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DIFFUSION NEAR A TENSILE CRACK

by

PETER JOHN LOOS

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

Franz R. Brotzen, Stanley O. Moore
Professor of Materials Science
Chairman

Rex B. McLellan, Professor of
Materials Science

Alan J. Chapman, Harry S. Cameron
Professor of Mechanical Engineering

Mary F. Wheeler, Professor of
Mathematical Sciences

HOUSTON, TEXAS

APRIL 1986
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1986
DIFFUSION NEAR A TENSILE CRACK

by PETER JOHN LOOS

ABSTRACT

In inhomogeneously stressed solid solutions, a force is exerted on each solute atom. The magnitude and direction of the force depend on the solute atom's chemical potential gradient. The chemical potential, in turn, depends on the local solute concentration and local stress state.

The forces exerted on the solute atoms cause them to be redistributed within the stressed body. This diffusion of solute atoms is described by Fick's laws. Near a tensile crack, the primary component of interstitial diffusion is directed radially inward, toward the crack tip. Solute atoms accumulate there. Such accumulation is necessary in order for embrittlement to occur. Embrittlement is most acute at a particular temperature, the one at which the radial component of solute mobility is at a maximum.

By introducing a zone of plastic deformation around the crack tip and by assuming that solute atoms do not interact, one obtains a critical material strength below which no embrittlement can occur. This critical strength has no explicit dependence on microstructure, applied stress or shape of the cracked body. Calculated values of the critical material strength and the temperature of most acute embrittlement are in reasonable agreement with experimental values, for the case of hydrogen in steel.

Solute accumulation within a particular microstructural feature leads to fracture of that feature, followed by repeated solute accumulation and fracture. An average crack growth rate can be calculated for this discontinuous process. The calculated growth rate curves, as a function of applied stress intensity, exhibit three distinct regions that are also observed in experimentally measured growth rate curves.
ACKNOWLEDGEMENTS

This research was sponsored in its entirety by Hughes Tool Company. Without the patience and support of King Crutchfield and Phil Kirk it would never have been possible.

Dr. Franz Brotzen suggested the subject of this thesis, and it was he and Dr. Alfred Seeger who laid the groundwork for this effort with their earlier unpublished work. Without the constant guidance of Dr. Brotzen this research would have never been completed. Dr. Mary Wheeler suggested the numerical methods that were employed and she helped to guide the development of the computer program. My wife Elizabeth helped with preparation of the manuscript.
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1. Definition of a Few FORTRAN Names
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1. INTRODUCTION

1.1 General Outline

The general purpose of this work is to achieve a better understanding of processes occurring at and near crack tips in material bodies subjected to externally applied stress. In particular, this work is limited to examining the effects that such stresses have on mobile solute atoms present in the material. It is believed that under some conditions the mobile solute atoms can travel toward and accumulate around the tips of cracks, thereby influencing their propagation.

The ultimate causes of such solute segregation are chemical potential gradients within the cracked body. In the present model, the chemical potential of an individual solute atom is determined completely by the local concentration of solutes and the local stress state in the material. Solute atoms, from a macroscopic perspective, are seen to flow toward configurations in which the total free energy of the system is minimized and in which the total entropy of the system is maximized.

These solute flows are described phenomenologically by Fick's first law of diffusion, which is the starting point of this investigation. Fick's second law and the present mathematical model are formulated in terms of a linear second order partial differential equation that is descriptive of the solute concentration in homogeneous and isotropic materials. In order to solve for the solute concentration and fluxes within the cracked body, the shape of the cracked body must be specified, along with the specific conditions prevailing on its boundary. In this investigation a simple cylindrical geometry and constant Dirichlet boundary conditions are assumed. They appear to be the simplest and most appropriate to the problem at hand. In a simple
but useful way the chosen conditions are used to describe surface cracks that have not been invaded by an active chemical environment, as well as clean internal cracks.

The differential equations that describe the solute distribution within the cracked body have the form of classical diffusion-convection equations. These are notoriously difficult to solve. To simplify matters, Fourier's method of separation of variables is used to change the two-dimensional problem into an eigenvalue problem in one spatial dimension. Then the steady state, time independent solutions for the solute concentration and solute flux are obtained in terms of the modified Bessel functions of the first and second kind. It is shown that eigenvalue zero usually dominates the steady state behavior of the system.

While the steady state solutions to the differential equation are readily obtained in terms of known analytic functions, the transient, time dependent behavior of the equation cannot be expressed so conveniently. It is necessary to calculate approximate numerical solutions to the transient behavior of the system. To accomplish this the domain in space and time is broken up into a grid, and the Galerkin finite element method is used to transform the differential equation into a system of linear algebraic equations describing the grid points. The algebraic problem is solved at each chosen point in time. Since the problem is reduced to one spatial dimension, it is possible to carry out the calculations on a personal computer.

Three sorts of results are obtained from the numerical calculations. First are the concentration profiles throughout the cracked body, at various points in time. The other results are
calculated from these concentration profiles. Second are the solute fluxes into the region surrounding the crack tip. Finally, and most useful of all, the total solute accumulation in the neighborhood of the crack tip is calculated. Taking these curves of solute accumulation (as a function of time) and choosing an appropriate criterion for the onset of fracture, one obtains crack growth rate curves. These growth rate curves constitute one of three primary results of this research.

The other primary results of this research concern the temperature at which embrittlement is most acute and the critical strength below which no embrittlement occurs. While the calculations of solute concentrations, fluxes and accumulations in the cracked body require explicit specification of the specimen geometry and boundary conditions, these two features of specimen embrittlement can be obtained without specification of these items.

The critical material strength is obtained from the turning point of the differential equation. By comparing the turning point of the differential equation (which has the units of distance, as described in section 3.2) with the radius of a particular zone of deformation surrounding the crack tip (described in section 3.1), the critical material strength for embrittlement is determined.

Finally, the temperature of most acute embrittlement is derived from the solute atom mobility. In uniformly stressed bodies, the solute mobility is independent of position. In the present inhomogeneously stressed body, solute mobility is redefined to include a dependence on position. This position dependent mobility reaches a maximum where the derivative of mobility with respect to temperature vanishes.

Some of the results can be compared with available experimental
data. For the case of hydrogen in iron, calculated values of the critical material strength for embrittlement and the temperature of most acute embrittlement are in reasonable agreement with the experimental data.

1.2 Purpose of the Investigation

This investigation initially had two main purposes. The first was to determine the initial flow rate of solute atoms into the neighborhood of a crack tip in a perfectly elastic material. More specifically, the quantity of interest was the time dependence of the initial flow rate at infinitesimal distances from the crack tip. Recently, Rauh and Bullough (1985) have published a solution for this flow rate, in which they neglect the small effects of solute concentration gradients very near the crack tip. In order to improve on their results one must retain the effects of concentration gradients and thereby obtain information on solute atom behavior that is valid over much larger regions of the cracked body and over much longer time spans. This has been done in the present finite element calculations. These calculations also allow for the presence of a plastically deformed zone surrounding the crack tip.

The second original purpose of this investigation was to shed some light on one particular sort of experimental data that is often recorded during fracture tests on metals in embrittling environments. The particular data referred to here is the measured time to failure. In many tests on smooth or blunt notched specimens, the only data collected during the test is simply the measured time from load application to total specimen failure.

In such tests, if failure is due to some embrittling species, the
time to failure must be the sum of three components. In order for embrittlement to occur, some minimum amount of embrittling material must be involved. First, the embrittling material must react chemically with and be deposited on the specimen's surface. This adsorption is a thermally activated process and requires a certain amount of time. Next, the embrittling material must diffuse through the bulk of the specimen to the crack tip or other embrittled site. This too is a thermally activated, time dependent process. Finally, the embrittling material must somehow react with the base material that is already present, and thereby reduce its load bearing capacity. This reaction must also be thermally activated and time dependent.

The time to failure is just the sum of these three parts. Generally, it is expected that one of the three processes is much slower than the other two, in which case it alone would almost completely determine time to failure. It is believed that in many situations the diffusion process is the slowest of the three. Consequently, the second main goal of this research was to quantify the contribution of the diffusion process to the total time to failure. This goal has been met to some extent; however, further significant progress awaits development of a failure criterion relating solute atom accumulation in the neighborhood of the crack tip to the initiation of crack growth.

Besides these main objectives, two others were never far from the forefront. For dozens of years it has been recognized that hydrogen embrittlement of steel is most acute near room temperature. The usual explanation is that the solute atom mobility reaches a peak near room temperature. Temperature values calculated from the usual mobility definition, however, are too high by a factor of two. One goal of this
research, therefore, has been to explain this discrepancy. This goal has been accomplished.

It has also been recognized for some decades that soft steel is generally immune to hydrogen or hydrogen sulfide embrittlement while steel with a tensile strength above roughly 110,000 psi is readily embrittled. The amount of research devoted to this phenomenon over the years has been astronomical, yet no satisfactory explanation of it has ever been offered. The present research provides a description of this embrittlement behavior.
2. BACKGROUND

Ultimately, the starting point for the present research is the work of Cottrell and Bilby (1949) in which they determined the drift of solute atoms to a dislocation line. The dislocation problem which they considered is in many respects analogous to the present crack problem. Perhaps the most significant difference between the two is the exact position dependence of the attractive forces between solute atoms and the defect line. This difference is quantitative rather than qualitative. Another difference between the crack problem and that of the dislocation is as follows. The dislocation problem is one of constant displacement, as characterized by Burger's vector. As solute atoms accumulate around the dislocation line, they relax its long range force field. The crack problem, on the other hand, is usually a constant load problem. In this case accumulating solutes do not ultimately relax the applied load or the stress field within the cracked body.

There are several profound similarities between the problem of solute segregation to a crack and solute segregation to a dislocation. The primary similarity is the form which Fick's second law assumes. Since this second order differential equation has the same basic form for the two cases, the same mathematical techniques can be used to derive exact solutions, or at least approximate ones. Another similarity between the crack and dislocation problems is the condition at the center of the line defect. In both crack and dislocation problems, the defect line initially acts as a sink for the solute atoms. The dislocation core is analogous to the plastic zone at the crack tip. Since neither the dislocation sink nor the crack tip sink can be infinite, they both eventually fill up with solute. Soon thereafter the
net flow of solutes toward the defect line slows and completely stops.

Very near either the dislocation or the crack tip, the elastic interaction between defect and solute atom becomes very large. Consequently, very near the defect line one can consider that only the elastic interaction is significant, and the effects due to solute concentration gradients can be ignored. This is the main limiting assumption made by Cottrell and Bilby (1949). Making this assumption, they calculated the flow rate of solute atoms into the neighborhood of a dislocation line. Their results, valid only for short time periods and very near the defect line, indicate that the accumulation of solutes near the dislocation increases as the 2/3 power of time. Cottrell and Bilby used their model of solute accumulation around dislocations to explain the strain ageing of iron.

Rauh and Bullough (1985) have used an approach almost identical to that of Cottrell and Bilby to determine the rate at which solute atoms accumulate around a crack tip. They made the same simplifying assumption that concentration gradients are negligible in the neighborhood of the line defect. In this way they arrive at the the accumulated amount of solutes near the crack tip. They find that it increases as the 4/5 power of time.

Ham (1959) significantly improved on the method of Cottrell and Bilby (1949). Investigating the dislocation problem, he retained in the differential equation the term containing the solute concentration gradient. Even near the dislocation line he did not neglect this term with respect to the elastic interaction term. Ham first solved the resulting differential equation in the steady state limit where all time derivatives vanish. His solution was in terms of the modified Bessel
functions of the first and second kind. Ham found that the more general
time dependent differential equation could not be readily solved using
known analytic functions. He therefore employed numerical techniques to
obtain those time dependent results for the solute atom concentration.
The work of Ham on the dislocation problem has served as a prototype for
the present investigation of solute segregation around crack tips.
3. THEORETICAL INVESTIGATION

3.1 The Problem in Two Spatial Dimensions

To begin this investigation the simple crack geometry shown in Figure 1 is chosen. The cracked body is assumed to be cylindrical in shape and infinite in thickness. The crack itself is assumed to be straight, sharp and of infinitesimal width with its tip lying along the axis of the cylinder and in the plane y=0. In a homogeneous, isotropic, perfectly elastic medium the stress fields surrounding the crack tip, as given by Hertzberg (1976), are

\[
\begin{align*}
\sigma_y &= K(2\pi r)^{-1/2}\cos(\theta/2)[1 + \sin(\theta/2)\sin(3\theta/2)] \\
\sigma_x &= K(2\pi r)^{-1/2}\cos(\theta/2)[1 - \sin(\theta/2)\sin(3\theta/2)] \\
\sigma_{xy} &= K(2\pi r)^{-1/2}\cos(\theta/2)\sin(\theta/2)\cos(3\theta/2)
\end{align*}
\]

where \( K \) is Irwin's stress intensity factor and where \( x, y, r \) and \( \theta \) are shown in Figure 1. Note the singularity in \( r \), of order 1/2. In this model \( K \) is dependent only on the externally applied load and the macroscopic crack geometry. For the infinitely thick body that was chosen, the plane strain condition is appropriate:

\[ \sigma_z = \nu(\sigma_x + \sigma_y) \]

where \( \nu \) is Poisson's ratio. The first invariant of the stress tensor, the hydrostatic stress, is readily seen to be

\[ P = \frac{1}{3}(\sigma_x + \sigma_y + \sigma_z) = (1+\nu)(K/3)(2/\pi r)^{1/2}\cos(\theta/2) . \]

In the two preceding equations, the plane stress case is obtained simply by setting \( \nu=0. \)

No real material can elastically accommodate these stresses that increase without bound as \( r \) goes to zero. The present investigation, therefore, allows for the presence of a small zone of plastic deformation surrounding the crack tip. In this zone all radial stress
components are assumed either to vary slowly so that their gradients are negligible (implicit in [3.1.5] below) or to be directed away from the crack tip (implicit in [3.1.7] below). Outside the deformed zone, the elastic conditions described by equations [3.1.1] prevail. The zone is assumed to have high dislocation densities and high concentrations of point defects such as vacancies and self-interstitials, the result of edge dislocation climb. These defects act as traps for the mobile solute atoms, and the dislocations can significantly increase the mobility of solute atoms when they are mobile or are present in sufficient numbers.

The zone is assumed cylindrical, of radius \( r_p \), with its axis lying along the crack tip. While the plastic zone shape is usually far from circular (especially in plane strain), the assumption of a circular zone is made to facilitate the calculations. Since the elastic stress components are most concentrated in the direction of crack growth, \( \theta = 0 \), the extent of the deformed zone in that direction is of primary importance.

Parker (1981) reviewed some simple plastic zone models. Those of Irwin (1958) and Dugdale (1960) are most appropriate for the case of plane stress. Modifying Irwin's model by replacing the yield strength \( \sigma_0 \) with the maximum tensile strength of the material, \( \sigma_T \), leaves

\[
[r_p = (K/\sigma_T)^2 (1/2\pi)]
\]

For an elastic – perfectly plastic material (in which there is no work hardening), the yield strength and the tensile strength have the same value and \( r_p \) coincides with the usual elastic-plastic boundary. In work hardening materials the tensile strength is greater than the yield strength, and the radius \( r_p \) is not the usual plastic zone radius. It does not depend on the material's yield strength for the following
reason: when stress in a material has just reached the yield point, the nonconservative movement of dislocations, as well as the creation of both dislocations and point defects is just beginning. At the yield point in work hardening materials there exist substantial stress gradients which can move mobile solute atoms. These gradients do not completely vanish until the maximum tensile stress is reached. Therefore, the maximum tensile strength of the material is used, not the yield strength. In Irwin's model the visually observed crack length is increased by the radius \( r_p \) so that the crack tip is considered to lie at the center of the plastic zone. The Dugdale plastic slit model, although it differs from the Irwin model in some important respects, leads to a formula similar to [3.1.4], where the factor \( 1/2\pi \) is replaced by \( \pi/8 \). In both models \( r_p \) is in the direction of crack growth. The most appropriate of Parker's models for plane strain are based on the Mises (1913) critical strain energy density and the Tresca (1864) critical resolved shear stress. More recently, Johnson and Mellor (1962) have discussed the Mises and Tresca yield criteria. In the direction of crack growth the Mises criterion yields

\[
[3.1.5] \quad r_p = \frac{(K/\sigma_t)^2(1-2\nu)^2}{4\pi} 
\]

while the Tresca model results in a value for \( r_p \) exactly twice as large. Again, the tensile strength has been used rather than the yield strength. Note that equations [3.1.4] and [3.1.5] both depend on the square of the ratio of stress intensity to tensile strength. It is also significant that, in the case of plane strain, \( r_p \) is particularly sensitive to another material property, Poisson's ratio. In all of the plastic zone models mentioned so far, the radius \( r_p \) can be written as

\[
[3.1.6] \quad r_p = Q(K/\sigma_t)^2 
\]
where $Q$ is a dimensionless number that depends on the macroscopic stress state (plane stress or strain) and some material properties.

Hutchinson (1968) and Rice and Rosengren (1968) have presented a more sophisticated model of plasticity near crack tips in work hardening materials. Their results are clearly more realistic than the earlier ones mentioned above, but the results cannot be written in a simple closed form since they are obtained only by numerical techniques. From the numerically derived curves, one feature is rather evident. In the direction of crack growth, the plastic zone radius is rather sensitive to material properties other than just the material strength. Rice (1973) presented some more recent computational results, in a form that can be used in the present investigation. For a blunt crack in a work hardening material with continuous displacements across the elastic-plastic boundary, he gives for the crack tip opening displacement (CTOD) the formula \[\text{CTOD} = (0.5 \text{ to } 0.9) \frac{K^2}{\sigma_0E} \] where $E$ is Young's modulus and $\sigma_0$ is the material yield strength. Rice also points out that the point of maximum hydrostatic tensile stress lies at a distance from the crack tip of about twice the CTOD, in the direction of crack growth. As a result, \[r_p = 2 \text{CTOD} = (1.0 \text{ to } 1.8) \frac{K^2}{\sigma_0E},\] which depends on the yield strength, unlike equations [3.1.4] through [3.1.6]. In this model it is implicitly assumed that the crack tip has been blunted by the emission of dislocations into the plastic zone.

Next, as discussed by Puls (1985) for the case of hydrogen in iron, it is assumed that the solute atom induces negligible shear in the lattice, so that dilatations caused by the solute atom control the interaction with the elastic stress field. This interaction of solute and stress field has been discussed in general terms by several authors,
among them Li, Oriani and Darken (1966); Rauh and Bullough (1985) and Puls. Besides this assumption of purely spherical dilatation, it is further assumed that the solute atom induces a volume change in the body which is independent of the local stress state. Under these assumptions the potential energy of the interaction, in the elastic region, is

\[ U(r,\theta) = -P \delta v \]

where \( U \) is the potential per solute atom and \( \delta v \) is the local dilatation of the elastic continuum by the solute atom. The negative sign indicates that the internal energy of the system is reduced by the interaction. In arriving at equation [3.1.8] it is assumed that other contributions to the total energy of the system which contain the square of a stress term divided by an elastic modulus are negligible. In the published literature such contributions are usually attributed to differences between the elastic moduli of solute and solvent materials. Strictly speaking, isolated solute atoms cannot be described by such bulk properties, so that one should refer instead to differences between the interatomic potentials of solute and solvent atoms. In [3.1.8], \( \delta v \) is not the partial molar volume \( \bar{v}_i = \partial v/\partial n_i \). Instead, as described by Hirth (1980), the two quantities are related by the expression

\[ \delta v = \bar{v}_i (1+\nu)/3N_a (1-\nu) \]

where \( N_a \) is Avogadro's number. Inserting [3.1.3] into [3.1.8] leads to

\[ U = -Br^{-1/2} \cos(\theta/2) \]

where \( B = (1+\nu)(K\delta v/3)(2/\pi)^{1/2} \). For any interstitial species in any lattice, \( \delta v \) is greater than zero; therefore, for cracks loaded in tension, \( U \) is a negative, attractive potential throughout the elastic region. This potential results in a flux of atoms, the density of which is \(-C(D/kT)\nabla U\) where \( D \) is a phenomenological diffusion constant, \( C \) is the solute atom concentration.
(number per unit volume) as a function of position and time, \( k \) is Boltzmann's constant, \( T \) is absolute temperature and grad is the gradient operator. The term \( (D/kT) \) represents the solute atom mobility, and the potential gradient is just the force acting on each solute atom. Because \( \text{grad}(U) \) is always positive, the entire flux density term is always negative, indicating a flux of atoms toward the crack tip.

An additional solute flux term arises from gradients in the solute concentration. It has the form \(-D\text{grad}(C)\). The total solute flux density, \( \vec{j} \), can therefore be written as

\[
[3.1.11] \quad \vec{j}(r,\theta,t) = -D[ \text{grad}(C) + C\text{grad}(U)/kT ]
\]

This modified version of Fick's first law accounts for the redistribution of solute atoms by an arbitrary potential \( U \). For the purposes of this investigation it is assumed that \( U \) is independent of both concentration \( C \) and time \( t \). From equation \([3.1.11]\) one can derive the equation of continuity, Fick's second law. It is readily found to be

\[
[3.1.12] \quad \partial C/\partial t = D( \text{div}[ \text{grad}(C) + C\text{grad}(U)/kT ])
\]

where \( \text{div} \) is the divergence operator. Equation \([3.1.12]\) is rewritten as

\[
[3.1.13] \quad \partial C/\partial t = \text{div}[ D\text{grad}(C) + uC ]
\]

where \( u \) is a velocity field defined by \( u=(D/kT)\text{grad}(U) \). In the form \([3.1.13]\) the equation begins to take on the characteristics of a fluid flow problem. Since \( \text{div}(\text{grad}(U))=0 \) it follows that the velocity field \( u \) has zero divergence. Equations \([3.1.11]\) and \([3.1.12]\) can also be written in the form

\[
[3.1.14] \quad \vec{j} = -C(D/kT)\text{grad}(\delta \mu) \quad \text{and} \quad \partial C/\partial t = \text{div}[ C(D/kT)\text{grad}(\delta \mu)]
\]

where \( \delta \mu = U + kT\text{log}(C) \) is the chemical potential of a solute atom relative to some constant reference state. Written in this form it is seen that chemical potential gradients are the sole driving
force for the redistribution of solute atoms.

Solutions to this linear second order parabolic partial differential equation must be subject to certain boundary conditions. For the present problem a particularly simple set of Dirichlet boundary conditions are chosen. First, it is assumed that the initial solute concentration (at time \( t=0 \)) in the cracked body is a constant \( C_0 \). It is further assumed that the outer cylindrical surface of the cracked body (at \( r=r_0 \)) is exposed to an infinite reservoir of solute whose concentration is also \( C_0 \). It is also assumed that the crack tip is an ideal sink for the interstitial solutes. This assumption is warranted only during some limited period of time prior to saturation of the sink by the accumulating solute atoms. In the present investigation, the sink actually consists of dislocations, vacancies and other defects distributed in the deformed zone. They are simply lumped together at the crack tip. Once the sink is saturated by solute atoms, the condition \( C(r=0)=0 \) is no longer appropriate. Then, the most appropriate boundary condition is that of no flow across the boundary \( r=0 \). This latter condition is mentioned briefly in section 4.2. Other boundary conditions must be imposed on the two crack faces.

Because the potential \( U \), the chosen configuration (Figure 1) and the assumed boundary conditions are all even functions of angle \( \theta \), the concentration \( C \) must also be an even function of angle. Finally, in situations where the reservoir of solute is allowed to enter the crack, the solute concentration on the crack faces becomes the constant \( C_0 \). These boundary conditions are summarized as:

\[
\begin{align*}
\text{for } t>0: & \quad C(r=0) = 0 \\
& \quad C(\theta=\pm\pi) = C(\theta=-\pi) \\
& \quad C(\theta=\pm\pi) = C(\theta=-\pi) = C_0
\end{align*}
\]

[3.1.15] environment-free crack

environment-filled crack
for all \( t \): \( C(r=r_0) = C_0 \)

[3.1.15] for all \( r \) and \( \theta \): \( C(t=0) = C_0 \).

The parabolic Dirichlet problem just described has no exact solutions that can be written in closed form, in terms of known analytic functions. One can seek approximate numerical solutions to this problem in two spatial dimensions; however, it is not efficient to do so.

3.2 The Problem in One Spatial Dimension and the Turning Point

In order to understand better the physical processes that are going on near the crack tip, the differential equation must be simplified. To begin, the independent variable \( C \), a function of position and time, is replaced by the new variable \( G \), also a function of position and time, defined by the expression

[3.2.1] \( C(r,\theta,t) = \exp(G-U^*) \) where \( U^* = U/2kT = -Ar^{-1/2}\cos(\theta/2) \).

This expression serves to define the coefficient \( A=B/2kT \), where \( B \) is defined in [3.1.10]. A potential \( U_0^* \) can also be defined by

\[ U_0^* = U^*(r=r_0) \]

Substitution [3.2.1] was used previously by Ham (1959), although in a slightly different form. From equation [3.2.1] one can readily see that

\[ \frac{\partial C}{\partial t} = \exp(G-U^*)(\frac{\partial G}{\partial t}), \]

\[ \text{grad}(C) = \exp(G-U^*)\text{grad}(G-U^*) \]

and \( \text{div}(\text{grad}(C)) = \exp(G-U^*)[\text{grad}^2(G-U^*) + \text{div}(\text{grad}(G-U^*))] \).

In these equations \( \text{grad}^2 \) denotes the scalar product of the gradient with itself. Using these substitutions, together with the facts that \( \text{div}(\text{grad}(U^*)) = 0 \) and \( \text{grad}^2(U^*) = A^2/4r^3 \), equation [3.1.12] becomes

[3.2.2] \[ D^{-1}(\frac{\partial G}{\partial t}) = \text{div}(\text{grad}(G)) + \text{grad}^2(G) - A^2/4r^3 \].
The further substitution $F = \exp(G)$ leaves

$$D^{-1}(\partial F/\partial t) = \text{div}(\text{grad}(F)) - (A^2/4r^3)F.$$  \[3.2.3\]

While this is valid in the elastic region of the specimen, it is not so inside the deformed zone. There, according to the plasticity model described by [3.1.5], grad($U^*$) effectively vanishes. In order to account for this in equation [3.2.2] or [3.2.3], set $A^2=0$ inside the deformed zone. Again, as described in section 3.1, this deformed zone is generally much smaller than the usual plastic zone which depends on the material yield strength. Since $F = \exp(G)$, the boundary conditions [3.1.15] become

$$F(r=r_0) = C_0 \exp(U^*_0)$$ \[3.2.4\]

for all $r$ and $\theta$: \[3.2.4\]

$$F(t=0) = C_0 \exp(U^*)$$

for $t>0$: \[3.2.4\]

$$F(\theta=\pi) = F(\theta=-\pi) \quad \text{environment-free crack}$$

$$F(\theta=\pi) = F(\theta=-\pi) = C_0 \quad \text{environment-filled crack}$$

On the crack faces, potential $U$ vanishes so that $C = F$ there. In the deformed zone grad($U$) vanishes, so within this zone $C = F$ also.

Next, Fourier's method of separation of variables, as described by Hildebrand (1962), is used to separate out the angular dependence. A calculation similar to the following one was described by Liu (1970).

The separation is accomplished by setting

$$F(r,\theta,t) = \sum_n d_n R_n(r,t)H_n(\theta)$$ \[3.2.5\]

where $n$ is the set of integers ($...,-3,-2,-1,0,1,2,3,...$). Also in equation [3.2.5] the angular dependence is contained only in the new function $H_n$, both the radial and time dependence are contained in $R_n$, and the $d_n$ are the constant Fourier coefficients. The separation constants (or eigenvalues) are denoted by $n$ and the sum is taken over all allowed values of those eigenvalues. In the following derivations
the subscripts \( n \) on the functions \( H \) and \( R \) will sometimes be omitted for simplicity. The derivations also require an expression for the operator \( \text{div}(\text{grad}) \). In the chosen circular coordinate system,

\[ 3.2.6 \quad \text{div}(\text{grad}) = \left( \partial^2/\partial r^2 \right) + r^{-1}(\partial/\partial r) + r^{-2}(\partial^2/\partial \theta^2) . \]

Combining equations [3.2.3], [3.2.6] and [3.2.5], multiplying both sides of the resulting equation by 4 and then separating variables in the usual way leads to the coupled equations

\[ 3.2.7 \quad \partial^2 H/\partial \theta^2 + n^2 H/4 = 0 \quad \text{and} \]
\[ 3.2.8 \quad D^{-1}(\partial R/\partial t) = R'' + r^{-1}R' - [ (A^2/4r^3) + (n^2/4r^2) ]R . \]

In the latter equation, primes (') denote the partial derivative with respect to \( r \). The general solution to the angular equation is

\[ 3.2.9 \quad H_n = g_n \sin(n\theta/2) + h_n \cos(n\theta/2) \]

where the \( g_n \) and \( h_n \) are arbitrary constants that are to be determined from the boundary conditions. In order that \( C \) be an even function of angle, all of the sine terms are eliminated by setting \( g_n = 0 \). As a result, equation [3.2.5] can be rewritten as

\[ 3.2.10 \quad F(r, \theta, t) = \sum_n d_n R_n(r, t) \cos(n\theta/2) \]

where the arbitrary constants \( h_n \) have been combined into the \( d_n \). The concentration formula therefore becomes

\[ 3.2.11 \quad C = \exp(-U^*) \sum_n d_n R_n(r, t) \cos(n\theta/2) . \]

Implicit in this equation is the assumption that the reservoir of solute atoms has not invaded the crack. The alternate assumption has also been considered, wherein the solute reservoir (environment) enters the crack and causes a constant solute concentration on the crack faces. This case will be addressed in a separate publication.

Next, using equation [3.2.11] the boundary conditions are rewritten in terms of the new dependent function \( R \). First consider the boundary at
r=0, for the perfectly elastic approximation. Since C(r=0) = 0 and \( U^* \) increases without limit as r vanishes, equation [3.2.11] requires that

\[
0 = \exp(\omega) \sum d_n R_n \cos(n\theta/2) \quad \text{or} \quad d_n R_n(r=0) = 0.
\]

[3.2.12]

Note that if a deformed region surrounds the crack tip, then \( U^*(r=0) \) is finite. According to the present model, \( U^*(r=0)=U^*(r=r_p) \). If C(r=0) is a finite constant, it follows that \( d_n R_n(r=0) \) is also a finite constant. If C(r=0) vanishes then so does \( d_n R_n(r=0) \). On the boundary at \( r=r_0 \) it is readily seen that equation [3.2.11] requires

\[
C_0 = \exp(-U^*_0) \sum d_n R_n \cos(n\theta/2).
\]

Using equation 9.6.34 of Abramowitz and Stegun (1964) it follows that

\[
d_n R_n(r=r_0) = C_0 I_n(-z_0)
\]

where \( z_0=\alpha r_0^{-1/2} \) and where \( I_n \) is the modified Bessel function of the first kind, of order n. In a similar manner the initial condition at \( t=0 \) leads to the requirement that

\[
d_n R_n(t=0) = C_0 I_n(-z)
\]

where \( z=\alpha r^{-1/2} \).

The solution to the radial equation [3.2.8] can be written as the sum of a steady state solution \( R^s \) and a transient solution \( R^t \). When this is done, the steady state solution must satisfy the time independent boundary conditions at \( r=0 \) and \( r=r_0 \), while the transient solution must satisfy the initial condition [3.2.14] and vanish on the boundaries \( r=0 \) and \( r=r_0 \). The steady state portion of [3.2.8] is just a modified Bessel equation, the general solution of which is of the form

\[
R^s = a I_n(z) + b K_n(z)
\]

where \( K_n \) is the modified Bessel function of the second kind of order n.

In the limit as r vanishes, both \( z \) and \( I_n(z) \) increase without limit.
Since boundary condition [3.2.12] requires that $R$ vanish at the origin, the constant coefficients $a_n$ must all be set to zero, leaving

$$[3.2.16] \quad d_n R_S = b_n K_n(z).$$

Condition [3.2.13] therefore becomes

$$[3.2.17] \quad d_n b_n K_n(z) = C_0 I_n(-z_0)$$

so that the constants are found to be

$$[3.2.18] \quad d_n b_n = C_0 I_n(-z_0)/K_n(z_0)$$

and finally,

$$[3.2.19] \quad d_n R_S = C_0 K_n(z)I_n(-z_0)/K_n(z_0).$$

Note that if $n$ is odd, then the right hand side (RHS) is negative. Using this result together with equation [3.2.11] leads to the steady state concentration distribution for the perfectly elastic approximation:

$$[3.2.20] \quad C^S = C_0 \exp(-U^*) \sum_{n} \cos(n\theta/2)K_n(z)I_n(-z_0)/K_n(z_0).$$

To simplify matters further, one can consider only those steady state concentrations $C$ which are independent of angle for large values of $r$. This means that at large distances from the crack tip neither the elastic stress fields described by equations [3.1.1] nor the presence of the crack itself influence solute concentration. At large distances from the crack tip, therefore, the solute concentration must approach the constant boundary value $C_0$. In this case [3.2.11] becomes

$$[3.2.21] \quad C(r>>A^2) = \sum_{n} d_n R_n(r,t) \cos(n\theta/2) = C_0.$$ 

This can only be satisfied by setting $d_n = 0$ for all $n \neq 0$, leaving

$$[3.2.22] \quad C(r,\theta,t) = \exp(-U^*)d_0 R_0(r,t).$$

The steady state solution for $R_0$ is found, as before, by setting $n=0$ and $(\partial R/\partial t)=0$ in equation [3.2.8], leaving

$$[3.2.23] \quad R'' + r^{-1} R' - (A^2/4r^3)R = 0.$$ 

The general solution of this equation is a linear combination of $I_0(z)$
and \( K_0(z) \). The boundary condition at \( r=0, C(r=0)=0 \), inserted into equation [3.2.22] gives

\[ 0 = \exp(\infty)d_0 R_0 \]

which can only be satisfied if \( R_0 = K_0(z) \). Next, the condition at \( r=r_0 \), \( C(r=r_0)=C_0 \), inserted into [3.2.22] leads to

\[ C_0 = \exp(-U_0^*d_0)K_0(z_0) \]

so that

\[ d_0 = C_0 \exp(U_0^*/K_0(z_0)) \]

As a result, the steady state concentration for the perfectly elastic approximation is found to be

\[ C^S(n=0) = C_0 \exp(-U_0^*+U_0^*)K_0(z)/K_0(z_0) \]

The one-dimensional equation [3.2.8] has another important property that must be demonstrated. To accomplish this the change of variable

\[ R(r,t) = r^{-1/2}L(r,t) \]

is made, which leads to the derivatives

\[ r^{-1/2}R' = L' - L/2r \]
\[ r^{-1/2}R'' = L'' - L'/r + 3L/4r^2 \]

Multiplying [3.2.8] by \( r^{-1/2} \), setting \( \partial R/\partial t = 0 \) and using the above substitutions leads to an equation for the new independent variable

\[ r^2L'' - L \left[ (A^2/4r) + (n^2 - 1)/4 \right] = 0 \]

This second order equation is in the so called normal form, and it has a single turning point. Morse and Feshbach (1953) and Bender and Orszag (1978) have discussed turning points of such differential equations in some detail. The turning point is used to describe systems in which fundamental particles are neither created nor annihilated. Physically, it is the point in space where a single particle's velocity vanishes. In a system composed of many randomly moving particles, an individual particle located at the turning point has an equal probability of moving
outward or inward. In a mathematical sense, the turning point is that point in space where the coefficient of the term linear in \( L \) vanishes. Here it is denoted \( r_v \) and is determined from

\[
(\alpha^2/4r_v^3) + (n^2 - 1)/4 = 0.
\]

This relation can only be satisfied if \( n=0 \) and \( r_v = A^2 \). If \( z_v \) is defined by \( z_v = A r_v^{-1/2} \) then a finite turning point occurs only if

\[
[3.2.30] \quad n = 0 \quad \text{and} \quad z_v = 1.
\]

For the case \( n=0 \), a solute atom for which \( z \) is greater than \( z_v \) has been trapped by the crack-tip stress field and cannot escape. This occurs because the position-dependent potential energy of the solute is greater than the thermal energy of the solute.

Another method of obtaining the turning point \( z_v = 1 \) is as follows. Consider a solute atom to be a simple harmonic oscillator, according to the law of Dulong and Petit. The thermal vibrational energy of such an oscillator in three dimensions is \( 3kT \), so in the present two dimensional model it is just \( 2kT \). If the oscillator is located at the turning point \( r_v \), in the direction of crack growth, then its potential energy \( U \) from equation \([3.1.10]\) is just \( U = -Br_v^{-1/2} \). The chemical potential of the oscillator is the sum of its potential and vibrational energy, equal to \( U + 2kT = -Br_v^{-1/2} + 2kT \). In order for the solute atom to embrittles the cracked material, it must be bound in some finite neighborhood of the crack tip by the elastic stress fields. In order for the solute atom to be bound there it is necessary that the total energy of the solute atom (equal to its chemical potential) must be negative. If the solute atom's energy is greater than zero, then the atom's motion is unbounded and no embrittlement can occur. Consequently, zero is the largest value of the chemical potential for which embrittlement is possible. From this it
follows that $Br^{-1/2}=2kT$ or $B/2kT=r^{1/2}$ or $A^2=r_v$. This is the same result that was obtained from the differential equation [3.2.28].

The trapping of solute atoms is analogous to the process by which the earth’s gaseous atmosphere is trapped by the planet’s gravitational field. The gravitational force field of the earth is completely independent of time, as is the force field of a crack under constant loading. On the other hand, the trapping of mobile solute atoms by an isolated dislocation is fundamentally different. The dislocation core represents a fixed displacement, not a fixed force. The force field associated with the fixed displacement vanishes as solutes accumulate.

Whether one considers the crack problem or the dislocation problem, in either case the solute atoms do not all have the same thermal energy. Instead their energies follow the Fermi-Dirac distribution, as described by Hirth and Lothe (1982). Nevertheless, for the present discussion it is assumed that all solute atoms have the same thermal energy and the same temperature.

The importance of the critical radius $r_v$ is investigated further by inserting the definition of $A$ into equation [3.2.30], yielding

$$r_v = \frac{(1+\nu)K\delta v/3kT}{2\pi}.$$

Solute atoms cannot be trapped by the crack-tip stress fields unless $r_v$ exceeds the size of the deformed zone, $r_p$. This must be so since the driving force, grad$(U)$, practically vanishes inside $r=r_p$. Using the critical strain energy density formula [3.1.5] leads to the inequality

$$r_v > r_p \quad \text{or} \quad \left(\frac{(1+\nu)K\delta v/3kT}{2\pi}\right)^2 = \frac{Q(K/\sigma_t)^2}{Q(K/\sigma_t)^2}.$$

Notice that the factor $K^2$ appears on both sides of the inequality. By eliminating both, the embrittlement condition becomes completely independent of the applied stress (or load) and completely independent
of crack length and other specimen geometry. Simplifying [3.3.32] leaves

\[ \sigma_e > 3(2\pi\alpha)^{1/2}kT/(1+\nu)\delta v \]

where \( Q \) is a dimensionless plastic zone size factor from equation [3.1.6] and \( \delta v \) is obtained from equation [3.1.9]. Accumulation of solutes, and hence embrittlement by them, cannot occur unless this condition is satisfied. Note that the condition for embrittlement depends primarily on the material strength, solute atom volume and absolute temperature. To a lesser extent it also depends on Poisson's ratio (or stress state) and the plastic zone size factor.

An alternate expression for the embrittlement condition can also be obtained from equation [3.1.7]. As before, setting \( r_v \) greater than \( r_p \), and using equation [3.1.7] in which the imprecise coefficient has been set to a value of 1.4 leaves

\[ (1+\nu)K\delta v/3kT)^2/\pi > 1.4(K^2/\sigma_0 E) \]

Eliminating \( K^2 \) from both sides and rearranging gives

\[ \sigma_0 > 2.8\pi(3kT)^2/E((1+\nu)\delta v)^2 \]

Note that inequality [3.2.35] for yield strength \( \sigma_0 \) depends on \( (kT/\delta v)^2 \) and \( E \) while inequality [3.2.33] for \( \sigma_e \) depends on \( (kT/\delta v) \) and not on \( E \).

Eigenvalues \( n \) other than zero are qualitatively different from \( n=0 \). By examining [3.2.29] it is readily seen that for \( n=1 \) or \(-1 \), the turning point is located at infinity. For values of \( n \) greater than one or less than negative one, \( r_v \) is not defined. Consequently, the trapping of solute atoms by the crack tip will be qualitatively different in any situation where the initial, boundary or other conditions which define the problem result in a significant contribution of eigenvalues other than \( n=0 \) to the solute concentration distribution. For example, if eigenvalue \( n=2 \) is of significance, then every solute atom in the entire
cracked body is irreversibly trapped by the crack tip stress field and will eventually collect at the crack tip. This will happen irrespective of both temperature and the material properties of solute and solvent.

Consequently, the equilibrium condition for embrittlement, either [3.2.33] or [3.2.35], is only valid for the case n=0. It does not adequately describe surface cracks that have been invaded by hostile environments, in which case it is anticipated that values of n other than n=0 are of increased importance. Conditions [3.2.33] or [3.2.35] would, on the other hand, be descriptive of precharged cracked specimens in inert environments or of internal cracks that never reach a free surface.

3.3 The Drift Approximation and the Solute Atom Flux

Bilby and Cottrell (1949) originally investigated the drift of solute atoms to an isolated edge dislocation. They assumed that very near the dislocation the singular elastic interaction between it and the solute atoms was so large that one could neglect the forces due to concentration gradients that also act on the solute atoms. The same limiting assumptions can be made for the present situation of solute-crack interactions near the crack tip. Taking equation [3.2.12] and setting grad(C)=0 leaves

\[3.3.1\] \( (\partial C/\partial t) = \text{div}( D \text{grad}(U/kT) ) \)

and since \( \text{div}(\text{grad}(U))=0 \) it follows that

\[3.3.2\] \( (\partial C/\partial t) = (D/kT)\text{grad}(C)\text{grad}(U) \).

where the gradients' scalar product is taken. Next, the definition of U from equation [3.1.10] and the definition of the gradient operator in circular coordinates
[3.3.3] \[ \text{grad} = \hat{r}(\partial/\partial r) + r^{-1}\partial/\partial \theta \] .

Here \( \hat{r} \) and \( \hat{\theta} \) are the radial and angular unit vectors. As a result,

[3.3.4] \[ \text{grad}(U) = (B/2r^{3/2})(\hat{r}\cos(\theta/2) + \hat{\theta}\sin(\theta/2)) \]

in the elastic zone and therefore [3.3.2] becomes

[3.3.5] \[ (\partial C/\partial t) = DAr^{-3/2}(\cos(\theta/2)(\partial C/\partial r) + r^{-1}\sin(\theta/2)(\partial C/\partial \theta)) \].

This equation is subject to the boundary conditions [3.1.15]. The only possible solution to equation [3.3.5] is a constant concentration; and, consequently, the only function \( C \) which can satisfy the boundary conditions is a discontinuous one. Therefore, assuming the crack tip is a perfect sink for solute atoms, inside a closed surface centered about \( r=0 \), the concentration is just \( C=0 \). Outside that closed surface, \( C=C_0 \).

The closed surface is described by a characteristic equation which relates the independent variables \( r, \theta \) and \( t \).

Rauh and Bullough (1985) have published an exact solution of equation [3.3.5]. For the equation of the characteristic they give

[3.3.6] \[ t(r,\theta) = 8DAr^{5/2}f(\theta) \]

where

[3.3.7] \[ f(\theta) = \left( 3(\sin(\theta)+\text{sgn}(\theta)-\theta)+2\sin(\theta)\sin^2(\theta/2) \right)/\sin^5(\theta/2) \].

From these results Rauh and Bullough calculate \( N(r,t) \), the total amount of solute that has accumulated inside a circle of radius \( r \) centered on the crack tip, after time \( t \). For the perfectly elastic medium they obtain the formula

[3.3.8] \[ N(r,t) = (5/2)(3\pi/4)^{1/5}C_0(2DAr)^{4/5} \]

which is independent of \( r \) and valid only in the limit as \( r \) goes to zero.

Equation [3.3.8] is a useful approximation of the solute atom behavior in a limited region of the cracked body, and only for a limited period of time. It is useful only in regions much closer to the crack tip than the particle turning point described in section 3.2, and it is
obviously of no use inside the deformed zone described in section 3.1. Furthermore, [3.3.8] is useful only during the period of time in which all concentration gradients practically vanish outside of this limited region.

Since Rauh and Bullough's results are of limited usefulness, other methods of determining the solute flux and the solute accumulation are called for. Fortunately, the solute flux can also be calculated from the concentration function [3.2.11] or its more specialized forms [3.2.20] and [3.2.26]. The starting point for the flux calculation must be equation [3.1.11] for the flux density $\mathbf{j}(r, \theta, t)$. The total flux through the circular surface at radius $r$, here denoted $J(r, t)$, is obtained as follows. First, the unit outer normal, $\hat{n}$, of the deformed zone's surface is just the radial unit vector $\hat{r}$. The differential area element of the deformed zone's surface is just $dS = rd\theta$. The flux through the surface is just the integral of the normal component of the flux density over the surface. It is given by

$$J(r, t) = \int \mathbf{j} \cdot \hat{n} ds = \int_0^{2\pi} j^r \hat{r} d\theta.$$  

The limits of integration are chosen to be 0 to $2\pi$ rather than $-\pi$ to $+\pi$. This is done out of convenience; however, either is acceptable. Since the flux density is given by [3.1.11] and the gradient operator is given by equation [3.3.3] it follows that the normal flux density through the surface at radius $r$ is given by

$$\mathbf{j}^r \hat{r} = -D(C' + (C/kT)U') = -D(C' + 2CU'^\prime)$$

where the primes denote the derivative with respect to $r$. Integrating over the surface gives

$$J = \int_0^{2\pi} -D(C' + 2CU'^\prime) d\theta.$$

Next, define $J = J_{\text{con}} + J_{\text{pot}}$ where
\[ J_{\text{con}} = -2\pi \int_0^{2\pi} C^* d\theta \quad \text{and} \quad J_{\text{pot}} = -2\pi \int_0^{2\pi} C U^* d\theta \]

and solve for the two parts separately.

Using [3.2.11] for the concentration function, \( J_{\text{con}} \) becomes

\[ J_{\text{con}} = -2\pi \int_0^{2\pi} (\partial/\partial r)(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d\theta. \]

Reversing the order of the differentiation and integration,

\[ J_{\text{con}} = -2\pi \int_0^{2\pi} (\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d\theta. \]

or integrating over \( d(\theta/2) \) instead of \( d\theta \),

\[ J_{\text{con}} = -2\pi \int_0^{\pi} (\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d(\theta/2). \]

Using equation 9.6.19 of Abramowitz and Stegun (1964), [3.3.15] becomes

\[ J_{\text{con}} = -2\pi Dr(\partial/\partial r)(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n I_n(z)). \]

Next, consider the flux term \( J_{\text{pot}} \). Inserting equation [3.2.11], the definition of \( C \), into the second of equations [3.3.12] and then using

\[ U^* = -z'\cos(\theta/2) \]

\[ J_{\text{pot}} = 2\pi \int_0^{2\pi} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2)z'\cos(\theta/2)d\theta. \]

Again exchanging the order of the integration and differentiation,

\[ J_{\text{pot}} = 2\pi Dr(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d(\theta/2). \]

Integrating over \( d(\theta/2) \) instead of \( d\theta \) leads to

\[ J_{\text{pot}} = 4\pi Dr(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d(\theta/2). \]

Noticing that \( (\partial/\partial z)\exp(z\cos(\theta/2)) = \cos(\theta/2)\exp(z\cos(\theta/2)) \) leads to

\[ J_{\text{pot}} = 4\pi Dr(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d(\theta/2). \]

or combining \( z' \) with \( (\partial/\partial z) \) yields

\[ J_{\text{pot}} = 4\pi Dr(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n \cos(n\theta/2))d(\theta/2). \]

Integrating as before leaves

\[ J_{\text{pot}} = 4\pi Dr(\sum_{n=0}^{\infty} \exp(z\cos(\theta/2))d R_n I_n(z)). \]

Combining \( J_{\text{pot}} \) from [3.3.22] and \( J_{\text{con}} \) from [3.3.16] leaves

\[ J(r,t) = -2\pi Dr(\sum_{n=0}^{\infty} R' r(t)I_n(z) - R r(t)I'_n(z)). \]

The constants \( d_n \) and the radial concentration function \( R_n(r,t) \) must
be specialized to satisfy the appropriate boundary, initial or other
conditions. The product \( \frac{d_n R_n(r,t)}{R_n(r,t)} \) can be determined by numerical
methods, as described in section 3.4. Alternately, these unknowns \( d_n \) and
\( R_n(r,t) \) can be taken from the steady state concentration distribution
given by [3.2.20]. In this perfectly elastic case \( d_n = C_0 I_n(-z_0)/K_n(z_0) \)
and \( R_n(r,t) = K_n(z) \). Consequently, equation [3.3.23] becomes

\[
[3.3.24] \quad J^S(r) = -2\pi r D C_0 \sum_n \left( \frac{I_n(-z_0)}{K_n(z_0)} \right) \left( K'_n(z) I_n(z) - K_n(z) I'_n(z) \right).
\]

Using the Wronskian relation for the modified Bessel functions (see p.
179 of Hildebrand (1962) or equation 9.6.15 of Abramowitz and Stegun
(1964)), equation [3.3.24] becomes

\[
[3.3.25] \quad J^S(r) = -2\pi r D C_0 z'(-1/z) \sum_n \left( \frac{I_n(-z_0)}{K_n(z_0)} \right)
\]

and using \( z' = -z/2r \) finally gives

\[
[3.3.26] \quad J^S = -\pi D C_0 \sum_n \left( \frac{I_n(-z_0)}{K_n(z_0)} \right).
\]

Note that \( J^S \) is a constant independent of radius \( r \) and, of course, time \( t \). For small values of \( z_0, z_0 \) much less than unity, only the term \( n=0 \)
contributes significantly to the sum, leaving the negative quantity

\[
[3.3.27] \quad J^S = -\pi D C_0/(-\log(z_0)).
\]

Note that \( J^S \) is time independent, as it must be, and that it also is
independent of position in the cracked body.

Another quantity of interest is the total amount of solute that has
accumulated inside the circular surface at radius \( r \), at some time \( t \).
This amount will be denoted \( N(r,t) \). Since the steady state flux [3.3.27]
is time independent, it is simply multiplied by \( t \), leaving a positive
quantity

\[
[3.3.28] \quad N^S(t) = \pi D C_0 t/(-\log(z_0)).
\]

For the general time-dependent case of equation [3.3.23], the
quantity \( N \) is determined by the integral
\[ [3.3.29] \quad N(r,t) = -\int J(r,t) dt = 2\pi D r \sum_n \int_0^t (R'_n(r,t)I'_n(z) - R_n(r,t)I'_n(z)) dt. \]

To anticipate one of the developments of section 3.4, it is assumed that a change of variable is made, so that \[ R_n(r,t) = P_n(r,t)I_n(z) \]. Inserting this in equation [3.3.23] and simplifying gives
\[ [3.3.30] \quad J(r,t) = -2\pi r D \sum_n (-1)^n I_n^2(z) P'_n(r,t). \]

This is valid for either the perfectly elastic or the elastic-plastic case. As \( n \) increases in [3.3.30], the values of \( I_n(z) \) decrease rapidly, so that the lowest values of \( n \) contribute the most to the sum.

Integrating [3.3.30] over time and dividing by \( \pi r^2 \) gives
\[ [3.3.31] \quad \frac{N(r,t)}{\pi r^2} = 2r^{-1} D \sum_n (-1)^n I_n^2(z) \int_0^t P'_n(r,t) dt. \]

The dimensionless quantity on the LHS of [3.3.31] is the total accumulation of solute atoms (per unit volume) inside radius \( r \). The integral \( \int_0^t P'_n(r,t) dt \) will be determined by numerical techniques.

3.4 The Modified Method of Characteristics

The previous sections of this chapter have dealt with approximations for the solute atom concentration which are valid only for very short or very long time periods. In some situations of practical importance neither approximation is useful. In these situations approximate numerical techniques must be employed. Toward this goal equation [3.2.8] is simplified by the change of variable \( R(r,t) = I_n(-z)P(r,t) \). From this, the derivatives
\[ R'/I_n = P' + (I'/I_n)P \]
and
\[ R''/I_n = P'' + (2I'/I_n)P' + (I''/I_n)P \]
are obtained, where the arguments of the functions have been omitted and where the primes again denote the derivative with respect to \( r \). These identities, together with the modified Bessel equation
[3.4.1] \[ r^2 I_n''(-z) + rI_n'(-z) - (n^2/4) + (z^2/4) I_n(-z) = 0 \]

lead to the new equation in P

[3.4.2] \[ P'' + (2I_n'(-z)/I_n(-z)) + (1/r) P' = D^{-1}(\partial P/\partial t) \]

The modified Bessel functions can be simplified by using \( I_n(-z) = (-1)^n I_n(z) \). Once that is accomplished, the derivative of the Bessel function is replaced using

[3.4.3] \[ I_n'(z) = z'(I_{n+1}(z) + (n/z)I_n(z)) \]

where \( z' = -A/2r^{3/2} \). All of this leaves

[3.4.4] \[ P'' - (1/r)(-1 + n + zI_{n+1}(z)/I_n(z)) P' = D^{-1}(\partial P/\partial t) \]

Next, the spatial domain from \( r=0 \) to \( r=r_0 \) is mapped onto the unit domain by the change of variable \( q=r/r_0 \). From this, \( r_0 dq = dr \) so that

[3.4.5] \[ D^* P'' - uP' = (\partial P/\partial t) \]

where the primes now denote the derivative with respect to \( q \) and where \( D^* =Dr_0^{-2} \). Also in this equation, \( u = u(q) \) is given by

[3.4.6] \[ u(q) = \langle D^*/q \rangle(-1 + n + zI_{n+1}(z)/I_n(z)) \]

where \( z = z_0 q^{-1/2} \). For \( n=0 \) and \( q \) sufficiently small, \( u \) is positive. On the other hand, for \( n=0 \) and \( q \) sufficiently large, \( u \) is negative. This change of sign is due to the turning point mentioned in section 3.2. For all values of \( n \) greater than zero, \( u \) is always positive. As long as \( D^* \) is approximately equal to or greater than the magnitude of \( u \), the resulting solutions for \( P(r,t) \) in equation [3.4.5] are smooth and slowly varying.

On the other hand, as \( q \) vanishes, \( u \) varies as \( q^{-3/2} \). In this limit \( P \) exhibits gradients which increase without limit, even though \( P \) never exceeds its constant finite boundary value.

No further simplifications of the time dependent equation [3.4.5] are possible. Since there are no known analytic solutions to the equation, approximate numerical solutions must be sought. The methods
employed here are the Galerkin (1915) finite element method and the method of characteristics. The latter has been described by Russell (1983) and Ewing and Russell (1981). The Galerkin method has been discussed in detail by Zienkiewicz (1977).

The characteristic referred to above is that of the first order elliptic equation

\[ 0 = uP' + (\partial P/\partial t) \]

which results from \([3.4.5]\) when \(u\) is very large. The characteristic is a particular curve in the \((q,t)\) plane, on which \((\partial q/\partial t) = -u\). It is depicted in Figure (2). The unit vector in the characteristic direction, \(\hat{\psi}\), is readily seen to be

\[ \hat{\psi}(q,t) = (-u\hat{q} + \hat{t})/S \]

where \(\hat{q}\) and \(\hat{t}\) are unit vectors in the \(q\) and \(t\) directions, respectively, and where \(S\) is the normalizing factor

\[ S = (1 + u^2)^{1/2} \]

From \([3.4.8]\) the directional derivative in the characteristic direction is found to be

\[ (\partial/\partial \psi) = ( -u(\partial/\partial q) + (\partial/\partial t) )/S \]

This can be easily verified by applying this directional derivative to both sides of equation \([3.4.8]\). Using \([3.4.10]\), equation \([3.4.5]\) can be rewritten as

\[ S(\partial P/\partial \psi) = D^P'' \]

To begin the discretization of this equation, \((\partial P/\partial \psi)\) is approximated by a backward implicit difference formula (see \([3.4.14]\) or \([3.4.15]\) below). First, define a fixed time step \(\Delta t\), and from it

\[ t^m = m\Delta t , \quad \bar{q} = q - u(q)\Delta t \quad \text{and} \quad \bar{q} = q - u(q)\Delta t . \]

Next, defining
\[ 3.4.13 \quad \mathbf{P}_m = \mathbf{P}(\mathbf{q}, t^{m-2}), \quad \mathbf{P}_m = \mathbf{P}(\mathbf{q}, t^{m-1}) \quad \text{and} \quad \mathbf{P}_m = \mathbf{P}(\mathbf{q}, t^m) \]

the difference formula for the directional derivative is expressed in
relatively compact notation as either
\[ 3.4.14 \quad S(\partial \mathbf{P}/\partial \psi) = (\mathbf{P}_m - \mathbf{P}_{m-1})/\Delta t \]
which is of first order accuracy in time or
\[ 3.4.15 \quad S(\partial \mathbf{P}/\partial \psi) = (3\mathbf{P}_m - 4\mathbf{P}_{m-1} + \mathbf{P}_{m-2})/2\Delta t \]
which is of second order accuracy in time. The second of the two
formulae is not considered further in this work, since the first is
considerably easier to implement and can be computed faster.
Furthermore, as described by Ewing and Russell (1981), the simpler
formula [3.4.14] is about as accurate as the more complicated one, due
to a "serendipitous interaction between the spatial flattening and
temporal sharpening" that occurred.

The Galerkin finite element method is applied to equation [3.4.11].
First, the inner product of two arbitrary functions \( w_1 \) and \( w_2 \), denoted
\[ [w_1, w_2] \], is defined to be the integral of the product of functions \( w_1 \)
and \( w_2 \) over the spatial domain, from \( q=0 \) to \( q=1 \). Next, a particular
weighting function, described below, is denoted as \( v \). Using these
definitions along with [3.4.14], equation [3.4.11] is rewritten as
\[ 3.4.16 \quad [\mathbf{p}_m, v] - D^x \Delta t [\mathbf{p}'_m, v] = [\mathbf{p}_{m-1}, v] \quad . \]
In this equation unknown quantities (at time \( t^m \)) are on the LHS of the
equation and known quantities (at time \( t^{m-1} \) or earlier) are all on the
RHS. Integrating by parts gives
\[ 3.4.17 \quad [\mathbf{p}'', v] = (\mathbf{p}'v)_0^1 - [\mathbf{p}', v'] \quad . \]
The Dirichlet boundary conditions that have been chosen do not force any
particular values of \( \mathbf{p}' \)(or flux) to occur on the boundary. Therefore
\( (\mathbf{p}'v)_0^1 \) is set to zero and [3.4.16] becomes
[3.4.18] \[ P^m, v' \] + D^* \Delta t[P', v', v'] = [P^{m-1}, v'] .

Had mixed or Neumann boundary conditions been chosen \( P' \) would not vanish on the boundary. In the following description of the Galerkin method, the constant boundary values of \( P \) are accounted for in another way.

It is important to note that the original differential forms [3.4.5] or [3.4.11] or the integral formulation [3.4.16] requires that \( P'' \) be defined at all points in the domain. On the other hand, after integrating by parts, equation [3.4.18] only requires that \( P' \) be defined throughout the domain. Equation [3.4.18] allows solutions which are less smooth than the previous formulations. It is known as the "weak" form of the equation. In this weak form of the equation restrictions on \( P \) have been relaxed while those on \( v \) have been made more restrictive.

Next, according to the Galerkin method, it is assumed that \( v=v(q) \) is a member, \( v_i \), of a set of functions which form a basis for \( P^m \). In this case \( P^m \) can be written as a linear combination of the functions \( v_i \):

\[ P^m = \sum_i a_i v_i(q) \]

for constants \( a_i \) and for \( i=(0,1,2,...N) \). From equation [3.4.19] the derivative of \( P^m \), denoted \( P^m' \), is readily seen to be

\[ P^m' = \sum_i a_i v'_i(q) . \]

Consider the factor \([P', v']\) appearing in equation [3.4.18]. Since \( P' \) depends on \( v' \), it follows that the inner product \([v'_i, v'_j]\) must be defined throughout the spatial domain, for arbitrary \( i \) and \( j \). Further inspection of [3.4.18] reveals that the inner product \([v_i, v_j]\) must also be defined throughout the domain. Consequently, the functions \( v_i \) and \( v'_i \) must all be square integrable on the unit domain. Since the boundary values of the dependent variable are known quantities, the weighting functions must all vanish on the boundary. The weighting functions \( v_i \) must therefore
be members of the Sobolev space $H^1_0$ on the unit domain.

The spatial domain is discretized using $N$ grid points. Each grid point is denoted $q_i$, where $q_0 < q_1 ... < q_i < q_{i+1} ... < q_{N-1} < q_N$. Since the unit domain is employed here, $q_0 = 0$ and $q_N = 1$. From these grid points, the grid spacing is defined by $h_i = q_i - q_{i-1}$. In the Galerkin formulation, the weighting functions $v_i$ are defined by

$$v_i = (q_{i+1} - q)/h_{i+1} \text{ for } q_i < q < q_{i+1}
$$

$$v_i = (q - q_{i-1})/h_i \text{ for } q_{i-1} \leq q \leq q_i.$$

Elsewhere the functions $v_i$ $(i=0,1,2,...N)$ all vanish, and so do their derivatives. Now, consider again equation [3.4.19]. At each node all weighting functions but one vanish, and the remaining one has a value of unity at the node. Consequently, at the nodes $a_i = P(q_i, t^m)$. Furthermore, since the boundary values of $P$ are known, it follows that all of the weighting functions $v_i$ must vanish on the domain boundary.

As a result of equations [3.4.19] and [3.4.20], the inner products are calculated to be

$$[P,v] = \sum_i a_i [v_i, v_j]$$

and

$$[P',v'] = \sum_i a_i [v_i', v_j']$$

where $j=(0,1,2,...N)$ and in general $j$ may or may not equal $i$. Inserting equations [3.4.22] into [3.4.18] leads to

$$\sum_i a_i \left( [v_i, v_j] + \Delta t \frac{\partial}{\partial t} [v_i', v_j'] \right) = [P^{m-1}, v_j].$$

Even though the remaining integrals are over the entire domain from $q=0$ to $q=1$, the weighting functions $v_i$ vanish everywhere except on the interval $q_{i-1}$ to $q_{i+1}$. On this interval, for each of the remaining integrals, three cases must be considered: $j=i-1$, $j=i$ and $j=i+1$. The integrals $[v_i, v_j]$ and $[v_i', v_j']$ are readily calculated and their values are given in the following table:
\[ \begin{align*}
[v_i, v_j] &= 
\begin{cases}
  h_{i+1}/6 & \text{if } i = i-1 \\
h_j + h_{j+1}/3 & \text{if } i = i \\
h_j/6 & \text{if } i = i+1
\end{cases}
\end{align*} \]

Note that [3.4.23] is really a system of \( N \) algebraic equations for
the \( N \) unknown quantities \( a_i \). Every factor appearing in [3.4.23], other
than \( a_i \), is known. At an arbitrary interior node \( j \), [3.4.23] gives

\[
[3.4.24] \quad a_{j+1}(h_{j+1}/6 - D^*\Delta t/h_{j+1}) + a_j((h_j+h_{j+1})/3 + D^*\Delta t(1/h_j + 1/h_{j+1}))
\]

\[ + a_{j-1}(h_j/6 - D^*\Delta t/h_j) = [P^{m-1}, v_j] \]

Replacing the \( a_i \) in equation [3.4.24] with \( P^m_i \), multiplying by \( h_j/D^*\Delta t \)
and defining

\[
[3.4.25] \quad F_j = [P^{m-1}, v_j] h_j/D^*\Delta t
\]

leaves [3.4.24] in the dimensionless form

\[
[3.4.26] \quad P^m_{j-1}(-1 + h_j^2/6D^*\Delta t) + P^m_j(1 + h_j/h_{j+1} + h_j(h_j+h_{j+1})/3D^*\Delta t) +
\]

\[ P^m_{j+1}(-h_j/h_{j+1} + h_jh_{j+1}/6D^*\Delta t) = F_j
\]

From [3.4.26] a system of linear algebraic equations is
constructed, having the form \( AP = F \) where the transpose of \( P \) and \( F \) are:

\[
P^T = (P_1^m, P_2^m, \ldots P_{N-1}^m)
\]

\[
F^T = (F_1 - A_0 P_0^m, F_2, F_3, \ldots, F_{N-2}, F_{N-1} - A_N P_N^m)
\]

In the formula for \( F^T \) there appear two boundary terms \( A_0 P_0^m \) and \( A_N P_N^m \).
These terms actually originate on the LHS of [3.4.26] but since they
contain only known quantities, they are moved to the RHS of the equation
and appear in \( F \). From [3.4.26] it is readily seen that

\[
A_0 = -1 + h_1^2/6D^*\Delta t
\]

\[
A_N = -h_{N-1}/h_N + h_{N-1}h_N /6D^*\Delta t
\]

The matrix \( A \) is square and tridiagonal. It has dimension \( N-1 \) by \( N-1 \). All
of the elements on the diagonal of \( A \) are positive. Since \( P \) is always
positive, it follows from [3.4.25] that the \( F_j \) are all positive as well.
While the system of equations defined by equation [3.4.24] would have produced a symmetric square matrix, the matrix $A$ which results from equation [3.4.26] is not symmetric. This is a consequence of multiplying both sides of equation [3.4.24] by $h_j$, in order to produce the dimensionless form that appears in [3.4.26]. Evidently dimensionless equations and symmetric square matrices are mutually exclusive. Since the grid points $q_i$ are fixed in space and since the diffusion constant is independent of time, the matrix $A$ must be recalculated only if the time step $\Delta t$ is changed. The system of linear algebraic equations is solved by Gaussian elimination and back substitution.

Evaluation of the integral appearing on the RHS of equations [3.4.23] through [3.4.26] requires a considerable amount of numerical computation. First, values of the dependent variable $P$ are known only at the nodes, while one of the terms in the integrand, $P_{m-1} = P(q_i, t^{m-1})$, must be evaluated at points between the nodes. This requires some form of interpolation.

In all of the computational results that are presented in this paper, simple linear interpolation is used. There are two reasons for this. First, linear interpolation requires less computation time. Second, the procedure is more robust than quadratic or higher forms of interpolation. Linear interpolation assures that each interpolated value of $P$ always lies between the nodal values of $P$ to the left and right of the interpolation point. Higher forms of interpolation can produce interpolated values of $P$ that are outliers, that is values which are either greater than or less than all of the nodal values of $P$ used in the interpolation. In the presence of large gradients in $P$, where $P$ changes rapidly from one node to the next, higher forms of interpolation
can contribute to artificial oscillations in the computed values of P. Linear interpolation largely eliminates this problem.

The linear interpolation is carried out using the calculated values of $\bar{q}$ for each node and time step. For each value of $\bar{q}$, the index of the node immediately to the left of $\bar{q}$ is determined. If the particular node has index $i$ then the interpolation is carried out according to

$$\overline{P}^{m-1} = a(\bar{q} - q_i) + b$$

where $a$ and $b$ are the constants

$$b = \overline{P}^{m-1}(q_i) \quad \text{and} \quad a = \frac{(\overline{P}^{m-1}(q_{i+1}) - \overline{P}^{m-1}(q_i))}{h_{i+1}}.$$

If the point $\bar{q}$ lies outside the domain $0 < q < 1$ then the boundary value of $P$ at the nearest domain boundary is used for $\overline{P}^{m-1}$.

Another note also concerns the integral on the RHS of equations [3.4.23] through [3.4.26]. The numerical integration must be carried out using some quadrature rule. For the present work the two-point Gaussian quadrature rule discussed by Carnahan, Luther and Wilkes (1969) is employed. The Gaussian integration was carried out as follows. The interval of integration (as before) is from $q_{j-1}$ to $q_{j+1}$. On that interval, the integral $[\overline{P}^{m-1}, v_j]$ becomes

$$[\overline{P}^{m-1}, v_j] = h_j \left( s_1 \overline{P}^{m-1}(\bar{q}_a) + s_2 \overline{P}^{m-1}(\bar{q}_b) \right)/2$$
$$+ h_{j+1} \left( (1-s_1) \overline{P}^{m-1}(\bar{q}_c) + (1-s_2) \overline{P}^{m-1}(\bar{q}_d) \right)/2$$

where $s_1 = (1-s_2) = (1 - 1/31/2)/2$ and $s_2 = (1-s_1) = (1 + 1/31/2)/2$ are the two Gauss points in each interval. The quantities $\bar{q}_a$, $\bar{q}_b$, $\bar{q}_c$ and $\bar{q}_d$ are given by

$$\bar{q}_a = q_{j-1} + s_1 h_j - u \Delta t(q_{j-1} + s_1 h_j)$$
$$\bar{q}_b = q_{j-1} + s_2 h_j - u \Delta t(q_{j-1} + s_2 h_j)$$
$$\bar{q}_c = q_{j+1} + s_1 h_j - u \Delta t(q_{j+1} + s_1 h_{j+1})$$
$$\bar{q}_d = q_{j+1} + s_2 h_{j+1} - u \Delta t(q_{j+1} + s_2 h_{j+1}).$$
These four quantities are just the images of the four Gauss points (two in each interval) propagated along the characteristic. Remember that integral [3.4.29] is multiplied by $h_j/D^*\Delta t$ as in equation [3.4.26].

The function $u$, containing the ratio of modified Bessel functions $I_{n+1}(z)/I_n(z)$ must be calculated repeatedly in determining $\bar{q}$. The most efficient method of obtaining this ratio is the continued fraction method of Blanch (1964), as embodied in a software package supplied by IBM (1970). Since the ratio of modified Bessel functions and and the diffusion coefficient are both independent of time, the entire coefficient $u(q)$ in equation [3.4.5] is also time independent. Note that in equation [3.4.29] the quantity $\bar{q}=q-u(q)\Delta t$ evaluated at the Gauss points appears repeatedly in the integration. To speed processing, the value of $\bar{q}$ at each Gauss point is calculated and stored in an array. The array must be recalculated only if the time step $\Delta t$ changes.

Based on the methods described in this section, a FORTRAN computer program was written. A listing of the program is included in Appendix I. The program solves the differential equation [3.4.5] on the unit domain, subject to the boundary conditions

$$P_n(q=0) = 0 \quad \text{for } t > 0$$
$$P_n(t=0) = C_0 \quad \text{for all } q$$
$$P_n(q=1) = C_0 \quad \text{for all } t .$$

These boundary conditions follow directly from [3.2.12] through [3.2.14] and the definition $R_n(r,t)=I_n(\bar{q}P_n(r,t))$.

From the computed values of $P_n(r,t)$ the program also calculates the solute flux into a circular zone of arbitrary radius $r$, according to equation [3.3.30] and the total solute accumulation according to [3.3.31]. The integration over time that appears in the latter equation
is carried out using the trapezoid rule:
\[
\int_{a}^{b} f(t) dt = \frac{(b-a)(f(a)+f(b))}{2}
\]

The FORTRAN program is to some extent menu driven, and it prompts the user to choose among various available options. The program allows a choice of two mesh types, on the unit domain. One is a power law mesh where \( q_i \) is proportional to some power of \( i \), and the other is a piecewise uniform mesh that is discontinuous at \( 2r_p \). The program also allows a choice of linear or quadratic interpolation. In either case integration is carried out using the two point Gaussian quadrature rule. In all of the calculations described below, linear interpolation and the power law mesh were employed.

The temporal mesh that is used in the calculations is not uniform, either. The program automatically generates a sequence of variable time steps, determined from input data in the following way. The time domain is from 0 to \( TF \), and the initial time step, \( DTO \), is defined by \( DTO = TF / NT \) where \( NT \) is typically a very large number. In most of the computations it was set to a value of about \( 2 \times 10^6 \). The span from \( DTO \) to \( TF \) is broken up into octaves, or periods in which time doubles. The number of octaves, \( X \), is just \( X = \log(TF/DTO) / \log(2) \). In the first few octaves of the time domain, the time step \( DT \) is held at the constant initial value \( DT = DTO \). In each subsequent octave the time step is doubled. If \( Y \) is the number of octaves over which \( DT = DTO \), then the total number of steps taken, denoted \( KNT \), is given by \( KNT = (2^Y - 1) + 2^{Y-1}(X - Y) \).

The calculation is therefore completed in a reasonable amount of time, and the flux and solute accumulation which are calculated at each time step can be stored in a reasonable number of memory registers.

It was inevitable that the notation used in the FORTRAN program
does not correspond exactly to the notation used in this section and the several preceeding ones. Table 1 lists several of the FORTRAN variable names, along with their counterpart in this theoretical development.
4. RESULTS AND DISCUSSION
4.1 The Turning Point as an Embrittlement Criterion

From the results of sections 3.2 and 3.3 it is clear that the eigenvalue $n=0$ is by far the most important one. Part of section 3.2 concerns the steady state situation in which the solute atom concentration approaches the constant value $C_0$ at large distances from the crack tip. In this situation it is determined that only the eigenvalue $n=0$ contributes to the concentration distribution. This determination is not revolutionary, since Ham (1959) found the same thing to be true for an isolated dislocation.

Section 3.3 concerns the flux of atoms into a circular zone surrounding the crack tip. Part of section 3.3 deals with the steady state situation in which the solute concentration is constant on the finite boundary $r=r_0$. It has been shown that only eigenvalue $n=0$ contributes significantly to the steady state flux of solute atoms, as long as $z_0$ is much less than unity. The quantity $z_0$ is much less than unity for any interstitial species in any macroscopic specimen as long as the temperature is not extremely low.

While $n=0$ dominates the steady state behavior of the system, it is also important to consider the time-dependent situation. The general time-dependent case was examined in section 3.3. There both the solute flux and the total solute accumulation were calculated. In equations [3.3.30] and [3.3.31] the sums over all values of $n$ contain the factors $I_n^2(z)P_n'(z)$. As $n$ increases, $I_n^2(z)$ vanishes rapidly. Next, consider the factor $P_n'(z)$. As seen in equations [3.4.5] and [3.4.6], increasing values of $n$ tend to sharpen slightly the propagating fronts which define $P_n(r,t)$. Increasing $n$ therefore causes a slight increase in the factor
$P_n'(z)$. This effect tends to offset the effect of the factor $I_n^2(z)$. From
the computational work in section 4.3, however, it is clear that for
small values of $z$ the term $I_n^2(z)$ dominates. To summarize, eigenvalue $n=0$
dominate the time dependent case as long as $z$ is much less than unity.

Another boundary condition that is not covered in this thesis (but
will be treated in subsequent work) is the situation in which the solute
concentration is a constant $C_0$ on the crack faces. This would be the
case if the solute reservoir (or active environment) invades the crack
and reacts with the crack faces. It is expected that this boundary
condition causes a significant contribution of eigenvalues other than
$n=0$ to the solute concentration distribution.

Recalling the embrittlement criterion developed in section 3.2, it
is necessary that the particle turning point, $r_y$, lie outside the
deformed zone of radius $r_p$ in order for embrittlement to occur. This
must be so for two reasons. First, solute atoms outside the turning
point are driven primarily by random thermal motion and are free to
move either toward or away from the crack tip. On the other hand, the
motion of solutes inside the turning point is dominated by the elastic
attraction to the crack tip. Any radial component of the solute motion
must be toward the crack tip. The second part of the argument is this:
the elastic attraction vanishes inside the deformed zone near the crack
tip. If the particle turning point lies inside the deformed zone then
there is no region of the specimen in which solute atoms are trapped,
they all have sufficient thermal energy to "boil away" from the crack
tip. If, on the other hand, the turning point lies outside the deformed
zone, then there exists a region between $r_p$ and $r_y$ where the elastic
interaction dominates. If a solute atom happens to fall into this region
it cannot escape.

For the dominant eigenvalue \( n=0 \), the critical strain energy density criterion for embrittlement, equation [3.2.33], is

\[
\sigma_t > 3(2\pi Q)^{1/2}kT/(1+\nu)\delta_v
\]

For the case of plane strain, embrittlement occurs at a lower strength level than for the case of plane stress. This is because the plastic zone size factor \( Q \) is smaller in plane strain than plane stress. Taking \( Q \) from [3.1.5] therefore leaves

\[4.1.1\] \[
\sigma_t > 2^{-1/2}3(1-2\nu)kT/(1+\nu)\delta_v
\]

and taking the local solute atom dilatation from [3.1.9] leads to

\[4.1.2\] \[
\sigma_t > 2^{-1/2}(1-2\nu)/(1-\nu)gN_a kT/\bar{v}_i(1+\nu)^2
\]

Estimating a value of 1/3 for Poisson's ratio leaves

\[4.1.3\] \[
\sigma_t > 2^{-1/2}gN_a kT/8\bar{v}_i
\]

The alternate embrittlement condition [3.2.35], due to Rice's (1977) plastic zone model, is

\[
\sigma_0 > 2.8\pi(3kT)^2/E((1+\nu)\delta_v)^2
\]

Taking the local solute atom dilatation from [3.1.9] leads to

\[4.1.4\] \[
\sigma_0 > (2.8\pi/E)(1-\nu)^2/(1+\nu)^4)(gN_a kT/\bar{v}_i)^2
\]

and estimating a value of 1/3 for Poisson's ratio leaves

\[4.1.5\] \[
\sigma_0 > (31.9\pi/E)(N_a kT/\bar{v}_i)^2
\]

Notice that equation [4.1.3] depends on the quantity \( N_a kT/\bar{v}_i \) while equation [4.1.5] depends on the square of the same quantity.

The predictions [4.1.3] and [4.1.5] can be tested for the case of hydrogen in body centered cubic iron at room temperature. Wagenblast and Wriedt (1971) give for the molar volume \( \bar{v}_i \) a value of 2.0 cc/mole. Puls (1985) has reviewed this and other published data for the partial molar volume of hydrogen in iron, at a variety of temperatures. All of the
tabulated values are in rough agreement with the data of Wagenblast and Wriedt. Finally, inserting $T=300$ Kelvin, and $E=207$ GPa along with the other constants, condition [4.1.3] becomes

\[ 4.1.6 \quad \sigma_t > 1000 \text{ MPa or 146,000 psi} \]

while [4.1.5] becomes

\[ 4.1.7 \quad \sigma_0 > 774 \text{ MPa or 112,000 psi} . \]

In mildly work hardening alloys similar to the material considered by Rice (1977), the ratio of yield strength to tensile strength is about 2/3, so that the last condition can be rewritten as

\[ 4.1.8 \quad \sigma_t > 1160 \text{ MPa or 168,000 psi} . \]

The tensile strength dependence of equation [4.1.3] and yield strength dependence of equation [4.1.5] on ambient temperature have been plotted in figure 3, over the temperature range 0 to 400$^\circ$ Kelvin. The data for hydrogen in steel (given above) have been assumed. For comparison purposes, the yield strengths of equation [4.1.5] have been multiplied by 3/2 to give approximate tensile strengths.

Hydrogen sulfide is one of the best known agents of hydrogen embrittlement. In aqueous solutions it reacts readily with iron-based alloys, forming iron sulfide and liberating hydrogen. As described by McCright (1977), the element sulfur acts as a poison to slow or prevent the recombination of atomic hydrogen into its molecular form. The atomic hydrogen that is produced in this way is readily adsorbed onto and absorbed into iron-based alloys.

Hydrogen sulfide is commonly found in all phases of the oil and gas industry. This corrosive gas occurs naturally in many rock formations where hydrocarbons are found, and it is frequently encountered in large quantities during the drilling of wells and the subsequent production of
hydrocarbons. Large amounts of structural steel are used in the drill string, well casing and production tubing. Of necessity, these structural steels are inexpensive low alloy materials. In such low alloy materials, the partial molar volume of dissolved hydrogen should be similar to the value measured by Wagenblast and Wriedt in their cold-swaged "Ferrovac E" material.

Over a period of several decades innumerable fracture tests have been carried out on these and other low alloy steels in $H_2S$ bearing environments. A review of some of the published data has been given by Carter and Hyatt (1977). The National Association of Corrosion Engineers (NACE) has developed a specification (NACE, 1981) for a buffered aqueous solution of $H_2S$ for use in testing the susceptibility of materials to embrittlement by $H_2S$. Based on laboratory and field tests (NACE, 1963), NACE has developed specifications (NACE, 1966) for metallic materials to be used in $H_2S$ bearing environments. In essence, the specification states that a material's hardness should not exceed 22 on the Rockwell "C" scale. Through a well-known table (ASTM, 1979) correlating hardness and tensile strength, 22 Rockwell "C" corresponds to a tensile strength of about 115,000 psi. This value can be compared directly with conditions [4.1.6] and [4.1.8]. In the first case the predicted value exceeds the NACE value by 26%, while in the second case the predicted value is 46% higher than the NACE value.

There is little to be done in the way of error analysis here. These errors of 26% or 46% could be completely accounted for by errors in the experimental determination of hydrogen's partial molar volume. Differences between the rather pure materials of Wagenblast and Wriedt (1971) and the low alloy steels examined by the NACE committee could
also account for the errors. They could also be accounted for in the estimated value of Poisson's ratio. While Poisson's ratio usually has a value of 1/4 to 1/3 for small elastic deformations, the value approaches 1/2 if the deformations are large and irreversible. Finally, it has been assumed that all solute atoms have the same thermal energy. In reality they exhibit a distribution of energies, according to the Fermi-Dirac distribution. This has not been accounted for in the present analysis. In light of these sources of error, it is remarkable that the discrepancy between theory and experiment is in the range of only 26% to 46%. It is possible that several sizeable errors have offset each other.

Carter and Hyatt (1977) have cited considerable evidence in support of the critical hardness value 22 Rockwell "C". See section 4.4.2 of their paper. They have also cited several experiments that seem to contradict the specified NACE hardness level. This contradictory evidence consists of H₂S fracture tests in which steel specimens softer than 22 Rockwell "C" had failed. In the majority of these tests, surface cracks full of H₂S were clearly present. Some resulted from the cracking of large inclusions present on the specimen's surface and others occurred when notched specimens were loaded past their yield point, initiating cracks at the notches. In these situations, one can attribute specimen failure to material deficiencies or overloading of the specimens, or one can attribute the failures to the influence of eigenvalues other than n=0.

It is well known that electrolytic hydrogen charging of specimens can also lead to embrittlement of materials softer than 22 Rockwell "C". Hirth (1980) pointed out that electrolytic charging can lead to very high hydrogen fugacities, and that such high fugacities cause fissure
formation at impurities. Oriani (1978) has also discussed electrolytic hydrogen charging in some detail. He estimates that cathodic charging can produce hydrogen fugacities as high as $10^6$ atmospheres, and can irreversibly degrade material properties. Materials that are severely damaged by such charging can fail at low strength levels, even when eigenvalue $n=0$ completely describes the system.

4.2 The Temperature Dependence of Embrittlement

It is well known that hydrogen embrittlement is most acute at temperatures near room temperature, about $300^\circ$ Kelvin. Carter and Hyatt (1977) reviewed some of the published experimental data for hydrogen and hydrogen sulfide embrittlement. For the former case they graph the temperature dependence of crack growth rates in hardened AISI 4130 steel. The crack growth rates reach a maximum at about $20^\circ$ centigrade. For the case of hydrogen sulfide, Carter and Hyatt show the time to failure of cold drawn AISI 1075 wire as a function of temperature. The data reaches a peak at about $30^\circ$ C.

The explanation of this behavior lies in the simplified differential equation [3.4.5], Fick's second law for the one dimensional problem. Since the dependent variable in that equation is the radial concentration function $P(r,t)$, it is first necessary to demonstrate the relationship between $P$ and the actual concentration $C$. First, note that according to equation [3.2.11]

$$C(r,\theta,t) = \exp(\zeta \cos(\theta/2)) \sum_{n} d_n R_n(r,t) \cos(n\theta/2).$$

Since $n=0$ is the dominant eigenvalue,

$$C(r,\theta,t) = d_0 \exp(\zeta \cos(\theta/2)) R_0(r,t).$$

Inserting the definition $R_0 = I_0(-\zeta)P(r,t)$ leaves
\[ C(r, \theta, t) = d_0 \exp(z \cos(\theta/2)) I_0(-z)P(r, t) \, . \]

In the region of the specimen where \( z \) is much less than unity, both the exponential function and the modified Bessel function \( I_0(-z) \) are approximately equal to unity. Consequently, for small \( z \)
\[ C(r, \theta, t) \approx d_0P(r, t) \, . \]

Since Fick's law is a linear differential equation, the constant \( d_0 \) can be absorbed into the variable \( P(r, t) \), so that concentration \( C \) and radial variable \( P \) are practically indistinguishable for small \( z \). This is true at positions outside of and well away from the turning point. This region encompasses the great bulk of the cracked body.

With this in mind, the differential equation for \( P \), equation [3.4.5], is now considered. All of the interesting stress dependent behavior of the differential equation is contained in the velocity field \( u \), given in equation [3.4.6]. In that equation the term \((D^*/q)(-1)\) arises from the choice of a circular coordinate system and is independent of the applied stress. Its temperature dependence is irrelevant. Also, as shown in the preceding section, the eigenvalue \( n=0 \) is by far the most important one, so a second term in the function \( u \) is also eliminated. This leaves only one term from \( u \) for further consideration. Denoting it by \( W \),
\[ [4.2.1] \quad W = (D^*/q)zI_1(z)/I_0(z) \, . \]

In this equation, both \( z \) and \( D^* \) have an implicit temperature dependence. Using \( z=Ar^{-1/2}=B/2kTr^{1/2} \), \( D^*=D/r_0^2 \) and \( q=r/r_0 \) leaves
\[ [4.2.2] \quad W = (B/2r_0^3/2)(D/kT)I_1(z)/I_0(z) \, . \]

In this form the velocity \( W \) is seen to be the product of a force (or potential gradient) and a mobility. Here the force is \( B/2r_0^3/2 \), which is independent of temperature and the mobility is \( D/kT \) multiplied by the
ratio of Bessel functions. This dimensionless ratio of Bessel functions must be contained in the mobility, since \( z \) is temperature dependent. As a consequence, the mobility is position dependent.

Substituting \( D = D_0 \exp(-G/kT) \) where \( G \) is the activation energy for diffusion and \( D_0 \) is the frequency factor leaves

\[
W = \left( \frac{B}{2} \right) r_0^3 \left( \frac{D_0 \exp(-G/kT)}{I_1(z)/I_0(z)} \right).
\]

The ratio of Bessel functions can easily be simplified in two limiting cases. For values of \( z \) much greater than unity, \( I_1(z)/I_0(z) \) approaches unity while for values of \( z \) much less than unity, \( I_1(z)/I_0(z) \) approaches a value \( z/2 \). The former case, that of large values of \( z \), corresponds to particles far inside the particle turning point. Such particles have already been trapped by the crack tip stress field. In order to understand the embrittlement process, we are not concerned with particles already trapped. Instead we must examine the mobility of untrapped, freely moving particles outside the particle turning point. This corresponds to the case of small \( z \). Using therefore \( I_1(z)/I_0(z) = z/2 \) in equation [4.2.2] leads to

\[
W = W_0 (kT)^{-2} \exp(-G/kT)
\]

where \( W_0 \) contains some quantities independent of temperature. The maximum mobility value occurs at the temperature where the mobility's derivative with respect to temperature vanishes:

\[
\frac{\partial W}{\partial T} = \left( \frac{\partial (kT)^{-1}}{\partial T} \right) \left( \frac{\partial W}{\partial (kT)^{-1}} \right) = 0
\]

or

\[
0 = W_0 \left( \frac{2}{(kT)^{-1}} \exp(-G/kT) + (kT)^{-2}(-G) \exp(-G/kT) \right).
\]

Multiplying both sides of the equation by \( \exp(G/kT)(kT/W_0) \) leads to the particularly simple result

\[
0 = 2 - G/kT \quad \text{or} \quad T^{\text{cr}} = G/2k
\]

where \( T^{\text{cr}} \) denotes the critical temperature where embrittlement is most
acute. Using the value of $G$ given by Kiuchi and McLellan (1983), $G=5700$ J/mole, leads to a value $T_{cr}=338^\circ$ Kelvin. This value is in good agreement with the data of Carter and Hyatt (1977) mentioned above. The differences between the calculated value, $338^\circ$ Kelvin, and the experimental data presented by Carter and Hyatt may be attributable to differences in activation energy between the AISI alloy steels and the relatively pure materials considered by Kiuchi and McLellan.

The usual definition of particle mobility does not contain the ratio of Bessel functions described above. Consequently, if the critical temperature for embrittlement is calculated from the usual mobility definition ($\text{mobility} = D/kT$), the resulting value is off by a factor of two. This long-standing discrepancy between theoretical and experimental results has been remedied by the present model.

The prediction of equation [4.2.5] cannot be valid for extremely short periods of time, especially if the initial solute concentration $C_0$ is particularly large. The reason is as follows. The first solute atoms to arrive at the site of embrittlement have travelled a short distance. It may well be that at time zero these solute atoms were located at $z/2$ or so. Clearly then, the assumption that $z$ is much less than unity is not true for the case in which a "sufficient" quantity of embrittling atoms are located close to the site of embrittlement at time zero. It is expected, however, that if an average embrittling atom travels from a distance of $z/10$ or so that equation [4.2.5] would then be valid.

4.3 Finite Element Calculations of the Solute Accumulation

During crack growth rate tests on precharged specimens, an incubation period is commonly observed between application of the load
and the onset of crack growth. In tests on smooth or blunt notched specimens, there is usually no attempt made to observe the onset of crack growth. Instead, the measured quantity is usually the total time to specimen failure. In many situations in which the applied load approaches the elastic limit of the specimen, this time to failure is only infinitesimally greater than the time to initiate crack growth. In the following discussion of incubation period, one can consider that the incubation period and the time to failure are essentially the same for highly loaded specimens either with or without sharp cracks. The discussion, however, applies only to precharged specimens in which no hostile environment has invaded the crack.

The observed incubation period (or time to failure) leads to an obvious choice for a failure criterion: crack propagation begins when the solute concentration in the deformed zone reaches some critical level. The incubation period, then, is just the period of time required for a "sufficient" amount of the embrittling solute to arrive in the neighborhood of the crack tip.

The "neighborhood of the crack tip" is troublesome to define. In this research it was initially hypothesized that the deformed zone was the most appropriate region. This hypothesis leads to the physically unrealistic result that crack growth rates decrease as applied stress intensity increases. Since this cannot be so, the hypothesis was abandoned. Following the criterion discussed by Rice (1977), a stress independent, microstructure dependent distance has been adopted. As discussed by Rice, the distance chosen must be "appropriate to the mechanism at hand." Since hydrogen embrittlement typically results in intergranular fracture, the obvious choice for a fixed microstructural
distance is the grain size. Consequently, in the calculations presented below, the average grain diameter is used as the appropriate distance.

In the computational work it is assumed that the crack tip is an ideal sink for solute atoms. The supposed sink is really composed of the distributed point and line defects that are generated in the deformed zone as a result of the irreversible plastic deformation. Instead of distributing these defects in some unknown, nonuniform manner through the deformed zone, they are simply lumped together at the crack tip.

The assortment of defects is actually saturable. A sufficient quantity of solute atoms will relax all of the long range stress fields associated with the defects. Once that happens, the assumed ideal sink at the crack tip is no longer appropriate. The appropriate condition should then be that of no flow across the boundary at r=0.

The only problem with this change of boundary condition is knowing the total amount of solute atoms required to saturate the sink. Since determination of this quantity is beyond the scope of the present investigation, the boundary condition at r=0 will be left as that of a perfect sink. The computer program, however, can be modified at some future date to account for the sink's saturation, once the information becomes available. It is by no means certain that this modification is necessary. It would certainly not be necessary if crack propagation occurs before the sink is saturated. If the sink were to saturate without crack propagation, and solutes were to continue accumulating in the neighborhood of the crack tip, still without crack propagation, eventually the equilibrium condition would be approached where the net flow of solute atoms stops. This equilibrium state was examined by Li, Orien and Darken (1966) and by Liu (1970). Once equilibrium is reached,
the net flow of solutes into and out of the deformed zone (and every other region of the specimen) simply vanishes.

Once a sufficient quantity of solute atoms have accumulated around the crack tip, some embrittlement mechanism must come into play, by which the fracture resistance of the material is reduced. In some materials the mechanism may be hydride formation. In others, at high temperature, it may be methane formation. The mechanism may be more indirect. The solute atoms may alter the long range stress fields of the dislocations and thereby enhance the localization of flow. Finally, the solute atoms might directly reduce the interatomic potentials that bind the solvent atoms together.

Whatever the embrittlement mechanism, there should be associated with it some activation energy. If this activation energy is significantly less than the activation energy for solute diffusion, then solute diffusion would be the rate limiting process. Conversely, if the activation energy for the embrittlement reaction is much greater than the activation energy for diffusion, then the embrittlement reaction would be rate limiting.

The incubation period between loading and crack advance is the sum of the two contributions. If diffusion is rate limiting, then it will dominate the incubation period. If the embrittlement reaction is rate limiting, then it dominates. Since the present investigation deals only with the diffusion process, the calculated incubation periods are only descriptive of systems in which diffusion is the rate limiting mechanism. It is important to note that if diffusion is the rate limiting process, as assumed here, then crack propagation cannot occur once the sink is saturated and the equilibrium state has been reached.
With all of these considerations in mind, some calculations were carried out using the finite element program shown in the appendix. The aim of these calculations is to show the dependence of the incubation period on applied load and material parameters. The FORTRAN program has been used successfully on three different models of personal computers (PC's) and one large mainframe system. All together, three different FORTRAN '77 compilers have been used with good success. Operation of the program on a PC is reasonably fast as long as the floating point arithmetic is carried out in hardware, not software. As a minimum, one disk drive and about 128 K bytes of memory are necessary to compile and run the program on a PC. All of the numerical results presented here were produced using an AT&T 6300 PC with the 8087 math coprocessor, 2 floppy disk drives and 640 K bytes of memory. The operating system was IBM PC-DOS version 3.0 and the compiler was the IBM Professional FORTRAN compiler version 1.00.

The required inputs to the program are listed in Table 2, along with a description of each. Some frequently used values are also mentioned. The data can be entered manually from the keyboard, or read directly from a data file. Output from the program is directed to the display screen, and as an option, it can also be sent to a printer, a disk file or both. The disk file is formatted so that it can be read and manipulated by the spreadsheet program "1-2-3" from Lotus Development Corp. Most of the figures attached to this thesis were produced using the Lotus software.

The output from the program consists of three primary sorts of results. The first consists of the concentration profiles on the unit domain, at several specified points in time. These concentration
profiles all have the same basic shape and propagate outward from the origin in the same fashion. An example of these concentration curves is shown in figure 4. The curves in figure 4, for eigenvalue EIG=0, describe hydrogen diffusion in steel at room temperature. They were calculated using the partial molar volume data of Wagenblast and Wriedt (1971) and the diffusivity data of Kiuchi and McLellan (1983). The applied stress intensity is 10 MPa sqrt(m) and the material tensile strength is 2 GPa. Under these conditions, the material could well be embrittled by hydrogen.

The solute flux into the crack tip region is calculated from the concentration profiles. Since the solute flux curves are of more immediate interest than the concentration profiles, several examples are included in figures 5 through 9. These five figures show solute flux as a function of time for hydrogen in steel. The tensile strength is 1.0 GPa and applied stress intensity values of 2.5, 5, 10, 20 and 40 MPa are used, respectively, in figures 5 through 9.

These solute flux curves exhibit several important features. First, for each of the eigenvalues, the flux values are initially small in magnitude and increase rapidly. Since the initial concentration is assumed uniform, all flux components should vanish at time zero. All of the curves reach a peak magnitude and thereafter decrease toward zero. As the eigenvalue number increases, the flux peak moves to shorter times. The influence of eigenvalue zero is more important than the others. In fact, the curves for eigenvalues 2 and greater have such a small amplitude they do not show up at all on these graphs. As time goes on, the curves for the eigenvalues other than zero vanish more rapidly than the curve for eigenvalue zero. The curves for eigenvalue zero seem
to approach the steady state values predicted by equation [3.3.27]. The main feature of figures 5 through 9 is the dependence on applied stress intensity, $S_{IFK}$. All of the curves reach a peak flux of about 6 or $7 \times 10^{-6}$ /sec. after about $1/4$ second. The flux values are in terms of the initial concentration $C_0$.

Taking the flux curves, integrating from time zero up to the present time and then dividing by the volume of the chosen crack tip region leaves $ACCUM$, the excess solute accumulation per unit volume in the region. Here, the volume of the region is just pi times the square of its radius. This volume is per unit length of crack. The accumulation curves corresponding to figures 5 through 9 are found in figures 10 through 14.

As an example, assume that crack propagation occurs when the accumulation in the deformed zone reaches 100 times the initial concentration. Lacking any known failure criterion, this one is assumed for illustrative purposes. If crack propagation occurs before sink saturation, then the incubation period (or perhaps time to failure) increases with applied stress intensity as shown in table 3. Also in table 3 the crack growth rate is calculated as follows. First, assume the crack jumps the fixed microstructural distance of 30 microns after the incubation time is reached. The crack tip is then surrounded by essentially new material with the constant uniform initial solute concentration. Again the solute atoms accumulate around the crack tip, and after another incubation period the crack jumps once more. The average crack growth rate is just the distance failed divided by the incubation period.

Notice in table 3 that for applied stress intensity values between
2.5 and 10 MPa $\text{sqrt}(m)$ the crack growth rate is independent of applied stress intensity. For applied stress intensities greater than 10 MPa $\text{sqrt}(m)$, the crack growth rate increases rapidly.

Numerous experimental results show a similar dependence of crack growth rates on applied stress intensity, that is a range of applied stress intensity values over which crack growth rate is independent (or nearly independent) of the applied stress intensity. Experimental results also show a threshold value of the applied stress intensity factor, below which growth rates rapidly vanish. Hirth (1980) and Oriani (1978) have reviewed these and other features of the experimentally determined crack growth rate curves.

Such a threshold does not appear in the numerical results, due to the ideal sink at the crack tip. The tiny deformed zone associated with small values of applied stress intensity can act as only a very weak, easily saturated sink. Numerical results suggest that the deformed zone associated with some infinitesimal applied stress intensity would saturate with solute atoms in an infinitesimally short period of time. Such saturation would soon result in no further solute accumulation around the crack tip. In this way a threshold value of applied stress intensity would be determined, below which the crack growth rate would vanish.

As a result, then, the numerically derived crack growth rate curves are characterized by three primary regions. One is the region of diffusion limited growth in which the growth rate is independent of applied stress intensity. Another region of the curve is that of high applied stress intensity, where the growth rates increase rapidly with increasing applied stress intensity. The final region of the calculated
crack growth curves is the region of sink saturation at low applied stress intensity, where the crack growth rates vanish with decreasing applied stress intensity. It is notable that experimentally obtained crack growth rate curves usually exhibit three similar regions, and have the same general shape, as described by Hirth (1980) and Orianì (1978).

In the present investigation there has been no experimental effort made to confirm the validity of numerically derived crack growth rate curves. Consequently, this portion of the present research must be considered unfinished, until some confirmation or rejection of the numerical results can be achieved.
5. CONCLUSIONS

The present research has produced three primary results. The first two are the critical material strength below which no embrittlement occurs and the temperature of most acute embrittlement. The third result consists of the numerically calculated rates of solute accumulation in the neighborhood of the crack tip, together with the average crack growth rates resulting from such solute accumulation. While the first two results have, to some extent, been confirmed by available experimental data, the third finding has not been confirmed by any specific experimental data and must be considered preliminary.

The critical material strength for embrittlement is derived using the concept of the particle turning point. The steady state differential equation that describes the diffusion of solute atoms is characterized by (among other things) its turning point. The turning point defines a closed surface surrounding the crack tip. This has been described in section 3.2 for the one dimensional case. If at any point the closed surface intersects the deformed zone surrounding the crack tip, then solute atoms in the equilibrium state cannot be trapped by the crack tip stress fields. Consequently, in the equilibrium state the cracked body cannot be embrittled by the mobile solutes. The equilibrium state is only reached after an infinite amount of time has passed. Since the cracked body will not be embrittled after an infinite amount of time, it cannot be embrittled after any shorter period of time either.

The present model of the turning point criterion needs further refinement. Principally, the model should account for the distribution of solute atom energies. This refinement would serve to reduce the calculated material strength for embrittlement. This should bring
calculated values into better agreement with the known experimental values.

To further test the turning point criterion it should be applied to other alloy systems, including solutions of hydrogen in various nonferrous alloys. At elevated temperatures carbon or other interstitials may be sufficiently mobile to cause embrittlement. Some of these should be examined also.

The temperature of most acute embrittlement coincides with a maximum in the solute atom mobility. In the cracked body, solute atom mobility varies with position. The usual mobility, D/kT, is modified by a dimensionless ratio of Bessel functions $I_{n+1}(Ar^{-1/2})/I_n(Ar^{-1/2})$ which contains a dependence on radial position $r$ and a dependence on temperature through parameter $A$. Solute atoms falling inward toward the crack tip spend the great majority of their time in a region of the cracked body where the ratio of Bessel functions can be approximated by the factor $A/2r^{1/2}$. Since $A$ contains $1/kT$, the solute mobility effectively depends on $D/(kT)^2$ which is at a maximum for $T=G/2k$ where $G$ is the activation energy for diffusion. While this result is in good agreement with the experimental data for hydrogen in steel, it must be tested in other alloy systems.

Finally, the finite element method allows calculation of solute atom accumulation in any region of the specimen. Such solute accumulations are often responsible for crack propagation. In order to make practical use of the solute accumulation data, some failure criterion must be chosen. An obvious choice is that crack propagation begins when the solute accumulation inside some microstructural feature reaches some critical value.
The repeated cycle of solute accumulation followed by brittle fracture of the microstructural feature leads to a relationship between crack growth rates and applied stress intensity. These crack growth rate curves possess two distinct regions. For low or moderate applied stress intensity, crack growth is diffusion limited and is independent of stress intensity. For relatively high stress intensity values, crack growth rates increase rapidly with stress intensity. Saturation of the crack tip deformed zone by solute atoms would lead naturally to a threshold stress intensity below which crack propagation would vanish. These three regimes of the crack growth rate curves are observed qualitatively in many experimental situations.

There are two inherent problems with numerical modeling of crack growth rate curves. Such numerical modeling requires the choice, a priori, of the fracture criterion and the criterion for sink saturation. Neither of these is particularly well understood. Any improvement in our understanding of crack propagation must be based on a better understanding of these phenomena.
FIGURE 1: The Macroscopic Crack Geometry

\( r \) = distance from crack tip
\( r_0 \) = specimen radius
\( r_p \) = deformed zone radius
\( \theta \) = angle from direction of crack advance

\( x \) and \( y \) are the independent variables in the rectangular coordinate system
FIGURE 2: The Characteristic Curve in the \((q,t)\) Plane. Note that \(y(q)\) is negative, \(S\) is the length of vector \(\psi\). \(\psi\) is determined at time \(t^m = m\Delta t\).
Figure 3: The Critical Strength's Dependence on Temperature, for the sharp crack model (see eqns. 3.2.33 and 4.1.3) and the blunt crack model (see eqns. 3.2.35 and 4.1.5). Yield strengths are multiplied by 3/2 to give approximate tensile strengths.
Figure 4: Typical Concentration Curves for Various Elapsed Times for Eigenvalue 0. This is the one dimensional concentration function $P(r,t)$ obtained by the finite element method. Along the horizontal axis is plotted $\log_{10}(q)$ where $0 < q < 1$. 

The graph shows the variation of concentration over time with different values of tensile and shear stress for a specific domain.
Figure 5: Solute Flux Through a Circle of Radius 30 Microns, Centered on the Crack Tip. For each eigenvalue, this flux is calculated using eqn. 3.3.30. Eigenvalue zero dominates. The tensile strength is 1 GPa and the stress intensity is 2.5 MPa sqrt(m). Along the horizontal axis is plotted log_{10}(time).
Figure 6: Solute Flux Through a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 5, except the stress intensity is now 5 MPa sqrt(m).
Figure 7: Solute Flux Through a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 5, except the stress intensity is now 10 MPa sqrt(m).
Figure 8: Solute Flux Through a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 5, except the stress intensity is now 20 MPa sqrt(m).
Figure 9: Solute Flux Through a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 5, except the stress intensity is now 40 MPa \text{sqrt(m)}. At this higher stress level the curve for eigenvalue 1 has a larger amplitude, but it is still smaller than the one for eigenvalue 0.
Figure 10: Solute Accumulation Inside a Circle of Radius 30 Microns, Centered on the Crack Tip. This dimensionless concentration $N(r,t)$ is calculated using eqn. 3.3.31. The tensile strength is 1 GPa and the stress intensity is 2.5 MPa sqrt(m). Along the horizontal axis is plotted $\log_{10}(\text{time})$. 

![Diagram of Solute Accumulation](image-url)
Figure 11: Solute Accumulation Inside a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 10, except the stress intensity is now 5 MPa sqrt(m).
Figure 12: Solute Accumulation Inside a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 10, except the stress intensity is now 10 MPa \text{sqrt(m)}.
Figure 13: Solute Accumulation Inside a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 10, except the stress intensity is now 20 MPa \sqrt{m}.
Figure 14: Solute Accumulation Inside a Circle of Radius 30 Microns, Centered on the Crack Tip. This is the same as Figure 10, except the stress intensity is now 40 MPa sqrt(m).
<table>
<thead>
<tr>
<th>variable</th>
<th>definition</th>
<th>FORTRAN name</th>
</tr>
</thead>
<tbody>
<tr>
<td>q</td>
<td>q=r/r₀</td>
<td>X</td>
</tr>
<tr>
<td>q̅</td>
<td>q̅=q−u(q)Δt</td>
<td>XCH</td>
</tr>
<tr>
<td>D</td>
<td>empirical constant</td>
<td>DO</td>
</tr>
<tr>
<td>D*</td>
<td>D*=D₀⁻²</td>
<td>DSTAR</td>
</tr>
<tr>
<td>D*Δt</td>
<td>see [3.4.16] and [3.4.28]</td>
<td>DTDT</td>
</tr>
<tr>
<td>n</td>
<td>see [3.4.4] and [3.4.6]</td>
<td>EIG</td>
</tr>
<tr>
<td>σₜ</td>
<td>tensile strength</td>
<td>TENSIL</td>
</tr>
<tr>
<td>r₀</td>
<td>specimen radius</td>
<td>XSPEC</td>
</tr>
<tr>
<td>K</td>
<td>stress intensity factor</td>
<td>SIFK</td>
</tr>
<tr>
<td>rₚ</td>
<td>see [3.1.5] with ν=1/3</td>
<td>XDZ</td>
</tr>
<tr>
<td>z</td>
<td>see [3.4.6]</td>
<td>Z</td>
</tr>
<tr>
<td>z₀</td>
<td>z₀=Ar₀⁻¹/²</td>
<td>ZO</td>
</tr>
<tr>
<td>u/D*</td>
<td>see [3.4.5] and [3.4.6]</td>
<td>COEF</td>
</tr>
<tr>
<td>A/K</td>
<td>= (B/2kT)/K</td>
<td>PARAM</td>
</tr>
<tr>
<td>zₚ</td>
<td>=Ar₀⁻¹/²</td>
<td>ZDZ</td>
</tr>
<tr>
<td>N/πr²</td>
<td>solute accumulation inside r=GSIZE</td>
<td>ACCUM</td>
</tr>
<tr>
<td>J(τ)</td>
<td>flux through circle of radius r=GSIZE</td>
<td>FLUXJ</td>
</tr>
<tr>
<td>pₘ⁻¹</td>
<td>see [3.4.13]</td>
<td>PCH</td>
</tr>
<tr>
<td>-</td>
<td>appropriate microstructural distance for the accumulation of solute atoms</td>
<td>GSIZE</td>
</tr>
<tr>
<td>-</td>
<td>GSIZE/XSPEC =</td>
<td>XGS</td>
</tr>
</tbody>
</table>
TABLE 2
Required Input Data for the FORTRAN Program

**INPUT LINE 1:**  IPRN, ILOTUS, ISTD, ISTEPS
**INPUT FORMAT:**  All four are integers

For printer output use IPRN=1. For output to a Lotus compatible disk file, use ILOTUS=1. To skip input line 2 and use the default values for all of that data, use ISTD=1. ISTEPS is the maximum number of time steps that you want to use. More than a few hundred time steps will take a while to compute. ISTEPS=128 for most of the calculations shown here.

**INPUT LINE 2:**  DO, SIFK, TENSIL, PARAM, XSPEC, GSIZE
**INPUT FORMAT:**  All six are real

These quantities are, respectively, the solute diffusivity, the stress intensity factor, the material tensile strength, a parameter described below, the specimen radius and an appropriate microstructural distance. The parameter PARAM=B/2KTK is determined from equation [3.1.10]. The values XSPEC=.05 m and GSIZE=.00003 were used in all of the calculations. The default values of these can be found about 45 lines into the program. ALL UNITS ARE MKS.

**INPUT LINE 3:**  TF, NT
**INPUT FORMAT:**  One real, one integer

TF is the final time. NT is used to determine the initial time step. The initial step is DTO=TF/NT. In most of the calculations NT=2**21=2097152 was employed.

**INPUT LINE 4:**  ITYPE, NS, NaN, INTERP
**INPUT FORMAT:**  All four are integers

These are, respectively, the mesh type, the number of segments in the unit domain, the number of segments inside the deformed zone and the type of interpolation: 1 for linear, 2 for quadratic. In all of the computations, these were set to values of 1, 512, 64, 1 respectively.

**INPUT LINE 5:**  FNAME, ICONOUT, NWRITE
**INPUT FORMAT:**  The first is character data, the others are integers

FNAME is the name for the Lotus compatible disk file. It must be in quotes. Lotus requires the extension .PRN. FNAME must be in a format acceptable to the operating system. To write concentration profiles to the disk file, use ICONOUT=1. Solute flux and accumulation data are always written to the disk file if it exists. NWRITE controls the amount of concentration data written to the disk file. For Lotus, NWRITE should be an integer multiple of 20. NWRITE larger than about 200 is pointless...
### TABLE 3
Calculated Incubation Periods and Crack Growth Rates

<table>
<thead>
<tr>
<th>Stress Intensity in MPa</th>
<th>Incubation Period in seconds</th>
<th>GSIZE or Distance Failed in microns</th>
<th>Crack Velocity in meters/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.</td>
<td>.012</td>
<td>30</td>
<td>3. x 10^{-3}</td>
</tr>
<tr>
<td>20.</td>
<td>.47</td>
<td>30</td>
<td>6. x 10^{-5}</td>
</tr>
<tr>
<td>10.</td>
<td>36.</td>
<td>30</td>
<td>8. x 10^{-7}</td>
</tr>
<tr>
<td>5.</td>
<td>36.</td>
<td>30</td>
<td>8. x 10^{-7}</td>
</tr>
<tr>
<td>2.5</td>
<td>36.</td>
<td>30</td>
<td>8. x 10^{-7}</td>
</tr>
</tbody>
</table>

Note: For all data, TENSIL=1. GPa

DO=7.4D-9 m^2/sec
PARAM=9.4D-11 Pa^{-1}
XSPEC=.05 m
REFERENCES


ASTM, 1979, Annual Book of ASTM Standards, Part 4, ASTM, Philadelphia, PA, see Table 3A, page 321


Mises, R. von, 1913, Gottinger Nachrichten, math.-phys. Kl., p. 582

Morse, P. M. and H. Feshbach, 1953, Methods of Theoretical Physics, vol. 2, McGraw-Hill, New York,


NACE, 1966, "Sulfide Cracking Resistant Metallic Materials for Valves for Production and Pipeline Service," Materials Protection, 2, p. 81, prepared by NACE committee T-1F, see also NACE publication 1F166, NACE, Houston, Texas


APPENDIX
The FORTRAN Finite Element Code

C Linear Galerkin code by PETER LOOS. Solution of the one-dimensional
C parabolic p.d.e. with unit domain and Dirichlet boundary conditions.
C The equation is dP/dt = DSTAR( P' - P*COEF) . The indep. variable is x
C and prime ('') denotes d/dx. Also, COEF = (Z*RATI+EIG-1)/x
C where RATI= I(EIG+1,Z)/I(EIG,Z) and Z= ZO/SQRT(x) . EIG, DSTAR and ZO
C are constants. I is the modified Bessel function of the first kind
C of integer order. Finite elements and the modified method of
C characteristics are used to convert the differential problem into a
C linear algebra problem of the form AP=F. The algebra problem must be
C solved at each time step. The time step varies as the program runs.
C Each time it changes, A is recalculated. Note that A is tridiagonal and
C positive definite. Two types of mesh are available to the user. All
C subroutines use IMPLICIT REAL*8 (A-H,O-Z) and IMPLICIT INTEGER*4 (I-N).
C
IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER*4 (I-N)
CHARACTER*17 FNAME
INTEGER*4 EIG
DIMENSION A(1025,3),F(1025),P(1025),ACOL2(1025),
'X(1025),H(1025),XCH(1025,2),NL(1025,2)
DIMENSION FLUXJ(1025,3),ACCUM(1025,3),KTIME(1025)
DIMENSION SIG(2),CSIG(2),PCHN(2),PCHNM1(2),BIVEC(7),XLOG10(20)
C
open(5, file='con')
C
open(6, file='con')
MAXNS=1024
MAXEIG=3
MAXREC=20
MAXKNT=1024
C
C Get input data. Parameter ZO depends on SIFK, PARAM and XSPEC. GSIZE
C is a pertinent microstructural size, possibly even the grain size.
C DSTAR depends on DO and XSPEC. The required diffuson constant DO,
C final time TF, stress intensity factor SIFK, material tensile strength
C TENSIL, constant parameter PARAM and specimen radius XSPEC are entered
C from the keyboard. IPRN is set to 1 if hard copy is desired. ILOTUS
C is set to 1 if data will be written to a disk file for later plotting.
C If ISTD=1, standard values of several parameters are used. ITYPE, NS,
C NDZ and XDZ define the spatial mesh. TF, NT and the available memory
C control the temporal mesh. INTERP determines whether interpolation is
C linear or quadratic.
C
1 WRITE(6,*) 'Input IPRN, ILOTUS, ISTD, ISTEPS.......
READ(5,*) IPRN, ILOTUS, ISTD, ISTEPS
IF(ISTEPS.GE.MAXKNT) GO TO 3
MAXKNT=ISTEPS
3 DO=7.4D-9
SIFK=10.D6
TENSIL=1.D9
PARAM=9.4D-11
XSPEC=5.D-2
GSIZE=30.D-6
IF(ISTD.NE.1) WRITE(6,500)
IF(ISTD.NE.1) READ(5,*) DO, SIFK, TENSIL, PARAM, XSPEC, GSIZE
WRITE(6,*) 'Input TF, NT...note DTO=TF/NT ............'
READ(5,*) TF, NT
WRITE(6,501)
READ(5,*) ITYPE, NS, NDZ, INTERP
IF(NS.GT.MAXNS) WRITE(6,*) 'Using NS= MAXNS=', MAXNS
IF(NDZ.LE.2.OR.NDZ.GT.NS-2) WRITE(6,*) 'Using NDZ(NS/2)
IF(ITYPE.EQ.3.AND.NDZ.GE.NS/2) WRITE(6,*) 'Using NDZ(NS/3'
ICOMPL=0
COEFMAX=1.D12
WRITE(6,502)
READ(5,*) ICOMPL, COEFMAX
5 IF(IPRN.EQ.1) OPEN(8,FILE='PRN')
IF(NS.GT.MAXNS) NS=MAXNS
IF(ITYPE.NE.3) ITYPE=1
IF(NDZ.LE.2.OR.NDZ.GT.NS-2) NDZ=NS/2
IF(ITYPE.EQ.3.AND.NDZ.GE.NS/2) NDZ=NS/3
IF(INTERP.NE.2) INTERP=1
IF(ILOTUS.NE.1) GO TO 7
C C Set up the files and parameters for the Lotus compatible data files
C
WRITE(6,505)
READ(5,*) NAME, ICONOUT, NWRITE
OPEN(3,FILE=NAME)
IF(NWRITE.GT.MAXKNT) WRITE(6,*) 'Using NWRITE=MAXKNT'
IF(NWRITE.GT.MAXKNT) NWRITE=MAXKNT
NDIVIS=MAXO(1,1+(NS-1-MOD(NS-1,NWRITE))/NWRITE)
NSREDU=1+(NS/NDIVIS)
LINES=IDINT((DBLE(NSREDU)-.001)/DBLE(MAXREC))+1
LRECL=NSREDU/LINES
LTERM=LINES*(LRECL-1)
LDELTA=LINES*NDIVIS
C C Initialize boundary points and boundary values. The domain in space is
C divided into NS segments and it has endpoints XLEFT and XRIGHT. At these
C boundary points the values of P are PLEFT and PRIGHT, respectively. Note
C that PLEFT changes with time. At time zero PLEFT=PTO and at later times
C PLEFT=PXO. Both depend on ICOMPL. EIG is the integer eigenvalue that
C results from the separation of radial and angular coordinates. Initially
C EIG=0, and it is incremented as the program runs. Note that none of these
C constants depend on EIG or time.
C
7 EIG=0
XLEFT=0.DO
XRIGHT=1.DO
PTO=1.DO
IF(ICOMPL.EQ.1) PTO=0.DO
PRIGHT=PTO
PXO=0.DO
IF(ICOMPL.EQ.1) PXO=1.DO
NSM1=NS-1
ZO=(PARAM*SIFK)/DSQRT(XSPEC)
XGS=GSIZE/XSPEC
ZGS=ZO/DSQRT(XGS)
XDZ=((SIFK/TENSIL)**2)/(36.*3.14159*XSPEC)
ZDZ=ZO/DSQRT(XDZ)
DSTAR=DO/(XSPEC**2)
EX1=DLOG(XDZ)/DLOG(DBLE(NDZ)/DBLE(NS))
EX3=XDZ*2.DO
XFAC3=(XRIGHT-(XDZ*2.DO))/(DBLE(NS-(NDZ*2.DO))
SIG(1)=.5*(1.DO-(1.DO/DSQRT(3.DO)))
SIG(2)=.5*(1.DO+(1.DO/DSQRT(3.DO)))
CSIG(1)=SIG(2)
CSIG(2)=SIG(1)

C Set up KNTDBLE. Later on in the program as the time stepping is carried
C out, if KOUNT < KNTDBLE, leave the time step as DT=DTO. If
C KOUNT > KNTDBLE, it's necessary to double DT=DTO*KOUNT every time KOUNT
C (or time) doubles. This insures the data will all fit in the available
C MAXKNT array locations and that a final result is obtained in your
C lifetime no matter how many time steps you call for.

C OCTAVES=DLOG(DBLE(NT))/DLOG(2.DO)
DO 10 N=2,31
LHS=MAXKNT
RHS=DBLE(2**M)* ( 1.DO+ (OCTAVES-DBLE(M))/2.DO )
IF(RHS.LE.DBLE(LHS)) KKK=M
IF(RHS.GT.DBLE(LHS)) GO TO 11
10 CONTINUE
11 KNTDBLE=2**KKK
IF(MAXKNT.GE.NT) KNTDBLE=MAXKNT

C Print out some data (to both screen and printer) to verify its accuracy
C
WRITE(6,700) DO,SIFK,TENSIL,PARAM,XSPEC,DSTAR,ZO,NDZ,XDZ,XGS,
ITF,NT,KNTDBLE,ITYPE,NS,NDZ,INTERP,COEFMAX
IF(ITYPE.EQ.1) WRITE(6,711) EX1
IF(ITYPE.EQ.3) WRITE(6,713) EX3
IF(IXLOTUS.EQ.1) WRITE(6,701) FNAME, ICONOUT, NWRITE
IF(IPRIN.NE.1) GO TO 12
WRITE(8,700) DO,SIFK,TENSIL,PARAM,XSPEC,DSTAR,ZO,NDZ,XDZ,XGS,
ITF,NT,KNTDBLE,ITYPE,NS,NDZ,INTERP,COEFMAX
IF(ITYPE.EQ.1) WRITE(8,711) EX1
IF(ITYPE.EQ.3) WRITE(8,713) EX3
IF(IXLOTUS.EQ.1) WRITE(8,701) FNAME, ICONOUT, NWRITE

C Set up nonuniform mesh in space: the location of node N is X(N) and
C H(N) is defined to be X(N)-X(N-1). ITYPE=1 is a power law mesh and
C ITYPE=3 is piecewise uniform with a discontinuity at XDZ. In either
C case, the node with index NDZ is located at XDZ. While setting up the
C mesh, determine where XGS is located. XGS=X(NGS)+EPSILGS*H(NGS+1)

C 12 XL=XLEFT
DO 14 N=1,NS
IF(ITYPE.EQ.1) X(N)=(DBLE(N)/DBLE(NS))**EX1
IF(ITYPE.EQ.3.AND.N.LE.(NDZ*2)) X(N)=XZ*DBLE(N)/DBLE(NDZ)
IF(ITYPE.EQ.3.AND.N.GT.(NDZ*2)) X(N)=(XZ*2.DO)+XFA3*
' DBLE(N-NDZ*2))
H(N)=X(N)-XL
XL=X(N)
IF(X(N).LT.XGS) NGS=N
14 CONTINUE
EPSILGS=(XGS-X(N(GS))/H(NGS+1)
C
C Initialize some of the constants and arrays that depend on EIG and time:
C KOUNT, ACCUTMP and FLUXTMP. KOUNT count up time steps DTO and KNT counts
C up time steps DT. Note that DT=DTO*KOUNT. NCHS is the
C segment in the domain where (for EIG=0) COEF changes sign. ACCUTMP and
C FLUXTMP are the solute accumulation (per unit volume of deformed zone)
C and the flux during the last time step. Iteration over the eigenvalues
C EIG is carried out between lines 18 and 213
C
18 KOUNT=0
KNT=0
KOUNTER=1
NCHS=0
ACCUTMP=0.DO
FLUXTMP=0.DO
FLUXREF=0.DO
ICHANGE=1
C
C Initialize as constants P(N). Also initialize SLOLD, the slope dp/dx at
C XGS. SLOLD is determined by a difference formula accurate to order O(dx**2)
C Note that F1, F2, NGSO and DENOMGS are used later on to calculate SLNEW.
P(NS)=PRIGHT
20 DO 25 N=1, NSM1
P(N)=PTO
25 CONTINUE
IF(EPSILGS.GT..5DO) GO TO 26
DENOMGS=(H(NGS)+H(NGS+1))/2.DO
F1=(.5O-EPSILGS)*H(NGS+1)
F2=(.5O-EPSILGS)*H(NGS+1)
NGSO=0
GO TO 30
26 DENOMGS=(H(NGS+1)+H(NGS+2))/2.DO
F1=(1.DO-EPSILGS)*H(NGS+1)+.5O*H(NGS+2)
F2=(EPSILGS-.5O)*H(NGS+1)
NGSO=1
30 SLRT=(P(NGS+NGSO+1)-P(NGS+NGSO))/H(NGS+NGSO+1)
SLLFT=(P(NGS+NGSO)-P(NGS+NGSO-1))/H(NGS+NGSO)
SLOLD=(SLLFT*F1/DENOMGS)+(SLRT*F2/DENOMGS)
C
C Now write EIG to all of the active output devices and write some
C descriptors to the screen and printer. Also write the appropriate node
C numbers and node locations into the Lotus file if ICONOUT=1.
C
WRITE(6,706) EIG
IF(IPRN.EQ.1) WRITE(8,706) EIG
31 WRITE(6,777)
WRITE(6,*) ' '  
IF(IPRN.EQ.1) WRITE(8,777)  
IF(ILOTUS.NE.1.OR/iconout.NE.1) GO TO 99  
DO 35 L=1,LINES  
LLO=1+(L-1)*NDIVIS  
LHI=LLO+LTERM*NDIVIS  
WRITE(3,300) EIG, (K, K=LLO, LHI, LDELT)  
35 CONTINUE  
DO 37 L=1,LINES  
DO 36 K=1,LRECL  
LLO=1+(L-1)*NDIVIS  
NLX=LLO+(K-1)*LDELT  
IF(NLX.GT.NS) GO TO 36  
XLOG10(K)=DLOG10(X(NLX))  
36 CONTINUE  
WRITE(3,305) (XLOG10(K), K=1,LRECL)  
37 CONTINUE

C Set up the LHS of the eqn. This is necessary only when DT changes.  
C The tridiagonal operator matrix A has been stored in a three column  
C matrix where col. 2 is the original diagonal, and 1 & 3 are the lower  
C and upper parts, respectively. Also note that A(1,1) and A(NSM1,3) are  
C used in satisfying the boundary conditions but they are not part of  
C the square matrix A. Here, A is not symmetric.  

99 PCHN(1)=0.DO  
PCHN(2)=0.DO  
DTO=DT/DIBLE(NT)

C Time iteration is carried out from line 100 to line 200

C 100 IF(ICHANGE.NE.1) GO TO 110  
DT=DTO*DIBLE(KOUNTER)  
DTDT=DTSTAR*DT  
PLEFT=PXO  
IF(KOUNTEQ.0) PLEFT=PTO  
DO 105 N=1,NSM1  
NP1=N+1  
A(N,1)=-1.DO+(H(N)*H(N))/6.DO*DTDT  
A(N,2)=1.DO+(H(N)*H(NP1)+H(N)*(H(N)+H(NP1)))/3.DO*DTDT  
A(N,3)=-(H(N)/H(NP1))+(H(N)*H(NP1))/6.DO*DTDT  
105 CONTINUE

C Set up the RHS of the equation. The integration is carried out using  
C the two point Gaussian quadrature rule. Since P is known only at  
C the nodes, we must interpolate values of P between nodes.  
C First, determine which nodes are used in the interpolation. There are  
C 2 interpolation points (the Gauss points) in each segment. COEF  
C is the coefficient of the convection term (the first derivative  
C term in the PDE) evaluated at the Gauss points. XCH is the distance  
C traveled along the characteristic for each segment, N, and Gauss point, J.  
C NL contains the index of the node to the left of XCH. XCH is recalculated  
C only if DT changes, as indicated by ICHANGE=1. If INTERP=1 use linear  
C interpolation instead of quadratic. PCHN(J) is the value of the
C interpolate for segment N and Gauss point J. Similarly, PCHNML(J) is
C the value for segment NM1.
C
110 DO 155 N=1, NS
   NM1=N-1
   F(NM1)=0.DO
   DO 149 J=1, 2
   PCHNML(J)=PCHN(J)
   IF(ITYPE.EQ.3) GO TO 125
   XNJ=X(N)-H(N)*CSIG(J)
   Z=Z0/DQSRT(XNJ)
   CALL GETCOEF(XNJ,Z,ZDZ,EIG,BIVEC,COEF,COEFMAX)
C In the next line determine where COEF changes sign,
C from + on the left to - on the right. Note: this only happens if EIG=0.
   IF(COEFF.GE.0.DO) NCHS=MAXO(N,NCHS)
113 XCHTMP=XNJ-COEFF*DTD
119 IF(XCHTMP.LE.XLEFT) GO TO 126
121 IF(XCHTMP.GE.XRIGHT) GO TO 127
125 IF(XCHTMP.GT.(XZDZ.DO)) REALNL=2.*DBLE(NDZ)+(XCHTMP-
   (XZDZ.DO))/XPAC3
   IF(XCHTMP.LE.(XZDZ.DO)) REALNL=XCHTMP*DBLE(NDZ)/XZD
GO TO 128
C Use negative node numbers to indicate interpol'n point outside the domain
126 NLTMP=1
GO TO 140
127 NLTMP=-NS
GO TO 140
128 NLTMP=IDINT(REALNL)
   IF(ITYPE.EQ.1) GO TO 140
   IF(NLTMP.EQ.0) GO TO 140
   IF(NLTMP.NE.NSM1) GO TO 130
   NLTMP=NLTMP-1
   GO TO 140
130 XLM1=X(NLTMP)-H(NLTMP)
   TEST1=XCHTMP-XLM1
   TEST2=X(NLTMP+2)-XCHTMP
   IF(TEST1.LT.TEST2) NLTMP=NLTMP-1
C Temporary values NLTMP and XCHTMP are stored in arrays NL(N,J) and XCH(N,J)
C These arrays don't have to be recalculated unless the time step or mesh
C changes or COEF is a function of time.
140 NL(N,J)=NLTMP
C XCH(N,J)=XCHTMP
C
C In the same DO loop do the interpolation, either quadratic or linear. The
C quadratic polynomial PCHN(XCH)= W(3)*XCH**2 +W(2)*XCH +W(1) leads to a 3 by
C 3 matrix equation of the form G(3,3)*W(3)=Y(3). The numbers are actually
C stored as individual constants, not arrays. For example, G(3,2) is stored
C as G32. This speeds processing somewhat. The linear case is simpler.
C
142 NLTMP=NL(N,J)
   IF(NLTMP) 143, 144, 145
143 IF(NLTMP.EQ.-1) PCHN(J)=PLEFT
       IF(NLTMP.EQ.-NS) PCHN(J)=RIGHT
       GO TO 149
144 IF(INTERP.EQ.1) GO TO 148
       G32=0.DO
       G33=0.DO
       Y3=PLEFT
       GO TO 146

C Note G31=G21=G11=1. always.
145 IF(INTERP.EQ.1) GO TO 148
       G32=X(NLTMP)
       G33=X(NLTMP)**2
       Y3=P(NLTMP)
146 G22=X(NLTMP+1)
       G23=X(NLTMP+1)**2
       Y2=P(NLTMP+1)
       G12=X(NLTMP+2)
       G13=X(NLTMP+2)**2
       Y1=P(NLTMP+2)

C Note G21=G31=0 at this point.
       G22=G22-G12
       G23=G23-G13
       Y2=Y2-Y1
       G32=G32-G12
       G33=G33-G13
       Y3=Y3-Y1
       GRAT=G32/G22

C Note G32=0. at this point.
       G33=G33-G23*GRAT
       Y3=Y3-Y2*GRAT
       W3=Y3/G33
       W2=(Y2-W3*G23)/G22
       W1=Y1-W3*G13-W2*G12
       PCHN(J)=W3*(XCH(N,J)**2)+W2*XCH(N,J)+W1
       GO TO 149

C
C If called for, do the linear interpolation in the same big DO loop.
C
148 PL=PLEFT
       IF(NLTMP.GT.0) PL=P(NLTMP)
       SLOPE=(P(NLTMP+1)-PL)/H(NLTMP+1)
       CONST=PL-SLOPE*(X(NLTMP+1)-H(NLTMP+1))
       PCHN(J)=SLOPE*XCH(N,J) + CONST
149 CONTINUE
       IF(N.EQ.1) GO TO 155

C
C Finally, set up the RHS of the equation, still in the same DO loop.
C
       F(NM1)=F(NM1)+ (.5/DTDT)*
       ' ( H(NM1)*H(NM1)* (SIG(1)*PCHNM1(1)+SIG(2)*PCHNM1(2))+
          H(NM1)*H(N)* (CSIG(1)*PCHN(1)+CSIG(2)*PCHN(2)) )

155 CONTINUE
C Use PXO here (not PLEFT) since these bddy terms come from the LHS of the
C equation where time is never zero.
156 F(1)=F(1)-PXO*A(1,1)
F(NSM1)=F(NSM1)-RIGHT*A(NSM1,3)

C Do the fwd elimination and back sub on A and F. While doing the back sub
C replace old P values with the new ones. Since matrix A doesn't change with
C time, avoid damaging its contents by using a temporary matrix, ACOL2,
C which is just column 2 of the original matrix A. Carry out arithmetic in
C ACOL2. Also increment KNT by 1 and KOUNT by KOUNTER and reset ICHANGE.
C
ACOL2(1)=A(1,2)
159 DO 160 N=2, NSM1
      ACOL2(N)=A(N,2)
      ARATIO=A(N,1)/ACOL2(N-1)
      ACOL2(N)=ACOL2(N)-A(N-1,3)*ARATIO
      F(N)=F(N)-F(N-1)*ARATIO
160 CONTINUE
P(NSM1)=F(NSM1)/ACOL2(NSM1)
DO 165 NBKSUB=1, (NS-2)
      L=NSM1-NBKSUB
      P(L)=(P(L)-P(L+1)*A(L,3))/ACOL2(L)
165 CONTINUE
      KOUNT=KOUNT+KOUNTER
      KNT=KNT+1
      ICHANGE=0

C Determine dT*dP/dx at XGS. SLOLD is the slope dP/dx at previous
C time T(KOUNT-1) and SLNEW is the slope at present time T(KOUNT).
C Integration over time is carried out just after line 176 by summing
C over all previous contributions. The accumulation ACCUTMP is per unit
C volume. The volume is that of a grain (or other appropriate
C microstructural feature) and it is cylindrical, of unit length.
C
      SLRT=(P(NGS+NGSO+1)-P(NGS+NGSO))/H(NGS+NGSO+1)
      SSLFT=(P(NGS+NGSO)-P(NGS+NGSO-1))/H(NGS+NGSO)
      SLNEW=(SSLFT*SLRT)/DENOMGS+(SLRT*SLRT)/DENOMGS
      IF(KOUNT.LE.2) CALL FLXFA(C,EIG,ZGS,XGS,BVEC,FACTOR)
176 FLXTMP=FACTOR*DSTAR*(SLNEW+SLOLD)/2.DO
      ACCUTMP=ACCUTMP-((FLXTMP/DT)/(3.14159*(XGS**2)))
      SLOLD=SLNEW
C Store appropriate data in the arrays FLUXJ, ACCUM and TLOG10. Later
C these arrays will be written to the disk file (if it is being used).
178 IF(ILOTUS,NE,1) GO TO 181
      FLUXJ(KNT,EIG+1)=FLXTMP
      ACCUM(KNT,EIG+1)=ACCUTMP
      KTIME(KNT)=KOUNT
C
C If KOUNT is an integer power of 2, write out data to the printer,
C screen and the Lotus file if they are active. The data written here
C includes the values of the unknown, P, and its slope, dP/dx . Also,
C determine where the propagating front is located. The front is defined to
C be that part of the domain where .05 < P < .95 . Then, write out the index
C of the leftmost and rightmost nodes where the front is located. This
C concentration data is written to the Lotus file only if ICONOUT=1 .
181 IF(KOUNT.GE.NT) GO TO 182
   RATA=DLOG(DBLE(KOUNT))/DLOG(2.DO)
   TSTA=MOD(RATA,1.DO)
   TSTA=TSTA*(1.DO-TSTA)
C If KOUNT is not an integer power of 2, go to 197 - don't write anything.
   IF(TSTA.GT.1.D-4) GO TO 197
182 NA=0
   IF(icompl.eq.1) NA=NS
   NB=NS
   IF(icompl.eq.1) NB=0
   DO 183 N=1, NS
   IF(icomp.1 .AND. P(N).LT..05) NA=MAXO(N,NA)
   IF(icomp.1 .AND. P(N).LT..05) NA=MINO(N,NA)
   IF(icomp.1 .AND. P(N).GT..95) NB=MINO(N,NB)
   IF(icomp.1 .AND. P(N).GT..95) NB=MAXO(N,NB)
183 CONTINUE
   NLFT=NA
   IF(icompl.eq.1) NLFT=NB
   IF(NRT.LT.NS/2) NRTOLD=NRT
   NRT=NB
   IF(icompl.eq.1) NRT=NA
184 WRITE(6,550) KOUNT, (P(K),K=NDZ-3,NDZ+3), FLUXTMP, ACCUTMP,
   NLFT, NRT
   IF(IPRN.EQ.1) WRITE(8,801) KOUNT, (P(K),K=NDZ-3,NDZ+3),FLUXTMP,
   ACCUTMP, NLFT, NRT
   IF(ILOTUS.NE.1.OR.ICONOUT.NE.1) GO TO 190
   DO 186 L=1, LINES
   LLO=L+(L-1)*NDIVIS
   LHI=LLO+LTERM*NDIVIS
   WRITE(3,302) KOUNT, (P(K), K=LLO, LHI, LDELTA)
186 CONTINUE
   WRITE(3,320) NLFT, NRT
   NLRGE=NRT
   IF(NRT.GE.NS/2) NLRGE=NRTOLD
   NLINE=IDINT(DBLE(MAXO(NLRGE+10,20))-.001)/DBLE(MAXREC)+1
   NRECL=MAXO(NLRGE+10,20)/NLINE
   DO 187 L=1, NLINE
   WRITE(3,321) (P(K),K=L,(L+(NRECL-1)*NLINE),NLINE)
187 CONTINUE
190 IF(KOUNT.GE.NT) GO TO 200
C While KOUNT is a power of 2, check to see if the time step needs to
C be doubled. Double it if KOUNT = or > KNTDBLE calculated earlier. If
C KOUNT < KNTDBLE, the time step stays DT=DTO. Otherwise, DT is doubled
C every time this point in the program is reached. The net effect is that
C 32 time steps double the elapsed time, once time=DTO*KOUNT is reached.
C
   IF(KOUNT.LT.KNTDBLE) GO TO 197
   ICHANGE=1
   KOUTER=KOUTER*2
C Show some temporary data on the screen, but later overwrite it.
197 WRITE(6,577) P(NDZ), KOUNT, FLUXTMP
C Go to 100 means take another time step.
   GO TO 100
Having reached the final time when KOUNT=NT, write some final information to the screen, printer. The flux data (as a function of time) is also written to the Lotus-compatible disk file.

200 SECOND=DTO*DBLE(KOUNT)
XCHS=X(NCHS)+.5*XH(NCHS+1)
RATCHS=XDZ/XCHS
WRITE(6,753) SECOND, X(NDZ), P(NDZ), NDZ, ACCUTMP
IF(IPRN.EQ.1) WRITE(8,753) SECOND, X(NDZ), P(NDZ), NDZ, ACCUTMP
IF(EIG.NE.0) GO TO 205
IF(NCHS.NE.0) WRITE(6,754) XCHS, NCHS, RATCHS
IF(NCHS.EQ.0) WRITE(6,*), ' COEF>0 at all Gauss points'
IF(IPRN.NE.1) GO TO 205
IF(NCHS.NE.0) WRITE(8,754) XCHS, NCHS, RATCHS
IF(NCHS.EQ.0) WRITE(8,*), ' COEF>0 at all Gauss points'

205 IF(EIG.LT.MAXEIG) EIG=EIG+1
IF(EIG.LT.MAXEIG) GO TO 18
WRITE(6,*), ' EIG=MAXEIG, WRITING DATA TO DISK AND RESTARTING ...'
IF(ILLOTUS.NE.1) GO TO 213
WRITE(3,350) XDZ, TENSIL, SIFK, DO, PARAM, XSPEC, XGS
DO 210 KT=1, KNT
TIMELOG=DLOG10(DTO*DBLE(KTIME(KT)))
ACC1=ACCUM(KT,1)
ACC2=ACCUM(KT,2)
ACC3=ACCUM(KT,3)
IF(IOUT.EQ.-1) ACC1=DLOG10(DABS(ACCUM(KT,1)))
IF(IOUT.EQ.-1) ACC2=DLOG10(DABS(ACCUM(KT,2)))
IF(IOUT.EQ.-1) ACC3=DLOG10(DABS(ACCUM(KT,3)))
WRITE(3,303) KTIME(KT), TIMELOG, FLUXJ(KT,1), ACC1,
*FLUXJ(KT,2), ACC2, FLUXJ(KT,3), ACC3
210 CONTINUE
213 GO TO 1
STOP

Formats 3xx are for Lotus, 8xx are for the printer, 5xx are for the console, 99x are for console output of intermediate data and 7xx are shared by both console and printer. Lotus requires format E, not D.

300 FORMAT('',"EIG='",I3,'='',20(4X,I6))
305 FORMAT('',"LOG10(X(N))'=',20(1X,E9.3))
302 FORMAT(1H ,I10,20(4X,F6.3))
303 FORMAT(1H ,I8,7(1X,E9.3))
320 FORMAT(1H ,''' NLFT='",I4,''' NRT='",I4)
321 FORMAT(1H ,'''0 to NRT'=',20(4X,F6.3))
350 FORMAT(1H ,7(2x,E8.2)/,
''...=XDZ ...=TENSIL ...=SIF ...=DO ...=PARAM ...=XSPEC ...=XGS''/,
''...=EIG=0''/,
'"EIG=2...''/,
''...=KOUNT...LOG10(T)...=FLUXJ...=ACCUM...=FLUXJ...=ACCUM'')
700 FORMAT(,'' DO()='",D8.2,'' SIFK()='",D8.2,'' TENSIL()='",D8.2,
'* PARAM()='",D8.2,'' XSPEC()='",D8.2,'' DSTAR()='",D8.2,
'* ZO()='",D8.2,'' XDZ()='",D8.2,'' ZDZ()='",D8.2,'' XGS()='",D8.2,/,
'* TF()='",D8.2,'' NT()='",I7,'' KNTDBLE()='",I3,/,
2 ITYPE=I2, NS=I4, NDZ=I4, INTERP=I2, COEFMAX=D8.2
711 FORMAT(1X(N) = (N/NS)**(F8.5)
713 FORMAT(1X(N) discon AT X='*,F8.5)
701 FORMAT(' The Lotus filename is ',A17,'ICONOUT=',I2, ' NWRITE=',I3)
706 FORMAT(I(X,/, ' EIG is now equal to ',I3)
753 FORMAT(' At T=',D9.3, ' sec, P(x=',F7.6, ')=' ,F10.8,
2 ' at N=',I3, ' Final ACCUM=',D10.4)
754 FORMAT( ' COEF=O for X>',D8.2, ' NCHS=',I4, ' and XDZ/XCHS=',D8.2)
777 FORMAT( ' T/DTO NDZ-3 NDZ-2 NDZ-1 NDZ NDZ+1 NDZ+2 NDZ+3 FLUXJ
2 ACCUM NLFT NRT')
500 FORMAT( ' Input DO, SIFK, TENSIL, PARAM, XSPEC, GSIZE in mks units'
2 ', ', for H in FE at 25 Centigrade use: ', /
2 ', ', DO = 7.4D-9 m**2/sec (KIUCHI and MCLELLAN data) ', /
2 ', ', TENSIL = 1.09 for drill string material ', /
2 ', ', PARAM=9.4D-11 1/Pa (WAGENBLAST & WREIDT data for dv and ', /
2 ', ', Poisson rat. =1/3 ', /
2 ', ', GSIZE=3.5D-5 for drill string material ', /
2 ', ', assuming plane strain & unit domain ', /
2 ', ', critical strain energy density model of plasticity ', /
2 ', ', so XGS = GSIZE/XSPEC ', /
2 ', ', .... and XDZ = (SIFK/TENSIL)**2 /36.*3.14159*XSPEC ', /
2 ', ',.... and ZO = PARAM*SIFK/SQRT(XSPEC)...... ', /
2 ', ',.... and DSTAR = DO/(XSPEC**2) ', /
501 FORMAT( ' Input ITYPE, NS, NDZ, INTERP..... ', /
2 ', ', If ITYPE=1 X(N)=(
2 ' N/NS)**(-LOG(XDZ)/LOG2)', ', ', If ITYPE=3 X(N) is discontinuous at
2 ', ', 2*NDZ or 2*XDZ ', ', ', Use NS-1 > NDZ > 1. If ITYPE=3 use NDZ <
2 ', ', NS/2 ', ', ', INTERP controls interp.- either linear(1) or quad(2) ', /
502 FORMAT( ' Input ICOMPL, COEFMAX ', /
2 ', ', If ICOMPL=1 solve for (1-P),
2 ', ', not P ', ', If COEF>COEFMAX use a constant coeff. COEF=COEFMAX' /
505 FORMAT( ' Input FNAME.PRN, ICONOUT, NWRITE..... ', /
2 ', ', Use quotes for 
2 ', ', the filename and use extension .PRN ', /
2 ', ', If ICONOUT=1 concentrati 
2 ', ', on data is written to FNAME.PRN according to NWRITE ', /
2 ', ', NWRITE a 
2 ', ',Iso controls writing of flux data to FNAME.PRN ', /
2 ', ', For ICONOUT=1 
2 ', ', use for NWRITE an integer multiple of 20 ', /
550 FORMAT(1H1,I7,7(1X,F5.3),2(1X,D9.3),2(1X,I3),/)
577 FORMAT(1H1,F5.3,I7,1X,I9.3)
801 FORMAT(1H ,I7,7(1X,F5.3),2(1X,D9.3),2(1X,I3))
END
C This subroutine calculates the function COEF appearing in the original
C differential equation. Other subroutines may be called.
C
SUBROUTINE GETCOEF(XNI,J,Z,ZN,DZ,EIG,BIVEC,COEF,COEFMAX)
IMPLICIT REAL*8 (A-H,0-Z)
IMPLICIT INTEGER*4 (I-N)
INTEGER*4 EIG
DIMENSION BIVEC(1)
IF(Z.LE.ZN) GO TO 1
RATI=0.DO
GO TO 2
1 RATI=1.DO
BI=1.DO
CALL IQ(Z,BI)
CALL INUE(Z,EIG+1, BI, BIVEC)
IF(EIG.NE.0) BI=BIVEC(EIG)
RATI=BIVEC(EIG+1)/BI
2 DEIGM1=DBLE(EIG-1)
   COEF=(RATI*Z+DEIGM1)/XNJ
   IF(COEF.GT.COEFMAX) COEF=COEFMAX
   RETURN
END

C This subroutine calculates the constant FACTOR in the solute flux.
C
SUBROUTINE FLXFAC(EIG,ZGS,XGS,BIVEC,FACTOR)
IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER*4 (I-N)
INTEGER*4 EIG
DIMENSION BIVEC(1)
BIGS=0.DO
IF(EIG.EQ.0) BIGS=1.DO
CALL IO(ZGS,BIGS)
IF(EIG.EQ.0) GO TO 1
CALL INUE(ZGS,EIG,BIGS,BIVEC)
BIGS=BIVEC(EIG)
1 FACTOR=2.*3.14159*(1-2#MOD(EIG,2))*XGS*BIGS*BIGS
   RETURN
END

C Bessel function subroutines are from IBM SSP ver. 3, mod. 1, 1969
C
SUBROUTINE IO(X,RIO)
IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER*4 (I-N)
RIO=DABS(X)
   IF(RIO-3.75) 1,1,2
1 Z=X*X*7.111111-2
   RIO=((( 4.5813E-3*Z+3.60768E-2)*Z+2.659732E-1)*Z+1.206749E0)*Z
   +3.089942E0)*Z+3.515623E0)*Z+1.
   RETURN
2 Z=3.75/RIO
   RIO= DEXP(RIO)/DSQRT(RIO)*(((((((3.92377E-3*Z-1.64763E-2)*Z
   +2.635537E-2)*Z-2.05706E-2)*Z+9.16281E-3)*Z-1.57565E-3)*Z
   +2.25319E-3)*Z+1.328592E-2)*Z+3.989423E-1)
   RETURN
END
SUBROUTINE INUE(X,N,ZI,RI)
IMPLICIT REAL*8 (A-H,O-Z)
IMPLICIT INTEGER*4 (I-N)
DIMENSION RI(1)
IF(N) 10,10,1
1 FN=N+N
   Q1=X/FN
   IF(DABS(X)-5.D-4) 6,6,2
2 AO=1.
   A1=0.
   B0=0.
   B1=1.
   FI=FN
3 FI=FI+2
   AN=FI/DABS(X)
   A=AN*A1+AO
   B=AN*B1+BO
   AO=A1
   BO=B1
   A1=A
   B1=B
   Q0=Q1
   Q1=A/B
   IF(DABS((Q1-Q0)/Q1)-1.D-6) 4,4,3
4 IF(X) 5,5,6
5 Q1=-Q1
6 K=N
7 Q1=X/(FN+X*Q1)
   RI(K)=Q1
   FN=FN-2.
   K=K-1
   IF(K) 8,8,7
8 FI=ZI
   DO 9 I=1, N
   FI=FI*RI(I)
9 RI(I)=FI
10 RETURN
END