain to be explored quantitatively. For example, the relaxation time for local equilibrium to be attained on the surface in the "rapid" separation case is not known.

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Figure Captions

- Fig. 1. Modes of boundary separation.
- Fig. 2 Stress-displacement curves corresponding to the processes of Fig. 1.
- Fig. 3 Schematic representation of system in states A, B, C and intermediate states. For (A) the interface is imagined to have contact with (B) or to be blocked from (C) a matter reservoir.
- Fig. 4 Work cycle representation of boundary separation process in μ - Γ space.
- Fig. 5 Work cycle representation of Fig. 4 with chemical potential of vapor coordinate added.
- Fig. 6 General separation path, from state O along adsorption isotherm for initial grain boundary to state F along adsorption isotherm for separated surfaces.
- Fig. 7 Work cycle for interface separation in three-component system.

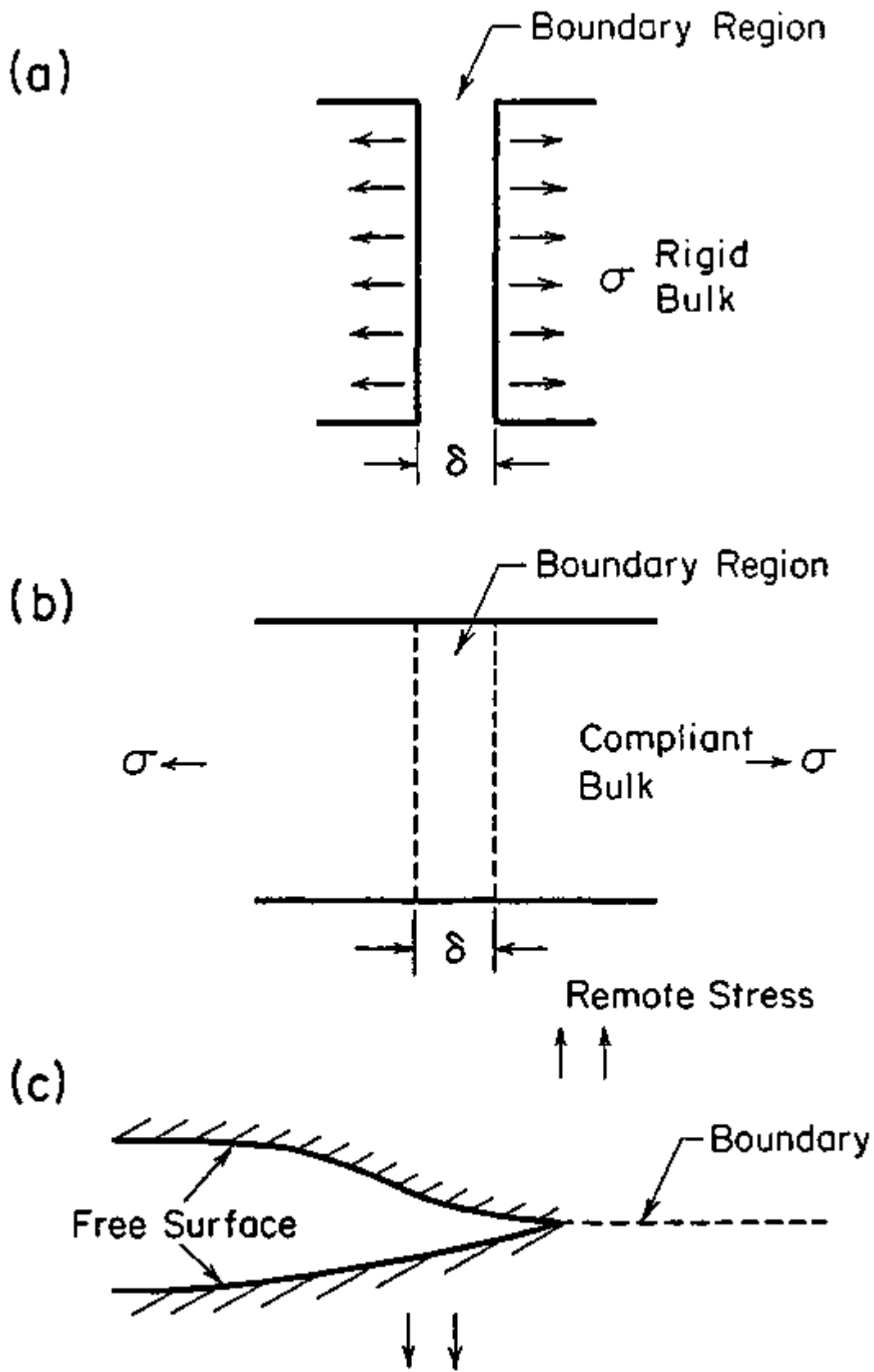


Figure 1

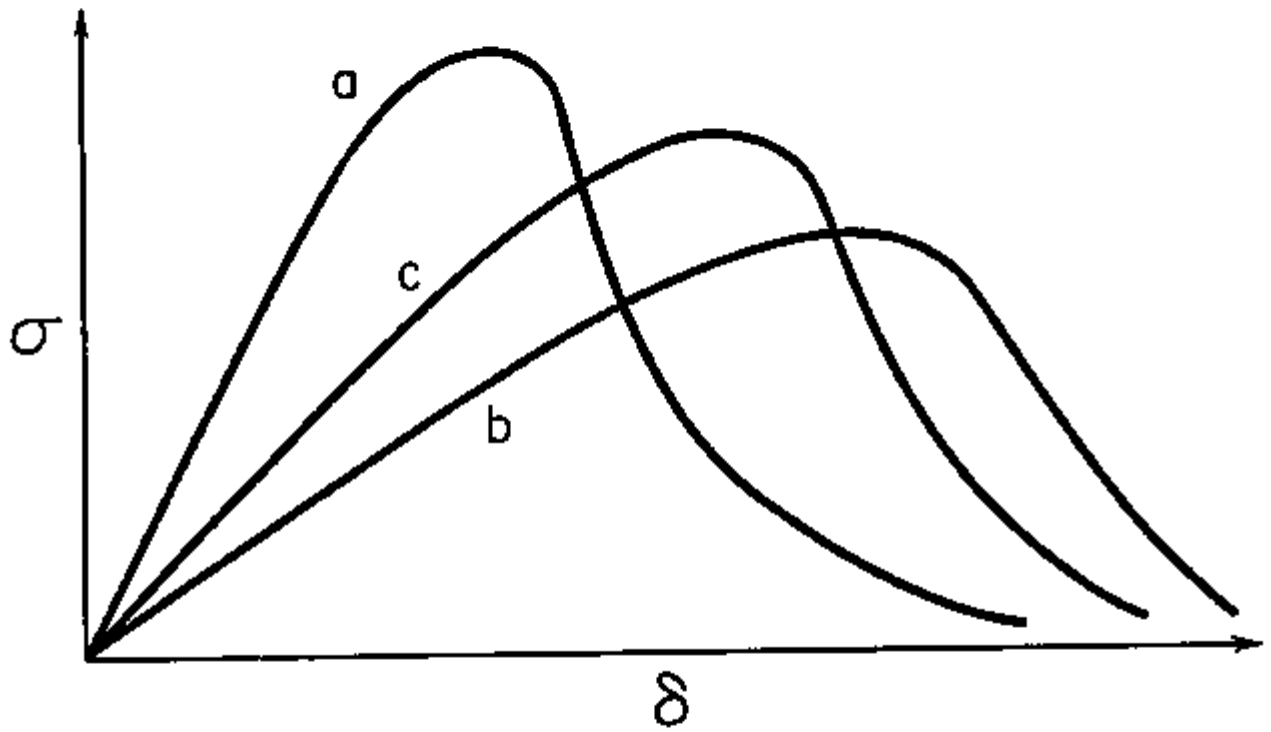


Figure 2

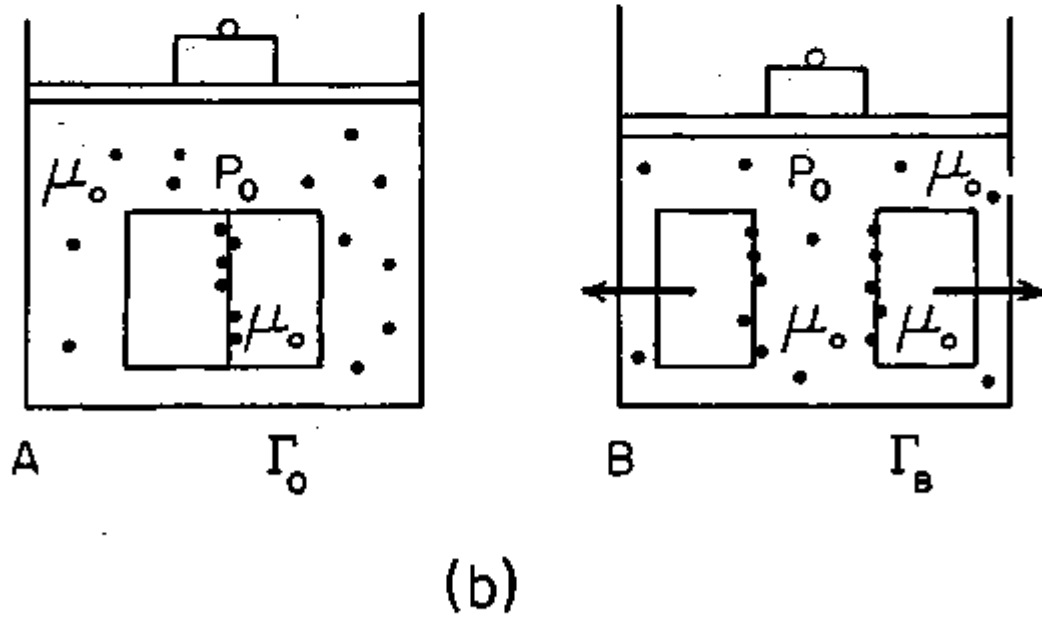
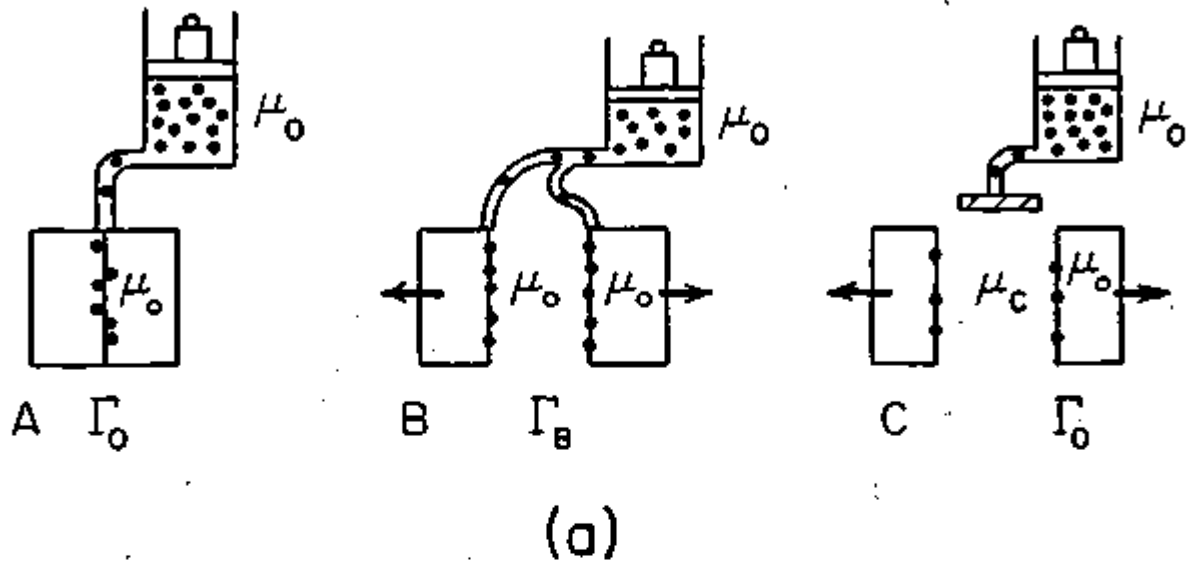


Figure 3

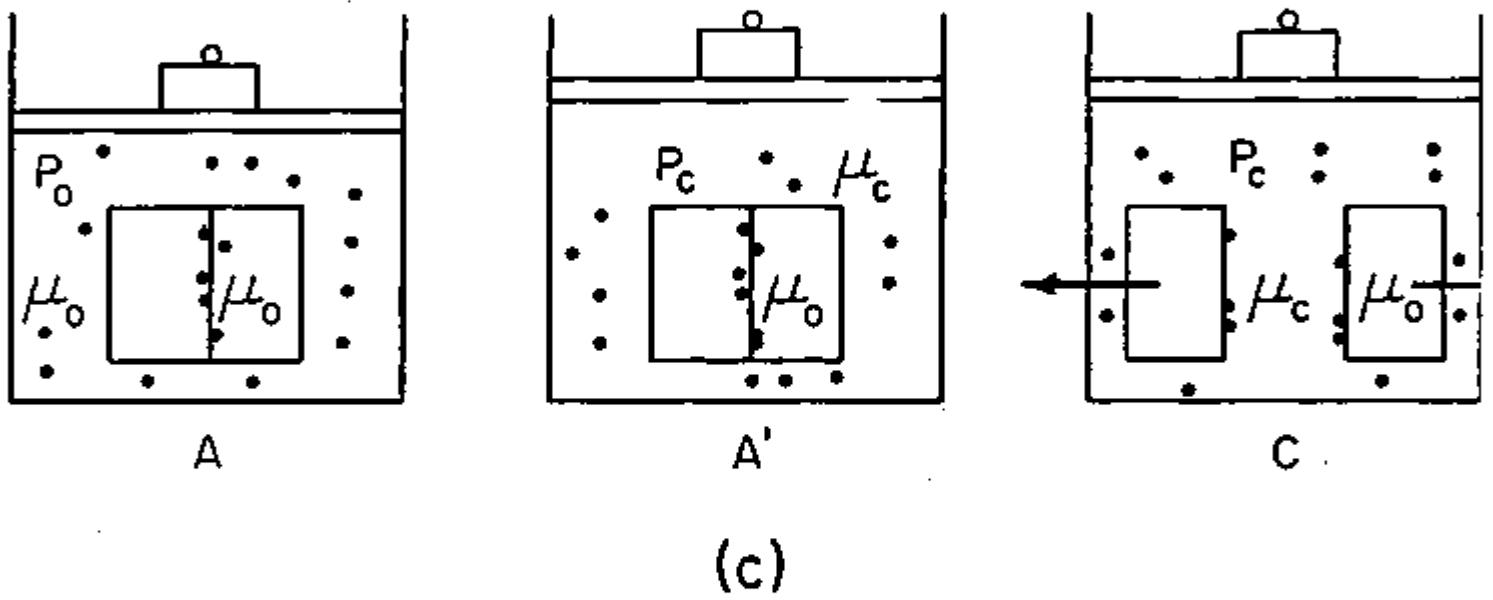
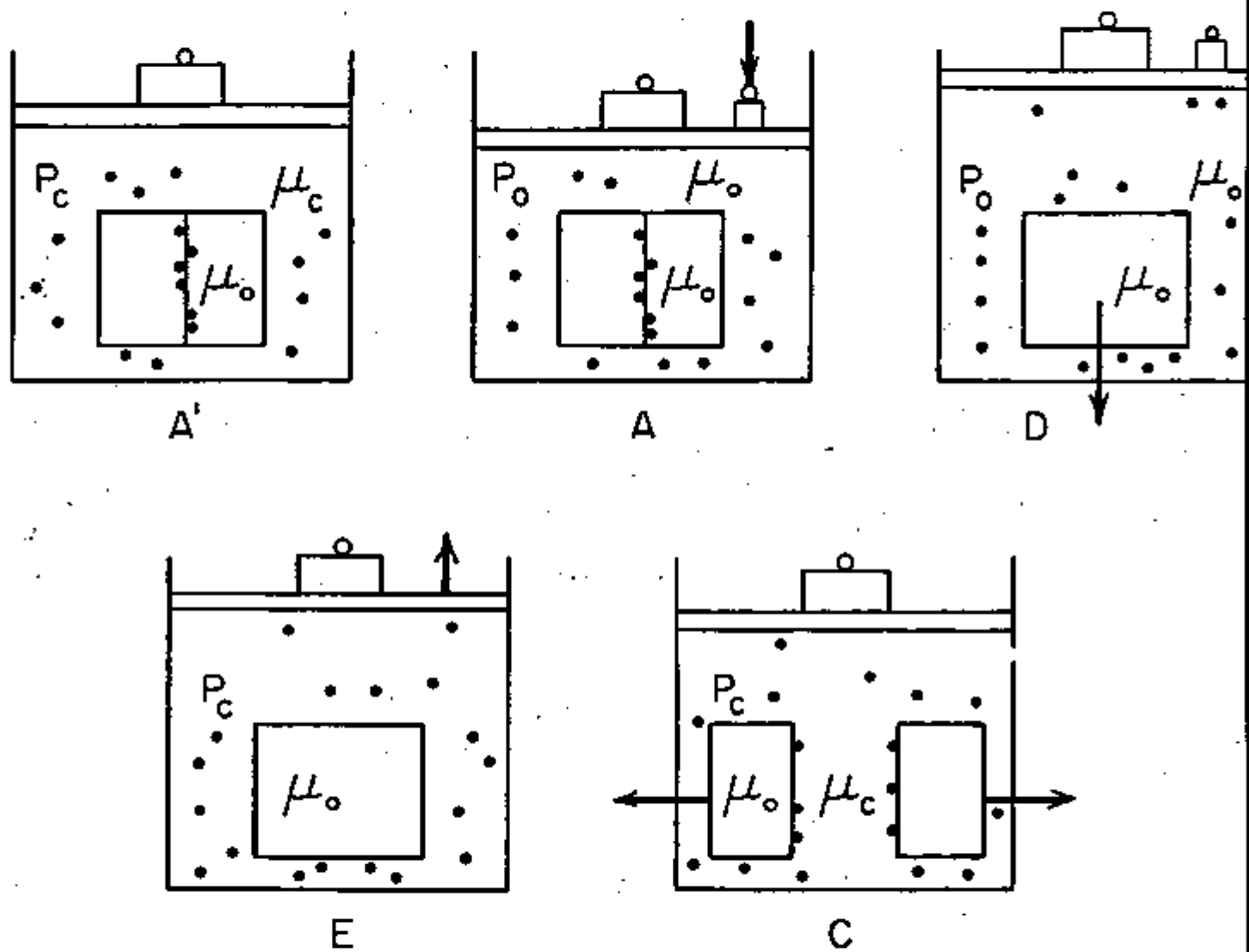


Figure 3
(Continued)



(d)

Figure 3
(Continued)

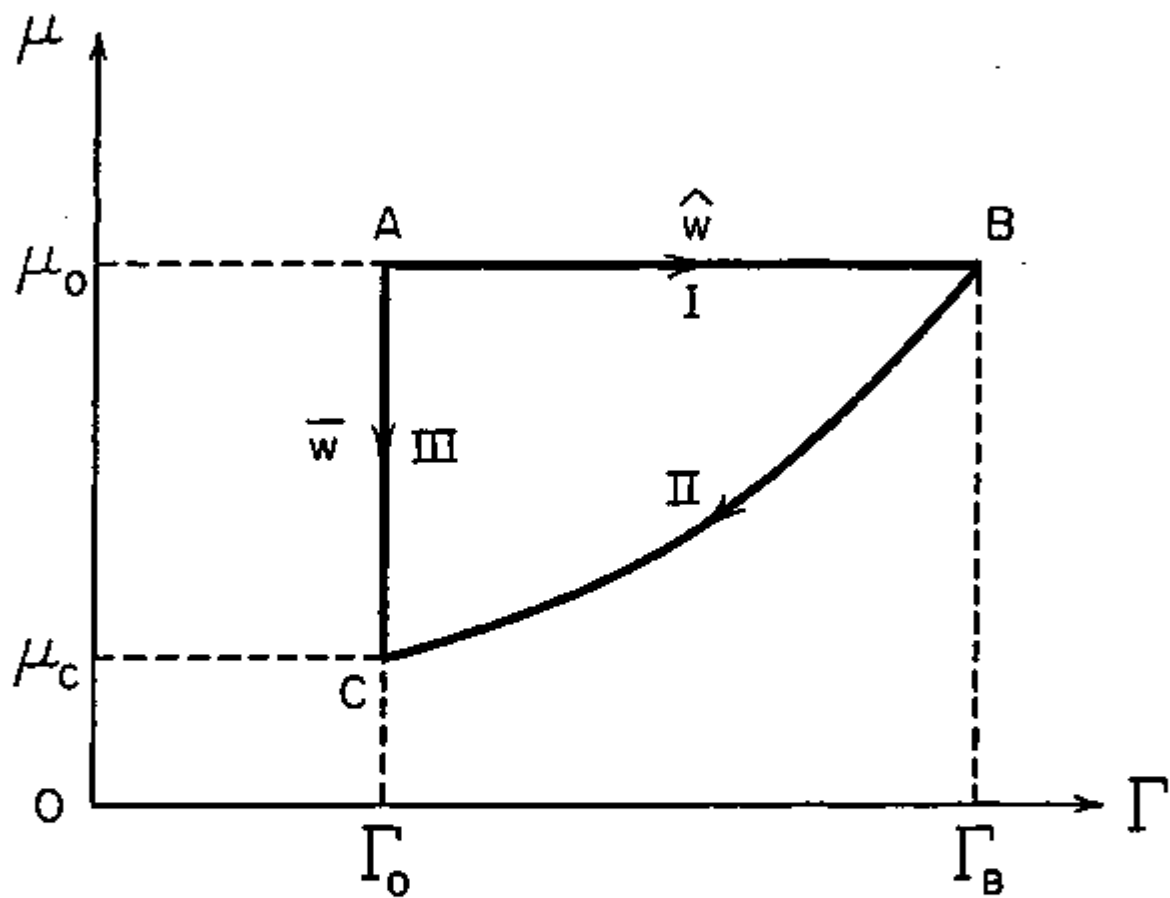


Figure 4

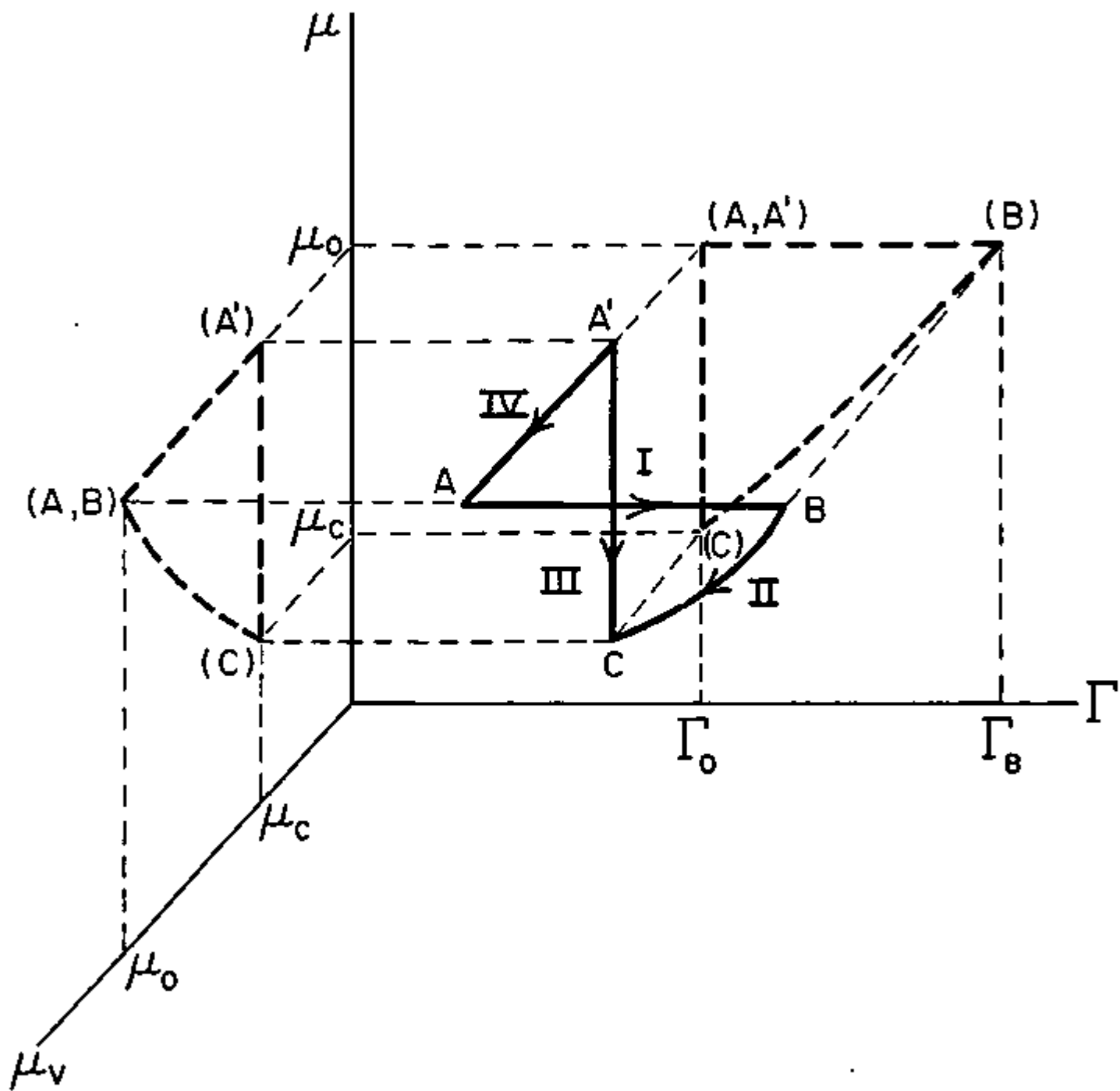


Figure 5

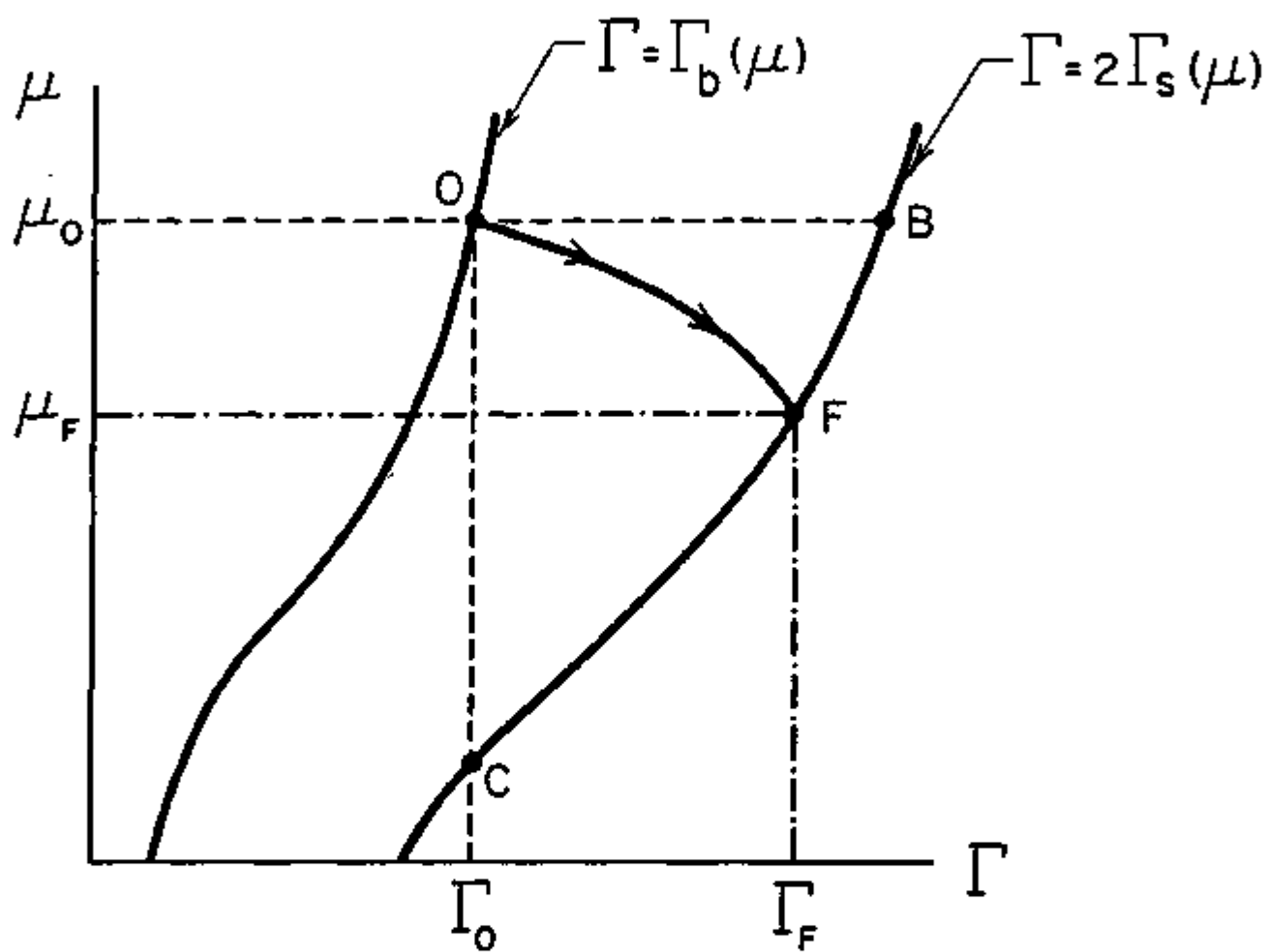


Figure 6

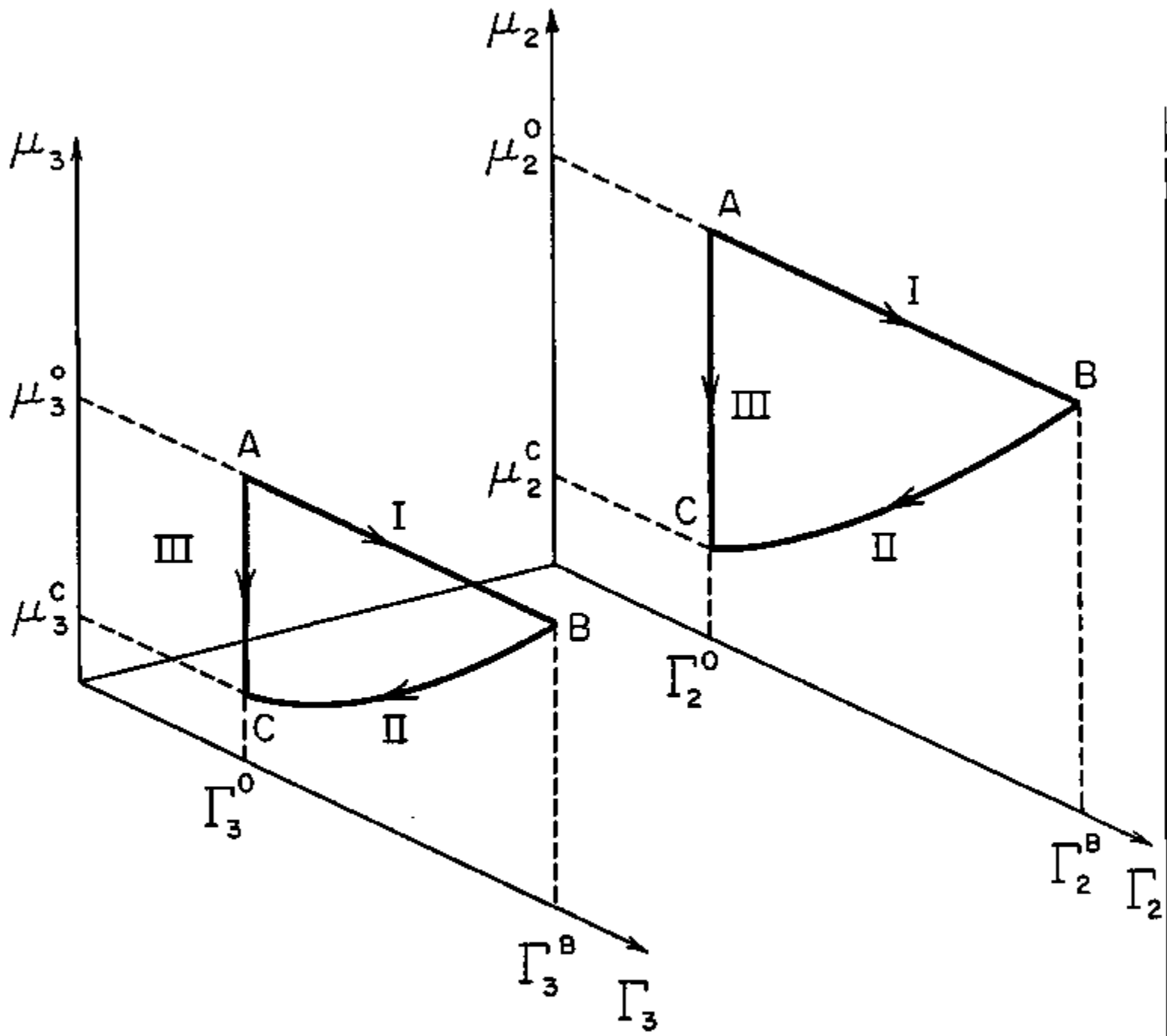


Figure 7