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Statistics of chemical and mechanical fractures of corroded solids

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ABSTRACT

The maximal penetration depth reached by a finite corrosion solution during the etching of a random solid is studied in a two-dimensional model. It is found that the statistical distribution of the maximal depth values follows a Gumbel law both through theoretical arguments and numerical simulation . When the maximal penetration of the corrosion front reaches the size of the sample, a chemical fracture occurs. It is shown that the probability of this chemical fracture obeys a law which is practically indistinguishable from the empirical Weibull law used to describe the statistics of mechanical fractures of brittle material. It is also shown that the statistics of the mechanical failure of a previously corroded sample follows a similar law.

KEYWORDS

INTRODUCTION

Chemical etching of disordered solids is an issue in several technological problems and in the theory of random systems. Etching can lead to the rupture of a sample if the etching

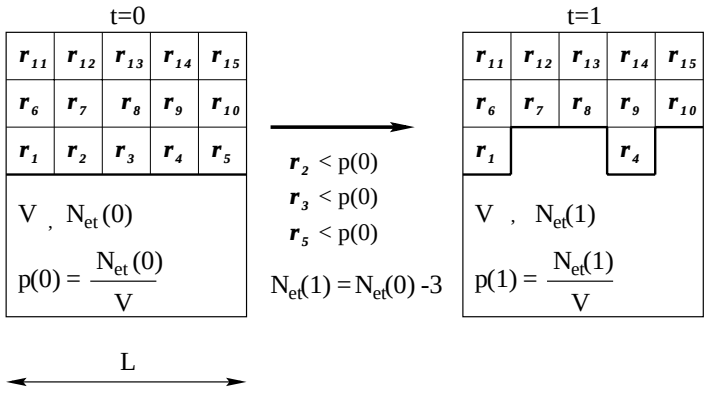

Figure 1: Sketch of the etching dynamics in a square lattice: the sites $2, 3, 5$ are etched at the first time-step as their resistances are lower than $p(0)$. At the same time the number of etchant particles in the solution decreases by 3 units, and a new part of the solid is uncovered.

solution is strong enough, or the solid thin enough. This is defined as a "chemical fracture". Its statistical behavior is studied here in a two-dimensional model. It is found numerically [1] as well as theoretically that the *chemical* fracture probability obeys Gumbel statistics [2] which is typical of an extremal variable. This law has been previously proposed by (e.g. [3, 4]) as a possible law fitting the statistics of *mechanical* fractures of samples under identical conditions of stress. The distribution found is hardly distinguishable from the Weibull distribution, which is the empirical law generally used to fit mechanical fracture statistics [5]. Furthermore, we show that the same statistics applies to the *mechanical* failure of a sample which has been *previously corroded* to some extent.

The Gumbel law is found through a study of the extremal properties of the etching front in a simple two-dimensional corrosion model previously introduced [6]. This model describes the chemical etching of a random solid by a finite volume of corrosive solution. It was inspired by an experimental study of pit corrosion of aluminum films [7] and reproduces the phenomenology of the experiment. It predicts that the etching stops spontaneously on a fractal liquid-solid interface as observed experimentally. The model dynamics are characterized by a progressive weakening of the corrosive power of the solution and a simultaneous progressive "hardening" of the solid-liquid interface. When this surface is too hard to be etched by the weakened solution, the corrosion stops. However, if the solid is too thin, it will have been fractured before the end of the process. In order to obtain the fracture statistics, one examines the probability that the maximal depth reached by the solution during the corrosion process is larger than the sample depth.

The etching model is recalled in Fig. 1 and is described as follows[8]:

1. The solid is represented by a lattice of sites exhibiting random "resistances to corrosion" $r_i \in [0, 1]$ uniformly distributed. It has a width L and a given fixed depth Y. At any time t the "etching power" of the solution is proportional to the etchant concentration

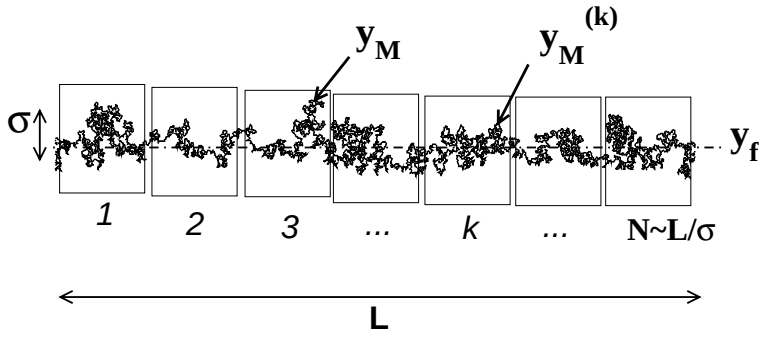

Figure 2: Final corrosion front: It is composed of $N \sim L/\sigma$ independent regions of size σ (σ can be considered as the correlation length of the system). The extremal front position y_M is indicated. It is the max between the N independent values of $y_M^{(k)}$ of each region.

$p(t)$. The etching solution has a finite volume V and contains an initial number $N_{et}(0)$ of etchant molecules. The initial etching strength is then $p(0) = N_{et}(0)/V$. Hereafter we choose $p(0) > p_c$, where p_c is the percolation threshold of the lattice.

2. The solution is initially in contact with the solid through the bottom boundary $y = 0$. At each time-step t, all surface sites with $r_i < p(t)$ are dissolved and a particle of etchant is consumed for each corroded site. Hence, at each time-step the concentration of the solution decreases.

At the beginning, the corrosion front stays quite smooth and advances layer by layer up to approximatively the time t_c when $p(t) = p_c$. In this regime one can show [8] that $p(t) = p_0 \exp(-t/\tau)$ with $\tau = V/L$. Therefore, this smooth part of the dynamics lasts for a period on the order of V/L reaching a depth $y_{lin.} \sim V/L$. After this regime the corrosion front becomes very irregular and finally stops at $t = t_f$. At t_f the etching power $p_f = p(t_f)$ is slightly smaller than p_c and the final corrosion front is fractal with dimension $D_f = 7/4$ up to a characteristic width $\Delta y = \sigma$ (see Fig. 2). As shown in [8], the model presents the scaling laws of Gradient Percolation [9] where the role of the gradient is played by the ratio L/V. This implies that σ can be seen as a percolation correlation length and $\sigma \sim (L/V)^{-1/D_f}$. The total front shown in Fig. 2 can then be considered as a juxtaposition of nearly independent fractal zones of lateral width σ. The total number of independent regions (hereafter σ-boxes) is $N \sim L/\sigma$. The maximal depth y_M reached by the front can be written as $y_M = \max_{k=1}^{N} y_M^{(k)}$, where $y_M^{(k)}$ is the maximal final depth reached by the corrosion in the k^{th} σ-box. The set of $y_M^{(k)}$ is then a collection of L/σ nearly independent and identically distributed random variables. Since σ is a percolation correlation length, we can say that the distribution of $y_M^{(k)}$ has an exponential tail with a characteristic scale y_0 of order σ. We have then to search y_M as the maximal value among a large set of independent and exponentially distributed identical random variables. Therefore, in the limit of large N, y_M has the following standard Gumbel distribution [2]:

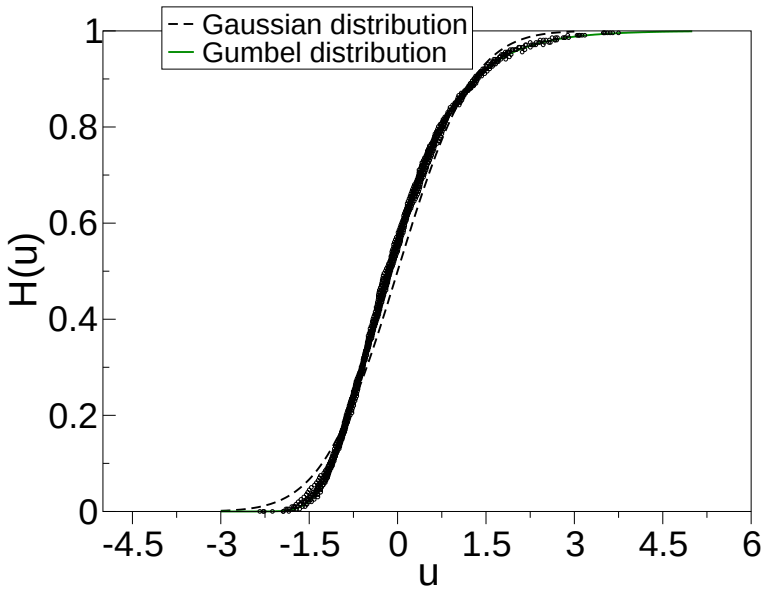

Figure 3: Integrated probability distribution for reduced y_M (zero mean and unitary variance) are compared with standard Gaussian and Gumbel distributions. The simulation results collapse on the Gumbel distribution given by Eq. (1) (continuous line, hidden by data points).

$$H(u) \equiv Prob\left(\frac{y_M - \langle y_M \rangle}{\Sigma} < u\right) = e^{-e^{-(bu+a)}} , \tag{1}$$

where Σ is the standard deviation of y_M, and $a \simeq -0.5772$ and $b \simeq \sqrt{1.64493}$.

The quantities $\langle y_M \rangle$ and Σ can be written[2]:

$$\langle y_M \rangle \simeq \left\langle y_M^{(k)} \right\rangle + 2y_0 \log N \tag{2}$$

$$\Sigma \simeq 2\, y_0 , \tag{3}$$

From the previous discussion, one can show also that:

$$\begin{aligned} y_f &\simeq c_1 V/L + c_2 (V/L)^{4/7} \\ \left(\left\langle y_M^{(k)} \right\rangle - y_f\right) &\sim \sigma \sim (V/L)^{4/7} \end{aligned} \tag{4}$$

where y_f is the average depth of the final corrosion front. In summary, (i) $[\langle y_M \rangle - y_f]$ scales as σ if L/σ is fixed, and (ii) $\langle y_M \rangle$ dependends linearly on $\log L$ for given σ. These theoretical results are confirmed by extensive numerical simulations. The direct numerical evidence for a Gumbel statistics is shown in Fig. 3, where the numerical probability distribution function of the reduced variable $[y_M - \langle y_M \rangle]/\Sigma$ is represented.

It is now possible to study the chemical fracture of a solid sample with finite depth Y. This fracture probability is then given by $Prob\,(y_M > Y)$:

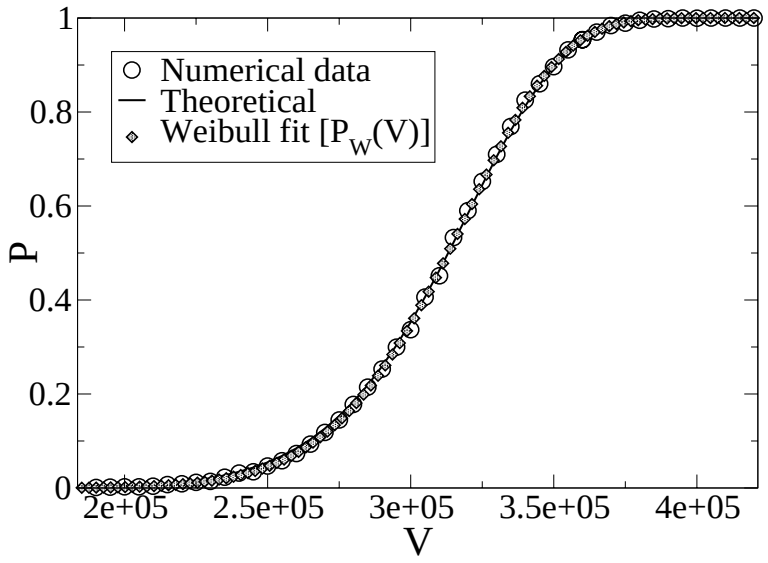

Figure 4: *Chemical fracture* probability $Prob\,(y_M > Y)$ as a function of the solution volume V which measures the "chemical force". Small circles are the numerical extimated probabilities. The line is the result of our theory. Diamond shaped points represent the fit of the fracture data with a Weibull law.

$$Prob\,(y_M > Y) = 1 - \exp\left\{ -A \left(\frac{L}{\Sigma}\right)^b \exp\left[\frac{b(y_f - Y)}{\Sigma}\right] \right\} , \tag{5}$$

where Eqs. (1), (2) and (3) have been used, and A is a positive constant.

By substituting y_M as a function of V/L, one obtains the chemical fracture probability distribution $P(V)$, as a function of the *chemical force* V for a given p_0 (i.e. the initial etchant concentration) and L. This distribution is determined but the value of A, which has to be fitted to the numerical fracture statistics (i.e. the fraction of simulation runs that break the sample as a function of V). The result is shown in Fig. 4. Also shown in the figure is a direct comparison of the best fit of a Weibull law [5] with the direct chemical fracture statistics. Here again the agreement is good. The Weibull law, introduced to describe the statistics of brittle materials failure, has the following form:

$$P_W(V) = 1 - e^{-\left(\frac{V - V_0}{V_1}\right)^m} , \tag{6}$$

where V represents an applied stress, V_0 is the minimal stress to have finite fracture probability, V_1 and m are suitable parameters. The extreme similarity between the Gumbel and Weibull behaviors observed in our model suggests that the underlying probabilistic structure controlling chemical and mechanical fracture could be the same. This would be a case of universality.

We now extend the analysis to the case of the *mechanical* failure of a partially corroded solid. Here this means that an uniaxial mechanical force F is applied to the lateral sides of a

sample which has been previously corroded up to $y_M < Y$. The most reasonable hypothesis is that the force produces the maximal stress at the point where the solid is the thinnest. The solids fails if this stress, equal to $F/(Y - y_M)$, is larger than a critical value s_c characteristic of the material. The failure probability is then equal to $P[y_M > (Y - F/s_c)]$. Therefore, in this model, even the *mechanical failure* of a corroded solid presents statistics related to the extremal Gumbel law. It is worth to note that this case of failure can be seen as the effect of a *stress under corrosion*, while it is *corrosion under stress* that is typically studied experimentally. The relationship between these two mechanisms requires further study.

ACKNOWLEDGEMENTS

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REFERENCES

[1] A. Baldassarri, *Statistics of Extreme Persistent Events*, Ph.D.Thesis, University of Paris XI, 1999.

[2] E.J. Gumbel, *Statistics of Extremes*, Columbia University Press, New York, 1958; J. Galambos, *The Asymptotic Theory of Extreme Order Statistics* (R. E. Krieger Publishing Co., Malabar, Florida, 1987).

[3] P. M. Duxbury, P. L. Leathand P. D. Beale, Phys. Rev. B **36**, 367 (1987).

[4] H. Herrmann and S. Roux, *Statistical models for the fracture of disordered media* (North-Holland ed., Amsterdam, Netherlands, 1990).

[5] W. Weibull, J. Appl. Phys. **18**, 293 (1951).

[6] B. Sapoval, S. B. Santra and Ph. Barboux, Europhys. Lett., **41**, 297 (1998). S. B. Santra and B. Sapoval, Physica A., 266, 160-172 (1999).

[7] L. Balázs, Phys.Rev. E **54**, 1183 (1996)

[8] A. Gabrielli, A. Baldassarri, and B. Sapoval, Phys. Rev. E, **62**, 3103 (2000).

[9] B. Sapoval, M. Rosso and J. F. Gouyet, J. Phys. Lett. (Paris), **46**, L149 (1985); B. Sapoval, M. Rosso and J. F. Gouyet, in *"The Fractal Approach to Heterogeneous Chemistry"*, edited by D. Avnir (John Wiley and Sons Ltd., New York, 1989).