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## Energy Variations in Diffusive Cavity Growth

JAMES R. RICE

Division of Engineering, Brown University, Providence, Rhode Island 02912

TZE-JER CHUANG\*

Fracture and Deformation Division, National Bureau of Standards, Washington, D.C. 20234

The assignment of boundary values for the chemical potential and the calculation of energy-release rates for the growth of creep cavities along grain boundaries by self-diffusion are discussed. For simplicity, it is assumed that the boundaries are flat and that surface and grain-boundary diffusion are the dominant transport mechanisms. As matter diffuses from the void surface into and along the grain boundary, misfit residual stresses are induced to alleviate the high stress concentration ahead of the cavity apex. As a result, the contribution of strain-energy terms to the chemical potential can be neglected in typical cases. Also, contrary to the Griffith crack-extension model, the energy dissipation incurred by diffusive removal of material from the cavity surface and deposition in the grain boundary is a major term in the energy transfers associated with cavity growth. The primary energy "sink" in diffusive cavity growth is shown to arise from the work done by the grain-boundary normal stress when matter is inserted in the near-tip region by diffusion, not from the loss of strain energy of matter that is removed from the cavity at its tip or from the work of bond separation. Thermodynamic restrictions on the angle formed by the void surfaces at their apex, where they join the grain boundary, are considered. Boundary values for the chemical potential are derived in a manner appropriate for arbitrarily large but elastic distortions of material near the cavity tip and, in contrast to most previous work in the area, the effects of surface tension (i.e. of "surface stress," as distinct from surface energy) are included.

### I. Introduction

WHEN subjected to creep conditions, polycrystalline materials tend to develop cavities at grain interfaces. Their growth and final coalescence lead to intergranular failure. The kinetics of cavity growth by diffusion has become a topic of extensive recent interest, and the literature does not fully agree on fundamentals of the subject. Hull and Rimmer<sup>1</sup> and others<sup>2–5</sup> considered the diffusive growth of an array of spherical-cap (or lenticular) cavities in a planar grain interface. This assumption as to cavity shape implies that surface diffusion is rapid enough that cavity growth is controlled only by grain-boundary diffusion. Further, the grains were assumed to be nondeforming (rigid) and it is predicted that the growth rate varies linearly with the applied stress. However, conditions do not always allow this quasi-equilibrium cavity shape and grain-boundary cavities sometimes have an elongated, cracklike shape. Hence, Chuang and Rice<sup>6</sup> and others<sup>7–10</sup> considered the other limiting case of a thin cracklike cavity growing in a grain boundary and established different relations between applied stress and growth speed.

In an overview of nonequilibrium models, Chuang *et al.*<sup>10</sup> examined the entire spectrum of interfacial void shapes in diffusive cavitation and concluded that, for many conditions, a cavity can grow from one extreme case of slow advance in a lenticular shape to the other extreme case of rapid advance in a cracklike shape. The growth mechanisms on which these analyses are based are such that under the action of the applied stress normal to the boundary where cavities are located, matter on the cavity surfaces is driven by surface diffusion toward the cavity apex and into and along the grain boundary.

Based on this kinetic model, it is worthwhile to investigate the thermodynamic forces driving a cavity. Indeed, several workers have studied chemical forces in a stressed body containing defects.

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\*Member, the American Ceramic Society.

Specifically, Stevens and Dutton<sup>11</sup> considered Griffith crack propagation by mass transport and formulated the thermodynamic potentials for incremental advance of a crack due to various diffusion paths. McCartney<sup>12</sup> and Heald and Speight<sup>13</sup> investigated the thermodynamic stability of a cavity and determined the shape at which subcritical growth can be maintained. Their studies are essentially limited to cases in which cavities are located in a perfect crystal. However, grain boundaries are perfect matter sinks (or vacancy sources) and the fact that voids are often observed at the grain boundary suggests that it plays an important role during nucleation and growth.

The objective of this paper is to reexamine the formulation of chemical potentials and the calculation of energy-release rates in cavity growth. The special features induced by the existence of grain boundaries are emphasized. Their action as matter sinks can change the whole picture of the formulation. Specifically, in contrast to Griffith cracks, it is shown that the strain-energy term in the chemical-potential expression can typically be neglected even in cavity growth in a relatively narrow cracklike shape. Also, it is shown that the major sink of energy in cavity growth is from the work of normal stresses on the effective opening of the grain boundary due to the addition of matter by diffusion.

Although the material is modeled here as an elastic solid, undergoing self-diffusion along interfaces, it is well to remember that the cavitation process is often accompanied by significant amounts of plastic creep flow through dislocation motion.<sup>14</sup>

## II. The Boundary Values of Chemical Potential

In phenomenological terms, diffusive fluxes of a substance are driven by thermodynamic forces generated by chemical-potential gradients. Consider a stressed body containing defects in the form of voids and grain boundaries and suppose, for simplicity, that the body consists of a single component which, again for simplicity, is taken as isotropic with respect to its elastic and surface-energy properties. Temperature is held constant and it is assumed that an unstressed matter reservoir, without defects, is available at the same temperature as the body. All thermodynamic potentials, including the chemical potential  $\mu$ , can arbitrarily be assigned the value zero in the reservoir. It is conventional to define  $\mu$  in units of energy per atom although the concepts are continuum in character and treat matter as being indefinitely divisible; atoms are merely a convenient unit for mass.

The classic work on establishing boundary values for  $\mu$  is that of Herring.<sup>15,16</sup> We follow here essentially his procedures, but three comments are in order. (1) Since it is assumed that matter is always added coherently to surfaces, at full composition equilibrium with the immediately adjoining bulk, there is no need to distinguish separate potentials for atoms and vacancies as he does. Indeed, Herring makes similar assumptions about matter addition, so that in the end the distinction is unnecessary and only  $\mu_a - \mu_v$  appears in his formulas ("a" denotes atoms, "v" vacancies). (2) Although Herring discusses carefully the difference between surface energies and surface tensions (i.e. surface stresses), in a context which assumes that surface energies are dependent on elastic strains of surface elements, in his evaluations of  $\mu$  he does not discuss energy changes that occur because adding matter will, in general, alter the strains along a surface. We derive expressions for  $\mu$  in a manner appropriate to arbitrarily large elastic distortions (important because some models for diffusive cavitation assume large strains at the cavity tip) and show, by a simple verbal argument in the following text and a more detailed analysis in the Appendix, that Herring's expressions do in fact remain valid so long as the terms within them are properly referenced to the current deformed state. (3) Although some of Herring's discussion of potentials is directed to (global) nonequilibrium states, notably to diffusion, his methods of evaluating  $\mu$  are phrased mostly in terms of conditions for equilibrium. Our methods are somewhat more in keeping with the spirit of irreversible thermodynamics although we tacitly adopt the notions of local thermodynamic equilibrium which are inherent to the accepted, if thereby limited, procedures of that subject.

Note that  $\mu$  is defined at any location within the stressed body

such that  $\mu \delta n$  is the reversible work of taking an infinitesimal element of matter, equivalent to  $\delta n$  atoms, from the reservoir and placing it at that location, whereas the displacements are fixed on the loaded external boundary. Equivalently,  $\mu \delta n = \delta F$ , where  $F$  is the total Helmholtz free energy of the body and, more generally, when matter is transferred without restrictions on the external boundary displacements,

$$\delta F = \delta W + \mu \delta n \quad (1)$$

where  $\delta W$  is the work of external loads. The present concern is with matter added to (or removed from) void surfaces and grain boundaries. If, collectively, they have an area in the current deformed configuration denoted by  $A$ , then  $\mu$  satisfies

$$\delta F = \delta W + \int_A \mu \delta N dA \quad (2)$$

for arbitrary additions of infinitesimal matter layers to  $A$ , consisting of  $\delta N$  atoms per unit (current) area. Expressions in the form of Eq. (2) arise in "internal variable" formulations<sup>17</sup> of inelastic processes in solids, due to structural rearrangements of constituent elements of material by diffusion or (with appropriate terms analogous to  $\mu \delta N$ ) slip, phase changes, etc. In applying Eq. (2) we will generally write  $\delta N = \delta t / \Omega$  where  $\delta t$  is the local thickness of the (coherently) added layer and  $\Omega$  is the local volume per atom in the deformed configuration. Further,  $F$  will be represented as  $F_e + F_s$ , where  $F_e$  is the elastic strain energy, of local density  $w$  per unit volume of the current deformed configuration, and  $F_s$  is the energy of interfaces, of density  $\gamma$  per unit (current) area ( $\gamma = \gamma_s$  on cavity surfaces and  $\gamma = \gamma_b$  on grain boundaries).

Consider the addition of a layer of matter of (variable) local thickness  $\delta t$  over some portion of a cavity surface, under circumstances for which the external boundary is fixed ( $\delta W = 0$ ). To obtain  $\mu$ ,  $\delta F$  must be calculated using contributions from the following sources: (i) a strain energy density  $w$  must be given to the added layer to make it fit coherently; (ii) the area of the surface changes such that, if additional elastic strains  $\delta \epsilon_{\alpha\beta}$  of surface elements are neglected,  $\delta(dA) = -(\kappa_1 + \kappa_2)\delta t dA$  by an easy geometric construction, where  $\kappa_1$  and  $\kappa_2$  are the principal curvatures and the sign convention is such that both would be positive on a spherical cavity; (iii) surface elements strain by  $\delta \epsilon_{\alpha\beta}$  causing a change in  $\gamma$  and an additional change in  $dA$ ; (iv) the tractions acting on the bulk solid immediately below the surface, which are in general nonzero whenever surface tensions exist, are carried through some additional displacements  $\delta u_i$  when matter is added, thus causing a change in strain energy of material external to the surface. Herring's<sup>15,16</sup> discussion makes no reference to (iii) and (iv). It is conducted as if the product  $\gamma dA$  is unaffected by the strains  $\delta \epsilon_{\alpha\beta}$ ; in such circumstances the contribution from (iii) would be zero and, because (see Appendix) the surface tensions vanish in these circumstances, there would also be no contributions from (iv). (Rice and Drucker<sup>18</sup> observed that, when matter is added or removed from an unstressed surface, the energy alteration analogous to (iv) is of second order in  $\delta t$ , hence zero for our present purposes.)

We evaluate  $\delta F$  as if  $\gamma dA$  were invariant to strain and then explain briefly (relegating a detailed analysis to the Appendix) why the result is valid in general. Hence the contributions to  $\delta F$  arise from (i) and (ii) and are

$$\delta F = \int_A w \delta t dA + \int_A \gamma_s [ -(\kappa_1 + \kappa_2) \delta t ] dA \quad (3)$$

If we now write  $\delta t = \Omega \delta N$  and compare with Eq. (2), it is seen that

$$\mu = w \Omega - \gamma_s (\kappa_1 + \kappa_2) \Omega \quad (4)$$

on a cavity surface. This expression is the same as that given by Herring, except that the strain-energy term which he neglects is now included, as long as it is understood that  $w$ ,  $\Omega$ ,  $\gamma_s$ , and the  $\kappa$ 's are referenced to the current deformed state where matter is added.

Now the generally untenable assumption that  $\gamma dA$  is invariant to surface strain is discarded and  $\delta F$  is calculated. Steps (i) and (ii) are first accomplished, while applying whatever system of (workless) forces is necessary to prevent occurrence of the surface strains  $\delta \epsilon_{\alpha\beta}$

and displacements  $\delta u_i$ . This procedure gives a  $\delta F$  exactly as in Eq. (3) and the net additional  $\delta F$ , associated with steps (iii) and (iv), is merely minus the work of removing this additional set of forces. But the final state of the system is one of elastic (as opposed to compositional, or surface shape) equilibrium, and at this state  $F$  is stationary with respect to elastic distortions. Hence, the net work of removing the set of constraining forces is a second-order quantity in  $\delta t$ , and the net contribution of (iii) and (iv) to  $\delta F$  is therefore zero to the first-order terms of interest. Hence Eq. (3) and, particularly, Eq. (4) for  $\mu$  are generally valid. A fuller analysis, necessarily of some mathematical complexity, is given in the Appendix. It is shown there that, when surface tensions exist,  $\delta F_e$  and  $\delta F_s$  separately contain terms of first order in  $\delta t$  (in addition to those already listed in Eq. (3)) but these terms are of opposite sign and cancel when  $\delta F = \delta F_e + \delta F_s$  is formed.

Throughout the body of the paper, derivations are often simplified by neglecting surface tension and the variation of  $\gamma dA$  with surface strain. The final results in each case are valid without these assumptions, if the terms are properly interpreted; details of complete derivations are given in the Appendix.

Consider now the addition of a matter layer  $\delta t$  to a flat grain boundary subject to tensile stress, again under conditions for which  $\delta W = 0$ . The layer must be given a strain energy appropriate for coherent fit and the boundary must be separated by the distance  $\delta t$  to allow the new matter, resulting in a change  $-\sigma \delta t dA$  of strain energy of the adjoining material, where  $\sigma$  is the normal stress ('true' stress, i.e. force per unit current area) acting on the grain boundary. Thus

$$\delta F = \int_A (w - \sigma) \delta t dA \quad (5)$$

and, writing  $\delta t = \Omega \delta N$ ,

$$\mu = w \Omega - \sigma \Omega \quad (6)$$

along a grain boundary. Again, this result agrees with Herring's, except that the strain-energy term is now included, so long as the terms are properly referenced to the current deformed state; the result remains valid when surface tension along the grain boundary and dependence of  $\gamma_b$  on strain are included (see Appendix).

Equation (6) emphasizes the necessity for care in defining quantities per unit volume or area of the deformed configuration. The difference between  $\sigma \Omega$  and  $\sigma \Omega_r$ , where  $\Omega_r$  is the value of  $\Omega$  in the unstressed reservoir, is itself of the same order as the strain-energy term  $w \Omega$  in Eq. (6). If, instead,  $\hat{w}$  is the strain energy per unit volume as measured in the unstressed state and  $\hat{\sigma}$  and  $\hat{\gamma}_s$  are, respectively, force and surface energy per unit area of the unstressed state (so that  $\hat{\sigma}$  is a 'nominal' stress), then it is straightforward to show that Eqs. (4) and (6) are modified to

$$\mu = \hat{w} \Omega_r - \hat{\gamma}_s (1 + \varepsilon_n) (\kappa_1 + \kappa_2) \Omega_r \quad (4a)$$

on the cavity surface and

$$\mu = \hat{w} \Omega_r - \hat{\sigma} (1 + \varepsilon_n) \Omega_r \quad (6a)$$

on the grain boundary, where  $\varepsilon_n$  is the strain of adjoining material elements in the direction normal to the surface being considered. Obviously,  $\hat{\sigma} \varepsilon_n$  is of the same order as  $\hat{w}$ , and hence great care is required in discussing the effect of strain-energy contributions to the chemical potentials.<sup>11,12,19,20</sup> Similar remarks apply to Eq. (4a) since  $\kappa_1 \gamma_s$  is generally of the same order as  $\sigma$  at a cavity tip (see below).

In a material capable of matter transport by diffusion,  $\mu$  must be continuous at the cavity apex where it meets the grain boundary; otherwise, an unbounded matter flux would result there. Hence, when the strain energy terms are negligible

$$\gamma_s (\kappa_1 + \kappa_2) = \sigma_0 \quad (7)$$

where  $\kappa_1$ ,  $\kappa_2$ , and  $\sigma_0$  are, respectively, the cavity surface curvatures as the apex is approached along the cavity walls and the grain-boundary normal stress as the apex is approached. Using this formula as an approximate estimate of stress near the apex, the relative importance of the strain-energy terms can be estimated. For simplicity, consider cylindrical voids under plane strain conditions ( $\kappa_1 = \kappa$ ,  $\kappa_2 = 0$ ) and assume linear elasticity. Then

$$w \approx \frac{1 - \nu^2}{2E} \sigma_0^2 \approx \frac{\gamma_s \kappa_0}{2E} \gamma_s \kappa_0 \approx \frac{b}{50 \rho_0} \gamma_s \kappa_0 \quad (8)$$

where  $b$  is the lattice spacing,  $\rho_0 = 1/\kappa_0$  is the radius of curvature of the cavity wall at the apex, and we use the estimate  $\gamma_s \approx Eb/25$ . Since  $\rho_0$  typically has values of 50 to 5000 $b$  (i.e. 10 nm to 1  $\mu$ m), the strain-energy term is negligible.

However, this result occurs because of the mobility of matter in the circumstances considered. Surface diffusion allows large values of  $\rho_0$  to be attained (e.g. compared to that for a flat Griffith crack). Also, misfit stresses induced by matter flow into the grain boundary effectively thicken the boundary near the tip, alleviating the stress concentration normally associated with cracks or cavities. Very different conclusions on the importance of  $w$  could arise when the cavity does not lie along, or itself constitute, a high-diffusivity path.

These latter circumstances seem to coincide with those assumed by Stevens and Dutton<sup>11</sup> and Dutton and Puls<sup>20</sup> for the diffusive growth of Griffith cracks and, at this point, it is interesting to compare the directions of matter flow in the proposed models. As Dutton and coworkers remarked, in the case of their Griffith crack-extension model, the chemical potential at the tip region is very high due to high strain-energy density developed in this region, and they considered that the first term in Eq. (4) dominates. Hence, they assumed that the direction of diffusion is away from the tip along the cavity surface. However, in the present model, based on the Hull-Rimmer model and its generalizations, misfit stress is induced and greatly reduces the stress concentration associated with a notch so that the second term of Eq. (4) dominates. The chemical potential at the cavity surface far from the tip is higher than at the tip region and the flow is then reversed toward the tip and into the grain boundary. Intuitively, this result must be true since in our model the grain boundary which lies ahead of the cavity tip is capable of accepting the matter previously diffused from the cavity surface, whereas in the Griffith model the cavity is regarded as being essentially the same as if it were located in a perfect crystal so that no sinks are available to accommodate the matter, and thus flow must carry atoms away from the tip. However, it remains an open question as to whether a full solution to the coupled equations of elasticity and diffusion would actually produce cavity growth in the narrow cracklike mode assumed in the Griffith model of Dutton and coworkers. Instead, it is possible that a full analysis would merely predict a rounding of the crack near its tip. In contrast, there are several complete solutions for modeling cavities along grain boundaries. These solutions predict growth, ultimately in a comparatively narrow cracklike mode,<sup>7,10,21</sup> but with negligible strain-energy terms at the tip as long as  $\rho_0 \gg b$ .

### III. Energy-Release Rate in Cavity Growth

In fracture-mechanics terminology, there is an energy-release rate associated with cavity growth. Since the published literature does not show total agreement, we examine here the computation of this rate and determine where the energy goes for diffusive crack growth. This computation is done with reference to a plane strain mode (i.e. cylindrical cavities or cracks) so that all works and energies are on a unit-thickness basis.

In the case of elastic-brittle crack growth without diffusion, as formulated within the Griffith context, an energy-release rate  $G$  is defined by

$$G \dot{a} = \dot{W} - \dot{F}_e \quad (9)$$

where  $a$  is crack length. Here it is customary to neglect surface-tension effects (whether they can be included consistently within a model for a mathematically sharp-tipped crack remains an open question), so that  $F_e$  is the ordinary strain energy of the cracked body, as computed from continuum elasticity theory, and  $G$  is given by the expression  $(1 - \nu^2) K^2 / E$  for an isotropic linear elastic solid. Further, in the Griffith model  $dF_s$  is written as  $(2\gamma_s - \gamma_b) da$  because, in an increment  $da$  of growth a length  $2da$  of the crack surface is created at the expense of length  $da$  of the grain boundary. Actually, this term should be written as  $(2\hat{\gamma}_s - \hat{\gamma}_b) d\hat{a}$ , where  $d\hat{a}$  is the growth increment as measured in comparison to some reference

configuration, and the  $\hat{\gamma}$ 's are based on the unit area of that configuration (the  $\hat{\gamma}$ 's are independent of surface strain when surface tensions vanish). Understanding the terms in this way gives, for the Griffith model of reversible crack growth,

$$dW = dF = dF_e + dF_s = dF_e + (2\gamma_s - \gamma_b)da \quad (10)$$

during growth, so that the required value of  $G$  is

$$G = 2\gamma_s - \gamma_b \quad (11)$$

It has been emphasized,<sup>22</sup> however, that the actual requirement of thermodynamics for quasi-static, isothermal crack growth should be phrased as the inequality  $\dot{W} \geq \dot{F}$  (i.e. the inequality assuring non-negative entropy production) which requires only that

$$\dot{W} - \dot{F} \equiv [G - (2\gamma_s - \gamma_b)]\dot{a} \geq 0 \quad (12)$$

for growth (or healing,  $\dot{a} < 0$ ), which is general enough to include lattice trapping with thermally activated growth at values of  $G$  which differ from Eq. (11). Here  $2\gamma_s - \gamma_b$  can be interpreted as the reversible work of pulling the interface apart against cohesive forces.

The formulation is rather different for the diffusive-growth process considered here, because there is no direct rupturing of cohesive bonds. It is assumed, consistent with procedures in the thermodynamics of diffusion, that  $\mu$  is defined as in Eqs. (4) and (6) during processes and that diffusive fluxes  $J$  are established on the cavity surface and grain boundary, such that  $J\partial\mu/\partial s < 0$ , where  $s$  is the arc length along the flow path. Consider a half-void of length  $a$  as in Fig. 1 and let  $\Gamma_b$  denote the grain interface and  $\Gamma_s$  the upper surface of the cavity. Then Eq. (2), which is regarded as an identity given the definitions of  $\mu$ , can be written with  $F = F_e + F_s$ , where

$$F_s = 2 \int_{\Gamma_s} \gamma_s ds + \int_{\Gamma_b} \gamma_b ds \quad (13)$$

and  $ds$  denotes an element of arc length. Hence, if an energy-release rate is defined as  $\dot{W} - \dot{F}_e$ , the rate is given by

$$\dot{W} - \dot{F}_e = \dot{F}_s - 2 \int_{\Gamma_s} \mu \dot{N} ds - \int_{\Gamma_b} \mu \dot{N} ds \quad (14)$$

Some rearrangements of this equation are useful. Note, however, that contrary to the case for Griffith cracks, the quantity like  $G$ , viz.  $(\dot{W} - \dot{F}_e)/\dot{a}$ , will not generally be simply a function of applied load and notch size but, as will be shown, will depend on details of the matter placement along the grain boundary. First, observing that  $J$  and  $\dot{N}$  are related by mass conservation,

$$\partial J / \partial s + \dot{N} = 0 \quad (15)$$

that  $\mu_s = \mu_b$ ,  $2J_s = J_b$  at the cavity apex, and that  $J$  vanishes at the left and right boundaries (the latter if the right boundary is a half-spacing between cavities), integration by parts leads to

$$\dot{W} - \dot{F}_e = \dot{F}_s + \left[ 2 \int_{\Gamma_s} (-J \partial \mu / \partial s) ds + \int_{\Gamma_b} (-J \partial \mu / \partial s) ds \right] \quad (16)$$

Hence the energy-release rate  $\dot{W} - \dot{F}_e$  supplies two terms, the first ( $\dot{F}_s$ ) being the energy which goes to cavity-surface creation and grain-boundary removal and the second being diffusive dissipation in the form of necessarily positive products  $(-J \partial \mu / \partial s)$ .

Next, elasticity theory shows that the rate of change in strain energy (calculated, e.g. as by Rice and Drucker,<sup>18</sup> Rice,<sup>23</sup> and Eshelby<sup>24</sup> when material is added or removed from surfaces) is

$$\dot{F}_e = 2 \int_{\Gamma_s} w \Omega \dot{N} ds + \int_{\Gamma_b} w \Omega \dot{N} ds + \dot{W} - \int_{\Gamma_b} \sigma \Omega \dot{N} ds \quad (17)$$

Here  $\Omega \dot{N}$  (generally positive on  $\Gamma_b$  and negative on  $\Gamma_s$ ) is the volumetric rate of matter addition per unit area or the rate of thickening  $i$ ; the first two terms represent the strain energy of the added matter and the last two the work of all applied tractions, both external and those  $(-\sigma)$  acting along the grain boundary. Equation (17) is written for the case when no surface tensions exist, consistent with Refs. 18, 23, and 24. The full form of the equation is given in the Appendix. We can also compute  $\dot{F}_s$ , where  $F_s$  is given by Eq.

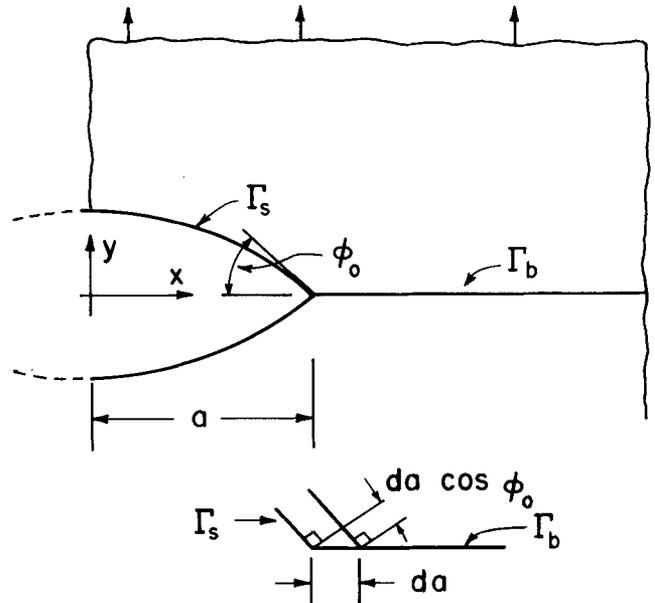


Fig. 1. Cylindrical void in grain boundary.

(13). Consistent with the neglect of surface tension in Eq. (17), in evaluating  $\dot{F}_s$  the effects of the surface strain rate  $\dot{\epsilon}$  on products of the form  $\gamma ds$  are neglected (again, see the Appendix for the full expression) and hence

$$\dot{F}_s = -2 \int_{\Gamma_s} \gamma_s \kappa \Omega \dot{N} ds + (2\gamma_s \cos \phi_0 - \gamma_b) \dot{a} \quad (18)$$

Here the integral represents the effect of adding matter at the rate  $i \equiv \Omega \dot{N}$  to the surface ( $i$  will generally be negative along  $\Gamma_s$  when the cavity is growing); as discussed earlier,  $-\kappa i ds = -\kappa \Omega \dot{N} ds$  is the rate of change of an arc  $ds$ , at a place where the curvature is  $\kappa$ , due to matter addition. The last term of Eq. (18) arises because the integral gives only the rate of change of  $F_s$  from matter addition (or removal) from the existing arc  $\Gamma_s$  but, as illustrated by the inset diagram in Fig. 1, it does not include the new surface element created during growth. As shown in the diagram, in cavity growth by  $da$  into the grain boundary, two arcs of length  $da \cos \phi_0$  ( $\phi_0$  is the angle between  $\Gamma_s$  and the negative  $x$  axis at the cavity tip) are added to the cavity surface and the grain boundary diminishes by  $da$ , thus leading to the last term of Eq. (18) for  $\dot{F}_s$ . The subscript "o" on this last term means that the  $\gamma$ 's refer to values at the cavity tip.

Summing Eqs. (17) and (18) gives

$$\dot{F} = \dot{F}_e + \dot{F}_s = \dot{W} + 2 \int_{\Gamma_s} (w - \gamma_s \kappa) \Omega \dot{N} ds + \int_{\Gamma_b} (w - \sigma) \Omega \dot{N} ds + (2\gamma_s \cos \phi_0 - \gamma_b) \dot{a} \quad (19)$$

and, as shown in the Appendix, this equation is correct generally, i.e. when surface tensions and associated dependences of products  $\gamma ds$  on surface strains are present. If surface tension  $\tau_s$  exists at the tip, the distribution of  $\sigma$  must be regarded as including a concentrated tension  $\tau_s \sin \phi_0$  at the tip in this formula and in Eqs. (23) and (24). As noted in the Appendix, however, there are grounds for arguing that  $\tau_s$  and  $\tau_b$  must vanish at the tip. If we now recall the definitions of  $\mu$  in Eqs. (4) and (6), recognizing that  $\kappa_1 = \kappa$ ,  $\kappa_2 = 0$  in the present case, and then compare Eqs. (14) and (19), we conclude that

$$(2\gamma_s \cos \phi_0 - \gamma_b)_o = 0 \quad (20a)$$

or

$$\cos \phi_0 = (\gamma_b / 2\gamma_s)_o \quad (20b)$$

during cavity growth. This expression is well known for the equilibrium angle  $\phi_0$  at the apex of a grain-boundary void. The same expression has generally been assumed to apply during growth; the

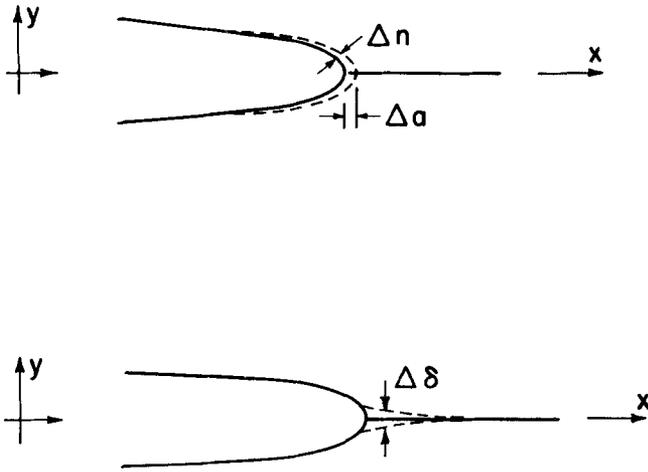


Fig. 2. Illustration of transfer of matter in diffusive cavity growth. In growth  $\Delta a$  a layer of local thickness  $\Delta n$  is removed from the cavity surface, and the grain boundary effectively thickens by a local amount  $\Delta \delta$  as a result of addition of matter.

present analysis provides a rationalization for this assumption.

On the other hand, Eq. (2), and hence Eq. (14), were assumed to apply as equalities during growth. If, instead, they were assumed to apply as inequalities in the form (notation of Eq. (2))

$$\dot{W} \geq \dot{F} - \int_A \mu \dot{N} dA \quad (21)$$

to allow for some form of entropy production at the cavity tip in addition to the diffusive entropy production ( $-J \partial \mu / \partial s$ ) already exhibited, e.g. in Eq. (16), then combining Eq. (14), with  $=$  replaced by  $\geq$ , and Eq. (19) (which remains valid as an equality) leads to

$$(2\gamma_s \cos \phi_0 - \gamma_b) \dot{a} \leq 0 \quad (22)$$

This inequality will be satisfied during cavity growth (i.e. when  $\dot{a} > 0$ ) only if  $\cos \phi_0 \leq (\gamma_b / 2\gamma_s)_0$ , that is, only if  $\phi_0$  is greater than or equal to the angle given by the equilibrium expression. During cavity shrinkage (i.e. sintering) it will be satisfied only if  $\phi_0$  is less than or equal to the result of the equilibrium expression. Consequences of the inequality version of the second law of thermodynamics are perhaps not often surprising but this case seems to be an exception. It might be expected that, because the cavity advances by the drawing-in of material to the grain boundary at the cavity apex, under action of applied stress,  $\phi_0$  might decrease from the value given by the equilibrium expression as  $\dot{a}$  increases from zero, and conversely. But thermodynamics prohibits this action. If there is to be any deviation from the equilibrium expression, it must be in the opposite sense. In these circumstances, it seems reasonable to assume that  $\phi_0$  always retains the value given by the relation for equilibrium and, as shown by Eq. (20), this assumption must necessarily be the case if the cavity apex does not constitute a "point source" of entropy production. We have been careful to use the phrasing "angle given by the equilibrium expression" rather than "equilibrium angle" in this discussion. For example, due to the dependence of the  $\gamma$ 's on surface strain it is possible that the angle  $\phi_0$  given by the equilibrium expression in a stressed solid would differ from the corresponding angle  $\phi_0$  in an unstressed solid.

As a final expression for the energy-release rate, which is perhaps most revealing in comparing different models, we may rearrange Eq. (17), which retains validity regardless of whether Eq. (21) is regarded as an equality or inequality, to read

$$\dot{W} - \dot{F}_e = \left[ 2 \int_{\Gamma_s} w(-\Omega \dot{N}) ds - \int_{\Gamma_b} w \Omega \dot{N} ds \right] + \int_{\Gamma_b} \sigma \Omega \dot{N} ds \quad (23)$$

(Since Eq. (17) neglects surface-tension effects, so does this equation. However, we show in the Appendix that this equation and, hence, our subsequent discussion in this section remain valid if  $F_e$  is replaced by a new quantity  $F_e'$  which is, in fact, a more logical quantity to use in calculating an energy-release rate, as  $\dot{W} - \dot{F}_e'$ , when surface-tension effects exist. Also, as noted previously,  $\sigma$  then includes the concentrated tension  $\tau_s \sin \phi_0$  at the tip.) Equation (23) can be interpreted using Fig. 2 where, in growing the void by some infinitesimal increment  $\Delta a$ , material of local thickness  $\Delta n$  is removed from the notch surface and the grain boundary effectively thickens by an amount  $\Delta \delta$ . Hence

$$\Delta W - \Delta F_e = 2 \int_{\Gamma_s} w \Delta n ds - \int_{\Gamma_b} w \Delta \delta dx + \int_{\Gamma_b} \sigma \Delta \delta dx \quad (24)$$

and this equation clearly shows the difference between the Griffith-like model envisioned by Stevens and Dutton<sup>11</sup> and the misfit model. In the former case, there is assumed to be no (or negligible) opening  $\Delta \delta$  ahead of the crack, and all of the energy release goes to the first term of Eq. (24), representing strain energy of material diffused away from the highly stressed notch surface. As remarked, it remains to be demonstrated that a model of this type will actually lead to cavity growth. On the other hand, in the Hull-Rimmer model and its generalizations, high stresses are alleviated by the misfitting material which effectively thickens the grain boundary at the notch tip. As shown (Section II), in this case the  $w$  terms are negligible and all of the energy release goes to the last term of Eq. (24), which represents work done by local stresses in opening the grain boundary to accommodate the diffused matter.

It is tempting to regard the left side of Eq. (24) as being  $G \Delta a$ , where  $G = (1 - \nu^2) K^2 / E$  is the usual energy-release rate of linear elastic fracture mechanics. However, this application is valid only in special cases, considered by Chuang,<sup>21</sup> of essentially steady-state growth in which the creep cavity is thin (i.e. cracklike in shape and in which all effective thickening of the grain boundary is limited to very near the void tip, with the diffused matter being accommodated by elastic distortion of the adjoining grains. In such cases Chuang shows, by developing numerically an explicit solution to the coupled (linearized) equations of elasticity and diffusion, that the  $G$  level to drive the void is always greater than the Griffith level of Eq. (11). Indeed, this is required by general considerations embodied in Eq. (16) (in which we may set  $\dot{F}_s = (2\gamma_s - \gamma_b) \dot{a}$  for the present case), since  $(-J \partial \mu / \partial s)$  is necessarily positive. Chuang's analysis suggests that  $K$  can never fall below  $\approx 1.7$  times the Griffith value and, by applying the  $J$ -integral,<sup>23-25</sup> he derived an equation analogous to Eq. (24), neglecting the  $w$  terms, and demonstrated that his numerical results for  $\sigma(x)$  and  $\delta(x)$  closely satisfied this equation.

#### IV. Total Energy Change due to Introducing a Cavity\*

Stevens and Dutton<sup>11</sup> considered the total energy change  $\Delta E$  due to introducing a cavity into a stressed body. In our notation  $E = F - W$ , where the external loads are assumed to be fixed so that  $W$  varies in proportion to the displacement of the loaded boundary. Following their classification, with slight modifications,  $\Delta E$  includes contributions from the following four sources (completely neglecting surface-tension effects): (1) change of energy due to void surface area introduced and lost grain-boundary area ( $\Delta F_s$ ), (2) elastic strain-energy change ( $\Delta F_e$ ) due to removal of material from the body to form a void, (3) work done by external loads ( $\Delta \bar{W}$ ) during removal of material, and (4) work done in processes of local matter rearrangement, such as by local stress fields when the matter removed from the void is deposited at the grain boundary ( $W'$ ). (All other possible sources such as dislocation, slip, etc. are neglected.) It is important to note, as was not emphasized by Stevens and Dutton, that the  $\Delta \bar{F}_e$  and  $\Delta \bar{W}$  terms calculated in steps (2) and (3) are not the total terms  $\Delta F_e$  and  $\Delta W$  (which, for example,

\*This section and Fig. 3 are based on a letter sent to R. Dutton in 1974 in response to his comments on Ref. 6.

enter into the energy release-rate expression). Both  $\Delta F_e$  and  $\Delta W$  include a contribution from the work  $W'$  in step (4) and, typically, this is a very significant term. Indeed, the work  $W'$  is analogous to the effect of the  $\sigma$  term in Eq. (6) for  $\mu$  on a grain boundary; the part  $-\sigma\Omega\delta N$  of  $\mu\delta N$  in Eq. (2) is essentially a work of type  $W'$ ; its importance has been shown in Eq. (24).

With the preceding classification of terms, the total energy change is

$$\Delta E \equiv \Delta F_s + \Delta F_e - \Delta W = \Delta F_s + \Delta \bar{F}_e - \Delta \bar{W} + W' \quad (25)$$

In fact, the specific terms  $\Delta \bar{F}_e$ ,  $\Delta \bar{W}$ , and  $W'$  depend on the sequence of operations and are different if matter (e.g. from a reservoir) is first inserted into the grain boundary, then an equivalent amount of matter is removed from the body to form the void and placed in the reservoir. The total effect,  $\Delta F_e - \Delta W$ , which these terms represent, is independent of sequence.

Consider a small elliptical cylindrical void lying along a grain boundary, as illustrated in Fig. 3 with its major axis normal to the direction of the uniaxial applied stress  $\sigma_\infty$ . The energy change  $\Delta E$  of this configuration is computed by cutting out the "volume"  $V$  (actually, an area in the 2-D model), thus creating a void on the boundary, and temporarily depositing it in an unstressed-matter reservoir. This operation produces the free energy changes  $\Delta F_s$ ,  $\Delta \bar{F}_e$ , and  $\Delta \bar{W}$ , where<sup>23</sup>

$$\Delta \bar{F}_e - \Delta \bar{W} = -[\pi(1-\nu^2)\sigma_\infty^2 a^2/E](1+d/2a) \quad (26)$$

The volume  $V$  is then removed from the reservoir and inserted into the grain boundary, thus adding a nonuniform layer of material of local thickness  $\delta$ , such that

$$\int_{\text{grain boundary}} \delta(x) dx = V = \pi ad \quad (27)$$

To obtain the  $W'$  term, the work done during the insertion process is calculated. This work includes that done on the surrounding material, plus that necessary to bring the strain energy of the material being inserted to the proper level. Let  $\sigma^a(x)$  be the normal tensile stress of an Inglis-type stress distribution induced by  $\sigma_\infty$  and let  $\sigma^b(x)$  be the final total stress that results after the matter  $V$  has been stuffed into the grain boundary. To compute  $W'$ , the grain boundary is cut, held in place by applying  $\sigma^a$ , and the stresses are quasi-statically altered until the cut has opened locally by  $\delta(x)$  (at which point the grain boundary stresses are  $\sigma^b(x)$ ). The  $W'$  is simply the (negative) work done on the surface of the cut during this operation and, assuming that the material is linearly elastic,

$$W' = -1/2 \int_{\text{grain boundary}} (\sigma^a + \sigma^b) \delta dx \quad (28)$$

The material  $V$  that is inserted into the opened cut must be stressed and thus there will be an additional part of  $W'$  related to the strain-energy increase in the inserted volume  $V$  at state (b) but this portion is insignificant when  $\sigma^b$  is small compared to  $E$ . Still, if  $\sigma^b$  is of the order of  $\sigma_\infty$  over the region where the matter is added, the term is of the order  $\pi(1-\nu^2)\sigma_\infty^2 ad/2E$ , which is of the same order as  $\Delta \bar{F}_e - \Delta \bar{W}$  of Eq. (26), unless  $d/a \ll 1$ .

There are two observations concerning  $W'$ . First, it is usually far larger than  $\Delta \bar{F}_e - \Delta \bar{W}$  and hence cannot be neglected. Suppose, for example, that the material is added uniformly over the entire grain boundary, so that  $\sigma^b = \sigma^a$  and both have average values of  $\sigma_\infty$ . Then

$$\begin{aligned} W' &= -\sigma_\infty V = -\sigma_\infty \pi ad \\ &= (\Delta \bar{F}_e - \Delta \bar{W})(E/(1-\nu^2)\sigma_\infty)(d/a)/(1+d/2a) \end{aligned} \quad (29)$$

and the factor multiplying  $(\Delta \bar{F}_e - \Delta \bar{W})$  will be much greater than unity unless  $d/a$  is of the same order as  $\sigma_\infty/E$ . Second, there is no unique value for  $W'$ ; it depends on how the matter is inserted. For example, concentration of the matter along a limited segment of the grain boundary could make  $\sigma^b$  large and negative there, so much so that  $W'$  could become positive (and indefinitely large). Also, adding matter only over the highly stressed portions of the grain boundary, so as to reduce  $\sigma^b$  to negligible values there, would produce a different expression for  $W'$  than Eq. (29). Since  $W'$  is not unique,

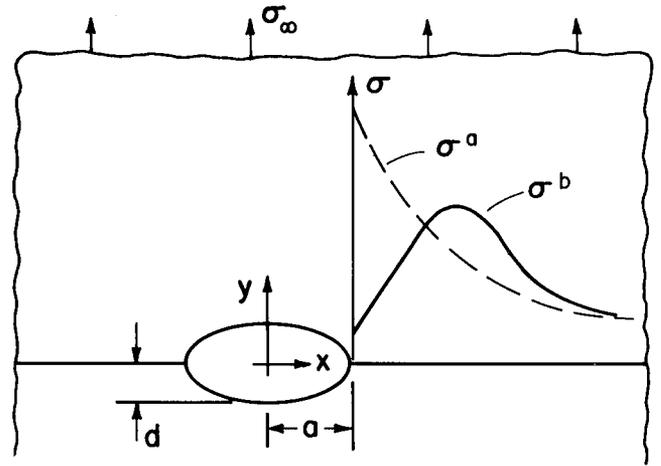


Fig. 3. Elliptical cavity in a linear elastic material;  $\sigma^a$  is the grain-boundary tensile stress when there is no matter placement in the grain boundary and  $\sigma^b$  results after placement.

neither are the terms  $\Delta F_e$  and  $\Delta W$  and, hence, neither is the net energy change  $\Delta E$ . Unique values result only for a given  $\delta(x)$ . In this sense, it is meaningless to talk about an energy-release rate (except in the limiting case of steady-state cracklike cavity growth (Section III)) unless it is understood that the distribution  $\delta(x)$  is determined by the coupled equations of elasticity and diffusion as part of the analysis.

## V. Discussion

Dutton and Puls,<sup>20</sup> commenting on the formulation presented by Charles,<sup>19</sup> equated the crack-extension force to the elastic fracture-mechanics strain-energy release rate  $G = (1-\nu^2)K^2/E$ . As indicated, the usual fracture-mechanics expressions are valid only in special circumstances. Essentially, their arguments were based on a Griffith-like crack model and treated the strain-energy term in Eq. (24) as dominant. We have pointed out, however, that when a crack is located in a grain boundary rather than in a perfect matrix, the grain boundary can accommodate the material being removed from the crack surface and thus relax the high stress concentration ahead of the crack tip. Hence the strain-energy contribution appears to be minor in the energy-release expression and the major portion comes from the work done by the boundary stress  $\sigma$  on the opening  $\Delta\delta$  as it appears in the last term of Eq. (24). Charles<sup>26</sup> noted in his reply that he believes that the "PV" work of insertion of a diffusible species in a highly stressed volume dominates in the stress rupture process, although he did not provide a full analysis as we do here.

Speight *et al.*<sup>8</sup> presented an intergranular crack-growth model based on the mechanisms discussed here. Rather than relying on a full solution of relevant equations, as by Chuang<sup>21</sup> and Vitek,<sup>7</sup> they imposed an approximate distribution  $\delta$  (see Eq. (1) of Ref. 8) to solve for the maximum stress in the grain boundary. Further, they attributed the energy-release rate to the "plastic work" done by  $\sigma_\infty$  on the crack volume ( $W' = -\sigma_\infty V$ ) as in Eq. (29). But we have shown that the work term  $W'$  depends on the distribution of  $\delta$  and their formulation does not appear to be fully consistent in this respect, although it is not clear how critically these assumptions affect their conclusions.

## VI. Conclusions

Precise expressions have been presented for chemical potentials on grain boundaries and free surfaces; in representative cases, the strain-energy contributions to these expressions are negligible for the diffusive growth of grain-boundary cavities. This result occurs because surface diffusion tends to round out a cavity near its tip and

grain-boundary diffusion generates misfit stresses to alleviate its stress concentration, reducing local stresses to the order of  $\gamma_s/\rho_0$ . An evaluation of expressions for the energy-release rate in diffusive cavity growth shows that the major energy sink is provided by the work of normal stresses on the grain boundary, as it is effectively thickened by matter addition, and not from the loss of strain energy of material diffused from the cavity tip. We discussed the computation of net energy changes associated with introduction of cavities and pointed out that the dominant term is dependent on details of the matter placement along the grain boundary. We also commented on restrictions placed by thermodynamics on the angle formed by cavity walls where they join the grain boundary.

## APPENDIX

### Surface-Tension Effects

At various points throughout the paper, surface-tension (or surface-stress) effects were ignored for ease of presentation, with reference to the Appendix. Let  $\theta^1$  and  $\theta^2$  be curvilinear coordinates in a surface (cavity surface, grain boundary) in some arbitrary reference configuration, and let  $g^{\alpha\beta}$  be the surface metric tensor ( $\alpha, \beta = 1, 2$ ) in this configuration. If the coordinate lines are regarded as being scribed onto the surface, in an elastic deformation the coordinates are convected and the metric tensor changes to  $g_{\alpha\beta}$ . The (covariant) components of strain are defined as

$$\varepsilon_{\alpha\beta} = (g_{\alpha\beta} - g^0_{\alpha\beta})/2 \quad (\text{A-1})$$

The contravariant components (on the convected coordinates)  $\tau^{\alpha\beta}$  of the surface-tension tensor are defined such that  $\tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA$  is the work of incremental elastic distortion  $\delta\varepsilon_{\alpha\beta}$  of an area  $dA$ . Since  $\gamma dA$  is the surface energy,

$$\tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA = \delta(\gamma dA) = \delta\gamma dA + \gamma g^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA \quad (\text{A-2})$$

where the  $g^{\alpha\beta}$ 's are the contravariant components of the metric, we obtain the well-known relation between surface tension and surface energy<sup>15,16,27</sup>

$$\tau^{\alpha\beta} = (\partial\gamma/\partial\varepsilon_{\alpha\beta}) + \gamma g^{\alpha\beta} \quad (\text{A-3})$$

which is valid for arbitrary deformation. Note that if  $\hat{\gamma}$  is defined by  $\hat{\gamma}dA_0 = \gamma dA$ , where  $dA_0$  is the area of the considered element in the reference configuration, then

$$\tau^{\alpha\beta} = (dA_0/dA)(\partial\hat{\gamma}/\partial\varepsilon_{\alpha\beta}) \quad (\text{A-4})$$

(For readers unfamiliar with curvilinear tensors: If the coordinate lines are locally orthogonal at the point considered and normalized so that  $d\theta^1$  and  $d\theta^2$  are equal to the associated changes in arc length along the surface, then  $g^{\alpha\beta}$  of Eqs. (A-2) and (A-3) is just the Kronecker tensor and  $\tau^{\alpha\beta}$  is the force acting in the  $\beta$  direction per unit length of a cut along the surface with outward normal in the  $\alpha$  direction. Also, when the reference configuration differs by an infinitesimal amount from the current configuration,  $\varepsilon_{\alpha\beta}$  is merely the classical strain tensor.)

Mechanical equilibrium equations for  $\tau^{\alpha\beta}$  are complicated<sup>28</sup> but it is known that the field equations of equilibrium are fully implied by the principle of virtual work, which is most convenient for our purposes. Let  $A$  denote a region of cavity surface with bounding contour  $C$ , let  $n_i$  be components (in 3-D space) of the outward normal to  $A$  (i.e. pointing away from the adjacent material), let  $\sigma^{ij}$  be the stress tensor acting immediately beneath the surface (Latin indices  $i, j$  have the range 1 to 3), and let  $T^\alpha$  be components of the surface tension acting normal to  $C$ . Hence the surface may be considered as a membrane loaded with forces per unit area  $-n_i\sigma^{ij}$  on  $A$  and forces per unit length  $T^\alpha$  along  $C$ . The principle of virtual work then requires that

$$\int_A \tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA = \int_C T^\alpha\delta u_\alpha dC - \int_A n_i\sigma^{ij}\delta u_j dA \quad (\text{A-5})$$

for arbitrary virtual displacement fields  $\delta u_i$  and associated virtual

surface strains  $\delta\varepsilon_{\alpha\beta}$ . Some well-known consequences are, for example, that

$$T^\beta = m_\alpha\tau^{\alpha\beta} \quad \tau^{\alpha\beta}\kappa_{\alpha\beta} = n_i\sigma^{ij}n_j \quad (\text{A-6})$$

where  $m_\alpha$  denotes the outward normal (in the tangent plane of the surface) to  $C$ , and  $\kappa_{\alpha\beta}$  is the surface-curvature tensor.

An equation identical to (A-5) can be written for an arbitrary area  $A$  of the grain boundary, where  $\tau^{\alpha\beta}$  and  $T^\alpha$  are tensions in the grain boundary, but now the integral involving  $\sigma^{ij}$  must be carried out over both sides of the grain boundary. Observe that when the grain boundary is flat, as considered here, the normal components of  $\sigma^{ij}$  are equal on both sides (and identical to  $\sigma$ ). This observation means that, for grain boundaries, we can write  $n_i\sigma^{ij}\delta u_j$  as  $n_i\sigma^{i\alpha}\delta u_\alpha$  where  $\delta u_\alpha$  are components of  $\delta u_i$  parallel to the boundary and  $\sigma^{i\alpha}$  are shear stresses in the immediately adjacent material. Observe that for symmetrically loaded boundaries, as in Figs. 1 to 3,  $\sigma^{i\alpha}$  will reverse sign on crossing the boundary and  $\sigma^{i\alpha}$  is generally nonzero whenever the surface tensions in the boundary are nonuniform.

To calculate  $\mu$  (Section II),  $\delta F$  was calculated when a layer of local thickness  $\delta t$  was added to cavity surfaces and/or grain boundaries, under conditions for which  $\delta W = 0$ . We write  $\delta F = \delta F_e + \delta F_s$  and observe that, when matter is added, there are associated displacements  $\delta u_i$  and strains  $\delta\varepsilon_{\alpha\beta}$  along  $A_s$  (the cavity surfaces) and  $A_b$  (the grain boundaries). The change in elastic strain energy is

$$\begin{aligned} \delta F_e = & \int_{A_s} w\delta t dA + \int_{A_b} w\delta t dA - \int_{A_b} \sigma\delta t dA \\ & + \int_{A_s} n_i\sigma^{ij}\delta u_j dA + \int_{A_b} n_i\sigma^{i\alpha}\delta u_\alpha dA \end{aligned} \quad (\text{A-7})$$

The first three terms were discussed in the body of the paper, the fourth corresponds to item (iv) in the list preceding Eq. (3), and the last three together give the change in strain energy of the material lying outside the added layers. The last integral on  $A_b$  covers both sides of the grain boundaries and it is noted that the normal stresses  $\sigma$  and shear stresses  $\sigma^{i\alpha}$  appear separately. Further, for symmetrically loaded grain boundaries,  $\delta u_\alpha$  is the same on both sides of the boundary. The change in  $F_s$  is

$$\begin{aligned} \delta F_s = & - \int_{A_s} \gamma_s(\kappa_1 + \kappa_2)\delta t dA + \int_{A_s} (\delta\gamma_s + \gamma_s g^{\alpha\beta}\delta\varepsilon_{\alpha\beta})dA \\ & + \int_{A_b} (\delta\gamma_b + \gamma_b g^{\alpha\beta}\delta\varepsilon_{\alpha\beta})dA \end{aligned} \quad (\text{A-8})$$

The first term was discussed in the body of the paper. The second two are contributions of type (iii) (preceding Eq. (3)), due to effects of elastic strain in changing  $\gamma$  by  $\delta\gamma$  and  $dA$  by  $g^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA$ . Using Eq. (A-2),

$$\begin{aligned} \delta F_s = & - \int_{A_s} \gamma_s(\kappa_1 + \kappa_2)\delta t dA + \int_{A_s} \tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA \\ & + \int_{A_b} \tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA \end{aligned} \quad (\text{A-9})$$

Mechanical equilibrium is expressed by the principle of virtual work in Eq. (A-5). We may write this equation separately for the grain boundaries and the cavities, taking  $C$  to be the arc where the two make contact. Summing these equations, we observe that contributions on  $C$  cancel (because of mechanical equilibrium between  $\tau_s$  and  $\tau_b$  at the cavity tip,  $2\tau_s \cos\phi_0 = \tau_b$ ) if there is a unique displacement  $\delta u_i$  at the tip. On the other hand, if there is matter addition  $\delta t (= \Omega\delta N)$  to the grain boundary at the tip, so that the vertical components  $\tau_s \sin\phi_0$  of  $\tau_s$  separate by  $\delta t$ , the sum of the two terms involving  $C$  is  $-\int_C \tau_s \sin\phi_0 \delta t dC$ . Hence the resulting "grand" form of the principle of virtual work is

$$\begin{aligned} \int_{A_s} \tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA + \int_{A_b} \tau^{\alpha\beta}\delta\varepsilon_{\alpha\beta}dA = & \int_C \tau_s \sin\phi_0 \delta t dC \\ & - \int_{A_s} n_i\sigma^{ij}\delta u_j dA - \int_{A_b} n_i\sigma^{i\alpha}\delta u_\alpha dA \end{aligned} \quad (\text{A-10})$$

where the last integral covers both sides of  $A_b$ . Since the actual field  $\delta u_i$ ,  $\delta \varepsilon_{\alpha\beta}$  associated with matter addition involves continuity of  $\delta u_\alpha$  across  $A_b$ , it can be taken as the field to be entered in this form of the virtual work equation. Now, when we sum Eqs. (A-7) and (A-9), to write  $\delta F = \delta F_e + \delta F_s$ , we find that because of Eq. (A-10), all the terms involving  $\tau^{\alpha\beta}$ ,  $\sigma^{ij}$ , and  $\sigma^{i\alpha}$  cancel one another. Hence

$$\delta F = \delta F_e + \delta F_s = \int_{A_s} [w - \gamma_s(\kappa_1 + \kappa_2)] \delta t \, dA + \int_{A_b} (w - \sigma) \delta t \, dA \quad (A-11)$$

where here, and in Eq. (A-16), for simplicity in the presentation of formulas, the integral involving  $\sigma$  is understood to include a "delta function" contribution to  $\sigma$  at the cavity tip due to the vertical component of concentrated tension,  $\tau_s \sin \phi_0$ , acting there.

Thus, if we write  $\delta t = \Omega \delta N$  and observe that  $\mu$  is defined by

$$\delta F = \int_{A_s} \mu \delta N \, dA + \int_{A_b} \mu \delta N \, dA \quad (A-12)$$

(in the case considered of matter addition under conditions for which  $\delta W = 0$ ), then we obtain at once Eqs. (4) and (6) in the body of the paper for  $\mu$ . Thus we see that, although the terms associated with  $\delta u_i$  and  $\delta \varepsilon_{\alpha\beta}$  make first-order contributions to  $\delta F_e$  and  $\delta F_s$  separately, they make only higher-order contributions to the total  $\delta F$ . There is, however, a curious result at the tip. Because  $\sigma$  has the delta-function contribution there, of integrated intensity  $\tau_s \sin \phi_0$ , we must conclude that  $\mu$  has a similar negatively infinite delta function form of integrated intensity  $-\tau_s \sin \phi_0 \Omega$  at the tip. We leave open the full interpretation of this conclusion. Certainly, to the extent that thermodynamics requires continuity of  $\mu$ , such a condition can be met only if the material adjusts its state of surface strain at the tip of a manner such that  $\tau_s$  (and hence  $\tau_b$ ) vanishes there.

In the discussion of plane strain growth of a cylindrical cavity, surface-tension effects were ignored in deriving Eqs. (17) and (18). Now we can drop indices on  $\tau^{\alpha\beta}$  and  $\varepsilon_{\alpha\beta}$ , writing  $\tau$  and  $\varepsilon$  for the components in the plane of deformation. With the previous discussion as background, the full version of Eq. (17) is readily seen to be

$$\dot{F}_e = 2 \int_{\Gamma_s} w \Omega \dot{N} \, ds + \int_{\Gamma_b} w \Omega \dot{N} \, ds + \dot{W} - \int_{\Gamma_b} \sigma \Omega \dot{N} \, ds + 2 \int_{\Gamma_s} n_i \sigma^{ij} \dot{u}_j \, ds + \int_{\Gamma_b} n_i \sigma^{ix} \dot{u}_x \, ds \quad (A-13)$$

where the integral on  $\Gamma_b$  covers both sides of the grain boundary and, as in Figs. 1 to 3, the  $x$  direction is parallel to the grain boundary. Here  $i$  and  $j$  range over  $x$  and  $y$ . Similarly, the full version of Eq. (18) is:

$$\dot{F}_s = - 2 \int_{\Gamma_s} \gamma_s \kappa \Omega \dot{N} \, ds + (2\gamma_s \cos \phi_0 - \gamma_b) \dot{a} + 2 \int_{\Gamma_s} \tau \varepsilon \, ds + \int_{\Gamma_b} \tau \varepsilon \, ds \quad (A-14)$$

Again, a grand form of the principle of virtual work may be written, analogous to (A-10):

$$2 \int_{\Gamma_s} \tau \delta \varepsilon \, ds + \int_{\Gamma_b} \tau \delta \varepsilon \, ds = - (\tau_s \sin \phi_0 \delta t)_0 - 2 \int_{\Gamma_s} n_i \sigma^{ij} \delta u_j \, ds - \int_{\Gamma_b} n_i \sigma^{ix} \delta u_x \, ds \quad (A-15)$$

Thus, when Eqs. (A-13) and (A-14) are added together the terms multiplying  $\dot{\varepsilon}$  and  $\dot{u}_i$  cancel and we obtain Eq. (19) in the body of the paper (which we remarked there to be valid in the general case when surface-tension effects exist, as long as  $\sigma$  is taken to include the concentrated tension at the tip—if, indeed, this is nonzero).

Finally, if Eq. (A-15) is used in (A-13), and then (A-13) is rearranged to the form of Eq. (23) in the body of the paper, we obtain

$$\dot{W} - \dot{F}_e' = \left[ 2 \int_{\Gamma_s} w(-\Omega \dot{N}) \, ds - \int_{\Gamma_b} w \Omega \dot{N} \, ds \right] + \int_{\Gamma_b} \sigma \Omega \dot{N} \, ds \quad (A-16)$$

(i.e. the same right side as Eq. (23)) if we define

$$\dot{F}_e' = \dot{F}_e + 2 \int_{\Gamma_s} \tau \dot{\varepsilon} \, ds + \int_{\Gamma_b} \tau \dot{\varepsilon} \, ds \quad (A-17)$$

When we recall that  $\dot{F}_e'$  can be written as the integral over the volume of the body of stress components times corresponding components of strain rate, these added terms seem to be appropriate and  $\dot{W} - \dot{F}_e'$  seems to be the obvious extension of the concept of an energy-release rate to cases in which surface tensions exist during cavity growth.

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