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An atomistic model of kinetic crack growth in brittle solids

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A general theory of kinetic crack growth in ideally brittle solids is developed from first principles. In setting up a basic model, emphasis is placed on the essential need to provide for the existence of an energy barrier to activated, non-linear crack motions at the atomic level. The picture is presented of an ideally brittle fracture crack in which sequential bond rupture occurs via the lateral motion of atomic kinks along the crack front. Approximate solutions to the equations of kink motion are then obtained from the discrete, "lattice trapping" theory of Thomson and co-workers. Assuming a classical distribution of kink sites, an expression for the steady-state crack velocity follows. A feature of the present theory is the formulation in terms of the fundamental energy-balance concept of Griffith, with two major advantages: in the first place, standard fracture-mechanics parameters, such as the mechanical-energy-release rate and the fracture-surface energy, enter into the description in a natural manner; in the second, the effect of extrinsic agents on activated kink motion is readily accountable, through a simple modification of the total energy function for the crack system. To illustrate the model, the case of a slowly growing brittle crack in the presence of an interacting ideal gas environment is treated in some detail.

1. Introduction

A large number of solids, of varying degrees of brittleness, are now known to exhibit the phenomenon of "kinetic", or "slow", crack growth. By slow, it is meant that the crack velocity is small (typically < 1 m sec^{-1}) compared with dynamic values (typically $\approx 10^3$ m sec^{-1}). Generally, it is found that the rate of slow growth tends to be highly sensitive to such variables as temperature, applied load, concentration of chemical environment, etc., suggesting a thermally activated process. The practical manifestations of this type of time-dependent process in engineering materials [1] have a vital bearing in "fail-safe" design of structural components; the very real possibility of a critical crack developing from a seemingly harmless flaw over an extended period of time has often been demonstrated in all too spectacular fashion. Yet despite a wealth of accumulated empirical data the fundamental nature of the mechanisms of rupture at the crack tip remains relatively unexplored, and it is only recently that a trend toward systematic studies of "model" fracture systems has emerged; the work of Wiederhorn and colleagues on the fracture behaviour of silica glasses and other ceramics in the presence of water environments [2] is worthy of mention as a step in this direction.

Perhaps the greatest obstacle to the understanding of kinetic fracture processes has been the lack of a satisfactory theoretical basis for describing crack-tip events at the atomic or molecular level. For the growth of any crack inevitably involves the rupture of cohesive bonds, and this necessarily implies a departure from linearity in the force-separation response of the solid. That is, crack growth is fundamentally a non-linear problem, for which a general analytical treatment is out of the question. Several simplistic crack-tip models have evolved over the years in an attempt to circumvent this difficulty, but it is only within the last half-decade that the calculations have reached the degree of refinement needed to predict the one feature essential to thermally activated crack growth, namely a periodically varying energy barrier. Notable among the more advanced

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models are those based on simple, discrete "lattice" representations of the solid, developed quasianalytically by Thomson and co-workers, and those based on "realistic" atomic structures, handled by computer simulation (for reviews, see [3, 4]). Bascially, one arrives at the following picture of an *ideally brittle fracture*:

(i) The crack is in thermodynamic, or "Griffith", equilibrium when, for a virtual increment in area, the work done by applied forces transmitted to the tip just balances the increase in reversible surface energy [5]. The "surface energy" may correspond to the intrinsic value for the solid, or to a reduced, interfacial value for the solid in contact with a chemical environment [6].

(ii) The crack advances or retreats from its equilibrium configuration by the sequential rupture of cohesive bonds across a well-defined plane. Associated with each atomic-scale jump is an energy barrier, i.e. the crack is "lattice-trapped", which effectively increases the "forward cleavage" surface energy [7, 8].

(iii) The crack profile is most realistically represented by a narrowing slit terminated by a line of bonds close to the rupture point [9]. The crack front itself contains "kinks", which provide "active" sites for preferential bond rupture; the kinks accordingly undergo lateral displacements along the crack front, and thereby facilitate crack growth [8].

(iv) The atomic motions of the kinks are enhanced by thermal fluctuations [8].

In this view, the key step in kinetic fracture reduces to a one-dimensional problem in statistical mechanics.

The prime aim of the present treatment is to establish a general theoretical framework for describing slow crack growth in brittle solids, using the atomistic picture outlined above as an underlying basis. The important case of chemically-enhanced growth will be taken as a useful illustrative application of the model. One interesting conclusion that derives from the analysis of this particular case is that slow fracture may actually be stimulated by environments normally considered to be non-corrosive. Another important adjunct is the existence of subsidiary kinetic steps in the overall chemo-rupture process; under certain conditions one of these subsidiary steps may become rate-controlling. The basic predictions of the theoretical model will be shown to be in accord with the qualitative features of published crack-velocity data.

2. Kink model of crack front

2.1. Background considerations

In devising a crack-tip model for an ideally brittle solid, certain requirements need to be met: first, the proposed structure should be capable of sustaining the crack without plastic flow; second, the model should reconcile with the soundly-based energy-balance concept of Griffith [5]; and finally, the model should make provision for incorporating thermally assisted extrinsic effects (e.g. the chemical effects already mentioned).

We may deal with the first point briefly. Recent attempts at a first-principles approach to this problem address two different aspects of the following question: given an atomically sharp crack, under what structural conditions might a shear instability be expected to occur in the stress field of the tip? One approach involves calculating whether the theoretical strength of the solid in shear (favouring off-plane slip deformation) is likely to be exceeded before the theoretical strength in tension (favouring in-plane crack extension) [10]. The other approach involves calculating the energy barrier to dislocation emission from the crack tip once shear failure does occur [11]. Both types of calculation indicate that cracks may grow entirely free of plastic blunting in certain solids, particulary those with strong covalent and ionic bonding. This indication is indeed confirmed by computer exercises in the diamond-structure crystals [9]. Definitive experimental evidence on the question is lacking, but a careful electron microscopic study of thinned fracture specimens of sapphire revealed no evidence for plastic flow around residual fissures [12]. The notion of the atomically sharp cleavage crack accordingly assumes a central standing in any fundamental discussion of brittle fracture mechanisms [3].

Turning to the second point, it is essential that the cornerstone of Griffith's theory, the surface energy term, be implicit in the crack-tip model. The usual way of setting up the model is to subdivide the crack system into two hypothetical *zones*: the non-linear, separation processes are considered to operate exclusively within a relatively small, inner zone immediately surrounding the crack tip; the linear elastic material in the surrounding, outer zone then serves the function of a medium for transmitting the applied forces to the inner regions. For instance, Orowan [13] effectively assumed the non-linear zone to contain a single bond, and considered the rupture of this bond in terms of the stress concentration at the tip of an elastic notch of atomic radius; by matching adjustable parameters of an empirical force-separation characteristic to the intrinsic surface energy, he was able to derive a criterion for fracture identical in form to that of Griffith. Barenblatt [14], on the other hand, argued that the non-linear crack-tip zone must extend over several atomic spacings along the crack interface in order that the crack be induced to close smoothly into a cusp (thus avoiding singularities in the stress field solutions for the surrounding linear medium); the work of separating material at the crack tip is expressed in terms of a "modulus of cohesion", an integral over the crack plane of a smoothed-out distribution of cohesive "closure stresses", with the status of an intrinsic surface energy once more implied. This essential equivalence between the macroscopic and crack-tip theories has in fact been confirmed in a rigorous manner by Rice [15], using an elegant path-independent line-integral formulation to compare the energetics of crack extension at the different levels.

However, it is important here to be aware of subtle differences in the dependence of the total surface energy function on crack area in the Griffith energy balance. The two models above actually represent limiting cases of crack-tip behaviour: the Orowan model views growth as an accumulation of discrete, independent bond-popping events, with attendant stepwise jumps in the total surface energy function (each jump corresponding to the energy of one bond); the Barenblatt model views growth as more or less continuous from one bond to the next, with strict proportionality between total surface energy and crack area. Thus, differences in the modelling reflect in the *fine structure* of the total surface energy term. This is only to be expected, for the particular conditions prescribed for the non-linear zone boundary must surely exert a strong influence on the atomic motions of the crack. What is at issue here is not the common energy-balance link with the Griffith theory, but rather the means by which the balance itself is effected. It is in this context that the "lattice models", based on quasi-one- and two-dimensional representations of a cracked crystalline array, offer new insight into kinetic processes. With their inbuilt provision for treating crack growth as a sequence of *discrete yet mutually interacting* bond-rupture events, these models indicate that the appropriate total surface energy function should exhibit an atomically periodic, smoothly varying fine structure [7, 8]. In this way the energy barrier requirement is met, and at the same time the fundamental Griffith concept remains intact.

This preservation of the Griffith theme bears strongly on our final point; the energy-balance concept, rooted in the first law of thermodynamics, provides the flexibility for dealing with extrinsic fracture processes via the simple incorporation of new energy terms. At the crack-tip, or mechanistic, level the operation of any thermally assisted bond-rupture process implies the existence of atomically localized "active" sites along the crack front. For the thermal energy needed to activate crack growth must clearly increase with the size of the basic kinetic unit, thereby ruling out the possibility of a rigid forward motion of the entire front of a macroscopic crack. The energetically favoured configuration is that of the kink, where traversal over the energy barrier manifests itself as a mobility of the active site along the front in much the same fashion as in the analogous cases of the dislocation line and the crystal growth step.

2.2. Energetics of kink configuration

We are now in a position to establish a semi-quantitative model of a kinked crack front. We begin with a formal statement of the Griffith concept. The total energy of a quasistatic crack system may be written as the sum of all terms which are affected by crack formation,

$$U = (-W_L + U_E) + U_S, \tag{1}$$

where W_L is the work of applied forces, U_E is the elastic strain energy in the system, and U_S is the total surface energy. It can readily be demonstrated that the mechanical energy, consisting of the bracketed terms in Equation 1, must decrease as the crack extends, while the surface energy must increase, thereby maintaining the energy balance. This leads us to the "fracture mechanics" formulation, with C the crack area,

$$\frac{dU}{dC} = \frac{d(-W_L + U_E)}{dC} + \frac{dU_S}{dC} = -G + 2\Gamma, \tag{2}$$

where G is the mechanical-energy-release rate (or crack-extension force) and Γ is the fracture-surface energy. For Griffith equilibrium we have a stationary value in the total energy, that is

$$G = 2\Gamma\,. \tag{3}$$

If $\mathrm{d}U/\mathrm{d}C$ be made negative ($G > 2\Gamma$) the crack extends, if made positive ($G < 2\Gamma$) the crack retracts. The advantages of this particular formulation are two-fold: first, standard elastic continuum solutions for the G term have been tabulated for a wide variety of crack geometries; second, Γ can generally be regarded as a material constant (in the event that the work of creating the new crack surfaces contains no dissipative component, Γ reduces to the reversible surface energy γ).

Next we consider the lattice crack models [7, 8]. The approach here is to represent a crystal structure by an array of static point masses linked by stretchable and bendable springs. In the interest of mathematical tractability the proposed arrays are necessarily oversimplistic, and the interatomic force function has to be taken as linear up to some critical rupture point. The models nevertheless allow automatically for interactions between the non-linear zone (now localised about the crack-tip bonds) and the surrounding lattice structure, and this is the vital ingredient which leads to the prediction of a smooth energy barrier to crack motion. Because of the discrete nature of the cracked system the equations of equilibrium reduce to fourth-order *difference* rather than *differential* equations, the exact solving of which may demand numerical techniques. However, the analysis may be conveniently simplified by an exploitation of the zone concept:

(i) The mechanical energy of applied forces and elastic elements resides mainly in the outer, linear zone surrounding the inner tip region (i.e. over distances large compared with atomic spacings), so that G may be evaluated as if the system were continuous.

(ii) The total surface energy is determined explicitly by the non-linear separation processes which operate within the non-linear zone, so that Γ must be expected to oscillate with atomic periodicity. A simple, harmonic function provides a useful first approximation.

The system to which these ideas are to be applied is depicted in Fig. 1. The crack is of unit width, so that if the front were to advance uniformly along the x-axis the general infinitesimal increment in area, δC, could be replaced by the increment in crack length, δc. Indeed, this is the situation given specific attention by Thomson *et al.* in their work. Their approximate solution to the lattice equilibrium equations reduces to

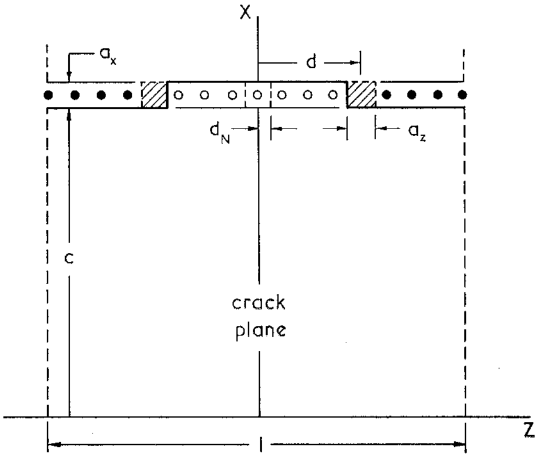

Figure 1 Schematic of crack plane, showing atomic crack extension by nucleation and expansion of kink pair. Closed circles denote unruptured bonds, open circles ruptured bonds, shading "active" bonds at kink sites. Longitudinal crack-length co-ordinate c, and lateral kink co-ordinate d, define the atomic crack-tip displacements. Dimensions a_x, a_y (out of page, not shown) and a_z are appropriate lattice spacings.

$$U_\mathrm{S} = 2\gamma c - \left(\frac{\gamma_{\mathrm{t}x} a_x}{\pi}\right) \sin\left(\frac{2\pi c}{a_x}\right), \tag{4}$$

where a_x is the lattice spacing along the x-axis, γ is the reversible surface energy and $\gamma_{\mathrm{t}x}$ is a trapping term for straight-ahead growth. From this equation we obtain the periodic fracture surface energy.

$$2\Gamma = \left(\frac{\partial U_\mathrm{S}}{\partial c}\right)_d = 2\left[\gamma - \gamma_{\mathrm{t}x} \cos\left(\frac{2\pi c}{a_x}\right)\right], \quad (x\text{-mode})\,. \tag{5}$$

However, if we invoke the mechanism of crack growth by kink motion, then the increment in crack area is replaced by $a_x \delta d$, with d an appropriate kink co-ordinate; the analogous fracture surface energy expression becomes

$$2\Gamma = \frac{1}{a_x}\left(\frac{\partial U_\mathrm{S}}{\partial d}\right)_c = 2\left[\gamma - \gamma_{\mathrm{t}z} \cos\left(\frac{2\pi d}{a_z}\right)\right] \quad (z\text{-mode})\,, \tag{6}$$

with the subscript z everywhere indicating the lateral mode of crack growth. In either of the two modes the crack is immobilized by the lattice within the "trapping range" $2\Gamma_- \leqslant G \leqslant 2\Gamma_+$, where we define

$$\Gamma_\pm = \gamma \pm \gamma_\mathrm{t}\,. \tag{7}$$

The γ_t parameters for the two modes must clearly depend on the detailed nature of the crystal structure, and would appear to require the computer for quantitative evaluation [16, 17]. However, it is generally fair to assume that $\gamma_{tz} < \gamma_{tx}$ [17], which means that kink motion will always occur provided suitable sources exist.

Let us assume for the moment that the required kink sources do exist. Recalling that G is insensitive to atomic-scale events within the crack-tip zone, and that γ, γ_t are material constants, we may insert Equation 6 into Equation 2 and integrate over d to get the energy associated with the motion of the kink,

$$U = U(c, d) = U(c) + U^*(d_N) + \left[(-G + 2\gamma)d - \left(\frac{\gamma_{tz}a_z}{\pi}\right)\sin\left(\frac{2\pi d}{a_z}\right)\right]a_x, \quad (d > d_N)\,. \quad (8)$$

The first two terms on the right-hand side of this equation relate to the boundary conditions for the particular kink configuration depicted in Fig. 1: in this case, where a source operating at $(c, 0)$ creates a kink pair by rupturing a bond ahead of an otherwise straight crack front, d_N refers to a critical kink co-ordinate for nucleation, and the asterisk denotes an activated state.

It is of interest to examine the effect of variations in applied loading, as manifested in the value of G, on the energy function for kink motion in Equation 8. We do this in Fig. 2, with plots covering the full range of trapping. The relative energy barriers for kink pair expansion (U_+^*) and contraction (U_-^*) indicate clearly the bias of the applied loading. Fig. 2c represents Griffith equilibrium, where forward and backward motions of the kinks are equally favoured. Invoking the condition $(\partial U/\partial d)_c = 0$ for the extrema in Equation 8, we obtain the activation energies

$$U_+^*(G) = U_-^*(G) = \frac{2\gamma_{tz}}{\pi N_A}\,, \quad (G = 2\gamma)\,, \quad (9)$$

where $N_A = 1/a_x a_z$ is the number of bonds intersecting unit area of crack plane. Figs. 2a and e represent trapping limits for forward and backward kink motions respectively; beyond these limits the crack proceeds spontaneously to a dynamic state. Figs. 2b and d represent intermediate trapping configurations. For small departures from Griffith equilibrium the activation energies contain a linear term in G,

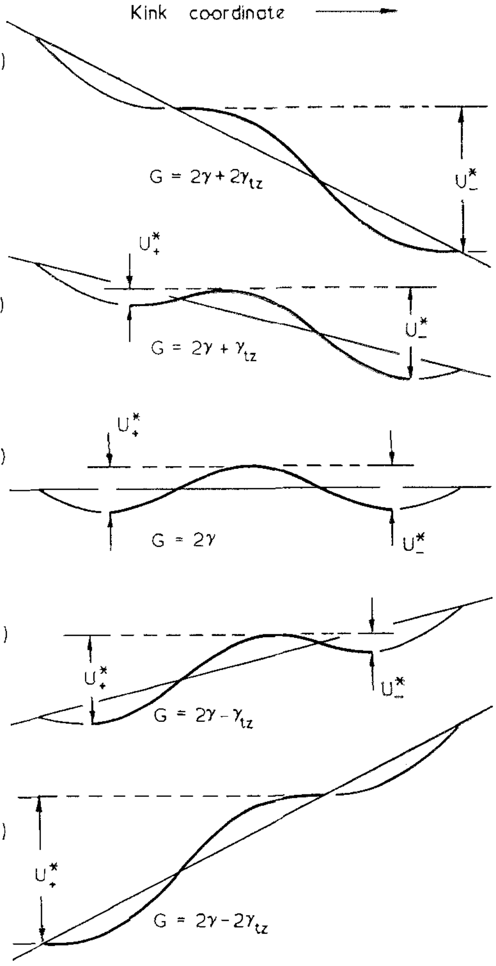

Figure 2 Potential energy diagrams for kink motion according to lattice model. Activation barrier for discrete motion through an atomic spacing is indicated by heavy curved line. Corresponding continuum behaviour is indicated by full, straight line. Sequence (a) to (e) represents states within the "trapping" range $2\Gamma_- \leq G \leq 2\Gamma_+$ for the crack, from which "escape" may occur via thermal fluctuations. Beyond the limiting states (a) and (e) the crack is free to advance or retreat dynamically.

$$U_\pm^*(G) = \frac{2\gamma_{tz}}{\pi N_A}\left[1 \pm \frac{\pi}{2}\left(\frac{-G + 2\gamma}{2\gamma_{tz}}\right)\right], \quad (|-G + 2\gamma| \ll 2\gamma_{tz})\,. \quad (10)$$

More generally, however, the activation energies are non-linear functions, as shown in Fig. 3.

Thus far we have effectively been dealing with a classical system at the absolute zero of temperature. We must now extend the description to include the effects of thermal energy on the crack response.

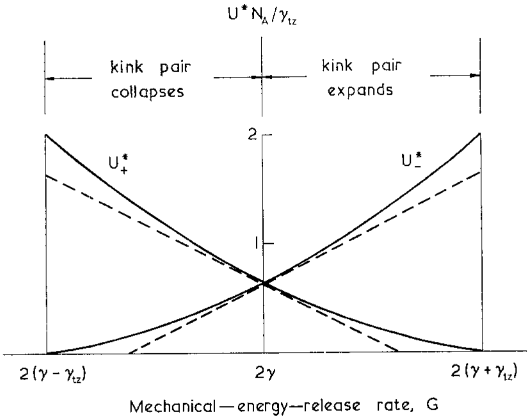

Figure 3 Activation energy for kink motion as function of mechanical-energy-release rate over trapping range. Full lines denote exact functions as determined from the extrema in Equation 8 (and as indicated in the previous figure), dashed lines denote the linear approximations of Equation 10.

3. Kinetics of kink model

The quantity which reflects most directly the action of kinetic processes in a fracture experiment is the forward crack velocity. Suppose that a population of kink sources along the crack front operates so as to produce a cumulative extension through δc. Then $\delta N = N_A \delta C = N_A \delta c$ bonds per unit width of crack will be ruptured, giving a crack velocity

$$v_c = \frac{dc}{dt} = \frac{1}{N_A}\left(\frac{dN}{dt}\right), \tag{11}$$

with dN/dt the bond-rupture rate per unit crack width. The bond-rupture rate will depend on the density of kinks. If this density be written as N_W^*/N_W, with N_W the number of crack-tip bonds along the unit crack front and the asterisk again denoting an "active" state, we have

$$\frac{dN}{dt} = N_W^* \nu_M^*, \tag{12}$$

ν_M^* being the frequency factor for rupture of a single active bond; the subscript M is used to imply that barrier traversal effectively imparts mobility to the kink.

To determine the kink concentration in Equation 12 it is necessary to look closely at the manner in which neighbouring kinks mutually interact to extend the crack [8]. We consider a steady-state situation in which kink pairs are nucleated thermally, and subsequently expand laterally to collide with and annihilate their neighbours (Fig. 4). The velocity of an individual kink is given as the product of the rupture rate of an active bond and the ensuing lateral displacement, that is ν_M^*/N_W. Then the mean collision time between mutually approaching neighbours is simply the mean kink spacing divided by the relative collision velocity, $(1/N_W^*)/(2\nu_M^*/N_W)$. Since the inverse of this quantity gives the collision rate per kink pair, and the density of such kink pairs is $\frac{1}{2}N_W^*/N_W$, the pair annihilation rate per bond becomes $\nu_M^* N_W^{*2}/N_W^2$. For a steady state, this annihilation rate must balance the nucleation rate, $\nu_N^* = \nu_M^* N_W^{*2}/N_W^2$, thus giving an equilibrium kink concentration

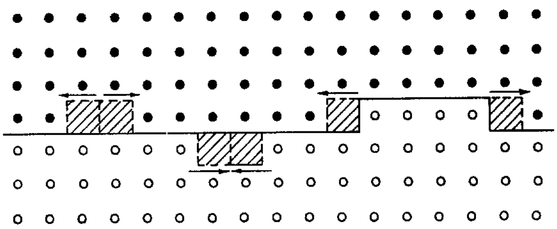

Figure 4 Model for kink interactions, showing schematic view of crack plane. Closed circles denote unruptured bonds, open circles ruptured bonds, shading kink sites. Arrows indicate kink motions corresponding to crack *extension.*

$$N_W^* = N_W\left(\frac{\nu_N^*}{\nu_M^*}\right)^{\frac{1}{2}}. \tag{13}$$

Inserting Equation 13 into Equations 11 and 12, we obtain

$$v_c = \frac{N_W}{N_A}(\nu_N^* \nu_M^*)^{\frac{1}{2}}. \tag{14}$$

A full treatment of the problem would, therefore, require an analysis of both the nucleation and the motion facets of kink mechanics. Generally, it would be expected that $\nu_N^* < \nu_M^*$, but since both processes may be regarded as involving the rupture of a single bond (Fig. 1) we assume to a first approximation that $\nu_N^* = \nu_M^* = \nu^*$ say, thus reducing Equation 14 to

$$v_c = \frac{N_W}{N_A}\nu^* = \nu^* a_x, \tag{15}$$

with $N_W = 1/a_z$, $N_A = 1/a_x a_z$. This approximation effectively ignores the attractive elastic interaction between the members of a newly created kink pair; however, the attendant overestimate in ν_N^* here should not be large for the more brittle, covalently-bonded solids in which structural distortion about the kink sites is relatively localized [17].

It remains only to relate the frequency factor in Equation 15 to the activation energies for the kink processes. If we assume the kink population to be determined by Maxwell-Boltzmann statistics we have

$$\nu^* = \nu_0 \left\{ \exp\left[-\frac{U_+^*(G)}{kT}\right] - \exp\left[-\frac{U_-^*(G)}{kT}\right] \right\}, \qquad (16)$$

where $\nu_0 \approx kT/h$ (k = Boltzmann's constant, h = Planck's constant, T = absolute temperature) is a lattice vibration frequency and the $U^*(G)$ terms are those plotted in Fig. 3. It will be noted that provision for both forward (bond breaking) and backward (bond remaking) fluctuations is included here. Combining Equations 16 and 15 gives the kinetic crack velocity,

$$v_c = v_c(G) = \nu_0 a_x \left\{ \exp\left[-\frac{U_+^*(G)}{kT}\right] - \exp\left[-\frac{U_-^*(G)}{kT}\right] \right\}. \qquad (17)$$

The function $v_c(G)$ is plotted in Fig. 5 (full line), for a typical value $U_+^*(2\gamma) = U_-^*(2\gamma) = 2\gamma_{tz}/\pi N_A = 25\ kT$ at Griffith equilibrium (Equation 9). Also plotted in Fig. 5 is the corresponding function with just the linear, forward activation term in Equation 10 included (dashed line), i.e.

$$v_c(G) = \nu_0 a_x \exp\left(-\frac{2\gamma_{tz}}{\pi N_A kT}\right) \exp\left(\frac{G - 2\gamma}{2N_A kT}\right),$$
$$(0 < G - 2\gamma \leqslant 2\gamma_{tz}) \cdot \qquad (18)$$

Notwithstanding the essential non-linearity of the intrinsic $U^*(G)$ functions in Fig. 3, Equation 18 stands as a useful working basis for describing kinetic fracture processes over a reasonable portion of the forward trapping range.

The above analysis is clearly open to considerable refinement. We have derived the key energy function in Equation 8 on the basis of an approximate solution to an oversimplified lattice representation, and have conveniently overlooked considerations of entropy terms and spurious sources or sinks (e.g. free surfaces intersecting extremities of the crack front) in the kink mechanics. The formulation nevertheless embodies certain desirable features:

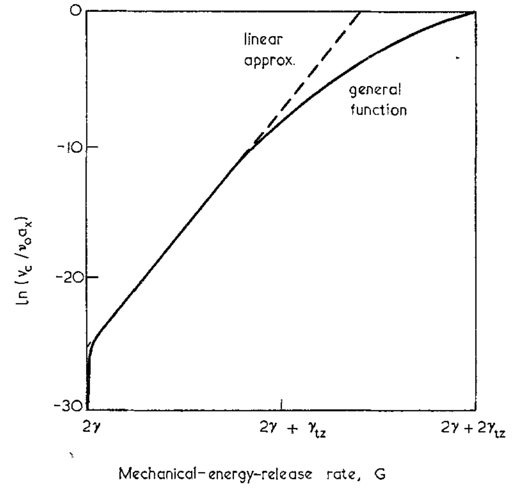

Figure 5 Crack velocity as a function of mechanical-energy-release rate over forward trapping range. Full line is exact representation of Equation 17, evaluated according to the activation energies U_+^* and U_-^* shown in Fig. 3. Note cut-off values $v_c = 0$ at $G = 2\gamma$, $v_c = \nu_0 a_x$ at $G = 2(\gamma + \gamma_t)$. Dashed line is approximate representation of Equation 17, using just the forward, linear activation energy $U_+^* (< U_-^*)$ from Equation 10. Plots for $U^*(2\gamma) = 25\ kT$.

(i) Equation 17 predicts a zero in the crack velocity ("fatigue limit") at true Griffith equilibrium, corresponding to equal forward and backward fluctuations of the kink energy barriers ($U_+^* = U_-^*$).

(ii) Equation 17 predicts an upper limit in crack velocity, $v_c \approx \nu_0 a_x \approx (5 \times 10^{12}\ \text{Hz}) \times (2 \times 10^{10}\ \text{m}) = 10^3\ \text{m sec}^{-1}$ ≈ dynamic velocities, corresponding to spontaneous forward crack growth ($U_+^* = 0$, $U_-^* \gg kT$).

(iii) There is provision, through the material parameters γ and γ_t, for incorporating the effects of extrinsic processes.

4. Chemically-enhanced kinetic crack growth

The presence of a chemical environment within a stressed crack system can lead to a very significant enhancement of kinetic crack growth. Such an effect must be given close attention in any practical consideration of material strength, for there are many chemical species in the everyday surrounds which inevitably have access to the vital crack-tip region via the open crack mouth. In this section we extend our previous treatment to cover the somewhat idealistic case of a single gaseous species diffusing along the crack interface and subsequently undergoing bond-rupture interactions at the crack tip. However, in adopting this particular situation as a case study it is well to appreciate that a multiplicity of possible alternative processes may, in principle, be incorporated into the general formulation in similar fashion [4].

4.1. Chemical modification of surface energy term

Let us suppose that the chemical rupture process can be described in terms of a generalised interaction between crack-tip bonds **B** and environmental molecules of species **A** according to

$$\eta \mathbf{A} + \mathbf{B} \rightarrow \mathbf{B}^* , \qquad (19)$$

where the asterisk denotes passage over the activation barrier into the ruptured state. This interaction facilitates lateral crack advance through one atomic spacing, with the η molecules of the depleted species **A** left *associated* with the broken bond on the new surfaces thus created; the reverse interaction conversely facilitates crack retreat, with the **A** molecules correspondingly *dissociated* from the surfaces. Recalling that forward extension of a crack front of unit width involves the rupture of $\delta N = N_A \delta c$ bonds, and noting that $\mathbf{B}^*$ accordingly increases at the expense of **B** and **A**, we may write the energy rate for the system crack + environment as

$$\frac{\mathrm{d}U}{\mathrm{d}c} = -G + (\mu_{\mathrm{B}^*} - \mu_{\mathrm{B}} - \eta\mu_{\mathrm{A}})N_{\mathrm{A}} , \qquad (20)$$

where the μ terms are appropriate chemical potentials. If we now identify the quantity $\mu_{\mathrm{B}^*} - \mu_{\mathrm{B}}$, representing the difference between "after" and "before" states of the crack-tip bond, with the surface energy function $2\Gamma'/N_{\mathrm{A}}$ for the bond, Equation 20 conveniently reduces to

$$\frac{\mathrm{d}U}{\mathrm{d}c} = -G + 2\Gamma' - \eta\mu_{\mathrm{A}}N_{\mathrm{A}} , \qquad (21)$$

in analogy with our original energy-balance Equation 2. We may then proceed through Equations 2 to 18 exactly as before, but with parameters γ' and γ_{t}' relating to the new equilibrium at the crack-environment interface; in the "linear, forward approximation" of Equation 18, we obtain a crack velocity function modified only by an exponential term in the chemical potential of the environmental species,*

$$v_{\mathrm{c}}(G) = \nu_0 a_x \exp\left(-\frac{2\gamma_{\mathrm{t}z}'}{\pi N_{\mathrm{A}}kT}\right) \exp\left(\frac{G - 2\gamma'}{2N_{\mathrm{A}}kT}\right) \exp\left(\frac{\eta\mu_{\mathrm{A}}}{2kT}\right) , \quad (0 < G - 2\gamma' \ll 2\gamma_{\mathrm{t}z}') . \qquad (22)$$

For an ideal gas at a given temperature the chemical potential assumes the standard form

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{s}}(T) + kT\ln\left(\frac{p_{\mathrm{A}}}{p_{\mathrm{A}}^{\mathrm{s}}}\right) , \qquad (23)$$

where p_{A} is the gas pressure at the crack tip and the superscript s denotes some reference state. We may note that μ_{A} relates only to the state of the environment, which in this case is assumed independent of the stress intensity at the crack tip, hence of G. This independence of G may not always obtain, however; for instance, stress-enhanced ion-exchange processes are known to have a significant influence on the nature of aqueous environments at crack tips in silicate glasses [18, 19]. Within the present assumption we may insert Equation 23 into 22, collecting various uncertain energy constants into a single term, U_0^*, to obtain

$$v_{\mathrm{c}}(G) = V(T)\left(\frac{p_{\mathrm{A}}}{p_{\mathrm{A}}^{\mathrm{s}}}\right)^{\eta/2} \exp\left(-\frac{U_0^*}{kT}\right) \exp\left(\frac{G}{2N_{\mathrm{A}}kT}\right) , \quad (0 < G - 2\gamma' \ll 2\gamma_{\mathrm{t}z}') , \qquad (24)$$

with $V(T)$ a slowly varying factor. The term $1/2N_{\mathrm{A}} = a_x a_z/2$ in the exponential factor for the mechanical-energy-release rate G may be regarded as having the status of an "activation area" for the kinetic crack motion.

Before continuing the analysis it might be timely to compare the present theoretical model with an earlier one proposed by Charles and Hillig [20] and developed by Wiederhorn [21]. This earlier model, originally conceived with glass/water systems specifically in mind but now widely applied in the interpretation of slow crack growth in a wide range of brittle systems in general, derives from the following starting assumptions: the basic chemical process is that of a normal corrosion reaction at standard temperature and pressure, but enhanced by the special conditions existing within the crack system; the activation barrier for this process is

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*The intrinsic, zero-interaction crack velocity Equation 18 appearing as the limiting case $\eta \rightarrow 0$.

lowered by an amount in direct proportion to the local stress intensity at the crack tip; the steady-state crack-tip profile is adequately approximated by portion of a smooth ellipse, the curvature of which tends to increase (by virtue of preferential chemical attack) toward atomic dimensions as the applied loading approaches the level for dynamic propagation. However, there are certain limiting features inherent in the "stress corrosion" model:

(i) The assumption that the crack-tip rupture process is strictly a stress-enhanced dissolution reaction seems unnecessarily restrictive. It would appear to exclude the possibility of slow growth effects in environments which are non-corrosive at the zero stress level [22]. The present formulation, on the other hand, overcomes this objection by allowing for the dominance of a reversed interaction (bond remaking) at stress levels below that corresponding to true Griffith equilibrium.

(ii) The notion of a smoothly rounded elliptical hole is in direct conflict with that of the ideally sharp cleavage crack. Such a continuum viewpoint has no inbuilt provision for a lattice-trapping characteristic, which means that the necessary energy barrier for activated crack growth has to be introduced into the description in a somewhat artificial manner.* The consequent linearity between logarithmic crack velocity and crack-tip stress intensity predicted by this model thus has no sound physical basis, nor is it always borne out by experimental data (although the variation of crack velocity with applied load is generally so great that it is difficult to draw any definite conclusion concerning the exact functional form from experimental data alone). Again, to explain a fatigue limit it is necessary to postulate corrosive blunting of the crack tip at low loads; in crystalline materials with marked surface energy anistropy, such as mica [6], it is not easy to envisage anything but an atomically sharp tip. Such difficulties do not arise in the discrete, lattice trapping models.

(iii) With its semi-empirical foundation, in which adjustable parameters can be determined only by curve fits to the data, the stress corrosion model is incapable of predicting *a priori* the magnitude of the crack-velocity function for a given system. By contrast, the corresponding parameters in the present theory may, in principle at least, be predetermined from purely structural considerations at the atomic level (although in reality, approximations in the treatment impose certain numerical uncertainties, as we shall indicate later).

4.2. Role of gas transport in fracture kinetics

As mentioned briefly in the Introduction, a complete description of kinetic crack growth requires a consideration of any subsidiary rate-dependent steps that may precede the key bond-rupture event. In the case of an ideal gas environment, we need to take into account the kinetics of molecular diffusion along the narrow crack interface between mouth and tip. This situation has been treated in detail elsewhere [4, 23], and we discuss only the essential results here.

Suppose once more that the operation of crack-front kinks produces a crack extension through δc. Then if the kinks are activated according to Equation 19, the arrival of δM interacting molecules of species **A** at the tip of a crack of width unity will give rise to the rupture of $\delta N = \delta M/\eta$ bonds. The basic crack velocity Equation 11 becomes

$$v_c = \frac{1}{\eta N_A}\left(\frac{dM}{dt}\right), \qquad (25)$$

with dM/dt the steady-state molecular flow rate per unit width of crack front. From the kinetic theory of gases we obtain [23]

$$\frac{dM}{dt} = \frac{\kappa a_y(p_A{}^0 - p_A)}{(2\pi mkT)^{\frac{1}{2}}}, \qquad (26)$$

where the lattice spacing a_y along the y-axis represents the "reaction cross-section" per unit width of front presented to the impinging gas molecules by the crack-tip bonds, the pressure differential $(p_A{}^0 - p_A)$ between crack mouth (source) and tip (sink) represents the driving force for the molecular flow, m is the molecular mass of the gaseous species, and κ represents an attenuation factor associated with the increasing incidence of retarding, diffuse molecule/wall collisions as the gas approaches the crack tip. The attenuation factor is a slowly-varying function of crack geometry, hence of the crack-extension force G, decreasing from unity (retardation-free value) as the crack becomes longer and narrower. However, we are not primarily concerned with the transport step here, and the function $\kappa(G)$ is in any case difficult to calculate accurately, so we shall simply regard κ

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*For example, by series expansion of the activation free energy in terms of the "crack-tip stress" retaining only *linear* terms.

as a constant to be determined empirically over any limited range of G. Combining Equations 26 and 25 then gives

$$v_c = \frac{\kappa a_y(p_A^0 - p_A)}{\eta N_A(2\pi mkT)^{\frac{1}{2}}}. \tag{27}$$

We may note the relative insensitivity of this result to applied load and temperature.

We now have two basic crack velocity functions, Equations 24 and 27, which may be connected via the unknown crack-tip gas pressure, p_A. To this end Equation 24 is rewritten in the form

$$v_c = v_r \left(\frac{p_A}{p_A^0}\right)^{\eta/2}, \tag{28}$$

where, at $p_A \rightarrow p_A^0$ ("instantaneous transport"),

$$v_r = V(T) \left(\frac{p_A^0}{p_A^s}\right)^{\eta/2} \exp\left(-\frac{U_0^*}{kT}\right) \exp\left(\frac{G}{2N_A kT}\right), \tag{29}$$

defines a *reaction-limited* crack velocity. Similarly, Equation 27 is rewritten as

$$v_c = v_t \left(1 - \frac{p_A}{p_A^0}\right) \tag{30}$$

where, at $p_A \ll p_A^0$ ("instantaneous interaction"),

$$v_t = \frac{\kappa a_y p_A^0}{\eta N_A(2\pi mkT)^{\frac{1}{2}}} \tag{31}$$

defines a *transport-limited* crack velocity. Eliminating p_A from Equations 28 and 30 gives us finally an implicit relation in the crack velocity,

$$\frac{v_c}{v_t} + \left(\frac{v_c}{v_r}\right)^{2/\eta} = 1 \tag{32}$$

for the overall two-step, transport-reaction process. The crack growth will then be reaction- or transport-controlled over different ranges of G: at low G values, $v_r \ll v_t$, $v_c \rightarrow v_r$, and conversely at high G values, $v_r \gg v_t$, $v_c \rightarrow v_t$. This justifies to some extent the approximations embodied in Equations 29 and 31, namely the forward, linear approximation corresponding to $0 < G - 2\gamma' \ll 2\gamma_{t_z}'$ in the reaction-controlled region, and the approximation that κ be independent of G in the transport-controlled region.

4.3. Comparison of theory with experimental crack velocity data

In seeking to obtain experimental verification of the above analysis, care needs to be exercised in the choice of a model crack system. Firstly, of course, it is necessary that the material under consideration be capable of sustaining an atomically sharp crack, preferably (in keeping with the lattice models) on a well-defined crystallographic cleavage plane. Then, it is also necessary that the appropriate gaseous species in the environment diffuse toward, and interact with, the active crack-tip bonds in essentially the manner specified in Sections 4.2 and 4.1 respectively. In particular, one has to be careful here not to adopt a system complicated by such effects as crack-tip plasticity, crack-tip/microstructure interactions (including interactions involving stress-enhanced migration of active point defects within the structure to the crack tip [24]), etc. Unfortunately, these restrictions are stringent, to the extent that very few of the crack velocity data accumulated in the literature are suitably pertinent to the present situation. We shall accordingly limit ourselves to a brief consideration of some published observations on the behaviour of the crack velocity function $v_c(p_A^0, G)$ for $(10\bar{1}2)$ fracture of sapphire in the presence of water vapour [25].

Fig. 6 makes the required comparison between theory and experiment for the $Al_2O_3(s)$–$H_2O(g)$ system. The experimental data represent a series of runs, at seven partial pressures of water vapour.* The corresponding theoretical curves are generated from the two-step Relation 32, in conjunction with Equations 29 and 31. Here we take $T = 300$ K and $p_A^s = 1.0 \times 10^5$ N m^{-2} as our standard state for the water vapour environment. Several of the other necessary parameters in Equations 29 and 31 are obtained from structural considerations, as follows. In the sapphire lattice [26] the oxygen atoms are arranged approximately in hexagonal close packing (O–O distance 0.27 nm). Between the close-packed layers exist octahedral interstices, two-thirds of which are occupied (in ordered manner) by the aluminium atoms (Al–O distance 0.19 nm). The simplest chemo-rupture interaction between the water molecules and the sapphire bond linkage across the crack plane is

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*The test environment in these experiments actually consisted of humidified nitrogen gas. We may recall (Section 4.2) that the flow rate of gas to the crack tip is limited by molecule/wall collisions, in which case each molecular species must diffuse independently of the other. Thus, presuming the nitrogen to be inert, the relevant pressure is the partial pressure of the reactive water vapour.

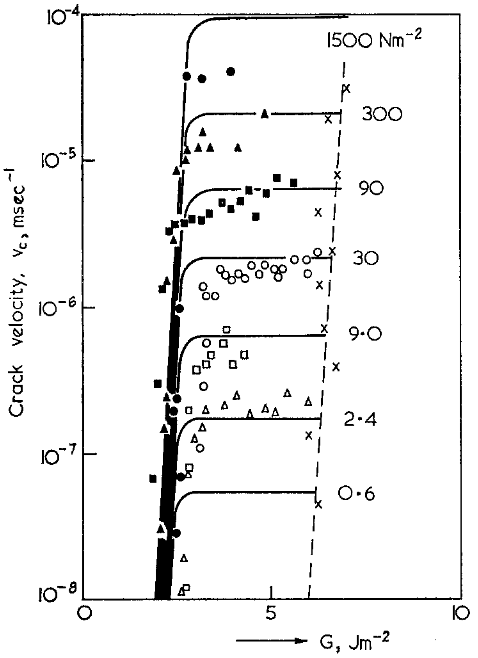

Figure 6 Comparison between theory (full lines) and experiment (data points) for $(10\bar{1}2)$ fracture of sapphire in water vapour (pressures indicated) at room temperature. Theoretical curves generated from two-step Equation 32. Experimental data from [25] (with mechanical-energy-release rates G converted from plotted "stress-intensity factors" K according to $G = K^2/E$, using $E = 3.5 \times 10^{11}$ N m^{-2} as Young's modulus for sapphire). At upper limit to trapping range crack accelerates toward dynamic state (dashed line).

$$(\text{-Al-O-Al-}) + (\text{H-O-H}) \rightarrow (\text{-Al-OH . HO-Al-}) \; ; \qquad (33)$$

that is, the strongly linking oxygens are replaced by weakly coupled hydroxyl pairs. This gives $\eta = 1$ in Equation 19. Also, we have $m = 3.0 \times 10^{-26}$ kg (H_2O), $a_y = 0.38$ nm (Al–O–Al bond length). To determine the bond density we note that, because of the incomplete aluminium occupancy, only two-thirds of the linking oxygens need be replaced by hydroxyl pairs in order for chemo-rupture to proceed; we obtain $N_A = 1.15 \times 10^{19}$ bonds m^{-2} [Al_2O_3 $(10\bar{1}2)$ plane]. The remaining unknowns may be reduced to just one dimensionless constant in each of Equations 29 and 31, to be matched empirically to the experimental data: in Equation 29 we collect all unspecified temperature-dependent terms into a single parameter $V'(T) = V(T) \exp(-U_0/kT)$, and set $V'(T) = 1.0 \times 10^{-16}$ m sec^{-1}; similarly, in Equation 31 we set $\kappa = 0.06$.

It is apparent from Fig. 6 that the theory is capable of accounting for the qualitative features of the applied load and pressure dependence of the crack velocity function for the kinetic fracture of brittle solids in a dilute gas environment. In particular, the distinctive transition in the $v_c(G)$ curve at given pressure and temperature is entirely consistent with the proposed transport-reaction process. However, for lack of an exact structural kink model for the sapphire/water system, we have been forced to resort to a semi-empirical approach in the present calculations, as a result of which little or no physical significance can be attached to *absolute values* of the generated functions. Extension of the critical analysis, for instance to the questions of the temperature dependence of the crack velocity and the existence of a static fatigue limit, would require, in addition to a more detailed kink model, more comprehensive experimental data than are at present available.

5. Concluding remarks

We have outlined a theory of kinetic crack growth for brittle solids, based on a model of an atomically kinked crack front. Unlike earlier treatments, the fundamental non-linearity of the bond-rupture process is accommodated in the formulation. In its immediate form, the model appears capable of predicting the crack velocity dependence on such key variables as applied loading, chemical concentration of reactive environmental species, temperature, etc. However, because of the present necessity to resort to approximate solutions for the atomic motions in oversimplistic lattice-crack structures, this capability is yet to be fully substantiated. Moreover, absolute predictions of the crack velocities lie beyond the scope of the model at this stage.

There is, accordingly, an apparent need for more detailed studies of model crack systems, from both theoretical and experimental standpoints. Here materials such as the diamond-structure crystals, with their highly brittle fracture characteristics, their relatively simple covalent bonding, and their current availability in near-perfect single-crystal form, present themselves as attractive candidates. Experimentally, the need is for more systematic accumulation of crack velocity data under controlled conditions of testing. Theoretically, more refined structural models are required to evaluate the essential parameters in the total energy functions for the kink displacements.

While it may be possible to gain some physical insight into these parameters from simple bond-energy arguments [4, 27], the general complexity of the problem would seem to demand the use of the high-speed computer. Sinclair's recent computations of the energetics of intrinsic kink motion in silicon (1 1 1) cleavage [17] are especially relevant in this context. Preliminary attempts to model environmental effects in a similar way, as with an interesting simulation of hydrogen interaction at crack tips in α-iron [28], serve to hint at some of the difficulties which beset investigations of the less simple kinetic fracture phenomena.

However, inadequacies in the details of the modelling should not be allowed to cloud the inherent generality of the present approach. The incorporation of extraneous effects into the description is facilitated via the retention of the Griffith energy-balance concept as an underlying theoretical basis for the model. Thus the interaction Equation 19 may be extended beyond the chemical interpretation of Section 4.1; for instance, "species **A**" may equally well be taken to represent such rupture-assisting agents as vacancies or interstitials within the solid structure, radiation particles or photons, etc. The problem reduces to one of rewriting the total energy function of the system to suit the appropriate new system variables, and thence proceeding with the analysis as before.

In principle, there is no reason why the basic ideas outlined here should not ultimately be extended to more practical systems, notably metallic and ceramic systems in which the complications of microstructure and glassy phases are the rule rather than the exception. Here it becomes a question of first identifying the various mechanisms which contribute to the overall crack growth process, and then determining the conditions under which each such mechanism might assume a rate-controlling role. This opens up a wide field for further study.

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