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An atomistic model of crack extension by kink propagation

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A model originally developed to characterize the extension and breakage of interatomic bonds at the tip of a propagating brittle crack is used to describe crack extension through a crystalline lattice by kink motion. Magnitudes of the effective kink barriers against crack extension and healing are computed as a function of lattice strain and are found to exhibit a marked asymmetry, relative to each other, in their strain dependences. In addition, decohesion effects associated with the presence of certain foreign atomic species are simulated, and it is shown that, for a broad range of relative bond-weakening, the kink barriers against both crack extension and healing are completely eliminated.

1. Introduction

Beginning with the work of Hsieh and Thomson [1], a number of simulations have been developed to describe brittle fracture in terms of atomic-bond breaking at the crack tip. These simulations are of two general types that can be regarded as two- or three-dimensional models.

In the two-dimensional case, a planar crack with a straight tip lying along a symmetry direction is propagated uniformly along its length. Periodic boundary conditions can then be employed along the crack-tip direction, and a large cylinder of atoms around the crack tip can be atomistically simulated, using pair potentials, with relatively few total atoms. In addition to the reversible work of separation (the surface energy of the created surfaces), a periodic irreversible energy barrier is encountered which is called the lattice-trapping barrier (LTB) [1]. Estimates of the magnitude of the LTB, based on such calculations, range from 15 per cent of the reversible work, for silicon in a 0 K (i.e., static) calculation [2], to about zero per cent for a Lennard–Jones solid in a dynamic, adiabatic simulation [3], with the temperature rising to about half the absolute melting point.

In the three-dimensional case, however, it is expected that the LTB is surmounted by the creation of double kinks [4, 5] analogous to those formed in dislocation motion over the Peierls barrier [6]. The energy required to form the double kinks must be less than that required to surmount the LTB, so that the *effective* LTB is less in the three-dimensional case. Indeed, for the low-driving-force, nearly reversible case, the lateral motion of kinks along the crack tip is expected to provide the activation barrier for the cracking process [4]. Preliminary calculations for silicon [4] and iron [7] do indicate that the effective LTB is nearly zero when a set of kinks is present at the crack tip. However, since the boundary conditions are not well defined for the kinked crack, atomic calculations of an extensive configuration would be difficult. In addition, pair potentials are expected to be less accurate for a complex configuration such as a kink. Consequently, a more empirical description is representative of the present state of understanding and should be valuable in providing insight into the kink-propagation process.

The features required of a model for a kink in a crack are (a) that it represents local bond breaking

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and (b) that it incorporates the compliance or constraint of the surrounding array of atoms, an effect which invariably lowers the energy for bond breaking relative to that for a pair of isolated atoms. Such a model was originally proposed by Thomson, Hsieh, and Rana [8] and was also treated by Fuller and co-workers [9–12]. They represented a Mode I crack by two chains of atoms. Adjacent atoms of the same chain were connected by flexible bonds, and the two chains were connected by stretchable parallel bonds between atoms of the different chains. The stiffness of the flexible bonds reflected the lattice compliance, and a breaking stretchable bond represented kink motion. The model was also used to describe extrinsic or chemically-assisted bond rupture [11, 12].

An alternate model for bond breaking in kink propagation is that suggested by Hirth [13], consisting of the extension of a linear four-atom chain, with adjacent atoms connected by non-linear bonds. The central bond is the one that breaks upon extension, with the two outer bonds representing the lattice compliance. An advantage associated with this simple model is that it can be treated in detail in an analytical manner. The model is reconsidered here, in a 0 K simulation, and some new results are obtained relative to the kink barrier for crack propagation. Effects of solute atoms on bond breaking are included in these studies in an essentially empirical manner. As in the original study by Hirth [13], the non-linear bonds are represented by Morse potentials, the Morse function having some physical basis as an interatomic pair potential [14, 15].

2. Development of the model

The basic model consists of a system of four point-mass atoms, arranged along a straight line by identical Morse-function "springs", as illustrated schematically in Fig. 1. Interactions beyond those involving first-nearest neighbours are not considered. The potential energy of interaction, v, associated with each of the springs is thus of the form

$$v(D, \alpha, r_e; r) = D\{\exp[-2\alpha(r - r_e)] - 2\exp[-\alpha(r - r_e)]\}, \quad (1)$$

where D, α, and r_e are the usual Morse-function parameters and r is the instantaneous length of a given spring (i.e, the distance between the two associated atoms). Assumptions relative to the model are that all three springs have the same set of values for α and r_e, that the two outer springs have the same value of D, but that the inner spring has value kD for this parameter, where k is a numerical parameter describing the strength of the inner bond relative to that of each of the outer bonds. We shall consider values of k within the range $0 < k \leqslant 1$.

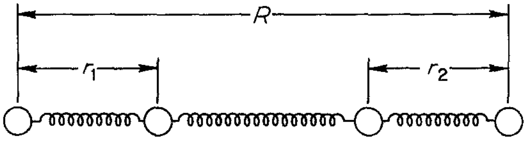

Figure 1 Schematic illustration of linear chain of four point-mass atoms that interact via Morse-function "springs".

Let us now consider what happens to the configuration of atoms as the length of the four-atom chain is altered as a result of the application of external forces, equal in magnitude and opposite in direction to the two end atoms. The overall length of the system, R, is supposed to change at a slow enough rate to ensure that the four-atom system remains in a state of quasiequilibrium, i.e., one of minimum net potential energy.

Let r_1 and r_2 be the lengths of the two outer springs, in which case the length of the inner spring must be $R - r_1 - r_2$ (see Fig. 1). It then follows, from Equation 1, that the net potential energy of the system, $U(r_1, r_2)$, is, for a given value of R,

$$U(r_1, r_2) = v(D, \alpha, r_e; r_1) + v(D, \alpha, r_e; r_2) + v(kD, \alpha, r_e; R - r_1 - r_2). \quad (2)$$

Now, consider some features of the variation of the function $U(r_1, r_2)$ with the co-ordinates r_1 and r_2. Of particular interest is the function $U(r, r)$, which is the potential energy that exists along the straight line $r_1 = r_2 \equiv r$ in a two-dimensional r_1–r_2 space. Those configurations for which $r_1 \neq r_2$ are asymmetric relative to the centre of the four-atom chain, and are not dealt with here in detail. Consider, however, the manner in which $U(r, r)$ varies along a direction perpendicular to this line. This is conducted by evaluating the function $U(r + \delta r, r - \delta r)$, where δr is a small increment of r. Thus, combining Equations 1 and 2, and expanding the resultant expression for $U(r_1, r_2)$ in a Taylor series about $r_1 = r$, and $r_2 = r$, taking the increment of r_1 to be δr and that of r_2 to be $-\delta r$, we obtain, through terms of fourth order in δr,

$$U(r+\delta r, r-\delta r) = U(r,r) + (D/y^2)[2(2-y)(\alpha\delta r)^2 + \tfrac{1}{6}(8-y)(\alpha\delta r)^4 + \ldots], \quad (3)$$

where

$$y \equiv \exp[\alpha(r-r_e)]. \quad (4)$$

Equation 3 shows that, provided the value of y does not exceed 2, the potential energy increases about the line $r_1 = r_2$, so that the system would tend, for this range of y, to remain situated on this line once it was placed thereon. If, however, $y > 2$, the system is unstable with respect to deviations from the line $r_1 = r_2$ and would spontaneously progress to an equilibrium configuration for which $r_1 \neq r_2$.

To illustrate the behaviour of the system within the range $y > 2$, consider the following example. Let the system be in a configuration such that $r_1 = r_2$, with $y > 2$. Now let the position of one of the two inner atoms fluctuate slightly. That fluctuation would then spontaneously develop, and an asymmetric equilibrium configuration would finally be reached in which the bond between that atom and its neighbouring end atom would be elongated or shortened, relative to its initial length, depending upon whether the initial fluctuation has been, respectively, a bond extension or bond shortening. Of course, the other two bonds would, in general, also change in length in the process, although the details of these changes are not discussed here.

The analysis that follows is restricted to the conditions $r_1 = r_2 \equiv r$ and $y \leqslant 2$, although some properties of the more general case are discussed in Appendix 1, together with application to a specific example. For the case of interest here, however, Equation 2 becomes

$$U = 2v(D, \alpha, r_e; r) + v(kD, \alpha, r_e; R-2r), \quad (5)$$

where $U \equiv U(r,r)$. y is always a positive number. The problem now is to determine the values of r, for given R, for which U is stationary.

Toward this end, Equations 1, 2, 4 and 5 are used to show that

$$U = D(By)^{-2}[k(y^6 - 2By^4) + 2B^2(1-2y)], \quad (6)$$

where

$$B \equiv \exp(3\eta e) \quad (7)$$

with

$$\eta \equiv \alpha r_e \quad (8)$$

$$e \equiv (R - 3r_e)/(3r_e). \quad (9)$$

In addition, note that Equations 4 and 8 can be combined to yield

$$y = \exp(\eta Z), \quad (10)$$

where

$$Z \equiv (r - r_e)/r_e. \quad (11)$$

It is clear that Z is simply the strain associated with each of the two outer inter-atomic bonds. Likewise, e is the strain associated with the entire four-atom chain. In addition, the variable y is a direct measure of the strain Z, since y increases monotonically with Z (after Equation 10); similar reasoning can be used to conclude that B is a measure of the net strain, e, of the four-atom chain (after Equation 7). In summary, Equations 6 to 11 comprise a convenient description of U in terms of unitless quantities y, B, η, Z, and e.

It should be noted that the smallest value that y can have, $y_{\min}$, is that for which $r = 0$, which corresponds to complete compression of the two outer bonds, and which, from Equations 10 and 11, is seen to be $y = \exp(-\eta)$. Moreover, assuming that spatial order among the four atoms is maintained, the largest possible value, $y^{(1)}_{\max}$, that y can have is that for which $r = R/2$, which corresponds to complete compression of the inner bond, and can be shown, using Equations 7, 9, 10 and 11, to be $y^{(1)}_{\max} = B^{1/2}\exp(\eta/2)$.

As indicated above, values of y for which $y > 2$ are not of interest. However, the allowable range for y can be restricted even further. As demonstrated in Appendix 2 (see Equation A8), real roots for y lying between zero and 2 can actually only exist within the subrange $0 < y \leqslant y^{(2)}_{\max}$, where $y^{(2)}_{\max} = (2/k)[1-(1-k)^{1/2}]$. Clearly, if $k = 1$, then $y^{(2)}_{\max} = 2$, but for $0 < k < 1$, the corresponding range for $y^{(2)}_{\max}$ is $1 < y^{(2)}_{\max} < 2$.

Now, for given e value (i.e., given R value), values of Z are desired for which U is stationary. Hence, the following derivatives, obtained using Equations 6 and 10, are needed:

$$\left(\frac{\partial U}{\partial Z}\right)_e = \frac{4D\eta}{(By)^2}[k(y^6 - By^4) + B^2(y-1)] \quad (12)$$

and

$$\left(\frac{\partial^2 U}{\partial Z^2}\right)_e = 4D\left(\frac{\eta}{By}\right)^2\left[2k(2y^6 - By^4) + B^2(2-y)\right]. \quad (13)$$

Consequently, the search for stationary values of U, for given a e value, is seen, from Equation 12, to be reduced to seeking physically acceptable roots of the following polynomial of degree six:

$$f(y) \equiv k(y^6 - By^4) + B^2(y-1) = 0. \quad (14)$$

Equation 13 can be used to help assess the nature of any stationary points, that is, to determine whether a given stationary point corresponds to a maximum, a minimum, or an inflection point.

Actually, the search for roots of the polynomial $f(y)$ can be somewhat simplified. First, as already demonstrated, y can be no smaller than $y_{\min}$ and no larger than either $y_{\max}^{(1)}$ or $y_{\max}^{(2)}$, whichever is the smaller. Second, one can apply Descartes' rule of signs [16] to $f(y)$ to immediately deduce that, since both k and B are positive, there can be, at most, three roots that are both real and positive.

Our interest in this work is primarily in the behaviour of the system upon extension, i.e., when $e \geqslant 0$; its characteristics under compression, for which $e < 0$, will not be considered in detail. For $e > 0$, it is a simple matter to show that $f(y_{\min}) < 0$ and $f(y_{\max}^{(1)}) > 0$. In other words, at minimum Z (for which $r = 0$), an incremental increase of Z would cause U to decrease. Similarly, at the maximum value of Z that is physically possible (for which $r = R/2$), an incremental decrease of Z would also cause U to decrease. On this basis, one can conclude that if only one root exists within the range $y_{\min} < y < y_{\max}^{(1)}$, that root must correspond to a minimum of the function $U(r, r)$. Roots for which $y \geqslant y_{\max}^{(2)}$ are not of interest, as discussed above. In addition, if three roots exist within this same range of y, then, except for special cases in which one or more of the roots may represent inflection points, the roots having the lowest and highest values of y correspond to energy minima, and the root at the intermediate value of y corresponds to an energy maximum. The limiting case, for which there exist three roots, two of which are equal, consists of an energy minimum that corresponds to the distinct root, and an inflection point that corresponds to the two roots of equal value. Depending upon the relative values of k, B, and η, the situation for compression of the system is somewhat more complex, but, as indicated above, is not considered here in detail.

Two particular cases will be considered here, i.e., when $k = 1$ and when $0 < k < 1$. The first corresponds to the situation in which all three springs are identical, and is the case originally considered by Hirth [13]. The second involves a weakening of the inner atomic bond (its maximum well depth being k times that of each of the two outer bonds), which can be regarded as a cohesion effect such as that which may occur in a real system because of the participation of a solute atomic species in the cracking process. Thus, comparison of results obtained from the two cases provides some insight into the manner in which such embrittling atomic species can affect bond breaking as a crack tip propagates through a lattice by kink motion.

3. Application of the model to special cases

3.1. Three identical bonds: $k = 1$

The case for which $k = 1$, which corresponds to a "pure" crystal, is particularly simple. For this special case, one can factorize Equation 14 to obtain

$$(y^3 - B)(y^3 - By + B) = 0,$$

so that the sixth-degree polynomial is reduced to two polynomials, each of degree three. The only real positive root of $y^3 - B = 0$ is

$$y_1 = B^{1/3}, \tag{15}$$

with y_1 being a real, positive root, since B is positive (after Equation 7). The roots of the polynomial $y^3 - By + B = 0$ can be easily deduced using Cardan's formulas. One thus finds that, for $B \geqslant 27/4$, there exist two physically acceptable roots of this latter polynomial; these can be expressed in the following form:

$$y_2 = 2\left(\frac{B}{3}\right)^{1/2} \cos\left(\frac{\phi}{3}\right) \tag{16}$$

and

$$y_3 = 2\left(\frac{B}{3}\right)^{1/2} \cos\left(\frac{\phi + 4\pi}{3}\right), \tag{17}$$

where

$$\phi = \cos^{-1}\left[-\left(\frac{27}{4B}\right)^{1/2}\right].$$

At the lower limit, when $B = 27/4$,

$$y_2 = y_3 = 3/2.$$

Finally, one can show that no real, positive roots of the polynomial $y^3 - By + B = 0$ exist for $B < 27/4$.

The nature of the various stationary points of the function U follows immediately from the reasoning presented in Section 2. The results thus obtained are summarized in Table I. The Z_i values are related to the respective values of y_i (with $i = 1, 2, 3$) via Equation 10. Similarly, the U_i values are related to the respective values of y_i via Equation 6, with $k = 1$. The lower bound of

TABLE I Properties of stationary points of U, for $k = 1$, along the line $r_1 = r_2$ and within the range $\exp(-\eta) \leqslant y_i \leqslant 2$, with $i = 1, 2, 3$. "Min", "Max" and "Infl" denote minimum, maximum and inflection points, respectively, in the variation of U with Z for given e value. Expressions for y_i are given in Equations 15 to 17

Range of B values	y_1	y_2	y_3	Relative Z values	Relative U values
$1 \leqslant B < 27/4$	Min	*	*	–	–
$B = 27/4$	Min	Infl	Infl	$Z_1 > Z_2 = Z_3$	$U_1 < U_2 = U_3$
$27/4 < B < B_G$†	Min	Max	Min	$Z_1 > Z_2 > Z_3$	$U_1 < U_3 < U_2$
$B = B_G$	Min	Max	Min	$Z_1 > Z_2 > Z_3$	$U_1 = U_3 < U_2$
$B_G < B < 8$	Min	Max	Min	$Z_1 > Z_2 > Z_3$	$U_3 < U_1 < U_2$
$B = 8$	Infl	Infl	Min	$Z_1 = Z_2 > Z_3$	$U_1 = U_2 > U_3$
$B > 8$	‡	‡	Min	–	–

*No real values for either y_1 or y_2 exist within this range of B.

†$B_G = 6.88$.

‡Both y_1 and y_2 are greater than 2 within this range of B, for which the system is unstable with respect to fluctuations about the line $r_1 = r_2$, as discussed in Section 2.

B (i.e., $B = \exp(-3\eta)$) corresponds to complete compression of the system to $R = 0$, that is, to $e = -1$.

The results obtained thus far, particularly those presented in Table I, can now be easily applied to determine the response of the four-atom chain to expansion under the influence of an externally applied force. However, one fact that is now obvious is that even for this very simple physical system, the mathematical analysis is relatively involved, and the behaviour of the system is correspondingly complex.

Consider, then, what happens as equal and opposite forces are applied to the two end atoms of the chain. In this regard, it is useful to observe what happens as the system undergoes a complete cycle of deformation, i.e., beginning from the stable configuration (with no applied forces), then pulled apart to $e \to \infty$, and then allowed to come together again to the stable configuration. It is convenient, along these lines, to consider régimes of the parameter B (which, as noted above, is a direct measure of e).

(*a*) $\exp(-3\eta) \leqslant B < 1$. This régime is not of particular interest. The only real root is y_1 and for this range of B the system is in a state of compression. For this root, one can show that all three bonds maintain equal strain as B is varied. The potential energy U is a monotonically decreasing function of B within this range.

(*b*) $B = 1$. The system exists in its stable configuration at this value of B. There remains only one real root, y_1, which characterizes the system at $B = 1$. One can show that, for this particular value of B, none of the bonds are strained, so that the system is in its lowest possible energy state, i.e., $U = -3D$.

3.1.1. Elongating the system

(*a*) $1 < B < 27/4$. As the system is slowly stretched within this range the atomic configuration remains described by the one real root, y_1.

(*b*) $27/4 \leqslant B < B_G$. For values of B within this range (the significance of B_G to be discussed below) three real roots appear. As can be seen from Table I, an inflection point of U appears at $B = 27/4$ at root $y_2 = y_3$; and then a maximum occurs at root y_2 and a minimum at root y_3 when B is increased beyond this value but still within the stated régime. Within this range of B values, the two minimum energies satisfy the inequality $U_1 < U_3$. Consequently, root y_1 would still be the most stable configuration if thermal activation were to permit occupancy of both states; the stable state consists of three equally strained bonds.

(*c*) $B = B_G$. The parameter B_G is defined as the value of B for which $U_1 = U_3$. Hence, for this particular value of B, the Griffith condition for reversible crack extension in the absence of a kink barrier is satisfied, The system is in local equilibrium relative to reversible crack extension, which means that, if the kink barrier were to be overcome by thermal fluctuations (such that the kink would extend by one atomic distance), the work done by applied forces would be exactly equal to that required to create an atomic increment of surface area. The magnitude of B_G was obtained using an iterative procedure, and it was found that $B_G = 6.88$. The kink barrier, $U_2 - U_1$, computed at the Griffith level, was $0.000894D$. The system itself remains characterized at B_G by root y_1 with the energy maximum existing at y_2 and the other minimum at y_3.

(*d*) $B_G < B < 8$. The system is still characterized by three roots. The energy maximum at y_2 persists as well as the minima at y_1 and y_3. Now, however, there is a net driving force for crack propagation, since $U_3 < U_1$. An effective kink barrier against crack propagation, $U_2 - U_1$, persists in this region, and irreversible crack propagation by kink motion can occur, within this régime, via thermal activation.

(*e*) B = *8*. At this point, the minimum that had existed at root y_1, noting that $y_1 = 2$ at this value of B, now becomes an inflection point, which coincides with root y_2 and is characterized by energy $-2.25D$. The energy minimum at root y_3 still exists, however, and has value of $-2.27D$ at this value of B. There is now no kink barrier, and the system should relax into this minimum-energy configuration, i.e., from root y_1 to y_3 (with $y_3 = 1.236$ at $B = 8$). This change is made at fixed B (i.e., fixed e) so that the internal energy of the system is reduced by an amount $E_{\text{irr}}^{(1)} = 0.02D$ with no external work being done by the forces applied to the end atoms. The process corresponds now to athermally surmounting the kink barrier against crack propagation, with the irreversible energy E_{irr}^{1} being dissipated thermally in the process. It can be seen, from Table I, that when the system relaxes from y_1 to y_3, the value of Z is reduced. This corresponds to an abrupt increase of the strain of the inner bond as the two outer bonds move closer to their unstrained conditions. For example, for the special case considered by Hirth [13], for which $\eta = 5$, the value of Z_1 at $B = 8$ was 0.139 which was reduced, at $B = 8$, to a Z_3 value of 0.0424, which corresponded to a strain variation of the inner bond from its initial value of 0.139 to a new and substantially higher equilibrium value of 0.331, corresponding to the bond-breaking process. This particular broken bond has not yet progressed to the point at which it contributes fully to the equilibrium surface energy.

(*f*) B > *8*. As the system is stretched further, the atomic configuration remains in the state characterized by y_3, i.e., the "broken-bond" state. The roots y_1 and y_2 are greater than 2 and would correspond to constrained minima, i.e., as measured along the path $r_1 = r_2$. However, in this range of y, as discussed earlier, the system is unstable with respect to variations about the line $r_1 = r_2$, and would progress toward an equilibrium state for which $r_1 \neq r_2$. One can show that $y_3 \to 1$ as $B \to \infty$, which corresponds to the two outer bonds approaching an unstrained state (i.e., $Z \to 0$), with the inner bond being virtually entirely broken. Of course $U \to -2D$ as $B \to \infty$, in which case the broken bond does contribute fully to the equilibrium surface energy.

Consequently, for elongation of the system, the net change of potential energy of the system in going from $B = 1$ to $B \to \infty$ is just D, which corresponds to the energy of the broken inner bond and simulates the surface energy created by kink motion. However, the net work done by the externally applied forces is higher, i.e., $D + E_{\text{irr}}^{(1)}$, where $E_{\text{irr}}^{(1)}$ is a positive quantity equal to the negative of the potential-energy change that occurred when relaxation of the system took place at $B = 8$. The energy $E_{\text{irr}}^{(1)}$ is a measure of the irreversibility of the bond-relaxation process.

3.1.2. Healing the broken bond

Next, consider what happens when the procedure is reversed, and the system is allowed to come together starting from $B \to \infty$. The system is initially in state y_3, which was its state after elongation had been completed. As before, pertinent régimes of B are considered (as delineated in Table I).

(*a*) B > *8*. The system is in state y_3 (with $y_3 < 2$).

(*b*) B = *8*. The system is in its energy minimum at root y_3, but y_1 and y_2 now are equal and constitute an inflection point.

(*c*) $\mathrm{B}_G < \mathrm{B} < 8$. The system remains in its energy minimum at y_3, but now there exists another minimum at y_1 and a maximum at y_2. Here $U_3 < U_1$ so y_3 remains at the lowest-energy configuration.

(*d*) $\mathrm{B} = \mathrm{B}_G$. Here y_1 and y_3 both correspond to energy minima and y_2 corresponds to a necessary maximum. Again, $U_1 = U_3$ and the system is in the same quasi-equilibrium configuration for reversible extension as when the state was being elongated.

(*e*) $27/4 < \mathrm{B} < \mathrm{B}_G$. Again, y_1 and y_3 correspond to energy minima and y_2 corresponds to an energy maximum. Now $U_1 < U_3$ and there is a net driving force for crack healing. The effective kink barrier, $U_2 - U_3$, can be overcome, in an irreversible healing process, by thermal activation.

(*f*) B = *27/4*. Roots y_2 and y_3 are now equal and constitute an inflection point, and a minimum now exists at y_1. In a way analogous to that seen in the elongation process at $B = 8$, the system is supposed to fall from the inflection point at y_3, which is characterized by energy $-2.333D$, into the minimum at y_1, characterized by energy $-2.335D$, at this fixed value of B. As a result, the strain of the two outer bonds increases as healing of the broken inner bond is partially accomplished. For the special case originally considered by Hirth [13], where $\eta = 5$, the strain associated with each of the two outer bonds increases from 0.081 at y_3 to 0.127 at y_1, which corresponds to a decrease of strain of the inner bond from 0.220 to 0.127. The accompanying change of potential energy of the system is $-E^{(2)}_{\mathrm{irr}}$, where $E^{(2)}_{\mathrm{irr}}$ is a positive quantity equal to $0.002D$, and is thus relatively small compared to that, $E^{(1)}_{\mathrm{irr}}$, for bond breaking. This process corresponds to athermally surmounting the effective kink barrier against crack healing, with the irreversible energy increment, $E^{(2)}_{\mathrm{irr}}$, being dissipated thermally.

(g) *$1 \leqslant B < 27/4$*. As B is further reduced, the system remains in state y_1, and the potential energy decreases until the unstressed equilibrium configuration is reached at $B = 1$, for which $U = -3D$.

Thus, when the broken inner bond is healed by going from $B \to \infty$ to $B = 1$, the potential energy of the system changes by $-D$, which corresponds to the energy gained in healing the broken inner bond, or, equivalently, to the removal of surface energy. However, the net external work done by the externally-applied force is higher, i.e., $-D + E^{(2)}_{\mathrm{irr}}$, with $E^{(2)}_{\mathrm{irr}}$ being a measure of the irreversibility of the bond-healing process. The net amount of work done by the externally applied force, in going from $B = 1$ to $B \to \infty$ and then back to $B = 1$, is *not* zero, but instead is $E^{(1)}_{\mathrm{irr}} + E^{(2)}_{\mathrm{irr}}$, which is the net energy change associated with the irreversible nature of the entire breaking-healing cycle.

The kink-barrier energies $U_{21} \equiv U_2 - U_1$ and $U_{23} \equiv U_2 - U_3$, for the case $k = 1$, are plotted in Fig. 2, as a function of B. These are shown over the entire range of B, that is, $27/4 \leqslant B \leqslant 8$, for which such barriers exist. Of course, U_{21} and U_{23} are the barriers against bond extension and healing, respectively. The decrease of U_{21}, as well as the increase of U_{23}, with increasing B, are both demonstrated. The barrier U_{23} is zero at $B = 27/4$, whereas U_{21} is zero at $B = 8$. In addition, the magnitude of U_{23} at $B = 8$ is simply $E^{(1)}_{\mathrm{irr}}$, whereas that of U_{21} at $B = 27/4$ is $E^{(2)}_{\mathrm{irr}}$.

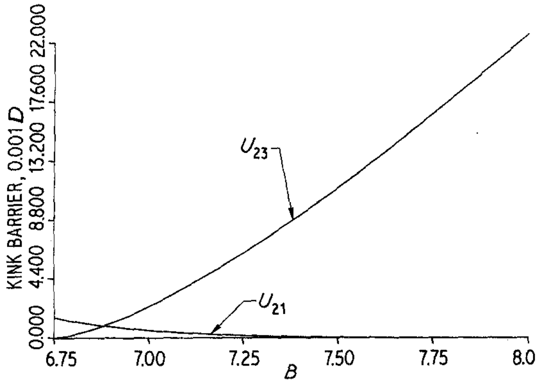

Figure 2 Variation of kink-barrier energies with lattice-strain parameter, B, for the case $k = 1$. The barrier against crack extension is U_{21} and that against crack healing is U_{23}.

Also illustrated in Fig. 2 is the pronounced asymmetry between the magnitudes of U_{21} and U_{23}. This asymmetry is a significant feature of this model and will be discussed in greater detail in Section 4.

3.2. Weakened inner bond: $0 < k < 1$

For values of k within the range $0 < k < 1$, roots of Equation 14 can, unfortunately, not be extracted by analytical means. Nevertheless, some general properties relative to the nature of the roots can be assessed by straightforward, albeit tedious, methods. These procedures are outlined in Appendix 2.

The following results are of particular interest:

(a) Within the subrange of k values $0 < k < 125/128$, there exists only one root of Equation 14 within the allowed range of y discussed in Section 2. That root corresponds, of course, to an energy minimum.

(b) Within the subrange $125/128 \leqslant k \leqslant 1$, the situation is more complicated, and there exist three roots for some values of $B > 0$. At $k = 125/128$, two roots exist for some values of $B > 0$. The nature of these roots is as discussed in Section 2.

A consequence of Result a is that when the system is elongated from its equilibrium configuration, for which $B = 1$ and $U = -(2 + k)D$, out to $B \to \infty$, for which $U = -2D$, it remains characterized by that same root for the *entire* range of B. Consequently, no irreversible change takes place, as occurred for the case $k = 1$, and the net work done by the externally-applied force is exactly equal to the increase of potential energy, that is, kD, which, of course, is the energy of the broken bond. Similarly, when B is taken from a large value approaching infinity, back to a value of unity, the system again remains characterized by that same root over the entire range of B. For any given value of B, the corresponding value of y is the same as that which had existed at that same value of B during elongation. Again, no irreversible change takes place, and the work done by the externally applied forces is $-kD$. Consequently, the net work done by the external forces, in first expanding the system and then healing the broken bond, is exactly zero.

For values of k within the range $125/128 \leqslant k \leqslant 1$, activation-energy barriers exist for certain values of B. A method for actually evaluating these values of B, for a given value of k, is presented in Appendix 2. (The case $k = 1$ was considered in detail above, using analytical methods.)

One special case is illustrated in Fig. 3. Here, the barriers U_{21} and U_{23} are plotted as a function of k, with the parameter B being fixed at the value $B = 7$. It is clear that U_{21} decreases and U_{23} increases as k decreases. Moreover, for this case, U_{21} vanishes at $k = 0.993$. One implication of this result is as follows. If the system were to be held fixed at $B = 7$, and the value of k were to be reduced from unity to some lesser value, say through the influence of a foreign atomic species, then, when k has decreased to a value of about 0.993, the barrier against bond extension would be zero, and the inner bond would spontaneously extend, the potential energy of the system dropping by an amount equal in magnitude to the barrier height U_{23} for this value of k, which is seen from Fig. 3 to be about $0.004D$. One can show that, for the special case where $\eta = 5$ (considered by Hirth [13]), the strain of the inner bond increases from 0.15 to 0.27 when this spontaneous change takes place.

4. Discussion

The simple model developed in this work has features that are characteristic of actual physical systems and that may aid our understanding of crack propagation in such systems. Work by Sinclair on silicon [4] provides one basis for comparison. In computer simulation, he found a two-dimensional lattice-trapping barrier for forward crack motion of about $0.25D$ (in our notation), but estimated a barrier reduced by a factor of ten for a crack with widely-spaced kinks, or about $0.025D$. This result compares favourably with the Morse-potential estimate of $0.02D$. Estimates of the bond-breaking relaxation, using various potentials [17], indicate that the Morse potential may be too "soft", with the result that the bond strain and the barrier for kink propagation may be overestimated in the present approach. On the other hand, the present model almost certainly overestimates the compliance of the surrounding medium for an actual kink, which would tend to compensate for the potential [13]. Thus, the agreement with the results of Sinclair [4] is within rough theoretical expectation and may be representative of the degree of approximation of the real physical situation.

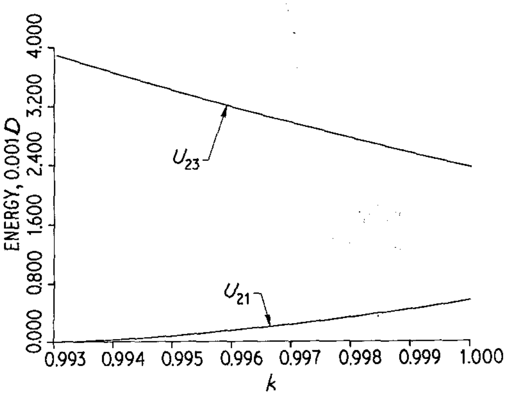

Figure 3 Variation of kink-barrier energies with k for the case $B = 7$. The barrier against crack extension is U_{21} and that against crack healing is U_{23}.

With the above provisos, the present results suggest several features which have not been revealed by previous models of crack propagation. Two-dimensional LTB calculations generally reveal nearly symmetric barriers for cracking and healing. The present kink-barrier calculations, while revealing a persistent barrier for crack extension or healing in the pure-crystal case, show a marked asymmetry in the magnitudes of the barriers, with that for healing being significantly larger than that for extension over most of the range of B for which barriers exist.

Another important aspect of this model is that the bond-breaking process is completely reversible when the middle bond has been sufficiently weakened, with the kink barriers against both crack extension and healing being eliminated. Indeed, this general behaviour was found to be relatively insensitive to the degree of weakening and persisted over a relatively broad range of k values, i.e., $0 < k < 125/128$. This simple model may help to explain the action of certain foreign atomic species (for example, metalloids on grain boundaries of an intergranularly fracturing metal) in enhancing crack propagation. This idea has been alluded to qualitatively in the analogous situation of reduction of kink-formation energy for a dislocation overcoming the Peierls barrier [18–20], where the solute atom is supposed to elastically disrupt the local periodicity of the Peierls configuration. The present work suggests that the kink barrier is reduced for very weak solute effects ($125/128 \leqslant k < 1$) but completely removed for stronger effects. The attendant reduction of the energy of crack propagation in the present model would suggest that solutes enhance decohesion of metal–metal bonds at the crack tip, with enhancement of crack propagation by kink motion occurring as a result. Of significance with respect to current theoretical considerations of such effects [21–24], the present model suggests that a solute which produces only a minimal reduction in equilibrium surface energy nevertheless suffices to completely remove the trapping barrier.

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Appendix 1: Some properties of the general potential-energy surface

Most of the analysis presented in the text is concerned with potential energy variations for which the value of y (after Equation 10) does not exceed 2. Some generalizations of this analysis are presented, here, together with application to a specific example. This procedure will also help clarify some of the results developed in the text.

We thus define

$$x_i = \exp(\eta Z_i), \tag{A1}$$

where

$$Z_i = (r_i - r_e)/r_e \tag{A2}$$

with $i = 1, 2$. Clearly, Z_i is the strain associated with bond i. If $r_1 = r_2$, then $r_1 = r_2 = r$, $Z_1 = Z_2 = Z$ (after Equation 11), and $x_1 = x_2 = y$ (after Equation 10). Combining Equations 1, 2, 7 to 9, A1 and A2, we obtain

$$\begin{aligned} U = DB^{-2}[&k(x_1^2 x_2^2 - 2Bx_1x_2) \\ &+ B^2(x_1^{-2} - 2x_1^{-1} + x_2^{-2} - 2x_2^{-1})]. \end{aligned} \tag{A3}$$

Equation A3 reduces to Equation 6 for bond-length variations constrained to take place along the line $r_1 = r_2$.

Equation A3 provides a general description of potential-energy variations for all values of x_1 and x_2 greater than zero. However, rather than carry out a detailed analysis of properties of this equation, we shall simply consider one specific example, namely, that for which $k = 1$ and $B = 7$. (The example depicted in Fig. 3 pertains to this same value of B.)

In Figs 4 to 6, the potential-energy "surface", defined in Equation A3, is plotted for this special case, as a function of x_1 and x_2 for various ranges of values of these two parameters, as well as for various orientations of the (x_1, x_2, U) co-ordinate axes, relative to the observer. In each of Figs 4 to 6, that portion of the potential-energy surface is

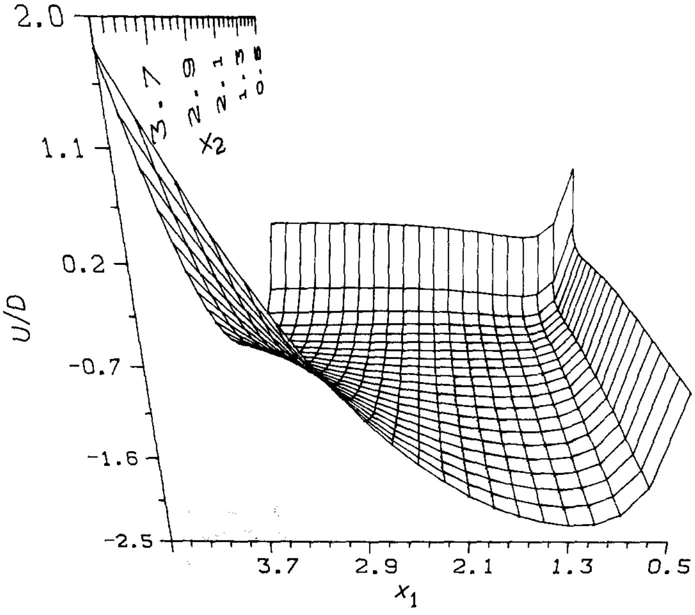

Figure 4 A view of the potential-energy surface (after Equation A3) for $B = 7$ and $k = 1$.

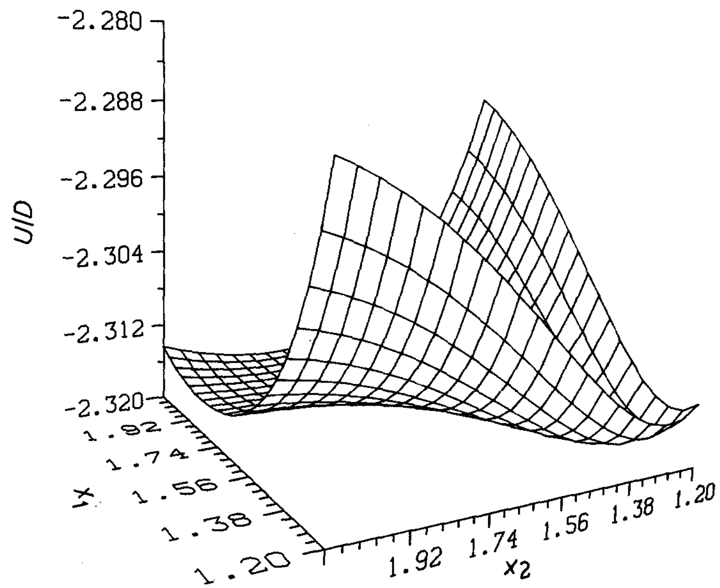

Figure 5 A view of a smaller portion of the potential-energy surface shown in Fig. 4, illustrating the two energy minima existing along the line $x_1 = x_2$.

illustrated that is bounded by the "cube" defined by the segments of each of the co-ordinate axes shown. A number of important features relative to bond extension can be deduced from Figs 4 to 6, as now discussed.

First, the range of x_1 and x_2 covered in Fig. 4 is relatively large, extending well into the régime for which the quantity y, treated in the text, is greater than 2. Indeed, if we follow the behaviour of U along the line $x_1 = x_2$, it can be seen that its variation about this line is generally consistent with Equation 3, that is, for small y, U increases about the line $x_1 = x_2$, whereas for larger values of y (specifically, $y > 2$, after Equation 3), U decreases about this line.

The "fine" structure of the potential-energy surface, that exists along the line $x_1 = x_2$ and within the region $y < 2$, cannot be distinguished in Fig. 3. Such structure, which for this special case consists of two energy minima and an energy maximum (see Table I), can, however, be resolved through a closer examination of the pertinent portion of the energy surface. Towards this end, consider Figs 5 and 6, noting first that the only difference between them is the position of the observer relative to the co-ordinate axes. Note also

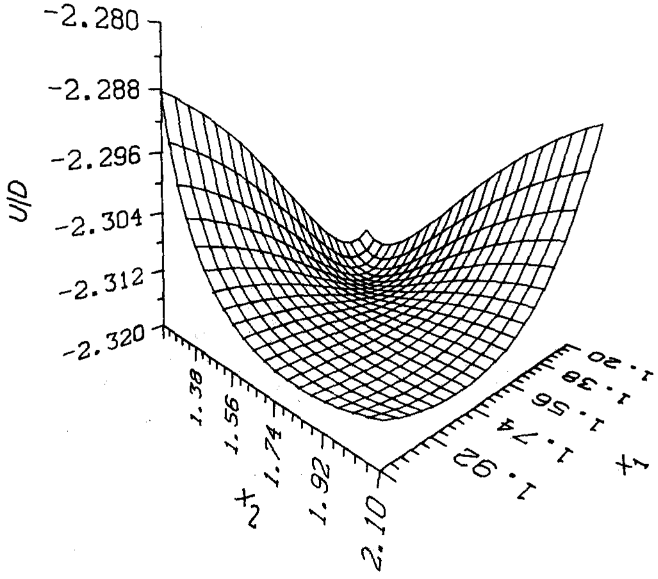

Figure 6 The same potential-energy surface shown in Fig. 5, but viewed from a different position.

that the energy range covered along the U-axis in Figs 5 and 6 is quite small compared to that covered in Fig. 4. The energy barriers against bond extension and healing are visible, particularly in Fig. 5, and the increase of potential energy about the line $x_1 = x_2$ can clearly be seen.

Appendix 2: Properties of stationary points of U for $0 < k < 1$

Some properties of the stationary points of the total potential energy, U, are determined for the case in which the inner bond is weakened, i.e., $0 < k < 1$. Only those values of y are considered that are real and lie within the range $0 < y \leqslant 2$. (Actually, the minimum value of y is $\exp(-\eta)$, as indicated in the text.)

For the sake of convenience, we set $A \equiv B^{-1}$ and $j \equiv k^{-1}$, in which case Equation 14 becomes

$$A^2y^6 - Ay^4 + j(y-1) = 0. \qquad \text{(A4)}$$

One can readily show, from Equation A1, that for given values of j and y, the quantity A is given by

$$A = [y \pm (y^2 - 4jy + 4j)^{1/2}]/(2y^3). \qquad \text{(A5)}$$

One can use Equation A5 to show that, for y restricted to the range $0 < y \leqslant 2$, real values of A exist only within the subrange

$$0 < y \leqslant y^{(2)}_{\max}, \qquad \text{(A6)}$$

where

$$y^{(2)}_{\max} \equiv 2[j - (j^2 - j)^{1/2}]. \qquad \text{(A7)}$$

One can use Equations A6 and A7 to express the acceptable range of y in terms of k rather than j, i.e.,

$$0 < y \leqslant (2/k)[1 - (1-k)^{1/2}]. \qquad \text{(A8)}$$

In addition, it follows, from Equation 7, that $A > 0$, so that only those values of A, denoted as A_+ and A_-, are of interest, where, using Equation A5,

$$A_+ \equiv [y + (y^2 - 4jy + 4j)^{1/2}]/(2y^3), \quad 0 < y \leqslant y^{(2)}_{\max} \qquad \text{(A9)}$$

and

$$A_- \equiv [y - (y^2 - 4jy + 4j)^{1/2}]/(2y^3), \quad 1 < y \leqslant y^{(2)}_{\max}. \qquad \text{(A10)}$$

The specific values of y for which Equation A4 is satisfied can be determined by plotting, for a given value of $j > 1$, the quantities A_+ and A_- as a function of y. Then, for a given value A_0 of A, the corresponding roots of Equation A4 are the intersections of the curves A_+ and A_- with the straight line $A = A_0$. Thus, by examining the manner in which A_+ and A_- vary with y, we can determine the number of such intersections, for given values of j. For example, it is clear that Equation 14 has exactly one root within the range of y given by Equations A6 or A8, for all $B > 0$ (the minimum value of B of interest actually being $\exp(-3\eta)$) and for all $0 < k < 1$, if and only if, A_+ is a monotonically decreasing function of y on its domain and A_- is a monotonically increasing function of y on its domain. Consequently, we shall next examine the manner in which A_+ and A_- vary with y on their respective domains.

First, we differentiate Equation A9 with respect to y to obtain

$$\mathrm{d}A_+/\mathrm{d}y = -y^{-4}[y + (y^2 - 5jy + 6j)/(y^2 - 4jy + 4j)^{1/2}], \qquad \text{(A11)}$$

where the right-hand side of Equation A11 is undefined at the upper limit of the range of y stated in Equation A9. Now,

$$y^2 - 5jy + 6j = y^2 - 4jy + 4j + j(2-y), \qquad \text{(A12)}$$

and it is clear that the right-hand side of Equation A12 is positive for y within the range stated in Equation A9. Consequently,

$$\mathrm{d}A_+/\mathrm{d}y < 0 \qquad \text{(A13)}$$

within the stated range of y, so that A_+ is a monotonically decreasing function of y within this range.

Next, we differentiate Equation A10 with respect to y to obtain

$$\mathrm{d}A_-/\mathrm{d}y = y^{-4}[-y + (y^2 - 5jy + 6j)/(y^2 - 4jy + 4j)^{1/2}], \qquad \text{(A14)}$$

where the right-hand side of Equation A14 is undefined at the upper limit of the range of y stated in Equation A10. Thus, we must examine the magnitude of

$$y^2 - 5jy + 6j \qquad \text{(A15)}$$

relative to that of

$$y(y^2 - 4jy + 4j)^{1/2} \qquad \text{(A16)}$$

over the domain of y covered by the function A_- and for all $j > 1$. Towards this end, we calculate the square of Expression A15 minus the square of Expression A16 and thus obtain the quantity $jg(y)$, where

$$g(y) \equiv (6-5y)^2 j + 8y^2 - 6y^3, \qquad \text{(A17)}$$

which is of interest to us within the domain of y covered by A_-. It is clear, for example, that $g(1) = j + 2$ and $g(y \to \infty) \to -\infty$. Similarly, it follows from Equations A7 and A12 and from the original definition of $g(y)$, that $g(y^{(2)}_{\max}) > 0$. Consequently, $g(y)$, always has at least one root greater than $y^{(2)}_{\max}$. By Descartes' rule of signs [16], the function $g(y)$ can have at most three real and positive roots of y. Therefore, either $g(y) > 0$ over the entire domain of y for the function A_- or $g(y)$ has two roots within this domain. The limiting case occurs when the value of j is such that $g(y)$ has two equal roots within this domain. The condition for equal roots is that the discriminant of $g(y)$ be zero. Before evaluating this discriminant, we make the change of variable

$$w \equiv 6 - 5y$$

in which case $g(y)$ becomes

$$g(y) = \tfrac{1}{125}\,[6w^3 + (125j - 68)w^2 + 168w + 144]. \qquad \text{(A18)}$$

Following Uspensky [25], the discriminant, Δ, of the right-hand side of Equation A18 is

$$\Delta = -576(\tfrac{1}{125})^4(t^3 - 49t^2 - 4536t + 232560), \qquad \text{(A19)}$$

where

$$t \equiv 125j - 68. \qquad \text{(A20)}$$

The three roots of the cubic polynomial in t in Equation A19 are $t = -68$, 57, and 60. From Equation A20, it is found that the corresponding values of j are $j = 0, 1$, and 128/125. Consequently, it readily follows that Equation A19 can be expressed as

$$\Delta = -\tfrac{576}{125}\, j(j-1)(j - \tfrac{128}{125}). \qquad \text{(A21)}$$

On the basis of the foregoing analysis, it is concluded that $g(y)$ has exactly one root (necessarily greater than $y^{(2)}_{\max}$) if $j > 128/125$, three roots, two of which are equal, for the limiting case of $j = 128/125$, and three distinct roots if $1 < j < 128/125$. In the last case, two of the roots lie between 1 and $y^{(2)}_{\max}$. For the limiting case of $j = 1$, $g(y)$ has three roots, two of which are equal. Therefore, for $j > 128/125$, the right-hand side of Equation A14 does not change sign within the domain of y for which A_- is defined (after Equation A10). Consequently, for this range of j and this entire domain of y, $g(y) > 0$, and since, within this range of y, $j^2 - 5jy + 6j > 0$ (after Equation A12), it follows that $\mathrm{d}A_-/\mathrm{d}y > 0$ under these same conditions. Thus, for $j > 128/125$, i.e., $0 < k < 125/128$, there exists only one root of Equation 14 within the range $0 < y \leqslant y^{(2)}_{\max}$. From the discussion presented in Section 2 it follows that this root must correspond to an energy minimum.

The situation for which $1 < j \leqslant 128/125$, i.e., $125/128 \leqslant k < 1$, is somewhat more complicated and will not here be analysed in detail. We do note that, for some values of $B > 0$, Equation 14 has two distinct roots for $j = 128/125$ and three distinct roots for $1 < j < 128/125$, within the range $0 < y \leqslant y^{(2)}_{\max}$. The relevant values of B could be readily determined, for given j, as follows. The corresponding A values are those that exist between the relative maximum and minimum of A_- that, in turn, exist for $1 < j < 128/125$. These are obtained by solving the expression $g(y) = 0$ (see Equation A18) and substituting the result into Equation A10. Of course, for the limiting case, $j = 128/125$, $g(y)$ has one distinct root within the range $0 < y \leqslant y^{(2)}_{\max}$ with two roots for Equation 14 existing within this allowable range of y. The nature of these roots (i.e., whether they correspond to maximum energy, minimum energy or an inflection point in energy) is as discussed in Section 2. One example, pertinent to this range of k, is that presented in Section 3, centred around Fig. 3.

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