Morphology and Rate of Fracture in Chemical Decomposition of Solids

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Self-fracturing of solids during chemical transformations is considered, and a first quantitative model of this widespread phenomenon is proposed. The analysis begins by considering the equilibrium of a single crack, and proceeds with the behavior of an ensemble of cracks. This enables one to solve the "selection problem" for this pattern-formation process and obtain formulas for the rate of crack-network propagation and for the diameter of the resulting blocks.

Pattern-formation studies, investigating how patterns emerge from a structureless environment, often focus on the *growth* processes [1,2]. Progress has been made in understanding crystal growth in solidification, diffusion-limited aggregation, viscous fingering in a Hele-Shaw cell, etc. Studies of important aspects of these problems are still under way [3]. Here we consider the widespread and somewhat opposite phenomena of solid-state *decomposition*, involving the fracturing of initially dense material. As with pattern-formation problems, the central question is the following: What physical characteristics of the originally homogeneous system prescribe the morphology and rate of propagation of the crack network?

Cracking patterns in nonequilibrium solids, recently considered as fractals [4–6], have long been of interest: Lord Rayleigh reported [7] fracture during gelatine film solidification. The diversity of crack networks in paints, drying mud, and in some geological objects is well known [8]. The chemistry of solids also provides a broad range of cases [9–12] in which cracking plays a key role: Chemical transformation causes internal stresses and numerous cracks, i.e., juvenile surfaces, which then may promote the reaction. This attractive scheme (cases of both positive [13] and negative [14] feedback) even gave rise to curious Daedalus inventions [13,14], but it remains a challenge for quantitative theory.

The simplest type of reaction, often complicated by fragmentation, is thermal decomposition of solids. As a result of a temperature increase, solid material loses some relatively volatile component, $(AB)_{\text{solid}} \rightarrow A_{\text{solid}} + B_{\text{gas}}$, so that shrinkage and misfit of specific volumes causes fracture. Optical observations demonstrate a distinct propagating front between the unbroken solid and a grainy product of reaction [9–12]. This propagation is determined by the interplay of three fields: the concentration of the mobile atoms $c(\mathbf{x})$, the internal stress tensor $\sigma(\mathbf{x})$, and some crack-network characteristic, like the average crack surface per unit volume $1/L(\mathbf{x})$. Rigorous mathematical treatment of such a problem is hopelessly complex, but reasonable physical assumptions enable one to simplify and solve it, as is shown below.

The progress of the front is limited by the transport of atoms B from the bulk of the crystal to the exterior [Fig. 1(a)]. Deep within the crystal these atoms move through simple diffusion. As they approach the front, they encounter cracks which allows easier passage. Eventually they arrive at the region of decomposed material from which their exit is quite rapid. To create a tractable "solvent loss" model, we assume that transport occurs in two stages. Until solvent atoms arrive at the propagating boundary, they diffuse, with diffusion constant D. Once at the border, they leave the crystal at a rate kc_b, where c_b is the boundary concentration of solvent atoms. It is further assumed that ahead of the moving boundary are numerous cracks of typical length L which are the precursors of the front. They set the typical length scale of broken blocks once the front passes, but do not themselves strongly influence the transport of solvent. The calculation proceeds in two stages. First, we will find the condition for a precursor crack to be in equilibrium. Next, we will find the spatial dependence of the concentration of solvent atoms, assuming the front travels at velocity v. Putting these two results together, with an additional dynamic assumption, completes the problem.

A single crack segment, adjacent to the topological border of the material, is affected by two factors: Elastic forces resulting from material shrinkage tend to open the crack, while molecular cohesion hinders crack growth. Since the diffusion is much slower than the unstable crack advance, we consider the crack in a state of
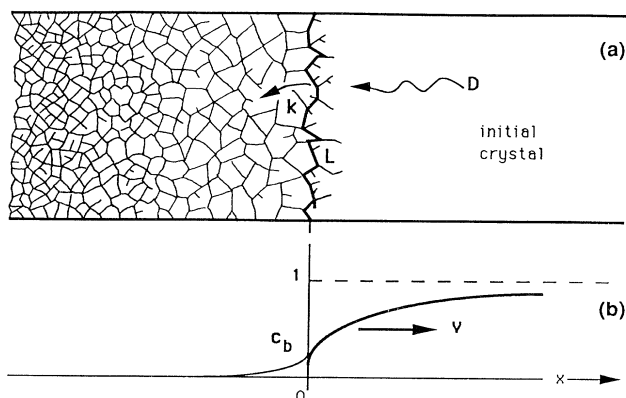

FIG. 1. Network of cracks propagating toward the interior of (a) the solid and (b) the corresponding concentration profile.

quasiequilibrium, where the tensile stress $\sigma(x)$ is balanced by the material toughness. In traditional terms of fracture mechanics [15–17] this means that stress intensity factor K (representing the weighted sum of the opening forces along the crack) takes the threshold value K_c,

$$K \equiv 2 \left[\frac{L}{\pi} \right]^{1/2} \int_0^L \frac{\sigma(x)\,dx}{(L^2 - x^2)^{1/2}} = K_c \,. \tag{1}$$

This balance corresponds to the extremum of a free-energy functional $F(L)$, which is more instructive from a physical point of view. A positive contribution to $F(L)$ is related to the new surface formation characterized by the work of fracture 2α. (Here α is the Gibbs surface tension for purely brittle fracture, when no irreversible processes take place.) A negative contribution to $F(L)$ is stress relaxation and, due to Irwin [15,16], the related "energy release rate" $dF/dL = -K^2(1 - v^2)/Y$ represents the elastic Lagrangian force acting on the crack. Using (1) and integrating over the crack length from zero to L we obtain
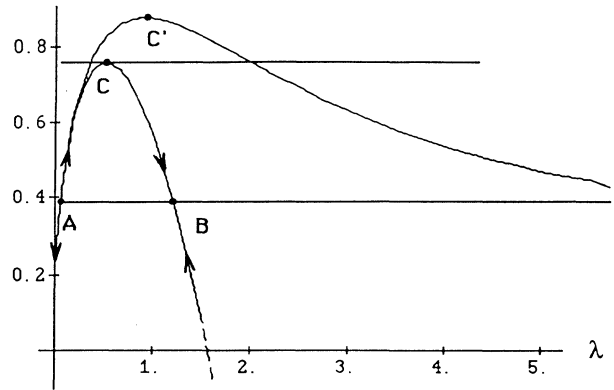

FIG. 2. Balance diagram for the brittle crack segment, corresponding to Eq. (6). Elastic opening force as a function of dimensionless crack length $\lambda \equiv (v/D)L$ is represented by the curves. The upper curve corresponds to the use of Eq. (4) for the concentration profile, while its linear approximation results in the lower curve. The material cohesion term does not depend on the crack length (horizontal lines).

$$F(L) = 2\alpha L - 4\frac{1 - v^2}{\pi Y} \int_0^L \int_0^L \sigma(x)\sigma(x') \ln \frac{(L^2 - x^2)^{1/2} + (L^2 - x'^2)^{1/2}}{|x^2 - x'^2|^{1/2}}\,dx\,dx' \,. \tag{2}$$

$F(L)$ is thus bilinear with respect to the stress field, and is reminiscent of the formulation [18] of free energy as a functional of the crack separation (offset field). Comparing Eq. (2) with Eq. (1) one can express K_c through more physical parameters [15–17]: $K_c = [2\alpha Y/(1 - v^2)]^{1/2}$.

We do not take into account the curvature of the cracks and their influence on one another. Furthermore, we consider only the typical stress component, neglecting the concentration inhomogeneity within the border plane. Thus the theory of thermal stresses (in a case of "solvent loss" the stress is also attributed to the decrease of molar volume proportional to the concentration changes) provides the simple local relation [19]

$$\sigma(x) = \beta Y[1 - c(x)], \quad \beta = \beta'/3(1 - v), \tag{3}$$

where β' is the volume shrinkage coefficient. This stress is what one should find to the right of the boundary if no precursor cracks were present, and it gives a reasonable estimate of the loading on the crack in Eq. (1) [20].

To estimate $c(x)$ we consider a diffusion on the half space $x \geq 0$ with desorption on the plane moving boundary [Fig. 1(b)], which is by definition connected with some (unknown) concentration value $c = c_b$. The steady-state solution in the moving coordinate system is

$$c(x) = 1 - (1 - c_b)\exp(-xv/D) \tag{4}$$

and mass flow continuity requires

$$v(1 - c_b) = kc_b \,. \tag{5}$$

The linear approximation of Eq. (4), $c(x) \cong c_b + x(1 - c_b)v/D$ at $x \leq D/v$, is sufficient for simple esti-

mates. Substituting it into Eqs. (3) and (1) one obtains

$$\frac{K_c}{2Y\beta} \left[1 + \frac{v}{k} \right] \left[\frac{\pi v}{D} \right]^{1/2} = \sqrt{\lambda} \left[\frac{\pi}{2} - \lambda \right], \tag{6}$$

where the dimensionless length $\lambda = (v/D)L$ is introduced. Equation (6) shows how the length of the crack depends upon the speed of front propagation. There are typically two real solutions λ (points A and B in Fig. 2). The smaller of these is unstable and a crack with this length would grow very rapidly until λ reaches the larger, stable value. Propagating solutions are allowed for a continuous range of values of v. At very low v, the length of the crack diverges like $v^{-1/2}$; as v increases the length shrinks, until beyond some speed v_c, corresponding to the maximum value of the right-hand side of Eq. (6), precursor cracks are no longer able to propagate. Thus, instead of a single solution we have a continuous family, posing a "selection problem": What determines the particular values of v and L observed in the fracturing process? This situation is typical in pattern formation studies [1,2].

Figure 3 provides equivalent representation in terms of the free-energy functional, based on more accurate use of Eq. (4) in Eqs. (3) and (2). The free-energy surface is plotted as a function of dimensionless crack length λ and stress-field spatial extent δ. On this diagram one can follow transformation of the $F(L)$ dependence from the increasing straight line in the unloaded media ($\delta = 0$) to the conventional Griffith inverted parabola in case of homogeneous loading ($\delta \to \infty$). There is a "peninsula of growth" in this picture with one coast $A'C'$ of mechani-
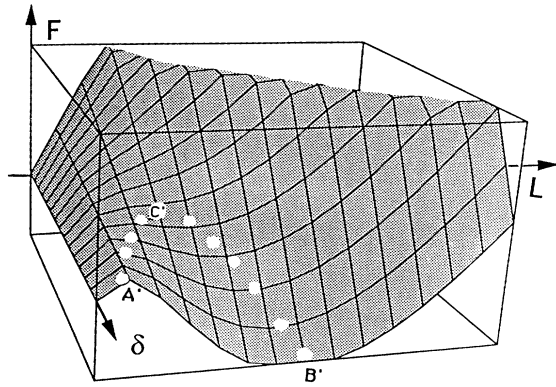
FIG. 3. Single crack free energy as a function of crack length and of the internal stress effective extent $\delta \equiv (D/\pi v)[2Y\beta(1-c_b)/K_c]^2$. Plot range: $0 < L < 5$ in units of D/v, $0 < \delta < 2$ and $-0.5 < F < 1$ in units of $2aD/v$. Light spots outline the "peninsula of growth."

cally unstable solutions and an opposite coast $B'C'$ of stable ones (cf. Fig. 2). Superficially, instead of a definite solution we have the whole branch $B'C'$ of possibilities. Both Figs. 3 and 2 represent single-crack behavior, while we should deal with an ensemble of segments evolving somehow within the propagating front (Fig. 1). This allows one to elucidate the crack-size selection mechanism.

To select the appropriate solution from the family, one must investigate the dynamics of the decomposition front. Certainly it cannot travel faster than v_c, since above this speed there is not enough stress (or concentration deficit) to permit precursor cracks, and the front must slow down. The basic dynamical hypothesis of this Letter is that the front travels in fact at v_c. The logic behind this assumption is that if the front travels slowly and the precursor cracks become long, the shorter segments will rapidly shatter the rear portions of the dense solid: that is, the front will rapidly begin to move ahead. The only natural velocity at which this process of acceleration can stop is v_c itself. The corresponding value is $\lambda_c = \pi/6$, as a result of which we obtain

$$L = \pi D/6v \tag{7}$$

and, from Eq. (6),

$$\frac{v}{k}\left(1 + \frac{v}{k}\right)^2 = \Delta, \quad \Delta \equiv \left[\frac{2\pi^2}{27}\right]\frac{D}{k}\left[\frac{Y\beta}{K_c}\right]^2. \tag{8}$$

Equations (7) and (8) essentially solve the problem. The principal parameter characterizing the solutions is Δ. It is most useful to examine two limiting cases. [The use of Eq. (4), instead of its linear approximation, would change the steady point C to C' in Fig. 2 and lead to slightly different numerical factors. In view of this, these factors

are omitted below.]

At $\Delta \gg 1$ (relatively fast diffusion) we obtain

$$v = k^{2/3}D^{1/3}(Y\beta/K_c)^{2/3}, \quad L = (DK_c/kY\beta)^{2/3}. \tag{9}$$

For $\Delta \ll 1$ the results from Eqs. (8) and (7) are

$$v = D(Y\beta/K_c)^2, \quad L = (K_c/Y\beta)^2. \tag{10}$$

Equations (9) and (10) relate self-fracturing rate and morphology with basic parameters of the decomposing system and deserve discussion here. One can naturally presume Arrhenius-type temperature dependence of the kinetic coefficients k and D. Then Eqs. (9) and (10) predict two regimes with different activation energies of the decomposition rate v, observable experimentally [11] at different temperatures.

As to morphology (L), we see a tendency that the closer the conditions are to equilibrium, i.e., the smaller k, the larger are the product blocks. (There is some similarity to the space correlations near the critical point of a phase transition.) Consideration of product-layer resistance to gas release, neglected before, would diminish k. According to (9), block sizes would increase while the product layer thickens toward the interior of the crystal (cf. Fig. 1). At the other extreme, if $k \rightarrow \infty$, the values of v and L attain those given in (10). This represents the limit of brittle fracturing, i.e., it results in the smallest blocks. Estimating the surface energy, which determines K_c, as $a \approx Ya/10$, where a is of the order of the atomic size (as is often assumed in the literature), one obtains roughly from Eq. (10) $L \approx a/\beta'^2$. Thus, a significant shrinkage may result in a rather disperse product of decomposition (e.g., $\beta' \approx 10\%$ and $L \approx 300$ Å in decomposition of barium chloride hydrate [11]). This estimation also fits the observations of Ref. [6], where for an "atomic" diameter $a \approx 3.4$ μm and for two-dimensional shrinkage coefficient $\beta' \approx 36\%$ one finds $L \approx 30$ μm.

We would like to be cautious in comments about possible self-organized criticality [21] in the fracturing-front propagation. There is a temptation to refer to the locations of the horizontal line in Fig. 2 below, above, and tangent to the point C as supercritical, subcritical, and critical states, respectively. Obviously, besides the estimated diameter, there is some distribution of the fragment dimensions; but the finite extent of the stress field (see descending parts of the curves in Fig. 2), located in the diffusion-depleted region, suppresses the long-tail power-law distribution of L, inherent in self-organized criticality phenomena [21,22]. The same local character of loading prevents the overwhelming growth of a single crack, which was proved to take place in a homogeneously loaded viscoelastic strip [15]. There is no contradiction with this thoroughly analyzed [23] conclusion, because in our case the network of cracks appears as a result of certain interplay between fracturing and diffusion.

To emphasize the pattern-*formation* aspect of fracturing we deliberately avoided possible heterogeneity of the

initial solid on any intrinsic length scale a (e.g., grain size). This heterogeneity can play a prominent role, being superimposed on the picture described above, with the results depending on the L/a ratio. In particular, for $L \gg a$ heterogeneity may lead [4,5] to some fractal dimension $d \geq 2$ of crack surfaces. Consequently, for small k the sinuosity of the boundary and corresponding enhancement of its surface area may be simply accounted for [24] by some geometrical factor $(L/a)^{d-2}$ in the right-hand side of Eq. (5). This would change the powers in Eq. (9), which become rational functions of d, while Eq. (10) essentially does not vary.

We realize how abstract and simplified our model of fracture in thermal decomposition is. Still we believe that the above considerations can provide valuable insights into this complex and widespread phenomenon. It is useful to rephrase our results in general terms of nonlinear thermodynamics: For a solid sample of initial size much larger than the estimated value L, chemical decomposition by trivial diffusion (thermodynamical branch [25]) necessarily results in a mechanical metastability of the material. Decomposition proceeds with the formation of a cracking pattern (dissipative structure [25]), whose propagation rate v and fragment size L are given by Eqs. (9) and (10).

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