

Statistical-thermodynamic approach to fracture

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We present a statistical-thermodynamic theory that associates fracture of a solid with the approach of a spinodal upon increasing stress. This formulation is illustrated by a one-dimensional model, and the temperature dependence of the nonlinear stress-strain relation and fracture stress is obtained. A two-dimensional network model is treated by both effective-medium theory and Monte Carlo simulations, showing metastability and the nucleation of microcracks.

The mechanisms and physical characteristics of fracture continue to attract the attention of many pure and applied researchers.¹ Recent work has focused on quasi-analytical methods to calculate the failure strength distribution for hierarchical and democratic load-sharing systems,² and on numerical simulation of the mechanical response of bond networks,^{3,4} including molecular-dynamics (MD) simulations at zero temperature.⁵ Finite-temperature MD computations have been carried out by Soules and Busbey and by Kieffer and Angell, for the case of uniaxial and isotropic imposed strains, respectively.⁶ Furthermore, Raj⁷ and co-workers have modeled intergranular fracture and cavitation in metals with the specific aim of estimating growth rates and low-cycle fatigue associated with inclusions and voids.

In most of the analytical and computational approaches mentioned above, the role of *thermal fluctuations* has been suppressed. In the work that we outline below, a *statistical-thermodynamic* formulation allows the temperature to enter from the outset. We treat the solid under stress as a *metastable state of equilibrium*, in analogy with the more familiar case of a supersaturated vapor. Fracture at a failure threshold corresponds to a metastability limit, or spinodal, just as does nucleation at the point of critical supersaturation. Nonequilibrium defects such as macroscopic cracks, dislocations, and impurities play the same role in decreasing overall strength that dust particles do in lowering the nucleation barrier. Here we concentrate on fracture induced in an ideal, defect-free crystal, that is, the *homogeneous* nucleation of fracture. A statistical-thermodynamic approach similar in spirit was presented first by Nishioka *et al.*⁸ and more recently by Englman and Jaeger.⁹ A field-theoretic formulation of the nucleation and growth of cracks under tension has been presented by Rundle and Klein,¹⁰ but theirs is a coarse-grained theory without explicit reference to the structure of crystal lattices or to the temperature dependence of fracture strengths. Related formulations of thermal effects have also appeared in the context of polymer systems; in particular, Termonia, Meakin, and Smith¹¹ have introduced temperature-dependent proba-

bilities into their simulation of strained networks, but because the bond breaking is not reversible, they are not describing a thermal equilibrium situation.

The application of equilibrium statistical thermodynamics to fracture is valid only if fracture occurs at an intermediate time scale, long enough that the system can achieve metastable equilibrium, and short enough that the solid does not undergo a phase transition to a liquid or gas. An equilibrium theory also requires that in the absence of fracture a stressed solid must display no hysteresis, such that the state of the system may be specified only by the temperature and the stress or strain. Iron whiskers appear to satisfy these requirements. They contain few defects (such as impurities or macroscopic cracks) and have stress-strain behavior that is reversible (i.e., no plasticity or fatigue) almost up to the fracture point.¹² Furthermore, whiskers under stress have been demonstrated to exist in a metastable state, in which the stressed whisker remains undamaged until it eventually fractures; this phenomenon was labeled "delayed fracture,"¹³ with a lifetime depending on the temperature and the applied stress.

We illustrate our approach through a schematic one-dimensional model of a solid under stress. Consider N harmonic springs, or bonds, arranged in parallel and subjected to a common strain ϵ . Let the i th bond be represented by the variable s_i , with $s_i = 0$ and $+1$ describing its broken and intact states, respectively. In the case where instead a stress is applied to the system, the applied load is shared democratically among all intact bonds. Thus the effective interaction range is infinite, and we expect mean-field-like behavior. With κ and D denoting the elastic modulus and dissociation energy associated with each bond, the system Hamiltonian resembles that of noninteracting spins in a field, $\mathcal{H} = \sum_i s_i (D - \frac{1}{2}\kappa\epsilon^2)$. It follows that the "magnetization," or fraction of intact bonds, is given by

$$\phi \equiv \frac{\langle \sum_i s_i \rangle}{N} = \frac{\exp[-\beta(\frac{1}{2}\kappa\epsilon^2 - D)]}{1 + \exp[-\beta(\frac{1}{2}\kappa\epsilon^2 - D)]}, \quad (1)$$

where β is the inverse temperature $1/T$ and we take $k_B=1$. The Helmholtz free energy per bond has the form $f(\phi, \epsilon) = (\frac{1}{2}\kappa\epsilon^2 - D)\phi + T[\phi \ln\phi + (1-\phi)\ln(1-\phi)]$. (2)

The final term is the entropy of mixing broken and intact bonds.

For experimental situations where an external stress σ is specified, it is appropriate to consider the (Legendre transformed) free energy

$$g(\phi, \sigma) \equiv f - \sigma\epsilon, \quad (3)$$

where

$$\sigma = \left. \frac{\partial f}{\partial \epsilon} \right|_{\phi, T} \quad (4)$$

is the thermodynamic stress. From (2) and (4) it follows that the stress-strain relation is

$$\sigma = \kappa\epsilon\phi, \quad (5)$$

where $\phi = \phi(\epsilon)$ is the equilibrium value given by (1). Substituting for ϵ from (5), we obtain the ϕ -dependent free-energy density at fixed stress:

$$g(\phi; \sigma) = -\frac{1}{2} \frac{\sigma^2}{\kappa\phi} - D\phi + T[\phi \ln\phi + (1-\phi)\ln(1-\phi)]. \quad (6)$$

Plots of this free energy for different values of the applied stress σ are shown in Fig. 1(a). Note that κ has been set equal to unity and that the quantities σ , D , and κ all have the same dimensions, namely energy per bond; the strain ϵ is dimensionless. In all cases the global minimum is the fractured (all bonds broken) state, $\phi=0$. For sufficiently small σ , $g(\phi)$ also has a *local* minimum at a value ϕ^* , with $0 < \phi^* \leq 1$. This local minimum in the free energy corresponds to a metastable state with a fraction ϕ^* of intact bonds. As σ is increased further, ϕ^* decreases, as does the free-energy barrier separating the local minimum from the *global* minimum at $\phi=0$. At $\sigma = \sigma_c$

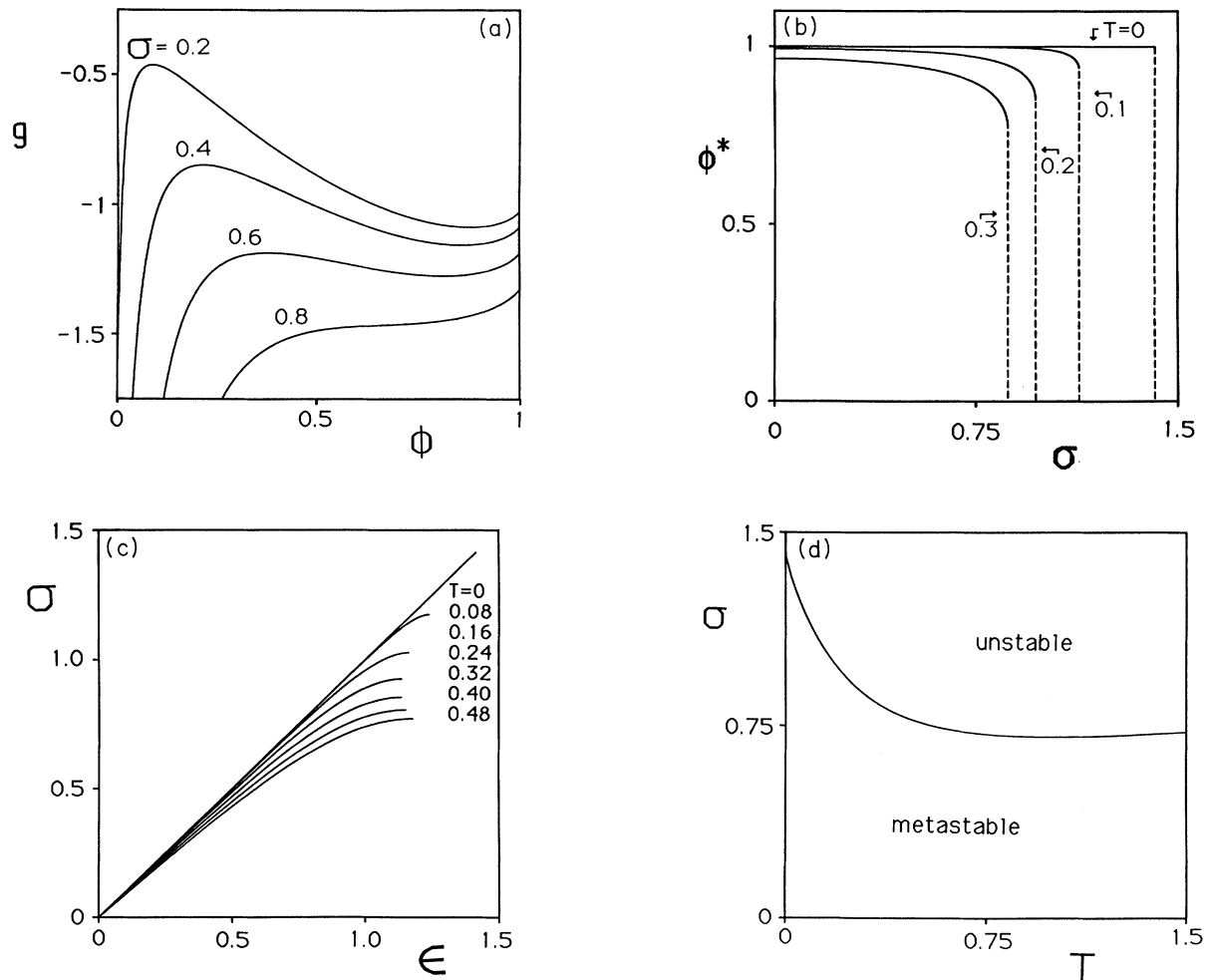


FIG. 1. For the one-dimensional model, (a) free energy g vs fraction of intact bonds ϕ for $T=0.5$, $D=1$, $\kappa=1$, and applied stress $\sigma=0.2, 0.4, 0.6$, and 0.8 . (b) Metastable minimum ϕ^* vs applied stress σ for $T=0, 0.1, 0.2, 0.3$. (c) Stress-strain relation σ vs ϵ , for $T=0.08, 0.16, 0.24, 0.32, 0.40$, and 0.48 . (d) Phase diagram in the σ - T plane.

the local minimum disappears: it is this limit of metastability, or spinodal, which we identify as the fracture threshold, where $\sigma_c(T, D, \kappa)$ is the ideal fracture strength.

Figure 1(b) shows ϕ^* versus σ for the particular choice $\kappa=D=1$ and several values of T . At $T=0$, no bonds break until they *all* break at the threshold $\sigma_c(T=0)$; in general, ϕ^* decreases continuously with σ until $\sigma=\sigma_c(T)$, at which it drops to 0. Similarly, Fig. 1(c) shows the corresponding σ versus ϵ (stress-strain) curves: only the $T=0$ curve is linear. The turnover point ($d\sigma/d\epsilon=0$) in the stress-strain curve is exactly the point where the metastable minimum at ϕ^* disappears in the plot of the free-energy $g(\phi)$.

Finally, in Fig. 1(d) we display the σ -vs- T phase diagram. The failure stress decreases with increasing temperature for $T < D$. In this regime, the curve agrees qualitatively with experimental data on the strength of iron whiskers.¹³ Over this same range, the failure *strain* first decreases and then increases with increasing temperature, and the nonlinear region of the stress-strain curve [Fig. 1(c)] becomes broader. This result should be compared with that of the mechanical model with initial random defects studied by Hassold and Srolovitz,³ who found a similar trend with increasing initial density of broken bonds. From Fig. 1(d) we see that the thermal fluctua-

tions have a significant effect on the fracture stress even at relatively low temperatures, e.g., σ_c decreases by 50% as T increases from 0 to only a few tenths of D .

The one-dimensional model can be generalized to higher-dimensional networks. For a two-dimensional triangular network with central forces, we can use effective-medium theory¹⁴ to express the elastic deformation energy as

$$E_{\text{def}} = \frac{1}{2} \kappa \epsilon^2 \frac{\phi - \phi_p}{1 - \phi_p},$$

where $\phi_p = \frac{2}{3}$, the elastic percolation threshold. Further analysis yields results qualitatively similar to the one-dimensional model. To go beyond this mean-field approximation, we carry out a Monte Carlo (MC) simulation of a two-dimensional network model. We represent a two-dimensional crystal as a triangular array of atoms connected by harmonic bonds. The network is fixed above and below with an applied overall strain $\bar{\epsilon}$, and with periodic boundary conditions connecting the right and left sides to make a cylinder. The total energy for a given configuration is $E(\{s_i\}) = \sum_i s_i (\frac{1}{2} \kappa \epsilon_i^2 - D)$, where as before s_i takes the values 0 or 1 to represent broken and intact bonds, respectively. The strain ϵ_i refers to the

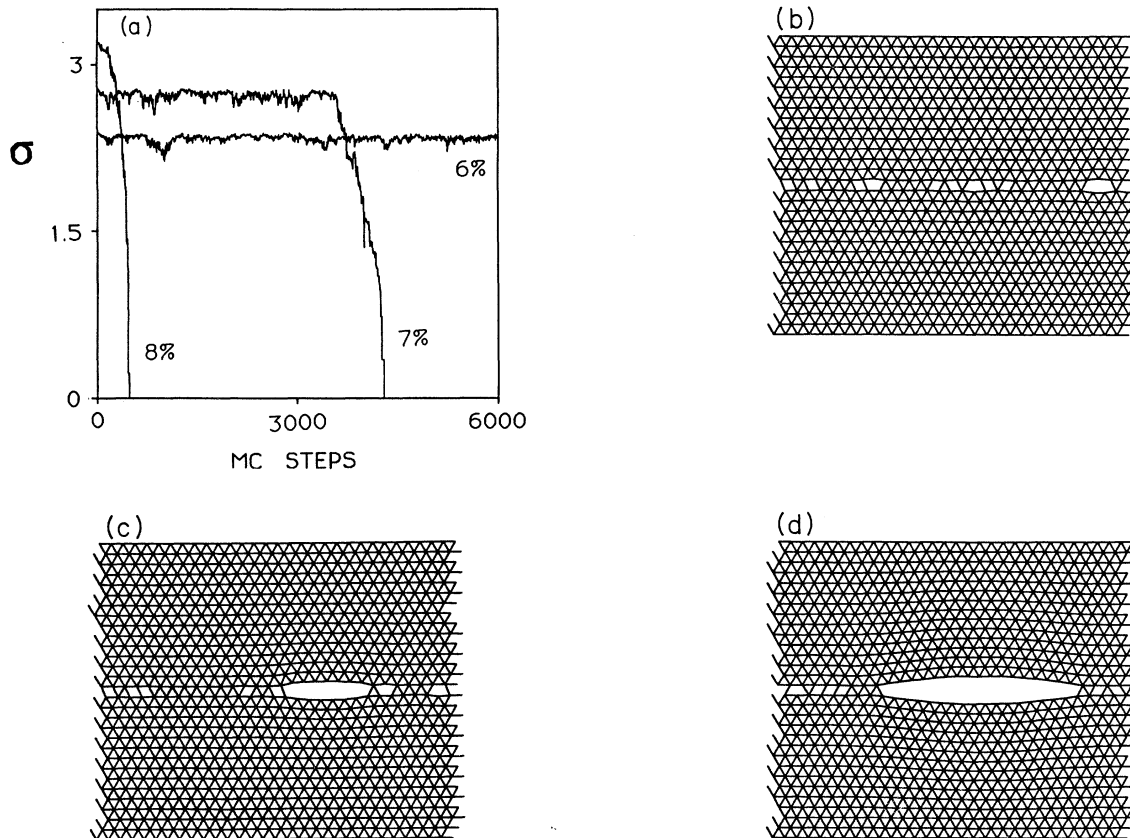


FIG. 2. For the two-dimensional model MC simulation, (a) stress σ vs MC steps for applied strain $\bar{\epsilon}=6\%$, 7% , and 8% . MC configurations for 7% strain, (b) in metastable equilibrium, (c) with a nucleated critical crack, and (d) showing propagation of the crack.

fractional extension of bond i . The bond states $\{s_i\}$ are the primary variables in the MC simulation, with the $\{\epsilon_i\}$ determined by mechanical equilibrium for a given configuration $\{s_i\}$. As a further simplification, we allow only the bonds on a single row in the center of the network to fluctuate. This central row of (approximately parallel) bonds appears similar to the one-dimensional model, but now—instead of democratic load sharing—the load is shared locally through the two-dimensional elastic strain field. This geometry corresponds to a crystal with a grain boundary where the bonds are much weaker than those in the bulk.

The simulation proceeds as follows: the initial condition is all bonds intact, $\{s_i=1\}$, with initial energy E_0 . Now a bond on the central row is chosen at random and broken, and the new mechanical equilibrium is calculated via the conjugate gradient method,¹⁵ with corresponding energy E_1 . The difference $\Delta E = E_1 - E_0$ is then used in the standard Metropolis algorithm to determine whether this first MC move is accepted.¹⁶ Then another bond on the central row is picked at random, its state is “flipped” (from intact to broken, or vice versa), the energy of the trial configuration is calculated, and this move is accepted or rejected as described above.

Our simulations were carried out on a 30×30 bond network with $\kappa=1$, $D=0.02$, and $T=0.01$ in arbitrary units, and for strains (uniaxial tension, with no shear component) in the range 0–10%. In the course of the MC simulation we monitor the stress σ , the vertical restoring force exerted by the network against its constraint. Figure 2(a) shows the evolution of σ during three simulations with different applied strains. For *small* enough applied strain, $\bar{\epsilon}=6\%$, the stress drops slightly and then remains essentially constant, indicating that a few bonds break but the network remains connected. For sufficiently *high* applied strain $\bar{\epsilon}=8\%$, the stress drops rapidly to zero, indicating that the network breaks into two pieces with virtually no delay. For an intermediate applied strain $\bar{\epsilon}=7\%$, the stress drops to a plateau value, remains essentially constant for some time, and then suddenly plunges to zero. We identify this behavior as relaxation to quasiequilibrium, followed by decay of the metastable state via nucleation of a microcrack that leads to fracture.

Figures 2(b)–2(d) show a sequence of MC configurations for the case of intermediate applied strain. In the first configuration, the system is in metastable equilibrium, and there are only small clusters of broken bonds generated by thermal fluctuations. In the second configuration, a large cluster of broken bonds, or microcrack, has nucleated. In the last configuration, the crack has begun to propagate across the network. Eventually the network breaks into two pieces.

Just as in studies of nucleation in the Ising model,¹⁷ we cannot associate a *real* lifetime with such a metastable state, because we have not explicitly included any kinetic mechanism for the nucleation process. We can, however, appeal to the Griffith¹⁸ theory of crack stability to estimate the size of the critical crack in the nucleation process, and to expose thereby the physical basis for metastability. We plot in Fig. 3 the energy \mathcal{E}_n of a configuration

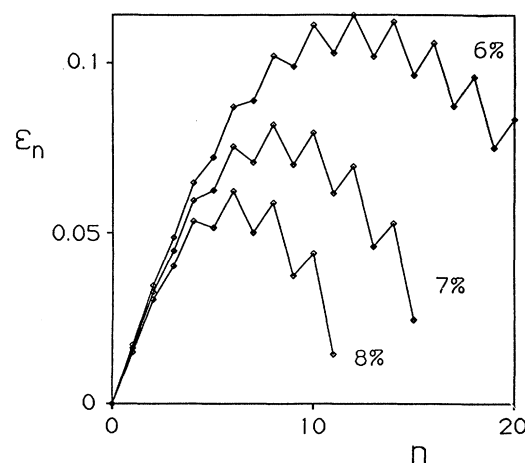


FIG. 3. Crack energy \mathcal{E}_n (in units of D) vs crack length n for applied strain $\bar{\epsilon}=6\%$, 7% , and 8% .

with a single cluster of n broken bonds on the middle row, with $1 \leq n \leq 20$, for several values of the applied strain in our triangular network. Here \mathcal{E}_n plays the role of the total energy in the Griffith picture, including terms analogous to the elastic strain energy and the line energy. The value n_c that maximizes \mathcal{E}_n is the critical crack size, which decreases with increasing strain, as does the effective energy barrier. We have also calculated from the MC simulations the size distribution of broken-bond clusters—or microcracks—prior to nucleation, and found that it agrees roughly with a Boltzmann distribution, e.g., the number of clusters of size $n \sim e^{-\mathcal{E}_n/T}$ for a given strain. The kinetics associated with nucleation of cracks over an energy barrier in real stressed crystals may, however, be complicated by surface reconstruction and other effects that inhibit crack healing.¹⁹

We are presently investigating fracture in a two-dimensional crystal via both MC and molecular-dynamics simulations, with a focus on metastability and nucleation of critical defects. We also intend to explore finite stress or strain rate effects and thereby test the range of validity of the statistical-thermodynamic approach. *Angular* force effects will also be studied, by comparing the simulation results for pair versus many-body potentials.

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