Force-induced breakdown of flexible polymerized membrane

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We consider the fracture of a free-standing two-dimensional (2D) elastic-brittle network to be used as protective coating subject to constant tensile stress applied on its rim. Using a Molecular Dynamics simulation with Langevin thermostat, we investigate the scission and recombination of bonds, and the formation of cracks in the 2D graphene-like hexagonal sheet for different pulling force $f$ and temperature $T$. We find that bond rupture occurs almost always at the sheet periphery and the First Mean Breakage Time $\langle \tau \rangle$ of bonds decays with membrane size as $\langle \tau \rangle \propto N^{-\beta}$ where $\beta \approx 0.50 \pm 0.03$ and $N$ denotes the number of atoms in the membrane. The probability distribution of bond scission times $t$ is given by a Poisson function $W(t) \propto t^{1/3} \exp(-t/\langle \tau \rangle)$. The mean failure time $\langle \tau_r \rangle$ that takes to rip-off the sheet declines with growing size $N$ as a power law $\langle \tau_r \rangle \propto N^{-0.17}$. We also find $\langle \tau_r \rangle \propto \exp(\Delta U_0/k_B T)$ where the nucleation barrier for crack formation $\Delta U_0 \propto f^{-2}$, in agreement with Griffith’s theory. $\langle \tau_r \rangle$ displays an Arrhenian dependence of $\langle \tau_r \rangle$ on temperature $T$. Our results indicate a rapid increase in crack spreading velocity with growing external tension $f$.

I. INTRODUCTION

Fracture in engineering materials is a long-standing topic of research due to problems that arise with technological applications and the ensuing economical implications. Thus, for decades a lot of attention has been focused on understanding the macroscopic and microscopic factors which trigger fracture. Recently, the interest and the need for better understanding of the interplay between elastic and fracture properties of brittle materials has been revived due to the rapidly developing design of advanced structural materials.

Promising aspects for applications include reversible polymer networks [1,2], and also graphene, that shows unusual thermomechanical properties [3,4]. Among other things, graphene, which is a honeycomb lattice packed with C atoms can be used as anti-corrosion gas barrier protective coating [5], in chemical and bio-sensors [6], or as efficient membrane for gas separation [7]. In all possible applications the temperature and stress-dependent fracture strength of this 2D-network is of crucial importance. Graphene has been investigated recently by Barnard and Snook [8] using ab initio quantum mechanical techniques whereby it was noted that the problems “has been overlooked by most computational and theoretical studies”.

An important example of biological microstructure is spectrin, the red blood cell membrane skeleton, which reinforces the cytoplasmic face of the membrane. In erythrocytes, the membrane skeleton enables it to undergo large extensional deformations while maintaining the structural integrity of the membrane. A number of studies, based on continuum-3, percolation- [10,12], or molecular level [14,15] considerations of the mechanical breakdown of this network, modeled as a triangular lattice of spectrin tetramers, have been reported so far. Many of these studies can be viewed in a broader context as part of the problem of thermal decomposition of gels [16], epoxy resins [17, 18] and other 3D networks both experimentally [16,18], and by means of simulations [19] in the case of Poly-dimethylsiloxane (PDMS).

The afore-mentioned examples illustrate well the need for deeper understanding of the processes of failure in brittle materials. Besides analytical and laboratory investigations, computer simulations [20,22] have provided meanwhile a lot of insight in aspects that are difficult for direct observations or theoretical treatment - for a review of previous works see Alava et al. [23]. Most of these studies focus on the propagation of (pre-existing) cracks, relating observations to the well known Griffith's model [24] of crack formation. A number of important aspects of material failure have found thereby little attention. Thus only a few simulations examine the rate of crack nucleation which involves long time scales necessary for thermal activation - see, however, [25,26]. Effects of system size on the characteristic time for bond rupture have not been examined except in a recent MD study by Dias et al. [27]. Also recombination of broken bonds has not been considered. These and other insufficiently explored properties related to fracture have motivated our present investigation of a free-standing 2D honeycomb brittle membrane by means of Molecular Dynamics simulation. In view of the possible applications as anti-corrosion and gas barrier coating, we consider a radially-spanned sheet of regular hexagonal flake shape so as to minimize effects of corners and unequal edge lengths that are typical for ribbon-like sheets. Tensile constant force is applied on the rim of the flake, perpendicular to each edge. By varying system size, tensile force and temperature, we collect a number of results which characterize the initiation and the course of fragmentation in stretched 2D honeycomb networks.

The paper is organized as follows: after a brief introduction, we sketch our model in Sec. II where we consider interactions between atoms in the brittle honeycomb membrane, define the threshold for bond scission, and also

\[ \langle \tau \rangle \propto N^{-\beta} \]

\[ W(t) \propto t^{1/3} \exp(-t/\langle \tau \rangle) \]

\[ \langle \tau_r \rangle \propto N^{-0.17} \]

\[ \langle \tau_r \rangle \propto \exp(\Delta U_0/k_B T) \]

\[ \Delta U_0 \propto f^{-2} \]
introduce some basic quantities that are measured in the course of the simulation. In Sec. III we present our simulation results, presenting briefly the results on recombination of broken bonds - III A, the distribution of bond scission rates over the membrane surface, the dependence of the Mean First Breakage Time (MFBT) before a bond scission takes place and of the mean failure time until the 2D sheet breaks apart on applied tensile force, and examine how these times depend on membrane size and temperature - III B. The formation of cracks at different cases of applied stress as well as their propagation in a 2D honeycomb brittle sheet are briefly considered in subsection III C. We end this report by a brief summary of results in Section IV.

II. MODEL AND SIMULATION PROCEDURE

A. The model

We study a coarse-grained model of honeycomb membrane embedded in three-dimensional (3D) space. The membrane consists of \( N \) spherical particles (beads, monomers) of diameter \( \sigma \) connected in a honeycomb lattice structure whereby each monomer is bonded with three nearest-neighbors except for the monomers on the membrane edges which have only two bonds (see Fig. 1 [left panel]). The total number of monomers \( N \) in such a membrane is \( N = 6L^2 \) where by \( L \) we denote the number of monomers (or hexagon cells) on the edge of the membrane (i.e., \( L \) characterizes the linear size of the membrane). There are altogether \( N_{\text{bonds}} = (3N - 6L)/2 \) bonds in the membrane. In our studies we consider symmetric hexagonal membranes (i.e., flakes) so as to minimize possible effects due to the asymmetric of edges or vortices at the membrane periphery.

![Figure 1: A membrane with honeycomb structure that contains a total of \( N = 54 \) beads and has linear size \( L = 3 \) (\( L \) is the number of hexagonal cells on the edge of the membrane). (right panel) A snapshot of a typical conformation of an intact membrane with \( L = 30 \) containing 5400 monomers after equilibration with no external force applied. Typical wrinkles are seen to form on the surface.](image)

For the analysis of our results we find it appropriate to divide the two-dimensional membrane network so that all bonds fall into different subgroups presented by concentric “circles” with consecutive numbers (see Fig. 1 [right panel]) proportional to their radial distance from the membrane center. To odd circle numbers thus belong bonds that are nearly tangential to the corresponding circle. Even circles contain no encompass radially oriented bonds (shown to cross the circle in Fig. 1). The total number of circles \( C \) in a membrane of linear size \( L \) is found to be \( C = (2L - 1) \). We use this scheme of labeling the groups of bonds that compose the membrane in order to represent our simulation results in appropriate way which relates them to their relative proximity to membrane’s periphery.

B. Potentials

The nearest-neighbors in the membrane are connected to each other by breakable anharmonic bonds described by a Morse potential,

\[
U_M(r) = \epsilon_M \{1 - \exp[-\alpha(r - r_{\text{min}})]\}^2. \quad (1)
\]

where \( r \) is the distance between the monomers. Here \( \alpha = 1 \) is a constant that determines the width of the potential well (i.e., bond elasticity) and \( r_{\text{min}} = 1 \) is the equilibrium bond length. The dissociation energy of a given bond,
$\epsilon_M = 1$, is measured in units of $k_B T$ where $k_B$ denotes the Boltzmann constant and $T$ is the temperature. The minimum of this potential occurs at $r = r_{\text{min}}$. $U_{\text{Morse}}(r_{\text{min}}) = 0$. The maximal restoring force of the Morse potential, $f_{\text{max}} = -dU_M/dr = \alpha M/2$, is reached at the inflection point, $r = r_{\text{min}} + \alpha^{-1} \ln(2) \approx 2.69$. This force $f_{\text{max}}$ determines the maximal tensile strength of the membranes bonds. Since $U_M(0) \approx 2.95$, the Morse potential, Eq. (1), is only weakly repulsive and beads could partially penetrate one another at $r < r_{\text{min}}$. Therefore, in order to allow properly for the excluded volume interactions between bonded monomers, we take the bond potential as a sum of $U_M(r)$ and the so called Weeks-Chandler-Anderson (WCA) potential, $U_{\text{WCA}}(r)$, (i.e., the shifted and truncated repulsive branch of the Lennard-Jones potential),

$$U_{\text{WCA}}(r) = \begin{cases} 4\epsilon [ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}] + \epsilon, & \text{for } r \leq 2^{1/6}\sigma \\ 0, & \text{for } r > 2^{1/6}\sigma \end{cases} \tag{2}$$

with parameter $\epsilon = 1$ and monomer diameter $\sigma = 2^{-1/6} \approx 0.89$ so that the minimum of the WCA potential to coincides with the minimum of the Morse potential. Thus, the length scale is set by the parameter $r_{\text{min}} = 2^{1/6}\sigma = 1$. The nonbonded interactions between monomers are taken into account by means of the WCA potential, Eq. (2). Thus, the nonbonded interactions in our model correspond to good solvent conditions whereas the bonded interactions make the bonds breakable when subject to stretching. External stretching force $f$ is applied to monomers at the membrane rim in direction perpendicular to the respective edge - Fig. 2a.

Before we turn to the problem of membrane failure under constant tensile force, we show here some typical elastic properties of the intact honeycomb network sheet that is used in our computer experiments - Fig. 2. In Fig. 2b, one can see an $S$-shaped variation of the stress - strain relationship with initial significant elongation at vanishing stress due to the straightening of the membrane wrinkles (ripples) that are typical for an unperturbed membrane - cf. Fig. 1b. This behavior is followed by a linear stress - strain elastic relationship where we measure the Young modulus $Y_r = 2.02 \times 10^{-2} \ [k_B T/a^2]$ or $Y_u = 2.95 \times 10^{-2} \ [k_B T/a^2]$, depending whether radial or uniaxial loading is applied. Eventually, for stronger stretching the elasticity of the network decreases as the anharmonicity of the bond potential comes into play. Moreover Fig. 2b indicates that the destructive strain of the whole membrane is considerably less in the case of uniaxial stretching.

In our work we have tried to develop the model which should serve as generic one for all kinds of 2D brittle-elastic networks with honeycomb orientation. We have been anxious to emphasize the common features of failure in materials with similar architecture but largely varying elasticity properties, e.g., from 1000 GPa graphene’s Young modulus compared to $4 \times 10^{-3}$ GPa for spectrin. Putting the value of a Kuhn segment ($\sigma = 1.44$ Å) and taking the thermal energy $k_B T = 4 \times 10^{-21}$ J at $T = 300$ K, we get from our simulation a Young modulus $\sim 0.03$ GPa which is ranged between typical values for rubber-like materials $0.01 \div 0.1$. Compared to ab initio simulations of graphene with linear size $L = 6$ which corresponds to 216 network nodes, our objects are about an order of magnitude larger, $L = 50$ and 2500 nodes, in units of elementary cells.
C. MD algorithm

As in our previous studies concerning scission kinetics of linear chains \[33, 34\] and bottle-brushes \[35\] we use a Langevin dynamics which describes the Brownian motion of a set of interacting particles whereby the action of the solvent is split into slowly evolving viscous (frictional) force and a rapidly fluctuating stochastic (random) force. The Langevin equation of motion is the following:

\[
m \dot{\vec{v}}_i(t) = \vec{F}_i(t) - m \gamma \vec{v}_i(t) + \vec{R}_i(t)
\]

where \(m\) denotes the mass of the particles which is set to \(m = 1\), \(\vec{v}_i\) is the velocity of particle \(i\), \(\vec{F}_i = (\vec{F}_M + \vec{F}_{WCA})_i\) is the conservative force which is a sum of all forces exerted on particle \(i\) by other particles in the system, \(\gamma\) is the friction coefficient and \(\vec{R}_i\) is the three dimensional vector of random force acting on particle \(i\). The random force \(\vec{R}_i\), which represents the incessant collision of the monomers with the solvent molecules, satisfies the fluctuation-dissipation theorem \(\langle \vec{R}_{\alpha}(t) \vec{R}_{\beta}(t') \rangle = 2 \gamma k_B T \delta_{\alpha\beta} \delta(t-t')\) where the symbol \(...\) denotes an equilibrium average and the greek-letter subscripts refer to the \(x\), \(y\) or \(z\) components. The friction coefficient \(\gamma\) of the Langevin thermostat is set to \(\gamma = 0.25\). Our simulation was performed in the weakly damped regime of \(\gamma = 0.25\) where effects of inertia are important. This value of \(\gamma\) is more or less standard in Langevin MD. However, we carried out additional simulation in the strongly damped regime for \(\gamma = 10\). No qualitative changes were discovered except an absolute overall increase of the rupture times \(\tau\) which is natural for a more viscous environment. The integration step is \(0.002\) time units (t.u.) and the time is measured in units of \(r_{\text{min}} \sqrt{m/\epsilon M}\). We emphasize at this point that in our coarse-grained modeling the solvent is taken into account only implicitly. In this work the velocity-Verlet algorithm is used to integrate the equations of motion.

Our MD simulations are carried out in the following order. First, we prepare an equilibrated membrane conformation, starting with a fully flat configuration, Fig. 1, where each bead in the network is separated by a distance \(r_{\text{min}} = 1\) equal to the equilibrium separation of the bond potential \((U_M + U_{WCA})\) [see Eq. 1 and 2]. The external constant force is switched on from the very beginning of the simulation. Then we start the simulation with this prepared conformation and let the membrane equilibrate with the applied force in the heat bath for sufficiently long time \((\approx 10^7\) t.u.) at a temperature that is low enough so that the energy barrier for scission is high and the membrane stays intact. This equilibration is done in order to prepare different starting conformations for each simulation run. Once the equilibration is finished, the temperature is raised to the working one and we let the membrane equilibrate at this temperature for roughly \(\sim 20\) t.u. We have checked that this time interval is sufficient for equipartition and uniform distribution of temperature to be established throughout the membrane sheet. Then the time is set to zero and we continue the simulation with this well-equilibrated membrane conformation checking for scission of the bonds.

We measure the elapsed time \(\tau\) until the first bond rupture occurs and repeat the above procedure for a large number of runs \((10^3 \div 10^4)\), starting each time with a new equilibrated conformation so as to sample the stochastic nature of rupture and determine the mean \(\langle \tau \rangle\) which we refer to as the mean first breakage time. In the course of simulation we also calculate properties such as the probability distribution of breaking bonds regarding their position in the membrane (a rupture probability histogram), the probability distribution function of the first breakage time \(W(\tau)\) (i.e., the MFBT probability distribution), the strain (extension) of the bonds with respect to the consecutive circle number in the membrane, as well as other quantities of interest.

In separate runs each simulation is terminated as soon as the honeycomb sheet disintegrates into two separate parts whereby the time it takes to “rip-off” the sheet is termed “mean failure time \(\langle \tau_f \rangle\) and measured. In order to monitor the propagation of cracks, we perform also individual runs labeling breaking bonds in succession and reconstructing the crack trajectory which is a laborious and rather involved problem.

D. Rupture criterion

An important aspect of our simulation is the recombination (self-healing) of broken bonds. The constant stretching force acting on the monomers at the membrane edges creates a well-defined activation barrier for bond scission. Direct analysis of the one-bond potential with external force, \(U_M(\tau) - f r\) indicates that the positions of the (metastable) minimum \(r_-\) and of the barrier (or hump) \(r_+\) are given by \[36\]

\[
r_{\pm} = \frac{1}{a} \ln \left[ \frac{2}{1 \pm \sqrt{1 - f}} \right]
\]

where \(a\) is the conservative force which is a sum of all forces exerted on particle \(i\) by other particles in the system, \(\gamma\) is the friction coefficient and \(\vec{R}_i\) is the three dimensional vector of random force acting on particle \(i\).
where the dimensionless force $\tilde{f} = 2f/a\epsilon_M$. For the range of tensile forces used in the present study one has typically $r_+ \approx 3r_{\min}$. The activation energy (barrier height) for single bond scission is itself given by $E_b = U(r_+) - U(r_-) = \epsilon_M \left\{ \sqrt{1 - \tilde{f}} + \frac{\tilde{f}}{2} \ln \left[ \frac{1 - \sqrt{1 - \tilde{f}}}{1 + \sqrt{1 - \tilde{f}}} \right] \right\}$

$$E_b = \epsilon_M \left\{ \sqrt{1 - \tilde{f}} + \frac{\tilde{f}}{2} \ln \left[ \frac{1 - \sqrt{1 - \tilde{f}}}{1 + \sqrt{1 - \tilde{f}}} \right] \right\}$$

One can easily verify that $E_b$ decreases with $\tilde{f}$. Since a bond may get stretched beyond the energy barrier and nonetheless shrink back again, i.e. recombine, in our numeric experiments we use a sufficiently large value for critical extension of the bonds, $r_h = 5r_{\min}$, which is defined as a threshold to a broken state of the bond. This convention is based on our checks that the probability for recombination (self-healing) of bonds, stretched beyond $r_h$, is vanishingly small, as demonstrated below. In our model we deal with $E_b/(k_B T) \approx 20$ which at 300 K and bond length $r_{\min} = 0.14$ nm corresponds to ultimate tensile stress $\sim 0.6$ GPa. This is a reasonable value for our membrane which is considerably softer than graphene with $\sim 100$ GPa and is ranged between typical values for rubber materials $0.03 \div 14$ GPa.

III. MD-RESULTS

We examine the scission of bonds between neighboring nodes in the network sheet with honeycomb topology, assuming thermal activation as a driving mechanism in agreement with early experimental work by Brenner [37] and Zhurkov [38]. In Fig. 3 we show a series of representative snapshots of a membrane of size $L = 10$ with $N = 600$ monomers taken at different time moments during the process of decomposition. Typically, the first bonds that break are observed to belong to the last (even) most remote circle as, for example, at $t \approx 171 t_u$. In Fig. 3 As mentioned above, these are the radially oriented bonds which belong to concentric circles of even number. Gradually a line of edge beads is then severed from the rest of the membrane and a crack is formed which propagates into the bulk until eventually a piece of the network sheet is ripped off, as in Fig. 3 at $t \approx 370 t_u$. As we shall see below, this mechanism of membrane failure, whereby an initial crack is formed parallel to the edge monomers, yet perpendicular to the tensile force, dominates largely the process of disintegration under constant tensile force. The process is, therefore, mainly described by two characteristic times, $\tau$ and $\tau_r$, which mark the occurrence of the first scission of a bond (MFBT) and that of the eventual breakdown of the flake into two distinct parts.

A. Bond recombination

As mentioned in Section III throughout in our studies of the brittle sheet breakdown we use a threshold for critical bond stretching (rupture criterion) $r_h = 5r_{\min}$. In the right inset of Fig. 4 we display the function $Q_h(h)$, which represents the probability distribution of bond stretching $h$ beyond the hump position $r_+$, given that a subsequent recombination has taken place. To this end one monitors for $10^4$ integration steps the length of each bond once the bond expands beyond $r_+$ and stores its maximal expansion, $h$, provided such a bond contracts again to $r < r_+$. Then $Q_h(h)$ is computed as the fraction of extensions to $h$ over the total number of recombination events. For each bond recombination one measures also the distribution of the respective self-healing times, $P_h(t)$, which is shown in Fig. 4 too. Both distributions are characterized by exponentially fast decaying tails, indicating that successful recombinations are possible after very short time interval $\approx 1.3 t_u$, and the possible stretching of a bond in such cases is minimal - about 0.19 $\div$ 0.5 beyond the energy barrier position at $r_+ \approx 2.96$, that is, significantly shorter than $r_h \approx 5$. We also find that recombination of bonds takes place seldom (roughly 1.5% over $\cdot 10^4$ runs of average length $\approx 437 t_u$ for a membrane composed of $N = 600$ beads). Yet as indicated below, allowing for self-healing events may significantly change the observed kinetics of membrane destruction. The left inset in Fig. 4 indicates that self-healing of bonds happens most frequently at the membrane periphery, $C = 19$, where bond stretching occurs most frequently.

B. Mean First Breakage Time

These conclusions, based on visual evidence from snapshots taken in the course of membrane decomposition, are corroborated in Fig. 5a where we show the probability distribution of a first rupture for all bonds in the honeycomb membrane flake as a 3D plot. It is seen that the scission rate is localized in the outer-most circle of radial bonds whereas bonds in the inner part of the membrane practically hardly break. Note that this is not a trivial effect since tension is distributed uniformly over all bonds in the equilibrated membrane so there is no additional propagation of
FIG. 3: Snapshots illustrate the process of bond breakage (crack generation) in different time moments for a membrane with $N = 600$ particles subject to external tensile force $f = 0.15$ at $T = 0.05$ and $\gamma = 0.25$. The force is applied to periphery monomers only and stretches the network perpendicular to its original edges.

the tension front from the rim towards the center. Fig. 5b also indicates a qualitative change in the rupture PDF when self-healing is not allowed for (by reducing the threshold position to that of the energy barrier - $r_h = 3.1$) in contrast to results where self-healing was fully taken into account - $r_h = 5$. Moreover, a closer inspection the new Fig. 5b indicates that scission of bonds with no self-healing takes place almost uniformly throughout the membrane while with self-healing it is concentrated only at the membrane periphery.

One can try to relate this finding to the distribution of strain within the network as shown in Fig. 6a and sampled for several strengths of the external stretching force $f$. In the case of strongest pulling, $f = 0.15$, the variation of the mean-squared bond length $\langle l^2 \rangle$ with distance from the membrane center (i.e., with consecutive circle number $C$) displays a well expressed saw-tooth behavior whereby the peaks correspond to bonds with radial rather than tangential orientation (odd $C$). The alternation of strongly / weakly stretched bonds modulates the overall gradual increase of the mean bond length with growing distance from the center. Evidently, the amplitude of the mean-squared bond length attains a pronounced maximum on the last circle of radially oriented network bonds. This distribution of strain is found to persist down to vanishing tensile force $f = 0$ - Fig. 6a. The distribution of first scission events is clearly seen in Fig. 6b, where we show it for several strengths of $f$. Evidently, with growing value of $f$ bonds happen to break also deeper inside the membrane although such events remain much less probable.
FIG. 4: Probability distribution $P_h(t)$ of maximal times (full circles), and $Q_h(h)$ of maximal bond lengths $h$ (circles, right panel of inset) before a recombination event in the stretched membrane with $N = 600$, $T = 0.1$, $\gamma = 0.25$ takes places. The exponential tail of $P_h(t)$ is fitted by blue line. The exponential decay of $Q_h(h)$ is given by red line. The left panel of the inset shows the healing probability $R_h$ vs. circle number $C$. The healing events under applied stress occur roughly 10 times less frequently than for $f = 0$.

FIG. 5: (a) Rupture probability histogram of flexible hexagonal membrane subjected to external tensile stress $f = 0.15$. (b) Scission probability histogram vs consecutive circle number for membrane pulled with $f = 0.125$ displayed for different rupture thresholds $r_h$ as indicated. Real rupture events ($r_h = 5.0$) are concentrated at the periphery whereas fictitious ones ($r_h = 3.1$) are distributed more uniformly all over the membrane. Here $N = 600$, $T = 0.05$ and $\gamma = 0.25$.

The variation of the MFBT $\tau$ with system size $N$ (i.e., with the number of monomers in the membrane $N = 6L^2$ where $L$ denotes the linear size of the flake) is shown in Fig. 7. For sufficiently large membranes one observes a power law decline of the MFBT, $\tau \propto N^{-\beta}$ with an exponent $\beta \approx 0.5 \pm 0.03$ for the tensile forces studied. If thermally activated bonds break independently from one another and entirely at random, then the MFBT $\tau$ measures the interval before any of the available intact bonds undergoes scission, that is, either the first bond breaks, or the second one, and so on which, at constant rate of scission, would reduce the MFBT $\tau \propto 1/N$ as observed for instance in the case of thermal degradation of a linear polymer chain [34]. A more comprehensively this simple result can be derived by means of the classical theory of Weibull. In the present system of a honeycomb membrane the bonds that undergo rupture are nearly all located at the rim of the flake and their number is proportional to $L$ so that with $\beta \approx 0.5$, cf. Fig. 7 and $N \propto L^2$, one obtains eventually the important result $\tau \propto 1/L$. This observation is in agreement with recent results of Grant et al. [29] who studied the nucleation of cracks in a brittle 2D-sheet. We should like to point
FIG. 6: (a) Variation of the mean squared bond length $\langle l^2 \rangle$ with consecutive circle number in a membrane with $N = 5400$ beads subjected to different strengths of the external force $f$ (as indicated in the legend). (b) Probability distribution of the first bond scission event vs circle number in a membrane with $N = 600$ beads at different strengths of the external force $f$ as indicated. For a force $f \leq 0.15$ the bonds from the last two outer circles (#18 and #19) in the membrane have the highest rupture probability. With increased strength of the pulling force $f \geq 0.175$ the bonds which are located in the circles #18 and #16 attain the highest rupture probability. Parameters of a heat bath are $T = 0.05$ and $\gamma = 0.25$.

out at this place that without self-healing, c.f., Fig. 5(b), rupture time goes as $\langle \tau \rangle \propto N^{-\beta}$, with $\beta \approx 1$ (not plotted here) in contrast to the observed exponent $\beta \approx 0.5$.

One should mention here an interesting analogy between the observed power-law dependence of the MFBT time on system size and the power-law decrease of life-time with system size in thermally activated breakdown of fiber bundles [30, 31]. While both in our honeycomb network as well as in the Fiber Bundle Model (FBM) the failure mechanism is related to redistribution of load on neighboring bonds (fibres) upon single rupture, bonds in our membrane are subject to a single scission threshold whereas in the FBM there is a random distribution of tensile strengths. As a result, one finds a single value of $\beta \approx 0.5$ and an Arhenian dependence of $\tau$ on temperature $T$ in our elastic-brittle honeycomb network (see below) while the exponent $\beta$ depends on the external load $f$ and on $T$ giving rise to a non-Arhenian $\tau$ vs. $T$ relationship.

Note that the decline of MFBT $\tau$ in a topologically connected brittle system is by no means a trivial one. In a recent study [33], using Molecular Dynamics (MD) simulation of a single anharmonic polymer chain subject to constant external tensile force, we found a rather complex interplay between the polymer chain dynamics and the resulting bond rupture probability distribution along the chain backbone. In a breakable chain (rather than 2D network) it was observed that the corresponding power $\beta \rightarrow 0$ as $N \rightarrow \infty$. A major role in this was attributed to nonlinear excitations as the possible origin for the observed increasing insensitivity of rupture time with respect to polymer length as the pulling force grows. One may thus conclude that nonlinear effects in bond scission are suppressed in 2D honeycomb networks.

One can also see from the inset in Fig. 7, that the MFBT $\tau$ decreases rapidly with growing stress $f$, that is, the energy barrier for rupture declines with $f$ in agreement with Eq. (5) and Zhurkov’s experiments [38]. The probability distribution of MFBT $W(t)$ is shown in Fig. 7(b). It is well described by a Poisson probability distribution function $W(t) = 5.57 \cdot 10^{-3} t^{1/3} \exp(-t/291.85)$.

C. Cracks and Mean Failure Time

The variation of $\tau_r$, the mean failure time of the membrane with system size $N$, shown in Fig. 8, displays also a power-law dependence on system size $N$, $\langle \tau_r \rangle \propto N^{-\phi}$, whereby $\phi$ undergoes a cross-over to a lower value beyond roughly $N > 300$. However, $\tau_r$ has different physical meaning. Following Pomeau [39], the failure time can be approximately identified with the nucleation of a crack of critical size $l_c$ given by Griffith’s critical condition [24, 40] assuming that crack propagation is much faster than the nucleation time. For a 2D-geometry consisting of a flat brittle sheet with a crack perpendicular to the direction of stress, the potential energy per unit thickness of the sheet
reads \( U = -\pi l^2 f^2 + 2\varepsilon l + U_0 \) where \( Y \) is the Young modulus, \( \varepsilon \) is the surface energy needed to form a crack of length \( l \), and \( U_0 \) is the elastic energy in the absence of stress \( (f = 0) \). This energy reaches a maximum for a critical crack length \( l_c = \frac{4Y\varepsilon}{f^2} \) beyond which no stable state exists except the separation of the sheet into two broken pieces. Thus, with a crack nucleation barrier \( \Delta U = \frac{4Y\varepsilon}{f^2} \) (in 3D \( \Delta U \propto f^{-4} \)), the failure (rip-off) time \( \tau_r = \tau_0 \exp(\Delta U_0/k_B T) \) as found in experiments with bidimensional micro crystals by Pauchard and Meunier [41] and in gels by Bonn et al. [42]. In Fig. 8b, we present the variation of \( \tau_r \) for membrane failure with stress \( f \) in good agreement with the expected relationship \( \Delta U \propto f^{-2} \). In addition, we show the variation of \( \tau_r \) with temperature, see inset in Fig. 8b, which is found to follow a well expressed Arhenian relationship with inverse temperature, in agreement with earlier studies [29, 40].

The end of the sheet rupturing process is marked as a rule by disintegration into two pieces of different size so it is interesting to assess the size distribution of such fragments upon failure. In the inset in Fig. 8a, we show a probability
distribution $S(n)$ of the sizes of of both fragments upon membrane rip-off. In a membrane composed of $N$ beads one observes a sharp bimodal distribution with narrow peaks at sizes $N_1 \approx 10$ and $N_2 \approx 140$. Evidently, for the adopted nearly radial direction - cf. Fig. 2h - of the applied tensile force one always finds a pair of one small and another very large fragment.

One can readily verify from the typical topology of the observed cracks in the membrane, presented in Fig. 9, that

(i) cracks emerge as a rule perpendicular to the direction of applied stress, and (ii) it is almost always the first row of nodes to which the tensile force is immediately applied that gets ripped off upon failure. Cracks that break the network sheet in the middle occur very seldom, in compliance with the sampled distribution of fragment sizes, $S(n)$.
in the inset of Fig. 8a. One would, therefore, predict a breakup of a protective cover spanned on the orifice of tube like the one shown in Fig. 9 to proceed immediately at the fixed orbicular boundary where the tensile force applies to the network. It is interesting to note that the geometry of cracks in the membrane shown in Fig. 9 appears very similar to the one observed in drying induced cracking of thin layers of materials subject to structural disorder [32].

The emerging cracks are expected to propagate with speed that increases as the strength of the external force is increased as the inset in Fig. 10a indicates. In fact, in Fig. 10b one observes typical curves comprising a series of short intervals with steep growth of the number of broken bonds per unit time and longer horizontal 'terraces' preceding the nucleation of a new crack. Even though the data, presented in Fig. 10a, is not averaged over many realizations, and, as Fig. 10b suggests, individual realizations of propagating cracks may strongly differ even at the same stress $f$, a general increase of the propagation velocity with growing external force $f$ - see inset - can be unambiguously detected, in agreement with earlier observations [20].

For our model membrane with computed Young modulus $Y \approx 0.02$ we get for the Rayleigh wave speed $c_R \approx 0.14$. Thus for most of the applied tensile stress values we observe crack propagation at speed less than $c_R$ - inset in Fig. 10b). As argued by [43] propagation speed cannot exceed $c_R$ because crack splits off into multiple cracks before reaching $c_R$. In contrast, Abraham and Gao in Ref. [44] have reported on cracks that can travel faster than the Rayleigh speed. Thus, our rough estimates (inset in Fig. 10) agree well with data from literature. Converting our results to proper metric units, with bond length $\sigma \approx 0.144$ nm and energy $\approx 20k_BT$ which yields 1 MD t.u. $\approx 10^{-12}$ s, we estimate the typical crack propagation speed $v_c \approx 50$ m/s. Note that mean crack speed for natural latex rubber was given as 56 m/s [45].

**IV. SUMMARY**

In the present work we have studied the bond rupture and ensuing fracture of a honeycomb brittle membrane subject to uniform radially applied external stretching forces for different values of force $f$, temperature $T$, and membrane size $N$. The most important conclusions that can be drawn from our Molecular Dynamics simulation can be summarized as follows:

- bonds scission in hexagonal 2D sheets with honeycomb structure of the underlying network under subjected to external pulling perpendicular to flake’s edges take place overwhelmingly at the sheet periphery
- The Mean First Breakage Time of breaking bonds depends on membrane size $N$ as a power law, $\tau \propto N^{-\beta}$ with $\beta \approx 0.50 \pm 0.03$.
- The failure time $\tau_r$ until a brittle sheet disintegrates into pieces follows a power law too, $\tau \propto N^{-\phi(f)}$, and an exponential decay $\tau_r \propto \exp(\text{const}/f^2)$ upon increasing strength of the pulling force, in agreement with Griffith’s criterion for failure.
- cracks emerge in the vicinity of membrane edges and typically propagate parallel to the edges, splitting the sheet in two pieces of size ratio of $\approx 7\%$.
- crack propagation speed is observed to increase rapidly with tensile force

We believe that these findings can be seen as generic also for 2D network brittle sheets of different geometry (hexagonal lattices, or quadratic lattices with second nearest-neighbor bonding) where similar interplay between elastic and fracture behavior is expected to take place. It is clear, however, that more investigations are needed before a full understanding of fracture in such systems is achieved.

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