Crumpling Damaged Graphene

I. Giordanelli, M. Mendoza, J. S. Andrade, Jr., M. A. F. Gomes, and H. J. Herrmann

1 ETH Zürich, Computational Physics for Engineering Materials, Institute for Building Materials, Wolfgang-Pauli-Strasse 27, HIT, CH-8093 Zürich, Switzerland
2 Departamento de Física, Universidade Federal do Ceará, Campus do Pici, 60155-760 Fortaleza, Ceará, Brazil
3 Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife-PE, Brazil

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Through molecular mechanics we find that non-covalent interactions modify the fractality of crumpled damaged graphene. Pristine graphene membranes are damaged by adding random vacancies and carbon-hydrogen bonds. Crumpled membranes exhibit a fractal dimension of $2.71 \pm 0.02$ when all interactions between carbon atoms are considered, and $2.30 \pm 0.05$ when non-covalent interactions are suppressed. The transition between these two values, obtained by switching on/off the non-covalent interactions of equilibrium configurations, is shown to be reversible and independent on thermalisation. In order to explain this transition, we propose a theoretical model that is compatible with our numerical findings. Finally, we also compare damaged graphene membranes with other crumpled structures, as for instance, polymerised membranes and paper sheets, that share similar scaling properties.

Keywords: Crumpling transition, graphene, vacancies, hydrocarbons, fractal dimension, self-affinity, non-covalent interactions

Graphene is a truly two-dimensional material of extraordinary mechanical and electronic properties [1–3]. It naturally forms ripples even at zero temperature, overcoming the restriction on long-range 2d order imposed by the Mermin-Wagner theorem [4]. Graphene sheets can be systematically damaged, for instance by creating vacancies through irradiation [5]. Remaining unsaturated carbon bonds are quite reactive but can be neutralized with hydrogen. Driven by thermal fluctuations, damaged graphene membranes (DGM) exhibit a tendency to crumple. How this crumpling takes place and on which ingredients it depends, is the subject of the present Letter.

Through sophisticated molecular mechanics simulations we show here that, for sufficient degree of damage, graphene sheets become fractal with a dimension that depends on the interaction range of the potential. Non-covalent interactions (NCIs) like van der Waals forces play such a dominant role, that they not only densify the molecular structure but even enhance the fractal dimension of DGM by over 20%.

We simulate DGMs using molecular mechanics with the adaptive intermolecular reactive bond-order (AIREBO) potential [6]. This many-body potential has been developed to simulate molecules of carbon and hydrogen. The AIREBO potential is defined by a sum over pairwise interactions,

$$\text{E} = \frac{1}{2} \sum_{i} \sum_{j \neq i} \left[ E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{ijkl}^{\text{TORS}} \right],$$

(1)

where $E_{ij}^{\text{REBO}}$ represents the covalent bonding interactions, $E_{ijkl}^{\text{TORS}}$ is the torsion term that ensures the correct dihedral angles, and $E_{ij}^{\text{LJ}}$ is a modified Lennard-Jones term accounting for the NCIs between the atoms [6]. $E_{ij}^{\text{LJ}}$ only acts between atoms if they are not connected directly or indirectly through covalent bonds within a range between 2 Å and 8.5 Å. The AIREBO potential is widely used for simulating molecules with more than $10^3$ carbon atoms, where ab initio simulations are computationally too expensive.

FIG. 1. Typical realization of a damaged graphene membrane (DGM) generated with a vacancy density of $p_v = 0.303$ and a system size of $L = 60$ Å. Green spheres represent carbon and white spheres hydrogen atoms. The initial configuration is shown in (a). The corresponding crumpled DGM after 1.8 ns at $T = 0$ K is shown in (b) without NCIs, and in (c) with NCIs.
The initial building block for our DGM is a quadratic graphene membrane (two-dimensional hexagonal carbon mantle) with a bond length of 1.4 Å and an initial edge length of L = 60 Å. To introduce disorder, we create vacancies by randomly removing carbon atoms, obtaining vacancy concentrations ranging from p = 0 to the critical percolation point pc = 0.303 for hexagonal lattices, which is the highest possible vacancy concentration that can be achieved for our purpose, because only small clusters remain for higher values of p. After damaging the graphene membranes with vacancies, we extract the largest connected cluster. This carbon cluster is chemically very reactive because some carbon atoms are left with less than three neighbours. We then reduce the reactivity of the system by adding hydrogen atoms. To each carbon atom with only two neighbours, we add two hydrogen atoms, one in positive and one in negative z-direction. Therefore, we do not saturate the benzene rings in the disordered hexagonal lattice, allowing to keep sp² hybridisation and the conjugated bonds. By applying this procedure, we obtain for p = 0 a graphene sheet where the open edges with dangling σ-orbitals are terminated by carbon-hydrogen bonds. The densities of these DGMs exhibit a power-law dependence on p.

We perform simulations with several realizations of DGMs for different vacancy densities p. We set the time step for the molecular mechanics simulation to 0.1 fs, which is sufficiently small to capture the carbon-carbon and the carbon-hydrogen interaction properly. In order to fix the temperature, we apply a Nosé-Hoover thermostat obtaining the equilibrium state of the DGM in the canonical ensemble (NVT). Each simulation begins with a flat DGM located in the x-y plane at a temperature of 800 K (see Fig. 1a). Subsequently, we cool down the structure gradually using a step size of 25 K, giving enough time for equilibration at each temperature (see Fig. 1b). To increase the precision during the last 25 K, we decrease the temperature step size to 5 K until we reach 0 K (see Fig. 1c). The equilibration time for each temperature step is chosen proportional to the number of carbon atoms contained in the DGM. Once the sheet reaches 0 K, we start performing the measurements for the fractal dimension. Finally, in order to analyse the influence of the NCI, we deactivate the EijLJ interactions of the potential described in Eq. (1), repeat all simulations, and compare the results with the corresponding ones obtained when NCIs are present.

The obtained DGM structures are characterized in terms of the gyration tensor and the fractal dimension. We first compute the center of mass, i.e. \( \vec{r}_{cm} = 1/M \sum_{i=1}^{N} m_i \vec{r}_i \), where M is the total mass of the structure (the mass of carbon atoms is set to 12 atomic units and the one of hydrogen atoms to 1 atomic unit), and shift the origin of the coordinate system to the center of mass frame. The gyration tensor is then obtained by

\[
S_{mn} = \frac{1}{M} \sum_{i=1}^{N} m_i \left( r_i^{(m)} - \bar{r}_m \right) \left( r_i^{(n)} - \bar{r}_m \right)
\]  

(2)

where \( m, n \in \{1, 2, 3\} \). This matrix is symmetric and, therefore, its eigenvalues \( \lambda_n \) are real and their associated eigenvectors orthogonal to each other. The eigenvalues \( \lambda_n \) correspond to the extensions in the direction of their eigenvectors. The sum of the eigenvalues gives the square of the radius of gyration, \( R_g^2 = \lambda_1 + \lambda_2 + \lambda_3 \). The radius of gyration \( R_g \) is an appropriate measure to quantify the compactness of various structures, like for instance organic molecules [7]. Furthermore, if the structure is fractal, \( R_g \) should relate with the mass \( M \) of the total DGM as a power law,

\[
R_g \sim M^{\frac{d_F}{D}}
\]

(3)

To obtain the fractal dimension we use the sand-box method through the relation \( M(r) \propto r^{d_F} \), where \( M(r) \) is the mass of the atoms contained in a sphere of radius r and origin at the closest atom to the center of mass (See Fig. S1 of the Supplementary Material). We compute \( M(r) \) in discrete exponential intervals, \( r_k = 1.05^k \), where \( k \in \mathbb{N} \). With the sand-box method we obtain a \( d_F \) for each single DGM.

Figure 2 shows the radius of gyration \( R_g \) for different temperatures and vacancy densities \( p \). We observe that \( R_g \) is strongly dependent on temperature and can vary.
The crumpling driven by mechanically compressing an isotropic elastic shell that contains a graphene membrane led to the same fractal dimension within error bars [17]. In contrast to region I, we observe that in region II the DGM extends in all three principal axes \((\lambda_3/R_g^2, \Lambda_3/R_g^2 > 0)\) being essentially isotropic close to the center of mass (See Supplementary Material Fig. S3). In this case, the sheets crumple resulting in a fractal dimension \(d_F = 2.71 \pm 0.02\), when all interactions between two atoms are considered. The three eigenvalues \((\lambda_n)\) do not change significantly in this region. Surprisingly, the simulations without NCI reveal a much smaller fractal dimension, \(d_F = 2.30 \pm 0.05\), showing that the NCI play a crucial role in compressing the DGMs. In principle, our simulation allows for the creation of new covalent bonds during the crumpling process. However, as shown in the Supplementary Material, and contrary to the significant influence of the NCIs, the impact of newly formed covalent bonds on the crumpled structure is practically negligible.

As depicted in Fig. 4, the crumpling transition takes place in the intermediate region II, for which \(0.1 < p < 0.22\). Close to \(p = 0.1\), some stronger deformations orthogonal to the original plane of the hydrocarbon sheet \((p = 0)\) become visible (as an increase in \(\lambda_3/R_g^2, \Lambda_3/R_g^2\)) and the DGM starts to expand stronger in one specific direction, as reflected by an increase of the ratios \(\lambda_1/\lambda_2, \Lambda_1/\Lambda_2\). However, the fractal dimension must be evaluated carefully due to the high anisotropy of the structure for low values of \(p\) (See Supplementary Material). Therefore, the continuous change in \(d_F\) in region II seems to be only a finite-size effect and thus we expect that this region will shrink to a transition point by increasing the system size, leading to a discontinuous change in fractal dimension in the thermodynamic limit.

Interestingly, similar fractal dimensions have been found experimentally for dry and fresh cream layers, \(2.65 \pm 0.10\) and \(2.45 \pm 0.15\), respectively [9], as well as theoretically for saturated hydrocarbon structures at the critical point of percolation, \(2.63 \pm 0.15\) [10]. In the first case, the fractal dimension is higher for dry layers because the water molecules between the polymerised membrane is evaporated. The interactions with water molecules seem to screen the NCIs within atoms of the polymerised membrane and, in analogy to our findings, produce a less compact structure. A well defined fractal dimension is also observed in many other crumpling processes such as paper sheets [11] and wires crumpled to spherical compact balls [12, 13], just to name a few [14, 15]. In Ref. [16], the authors studied self-avoiding surfaces as possible models of rapidly polymerising polymer membranes and found that self-avoiding surfaces might act similarly to DGM without NCI, where only the short-range covalent-bond repulsion is left. As a consequence, the reported Monte Carlo simulations produced self-avoiding surfaces with \(d_F = 2.35 \pm 0.05\), which is in agreement with our results. The crumpling driven by mechanically compressing an isotropic elastic shell that contains a graphene membrane led to the same fractal dimension within error bars [17].

One can develop an effective theory to explain the frac-
FIG. 4. Fractal dimension $d_F$ computed with the sand-box method for different fractions of vacancies $p$. The values of $d_F$ correspond to averages over 40 realizations of DGMs for $p < 0.1$ and 100 realizations for all other values of $p$. The blue circles correspond to the DGM after equilibration considering all the interactions. The dashed blue line indicates the average of $d_F$ calculated over the values within region III. The red diamonds correspond to $d_F$ after equilibration in absence of NCIs. The dashed red line is the average of $d_F$ without NCIs for region III. The green squares result from simulations that were first performed with all interactions and, after that, equilibrated again without NCI. The black triangles correspond to simulations that were first performed without NCIs and, after that, equilibrated again considering all interactions.

delimit three characteristic regions, depending on the degree of damage imposed to the graphene sheets: in region I ($p < 0.1$), the DGM is only extended in two principal axes and $d_F \approx 2$; in region II ($0.1 < p < 0.22$), a system size dependent transition occurs from a two-dimensional (flat) to a three-dimensional object (crumpled); and in region III ($p > 0.22$), we observe essentially isotropic and crumpled DGM. The crumpled graphene sheets are self-similar, with a fractal dimension of $2.71 \pm 0.02$ and $2.30 \pm 0.05$ for simulations with and without NCIs, respectively. From this last result, we deduce that the NCI play a crucial role in the crumpling process during compression of DGMs. Finally, we also provide a phenomenological model that describes qualitatively our numerical findings. We expect an experimental confirmation of our results to be, in principle, realizable in two steps: i) the vacancy creation in pristine graphene, and ii) the binding of hydrogen atoms to graphene sheets with vacancies. The first step could be carried out with electron or ion irradiation [19, 20], whereas the second step could be performed by exposing the graphene membrane with vacancies to a cold hydrogen plasma [21]. Finally, the effect of NCIs on the crumpling process might be duly attenuated by submerging the DGMs in an appropriate solvent.

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Supplementary Material: Crumpling Damaged Graphene

I. Giordanelli,1,∗ M. Mendoza,1, † J. S. Andrade, Jr.,1,2, † M. A. F. Gomes,3, § and H. J. Herrmann1,2, ¶

1ETH Zürich, Computational Physics for Engineering Materials, Institute for Building Materials, Wolfgang-Pauli-Strasse 27, HIT, CH-8093 Zürich, Switzerland
2Departamento de Física, Universidade Federal do Ceará, Campus do Pici, 60455-760 Fortaleza, Ceará, Brazil
3Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife-PE, Brazil

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This supplementary material contains some additional details regarding the fractal dimension measure, the anisotropy and asphericity of crumpled damaged graphene sheets, the contribution of newly formed covalent bonds and the derivation of the theoretical model presented in the paper.

Fractal dimension

In order to determine the fractal dimension systematically and consistently, in the case of the sand-box method, we have to determine first the power-law range for each DGM separately. A least-squares fit to the data is then applied and the resulting exponents are averaged over all DGM realizations.

\[
\ln(M) = a \ln(R) + b
\]

\[
\ln(R) = a_R g, \quad a = 0.19, \quad R_g \text{ as appropriate values for the lower and upper threshold, respectively. The dashed green lines delineate the thresholds of the scaling region. The fractal dimension for this particular case is } 2.71 \pm 0.03 \text{ and corresponds to a graphene sheet with } p = 0.28.
\]

In Fig. S2 we show the largest sphere used by the sand-box method. The structure is between the flat and the crumpled state. We clearly see that the DGM is still two-dimensional with some ripples and the spheres of the sand-box method contain regions where there are no atoms. On the contrary, in Fig. S3 we see that the sphere is completely contained in the DGM.

Ensemble method

We provide further evidence that the crumpled DGM is fractal using an additional method, which we will call the ensemble method. It is based on the relation between the radius of gyration \( R_g \) and the mass \( M \) of the DGM as expressed by Eq. (3). Different system sizes are required for this method. Small system sizes have a very small isotropic core and are thus not appropriate for measuring the fractal dimension. In contrast, large system sizes would produce accurate results but at a very high computational cost. Therefore we focus on intermediate system sizes in the range of 24—60 Å. We observe that the fractal dimension increases in region II as it does with the sand-box method (see Fig. S4). However, the plateau obtained with the sand-box method (seen in region III of Fig. 4) is more pronounced than with the ensemble-method seen in Fig. S4.
FIG. S3. DGM at $p = 0.28$. The green points represent carbon atoms, the blue points hydrogen atoms and the red point the center of mass. The radius of the sphere corresponds to the radius of gyration and covers the isotropic core of the structure.

FIG. S4. Fractal dimension computed with Eq. (3) (ensemble method) for sheets of different initial sizes ranging from 24 to 60 with NCIs.

**Cooling process and fractal dimension**

From Fig. S5 we see that as we decrease the temperature of the samples we converge to the fractal dimension $d_F$.

**Anisotropy and asphericity**

The eigenvalues of the gyration tensor are also useful for computing several shape descriptors. Shape descriptors of particular interest are the relative shape anisotropy $\kappa^2$ and asphericity $b$ (see Fig. S6). The former is a measure for anisotropy and can reach values between 0 and 1. The value 0 occurs when all particles are spherically symmetric and thus the structure is completely isotropic, 0.25 occurs when the particles lie on a plane, and 1 occurs when all points lie on a line. We observe that $\kappa^2$ reaches a value of 0.25 for $p = 0$ and decreases for higher values of $p$, providing evidence that the DGM is more isotropic for large values of $p$. The asphericity $b$, which is the second shape descriptor considered, is a quantity that is 0 for particles that are spherically symmetric. We observe that the asphericity is also decreasing as a function of $p$ with a turning point in region II, which is the region where the DGM crumples.

**Contribution from new covalent bonds**

In this section we study the evolution of the covalent bonds. It is reasonable to believe that possibly newly-formed covalent bonds increase the compactness of the structure. It might be also possible that during the evolution, some new covalent bonds are temporarily created. They could play an important role in the crumpling transition.

To address these questions we modified the simulation such that, whenever new covalent bonds are formed, a force is produced that, tries to separate the covalent bonds again. This does not allow the DGM to keep
newly-formed covalent bonds. Figs. S7 and S8 clearly show that the impact of newly formed covalent bonds is negligible. There are some new bonds which are created, but they disappear again some time steps later.

**Theoretical model**

An effective theory can be formulated to explain the fractal dimensions obtained from our simulation results. The mass-size scaling $M \propto R^{2.3}$ valid for DGM in absence of NCIs is reminiscent of many other situations including DLA growth [1], aggregating proteins [2], crumpled paper [3], ensemble average of large groups of proteins [4], and DNA in chromosomes [5, 6], all of satisfying $M \propto R^{2.5}$, differing $\approx 8\%$ in the scaling exponent. The recurrence of $d_F$ for these structures, in spite of chemical and physical peculiarities, suggests a common underlying origin. In fact, a mean-field phenomenological model using an entropic elastic energy $U_S = AR^2$ [7], and a two-body repulsive energy $U_{SA} = B\rho^2V$ can explain this scaling. In the last term, $\rho$ is the average density given by mass/volume $= M/V$, with $V \propto R^3$, and consequently, $U_{SA} = BM^2/R^3$. The entropic energy favours collapsed configurations of the system, but the second term, due to self-avoidance interactions, favours open, more extended, configurations of the sheet. Physically, the prefactor $A$ in $U_S$ is expected to depend on the percentage of vacancies as $p^z$, with $z > 0$; that is, the entropy of the sheet increases with the damage level. After minimisation of $E = U_S + U_{SA}$ with respect to $R$, the mass-size relation $M \propto R^{2.5}$ follows straightforwardly. If NCIs expressed through a modified Lennard-Jones potential are present, their attractive part that decays as $1/R^6$ tends to combine with the positive $U_{SA}$ term leading to a repulsive potential that effectively behaves more singularly.
Our candidate for this composition of energies is a four-body energy which decays as $U^{NCI}_{SA} = C \rho^4 V = CM^4 / R^9$. According to this qualitative model, in order to explain the crumpling transition observed in DGM in the presence of NCI, we conjecture that the relevant energy $E$ of the damaged sheet has the form $E = AR^2 + CM^4 / R^9$, which after minimisation leads to $M \propto R^{2.75}$, in conformity with Fig. 4, i.e. the attractive part of the non-covalent interaction favours more compact conformations with a greater fractal dimension, and the radius of gyration $R_g = (9C/2A)^{1/11} M^{4/11}$ is expected to scale inversely with $p$ (as $p^{-2/11}$), as suggested by Fig. 2. For completeness, Fig. 4 shows that there is reversibility between the processes leading to the conformations with fractal dimensions $d_F = 2.71 \pm 0.02$ and $d_F = 2.30 \pm 0.05$, i.e. with and without NCIs, respectively. Thus, if the steady-state configuration is initially obtained with NCI, the sudden elimination of this interaction restores the less compact structure with $d_F = 2.30$, and vice-versa.

* gilario@ethz.ch
† mmendoza@ethz.ch
‡ soares@fisica.ufc.br
§ mafg@ufpe.br
¶ hjherrmann@ethz.ch