We use molecular dynamics to study the nucleation of cracks in a two dimensional material without pre-existing cracks. We study models with zero and non-zero shear modulus. In both situations the time required for crack formation obeys an Arrhenius law, from which the energy barrier and pre-factor are extracted for different system sizes. For large systems, the characteristic time of rupture is found to decrease with system size, in agreement with classical Weibull theory. In the case of zero shear modulus, the energy opposing rupture is identified with the breakage of a single atomic layer. In the case of non-zero shear modulus, thermally activated fracture can only be studied within a reasonable time at very high strains. In this case the energy barrier involves the stretching of bonds within several layers, accounting for a much higher barrier compared to the zero shear modulus case. This barrier is understood within adiabatic simulations.

I. INTRODUCTION

While our current understanding of fracture begins with the ideas of Griffith in 1921 [1], the study of its atomic mechanism has attracted a large amount of attention in recent years. For example, corrections to Griffith’s results for a crack in a brittle material have been proposed and verified with atomistic simulations [2, 3, 4]. Also, large scale simulations have been used to study dynamical fracture [5, 6, 7]. This increase in interest in fracture is partly due to computer simulations which promise an understanding at the atomic level description of the phenomena. However simulations face a fundamental problem [8, 9]: many atomic deformations are thermally activated and therefore involve long timescales which are difficult to simulate.

Most simulations overcome this problem by studying fracture with a pre-existing crack. In that case, crack growth is a driven phenomena and there is no energy barrier to be overcome. Only a few simulations have been used to study the formation of cracks at non-zero finite temperature without pre-existing cracks: void formation has been observed in 3D simulations of strained binary Lennard-Jones systems [10], and simulations for the rate of crack nucleation have been performed in a 2D spring network [11]. Experimentally, the rate of crack nucleation in heterogeneous materials has been found to obey an Arrhenius law with an energy barrier scaling according to Griffith’s results [12, 13].

In the present work, we address the nucleation of cracks in a brittle two-dimensional material, i.e. a sheet with a thickness of one atomic layer, through Langevin dynamics. The rate constant for the nucleation of cracks follows an Arrhenius law, from which the energy barrier is extracted. Two situations in a square lattice are studied: atomic interactions restricted to first neighbours and interactions extended to second neighbours. In the former case, the shear modulus of the solid is zero and the energy barrier is shown to be independent of system size: the breakage of a single bond propagates to the rest of the solid without any cost. In the latter case the shear modulus is non-zero and a finite size crack has to nucleate before rupture can propagate throughout the system. These two situations will be referred to as chain-like and solid-like models, respectively.

This paper is organized as follows. In the next section we describe the models used in this paper followed by a description of how simulations are carried out. In section IV we present the results for the chain-like and solid-like models. The latter is physically more relevant to describe brittle materials and we discuss its energy barrier in the context of Griffith theory in section V. Our conclusions finalize the paper.

II. MODEL

A stretched one dimensional chain has been previously used as a simple model for breakage of polymers [14, 15, 16, 17, 18, 19]. Here we extend this model to study fracture in 2D brittle solids by bonding the chains to each other such as to form a square lattice – see Fig. 1. We study samples containing $M$ chains which are made of $N = 100$ atoms each. Those chains are stretched in the horizontal direction: their constant length is $N(a+s)$, where $a$ is the equilibrium bond length and $s$ is the applied strain. By constraining the dynamics of atoms along the applied strain the system cannot form topological defects and the only mechanism for stress relaxation is fracture. Also, by choosing the constraint along the applied strain, we expect to be sampling the meaningful pathway for fracture while speeding up the simulation time. This is verified later in section IV where we perform one set of simulations without this constraint.
A square lattice can be made isotropic by choosing the elastic constant between first neighbors to be twice as large as the elastic constant between second neighbors \(20\). To fulfill this condition we chose the following form for the Lennard-Jones potential between first neighbors:

\[
V_f(r) = \epsilon [(a/r)^{12} - 2(a/r)^6],
\]

and

\[
V_s(r) = 4\epsilon_s[(a_s/r)^{12} - (a_s/r)^6],
\]

for second neighbors. We use \(\epsilon = 1\) and \(\epsilon_s = 36/228\epsilon\) for the binding energies and \(a = 1\) and \(a_s = \sqrt{2}\) for the equilibrium lengths.

The dynamics of this system are obtained by solving a set of Langevin equations for the position \(x_{i,j}\) of each atom:

\[
m \frac{d^2 x_{i,j}}{dt^2} = \sum_{k,l} F(x_{i,j} - x_{k,l}) - \eta \frac{dx_{i,j}}{dt} + f_{i,j}(t)
\]

where \(F(x)\) is the force computed from the potential, \(m\) is the atomic mass and \(\eta\) is the friction coefficient. The random force \(f_{i,j}(t)\) is related to \(\eta\) by the fluctuation-dissipation theorem.

Periodic boundary conditions in the horizontal direction imply \(x_{0,j} = x_{N,j}\) and \(x_{N+1,j} = x_{1,j}\) for all \(j\). Periodicity is also imposed in the vertical direction to ensure that all chains are equivalent: \(x_{i,0} = x_{i,M}\) and \(x_{i,M+1} = x_{i,1}\). For simplicity we use reduced units. Energy is given in units of \(\epsilon\), distance is given in terms of \(a\), and time is given in units of the smallest phonon oscillation period \(P = 2\pi/(12\sqrt{(2\epsilon/ma^2)})\) of an intact chain \(14\). Mass is written in terms of \(m\) and the friction coefficient is tuned to \(\eta = 0.25(2\pi/P)\).

Initially all the horizontal bonds have the same length \(a + s\) and all vertical bonds are at their equilibrium length \(a\). The velocity of each atom is chosen randomly according the Boltzmann distribution. The dynamics of the system are obtained by solving numerically the set of equations \(3\) using the velocity-verlet algorithm \(21\) until the solid ruptures.

**III. SIMULATION**

In Fig. 2 (upper panel) we show the time dependence of the potential energy for the solid-like model. This energy fluctuates around its initial value showing that the initial stretched state is a configuration at a local energy minimum. Rupture occurs at about 2750 units of time when the energy of the system drops abruptly. This shows that the system is been driven towards an equilibrium state with lower energy. In panels A,B,C and D of this figure, we shown atomic configurations in panels A,B,C and D are shown.
towards rupture. In particular we measure the characteristic time of rupture and analyze this quantity from the point of view of thermally activated systems.

To compute the characteristic time of rupture \( \tau \) we use an ensemble containing \( S_N = 60 \times 100 \), \( S_0 = 500 \) samples for the solid-like model. Those samples differ from each other by the sets of initial velocities and random forces \( f_{i,j}(t) \). We will need to choose a value of the order parameter \( \phi \) which we will associate with irreversible rupture. The characteristic time for the incipient crack to reach a particular size is computed by tracking the number of chains \( S(\phi, t) \) whose order parameter has not yet reached the value \( \phi \) at time \( t \). For a fixed value of \( \phi \) this function decreases exponentially with time, \( S(\phi, t) = S_0 \exp(-t/\tau(\phi)) \). The characteristic time \( \tau(\phi) \) depends on \( \phi \) and is obtained from a fit of \( S(\phi, t) \) to the numerical data. The time that characterizes rupture in an irreversible manner depends on the arbitrary choice of the cutoff value \( \phi_c \) which we associate with rupture. To chose this cut-off we show in Fig. 3 the dependence of \( \tau \) on \( \phi \). Two distinct regimes are apparent. The first regime occurs when \( \phi \) is smaller than \( \sim 65.8 \) (in units of \( a \)). In this regime, \( \phi \) increases very slowly with time. The underlying physics of this regime is the competition between thermal fluctuations, which are responsible for increasing crack length, and the restoring force on the atomic bonds. The second regime occurs when the order parameter \( \phi \) is greater than 65.8. Here, \( \tau(\phi) \) has reached a plateau, and \( \phi \) increases very rapidly with time. Stress relief of the material’s bulk is the driving force of this regime which requires a larger crack and therefore produces a fast increase in \( \phi \); irreversible rupture has occurred. So, from

In Fig. 3 we can determine the value of \( \phi \) for which rupture becomes irreversible. This value is \( \phi_c = 65.8 \).

IV. RESULTS

The nucleation of cracks can be thermally activated \[8, 9, 11\] such that their occurrence is typical of an Arrhenius process. Mathematically the characteristic time of rupture \( \tau \), the inverse of the nucleation rate, reads:

\[
\tau = \tau_0 \exp \left( \frac{E_b}{k_b T} \right) \tag{4}
\]

where \( k_b T \) is thermal energy, \( E_b \) is the energy barrier the system has to overcome, and \( \tau_0 \) is the inverse of the attempt frequency to rupture. The attempt frequency depends on the vibration frequency of the system in the metastable wells of the energy landscape through the local curvature of the energy surface \[23, 24\]. It also depends on the friction coefficient in the Langevin equation \[24\]. In this section we study the dependence of \( \tau \) on temperature for the chain-like and solid-like models to extract both \( E_b \) and \( \tau_0 \), which are intrinsic quantities of the system being studied.

A. Chain-like model

In Fig. 4, we show the temperature dependence of \( \tau \) for different system sizes \( M \). The strain of this system is set to \( s = 0.05 \). For each system size, \( \tau \) increases exponentially with \( 1/k_b T \) – in agreement with Eqn. 4. The energy barrier \( E_b \) and the pre-factor \( \tau_0 \) were extracted from fits to those results. Changing system size strongly
affects the pre-factor but has no effect, within error bars, on the energy barrier – as can be seen in Figures 4(b) and (c) respectively.

The dependence of the pre-factor on system-size can be understood qualitatively within the scope of a nucleation theory for fracture. Intuitively, $\tau_0$ is proportional to the average time between two consecutive attempts to nucleate a crack. Assuming that cracks can nucleate in each of the $M$ chains of the system, then $\tau_0 = 1/M$ \cite{26, 27}. Fig. 4(b) shows the good agreement of simulation with this inverse relation.

The energy barrier can be understood quantitatively by assuming that parallel chains are independent from each other. Under this assumption, the energetic cost $E$ of elongating one atomic bond in a single layer is given by \cite{14, 15, 17}:

$$E(\phi) = V(a + s + \phi) + (N - 1)V\left(a + s - \frac{\phi}{(N - 1)}\right)$$  \tag{5}

where $\phi$ is the deviation of the broken bond length from its strained elongation and $V(x)$ is the potential energy of an atomic bond. Equation 5 corresponds to the sum of potential energy of all the bonds in the layer precursor of fracture. This equation considers that while one of the bonds increases towards rupture by an amount $\phi$, the other bonds of the same layer relax by an amount $\phi/(N - 1)$ towards their equilibrium value. For the parameters used in Fig. 4 i.e. $N = 100$ and $s = 0.05$, Equation 5 predicts an energy barrier of 0.0564. This is in good agreement with our simulations where the barrier is approximately 0.054 for all system sizes.

Independence of parallel chains is the key assumption to explain fracture in the chain-like model. This assumption can be understood as follow. Since the shear modulus of this model is zero, no energetic cost is associated with sheared configurations in the linear regime. Therefore, an individual atomic layer can proceed towards fracture independently of neighbouring layers until non-linear effects become relevant. The energy barrier opposing this process is related to the cost of increasing the length of one of the bonds of the layer – independently of other layers. Only when this bond becomes large enough, neighbouring layers are driven towards rupture in a domino-like process.

Eqn. 5 results from the competition between the energetic cost of extending one bond length of the chain and the energetic gain of relaxing the remaining bonds. This contrasts with Griffith’s calculation where the barrier is related to the cost of creating more surface and the energetic gain due to reducing the strain in the bulk of the material. Thus, despite its use in the literature, the square lattice with only first neighbour interactions is a poor model for fracture in a solid and Griffith’s theory does not apply to this system.

We now study the solid-like model. In Fig. 5(a) we show the temperature dependence of $\tau$ for different system sizes $M$ and applied strain $s = 0.065$. As in the previous model we study this system by fitting the time of fracture to Eqn. 4, obtaining the energy barrier $E_b$ and the pre-factor $\tau_0$ for each system size. Those results are shown in Fig. 5(b-c).

The pre-factor, Fig. 5(b), presents two regimes: for systems containing less than 15 chains, i.e. $M < 15$, $\tau_0$ increases with system size; however for $M > 15$, the pre-factor decreases as system size increases. Those behaviors are related to finite size effects. When $M < 15$, the relaxation region around the crack is of the same size as the system. On the other hand, increasing the size of the solid above 15 layers implies that more nucleation sites are available for rupture, and $\tau_0$ decreases with $M$, as in the previous model \cite{26, 27}. A quantitative assessment of the pre-factor would involve the generalisation of Kramer’s result to higher dimensions \cite{28}. This calculation was performed successfully to study rupture in a one-dimensional chain \cite{14} but its application to the present model is beyond the scope of this paper.

In Fig. 5(c) we show the energetic cost for nucleating a crack in the solid-like model as a function of system size $M$. For solids smaller than $M = 15$, the energy barrier increases considerably with system size: more than 150% in Fig. 5(c); while for solids larger than $M = 15$, the increase is only marginal and show a saturation trend at $E_b \sim 0.14$ – indicating that finite-size effects become negligible. This value is comparable to the adiabatic bar-
rier. This barrier is computed by extending the length of one bond in small steps and restraining it until the other bonds are relaxed at zero temperature. In this process the energy increases until the critical crack is formed. The maximum energy seen in this process corresponds to the energy required to nucleate the crack at zero temperature. This adiabatic energy for the different system sizes is represented by squares in Fig. 5. Notice that the barrier obtained in our simulations is smaller than the adiabatic energy barrier by about 23%. A smaller simulated barrier compared to the adiabatic case has also been observed for one dimensional systems [10]. A possible explanation for this discrepancy might be that a zero temperature calculation does not account for entropy which plays a role in the free energy opposing rupture in system with multiple degrees of freedom.

One important simplification imposed in our model with respect to two-dimensional solids consists in constraining the dynamics of atoms to one dimension. However by imposing this constraint along the direction of applied stress, we expect to be sampling the meaningful pathway for rupture of a 2D-solid. To verify this statement we performed a set of simulations on a M × N = 50 × 100 system where the constraint on the motion of atoms was removed. The results of those simulations are shown in Fig. 5 (b-c) and are referred to as full 2D. Notice that the full 2D system has a much lower pre-factor than our constrained system. A discrepancy in the pre-factor is expected since it is related to the vibration of the system, and therefore its dynamics, which is different in both models. However the energy barrier of our constraint model and the full 2D are equal within error bars. We are therefore confident that our constrained model can be used to study the energetic behavior of 2D solids. In the next section we discuss the simulated energy barrier in the context of Griffith theory for rupture and adiabatic simulations.

V. SOLID-LIKE MODEL AND GRIFFITH

The introduction of a crack of size L in a solid characterized by a Young’s modulus E and a stress σ will result in a stress-energy relief of πσ²L²/2E. But this crack will also involve a cost of 2γL, where γ is a surface energy, such that the dependence of the energy on the crack size L is [13]:

\[ E_G(L) = -\frac{\pi L^2 \sigma^2}{2E} + 2\gamma L. \]  (6)

This potential energy reaches a maximum when \( \partial E_G(L)/\partial L = 0 \). This occurs at the critical value \( L_G = 2E\gamma/(\pi\sigma^2) \). Beyond this crack length, the crack propagates spontaneously to reduce the bulk strain in the material until the solid is broken in two pieces. The barrier for crack nucleation occurs at this critical length: \( E_G(L_G) = \frac{2\gamma^2E}{\pi\sigma^2} \) or \( \frac{2\gamma^2E}{\pi\sigma^2} \). The Young modulus of the solid-like model is \( E = 77.91 \) (in units of \( \epsilon_f/a^2 \)) and the energy necessary to create two surfaces \( 2\gamma \) is equal to the energy of two weak and one strong bond per inter-atomic distance: \( \gamma = 0.6587 \). For a strain \( s = 0.065 \), the Griffith energy barrier is \( E_G = 0.837 \), that is, approximately six times the value obtained from our statistical simulation.

It is of no surprise that Griffith’s calculation is not valid for large strains. First, because in this highly stretched regime, linear elasticity theory is not valid. Second, for strains larger than 0.04 only one atomic layer needs to be completely broken in order to initiate the rupture process. In other words, while in Griffith’s regime the mechanism behind rupture is the competition between the formation of new surface and stress relaxation, the physics of rupture in the highly stressed regime is the competition between stress relaxation and bond stretching at the formation of the incipient crack.

To understand the range of validity of Griffith calculation, we performed adiabatic relaxation (\( T = 0 \)) where bonds were mathematically cut within a line perpendicular to the applied strain. After cutting those bonds, atoms were relaxed until the force on each one of them was smaller than \( 1 \times 10^{-5} \). To avoid finite-size effects we increased the size of the system from \( N=100 \) at \( S=0.04 \) to \( N=600 \) at \( S=0.01 \). The relative energy barrier computed from this process with respect to Griffith barrier is shown in Fig. 6. This Figure shows that for strains below 0.04, the adiabatic barrier differs at most by 30% from the Griffith barrier. On the other hand, for strains beyond 0.04 those barriers are several times different and this difference increases with strain. In the inset of Fig. 6 we also show in a log-log scale the dependence of the energy barrier on strain. For strains below 0.04, those
quantities scale with an exponent of -2.26. This is very close to the exponent predicted by Griffith’s theory: -2. The behavior at higher strains deviate from this scaling. This clearly shows that for our model Griffith’s theory is valid for strains smaller than 0.04. We note that the calculation of the energy barrier with strain dependent Young modulus and surface tension – as described in Ref. [6] – gave results in greater disagreement than the ones of Griffith.

VI. CONCLUSION

Due to its simple dynamics and large system size, our atomistic simulation of the nucleation of cracks in thin brittle sheets is an ideal system for the study of noise activated processes and nucleation theory. In particular, we found that the energy barrier for crack nucleation in a square lattice with only first-neighbor interactions is comparable to the barrier of one-dimensional chains due to the zero shear modulus of this system. For the more interesting case where second-neighbor interactions are incorporated into the model, we found an agreement between the simulated energy barrier at high strains and the one computed from an adiabatic relaxation. This barrier involves several layers, accounting for a much higher barrier compared to the case of isolated chains. We believe that extensions of the present study such as to investigate nucleation of pre-existing cracks would be a valuable contribution to understand fracture.

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