JOURNAL OF MATERIALS SCIENCE 12 (1977) 1950–1954

Van der Waals interactions between brittle cracks and gaseous environments

B. R. LAWN
Department of Applied Physics, School of Physics, The University of New South Wales, Kensington, N.S.W. 2033, Australia

The role of van der Waals forces in crack-tip decohesion is considered for a sharp-crack system in a gaseous environment. Simplistic calculations of the interaction between a single gas molecule and the two confining walls of the crack indicate the existence of a potential well close to the tip region. Diffusing gas molecules are thereby predicted to experience a significant attraction toward the crack-tip bonds, where they become "trapped" in a state of "interfacial physisorption". Provided diffusing molecules are not so large that they cause obstruction at the crack walls, this trapping state may constitute an important precursor to subsequent chemical steps in the overall decohesion process.

1. Introduction

The interaction between a reactive environment and a propagating crack constitutes one of the great problems in fracture theory. It is not unreasonable to say that most of the vast amount of work reported on this subject in the literature has little underlying physical basis: the general approach has been overwhelmingly empirical and engineering-oriented. Nevertheless, with the recent emergence of highly idealized working models of the crack tip [1–3], the way appears to be opening to a fundamental understanding of environmentally assisted crack-tip mechanisms at the molecular level. All of these models derive from the "sharp-crack" notion, in which a brittle crack is viewed as propagating by the sequential rupture of separation-plane bonds. The environmental problem reduces to one of intrinsic interaction processes between intruding molecules and stressed crack-tip bonds, i.e. toward the realm of surface- and solid-state science [4]. The fracture behaviour of "real materials" may then be pictured in terms of perturbations on idealized behaviour. In this context it is interesting to note Thomson's most recent extension of the sharp-crack concept to the important but complex problem of hydrogen embrittlement in ductile steels [5].

An important feature of the sharp-crack approach is the identification of a "cohesive zone" at the crack tip. Within this zone the essential bond-breaking events responsible for crack advance take place. There are certain instances where one may adequately describe the fracture mechanics without any detailed knowledge of the cohesive zone processes at all. A good example is where the diffusion of environmental species to the cohesive zone constitutes the slow step in a two-stage, transport/decohesion kinetic process, and thereby controls the crack velocity [4]. While the existence of such secondary kinetic steps is acknowledged, it is the events within the cohesive zone that must ultimately determine the fundamental nature of the crack growth.

The cohesive zone itself will generally involve a sequence of sub-steps: (i) "trapping" of environmental molecules or atoms at the crack tip via some mechanism akin to physical adsoprtion; (ii) passage into the chemisorbed state (with molecular dissociation contributing to an energy barrier) at the exposed crack-tip bonds, thereby reducing the cohesion across the separation plane; (iii) if the chemisorption process in itself does not part the bonds beyond the breaking point, subsequent permeation into the solid, with preferred diffusion and further attendant decohesion along the highly tensile separation plane. Secondary, but not necessarily unimportant, effects may be envisaged as a result of interactions between the penetrating chemical species and defects, notably dislocations. Which of these sub-steps assumes a controlling role in any given fracture situation will depend on the material/environment system under consideration.

In this work we consider the first of these sub-steps: what mechanisms exist for ensuring the accessibility of diffusing molecular species to the crack-tip region? A simplistic model is described for a material containing a sharp crack in the presence of an ideal-gas environment. Consideration of van der Waals interactions leads to the postulate of a decohesion precursor state in which diffusing molecules are "sucked" into the cohesive zone.

2. The physical interaction model

Molecules in a gas environment are free to enter the mouth of a crack and flow toward the tip region [6]. Initially, for a sufficiently wide crack, the transport will be controlled by intermolecular collisions within the gas itself. As the crack walls narrow down to separations comparable with the mean free path for the gas, however, collisions between molecules and crack walls become more frequent. Owing to diffuse scattering, these molecule/wall collisions give rise to a retardation in the transport, so-called "Knudsen" or "free molecules do begin to experience the influence table to physical adsorption/desorption processes at the saturated crack walls: van der Waals interactions have come into play. At the same time the equation of state for the ideal gas remains essentially unaltered until the collision distance, as determined by the crack wall separation, approaches molecular dimensions [7]. Once the gas molecules do begin to experience the influence of van der Waals forces from both crack walls simultaneously they enter a new, effectively two-dimensional state of "interfacial physisorption". This state of physisorption between the saturated walls will persist until the diffusing molecules encounter newly exposed, highly stretched bonds at the crack tip.

To quantify this picture we begin with the postulate that the profile of the crack surfaces is a smooth parabola, in accordance with the near-field prediction of continuum mechanics for slit-like cracks [8]. This is not likely to provide an accurate representation, for the true geometry must surely depend on such factors as the relative sizes of adsorbent and adsorbate atoms, the nature of the bonding between these atoms, structural arrangement (or rearrangement) of the chemisorbed layers on the saturated crack walls, etc. Nevertheless, the parabolic approximation enables us to demonstrate the essential features of the van der Waals interaction with minimal complexity. Using the co-ordinate system of Fig. 1 we may write the basic crack-profile formula (plane strain), using subscript W to designate the crack walls,

$$y_W = [(8/\pi)^{1/2}(1-\nu^2)K/E]x_W^{1/2}, \qquad (1)$$

where E is Young's modulus, ν is Poisson's ratio and K is the stress intensity factor. The stress intensity factor determines the intensity of the near field about the crack tip, and is a useful parameter for specifying the level of loading on the crack system [8].

Next we look at the form of the van der Waals interactions between crack walls and gas molecules. Again we resort to approximation, for a proper analysis involves summation procedures in the forces which are far from straightforward [9]. We simply take the field to be calculable as the sum of two independent interactions between a single point molecule and each of two parallel semi-infinite half-bodies (molecule/molecule and wall/wall interactions ignored). This geometrical representation should be reasonable for small molecules, narrow cracks, i.e. $R \ll y_W \ll x_W$, where R is the van der Waals radius of the molecules [10].

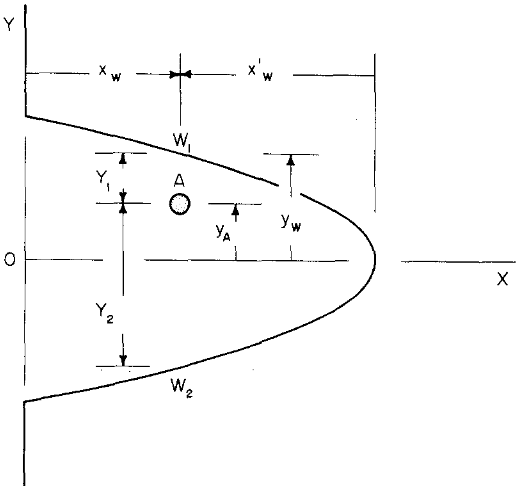

Figure 1 Co-ordinate system for gas molecule A between crack walls W_1 and W_2.

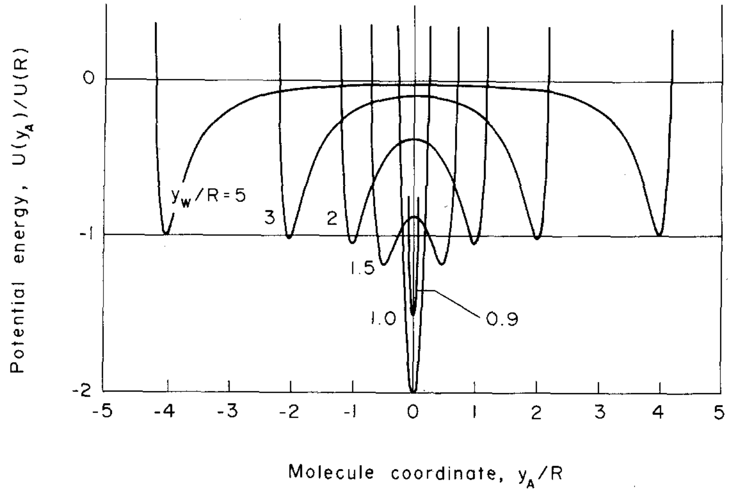

Figure 2 Reduced plot of potential energy function $U(y_A)$ for several values of crack-wall separation parameter y_W.

Thus for the interaction between molecule A and wall W_1 in Fig. 2 the potential energy is [9]

$$U(Y_1)/U(R) = -\tfrac{3}{2}(R/Y_1)^3 + \tfrac{1}{2}(R/Y_1)^9, \quad (2)$$

with a similar expression for the interaction with wall W_2; here the transformation relations

$$Y_1 = y_W - y_A, \; Y_2 = y_W + y_A \quad (3)$$

provide convenient molecule/wall co-ordinates. In Equation 2 the first term is the attractive (van der Waals) component of the interaction, and the second term is the repulsive (electron-cloud overlap) component. The values of R, and hence of $U(R)$, will be determined by the dipole properties of the constituent parts of the total system, and have a physical interpretation in terms of an adsorption configuration where no electron transfer is involved. If now we add the van der Waals contributions to the field from the two walls we obtain, at any given crack-wall separation,

$$\begin{aligned} U(Y_1, Y_2)/U(R) &= -\tfrac{3}{2}[(R/Y_1)^3 + (R/Y_2)^3] \\ &\quad + \tfrac{1}{2}[(R/Y_1)^9 + (R/Y_2)^9] \\ &= [U(y_A)/U(R)]_{y_W}. \quad (4) \end{aligned}$$

A plot of this potential energy function is given in Fig. 2. It is seen that as the crack-wall separation diminishes toward van der Waals dimensions, i.e. as $y_W \to R$, the potential well becomes correspondingly narrower and deeper. Ultimately, at $y_W < R$, the minimum in the well rises again, but by this stage the geometrical assumptions implicit in Equation 2 have lost their validity.

Thus as the incoming gas molecules enter the region of significant van der Waals interaction they experience an effective force driving them further toward the crack-tip bonds. This is perhaps most easily demonstrated by combining the van der Waals and crack-profile equations to evaluate the potential energy as a function of distance along the interfacial symmetry plane: accordingly, from Equations 1, 3 and 4 we have

$$\begin{aligned} [U(x'_W)/U(X')]_{y_A=0} &= -3(X'_W x'_W)^{3/2} \\ &\quad + (X'/x'_W)^{9/2}, \quad (5) \end{aligned}$$

where we have made the convenient substitution

$$X' = (\pi/8)[E/(1-\nu^2)K]^2 R^2. \quad (6)$$

Equation 5 is plotted in Fig. 3. The van der Waals attractions "suck" the molecules into the potential well until at $x'_W = X'$ (corresponding to $y_W = R$) the attractions are just balanced by the electron-cloud overlap repulsions: the minimum in Fig. 3 therefore represents a "trapping" state for the physically adsorbed molecules.

3. Implications of the model

The model described above bears on certain important aspects of the cohesive zone problem. The question of the accessibility of the environmental gas molecules to the crack tip is the most obvious of these. On this point it is well to re-emphasize the approximate nature of the potential well calculations, particularly as the scale of events becomes confined to atomic dimensions. For instance, the crack walls will certainly not be smooth and continuous, but will tend instead to show a periodic atomic structure characteristic of the adsorbed layer [11]. Depending on the shape of the dif-

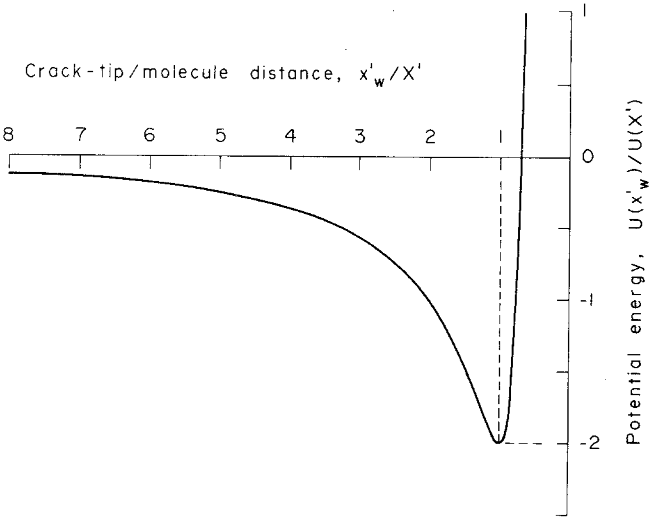

Figure 3 Showing potential energy variation for molecule/wall configuration as function of distance from crack tip.

fusing molecule, crystallographic "surface channels" may well provide even more enhanced migration to the crack tip. Such anisotropic effects might manifest themselves as preferred directions of crack propagation in certain material/environment systems. Notwithstanding these possible complications, the model stands as a useful basis for assessing the role of conventional fracture mechanics parameters, most notably the stress-intensity factor (e.g. through X' in Equations 5 and 6, in the precursor stages of crack-tip decohesion.

Given the interpretation of X' in Fig. 3 as the equilibrium distance between trapped gas molecules and exposed crack-tip bonds, the question arises as to the probability of passing into the next stage of the overall decohesion process. Clearly, X' must be sufficiently small, of the order of atomic dimensions, so that electron transfer can occur. The well-studied material/environment crack system glass/water [12] certainly satisfies this condition, as may be seen by inserting $E = 70\,\text{GPa}$, $\nu = 0.25$ and $K = 0.5\,\text{MPa}\,\text{m}^{1/2}$ (sub-equilibrium value) for glass, along with $R = 0.2\,\text{nm}$ (van der Waals radius of oxygen atoms [10] for water molecules, into Equation 6 to get $X' \approx 0.3\,\text{nm}$. Molecules larger than water would of course be trapped further from the tip, so that the probability of chemical interaction would be correspondingly diminshed. An interesting situation might then arise if a particular gaseous environment were to contain more than one species: a larger species, even though possibly a minor constituent of the gas, may well cumulate at some relatively large distance from the crack tip, thereby restricting the passage of the smaller species (crack-tip "poisoning").

It may be noted that there is nothing in the present model to restrict lateral motion of the gas molecules. Thus on reaching the bottom of the van der Waals potential well in Fig. 3 a given molecule is free to migrate along the crack front and "search" for active reaction sites. The chance of a successful chemical interaction will clearly increase with the lifetime of the moelcule in the trapped state. According to Maxwell–Boltzmann statistics the probability of thermal fluctuations attaining the necessary intensity to desorb the molecule from the crack tip is [11]

$$\nu_d \approx \nu_0 \exp\,[-2U(R)/kT] \tag{7}$$

with ν_0 a basic lattice vibration frequency, k the Boltzmann constant and T the temperature; the corresponding lifetime in the bound state is therefore

$$\tau_d \approx \tau_0 \exp\,[2U(R)/kT]\,, \tag{8}$$

τ_0 being a lattice vibration period. For a typical van der Waals energy, $U(R) \approx 5kT$, we compute $\tau_d \approx 2 \times 10^4 \tau_0$. We may note that the factor of two in Equation 8, arising from the field-overlap situation near the crack tip, is responsible for an increase by a factor ≈ 150 in the lifetime of the physisorbed state for the particular energy quoted. Van der Waals trapping may therefore be seen as a mecahnism for promoting the onset of chemical decohesion at the crack tip.

Acknowledgements

This work was stimulated by extensive discussions with R. Thomson and E. R. Fuller. Partial support of the project was provided by the U.S. Office of Naval Research under Contract No. NR-032-535.

References

1. R. THOMSON, C. HSIEH and V. RANA, *J. Appl. Phys.* **42** (1971) 3154; C. HSIEH and R. THOMSON, *J. Appl. Phys.* **44** (1973) 2051.
2. E. SMITH, *J. Appl. Phys.* **45** (1974) 2039; *Mat. Sci. Eng.* **17** (1975) 125.
3. J. E. SINCLAIR and B. R. LAWN, *Proc. Roy. Soc. Lond.* **A329** (1972) 83.
4. B. R. LAWN and T. R. WILSHAW, "Fracture of Brittle Solids" (Cambridge University Press, Cambridge, 1975), Chapter 8; B. R. LAWN, *J. Mater. Sci.* **10** (1975) 469.
5. R. THOMSON, to be published.
6. B. R. LAWN, *Mat. Sci. Eng.* **13** (1974) 277.
7. R. D. PRESENT, "Kinetic Theory of Gases" (McGraw–Hill, New York, 1958) Chapter 4.
8. B. R. LAWN and T. R. WILSHAW, "Fracture of Brittle Solids" (Cambirdge University Press, Cambridge, 1975) Chapter 3.
9. J. N. ISRAELACHVILI, *Contemp. Phys.* **15** (1974) 159.
10. L. PAULING, "The Nature of the Chemical Bond" (Cornell University Press, Ithaca, 1960), Chapter 7.
11. J. M. BLAKELY, "Introduction to the Properties of Crystal Surfaces" (Pergamon Press, Oxford, 1973) Chapter 7.
12. S. M. WIEDERHORN, *J. Amer. Ceram. Soc.* **50** (1967) 407.

Received 16 March and accepted 4 April 1977.