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Development of Interatomic Potentials for Large Scale Molecular Dynamics Simulations of Carbon Materials under Extreme Conditions

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Development of Interatomic Potentials for Large-Scale Molecular Dynamics Simulations of Carbon Materials under Extreme Conditions

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Abstract

The goal of this PhD research project is to devise a robust interatomic potential for large-scale molecular dynamics simulations of carbon materials under extreme conditions. This screened-environment dependent reactive empirical bond order potential (SED-REBO) is specifically designed to describe carbon materials under extreme compressive or tensile stresses. Based on the original REBO potential by Brenner and co-workers, SED-REBO includes reparametrized pairwise interaction terms and a new screening term, which serves the role of a variable cutoff. The SED-REBO potential overcomes the deficiencies found with the most commonly used interatomic potentials for carbon: the appearance of artificial forces due to short cutoff that are known to create erroneous phenomena including ductile fracture of graphene and carbon nanotubes, which contradicts the experimentally observed brittle character of these materials. SED-REBO was applied in large scale molecular dynamics simulations of nanoindentation of graphene membranes and shock-induced compression of diamond. It was shown in the first computational experiment that graphene membranes exhibit a non-linear response to large magnitude of indentation, followed by a brittle fracture in agreement with experiments. The strength of graphene was determined using the kinetic theory of fracture, and the crack propagation mechanisms in the material were identified. It was found in large-scale shock simulations that SED-REBO improves the predictive power of MD simulations of carbon materials at extreme conditions.
Chapter 1

Introduction

At the crossroad of theory and experiment, computer simulations play a key role in material science by both validating theoretical predictions and supplementing experimental findings at conditions that are sometimes difficult or even impossible to reach in experiment. Depending on the time and length scales of the investigated phenomena, various simulation techniques can apply to various modeling hierarchies, often sacrificing accuracy while increasing simulation times and system dimensions. For example, although ab initio or first-principles methods solve the Schrödinger equation for electrons within the atoms and solids, they are limited to systems of just a few hundred atoms. In contrast, finite element methods treat the materials at meso and macro time and length scales but fail to provide the underlying mechanisms at the atomic scale. Of course, the choice of a specific simulation technique is entirely guided by the nature of the investigated phenomena. In contrast to first-principles methods, molecular dynamics (MD) simulations efficiently describe systems consisting of hundreds of millions of atoms at the nano-meter and nano-second length and time scales [2–4]. The first MD simulations were performed in the late fifties to early sixties by Alder, Rahman and others [5–8]. Currently MD is still a very powerful method that is used to investigate a wide variety of problems, including testing of theoretical models and potential functions [3, Sections 2.2 (by Y. Mishin) and 2.4 (by J. Justo)], diffusion and adsorption processes [9, 10], determination of materials’ phase diagrams [11, 12], phase coexistence and phase transitions [13, 14], equilibrium structures and dynamics of polymer chains [15, 16], structure determination and dynamics of proteins [17, 18], hydrodynamic instabilities [19, 20] and many other phenomena. One of the first published MD
Figure 1.: Hierarchy of computational models (from Ref. [1]).
works was notably Rahman’s study of the motion of argon gas molecules using a simple Lennard-Jones potential to describe the atomic interactions [8]. In this seminal work, the atoms were represented as spheres interacting according to a specified potential function $V(r)$, and obeying Newton’s classical equations of motion, thus being represented in the microcanonical ensemble of statistical mechanics (NVE). Through the use of thermostat or barostat, the simulations can also be ran within the canonical (NVT) or isobaric-isothermal (NPT) ensembles. As a result, the method yields the full dynamical description of a system, including trajectories and velocities of each atom, thus allowing calculation of the thermodynamical properties of the system, such as energy, temperature, pressure, etc. The algorithm for a MD simulation can be summarized in the following way, see Fig. 2.

Provided that the potential energy and the initial atomic positions for a system are known, the forces acting on each atom are calculated. The atomic positions are then updated at a time $t + \Delta t$, where $\Delta t$ is chosen to be small enough to allow for numerical differentiation based on various schemes of Taylor expansion, see Fig. 2. The most popular “integrator”, or update method, is the Verlet algorithm, where the positions and velocities at $t + \Delta t$ are calculated using positions at $t$ and $t - \Delta t$, as well as the accelerations at $t$:

$$
\vec{r}(t + \Delta t) = 2\vec{r}(t) - \vec{r}(t - \Delta t) + \vec{a}(t)\Delta t^2 \quad (1.1)
$$

$$
\vec{v}(t + \Delta t) = \frac{\vec{r}(t + \Delta t) - \vec{r}(t - \Delta t)}{2\Delta t} \quad (1.2)
$$

while another method, the velocity Verlet scheme, uses only positions, velocities and accelerations at time $t$:

$$
\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t) + \frac{1}{2} \vec{a}(t)\Delta t^2 \quad (1.3)
$$

$$
\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\vec{a}(t + \Delta t) + \vec{a}(t)}{2} \Delta t \quad (1.4)
$$

Both methods incur error of the order of $\Delta t^2$. Other techniques have also been proposed,
Initial positions $\vec{r}_i$
potential function $V(r)$
calculate forces:
$\vec{f}_i = -\nabla V(r_i)$
update positions and velocities
$\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{1}{2} \vec{a}(t)\Delta t^2 + \ldots$
$\vec{v}(t + \Delta t) = \vec{v}(t) + \vec{a}\Delta t + \ldots$
update time: $t = t + \Delta t$

Figure 2.: Description of the stages in MD simulations.
see for instance Ref. [21] for a presentation of some integration methods. One of those is the Beeman algorithm, which improves accuracy by implementing numerical integration with an error $\sim \Delta t^3$. However, this increased precision comes with the price of an increased number of arithmetic operations and associated computational cost.

Although MD is traditionally applied to simulate fast atomic-scale materials processes, it has recently been extended to the simulation of relatively slow processes by using accelerated molecular dynamics” (AMD) methods. The idea behind AMD is that the frequency of rare events follow transition state theory: the system visits several states by overcoming energy barriers, the frequency of hopping guided by the transition rate as is nicely illustrated by a diffusion process, where an atom hops from one site to the next at a certain frequency. The rates are determined by such parameters as the height of the energy barrier and the temperature. Each of the AMD techniques aims at increasing the rate of transition, either by lowering the barrier (hyperdynamics [22]), increase of the temperature (temperature accelerated MD [23]), or by running copies of the system in parallel to increase the chance of occurrence of the event (parallel replica [24]). For a detailed review on AMD techniques, see [25].

As can be seen from Fig. 2, the interatomic potential is a key component of the MD technique, and a realistic outcome from the MD simulation requires an accurate potential function $V(r)$. It must satisfy several conditions [26]: it must be flexible enough to fit a certain number of properties (compiled in the fitting database), transferable (should work for conditions not included in the fitting database), accurate, and fast. The first potential to be used in MD simulations is the Lennard-Jones potential:

$$V_{LJ}(r) = 4\epsilon \left[ \frac{\sigma}{r^{12}} - \frac{\sigma}{r^6} \right]$$

(1.5)

describing the interactions between two atoms separated by a distance $r$. Here $\epsilon$ controls the strength of the potential and $\sigma$ defines the length scale of the interactions. This empirical
Figure 3.: Lennard-Jones potential $V_{LJ}(r)$. $V_{LJ}(r)$, repulsive and attractive functions. This particular potential was constructed with the parameters $\epsilon = 10$ eV, and $\sigma = 2$ Å.
form combines a repulsive $r^{-12}$ interaction which represents the strong repulsion of the core electrons (Pauli exclusion principle) and a long range attractive $r^{-6}$ van der Waals interaction, thus providing a realistic potential for the atoms separated by an equilibrium distance $r_{eq} = 2^{1/6}/\sigma$, see Fig. 3. Using such a simple potential function, the forces are easily calculated by analytical differentiation of $V(r)$: $\vec{f}_i = -\vec{\nabla}V(r_i)$. Nonetheless, in spite of its popularity, the simplistic LJ model, it is unable to reproduce the properties of ionic, metallic or covalently bonded solids. In particular, covalent bonding is caused by the sharing of electron pairs between the two atoms that form the bond. In order to describe the covalent solids, including carbon systems, a more complex potential is required, accounting for both $\sigma$ and $\pi$ bonding, as well as their angular and coordination dependencies. Covalent bonding is the strongest among all other types of bonding, and can form single, double or even triple bonds. Several potentials for covalently-bonded carbon systems have been proposed and used over the years some of which are reviewed in Chapter 2. Most of them originate from the early works of Abell [27] and Tersoff [28], who proposed to described the interaction between carbon atoms as the sum of the repulsive and attractive interactions:

$$E_i = \sum_j \left( V_{rep}(r_{ij}) + b_{ij}V_{att}(r_{ij}) \right)$$

(1.6)

where $V_{rep}$ and $V_{att}$ are the repulsive and attractive pairwise functions, and $b_{ij}$ is the “bond order” term, which takes into account the angular and coordination dependence of the covalent bonding. The $b_{ij}$ term is at the heart of the Abell-Tersoff potentials, its form having various representations. The reactive empirical bond order potential (REBO [29]), the adaptive intermolecular REBO (AIREBO [30]) potential, the environment dependent interatomic potential (EDIP [31]), the long range carbon bond order potential (LCBOPII [32]) and the analytic bond order potential (BOP [33]) will be presented in Chapter 2.

In addition to a serious concern of transferability - that is the ability of the potential to describe phenomena not included within the fitting procedure - most interatomic poten-
tials lack accuracy when considering carbon materials under extreme conditions, including extreme temperature, tensile or compressive stresses. This is because they were mainly designed to reproduce properties near equilibrium. Therefore, devising carbon potentials that properly describe systems under extreme conditions represents a true challenge.

Extreme conditions are very interesting: they allow the testing of limits for existing models to describe fundamental physical properties, models which in turn may help explain complex phenomena that are difficult or even impossible to probe experimentally. Such phenomena include shock compression of diamond [34–37], formation of nanodiamonds under pressure [38], carbon sputtering [39] or collision of carbon clusters in interplanetary dust [40, 41], as well as properties of amorphous carbon films generated through melting and fast cooling of the melted state [42–44]. A good carbon interatomic potential would be highly desirable for the investigation of the properties of carbon nanotubes (CNT) and graphene membranes, for applications in nano electromechanical systems (NEMS). Those applications involve the behavior of the materials under strong compression or stretching [45–47]. Standard interatomic potentials display poor behavior under extreme conditions, because they were specifically designed to describe the materials behavior at normal conditions.

This dissertation describes the work performed to develop a carbon interatomic potential for simulations of materials at extreme conditions. Chapter 2 reviews existing interatomic potentials, Chapter 3 reports the development of the novel screened environment dependent reactive empirical bond order (SED-REBO) potential [48]). It was specifically designed to investigate the properties of carbon systems under extreme conditions, and includes reparametrized pairwise functions, an increased cutoff distance, and a screening function that plays the role of an effective cutoff to filter out unphysical interactions. The construction, validation and applications of the SED-REBO potential are also discussed in Chapter 3.

In Chapter 4, the SED-REBO potential is applied to investigate the behavior of graphene
membranes under indentation, a study closely related to experimental probing of such membranes by an atomic force microscope (AFM) tip. The results obtained using the SED-REBO potential are compared to the predictions made by using the original REBO potential, highlighting the importance of the new developments.

Finally, in Chapter 5, the SED-REBO potential is used to investigate the response of diamond single crystal to shock compression. The SED-REBO predictions are compared with those provided by a recently developed potential (LCBOPII). Distinct shock regimes were investigated, and the results were compared to experiment.
Chapter 2
Interatomic Potentials for Carbon

2.1 The Reactive Empirical Bond Order Potential: REBO

REBO was developed by Brenner [49] in 1990, using the Abell-Tersoff bonding formalism [27, 28], and later underwent further improvements [29]. The potential was originally designed to model chemical vapor deposition (CVD) of diamond. Since then, it has been applied to a wide range of problems involving carbon and hydrocarbon systems, including growth mechanisms and properties of amorphous and diamond-like carbon films [42, 43, 50], friction [51, 52] and fracture [53, 54] of diamond crystals, tribological properties and indentation response of carbon materials such as amorphous carbon, graphene, carbon nanotubes (CNT) [47, 55–59], nanomechanical response and properties under stress of CNT [45, 60–66] and graphene membranes and graphene nanoribbons [67–74], growth mechanisms of CNT [75], properties of carbon nanostuctures [76], to mention a few.

The state of the art “second generation” of REBO includes contributions of torsional and dihedral angle terms, is presented here. The potential consists of three major components: pairwise attractive ($V_A$) and repulsive ($V_R$) functions, and a bond-order term $b_{ij}$ which accounts for the angular and coordination dependence of the carbon covalent bonds. The bond order term also includes torsional and $\pi$ conjugation terms. Within this model, the energy of an atom $i$ surrounded by neighbors $j$ is calculated as:

$$E_i = \sum_{j \neq i} f_c(r_{ij}) \left( V_R(r_{ij}) + b_{ij} V_A(r_{ij}) \right)$$  \hspace{1cm} (2.1)
where $f_c(r)$ is a switching function, which is applied in the interval of interatomic distances between some distance $r_1 < r < r_c$; $r_1 = 1.7 \text{ Å}$ and $r_c = 2 \text{ Å}$. The cutoff radius $r_c$ is used to determine whether or not two atoms are interacting. For $r > r_c$, $E = 0$, therefore to ensure the continuity of the potential function at $r_c$, $E \to 0$ when $r \to r_c$. Otherwise discontinuities in energy and forces would cause non-physical behaviors. This is realized by “switching off” the interactions using $f_c(r)$, the switching starting at $r = r_1$. The switching function itself can be expressed in many forms, among which Brenner chose the following:

$$f_c(r) = \begin{cases} 
1 & \text{if } r < r_1 \\
\frac{1}{2} \left[ 1 + \cos \left( \pi \frac{r - r_1}{r_c - r_1} \right) \right] & \text{if } r_1 \leq r < r_c \\
0 & \text{if } r \geq r_c 
\end{cases}$$ (2.2)

where $f_c$ satisfies the conditions $f_c(r_1) = 1$ and $f_c(r_c) = 0$, while possessing a smooth behavior in between. The attractive ($V_A$) and repulsive ($V_R$) pairwise functions from Eq. 2.1 are expressed as:

$$V_A(r) = (1 + Q/r) A e^{-\alpha r}$$ (2.3)
$$V_R(r) = \sum_{n=1}^{3} B_n e^{-\beta_n r}$$ (2.4)

The bond order term $b_{ij}$, the fundamental part of Abell-Tersoff models, is expressed as:

$$\bar{b}_{ij} = \frac{1}{2} \left( b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi} \right) + b_{ij}^{\pi}$$

$$b_{ij}^{\sigma-\pi} = \left[ 1 + \sum_{k \neq i, j} f_c(r_{ik}) g(\cos(\theta_{ijk})) + P_{ij}(N_i) \right]^{-\frac{1}{2}}$$ (2.5)

where $b_{ij}^{\sigma} = \Pi_{ij}^{RC} + b_{ij}^{DH}$, sum of conjugation and dihedral terms, describes the chemistry of radical and conjugated carbon systems, $g$ is the angular function, necessary to describe
covalent bonding, and $P_{ij}$ is an empirical correction function of the number of carbon neighbors $N_i$, which is calculated as:

$$N_i = \sum_{k \neq i,j} f_c(r_{ik})$$  \hspace{1cm} (2.6)$$

The parameters for the attractive and repulsive functions are summarized in table 1, page 13. The angular function $g(\cos \theta)$, was parametrized using carbon solids (graphene and diamond) and hydrocarbon molecules as a fitted database. All the parameters of the model were obtained by extensive search of the parameters allowing the REBO potential to describe a wide variety of situations involving carbon materials. Nonetheless, it is highly unrealistic to think that an empirical potential will be perfectly transferable, in other words will yield accurate results in situations not anticipated or simply not taken into account during the parametrization phase of the potential. As an example, it is known that the liquid and amorphous phases are poorly described by the REBO potential [31, 42–44], which could be simply explained by the fact that these systems were not of the primary interest for the developers of the potential. In order to improve the transferability, the behavior of carbon systems under high compression or stretching is also to be taken into account, as it will be discussed later.

2.2 Other Potentials: AIREBO, EDIP, LCBOPII, BOP

Several other carbon potentials were introduced. The most notable among them are the adaptive intermolecular REBO (AIREBO [30]) potential, the environment dependent interatomic potential (EDIP [31]), the long range bond order potential for carbon (LCBOPII [32]) and the analytic bond order potential (BOP [33, 77]). Apart from AIREBO, which could be considered as an extension of the REBO potential, the other potentials involve completely different functional forms. In fact, due to the empirical nature of the potentials, involving many functions and ad hoc corrections determined through extensive fitting, improving one
Table 1: Parameters for the repulsive ($V_R$) and attractive ($V_A$) functions in REBO. For Eq. 2.3 and 2.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>12.388.791.977.9 eV</td>
</tr>
<tr>
<td>$B_2$</td>
<td>17.567.406.465.0 eV</td>
</tr>
<tr>
<td>$B_3$</td>
<td>30.714.932.080.6 eV</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>4.720.452.3127 Å⁻¹</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>1.433.213.2499 Å⁻¹</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>1.382.691.2506 Å⁻¹</td>
</tr>
<tr>
<td>$Q$</td>
<td>0.313.460.296.083 Å</td>
</tr>
<tr>
<td>$A$</td>
<td>10.953.544.162.17 eV</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>4.746.539.060.659 Å⁻¹</td>
</tr>
</tbody>
</table>
aspect *e.g.* achieving accurate description of $\pi$-bonding entails quality reduction of other key properties. Therefore, improving the predictive power of a potential is a challenging task.

### 2.2.1 AIREBO

The adaptive intermolecular REBO (AIREBO) potential was developed by Stuart, Tutein and Harrison based on the second generation REBO potential [29], although it was published earlier. The potential aims at improving a description of non-bonded interactions in the systems where they play a key role, *e.g.* liquid and amorphous solids and graphite. It has been applied to study compressed CNT filled with $C_{60}$ (buckminsterfullerene) molecules [78], the bombardment of silver by $C_{60}$ molecules [79], the stress-induced warping of graphene sheets and nanoribbons [67]. To take into account the non-bonded interactions, a long-range 12-6 Lennard-Jones (LJ) potential is added to the total energy calculation, Eq. 2.1:

$$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

(2.7)

Instead of a simple distance-dependent additive interaction, the LJ term is turned on and off *via* a more complex process, taking into account, in addition to interatomic distance $r_{ij}$, the strength of the bonding interaction between the two atoms, and the local environment of the bond. Therefore, the LJ energy for a pair $i - j$ is written as:

$$E_{LJ}(r_{ij}) = S(t_r(r_{ij})) S(t_b(b^*_{ij})) C_{ij} V_{LJ}(r_{ij}) + \left[ 1 - S(t_r(r_{ij})) \right] C_{ij} V_{LJ}(r_{ij})$$

(2.8)

where $S(t)$ is a switching function:

$$S(t) = \Theta(-t) + \Theta(t) \Theta(1 - t) [1 - t^2(3 - 2t)]$$

(2.9)
Θ(t) is the Heaviside step function, and the \( S(t) \) function smoothly switches between the values of 0 \( (t > 1) \) and 1 \( (t < 1) \) using the dimensionless scaling functions:

\[
t_r(r_{ij}) = \frac{r_{ij} - r_{ij}^{LJ min}}{r_{ij}^{LJ max} - r_{ij}^{LJ min}} \quad (2.10)
\]
\[
t_b(b_{ij}) = \frac{b_{ij} - b_{ij}^{min}}{b_{ij}^{max} - b_{ij}^{min}} \quad (2.11)
\]

The bond order term \( b_{ij}^* \) appearing in Eq. 2.8 is actually a fictitious bond order, because the atoms involved are beyond the short-range interaction distance. It is \( b_{ij}^* \), calculated as:

\[
b_{ij}^* = b_{ij} \big|_{r_{ij}=r_{ij}^{min}} \quad (2.12)
\]

Finally, \( C_{ij} \) is a switching function which takes into account the local connectivity of the atoms, reflecting the fact that the interactions between first and second neighbors are already well described by the REBO part of the potential. Therefore \( C_{ij} \) ensures that that the LJ part is included only for the cases where the energy between the pair would otherwise be omitted. The parameters of the potential for the short range interactions are the same as for REBO (see table 1 on page 13). For the LJ part, they are given in the table 2.

### 2.2.2 EDIP

The environment dependent interaction potential (EDIP [31]) for carbon was developed by Nigel Marks, based on its predecessor, EDIP for silicon [80, 81]. EDIP for silicon is one of the most popular interatomic potentials for MD simulations of Si, including investigation of the structure and properties of amorphous silicon [82], the amorphization mechanisms and defect structures of Si [83], the interaction of vacancies with dislocations in crystalline Si [84], and the mechanisms of epitaxial growth [85]. The EDIP for C potential was originally introduced originally to study amorphous and liquid quenched carbon systems, for which it yields results in better agreement with experiments than REBO po-
Table 2: Parameters for the LJ part of the potential in AIREBO. For Eqs. 2.7, 2.10, 2.11 and 2.12 (for carbon-carbon interactions only).

<table>
<thead>
<tr>
<th>( \epsilon_{ij} )</th>
<th>0.00284 eV</th>
<th>( \sigma_{ij} )</th>
<th>3.40 Å</th>
<th>( r_{min} )</th>
<th>1.7 Å</th>
<th>( r_{max} )</th>
<th>2.0 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{min}^{LJ} )</td>
<td>( \sigma_{ij} )</td>
<td>( r_{max}^{LJ} )</td>
<td>( 2^{1/6} \sigma_{ij} )</td>
<td>( b_{min} )</td>
<td>0.77</td>
<td>( b_{max} )</td>
<td>0.81</td>
</tr>
</tbody>
</table>
tential [44, 86]. It was also used to simulate diamond-like carbon [87] and elasticity of carbon nanotubes [88]. The functional form differs from Tersoff-like potentials in that it does not invoke the notion of “bond-order” acting on the attractive part of the potential (see Eq. 2.1). Instead, the energy of an atom \(i\) is divided into three components: a two-body pair interaction, a three-body angular penalty function, and a generalized coordination function (included in the three-body term):

\[
E_i = \sum_j U_2(r_{ij}, Z_i) + \sum_{j<k} U_3(r_{ij}, r_{ik}, \theta_{jik}, Z_i),
\]

(2.13)

where \(Z\) is the atomic coordination, and \(U_2\) is a short-range pair potential described as:

\[
U_2 = \epsilon \left[ \left( \frac{B}{r} \right)^4 - \exp(-\beta Z^2) \right] \exp \left( \frac{\sigma}{r - a - a'Z} \right).
\]

(2.14)

The term in \(-\beta Z^2\) describes the bond order and \(a'\) controls a variable cutoff allowing better agreement with the first-principles data used by Marks. The three-body term \(U_3\) is Eq.2.13 contains radial and angular-dependent terms:

\[
U_3(r_{ij}, r_{ik}, \theta, Z) = \lambda(Z)g(r_{ij}, Z)g(r_{ik}, Z)h(\theta, Z)
\]

(2.15)

with

\[
\lambda(Z) = \lambda_0 \exp[-\lambda'(Z - Z_0)^2]
\]

(2.16)

\[
g(r, Z) = \exp[\gamma/(r - a - a'Z)]
\]

(2.17)

\[
h(\theta, Z) = 1 - \exp\left( -q[\cos\theta + \tau(Z)^2] \right)
\]

(2.18)

\(\tau(Z)\) describes the angular penalty differentiating between the structures containing 180°, 120°, 109.5° and 90° bond angles, which correspond to coordinations 2 (dimer or linear chain), 3 (graphene/graphite), 4 (diamond) and 6 (simple cubic) respectively. The parame-
ters of the potential are shown in table 3, page 19.

2.2.3 LCBOPPII

The long-range carbon bond order potential (LCBOPPII) was developed by Los et al. [32] to provide an accurate description of the various solid and liquid phases of carbon in the high temperature and high pressure regimes (up to 100 GPa and 10,000 K). With respect to the REBO potential, LCBOPPII contains a long-range energy term that accounts for the van der Waals interactions that are at play for graphitic systems (repulsive interaction between graphene sheets in compressed graphite), as well as a medium-range energy term which improves the reactive properties. This potential has been successfully used to study liquid carbon [89], determine the melting line of graphite [90], investigate the formation and thermodynamic properties of nanocarbons in detonation conditions [38, 91], and simulate the thermally activated graphitization of nanodiamonds in vacuum [92]. The potential form is:

\[
E_i = \frac{1}{2} \sum_{j \neq i} \left( S_{\text{down},ij} V_{ij}^{sr} + \frac{1}{Z_{\text{mr},ij}} S_{\text{up},ij} V_{ij}^{mr} + S_{\text{up},ij} V_{ij}^{lr} \right)
\]

(2.19)

where \( V_{ij}^{sr}, V_{ij}^{mr} \) and \( V_{ij}^{lr} \) describe the short, medium and long-range contributions which are functions of the interatomic distance \( r_{ij} \). Each contribution is triggered by the switching functions, \( S_{ij}^{\text{down}} = S_{ij}^{\text{down}}(r_{ij}) \) and \( S_{ij}^{\text{up}} = S_{ij}^{\text{up}}(r_{ij}) \), which are defined as:

\[
S_{ij}^{\text{down}}(x) = \Theta(-x) + \Theta(x)\Theta(1 - x)(1 + 2x + px^2)(1 - x)^2
\]

(2.20)

\[
S_{ij}^{\text{up}}(x) = 1 - S_{ij}^{\text{down}}(x)
\]

(2.21)

where \( \Theta(x) \) is the Heaviside step function, \( p \in [-3, 3] \) a parameter to adjust the shape of the switching, \( a \) the dimensionless quantity function of the variable \( q \) (the interatomic
Table 3: Parameters for the EDIP potential. For Eqs.2.14, 2.16, 2.17, 2.18.

<table>
<thead>
<tr>
<th></th>
<th>Two-body</th>
<th>Three-body</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\epsilon = 20.09 \text{ eV}$</td>
<td>$Z_0 = 3.615$</td>
</tr>
<tr>
<td></td>
<td>$B = 0.9538 \text{ Å}$</td>
<td>$\lambda_0 = 19.86 \text{ eV}$</td>
</tr>
<tr>
<td></td>
<td>$\sigma = 1.257 \text{ Å}$</td>
<td>$\gamma = 1.354 \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 0.0490$</td>
<td>$\chi' = 0.030$</td>
</tr>
<tr>
<td></td>
<td>$a = 1.892 \text{ Å}$</td>
<td>$q = 3.5$</td>
</tr>
<tr>
<td></td>
<td>$a' = 0.170 \text{ Å}$</td>
<td></td>
</tr>
</tbody>
</table>
distance \( r_{ij} \) in Eq. 2.19) switching between \( q_{\text{min}} \) and \( q_{\text{max}} \):

\[
x = x(q) = \frac{q - q_{\text{min}}}{q_{\text{max}} - q_{\text{min}}}
\]

(2.22)

The short-range contribution in Eq. 2.19 has a form similar to REBO, with:

\[
V_{ij}^{sr} = V_{R}^{sr}(r_{ij}) - B_{ij}V_{A}^{sr}(r_{ij})
\]

(2.23)

with

\[
V_{R}^{sr}(r) = A e^{-\alpha r}
\]

(2.24)

\[
V_{A}^{sr}(r) = B_1 e^{-\beta_1 r} + B_2 e^{-\beta_2 r}
\]

(2.25)

The bond order term is written as:

\[
B_{ij} = (b_{ij} + b_{ji})/2 + F_{ij}^{\text{conj}} + A_{ij} + T_{ij}
\]

(2.26)

where \( F_{ij}^{\text{conj}} \) and \( T_{ij} \) are the conjugation and torsional terms, and \( A_{ij} \) is the contribution that takes into account the presence of occupied anti-bonding states. It is similar to REBO’s form (Eq. 2.5), with the addition of the new anti-bonding contribution (\( b_{ij}^{\pi} \) in REBO contains both the conjugation and the torsion terms). The \( b_{ij} \) term in (2.26) contains the angular dependent function \( G(\cos(\theta, N_{ijk})) \) which is more elaborate than in REBO, and involves the local coordination \( N_{ijk} \):

\[
b_{ij} = \left( 1 + \sum_{k \neq i,j} S_{N}^{\text{down}}(r_{ik}) H(\delta r_{ijk}) G(\cos(\theta_{ijk}, N_{ijk})) \right)^{-1/2}
\]

(2.27)
The long-range potential $V^{lr}$ in Eq. 2.19, is given by:

\[ V^{lr}(r) = \left[ \Theta(r_0 - r) V_1^{lr} + \Theta(r - r_0) V_2^{lr} \right] S_{\text{down}}^\text{lr}(r) \] (2.28)

with

\[ V_1^{lr} = \epsilon_1 \left( e^{-2\lambda_1(r - r_0)} - 2e^{-\lambda_1(r - r_0)} \right) + v_1 \] (2.29)

\[ V_2^{lr} = \epsilon_2 \left( e^{-2\lambda_2(r - r_0)} - 2e^{-\lambda_2(r - r_0)} \right) + v_2 \] (2.30)

The parameters for the long and short range potential are gathered in the table 4. Finally, the middle-range environment dependent potential $V^{mr}$ describes attractive forces by taking into account the bond angles and the existence of dangling bonds in the local environment of the bond $i - j$ via a complex combination of switching functions and polynomial form terms (see [32]).

### 2.2.4 BOP

A new direction for carbon potentials was proposed by Oleynik and Pettifor in the form of the analytic bond order potential (BOP, [33, 77, 94]). The potential has his roots in the tight-binding (TB) model, and proposes analytical rather than purely empirical form for the bond order. It was first introduced to improve the poor description of $\pi$-bonding offered by REBO, and to increase the transferability of the potential. Using functional forms derived from the theory, it offers the solution to devise a potential which should be less empirical, thus avoiding an excessive fitting of the database of carbon properties. By analogy with the TB model, the energy of a bond $i - j$ is the sum of a repulsive pairwise interaction $U_{\text{rep}}$
Table 4: Parameters for the LCBOPII potential. For short and long-range functions (Eqs. 2.19, 2.25, 2.27, 2.28, 2.30), from Refs. [32, 93]).

<table>
<thead>
<tr>
<th>SR</th>
<th>$S_{sr}^{down}$</th>
<th>( q = r_{ij} )</th>
<th>( q_{min} = 1.7 )</th>
<th>( q_{max} = 2.0 )</th>
<th>( p=3.0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( V_R )</td>
<td>( A = 53,026.926 )</td>
<td>( \alpha = 6.747,509 )</td>
<td>( \beta_1 = 6.245038 )</td>
<td>( B_2 = 34.071425 )</td>
</tr>
<tr>
<td></td>
<td>( V_A )</td>
<td>( B_1 = 27618.357 )</td>
<td>( \beta_1 = 6.245038 )</td>
<td>( B_2 = 34.071425 )</td>
<td>( \beta_2 = 1.197128 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( B_{ij} )</th>
<th>$S_{N}^{down}$</th>
<th>( q = r_{ij} )</th>
<th>( q_{min} = 1.7 )</th>
<th>( q_{max} = 2.0 )</th>
<th>( p=-3.0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_1 )</td>
<td>( r_1^{lr} = 5.5 )</td>
<td>( v_1 = 3.475,378 )</td>
<td>( \epsilon_1 = 6.093,133 )</td>
<td>( \lambda_1 = 1.359,381 )</td>
<td></td>
</tr>
<tr>
<td>( V_2 )</td>
<td>( r_2^{lr} = 6.0 )</td>
<td>( v_2 = 0.0 )</td>
<td>( \epsilon_2 = 2.617,755 )</td>
<td>( \lambda_2 = 2.073,944 )</td>
<td></td>
</tr>
<tr>
<td>( V_1/V_2 )</td>
<td>( r_0 = 3.716,163 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.: Self-returning hoping paths for BOP. Paths of length two (a) and four (b, c, d). Atoms $k$ and $k'$ contribute to the $i-j$ bond order on the $i$ side. Similarly, hoping on neighbors on the $j$ side will contribute as well.
and a bonding $U_{bond}$ terms:

\[
U_{rep,ij} = U_{rep}(r_{ij}) \tag{2.31}
\]
\[
U_{bond,ij} = \frac{1}{2} (h_{ij,\sigma} \Theta_{ij,\sigma} + h_{ij,\pi} \Theta_{ij,\pi}) \tag{2.32}
\]

Within the fourth moment of the density of states approximation, using the Green’s function formalism, Oleynik and Pettifor showed that the bond order terms $\Theta_{\sigma}$ and $\Theta_{\pi}$ can be expressed analytically, in terms of the fundamental hoping integrals of the TB model: $ss\sigma$, $pp\sigma$, $pp\pi$. If the reduced TB model is used, then $sp\sigma = \sqrt{|ss\sigma| \times pp\sigma}$ [33], and the other hoping integrals are expressed as:

\[
ss\sigma = \frac{1}{1 + p_\sigma} h_{ij,\sigma} \tag{2.33}
\]
\[
pp\sigma = \frac{p_\sigma}{1 + p_\sigma} h_{ij,\sigma} \tag{2.34}
\]
\[
sp\sigma = \frac{\sqrt{p_\sigma}}{1 + p_\sigma} h_{ij,\sigma} \tag{2.35}
\]

and $pp\pi = h_\pi(r)$. $sp\sigma/pp\sigma = \sqrt{p_\sigma}$ and $h_{ij,\sigma} = h_\sigma(r_{ij})$. These parameters can be accurately fitted to first-principles data, using the fact that TB can describe the first-principles band structure of ideal solids quite well. The $\sigma$ part of the bond order between two atoms $i$ and $j$ can be expressed as:

\[
\Theta_{ij,\sigma} = \frac{1}{\sqrt{1 + \frac{2\Phi_{2s} + \delta^2}{1 + \sqrt{(\Phi_{4s} - 2\Phi_{2s}^2 + \Phi_{2s}^4 + \Phi_{2s}^4)/\Phi_{2s}^2}}}} \tag{2.36}
\]

where

\[
\delta = \frac{\Delta_{sp}}{2(h_\sigma(r_{ij}))^2 (1 + p_\sigma)^2} \tag{2.37}
\]

where $\Delta_{sp}$ takes into account the non-zero energy difference between the $s$ and $p$ atomic energy levels in carbon: $\Delta_{sp} = 2(E_p - E_s)^2$. In the expression (2.36) $\Phi_{n\sigma}$ represents the
contribution of the self-returning hoping integrals of length \( n \) (\( n = 2 \) or \( 4 \) within the fourth moment approximation), on site \( i \), shown in figure 4, and \( \Phi_{n\sigma} = 1/2(\Phi_{n\sigma}^i + \Phi_{n\sigma}^j) \)). The contributions themselves, for atom \( i \) bonded to \( j \), are calculated as:

\[
\Phi_{2\sigma}^i = \sum_{k \neq i,j} [g_\sigma(\theta_{jik})]^2 \hat{h}_\sigma^2(r_{ik})
\]

where \( k \) is a neighboring site of \( i \). \( \hat{h}_\sigma \) is the normalized bond integral \( h_\sigma(r_{ik})/h_\sigma(r_{ij}) \), and \( g_\sigma(\theta) \) is the angular function given by:

\[
g_\sigma(\theta) = \frac{p_\sigma}{1 + p_\sigma} \left( \frac{1}{p_\sigma} + \cos(\theta) \right)
\]

The four hop term \( \Phi_{4\sigma} \) is expressed as the sum of three contributions, reflecting the three different paths shown in Fig. 4-(b, c, d):

\[
\Phi_{4\sigma}^i = \sum_{k \neq i,j} [g_\sigma(\theta_{jik})]^2 \hat{h}_\sigma^4(r_{ik}) + \sum_{k,k' \neq i,j} g_\sigma(\theta_{jik}) g_\sigma(\theta_{kik'}) g_\sigma(\theta_{k'ij}) \hat{h}_\sigma^2(r_{ik}) \hat{h}_\sigma^2(r_{ik'})
\]

\[
+ \sum_{k,k' \neq i,j} g_\sigma(\theta_{jik}) g_\sigma(\theta_{ikk'}) [g_\sigma(\theta_{jik})]^2 \hat{h}_\sigma^2(r_{ik}) \hat{h}_\sigma^2(r_{kk'})
\]

The \( \pi \) bond order, is calculated as:

\[
\Theta_{ij,\pi} = \frac{1}{\sqrt{1 + \Phi_{2\pi} + \Phi_{4\pi}}} + \frac{1}{\sqrt{1 + \Phi_{2\pi} - \Phi_{4\pi}}}
\]

which includes two and four hop contributions:

\[
\Phi_{2\pi} = \frac{1}{2} \sum_{k \neq i,j} \{ \sin^2\theta_{jik} \frac{p_\sigma}{1 + p_\sigma} \hat{h}_\pi^2(r_{ik}) + (1 + \cos^2\theta_{jik}) \hat{h}_\pi^2(r_{ik}) + (i \leftrightarrow j) \}
\]

\[
\Phi_{4\pi} = \frac{1}{4} \sum_{k,k' \neq i,j} \{ \sin^2\theta_{jik} \sin^2\theta_{kik'} \hat{\beta}_\pi^2 \hat{\beta}_\pi^2 + \sin^2\theta_{jik} \sin^2\theta_{kik'} \hat{\beta}_\pi^2 \hat{\beta}_\pi^2 + (i \leftrightarrow j) \} \cos2(\phi_k - \phi_{k'})
\]
where 
\[
\hat{\beta}_{ik} = \left[ p_\sigma / (1 + p_\sigma) \right] \left[ \hat{h}_\sigma (r_{ik}) \right]^2 - \left[ \hat{h}_\sigma (r_{ik}) \right]^2.
\]

The term \( i \to j \) implies that an extra contribution is added, by replacing \( i \) by \( j \). The last term accounts for the dihedral contribution: \( \phi_k - \phi_{k'} \) is the angular difference between the \( kij \) and \( ijk' \) planes, where \( k \) is neighbor of \( i \), and \( k' \) is neighbor of \( j \). All the "hatted" integrals have been normalized: 
\[
\hat{h}_x (r_{ik}) = h_x (r_{ik}) / h_x (r_{ij}).
\]

Although BOP has not been implemented in an efficient, large-scale oriented, MD code yet, the results obtained so far are very encouraging: they show agreement between the exact TB bond orders and the BOP derived values within 1% (for the \( \sigma \) part), and 10% for the \( \pi \)-part, whose contribution is much less than that of \( \sigma \). Therefore BOP is a very promising candidate for the development of a robust and transferable interatomic potential for carbon.

### 2.3 Beyond the First Nearest-Neighbor Model: Screening

One of the failures of the standard interatomic potentials is a poor description of bond breaking events under high tensile stress. This behavior is due to artificial forces arising from switching functions used in the potentials to switch off the atomic interactions beyond the predefined cutoff distance \( r_c \) and serves two goals. First, it allows to work within a simplified nearest neighbor (NN) model for ideal (i.e. not too stretched nor compressed) materials, the cutoff being typically chosen between the first and second NN distance. Secondly, introducing a cutoff allows the building of so-called neighbor lists in MD codes, which determine which atoms are interacting, thus eliminating considerable amounts of calculations by omitting interactions considered unnecessary. However, under high stretching conditions the atoms interact within the region where switching is active, and are, therefore, subject to artificial forces. Specifically, in the case of the REBO potential, switching introduces an additional maximum in the forces within the switching region, causing a strengthening of the bonds, and an incorrect description of bond breaking processes. A common illustration of the consequences of this artificial response is the erroneous prediction of a
ductile fracture of CNT and graphene under tensile stress, in complete disagreement with experimental observations [45, 46, 95]. A discussed attempt to improve the description of bond breaking events in carbon materials is to conserve the computationally efficient REBO potential, and increase the cutoff distance [46, 96, 97] to encompass the critical bond length without the influence of switching. This critical bond length (spinodal point $r^*$) is the inflexion point of the binding energy curve after equilibrium, characterizing the mechanical instability of the material. This procedure, while providing a simple approach to the problem, still exhibits critical limitations: the potential is not designed for high-strain regimes, and therefore can lack accuracy at these large interatomic distances. More importantly, fracture phenomena characterized by crack opening and propagation necessitate a valid description of the atomic interactions even after the bond is broken, at distances where it will still suffer from the artificial forces due to switching [98].

In order to accurately describe bond breaking under stretching and subsequent events, the following must be satisfied: one must ensure the accurate description of the atomic interactions up to the spinodal point $r^*$, and also eliminate the artificial behavior caused by the switching function. Indeed, the derivative of the potential must be maximum at $r^*$ (characteristics of the spinodal point), which prevents the use of switching. If this condition is not satisfied, as with the “increased cutoff” method, described in the previous paragraph, then the validity of every post-breaking event is questionable due to artificial forces. However, the necessary condition, that is the potential is zero at some cutoff distance $r_c$, should be imposed under the constraint the maximum of the first derivative occurs at $r^* < r_c$. To do so, a much larger value for $r_c$ must be used, the minimum value for $r_c$ being defined by the condition $d^2E/dr^2 = 0$ at $r^*$. Then, a procedure must be introduced to conserve the nearest-neighbor nature of the potential by removing second and farther NN from the calculation of energy and forces. This task is accomplished by introducing the concept of screening.

Baskes [99–101] was the first to discuss and implement the idea of screening of the
interatomic interactions while devising the modified embedded atom potential for metals (MEAM). The idea is to discriminate between 1st and farther nearest-neighbors by looking at the local environment of a bond, the screening function playing the effective role of a variable cutoff. Thus the cutoff can be set to large enough distances to include critical bond-breaking phenomena, while guaranteeing a valid description of the atomic interactions at distances less than the cutoff distance. The screening was later used within the tight-binding framework [102–104] and was used in the construction of a new silicon potential [105]. Such MEAM-type screening was recently implemented in two carbon potentials [95, 106]. Pastewka and coworkers [95] discussed the failure of common carbon potentials in describing the bond breaking events, and notably illustrated the ductile fracture of CNT contrary to experimental observations. Their modified REBO potential possesses a complex screening formulation: in addition a MEAM type screening function, the screening is switched on or off depending on the location of the neighboring atom \( k \) in one of four distinct regions surrounding the bond \( i - j \). To implement this switching, the potential keeps and even adds more of the switching functions, which produce dramatic effects in the performance of the REBO potential: the occurrence of artificial forces within the switching region. Kumagai et al. [106] also introduced screening in a REBO-type potential, but made substantial changes in the original terms with the purpose of improving the description of amorphous carbon systems. The changes include removal of the corrections terms introduced by Brenner and coworkers for the \( \Pi \) conjugation, and an addition of a dihedral contribution. The effect of such substantial modifications on description of single, double or triple bonds in carbon materials remains unclear. Moreover, the potential still uses the switching functions, which introduce artificial maxima of the forces within the switching region, similar to what was done in Ref. [95]. The two potentials use complicated screening scheme. Moreover, Pastewka and co-workers used a fixed cutoff screening, the negative effect of this being that the interatomic interactions will be unscreened regardless of the presence of a screening atom \( k \) below a certain interatomic distance between atoms.
$i$ and $j$. This not only defeats the purpose of dynamical screening, or determination of the effective cutoff of interactions depending on the evolution of the local environment, but also retains the same flaw as the original REBO potential: the introduction of second and further NNs at large compressions, causing a sudden unphysical increase in energy and forces.
Chapter 3

The Screened Environment Dependent Reactive Bond Order (SED-REBO) Potential

3.1 SED-REBO functional form

The new REBO-type interatomic potential is designed in this PhD project for the simulations of carbon systems under extreme stress conditions. It utilizes several critical elements. First, the cutoff of the interactions is set at $r_c = 3.3 \, \text{Å}$, which includes the distances critical for bond breaking, notably in graphene. Since, as discussed in the previous chapter, a large cutoff means that many interactions contribute to the atomic energy, a “variable cutoff” is necessary in order to maintain the 1st NN nature of the potential, and was implemented by including a screening function in the potential. To impose continuous energy and forces even as a neighboring atom enters or leaves the switching region, the specially designed form of screening function was developed. The pairwise attractive and repulsive contribution were fitted to density functional theory (DFT) data, including very small and large interatomic distances, enabling the transferability of the potential in both the high-compression and high-tensile stress regimes. These regimes were not included in the original REBO potential fitting database, explaining the limitation of this potential under extreme stress conditions. And finally, analytic rational functions were used to represent the pairwise contributions, thus guaranteeing both computational efficiency (by avoiding the use of computationally costly transcendental functions), and great flexibility in the fitting procedure. In addition, the analytic form of the rational function was designed to avoid using a switching function for the pairwise contributions by embedding the desired switching behavior directly into the functional form. In contrast to the artificial response
displayed by REBO potential at large distances (caused mainly by the sharp switching at relatively small interatomic distances), the SED-REBO potential provides a smooth and continuous behavior of the energy and its derivatives (*i.e.* forces). This last point is particularly important to achieve conservation of energy in MD simulations involving bond breaking and remaking and crack propagation. Each of the points discussed here will now be presented in detail.

The general form of the potential is very similar to REBO’s, apart from the use of the environment dependent screening function $S_{ij}$ instead of the pairwise switching function $f_c(r_{ij})$:

$$E_i = \frac{1}{2} \sum_{j \neq i} S_{ij} \left[ V_R (r_{ij}) + b_{ij} V_A (r_{ij}) \right]$$

where $V_A$ and $V_R$ are the attractive and repulsive pairwise functions, $b_{ij}$ is the bond-order term, and $S_{ij}$ is the screening function determined by the local environment surrounding the bond $i - j$. The latter acts in the following way: a bond between two atoms $i$ and $j$ should not be screened if there is no atom $k$ in the neighboring of the bond ($S_{ij} = 1$). If an atom $k$ comes close to the $i - j$ bond, the strength of this bond should gradually decrease ($S_{ij} \leq 1$), as new bonds are formed between $i$ and $k$ and/or $j$ and $k$. This weakening of the $i - j$ bond is quite intuitive and can be related to the quantum mechanical concept of the overlap of the atomic orbitals that create a chemical bond. In the limiting case of $k$ in between $i$ and $j$, the the $i - j$ interaction should be completely screened *i.e.* $S_{ij} = 0$. Screening is illustrated in Fig 5. The screening factor $S_{ij}$ of the $i - j$ bond is calculated as a function of the position of the neighboring atom $k$. In the initial configuration (on the left), the $i - k$ distance is smaller than $r_{ij}$, therefore the atom $k$ screens the $i - j$ bond. As $k$ is moved up, its influence diminishes, and finally the $i - j$ is not screened at all. The form of the screening function, which depends on the bond length $r_{ij}$ and the surrounding
Figure 5.: Screening factor $S_{ij}$. Value of $S_{ij}$ depending on the position of a neighboring atom $k$. The distance between $i$ and $j$ is kept constant, while the distance of $k$ perpendicular to the $i - j$ bond increases. The two extreme configurations ($S_{ij} = 0$ and $S_{ij} \sim 1$) are showing the main (solid) and screened (dashed) bonds.
environment, is similar to that used in Ref. [105], and has the following form:

\[ S_{ij}(r_{ij}, \text{env.}) = \exp\left(-\sum_{k \neq i,j} (g_{ijk})^n\right) \]  

(3.2)

where \( k \) is a neighbor to atoms \( i \) and \( j \), and \( g_{ijk} \) is calculated as

\[ g_{ijk} = \begin{cases} \frac{r_{ij}}{\bar{R}_{ik} + \bar{R}_{jk} - r_{ij}} - \frac{1}{2}, & \text{if } \bar{R}_{ik} + \bar{R}_{jk} \leq 3r_{ij} \\ 0, & \text{else} \end{cases} \]  

(3.3)

with \( \bar{R} = \frac{r}{1 - (r/r_c)^m} \)  

(3.4)

The condition in Eq. 3.3 represents an ellipsoid around the \( i-j \) bond, which contains the neighbor atoms participating in the screening. Eq. 3.4 defines a renormalized distance, which we found is critical to ensure the continuity of the energy function when a neighboring atom is approaching the interaction region defined by the cutoff distance. A simple case of a symmetric configuration \( r_{ik} = r_{jk} \) is displayed in Fig. 6-a. The red semi-ellipse denotes the screening region involving neighbor atoms participating in the screening of the \( i-j \) bond. The dashed and dotted semi-circles represent the cutoff region \( r \leq r_c \) for atoms \( i \) and \( j \) respectively. Therefore, an atom will only be seen by the potential as it enters the cutoff region, and will participate the screening when it belongs to both circles and the ellipse (darker region around the bond). As the atom \( k \) starts to interact with atoms \( i \) and \( j \) (i.e. \( r_{ik} = r_{jk} \leq r_c \)), the original screening function from Ref. [105] gives \( S_{ij} \neq 1 \) and therefore causes a discontinuity that should be avoided for energy conservation purpose. Instead, Fig. 6-b shows that the renormalized distance introduced by us diverges when the atom \( k \) first enters the interaction range, mimicking an infinitely far away atom and thus ensuring that the \( i-j \) bond will first be unscreened. We used \( r_e = r_{ij} = 3.0 \) Å and \( n = 5 \) for Ref. [105]. Apart from the renormalization, effective for \( r \sim r_c \), the screening procedure
depends on the ratio of the atomic distances rather than their absolute values. For example, by considering the simple triangle $ijk$ shown in Fig.6-a, it is obvious that the screening will be the same if the distances are uniformly scaled up or down. This is the desired behavior we aim to achieve: under either compression or stretching, the atoms keep the same local environment of first, second and further NNs.

The adjustable parameters $n$ and $m$ in Eq. 3.2 and 3.4 determine the “strength” of the screening and the rate at which the renormalized distances. In the current implementation of the SED-REBO potential, specifically aimed at producing the most accurate results for tensile stress of graphene, different values for $n$ and $m$ were determined in the “membrane pull-out” test (see 3.2.4, page 49), by fitting the DFT data. However, it was found that the results were insensitive to the specific values of parameters, the test yielding surprisingly good results without substantial fitting. The bond order function $b_{ij}$ in Eq. 3.1 is defined as in Ref. [29], except that the switching function $f_c(r_{ij})$ is replaced by the product $f_c \times S_{ij}$, the screening allowing to discriminate between first and second and farther NN:

$$b_{ij} = \frac{1}{2}(b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}) + b_{ij}^{\rho}$$

$$b_{ij}^{\sigma-\pi} = \left[ 1 + \sum_{k \neq i,j} f_c(r_{ij}) \times S_{ij}(r_{ij}, r_{ik}, r_{jk}) \times \right. \left. G(\cos(\theta_{ijk})) e^{\lambda_{ijk}} + P_{ij}(N^C_i) \right]$$

$$b_{ij}^\pi = \pi_{ij}^{RC} + b_{ij}^{DH}$$

The reason why the switching function is still used here is the following: the bond order in REBO potential is a simplified second moment approximation of the full bond order [33, 77, 94]. Therefore this empirical function does not possess a proper behavior at cutoff distance (REBO’s bond order is distance independent). A switching function was introduced to ensure continuous behavior as an atom enters the cutoff distance. The expressions of the quantities $\lambda_{ijk}$, $N^C_i$, the spline $P_{ij}$, the angular term $G(\cos(\theta))$, and the
Figure 6.: Effect of the renormalized distance $\bar{R}$. $\bar{R}$ is defined by Eq. 3.4. a) Configuration where atom $k$ contributes to the screening of the bond $i - j$. Semi-ellipse: region where screening is on; dashed and dotted circles: the cutoff regions $r_c$ for $i$ and $j$. b)-top: $S_{ij}$ as $k$ is brought closer. Dashed blue line: $r_{jk} = r_{ik} = r_c$. b)-bottom: the renormalized distance $\bar{R}_{jk}$ approaches infinity as $r_{ik} \to r_c$, insuring a smooth transition between the unscreened/screened regimes. Distances A, B, C correspond to points in a).
conjugation and dihedral contributions $\pi^{RC}$ and $b^{DH}_{ij}$, are given in 2.1, page 10, and the original second-generation REBO potential paper [29]. These terms were kept as in Ref. [29], except of replacing the switching function $f_c(r_{ij})$ by the product $f_c \times S_{ij}$. Modification of the internal structure of the bond order was specifically avoided in this work, thus allowing to focus on the accurate description of bond-breaking in graphene under large tensile stress.

The switching function is defined as:

$$f_c(r) = \begin{cases} 
0, & \text{if } r \geq r_{\text{max}} \\
1, & \text{if } r \leq r_{\text{min}} \\
1 - \chi^3 (6\chi^2 - 15\chi - 10), & \text{else}
\end{cases} \quad (3.8)$$

$$\chi = (r - r_{\text{min}}) / (r_{\text{max}} - r_{\text{min}}) \quad (3.9)$$

The polynomial form, similar to that used in Ref. [30], has an advantage over the original cosine function used by Brenner (Eq. 2.2) by providing continuity of the function and its first and second derivatives at both $r = r_{\text{min}}$ and $r = r_{\text{max}}$. Therefore, the energy, forces and their derivatives are continuous. Finally, the repulsive and attractive terms are expressed as analytical rational functions of the form:

$$V(r) = \frac{\bar{r}^3}{r_{A_1} r_{A_2}} \times \frac{A_2 + A_3 \bar{r} + A_4 \bar{r}^2 + A_5 \bar{r}^3 + A_6 \bar{r}^4}{1 + B_3 \bar{r} + B_4 \bar{r}^2 + B_5 \bar{r}^3 + B_6 \bar{r}^4} \quad (3.10)$$

where $\bar{r} = r_c - r$. By using $\bar{r}$ instead of $r$, we ensure that the pairwise contributions, their first and second derivatives, automatically approach zero continuously at the cutoff distance $r_c$. Therefore the switching function is not used in Eq. 3.1, this excluding the artificial forces present in REBO potential (see Fig. 7 and 8). The pairwise interactions were fitted to DFT binding energy of graphene and diamond up to large distances.

The fitting procedure includes fitting the DFT binding energy curves for graphene and diamond using SED-REBO equation 3.1 with $S_{ij} = 1$ for 1st NN and 0 for all further NNs.
Figure 7.: Binding energy and its derivative for graphene. Comparison between DFT, REBO and SED-REBO potentials. The short cutoff and sharp switching in REBO potential causes a sudden increase of the interatomic force \( F_{CC} = -\frac{dE}{dr} \) at both the onset of the switching region 1.7Å and at short distances where second nearest neighbor start to contribute. SED-REBO potential, using a large cutoff and screening function, yields a very good agreement with DFT at both large and small interatomic distances.
Figure 8.: Binding energy and its derivative for diamond. Comparison between DFT, REBO and SED-REBO potentials. The deficiencies of REBO potential for both large and short interatomic distances as well as the accuracy of SED-REBO appear as in figure 7.
Table 5: Parameters for the repulsive ($V_R$) and attractive ($V_A$) pairwise functions in SED-REBO. For Eq. 3.10.

<table>
<thead>
<tr>
<th></th>
<th>$V_R$</th>
<th>$V_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$-1.4015028876548725E+0$</td>
<td>$-5.8766423956332570E-1$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$-1.8451246490858871E-3$</td>
<td>$-3.4940420183651895E+2$</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$2.743819550908305E+0$</td>
<td>$2.2350994593996063E+2$</td>
</tr>
<tr>
<td>$A_4$</td>
<td>$-3.9240134039225447E+0$</td>
<td>$1.8934007661360351E+2$</td>
</tr>
<tr>
<td>$A_5$</td>
<td>$-9.2436902389896866E-2$</td>
<td>$-1.7059931048598986E+2$</td>
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<tr>
<td>$A_6$</td>
<td>$1.3824581638942655E+0$</td>
<td>$1.1038890923066369E+1$</td>
</tr>
<tr>
<td>$B_3$</td>
<td>$2.8387400227469719E+0$</td>
<td>$7.6793759652105507E+1$</td>
</tr>
<tr>
<td>$B_4$</td>
<td>$-3.4344501165956176E+0$</td>
<td>$-5.635412519270104E+1$</td>
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<tr>
<td>$B_5$</td>
<td>$8.8256300370290830E-1$</td>
<td>$7.6561136064499777E+0$</td>
</tr>
<tr>
<td>$B_6$</td>
<td>$1.4842099244501433E-1$</td>
<td>$4.9866851900049216E+0$</td>
</tr>
</tbody>
</table>
Because graphene and diamond are the most stable forms of carbons, this set of fitting data appears to be sufficient for a realistic description of the interatomic interactions in carbon condensed phase. The bond-order $b_{ij}$ was calculated by the original REBO potential and was kept constant for all distances except of those in switching region. This is because $b_{ij}$ depends only on the angle between the bonds, which do not change during homogeneous expansion of the lattice. By matching this simplified form to DFT results, we were able to extract the “theoretical” attractive and repulsive pairwise dependencies, which were then fit to analytical functions. As discussed earlier in this section, these functions are rational polynomials, see Eq. 3.10, which offer many advantages: the possibility to embed the smooth approach to zero at the cutoff distance, the continuity of the first and second derivatives, high flexibility necessary for the accurate fit, and the cost effectiveness during MD simulations due to avoiding the use of transcendental functions during the calculations. Technical details of the fitting procedure can be found in [107]. DFT data up to $\sim 2.7 \text { Å}$ were used, along with a constraint imposing the monotonic behavior of the first derivatives of $V_A$ and $V_R$, added to ensure smooth regular behavior. The results of the fit are shown in Figs. 7 and 8. The coefficients for Eqs. 3.2, 3.4, 3.9, 3.10 are summarized in tables 5 and 6, on pages 39 and 41. The other parameters of the SED-REBO potential are the same as in the REBO potential.

3.2 SED-REBO Validation

3.2.1 Graphene and diamond properties

The first validation test of the potential is concerned with the elastic properties of graphene and diamond, see table 7 on page 44. As was presented in Figs. 7 and 8, SED-REBO potential binding energies and forces are very close to the DFT data. The forces are critically important since the ultimate strength $\sigma^*$ of the material is obtained at the maximum (spinodal point) of the $dE/dV$ curve (derivative of the energy with respect to the volume)
Table 6: Additional parameters for the SED-REBO potential. For Eqs. 3.2, 3.4, 3.8, 3.9.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$r_{\text{min}}$</td>
<td>3.0 Å</td>
</tr>
<tr>
<td>$r_{\text{max}}$</td>
<td>3.3 Å</td>
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<tr>
<td>$r_c$</td>
<td>3.3 Å</td>
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<td>$n$</td>
<td>5</td>
</tr>
<tr>
<td>$m$</td>
<td>48</td>
</tr>
</tbody>
</table>
Figure 9.: Pressure and ultimate strength of diamond and graphene. Obtained by volume (diamond) and surface (graphene) derivative of the energy. The ultimate strength of the material is defined by the pressure at the spinodal point, point of mechanical instability.
for a 3D material or $dE/dA$ curve (derivative with respect to the area) for a 2D material such as graphene. The 2D ($\sigma$) and 3D ($P$) pressures for graphene and diamond are plotted in figure 9 and the maximum of the curve defines the ultimate strength $\sigma^*$ reported in table 7. The strength of graphene obtained with SED-REBO potential compares very well to DFT data, a tremendous improvement over REBO potential. Our results are also compared with experimental results obtained from indentation of graphene membranes [108]. Due to the difficulty of measuring stresses in experiment, the experimental strength was obtained indirectly by supplementing the experimental data with finite element method (FEM) simulations. Although the strength of diamond under uniaxial compression was reported in experiment (between 60 and 120 GPa depending on the crystal orientation and experimental conditions [109, 110]), experimental strength of diamond under hydrostatic expansion is unknown. The elastic constants $C_{12}$ and $C_{44}$ obtained using the original REBO potential were recalculated by us due to some errors and inconsistencies in previous publications. For example, Brenner et al report a value of 100 GPa for $C_{12}$, and 680 GPa for $C_{44}$ [29]. In contrast, Stuart et al [30] reports $C_{12} = 120$ GPa, and $C_{44} = 720$ GPa, citing discussions with Brenner and co-workers. Therefore, the $C_{12}$ value reported by Brenner seems to be a misprint. The difference between the values of $C_{44}$ can be attributed to different methods of calculation of $C_{44}$. The elastic modulus $E^{2D}$ for graphene was obtained by fitting the linear part of the stress-strain curve upon equibiaxial expansion. The bulk modulus $B_0$ and its derivative $B'_0$ for diamond were obtained via a Birch-Murnaghan fit.

### 3.2.2 Binding energy curves for other crystal structures of carbon

We also calculated the binding energy curves for several other carbon crystal structures and determined their relative structural stability as judged by the corresponding minima of the binding energy for the following crystalline structures: dimer, linear chain (LC), simple cubic (SC), face-centered cubic (FCC) and based-centered cubic (BCC). While some of these forms are less than likely to be observed in nature, others such as the linear chain structure
Table 7: Results from binding energy curves and elastic properties for graphene and diamond. Comparison of results obtained from experiments, DFT calculations, and REBO and SED-REBO potentials.

<table>
<thead>
<tr>
<th></th>
<th>SED-REBO</th>
<th>REBO(^1)</th>
<th>DFT(^2)/Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_0) (Å)</td>
<td>1.422</td>
<td>1.420</td>
<td>1.42 / 1.42(^3)</td>
</tr>
<tr>
<td>(C_{11}) (GPa)</td>
<td>1011</td>
<td>1055</td>
<td>1073(^4) / 1109(^5)</td>
</tr>
<tr>
<td>(C_{12}) (GPa)</td>
<td>143</td>
<td>147</td>
<td>181(^4) / 139(^5)</td>
</tr>
<tr>
<td>(E^{2D}) (N/m)</td>
<td>380</td>
<td>387</td>
<td>373 / 340(^6)</td>
</tr>
<tr>
<td>(\sigma_{Gr}^*_G) (N/m)</td>
<td>30.4</td>
<td>102.0</td>
<td>32.2 / 42(^6)</td>
</tr>
<tr>
<td>Diamond</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_0) (Å)</td>
<td>1.549</td>
<td>1.544</td>
<td>1.547 / 1.547(^3)</td>
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</tr>
<tr>
<td>(C_{12}) (GPa)</td>
<td>77</td>
<td>126</td>
<td>127 / 125(^7)</td>
</tr>
<tr>
<td>(C_{44}) (GPa)</td>
<td>512</td>
<td>470</td>
<td>573 / 576(^7)</td>
</tr>
<tr>
<td>(B_0) (GPa)</td>
<td>424</td>
<td>441</td>
<td>447 / 442(^7)</td>
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<tr>
<td>(B'_0)</td>
<td>3.0</td>
<td>4.7</td>
<td>3.9 / 4.0(^8)</td>
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<tr>
<td>(\sigma_{Dia}^*_G) (GPa)</td>
<td>90.0</td>
<td>360.0</td>
<td>80.2 / -</td>
</tr>
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</table>

\(^1\) Recalculated
\(^2\) This work, DFT calculations using the \textit{DMOL}\(^3\) package (unless specified)
\(^3\) from Ref. [111]
\(^4\) from Ref. [112]
\(^5\) from Ref. [113], using 3.34 Å as the thickness of graphene for conversion from N/m
\(^6\) from Ref. [108]
\(^7\) from Ref. [114]
\(^8\) see Table I in Ref. [115]
Figure 10.: Binding energy for several arrangements of carbon obtained with SED-REBO. Symbols indicate equilibrium bond length and energies obtained from DFT calculation: *, o, ∅, □, △, ▽ for LC, graphene, diamond, SC, BCC and FCC respectively.
Table 8: Equilibrium bond length and energies for various carbon structures. The binding energy of diamond is taken as reference.

<table>
<thead>
<tr>
<th></th>
<th>SED-REBO</th>
<th>REBO</th>
<th>Ref. [106]</th>
<th>DFT&lt;sup&gt;1&lt;/sup&gt;</th>
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<td>$r_0$ (Å)</td>
<td>$E_0$ (eV)</td>
<td>$r_0$ (Å)</td>
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<tr>
<td>Dimer</td>
<td>4.580</td>
<td>1.349</td>
<td>4.265</td>
<td>1.325</td>
</tr>
<tr>
<td>LC</td>
<td>1.380</td>
<td>1.353</td>
<td>1.253</td>
<td>1.332</td>
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<tr>
<td>Graphene</td>
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<td>-0.025</td>
<td>1.420</td>
</tr>
<tr>
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<td>1.549</td>
<td>0.000</td>
<td>1.544</td>
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<tr>
<td>SC</td>
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<td>1.860</td>
<td>-</td>
<td>-</td>
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<td>BCC</td>
<td>4.154</td>
<td>2.019</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FCC</td>
<td>4.241</td>
<td>2.079</td>
<td>-</td>
<td>-</td>
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<sup>1</sup> This work, using the DMOL<sup>3</sup> package, unless specified

<sup>2</sup> From Ref.[114]
has been predicted to exist by the theory [116] and was found in experiments [117–119]. In addition, it is important to verify that our potential provides the correct equilibrium geometries for these carbon crystal structures. The equilibrium energies and corresponding interatomic distances within perfect crystal are calculated by REBO and SED-REBO potentials and compared to DFT and experimental data, as well as other theoretical work of Kumagai and co-workers who employed another screened REBO potential [106], see Table 8, page 46. Ref. [106] provides a better agreement with DFT for the linear chain configuration, but SED-REBO potential performs better for SC, FCC and BCC structures. It can be seen in Fig. 10 and table 8 that even though the specific data for crystal structures other than graphene and diamond were not included in our fitting database, SED-REBO potential predicts the structural stability in remarkably good agreement with DFT calculations.

### 3.2.3 Graphene ribbon “pull-out” experiment

In order to look at the bond breaking by the SED-REBO potential, a simple model exhibiting such phenomena was used: a single atom is pulled out of a graphene ribbon edge. The system consists of a rectangular piece of graphene (7×3 four-atoms unit cells, 84 atoms), with periodic boundary conditions (PBC) on the lateral directions and free top boundary at the graphene edge. A row of two atoms is pinned at the bottom of the sample, and one single atom is pulled out of the top side (see Fig. 11, insert). Similarly to the computational experiment of the previous section, the pulled atom is moved by increments of 0.05 Å and the whole system is relaxed at each step using the CG algorithm. The energy change per atom during the entire process is given in Fig. 11 for REBO, SED-REBO and DFT. The difference of the responses between REBO and SED-REBO potentials is striking. With REBO potential, the energy per atom increases with sudden jumps with amplitudes five times higher than for those calculated by SED-REBO potential.

A careful investigation (see Fig. 12) of REBO calculations reveals artificial behavior
Figure 11.: Graphene ribbon “pull-out” computational experiment. Energy per atom during the pulling of the central atom. Insert: side view of the system. The color shows the fixed edges (red) and the atom being pulled (blue). PBC are applied on the lateral dimensions. Letters characterize special events detailed in Figs. 12 and 13.
consisting of a “thread” of carbon atoms accompanied by a substantial drop in energy each time when an atom is extracted from the bulk of the graphene and added to the chain. Thus, any breaking process simulated by REBO including a crack propagation will involve formation of carbon chains. At the end of the pulling process, when the chain is eventually broken, the lattice is greatly affected by the events exhibiting a substantial remnant plasticity (Fig. 12). The “cold” energy curve of graphene (see Fig. 7) explains the origin of such phenomena: due to the switching function, the forces between the atoms increases suddenly, up to a value much higher than it should be as seen from comparison with DFT. This results in an artificial strength enhancement of the C-C bonds for large interatomic distances within the switching region. In particular large unbroken hexagons are formed in graphene lattice, as is seen on Fig. 12 (d) and (e). In contrast, the SED-REBO potential exhibits a simpler breaking mechanism in close agreement with DFT: the bonds between the pulled atom and its neighbors break first, followed by a relaxation of the free boundary of the graphene containing now one vacancy, see Fig. 13.

3.2.4 Graphene membrane “pull-out” experiment

The purpose of this computational test is to simulate the bond-breaking phenomena occurring during indentation of a circular graphene membrane by a point-like indenter. The edges of the membrane, consisting of two outer layers of atoms, are fixed. At each indentation depth \( \delta \), the central carbon atom of the membrane is pulled down and fixed, while the rest of the structure is relaxed using the CG algorithm (see Fig. 14). The relatively small system used (\( \sim 10\text{Å} \) in diameter) allowed us to perform calculations of the same system using first-principles methods, thus allowing a direct comparison of SED-REBO potential with DFT. The energy per atom at each step is plotted as a function of displacement of the central atom in Fig. 15. It is clearly seen that the behavior of the membrane as the central atom is pulled down differs greatly for the two interatomic potentials - SED-REBO and REBO. The REBO potential shows an increase of the per-atom energy about five times.
Figure 12.: Evolution of the ribbon during the pull-out experiment with REBO. Snapshots (a) to (f) correspond respectively to events A to F on Fig. 11.
Figure 13.: Evolution of the ribbon during the pull-out experiment with SED-REBO. Snapshots (a), (b), (c) corresponds respectively to events A, B and C on Fig. 11.
Figure 14.: Membrane “pull-out” computational experiment. (a): top view of the initial system. The color shows the fixed edges (red) and the central atom being pulled (blue). (b), (c) and (d): side view of the membrane a moment before failure, with REBO and SED-REBO potentials, as well as DFT.
Figure 15.: Energy per atom during the membrane pull-out computational experiment. Comparison between REBO, SED-REBO potentials and DFT results.
larger than that predicted by the SED-REBO potential. In fact, in the REBO computational experiment, the pulling of the central bond results in the stretching of almost all bonds of the membrane, causing a large increase in the total energy. After the bond length between the central atom and its neighbors is increased up to the bond length corresponding to switching region, the artificially large forces will let the neighboring atoms to pull their next neighbors, which then pull their neighbors, etc. Thus a large number of atoms are involved in the membrane response causing a substantial increase in the energy. On the contrary, SED-REBO potential predicts correct behavior: the bond length between the central atom and its first nearest neighbors increases until a critical bond length corresponding to bond breaking is reached. The further nearest atoms located away from the center are insignificantly affected, see Fig. 14 for a picture of the membrane geometry right before failure. The comparison with DFT data shows that the SED-REBO predicts the correct response. As was mentioned earlier, the various values of SED-REBO parameters $n$ (strength of screening) and $m$ (speed of divergence of the renormalized distance, Eq. 3.4) were explored in this pull-out test. It was shown that they hardly affect the behavior at bond breaking. The excellent agreement between DFT and SED-REBO energy change curves demonstrates excellent capabilities of the SED-REBO potential in describing the behavior of carbon systems at extreme conditions.

### 3.3 SED-REBO-S for shock compression of diamond

The benefits of SED-REBO potential can also be demonstrated in case of large compression of carbon materials. As discussed earlier, compression involves reduction of first, second and farther nearest neighbor distances. Within the REBO fixed cutoff framework, the compression brings these atoms into the calculation, resulting in a sharp unphysical increase in total energy, see, for example, the sharp increase of REBO potential binding energy curve at interatomic distances $r_{cc} \sim 1.1 - 1.2$ Å in Fig. 7. The screening function employed in SED-REBO allows us to avoid this phenomena by keeping the model to 1st NN only, thus
Table 9: Parameters for the repulsive ($V_R$) and attractive ($V_A$) functions in SED-REBO-S.
For Eq. 3.11.

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<tr>
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<tr>
<td>$A_9$</td>
<td>$5.42827 \times 10^0$</td>
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Figure 16.: Binding energy for diamond with SED-REBO-S. Comparison between DFT, and REBO, SED-REBO and SED-REBO-S potentials, the short-cutoff version of the potential specifically designed to investigate large compression in carbon materials.
Figure 17.: Uniaxial response of diamond to shock compression in ⟨110⟩ direction. Energy and longitudinal stress $\sigma_{xx}$ response. The SED-REBO calculations were performed with the short-cutoff version, SED-REBO-S.
providing a critical advantage compared to REBO, in the investigation of shock induced compression of diamond single crystals.

The SED-REBO potential presented above can be applied to both stretching and compression of carbon materials. However, in the particular case of large compressions, using large cutoff distance will result in a substantial computational expense by bringing many unnecessary calculations involving further nearest neighbors, which will be eventually discarded to keep first-nearest neighbor atoms only. Thus, a version of the SED-REBO potential, SED-REBO-S, was developed which utilizes a shorter cutoff, thus allowing to save computational time while investigating the response of diamond to shock compression [37]. The parameters of the SED-REBO-S potential must be determined in a separate fitting because the switching off of the interactions at interatomic distances above cut-off distance is embedded in the functional form of the pairwise functions, see Eq. 3.10. Therefore, the cutoff is now a parameter of the potential, and changing its value entails changing the parameters of the pairwise functions. The functional form is the same as described earlier (Eq. 3.1), only the cutoff distance, changed to 2.0 Å for SED-REBO-S, and the forms for the attractive and repulsive pairwise interactions differ. The latter is given by the function:

\[
V(r) = A_0 \bar{r}^{A_5} \times \exp\left(A_1 \bar{r}^{A_7}\right) + A_2 \bar{r}^3 + A_3 \bar{r}^4 + A_4 \bar{r}^5 + A_6 \bar{r}^6 + A_8 \left(\frac{\bar{r}}{r^2}\right)^{A_9}
\]

(3.11)

where \( \bar{r} = r_c - r \) and the coefficients \( A \) are given in table 9, page 55. The new binding energy curve for diamond is presented in Fig. 16. It should be noted that the position of the spinodal point for SED-REBO-S is different from both, SED-REBO and DFT. This is insignificant for compression situations, as the proper description of spinodal point is critically important only for bond-breaking phenomena under tensile loads. In the case of compressed material, the spinodal point can not be reached as this bond length corresponds to second and third NN atoms in uncompressed material. By construction these atoms are
completely screened out and will not contribute to the SED-REBO-S potential function. By design, the SED-REBO-S potential describes well large hydrostatic compressions of diamond. However, the shock compression of diamond [109, 110] involves uniaxial compressions. The behavior of SED-REBO-S under uniaxial loads is shown in Fig. 41, including the energy and longitudinal stress for diamond static compression in the high-symmetry direction $\langle 110 \rangle$. The SED-REBO-S potential displays much better behavior than the REBO potential. The latter exhibits a sudden increase in energy at a relatively moderate compression ratio $V/V_0 \approx 80\%$ due to the appearance of second NN atoms within the fixed cutoff distance. In contrast, the SED-REBO-S potential displays a much smoother response up to very high compressions. When compared to DFT, SED-REBO-S exhibits some deviations. This is related to the fact that the bond-order expression was taken from the original REBO potential [29] without any substantial changes. However, the uniaxial compressions bring new atomic geometries, significantly different from those in uncompressed diamond and graphene, which were primarily used in fitting the angular function $G(\cos(\theta))$ in the bond-order. This limited sampling of the bond angles during the fitting of the original REBO is the cause of deviations from DFT at large compressions as none of such atomic configurations were included in the fitting database. Such improvements of the bond order under high compressions will be the subject of future work.
Chapter 4  
Atomistic Simulations of Nanoindentation of Graphene Membranes

4.1 Introduction

One of the important applications of the SED-REBO potential developed in this work is the simulation of nanoindentation of graphene membranes. The pioneering experimental work by Geim and Novoselov on graphene exfoliation and the discovery of its extraordinary properties [120] has triggered an enormous scientific interest. Graphene is a one atom thick layer of carbon atoms arranged in a honeycomb lattice, and possesses exceptional electrical, optical and magnetic properties. In collaboration with Geim and Novoselov, Meyer and co-workers investigated the structure of graphene suspended membranes [121]. Those membranes exhibit exceptional mechanical properties, as shown in recent work by Lee and co-workers [108], which make graphene one of the best candidates for the development of new nanoelectromechanical (NEMS) devices [122–124]. The nanoindentation of graphene membranes, which probes the mechanical properties of materials, demonstrated that graphene is one of the strongest materials known to man [108]. The exceptional strength of graphene allows the design of unique NEMS devices such as pressure sensor and resonators [125, 126]. For this purpose, investigation of graphene’s mechanical properties, including response of graphene membranes to mechanical loading is of great interest.

The elastic properties of graphene have been investigated by several computational methods using different types of loading such as uniaxial stretching, bending, etc. These methods include finite element methods (FEM) [127, 128], first-principles simulations [113, 129, 130], molecular dynamics and molecular mechanics simulations using empirical in-
teratomic potentials [47, 68, 72, 131–134] or force-fields [127, 135], tight-binding (TB) atomistic simulations [136], and multiscale simulations such as coupled quantum mechanical/molecular mechanical (QM/MM) [137]. In addition, closed-form solutions to the equations of continuum mechanics, using the REBO interatomic potential, have been obtained [68, 74, 127, 138–141]. Specific example of nanoindentation modeling includes a domain-reduction multiscale model by Medyanik et al. [132] applied to simulate the indentation of a large hexagonal graphene sheet. They obtained the membrane profile as well as the indentation curve; Xu and Liao [127], who compared the closed form, MD and FEM results, found reasonable agreement between the three methods; Duan et al [135] used force fields to simulate indentation of a circular graphene sheet by a central point-load and found discrepancies between the model and theoretical elastic plate solution at large deflections. Neek-Amal and Peeters [47] used MD simulations to obtain indentation curves for circular graphene membranes indented by a pyramidal tip and reproduced the non-linear response observed in experiment [108].

Previous studies have also focused on the breaking strength of graphene: Cadelano et al. [136] obtained the stress-strain relation for equibiaxial stretching of a graphene sheet and found excellent agreement with experiment. The breaking strength of graphene nanoribbons under loading in zig-zag or armchair direction was determined independently by MD simulations and first-principles methods, which demonstrated the anisotropy of graphene’s response under uniaxial stretching [64, 130]. Zhao and Aluru used the kinetic theory of fracture to investigate the dependence of graphene’s strength in both directions as a function of temperature and strain-rate [134], while Min and Aluru performed a similar analysis in the case of shear deformations [72]. The general case of the fracture of brittle materials was recently reviewed by Vanel and coworkers [142]. An idealized quasi-1D discrete model was first presented by Thomson [143], showing that under sufficient stress, cracks initiated by bond-breaking can propagate in the material by loading the neighboring bonds (“lattice trapping”). Holian and coworkers then investigated the mechanisms
of crack propagation in various 2D and 3D lattices [144–147]. Terdalkar et al. [133] presented the results of nudge elastic bands calculations of crack propagation in graphene, and found that the process consists of alternating and competing events of bond breaking and rotations. Khare et al. [137] used a QM/MM method to confirm the lattice trapping effect during the propagation of a crack in graphene introduced by Thomson.

In this chapter we investigate these different but related phenomena which are critical for the design of NEMS, including the response of graphene membranes to large indentations, the subsequent membrane failure quantified by the strength of the material, and the following process of crack propagation which completely destroys the membrane. The nanoindentation response, failure and crack propagation in graphene under nanoindentation were investigated using MD simulations, with both REBO and SED-REBO interatomic potentials. We first obtained the indentation curves (load vs. indentation depth) and stress-strain curves for the central part of the membrane, which define the mechanical response of graphene to loading. But the characterization of the failure of the membrane necessitates a more thorough approach. This is because the failure under a critical load and associated strength of the material is a dynamical process in which parameters such as the waiting time to failure, strain-rate or even temperature should be accounted for [134]. We thus used the kinetic theory of fracture to determine the breaking strength of graphene. Finally, we were able to investigate with an atomic-scale and sub-picosecond resolutions the mechanisms of crack initiation and propagation that occur after the failure and destroy the membrane.

4.2 Computational methods

The REBO and SED-REBO potentials were implemented in the MD code LAMMPS [148] that was used to carry out the simulations. The samples consisted of circular membranes of diameter D (from 100 to 3000 Å) plus two layers of clamped atoms, whose position was fixed during the whole simulation in order to mimic the experimental conditions of a suspended clamped membrane. The center of the membrane coincides with the center of
an carbon hexagon. Then an indentation depth was imposed to the membrane according to the theory of elasticity of circular plates under central point load [149]. An indenter was then inserted in the system, represented by a repulsive spherical potential:

\[ V(r) = K \ast \theta(R - r) * (R - r)^3 \]  \hspace{1cm} (4.1)

where \( K \) is the specified force-constant, \( R \) the radius of the indenter and \( r \) the distance of the atom to the center of the indenter. This ideal representation of real AFM indenteres used in experiments (AFM tip) makes sense as it prevents the chemical reactions between the tip and the indented medium, which is achieved in experiment by passivating the tip.

Once the the indenter is applied, the system was relaxed to account for its finite rather than point-like size and the discreteness of the sample, which are often assumed when ideal continuum elastic medium theory is applied [149]. All simulations were ran within the NVT ensemble with a timestep of 1 fs, and the atomic energy and stress-tensor components for each atom were recorded for analysis. The stress tensor for the atom \( i \) was calculated using the virial theorem [150]:

\[ S_{ab}(i) = -\left[-m v_{ia} v_{ib} + \frac{1}{2} \sum_{j=1}^{N} (r_{ia} F_{ib} + r_{ib} F_{ia}) \right] \]  \hspace{1cm} (4.2)

where the indices \( a, b, \) and \( c \) take the values \( x, y, \) and \( z, \) resulting in the six-component pressure tensor \( S = \{ S_{xx}, S_{yy}, S_{zz}, S_{xy}, S_{xz}, S_{yz} \}. \) The first term in Eq.4.2 represent the kinetic energy contribution, the second term involves forces from neighbors of \( i. \) \( r_1 \) and \( r_2 \) are the positions of the two atoms, and \( F_1 \) and \( F_2 \) the pairwise forces acting on each atom.

Using the stress tensor \( S_{ab}, \) the atomic pressure on atom \( i \) is calculated as:

\[ P(i) = \frac{1}{3} \sum_{a=x,y,z} S_{aa} \]  \hspace{1cm} (4.3)

and has dimension pressure \( \times \) volume expressed in eVs. In order to recover the familiar
pressure units one needs to define the volume per atom. Since the indentation by a finite-
size indenter is characterized by a highly non-uniform stress distribution, the definition of
a local surface related to the atomic stresses is ambiguous. Therefore the units used in this
chapter are pressure $\times$ volume. When comparing with the experiment, the N/m units will be
used, because the calculation of the actual pressures requires the definition of the thickness
of graphene, which remains a challenge and a subject of controversy [45].

The indentation curves were obtained with the following method: at each indentation
depth, and after the initial preparation described above, the membrane was heated to 1000
K (5 ps), cooled down to 0 K (10 ps), and finally relaxed using the conjugate gradient
method. The heating process was introduced to equilibrate the system by acceleration of
the transient physical processes, but since the whole system is then slowly cooled down
and relaxed, the results should be considered as “cold” calculations.

4.3 REBO nanoindentation results

The indentation curves obtained from the computational nanoindentation experiments are
shown in Fig. 18. As a function of indentation depth, each curve exhibits a similar behavior:
a linear response of the load force at small indentations followed by a rapid non-linear rise,
until the appearance of defects. Figure 19 shows the state of the membrane at several
indentation depths. Only the region near the indenter is shown. We see that defects are
formed under the indenter, but the membrane is not open yet, as all atoms are still in contact
with the indenter. The membrane therefore behaves as a ductile material: the material
undergoes plastic deformations that lower the measured load gradually, eventually causing
failure, as opposed to a sudden failure of the membrane in case of brittle fracture. Another
striking observation is the presence of numerous, multi-atom carbon chains. These chains
have been discussed earlier in the validation part of the potential, and shown to be a pure
artifact of REBO. As the number of defects increases, the force exerted on the indenter,
directly related to the tip/surface contact area, increases slower and slower, before reaching
Figure 18.: Indentation curves from MD simulation with REBO. Force versus indentation depth for the two membrane subsets: small diameter membranes (a) and large diameter membranes (b). $D$ is the membrane diameter and $R$ is the indenter radius, both in Å.
Figure 19.: Central part of the membrane at different indentation depths. Dimensions are $D = 2000 \, \text{Å}$, $R = 100 \, \text{Å}$, and snapshots were taken at different indentation depths: a - 270 Å, b - 300 Å, c - 320 Å, and d - 350 Å. The linear size is about 300 Å. Coloring is according to the atomically-resolved potential energy, increasing from dark blue to red.
Figure 20.: Central part of the membrane during dynamic indentation. Dimensions are $D=2000\ \AA$, $R=100\ \AA$, and snapshots were taken at different indentation depths: a - 297; b - 297.5; c - 298; d - 298.5; e - 300; f - 305; g - 310; and h - 350\ \AA. The coloring depicts the atomically-resolved pressure (increasing from dark blue to red).
a plateau, and eventually decreasing to zero after a complete breaking.

Using a subset of small diameter membrane membranes, we found that the curves are almost identical up to the points where defects start to appear (Fig. 18-a). This is the consequence of the fact that the tip diameter is small compared to the diameter of the membrane. The deformations are determined by the magnitude of the load only (point indenter approximation) rather than the finite contact area with the tip. This is in agreement with theoretical results on circular clamped elastic membranes, and experimental observations, which showed that the load vs indentation relation obeys:

\[ F(\delta) = a \delta + b \delta^3 \]  

(4.4)

where \( \delta \) is the deflection of the membrane, \( F \) the load, \( a \) a coefficient proportional to the initial prestress in the membrane [151] and \( b \) varies as \( D^{-2} \), the diameter of the membrane [152]. The indenter radius is not a variable in this equation. The same was observed for the “large” subset (Fig. 18-b). An accurate sampling of indentation depths was performed for the membrane of diameter \( D = 2000 \) Å and indenter radii \( R = 100 \) Å and \( R = 50 \) Å. Due to a substantial computational cost, fewer points were calculated for the two other membranes (2500 and 3000 Å). This was done mostly to validate the previous results extended to the samples of larger size approaching experimental dimensions.

In order to observe the fracture mechanisms, dynamical nanoindentation experiments were performed, using the 2000 Å diameter graphene membrane and 100 Å indenter radius. The dynamic indentation started from the initial indentation depth \( \delta = 230 \) Å. Under this initial indentation, the membrane was relaxed under static loading to prepare the initial configuration and the sample has been inspected to make sure that defects are absent. Then, a constant velocity \( 2.5 \) Å/ps was applied to the indenter until it reached an indentation depth 350 Å. The MD indentation simulations were performed at a constant temperature of 300 K using the NVT ensemble. During the run, atomically-resolved stresses and potential energies of the atoms were recorded for further analysis. The membrane breaking occurred at
a smaller indentation depth compared to the static indentation experiments, thus exhibiting
the importance of the dynamic effects during the defect formation in the membrane under
the indenter. The rate of the indentation, 2.5 Å/ps, is fast compared to experiment and this
may also cause earlier failure.

Figure 20 shows the pressure distribution under the indenter at several stages of the dy-
namical indentation. Clearly, the loading pressure is concentrated in the area immediately
under the indenter. The local potential energy can be seen increasing, due to the stretching
of the bonds under increasing load, until the first defect appears, see Fig. 20-b. This does
not occur exactly at the center of the membrane due to the statistical nature of the pro-
cess involving thermal fluctuations. Once the localized defect appears, the fracture rapidly
grows by releasing the elastic energy and pressure by breaking the graphene bonds, see
Fig. 20-c, and 20-d. The very localized distribution of energy and pressure within a rather
small membrane/tip contact area could explain the experimental observation that the break-
ing strength does not depend on the membrane diameter. As long as the membrane diameter
is large compared to the tip radius, the only atoms affected by the indentation are those that
are under the indenter. In our computational experiments, independence of the breaking
strength on the indenter radius has not been clearly established. Eventually, the growth of
the crack initiated by fracture continues to propagate and causes complete breaking of the
membrane, see progressive snapshots e, f, g, h in Fig. 20.

4.4 SED-REBO nanoindentation results

The non-physical ductile fracture of graphene produced by the REBO potential, as was
also reported for carbon nanotubes [45, 46, 95]. This fact served as a motivation for the
development of the SED-REBO potential. Therefore, the SED-REBO potential has been
applied to investigate the response of graphene membranes to indentation. In addition to
the indentation curves, the strength of graphene was determined, and the mechanisms of
crack propagation after failure were established.
4.4.1 Indentation curves

Figure 21 displays the indentations curves obtained using the SED-REBO potential, with the method discussed earlier in this chapter. Membranes with diameters $D = 400, 600, 800 \, \text{Å}$, and indenter radii $R = 10, 20, 30 \, \text{Å}$ were used. The load response is seen to exhibit a non-linear response ($\sim \delta^3$) at high $\delta$, in agreement with experimental observation and non-linear elasticity theory predictions [108], REBO results, as well as other recent computational experiments [47]. The $D^{-2}$ dependence of the non-linear coefficient in Eq. 4.4 is shown in Fig. 22.

As expected SED-REBO simulations demonstrate the brittle character of graphene, see Fig. 21. Each sample, was visually inspected after the relaxation, and showed no defect appearing until the critical load/depth $\delta^*$ is reached. For $\delta > \delta^*$, large cracks cause the complete failure of the membrane. Britleness was also observed in experiments, and this point exhibits in a stunning fashion the importance of using interatomic potentials tailored to the conditions of the computational experiment: as shown in the previous section, previous work with REBO showed that many defects and long linear carbon chains were created during the indentation process, without causing the failure of the membrane. In other words REBO yields an unphysical ductile failure of graphene. SED-REBO predicts the correct behavior for graphene failure.

The investigation of the stress-strain response at the center of the membrane revealed a new and important result: for the atoms directly under the indenter, the loading process is virtually identical to equibiaxial stretching of a flat infinite graphene sheet. Fig. 23 shows that the stress-strain data extracted from our indentation simulations lie, up to very large strains, on top of the cold curve obtained for the uniform expansion of a flat graphene sheet at 0K. Similarly, indentation simulations at 1000 K (on smaller samples in order to save substantial computational time) and equibiaxial expansion of graphene performed at the same temperature, confirmed the results obtained in the cold case (see Fig. 23). Therefore we conclude that the stress-strain response at the center of the membrane is, as would be
expected, temperature dependent, but surprisingly also curvature independent. As a side note, for indenter sizes smaller than 10 Å, the curvature starts to play a role, as will be discussed in the next section.

### 4.4.2 Breaking strength

The indentation curves are nonetheless insufficient to determine the breaking strength of graphene. Indeed only a lower bound of the critical load/depth can be extracted, since performing a continuous indentation at rates relevant to experiments would involve considerable computational costs. In addition, the link between the load and the stress in the material used in [108] is based on the theory of continuous mechanical plates, not well suited for our atomistic simulations.

Instead, the breaking of graphene under indentation must be defined using the kinetic theory of bond fracture, and it depends not only on the temperature but also the waiting time to failure. According to Zhurkov’s work [153, 154], the failure time (average time required for the breaking of bonds) of a brittle material sample having a number \( n_s \) of bonds under a constant stress \( \sigma \), is given by the following equation:

\[
\tau = \frac{\tau_0}{n_s} \exp\left(\frac{U_0 - \gamma \sigma}{k_B T}\right)
\]

where \( \tau_0 \) is the typical vibrational time of chemical bonds in solids, \( U_0 \) the dissociation energy of graphene, \( \gamma = qV \) with \( q \) the coefficient of local overstress and \( V \) the activation volume, \( k_B \) the Boltzmann constant and \( T \) the temperature of the system. \( U_0 - \gamma \sigma \) represents the energy barrier to overcome in order to yield bond breaking, see the schematic in Fig. 24. Theoretically [142], Eq. 4.5 can be obtained from Eyring’s reaction-rate theory equation by neglecting the last term representing the small probability of self-healing (i.e.
Figure 21.: Indentation curves from MD simulations with SED-REBO. Crosses represent the highest load/depth reached before failure. A cubic fit was performed, in agreement with previous works for large indentation depths.
Figure 22.: Parameter $b$ from the non-linear fit of the indentation curves. See Eq. 4.4, Fig. 21. Triangles are from Neek-Amal and Peeters’ work with REBO [47] and data are fit according to $D^{-2}$ as proposed by [152].
Figure 23.: Stress - strain curves for graphene. Symbols were obtained from simulations of a circular membrane of diameter $D$ and indenter radius $R$ (first and second number respectively, in Å). The lines were obtained from equibiaxial expansion of an infinite graphene sheet.
Figure 24.: Energy barrier for bond breaking under external stress. $r_0$ is the equilibrium interatomic distance.
\[ k \approx \frac{1}{\tau_0} \exp \left(- \frac{U_0}{k_B T} \right) \left[ \exp \left( \frac{\gamma \sigma}{k_B T} \right) - \exp \left( - \frac{\gamma \sigma}{k_B T} \right) \right] \] (4.6)

In the case of constant temperature and a stress uniformly distributed in the sample, the failure time is simply \( \tau = 1/k \). However, in general conditions including time-dependent loading and non-uniform stress distribution, the failure time must be determined by solving the equation:

\[ \int_0^\tau k(\sigma, t, T) \, dt = 1 \] (4.7)

For a time-independent stress uniformly loading \( n_s \) number of bonds at fixed temperature, this equation reduces to 4.5. Equation 4.7 can be used to define a breaking strength \( \sigma^* \) of the sample for a given strain rate and/or spatial stress distribution. In the last case the breaking strength can be defined as the maximal stress, for instance under the tip of an indenter, resulting in bond failure in the sample for the prescribed failure time. It is important to note that such defined failure time is essentially the average waiting time for the formation of an atomic-size crack by bond breaking, and does not include the time required for the following processes of crack growth and propagation. However, these processes take a much shorter time, as our simulation of indentation shows.

In experiment and MD simulation the failure time can be obtained by averaging the breaking times over an ensemble of samples, which are distributed with the density:

\[ \rho(t) = k \exp (-kt) \] (4.8)

Since 4.8 represents a probability of failure as a function of the applied stress, a statistical study is necessary in order to determine the failure time vs stress. Indeed, the stress \( \sigma \) and the waiting time \( \tau \) are not independent variables: the longer the waiting time, the higher the probability to break at a stress much lower than the ideal (intrinsic) breaking strength.
Figure 25.: Breaking times (logarithmic scale) vs applied stress for a graphene membrane under indentation. The system consists of graphene membrane of diameter D=100 Å and an indenter of radius R=20 Å, at T=1000 and 300 K. The critical stress corresponds to the applied planar stress on the central carbon hexagon of the membrane. The lines are fit to the exponential relation (4.5).
of the material. Such effect is illustrated in Fig. 25 which shows the distribution of failure times as a function of the applied stress. It can be seen that, as expected from Eq. 4.5, the stress necessary to break a bond \((i.e. \text{the breaking strength } \sigma^*)\) diminishes as the waiting time increases. However an accurate evaluation of \(\sigma^*\) for a given waiting time to failure necessitates a rigorous statistical analysis of the breaking strength distribution, and the extrapolation to larger waiting times must be done with particular caution.

Table 10 gives the breaking strength \(\sigma^*\) for graphene under equibiaxial expansion and indentation at various temperatures. The breaking strength at 0 K (ideal strength) for a flat membrane was determined from the maximum of the stress-strain curve. For non-zero temperatures, since the material can break at stresses below its “true” strength due to thermal fluctuations, the value was obtained by extrapolating a fit of the stress-strain curve to a non-linear function \(\sigma = ae + be^2\). For the indentation results, we extrapolated from the rough fit presented in Fig. 25. Nonetheless, it should appear clearly that while \(\sigma^*\) for graphene under indentation approaches the value obtained for an infinite sheet of graphene for very short waiting time, the strength diminishes importantly if the waiting time is even only of the order of the nanosecond. Therefore, in order to design reliable NEMS and MEMS, the required strength of the material should take into account the relevant time scale of operation of the device. As a comment, our results are over 25% lower than the reported from experiments, despite very good agreement with first-principles calculations. In addition, authors of the experiment consider the material to be nearly free of defects, as our computational samples. It should thus be mentioned that the experimental result was only obtained indirectly, through notably the use of finite element methods (FEM) \[108\], which could explain the discrepancy.

Our method to determine the breaking strength of graphene \(\sigma^*\) under indentation is the following: stress is applied to a membrane \((D = 100 \text{ Å})\) by an immobile indenter, during a NVT run at 1000 K. During the simulation time of 12 ps, a positive outcome is reported as a failure (characterized by an immediate sharp drop of the atomic pressure), after at least 4 ps.
Ideally the strength should be defined in the interval \( [\tau, \tau + \delta \tau] \), nonetheless the exponential dependence illustrated in Fig. 25 indicates that the deviation of \( \sigma^* \) would be very small within a short interval such as 8 ps. Using multiple initial conditions, a distribution of the stresses at failure is built, of which the average gives the breaking strength \( \sigma^* \), for \( t \in [4, 12] \) ps (see figure 26). The short waiting time, as well as the high temperature, are dictated by computational costs; during an experiment, those conditions would rather be room temperature and of the order of microseconds. The \( \sigma^* \) vs \( R \) dependence is shown in Fig. 27-a. The atomic pressure in our calculations is obtained from the virial theorem and therefore has the dimension of an energy. We chose to keep it in such units in order to avoid the non-trivial definition of the atomic surface or volume under the indenter. The curve follows two trends: increases first, then decreases slowly after reaching a maximum for \( R = 15 \) Å.

Increase can be explained by the very small size of the indenter, comparable to inter-atomic bond distances in graphene, resulting in the curvature and therefore weakening of the bonds. As an example, for \( R = 5 \) Å, the average bond order in the central ring is decreased by about 1% compared to flat graphene. Such effect would reduce the ideal strength of graphene under equibiaxial expansion by about 5%, which corresponds approximately to the amount in Fig. 27. As \( R \) increases the curvature becomes less and less influential and therefore the sheet approaches its maximum strength. The following part shows now a decrease of the strength which is explained by another phenomena. Eq. 4.5 expresses the failure time in the case of a uniform distribution of the stresses over equivalent sites, each of these \( n_S \) sites having an equal probability to break. The more sites, the higher the probability to break even at lower stresses and thus the smaller the breaking strength. But in the case of a spherical indenter, the stresses are actually distributed non-evenly over the contact area, decreasing as the distance from the center the sheet increases. Therefore the membrane now consists of a certain number of non equivalent sites each having its own probability of failure. The modified equation based on 4.7 for a continuous distribution is
Table 10: Breaking strength of graphene. $\sigma^*$ (in N.m$^{-1}$) from equibiaxial expansion of infinite flat sheet and indentation of circular clamped membranes.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Equibiaxial Expansion</th>
<th>Indentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>DFT$^1$</td>
</tr>
<tr>
<td>0 °K</td>
<td>31.6</td>
<td>33.5</td>
</tr>
<tr>
<td>300 °K</td>
<td>30.0$^4$</td>
<td>-</td>
</tr>
<tr>
<td>1000 °K</td>
<td>27.2$^4$</td>
<td>-</td>
</tr>
</tbody>
</table>

1 This work, using the DMOL$^3$ package
2 Estimated from exponential fit in Fig. 25
3 From Ref. [108]
4 Extracted from stress-strain curves
Figure 26.: Determination of the breaking strength by statistical average. $N_T$ is the total number of simulations run for the given stress (atomic pressure, in eV). $N^*$ is the number of positive outcomes (i.e. failure for $t \in [4, 12]$ ps). The weighted average of $N^*/N_T$ gives the breaking strength $\sigma^*$. Present data are for $D = 100$ Å, $R = 10$ Å.
given by:

\[
\int_0^\infty dr \int_0^{1/\tau} k[T, \sigma(r)] dt = 1 \quad (4.9)
\]

or, in the case of discrete lattice with \(n\) non-equivalent sites \(i:\)

\[
k_i = \frac{n_{s_i}}{\tau_0} \exp \left( -\frac{U_0 - \gamma \sigma_i}{k_B T} \right) \quad (4.10)
\]

\[
\int_0^{1/\tau} \sum_{i=1}^n k_i[T] dt = 1 \quad (4.11)
\]

it can then be shown that this expression reduces to:

\[
k = \frac{1}{\tau_0} \left\{ \sum_{i=1}^n n_{s_i} \exp \left( -\frac{U_0 - \gamma \sigma_i}{k_B T} \right) \right\} = \sum_{i=1}^n k_i \quad (4.12)
\]

So it is expected that for a distribution stresses over an extended area, the multiplication of sites results in an increase of the failure rate (i.e. the failure time \(\tau = 1/k\) decreases); or, since this failure time is a fixed parameter in our computational experiment, the stress on the first ring should decrease.

In the present experiment, the stress is distributed over an area which size depends on the indenter radius. Figure 27-b shows the stress on the first non-equivalent sites under the indenter (first sites correspond to the central hexagon of the membrane, directly under the indenter). For \(R = 5\), the stress on the second atomic ring (second-closest atoms to the center of the membrane), is decreased by over 20% compared to the first ring, making it very unlikely for the failure to occur out of the central ring. However for \(R = 20\) and more, the stress is lowered by less than 10% on the fifth ring, offering considerably more sites for the failure to occur (see Fig. 27-b), and therefore lowering the breaking strength. Such effect was not noticed in experiment where very large tips were used (over 150 \(\text{Å}\) in radius) however from our results the strength variation is only a few percents between \(R = 15\) and \(R = 30\) \(\text{Å}\), well below the experimental uncertainty (nearly 10 \%[108]).
Figure 27.: Breaking strength vs tip radius and stress distribution. a: Breaking strength, line is a guide to the eye. b: Stresses over the first 5 rings of atoms. Ratio of the average stress over ring $i$ to the maximum stress $\sigma_0$. 
4.4.3 Crack propagation in graphene

After the initial bond fracture in the contact area, a crack propagates rapidly causing the failure of the membrane (Fig. 28). The pressure released from the bond breaking event is transferred to the neighboring bonds, causing them to break subsequently. The strong symmetry of the graphene unit cell and isotropy of the stress distribution in the vicinity of the center of the membrane favors a linear propagation of the crack, sustained by the local stress field. The observed propagation speed (4 to 5 km/s) is well below the reported sound speed in graphene (\(\sim 20\text{km/s}\)). The time between each bond breaking event is explained by the discreteness of the medium, and is predicted by theoretical models describing “lattice trapping” mechanisms where the crack can remain stable until the stress concentration transferred to the next bond is sufficient to cause it to fail [143]. It is to be noted that as a crack is initiated, it will continue to propagate up to the boundary of the contact region, causing a catastrophic failure of the sheet, and therefore expressing the brittle character of graphene membranes.

In addition to linear propagation of the crack, branching has also been observed (see Fig. 29). Since the stress load is concentrated on the bonds at the head of the tip, fluctuations can cause one of the bonds located at \(\pm 60^\circ\) of the crack propagation direction to fail first. At this point, a new propagation path is opened. In theory the three bonds at the head of the crack tip can fail simultaneously, but as the local pressure is drastically reduced by each bond breaking, the propagation pathways become competitive, and only two at most can remain. As the crack reaches the regions of lower stress, the load concentration is no longer sufficient to initiate further bond breaking, and the propagation stops. The different propagation pathways are summarized in Fig. 30.

Recent work on crack propagation in graphene showed that both bond breaking and rotation occurred during the growth of a crack in graphene, the second giving rise to Stones-Wales (S-W) defects consisting of 5-7 ring structures [133]. Such phenomena has not been observed in the present work, but a few important differences between the two studies
Figure 28.: Chronology of the membrane breaking and crack growth with SED-REBO. D=100 Å and R=30 Å. Frames size $\sim 50 \times 40$ Å². 

a: $t = t_0$, the circle indicates the first bond to break. 
b: A fracture opens and starts propagating linearly. 
c: Splitting of the crack on the left side. 
d: The crack on the left side now propagates linearly in the two directions opened earlier, new splitting occurs on the right side. 
e: One the cracks opened in c changes its direction, without splitting. 
f: $t = t_0 + 2$ ps, the crack does not evolve anymore.
Figure 29: Crack branching mechanisms. Top: average atomic pressure and bond length for each of the bonds involved in the branching. Bottom: chronology of the branching event. Colored ellipses identify bonds with respect to top graph. Color reflects the atomic pressure.

a) $t = 0.25 \text{ ps}$: the breaking of the previous bond (bond 3) causes the pressure to increase on the three bonds ahead of the crack.

b) $t = 0.30 \text{ ps}$: bond 4-a is the first to break, followed rapidly by the neighboring bonds (4-b and *) before the pressure drop caused by the initial bond breaking is felt. There are three competing cracks pathways.

c) $t = 0.43 \text{ ps}$. The pressure drop on both sides of bond (*) prevent crack growth. The bond healed and pressure drops to zero, because of full relaxation of the bond.
Figure 30.: Pathways of crack propagation. a: linear, b: linear plus 60° branching, c: symmetric branching (±60° split), d: 60° direction change.
should be pointed out. Firstly, the interatomic potentials used in the simulations differ, and so can the defect formation energy. Secondly, the curved geometry of the membrane in our work induces a non-uniform stress distribution in the membrane, and a limited length and time of propagation for the crack. Finally, and perhaps the most important point, the 2-D constrained geometry in [133] prevents the medium from possible out-of-plane relaxations, causing a relief of the local pressure. Earlier results obtained by means of coupled quantum/molecular mechanical modeling reported “moderate lattice trapping”, but did not mention the occurrence of bond rotation causing the formation of S-W defects [137].

4.5 Conclusions

In summary, we investigated the response of graphene membranes to nanoindentation, up to and beyond the failure point. By using the newly developed SED-REBO potential, a brittle fracture of graphene was observed, as opposed to the ductile failure observed with the REBO potential 31. This result highlights the fact that interatomic potential must be carefully used for far-from-equilibrium conditions, since the potentials are often not designed to perform under extreme conditions.

The SED-REBO potential allowed to reproduce the experimental result of a non-linear response of the membrane to large indentation ($\sim \delta^3$ dependence of the load). The critical strength of graphene under these conditions was determined, and it was shown that this quantity, rather than being a “universal” property of the material, depends on both the temperature, and perhaps more importantly, on the waiting time to failure. This last point should be taken into account when the aim is to devise mechanical devices, since the strength of the material will depend on the specific usage (duration of loading in the case of a pressure sensor for instance).

In addition, the MD simulations were used to describe the failure mechanisms of the membrane following the initial bond-breaking event. Subsequently, the broken bond gives rise to a crack when neighboring bonds in turn are broken. The crack propagates as the load
is transferred form one bond to the next, mostly in a linear fashion. Nonetheless, branching of the crack is possible, following the high symmetry directions of the graphene unit cell.
Figure 31.: Comparison of REBO and SED-REBO results for indentation of large-scale membranes. Left: Indentation curves from MD simulations of nanoindentation of circular graphene membranes ($D = 800$ Å) by a spherical indenter ($R = 30$ Å). Solid symbols represent depths for which defects are observed. Right: Snapshots from the central part of the membrane (about $120 \times 100$ Å$^2$). a)-b) REBO potential for $\delta = 110$ Å and 120 Å respectively. c)-d) SED-REBO potential for $\delta = 100$ Å and 105 Å.
Chapter 5
Molecular Dynamics Simulations of Shock Compression of Diamond

5.1 Introduction

The unique features of shock waves, characterized by the high pressure, temperature, and strain rate achieved within the shock front, may result in a wide range of material responses: elastic and plastic deformations, amorphization, polymorphic and melting phase transitions [155–158]. Because of the high strength and strong orientation dependence of covalent bonding, one might expect different and richer dynamic responses in covalent crystals compared for instance to the extensively studied metals [159–162]. The exceptional mechanical properties of diamond in particular, such as its bulk modulus being the highest among all elemental solids and its substantial resistance to shear deformations [163], make it an ideal candidate to probe the different regimes of shock wave propagation in covalently bonded materials.

In early experiments performed at relatively low shock pressure (up to 600 GPa) [164, 165], researchers observed split two waves when diamond is shocked along nearly ⟨111⟩ crystallographic direction and a single wave in ⟨100⟩ direction. Experiments exploring very high pressure (up to 3500 GPa) [166–171] were focused on the phase transition of diamond to liquid or to the high-density solid phase BC8. Unlike for low pressure, where the response may depend greatly on the orientation of the sample due to the symmetry of the unit cells, which causes varying resistance to longitudinal and shear stresses, at such high pressures (> 1 TPa) the material behaves mostly isotropically. Such regimes also prevent the observation of elastic or split elastic-plastic shock waves, occurring at much
lower pressures, and accordingly these later experiments reported single shock wave structure exclusively. Only recently [110], McWilliams et al. discovered the split elastic-plastic two waves structure for all crystallographic directions, ⟨100⟩, ⟨110⟩ and ⟨111⟩, at longitudinal stress up to 800GPa. In addition, Lang and Gupta [109] reported results from shock compression experiments on diamond ⟨110⟩ and also reported split two waves corresponding to an elastic and inelastic response. Regarding the theoretical studies, first-principles calculations have been performed in order to explore the high-pressure part of the phase diagram of carbon [172–174] and the shock Hugoniot of diamond [175]. Nonetheless, the limitations of sample size and simulation time inherent to first-principles methods prevent the understanding of the rich mechanisms causing the transformation of the material at the atomic scale upon dynamical loading.

For this reason, the molecular dynamics (MD) modeling technique is ideally suited to investigate the rich physics of shock: the time (sub-nanosecond) and length (less than 100 nanometers typically) scales at which the shock induced transformations occur within the shock front coincide with the resolution of MD.

Shock simulations were first run with the REBO potential, although the reliability of the potential’s predictions in the high-pressure/temperature regimes characteristics of shock remains questionable. Nonetheless, REBO is a widely used potential for carbon, computationally efficient, and one of the best tools available to investigate the response of carbon materials. In addition, REBO in the high pressure regimes can be considered as a theoretical model for other materials which response coincides with that of “REBO-carbon”.

Furthermore, we are presenting a comparative study of the performance in shock simulation of two recently developed, “beyond-REBO”, interatomic potentials for carbon: the screened environment dependent REBO (SED-REBO [48]) and the long range carbon bond-order potential (LCBOPII [32]). The accuracy of the potentials is assessed by comparing the results of static uniaxial compression, which mimic the conditions realized within the shock front, to density functional theory (DFT) results. Moreover, large-scale
molecular dynamics (MD) simulations of shock were ran with the two potential in the ⟨110⟩ crystallographic direction, uncovering unusual responses that will be discussed. A particular focus is brought on a split elastic-elastic response observed with SED-REBO, characterized by a polymorphic phase transition, and contrasted to the response of LCBOP2 under similar shock conditions.

5.2 Preliminary: REBO results

To simulate shock wave propagation, we employed two different methods. One of them is a standard piston simulation where the compression is applied by a short ranged repulsive potential, equivalent to a piston with infinite mass, located at the left boundary of the simulation box. At the beginning of the simulation, the atoms of the entire sample are given the initial velocity (−u_p) towards the piston. Subsequent collision of the left boundary of the crystal with the piston launches a planar shock wave front, which propagates back into the crystal at shock velocity (u_s). The other method is called Moving Window (MW) technique [176, 177]. As the name suggests, an “observing window” is moving alongside the shock wave and focused upon the shock wave front. As a prerequisite, the initial speed of the atoms shall be set equal to opposite of shock velocity −u_s. An obvious advantage of this method over standard piston simulation is that the simulation time is no longer limited by the size of the box, as opposed to regular piston simulations where the initiated shock wave can only propagate until it reaches the opposite boundary of the simulation box. Therefore the observation time is limited, and it is not guaranteed that the material is in a steady state, rather than experiencing some transition. Thus, a more accurate description of steady shock wave propagation can be achieved by MW technique. However, MW technique can not simulate non stationary two-waves regime of shock wave propagation. Here we compliment piston simulation with MW technique in order to obtain a full picture of shock wave propagation in different regimes.

Most of the simulations were performed using a sample size of 100 × 11 × 11 nm³.
The longest dimension is set along the shock direction $x$ and corresponds to the shock compression direction $\langle 110 \rangle$. Periodic boundary conditions (PBC) are applied along the $y$ and $z$ axis, corresponding to the $\langle \overline{1}10 \rangle$ and $\langle 001 \rangle$ directions respectively. Nonetheless, since PBC act an extra geometrical constraint on the material by preventing large-scale relaxations, several samples with larger dimensions ($200 \times 22 \times 22 \text{nm}^3$ and $400 \times 22 \times 22 \text{nm}^3$) were used to investigate regimes at which important plastic deformations occur. During the simulations, local variables such as temperature, stresses, mass velocity, density and local potential energy are calculated by spatial averaging over a 1-D grid of bins along the x-direction.

For all non-split shock-wave regimes, the simulations were done using MW technique. But for split shock-wave regimes, the first, faster elastic shock wave front was calculated using MW technique; the second, slower shock wave front was extracted from piston simulations even if the latter case can provide both profiles. This is done in order to improve the accuracy of the data because MW simulations are in general more accurate. Specifically, MW which uses shock velocity as an input parameter provides more accurate calculations of the piston velocity. In contrast, the piston simulations face substantial difficulty in the accurate determination of both elastic and plastic shock wave velocities due to the necessity of tracking the shock wave fronts.

### 5.2.1 $u_s - u_p$ and $P - V$ shock Hugoniot

The different regimes of material response to shock compression for diamond in the $\langle 110 \rangle$ direction were classified using the $u_s - u_p$ and $P - V$ shock Hugoniot (Fig. 32). As the piston velocity increases, five distinctive regimes of shock wave propagation were observed:

- (I) Single elastic wave for $u_p < 2 \text{ km/s}$ and $\sigma_{xx} < 126 \text{ GPa}$;
- (II) Split two elastic shock waves for $2 < u_p < 4.1 \text{ km/s}$ and $126 < \sigma_{xx} < 278 \text{ GPa}$;
- (III) Single elastic wave for $4.1 < u_p < 4.82 \text{ km/s}$ and $278 < \sigma_{xx} < 340 \text{ GPa}$,
Figure 32.: $u_s - u_p$ and $P - V$ shock Hugoniot for $\langle110\rangle$ diamond with REBO. Top: diamond $\langle110\rangle$ $u_s - u_p$ shock Hugoniot: shock velocity versus particle velocity. I-V refer to the shock wave regimes: single elastic wave of phase A diamond, split two elastic waves, single elastic wave of phase B diamond, split elastic-plastic shock waves, and two-zone elastic-plastic single shock wave respectively. Triangles, squares, diamond, and open and full circles describe the state of the material. Crosses and plusses are experimental results from [164] and [110]. Bottom: diamond $\langle110\rangle$ $P - V$ shock Hugoniot: longitudinal stress versus compression ratio. Points are data from shock simulations. Lines connecting them are for visual purpose. Symbols and roman numbers have the same meaning as in the top figure. Dotted lines are Rayleigh lines, illustrating the occurrence of single elastic wave in phase B diamond, and single two-zone elastic-plastic shock wave (regimes III and V respectively).
• (IV) Split, elastic-plastic shock waves for \(4.82 < u_p < 6.46 \text{ km/s}\) and \(340 < \sigma_{xx} < 388 \text{ GPa};\)

• (V) Two-zone elastic-plastic single shock wave, \(u_p > 6.46 \text{ km/s}, \sigma_{xx} > 388 \text{ GPa}.$

The elastic regime I corresponds to a single elastic wave propagating with velocity close to the longitudinal sound speed \(c_l = 18.96 \text{ km/s},\) calculated from REBO elastic constants [29], which corresponds to the first triangle at \(u_p = 0\) in Fig. 32, top. The \(u_s-u_p\) relation can be fitted by the linear relation \(u_s = c_l + au_p.\) In the limiting case of a linear dependence of the pressure \(P\) on the compression ratio \(\epsilon,\) the fitting parameter \(a\) is equal to 0.5. According to our results, \(a = 0.65,\) which results in a relatively small deviation from this linear regime of \(P - \epsilon,\) with a slow increase of the shock speed with the piston velocity in the pure elastic wave regime I.

In regime II, a shock-induced transition occurs which results in the splitting of the front into two waves: a faster elastic precursor followed, surprisingly, by another slower but also elastic wave. The leading elastic precursor produces normal compressed diamond (with \(0.91 < V/V_0 < 1),\) but the crystal after the second shock wave front consists of two different elastic phases: normal “low-pressure diamond” (phase A) and new “high-pressure diamond” (phase B) (see Figs. 33 and 34). In other words the crystal undergoes a stress-induced polymorphic phase transition behind the second shock wave front. Such polymorphic phase transition in carbon has been previously reported in the literature. If new forms of diamond have been observed mostly during shock compression experiments of graphite [178–180], the particular hexagonal diamond has also been identified in the case of shock compression of diamond [181]. Nonetheless, the high-pressure phase described here differs from hexagonal diamond in its structure, and the time scale for the kinetic transformation reported in [181](of the order of nanoseconds) is not compatible with the current observation. In regime III, a single elastic wave of phase B diamond is observed. In regime IV, an elastic precursor with phase B moves faster than the following plastic shock
wave, which leads to shock splitting. Regime V is the new regime of shock wave propagation which involves an elastic wave of phase B diamond followed by the plastic wave, both moving with the same velocity, and therefore a constant separation between two fronts. With further increase of particle velocity, the front separation reduces, and the plastic wave transforms into a melting shock wave. The results are compared to experimental data from Refs. [110, 164], showing good agreement for the elastic response, but discrepancies at higher piston velocities. Also it should be noted that the nature of the second wave for $2 < u_p < 4.1 \frac{km}{s}$ differs: REBO gives a phase coexistence, while experimentalists usually describe a plastic wave. Since REBO was not designed for high pressure phases, it should not be a surprise that disagreement with experiment could arise.

The regimes I-V can also be identified by specific ranges of longitudinal stress read from the P-V Hugoniot, which provides additional information about the different regimes (see Fig. 32, bottom). Regime I corresponds to the lowest stresses, for which the $P - \epsilon$ relation is almost linear, as mentioned above. Therefore the velocity of the wave remains nearly constant and close to the longitudinal sound speed in the solid, as shown by the superposition of the data with the Rayleigh line joining the origin ($P = 0$, $\epsilon = 1$) and the $P_A - \epsilon_A$ point, where $P_A$ is the critical pressure for the pure elastic regime. A constant velocity for the single elastic shock wave agrees with experimental results [110].

When the stress reaches the critical stress $P_A = 126$ GPa, split two elastic shock waves appear, indicating the onset of regime II. As presented in the previous section, the second elastic wave is composed of a coexistence of phases A and B diamond shown by squares between $P_A$ and $P_B$ in Fig. 32, bottom. The slope of the corresponding branch of the Hugoniot is smaller than that of the branch I for $P < P_A$, indicating that the second elastic wave moves slower than the first wave, and hence the splitting. The proportion of phase B in the second elastic wave increases with the stress, until the phase transition is complete at $P_B = 249$ GPa, corresponding to the cusp of the curve. There, the material in the second shock consists of phase B diamond exclusively. Afterward, the rapid increase of the stress,
due to low compressibility of the high-pressure phase B, results in the increase of the second elastic wave velocity, see Fig. 32, top, until it overdrives the first one at the onset of regime III ($P = 278$ GPa). Consistently, this onset point lies on the extension of the straight Rayleigh line between the origin and $P_A$, indicating that the second wave consisting of pure phase B has “caught up” with, and will now overcome, the elastic precursor made of regular phase A diamond. Consequently, in regime III only one elastic shock wave with pure phase B is observed. As the stress further increases, the Hugoniot Elastic Limit (HEL) is reached at $P_{HEL} = 340$ GPa, where plastic deformation starts to occur and the shock response enters regime IV. In this regime, the crystal is compressed quickly to a metastable phase B at pressure $P_{HEL}$, then changes to plastic state shown as open circles in Fig. 32. Similarly to regime II, two split shock waves are observed, only now with a precursor made of phase B diamond pinned at the pressure $P_{HEL}$, and a slower following plastic wave. Finally, when the longitudinal stress increases above 450 GPa, the plastic wave overdrives the elastic precursor corresponding to the Rayleigh line origin-$P_{HEL}$ and a single two-zone elastic-plastic wave propagates in regime V. We will now describe in more details the peculiar responses that we presented here: the elastic response and the associated polymorphic phase transition in regime II and III, the split elastic/plastic show waves of regime IV, and the newly discovered two-zone single elastic shock wave of regime V.

5.2.2 Elastic response of diamond in regimes II and III

Regimes II and III are characterized by a stress-induced polymorphic phase transition [182, Chapter 8, (by N. M. Kuznetsov)]-[158, Chapter 6], from normal phase A to high-pressure phase B diamond. In regime II, the shock wave splits into a fast elastic precursor of uniaxially compressed normal diamond and a slower second elastic wave where phase A and B are coexisting. Fig. 33 shows a typical snapshot of the state of the material in this regime. In this example, the shock wave is propagating from left to right with piston velocity 2km/s. The structure in the profiles of the physical variables $\sigma_{xx}$ (longitudinal stress), $\tau_{xy}$ and $\tau_{xz}$
Figure 33.: Split elastic-elastic shock waves in diamond with REBO: atomic structure and shock profile. Top panel: snapshot of diamond sample at \( u_p = 2 \text{ km/s} \) corresponding to regime II: Split elastic-elastic two shock waves. Atomic structure is colored by potential energy of atoms. Bottom panel: longitudinal and shear stresses as a function of the position along shock direction. Diamond is undergoing a phase transition from low-pressure phase A to a mixture of phase A and high-pressure phase B within second elastic wave.
Figure 34.: Phase coexistence in shock compressed diamond with REBO. Top panel: snapshot of stripe zone with $V/V_0 = 0.84$ from Fig. 33, illustrating phase separation. A slice of diamond atomically viewed in $\langle 110 \rangle$ direction. Low-pressure, low-energy phase A where the normal strain is $\epsilon_x = 0.079$ is colored in black; high-pressure, high-energy phase B, with normal strain $\epsilon_x = 0.211$, in red. Bottom panel: Normalized energy distribution of atoms in the part of the sample shown in top panel.
(shear stresses) at the beginning of the first elastic front in Fig. 33 is due to the perturbations created by the piston at the beginning of shock compression and will eventually disappear after enough time as seen in our MW simulations. Two distinct shock wave fronts moving at different speeds are clearly marked by the two-step sharp changes in physical quantities including potential energy of the atoms and stresses. The slower shock wave that moves at velocity $14.3 \text{ km/s}$ leaves regular colored stripes behind its front. Magnified atomic view (and color enhancement) of this region shown in top panel of Fig. 34 indicates that there are no broken bonds, no change in coordination number, no point defects, slipping planes or dislocation loops behind the second shock wave front. Although they resemble shear bands [183] produced by plastic deformations, they are in fact subdomains of two crystalline polymorphs: low-pressure phase A and high-pressure phase B diamond. Both phases are produced by uniaxial compression in $⟨110⟩$ direction, and they are distinguishable by local strains in $x$ and $z$ directions, the relative position of the atoms in the unit cell and energies of atoms. The subdomain structure is formed by cooperative displacements of atoms resulting in such phase separation. While the alternating A-B domains have the same longitudinal stress, they have different atomic potential energies due to different strains, as can be seen from the energy distribution in the bottom panel of Fig. 34. Phase A is lower than phase B in atomic potential energy. The coexistence of unit cells with different atomic structure is characteristic of polymorphic phase transitions. The transition is complete at the onset of regime III ($P = 278$ GPa), and the second wave becomes faster than the precursor causing only a single shock wave to propagate, as discussed in the previous section. At this point all the material in the second wave has turned in phase B diamond, see Fig. 35.

The mechanism underlying this phase transition can be understood by examining the static stress-strain dependency of diamond upon uniaxial compression. As illustrated in Fig. 36, the schematic cold longitudinal stress curve 1-A-C-B is not monotonic with respect to compression ratio $V/V_0$ which specifies the total strain at fixed transverse dimensions of the sample (first-principles and REBO cold curves for diamond $⟨110⟩$ can be found
Figure 35.: Phase transition in the elastic-elastic regime with REBO. Evolution of the composition of the second wave. From top to bottom, profiles corresponding to $u_p = 2$, 3 and 4 km/s respectively. As the piston velocity increases, the proportion of phase B diamond increases, until the transition is complete for $u_p = 4$ km/s. Coloring reflects the atomic potential energy, in eV.
Figure 36.: Schematic of cold compression curve in ⟨110⟩ direction in REBO diamond. Longitudinal stress vs compression ratio. Phase separation occurs due to the non-monotonic behavior of the line 1-A-C-B. The states located between A and C are metastable, corresponding to low-pressure phase diamond; the states between C and B (dotted line) are mechanically unstable. The onset of phase transition is at point A, which corresponds to low-pressure phase; any point on the A-B segment corresponds to phase coexistence of phases A and B; at point B (high-pressure phase) the whole sample is in phase B.
in [184]). Therefore, when the system is slightly compressed, it remains homogeneous until the critical stress at point A, measured to be around 126 GPa, is reached. Further static compression of one-unit-cell system will show an increase of stress until it reaches the local maximum at point C. Somewhere within section A-C, \( \frac{\partial^2 P}{\partial V^2} \) becomes negative, which prohibits the formation of compressive shock waves [155]. Later on, the stress reduces upon compression until the second critical point B is reached. In section B-C, compressibility of the crystal is therefore negative which leads to the mechanical instability of these states. In the case of a realistic many-unit-cell system under finite temperature, the branch A-C is not realized because the metastable states between A and C with homogeneous density are transformed into a mixture of two-phases, phase A and B, corresponding to the points of the segment A-B of Fig. 36, which are arranged in ordered, domain structure, see Fig. 34. As the total strain \( 1 - V/V_0 \) increases, the fraction of phase B increases and phase A completely disappears at the end of the segment A-B. A detailed discussion of the characteristics and mechanisms associated with this phase transition in REBO-diamond can be found in [36].

### 5.2.3 Elastic-plastic split shock waves in regime IV

In regime IV (4.82 < \( u_p < 6.46 \) km/s and 340 < \( \sigma_{xx} < 388 \) GPa), the shear stresses in the material become large enough to induce plastic deformations. As a result, the shock wave splits into two waves: a faster elastic wave consisting of pure phase B diamond, as a continuation of regime III, and a slower following plastic wave. The pressure in the elastic precursor remains pinned at near the HEL (\( P_{HEL} = 340 \) GPa), and its velocity is therefore nearly constant. An example snapshot is shown in Fig. 37, for shock compression generated by a piston moving at 6 km/s towards the right. On the top panel, atomic structure, colored by local energies of atoms, displays two distinctive fronts. Figure 37 shows the leading elastic wave moving at 23.8 km/s while the following plastic wave moves with 20.3 km/s, and is the place of plastic deformations. As seen in the bottom panel of Fig. 37, plasticity
Figure 37.: Split elastic-plastic two shock waves with REBO: atomic structure and shock profile. Top panel: snapshot of diamond sample at $u_p = 6 \text{ km/s}$ corresponding to regime IV: Split elastic-plastic two shock waves. The elastic (phase B) and plastic parts of the sample are represented by different colors according to potential energy of the atoms. Bottom panel - longitudinal and shear stresses as functions of position along shock direction.
results in the increase of longitudinal stress and reduction of shear stresses, characteristic of occurring relaxations, immediately after the second shock front (see the profiles at ∼600 Å). Fluctuations of the physical quantities behind the second front in the profiles are due to the random distribution of localized regions of plastic deformation within the sample.

5.2.4 Two zone elastic-plastic shock wave in regime V

In regime V, the two-zone elastic-plastic single wave was found. This single wave is characterized by a constant separation between elastic and plastic fronts since they move with the same speed. For instance, when particle speed is \( u_p = 6.97 \text{ km/s} \), both wave fronts move at \( u_s = 25 \text{ km/s} \) with a constant separation of 60 Å, see Fig. 38. This separation slightly fluctuates in time due to dynamic interactions between elastic and plastic fronts. The same single two-zone elastic-plastic shock wave structure was recently found in MD simulations of shock propagation in Lennard-Jones (LJ) and aluminum [177], showing that this phenomena is a naturally occurring response in shock compressed materials. Similar to regime (IV), the shear stresses reduce after the plastic wave front. The state of the material in different zones is shown in Fig. 39. As the shock wave propagates from left to right, there are four representative regions. Starting from right, the region with dark color (lowest energy) corresponds to the unperturbed perfect diamond lattice, and is followed by a region were the material is composed of phase B diamond, in an over-compressed state. This metastable state (since compressed above the HEL) is represented by the extension of the second elastic branch of the P-V Hugoniot above the HEL in Fig. 32. At the end of the elastic zone with phase B, lattice deformation start to form a plastic shock front resulting in relaxation of the shear stresses, similar to Fig. 37. At the beginning of the plastic zone, plastic deformations starts to generate nucleation seeds for further amorphization processes visible in the left-most panel of Fig. 39. The amorphization processes are clearly seen in the localized regions far behind the shock wave front [34]. In this regime, the shock inten-
Figure 38.: Two-zone elastic-plastic shock wave in diamond with REBO: shock profile. Stress profile for $u_p = 6.97 \text{ km/s}$, corresponding to regime V: Two zone elastic-plastic single shock wave. As a result, the two wave fronts move at the same speed $u_s = 25 \text{ km/s}$ and separated by 60 Å.
Figure 39.: Two-zone elastic-plastic shock wave in diamond with REBO: atomic structure. Structure of diamond sample at $u_p = 6.97$ km/s corresponding to regime V: Two-zone elastic-plastic single shock wave. The atoms and bonds are colored according to the potential energy of the atoms. Shock wave propagates from left to right. Bottom panel: the whole sample; Middle panel: view from $⟨001⟩$ direction ($z$-axis); Top panel, view from $⟨110⟩$ direction ($y$-axis). From the right to the left, the material transforms from uncompressed state to metastable high-pressure phase B (above HEL), to plastic deformed state, to plastic state with amorphized cluster inclusions.
Figure 40.: Distance between elastic and plastic wave fronts as a function of longitudinal stress in two-zone elastic-plastic regime. When the stress approaches HEL, the distance diverges: the size of the elastic zone approaches infinity, so no plasticity is observed.
sity is large enough to initiate bond breaking processes. For particle velocities greater than 7 km/s, melting starts to occur in the plastic region which results in complete relaxation of the shear stresses to zero.

The elastic front is supported by acoustic waves emitted by plastic deformations within plastic front. These waves propagate towards elastic front and maintain the stress in the elastic zone above the HEL. The same coupling mechanism of elastic and plastic fronts is discussed in details for two-zone single shock waves in metals and LJ crystal in Ref. [177]. The distance between the two fronts depends on the average stress in the elastic zone. As demonstrated in Fig. 40, the stresses in the elastic region are over $P_{\text{HEL}}$, causing overcompressed metastable states of phase B. With the reduction of stress, the distance between two wave fronts increases accordingly, and as the stress reaches the critical stress $P_{\text{HEL}} = 340$ GPa, the distance approaches infinity. While for stresses below $P_{\text{HEL}}$, regime (IV) of split elastic and plastic shock waves was observed, as discussed above. This critical stress therefore characterizes the lower bound of longitudinal stress above which elastic-plastic transition and amorphization occur, consistent with Fig. 32.

5.3 Using beyond-REBO potentials: comparative study between two recently developed interatomic potential: SED-REBO and LCBOPII

Two recently developed potentials for carbon, SED-REBO and LCBOPII, were used to run MD shock simulations of diamond. The comparative study aims at assessing the advantages of the potentials over REBO, as well as identifying potential (and therefore model) independent features.

5.3.1 Uniaxial compressions

Uniaxial cold (0 K) compressions represent the most important test to perform in order to assess the validity of the interatomic potentials for shock wave simulations. Indeed, such compressions allow the direct comparison with DFT results, and offer a good first approx-
Figure 41.: Results from static uniaxial compressions along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. Along the $\langle 110 \rangle$ direction, the non-monotonic behavior of the longitudinal stress observed with DFT is reproduced by both potentials and suggests unusual dynamic responses. Dashed lines for the shear along $\langle 110 \rangle$ show the difference between the two components ($\tau_{xy}$ and $\tau_{xz}$).
imation of the Hugoniot for weak shock wave, where cold effects dominate over kinetic contributions. Within the shock front, almost instantaneous compressions are imposed to the sample, and the short time scale characterizing the front forbids extensive relaxations. 1D compressions were performed for the three high-symmetry directions of the diamond primitive cell ($\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$), using unit cells containing 8, 8 and 16 atoms respectively. The influence of the cell size was also ascertained by using unit cells twice larger in each dimension, without any noticeable effect. The compression was simulated by scaling the unit cell size and atomic positions for each compression step (1%). At each step, the structure was relaxed using a conjugate gradient or steepest descent algorithm. In order to avoid metastable states caused by the instantaneous scaling, a progressive scheme was also employed: the compressed structure obtained after relaxation at step $n$ was scaled and used as the starting configuration for step $n + 1$. Again, no important effect was noticed when comparing the results obtained by either method. The resulting binding energies, longitudinal and shear stresses are presented in Fig. 41, for the three directions.

SED-REBO is very similar to the REBO potential when the screening is not activated (i.e. at low compression). The main features of the DFT stress-strain relation are qualitatively reproduced, but the stresses are in general largely underestimated. In particular, the local maximum of the longitudinal stress in $\langle 110 \rangle$ appears at $V/V_0 = 0.86$ and $\sigma_{xx} = 152$ GPa with SED-REBO, compared to $V/V_0 = 0.71$ and $\sigma_{xx} = 600$ GPa with DFT. Similarly, the non monotonic behavior of the shear stresses (still $\langle 110 \rangle$) is reproduced but the position of the minimum is shifted ($V/V_0 = 0.77$ vs 0.69), and we even notice that it becomes negative. Comparable trends are noticed along $\langle 111 \rangle$.

LCBOPPII reproduces the main features of the stress-strain curves, in particular the position of the extrema, although the potential noticeably overestimates stress at large compression. For $\langle 110 \rangle$ the local maximum for $\sigma_{xx}$ is located at $V/V_0 = 0.72$ and $\sigma_{xx} = 924$ GPa (vs $V/V_0 = 0.71$ and $\sigma_{xx} = 600$ GPa for DFT). The $\langle 110 \rangle$ shear stress shows almost indistinguishable behavior from DFT due to compensation of errors on the longitudinal and
transverse stresses. For ⟨100⟩ and ⟨111⟩ the potential yields excessive longitudinal stresses at large compression due to the insertion of the second neighbors into the NN cut-off distance.

These results show that both potentials offer an improvement over REBO along the three directions, limiting the sudden increase in energy and stress due to second neighbors entering the NN cut-off. This effect is especially visible in the ⟨110⟩ direction, where it occurs at relatively low compression ($V/V_0 = 0.8$). Therefore the results obtained for high compression ranges with these potentials are expected to offer more reliability than with REBO. Nonetheless, the behavior of diamond under uniaxial compression still lacks agreement when compared to DFT results. SED-REBO underestimates the stresses and the extrema of the stress-strain curves occur at too low compression rates, suggesting that structural transitions may occur at relatively low strain. With LCBOP II on the other hand, the extrema of the longitudinal and shear stresses are accurately reproduced in terms of compression ratio but the value of the stress itself is overestimated, suggesting increased resistance to transitions during shocks.

### 5.3.2 Isothermal compressions

Isothermal uniaxial compression simulations on large samples are used to get rid of two important constraints of the previous cold compression study: i) at finite temperature, the thermal fluctuations reduce the possibility of trapping the system into metastable states, and ii) large sizes reduce the periodic boundary condition artifacts, that is the artificial constraints on the small unit cells which prevent extensive rearrangements of the atomic structure, for instance via phase transitions or formation of local or extended defects. With SED-REBO we used a progressive compression procedure, rescaling the final structure obtained at step $n$ to start the simulation at step $n + 1$, with a compression step of 1%. This method is close to the true dynamical process but assumes that the thermodynamic equilibrium has been reached before moving to the next compression step. With LCBOP II,
Figure 42.: Binding energy and longitudinal stress for isothermal compression in ⟨110⟩. Evolution upon isothermal compressions, compared to results from cold calculations. The Hugoniot elastic limit (HEL) was obtained from large-scale MD shock simulations.
Figure 43.: Evolution of the material during isothermal compression. See also Fig. 42. The compressions yield pressures of 90 (360), 170 (420) and 300 (640) GPa in SED-REBO (LCBOPII) respectively. For SED-REBO, the coloring reflects the solid-solid phase transition: low-pressure phase A (white), high-pressure phase B (red). The green color illustrates the tip of the B phase growth.
the procedure had to be parallelized due to computational cost. Therefore each simulation was treated independently by directly rescaling a perfect diamond unit cell to the desired compression rate. This rate was sampled every 4% in the purely elastic regime and every 2% in the plastic regime. For some key structures with plastic transformations, we ran a second simulation recompressing the closest equilibrated sample with lower rate, and we found no significant difference in equilibrium energy, stress or structure, which overruled the existence of metastable states and validated our procedure.

The resulting binding energy and longitudinal stress curves with focus on the main structural transitions are presented in Figs. 42 and 43 respectively: they show a shift of the maximum of the longitudinal stress down to 120 GPa for SED-REBO and 560 GPa with LCBOPPII, corresponding to compression rates $V/V_0$ of 0.91 and 0.78 respectively. From a structural point of view, SED-REBO yields a polymorphic phase transition to a state consisting of two coexisting diamond phases: a low-pressure phase A (or “regular” diamond elastically compressed) and a high-pressure phase B, consisting of $sp^3$ bonded carbon similar to diamond but with distorted bond angles. This phase transition occurs without any plastic deformations in the sample since the stress remains below the Hugoniot elastic limit (HEL), and the ratio of B/A increases with pressure until the transition is completed at 300 GPa ($V/V_0 = 0.74$). With LCBOPPII the peak stress remains larger than the HEL which leads to localized plastic deformations rather than solid-solid phase transitions for moderate compression regimes ($V/V_0 = 0.76$). For larger compression rates, increasing amorphized fractions of the sample are obtained. For both potentials, the addition of temperature and increasing of the system size led to relaxation of the stress thanks to profound structural transformations. We expect the observation of very different responses during large-scale MD shock simulations with the two potentials: appearance of plasticity with LCBOPPII, as opposed to a possible polymorphic phase transition with SED-REBO.
Figure 44.: $u_s - u_p$ shock Hugoniot for (110) diamond with SED-REBO and LCBOPI. Comparison with experimental results from [110]. A and B refer to the low and high-pressure elastic phases observed with SED-REBO.
5.3.3 Regimes of Shock propagation

In order to perform MD simulations of shock compression, the sample is aligned such that the direction of the shock lies along the x-axis. Periodic boundary conditions (PBC) are applied on the lateral dimensions, and the initially perfect sample is given an initial velocity $-u_p$ (piston velocity) toward an infinite potential wall. The collision gives rise to a shock propagating in the material at a velocity $u_s$ (shock velocity). Samples of size $12 \times 12 \times 60 \text{ nm}^3$ were used in the SED-REBO simulations, while samples used with LCBOPPII possess typically smaller transverse sizes ($1 \times 1$ and $2 \times 2 \text{ nm}^2$) due to the extra computational cost of the potential. The influence of the sample size was investigated using sample sections up to $10 \times 10 \text{ nm}^2$ for particular cases, showing minor differences in the speed and structure of the shock wave. The piston velocities imposed in our simulation range from 1 to 10 km/s. The resulting $u_s = f(u_p)$ Hugoniot is plotted in Fig. 44 from which it can be noticed that both SED-REBO and LCBOPPII yield results that agree reasonably well with experimental data for the purely elastic branch of the Hugoniot. For each potential, we will detail the different regimes of shock propagation.

SED-REBO

The shock profiles obtained with SED-REBO are presented in Fig. 45 and can be decomposed in four different regimes:

- elastic response for $u_p = 1 \text{ km/s}$ (Fig. 45-a),

- split elastic-elastic shock waves for $1 < u_p \leq 5 \text{ km/s}$ (Fig. 45-b),

- split elastic-plastic shock waves for $5 < u_p \leq 8 \text{ km/s}$ (Fig. 45-c),

- single elastic-plastic shock wave, followed by a slow amorphization front for $u_p \geq 8 \text{ km/s}$ (Fig. 45-d).
Figure 45: SED-REBO shock profiles for various piston velocities. Profiles (particle velocity, longitudinal and shear stresses) for $u_p = 1, 3, 6$ and $8$ km/s are shown in a, b, c and d respectively. I, II, and III label regions of different states of the material discussed in the text.
For $u_p = 1 \text{ km/s}$ a trivial elastic shock wave is observed. A split elastic-elastic regime occurs for $1 < u_p \leq 5 \text{ km/s}$ where the shock consists of two fronts moving at different velocities. Results for piston velocity $u_p = 3 \text{ km/s}$ are shown in Fig. 46. As can be seen from the velocity or pressure profiles, the shock clearly consists of two distinct zones (marked I and II), and the two shock waves are moving at different velocities causing the split ($v_I = 19.8 \text{ km/s}$, $v_{II} = 14.6 \text{ km/s}$). Remarkably, the second wave is not the place of plastic deformations as is commonly seen in split shock wave regimes. Rather, the structure of the second wave displays the coexistence of two elastically compressed phases of diamond. The pressure profile confirms that shear stresses are not all relaxed. If one component decreases, it is to the expense of the increase of the other. The snapshot shown in Fig. 46-a shows the two phases, labeled “low-pressure phase A” and “high-pressure phase B” respectively. The occurrence of this polymorphic phase transition agrees with the results obtained from the isothermal uniaxial compressions, and the pressure/compression ratio agrees with the results presented above ($V/V_0 = 0.82$, $P = 175 \text{ GPa}$, vs 140 and 170 GPa for cold and 300 K isotherm respectively), showing that the material is in thermodynamical equilibrium. As the piston velocity increases, the proportion of the new B phase in the second shock increases as well, and the width of the precursor shock decreases. At $u_p = 5 \text{ km/s}$, the width of the first shock is less than 2nm, and the rear material has completely turned into B phase diamond. $5 < u_p < 8 \text{ km/s}$ corresponds to a split elastic-plastic regime: the precursor consists only of phase B while plasticity occurs at the rear in the form of local defects causing reduction of the shear stresses (Fig. 47). The material in slightly deformed, although the structure is still very close to the same B phase. We nonetheless label it as plastic to contrast this regime from the elastic-elastic shock response. In addition, the pressure profile shows that relaxations occurs in the second region, characteristics of a non-elastic state of the material. The speed of the second-wave is slower than that of the precursor, causing the split ($v_I = 21.0 \text{ km/s}$, $v_{II} = 18.9 \text{ km/s}$). With increasing piston velocity, the relative speed of the second wave increases compared to the elastic precursor, until finally it overcomes
Figure 46.: Split elastic-elastic shock waves in diamond with SED-REBO: atomic structure and shock profile. a: shock profile in shock initiated by $u_p = 3 \text{km/s}$. I and II correspond to regions in Fig 45-b,c: snapshots from region II (elastic A+B) and I (elastic A) respectively. The different cell structures are highlighted in red, while the phases boundary is drawn in thick black.
it. At this stage, only one single wave is observed, with only a remnant elastic front only a few nm wide. With further increase of the piston velocity, we observed the development of an amorphization front at the back of the sample. The profiles in Fig. 48-a show a single two-zone structure composed of a purely elastic precursor 2 to 3 nm wide, followed by the plastic front. Both fronts have a the same speed, and shear stresses are starting to relax in the plastic region. But farther, dislocations and nuclei of local amorphization appear, causing more drastic relaxation, until complete amorphization of the material at the back. Figs. 48-b,c,d show snapshots taken at different distance from the the elastic front. In 48-d, the uncompressed material can be seen on the right, in contrast to the elastic B phase on the left. In 48-c, the material undergoes local deformations causing relaxation of the shear stresses, but amorphization nucleation seeds can also be observed. Therefore the second region consists of a mixture of subdomains with deformed diamond and amorphous-like carbon. After growth of the amorphization seeds, the sample completely loses order and looks like amorphous carbon (48-b). The speed of the amorphization front is very small compared to the elastic front, and in fact it is propagating sub-sonically in the material ahead. Therefore it is not a shock-wave, and this response can be described as a single two-zone structure: a very narrow elastic precursor followed by a plastic wave with a very wide (∼ 30 nm) plastic front, which is the place of slow relaxation of the shear stresses.

**LCBOPII**

As for uniaxial compression, the LCBOPII response to shock compression differs substantially from the SED-REBO response and may be divided in three distinct regimes:

- a purely elastic regime for $u_p \leq 5$ km/s (Fig. 49-a),

- a split elastic-plastic regime for $5 < u_p < 9$ km/s (Fig. 49-b),

- an “anomalous” elastic regime followed by a plastic regime for $u_p > 9$ km/s (Fig. 49-c)
Figure 47.: Split elastic-plastic shock waves in diamond with SED-REBO: atomic structure and shock profile. a: shock profile in shock initiated by \( u_p = 6 \text{ km/s} \). I and II correspond to regions in Fig 45-b, c: snapshots from region II (plastic B) and I (elastic B) respectively.
Figure 48.: Two-zone elastic-plastic shock waves with amorphization front in diamond with SED-REBO: atomic structure and shock profile. a: shock profile in shock initiated by $u_p = 8$ km/s. I, II and III correspond to regions in Fig 45-b,c,d: snapshots from region III (amorphous), II (plastic B), and I (pristine and elastic phase B diamond) respectively.
Figure 49.: LCBOP II shock profiles for various piston velocities. Profiles (particle velocity, longitudinal and shear stresses) for $u_p = 3, 6, \text{ and } 9 \text{ km/s}$ are shown in a, b and c respectively. I and II label regions of different states of the material discussed in the text.
The elastic regime is characterized by a single wave with constant particle velocity (Fig. 49-a), longitudinal pressure and shear stresses. It is particularly long-lived with respect to SED-REBO (up to 5 km/s) which reflects the high stiffness evidenced in uniaxial compression simulations. The transition to the split elastic/plastic regime is found above 5 km/s and results in a two wave structure (Fig. 49-b). Behind the elastic precursor, the shocked sample undergoes strong plastic deformations causing a progressive vanish of all shear stresses. The transformation is highlighted by the snapshots in Fig. 50-a showing the formation of plastic seeds. Contrary to SED-REBO, no sign of an elastic/elastic phase transition were found during these simulations. Increasing the particle velocity results in decreasing the thickness of the elastic transient zone until the usual single wave is recovered (Fig. 50-c), which is usually the sign of an overdriven process; however with LCBOP II a peculiar behavior is observed since the shear stresses do not cancel as they usually do for overdriven plastic processes. Instead, the structure observed in Fig. 50-b shows the formation of nanometer-sized crystalline domains, with slightly tilted orientations, and separated by thin layers of amorphous or liquid carbon. The range of compression achieved under this regime corresponds to the minimum in longitudinal and shear stress observed under uniaxial compression (35 % compression rate). The minimum in shear stress inhibits the nucleation of plastic deformations and makes the compression nearly purely elastic. This elastic response beyond the HEL was reported in earlier studies with the REBO potential as an “anomalous elastic response” at a compression ratio close to 25 % [34]. However a recent reinterpretation overruled the existence of this phenomena with REBO: Ref. [36] shows that the “plastic” regime described in [34] for $V/V_0 <25\%$ actually corresponds to the split elastic-elastic regime observed with SED-REBO, but was erroneously interpreted as an elastic-plastic regime due to the shear bands observed at the interface between phase A and B (see Fig. 46): the subsequent full transition to phase B diamond at $V/V_0 =25\%$ was then spuriously interpreted as the occurrence of an anomalous elastic regime. This misinterpretation is less likely with LCBOP II since the occurrence of the anomalous elas-
tic regime is clearly preceded by an elastic-plastic transition.

\[ P - V \text{ Hugoniot and comparison with experiment} \]

The Hugoniot curves of SED-REBO and LCBOPPII are plotted in Fig. 51 and compared to the recent experimental results of Mc Williams et al [110]. Although the agreement is good for both potentials in the elastic regime (up to 200 GPa), only SED-REBO seems to yield reasonable agreement for the plastic regime in terms of shock pressure, although the existence of distinct elastic/plastic branches cannot be confirmed by experiments. In turn LCBOPPII is clearly too stiff, as suggested by the uniaxial compression results, yielding pressures too high for the plastic branch of the Hugoniot.

The most striking discrepancy between our simulations and the experimental results is the large overestimate of the HEL with both potentials (experiments yield value close to 90-100 GPa). The polymorphic phase transition observed with SED-REBO occurs in this range of pressure (~90 GPa), however the fact that no such phase transition has been reported experimentally suggests that the agreement between these two values should be fortuitous: therefore in order to estimate the SED-REBO HEL value we chose the onset of plasticity criterion, leading to a value much higher (~400 GPa) and comparable to the LCBOPPII value (~450 GPa). Such discrepancies between simulations and experiments are usual and can arise either from i) a too stiff behavior of the potentials, ii) insufficient time and length scales of the simulations resulting in unstationary shock waves, or iii) the perfect structure of the simulated samples when experimental samples may contain large concentrations and variety of defects which can act as a nucleation seeds for plasticity. In this case we believe the major reasons for this disagreement lies in the stiffness of the potentials and the absence of defects in the shocked samples. The better agreement of SED-REBO with the experimental Hugoniot could then be only coincidental and arise from the observed solid-solid phase transition which would mimic structural defects and spuriously activate plasticity. We tried to test this hypothesis with LCBOPPII by inserting some lo-
Figure 50.: Split elastic-plastic shock waves and single anomalous elastic shock wave with LCBOPPI: atomic structures. a- Top: atomic structure in shock initiated by $u_p = 8$ km/s. I and II correspond to regions in Fig. 49-c. Bottom: snapshots from region II (plastic) and I (elastic) respectively. b- Top: atomic structure in shock initiated by $u_p = 9$ km/s. Bottom: snapshots at various distances from the shock front, showing that the atomic structure is globally conserved, and that plastic deformations are absent (anomalous elastic).
Figure 51.: $P - V$ shock Hugoniot for $\langle 110 \rangle$ diamond with SED-REBO and LCBOPII. McWilliams refers to experimental points taken from ref. [110]. The green dashed line (Rayleigh line) corresponds to the response shown in Fig. 45-d: single two-zone elastic-plastic wave, and rising amorphization front. The slow speed of the amorphization is highlighted by the decrease of the slope of the Rayleigh line past the plastic branch.
calized (voids, insertions, or void-insertion pairs) and large scale defects (stacking faults): none of our defected samples changed substantially the shock properties (shock velocities, stress, density) which suggests further improvements of this potential in order to reduce its stiffness.

5.4 Conclusions

This combination of static and shock compression along the $\langle 110 \rangle$ direction with the SED-REBO and LCBOPPII potentials yield contradictory results when compared to the available first-principles or experimental reference data. 1D compression points to a better description of the longitudinal and shear stresses with the LCBOPPII potential with a correct description of the positions of the various extrema and better quantitative estimates, although notably overestimated, of the stress intensities. SED-REBO shows too weak behavior with too low stress intensities and extrema located at too low compression rates.

In turn, shock compression simulations show good agreement of the SED-REBO Hugoniot data with available experiments, when LCBOPPII is too stiff and largely overestimates the shock pressures. Both potentials largely overestimate the HEL (400-450 GPa vs 100 GPa experimentally) which may suggest further developments to improve the description of the plastic regime.

Despite these disagreements, we found both SED-REBO and LCBOPPII offer improvement over REBO, although none was originally designed nor fitted for shock compression applications. Therefore the present results should be regarded as encouraging with regards to possible improvements of these potentials for subsequent shock compression studies.
References


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