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Combining a reactive potential with a harmonic approximation for molecular dynamics simulation of failure: construction of a reduced potential

I G Tejada[1], L Brochard[1], G Stoltz[2,3], F Legoll[1,3], T Lelièvre[2,3] and E Cancès[2,3]

[1] Université Paris-Est. Laboratoire Navier (UMR 8205), CNRS, ENPC, IFSTTAR. 6 & 8 avenue Blaise Pascal 77455 Marne-la-Vallée, France.
[2] Université Paris-Est. CERMICS, École des Ponts ParisTech (ENPC). 6 & 8 avenue Blaise Pascal 77455 Marne-la-Vallée, France.
[3] INRIA Rocquencourt, MATHERIALS research-team, 78153 Le Chesnay Cedex, France.

E-mail: `ignacio.tejada@enpc.fr`

Abstract. Molecular dynamics is a simulation technique that can be used to study failure in solids, provided the inter-atomic potential energy is able to account for the complex mechanisms at failure. Reactive potentials fitted on ab initio results or on experimental values have the ability to adapt to any complex atomic arrangement and, therefore, are suited to simulate failure. But the complexity of these potentials, together with the size of the systems considered, make simulations computationally expensive. In order to improve the efficiency of numerical simulations, simpler harmonic potentials can be used instead of complex reactive potentials in the regions where the system is close to its ground state and a harmonic approximation reasonably fits the actual reactive potential. However the validity and precision of such an approach has not been investigated in detail yet.

We present here a methodology for constructing a reduced potential and combining it with the reactive one. We also report some important features of crack propagation that may be affected by the coupling of reactive and reduced potentials. As an illustrative case, we model a crystalline two-dimensional material (graphene) with a reactive empirical bond-order potential (REBO) or with harmonic potentials made of bond and angle springs that are designed to reproduce the second order approximation of REBO in the ground state. We analyze the consistency of this approximation by comparing the mechanical behavior and the phonon spectra of systems modeled with these potentials. These tests reveal when the anharmonicity effects appear. As anharmonic effects originate from strain, stress or temperature, the latter quantities are the basis for establishing coupling criteria for on the fly substitution in large simulations.

1. Introduction

As many macroscopic failure mechanisms in materials, such as fracture or plastic deformation, originate at the atomic scale (bond breaking, vacancies, dislocations) it is natural to study failure at such scale [1]. However, atomistic modeling is computationally expensive because models usually contain an extremely large number of particles and because events at atomic scale require complex modeling. Ab initio approaches (i.e. based on first principles) have a good predictive ability, but a high computational cost which limits their use to small systems and time scales. Molecular dynamics (MD) is an alternative technique that makes it possible

to simulate larger systems. It is used to calculate the motion of atoms (e.g. following the Hamiltonian dynamics) once a model for their mutual interactions is postulated. The interatomic potential used is what mostly determines the physical validity and the computational cost of the simulation.

Reactive potentials [2, 3, 4, 5, 6] are classical potentials that allow bonds to break and form. This is done by empirically modeling the effect of the current atomic environment on interaction forces, which is essential at failure when the atomic structure is strongly rearranged. However the reactive ability is useless in regions where the atomic structures are close to the ground state and the material behaves elastically. Substituting there the reactive potential by a non-reactive approximation makes it possible to get the same macroscopic response of the model while considerably reducing the computation time. This technique has been used, for instance, to study dynamic crack propagation in a silicon single crystal [7], but the existing approaches lack a detailed methodological investigation and a proper validation. To make further progress in this direction we discuss here a coupling method between a reactive bond-order potential and a harmonic potential.

2. Theoretical background

Graphene is a material made of carbon atoms arranged in a two-dimensional honeycomb lattice with unique physical properties. In this work, we use it as a simple case study to illustrate our methodology. In this respect, we do not pay attention to out-of-plane bending or vibration modes, and we use the 2nd-generation reactive empirical bond-order potential [8], REBO, as implemented in [5]. It accounts for the angular forces and gives the correct cohesive energy and equilibrium lattice constants of graphene, but is known to only imperfectly reproduce its elastic constants and phonon spectra [9]. REBO is a reformulation of Brenner-Tersoff potentials [3, 4], that are in turn based on Abell's formalism [2] in which the binding energy is produced by pairwise nearest-neighbor interactions that depend on the local atomic environment.

In the ground state (i.e., the system unstressed at 0 K), the potential energy is minimum and it can be expanded in terms of the powers of the atomic displacements around their equilibrium positions. The harmonic approximation consists in truncating the Taylor expansion after quadratic terms. The Hessian of the potential energy is the so-called force constants matrix [10], Φ.

We seek a substitute for REBO interactions such that, close to the ground state, both the original potential and its harmonic approximation provide the same (or very close) forces. Accordingly, their Hessians must be the same, or very close. We consider harmonic potentials made of harmonic springs (bond interactions between pairs of atoms) and angles (angle interactions between triplets of atoms), widely implemented in MD codes. The analytical expressions for the potential energies respectively are: $E_s = (1/2)\, K_s\, (r_s - r_{\mathrm{eq},s})^2$ and $E_a = (1/2)\, G_a\, (\theta_a - \theta_{\mathrm{eq},a})^2$. The topology of the network of springs and angles as well as the values of the parameters K_s, $r_{\mathrm{eq},s}$, G_a and $\theta_{\mathrm{eq},a}$ are fitted so that the Hessian of that harmonic potential is exactly equal to that of REBO in the ground state. Note that the harmonic potential is not a quadratic function in terms of the current positions of the atoms but in terms of bond lengths r_s and angles θ_a.

The use of a substitute potential affects the bulk properties of graphene. As we focus on fracture tests, we analyze the mechanical behavior, i.e. the static strain-stress relation, and the phonon dispersion curves, i.e. the dynamics of the atomic vibrations, which are both essential to the failure mechanisms of materials. If the substitute potential reproduces the Hessian of REBO in the ground state, then their mechanical behaviors and phonon spectra deviate only when the second order expansion fails approximating the REBO potential, e.g. because of excessive anharmonicity due to large strains and/or large temperatures.

The desired hybrid model consists of a reactive zone close to the crack tip (REBO

interactions), a non-reactive zone (harmonic interactions) far from the crack tip and a transition zone which serves for the computation of the REBO potential (because of the range of the interactions) and for a smooth transition between the potentials.

3. Methodology

In order to set the parameters of springs and angles, we follow the algebraic method proposed by Mounet [11] to enforce the acoustic sum rules and index symmetries on the Hessian of carbon allotropes obtained with density-functional perturbation theory. First a dot product between two matrices is defined as $\Phi \cdot \Psi = \sum_{i\alpha j\beta} \Phi_{i\alpha j\beta} \Psi_{i\alpha j\beta}$, where i, j label atoms $(1, \cdots, N)$ and α, β represent the in-plane coordinates (x, y). The associated distance is $\mathrm{d}(\Phi, \Psi) = \sqrt{(\Phi - \Psi) \cdot (\Phi - \Psi)}$, so that minimizing such distance is equivalent to applying a least squares method. The methodology for finding the optimal potential parameters for a simplified harmonic potential (valid for non-crystalline structures too) is as follows:

- Compute the force constants matrix with REBO potentials in the ground state: Φ^{REBO}.
- Use the same geometry of the system in its ground state for the harmonic approximation (e.g. a honeycomb lattice of constant $a \simeq 2.4$Å for graphene).
- Prescribe a topology of harmonic interactions between atoms produced by springs and angles.
- Construct a basis for the approximated solutions. The contribution of each prescribed interaction to the whole approximated Hessian Φ^{HARMO} is known and depends on the corresponding constant, in such a way that we can write: $\Phi^{\mathrm{HARMO}} = \sum_s K_s \Phi_s^{\mathrm{spring}} + \sum_a G_a \Phi_a^{\mathrm{angle}}$. Thus $\left\{\Phi_s^{\mathrm{spring}}, \Phi_a^{\mathrm{angle}}\right\}$ is the basis of the subspace of approximated solutions.
- Orthonormalize the basis $\left\{\Phi_s^{\mathrm{spring}}, \Phi_a^{\mathrm{angle}}\right\} \rightarrow \{U_I\}$.
- Take Φ^{HARMO} as the projection of Φ^{REBO} onto the orthonormalized basis. $\Phi^{\mathrm{HARMO}} = \sum_I (\Phi^{\mathrm{REBO}} \cdot U_I) U_I$ is the element closest to Φ^{REBO} in the subspace of approximated models. If $\mathrm{d}\left(\Phi^{\mathrm{REBO}}, \Phi^{\mathrm{HARMO}}\right) = 0$, then the prescribed interactions are able to exactly reproduce the original force constants matrix.
- Express Φ^{HARMO} in the original basis, and get the constants of the springs to use.
- Optional: if the system is a crystal, the approximated model can be symmetrized to use fewer constants.

Once the approximated model is known, we use MD simulation to compare the mechanical behavior of both models. The graphene sheet is deformed in one direction (zig-zag or armchair) while the perpendicular one is left undeformed. At each deformed configuration, the energy is minimized and the stress is computed as $\sigma_{\alpha\beta} = \sum_i^N r_{i\alpha} f_{i\beta}/A$, where A is the area of the sheet, $f_{i\beta}$ the β-component of the total force per unit of length acting on particle i, and $r_{i\alpha}$ the α-component of its position vector. The engineering strain is defined as $\varepsilon_\alpha = (L_\alpha - L_{\alpha,0})/L_{\alpha,0}$, where $L_{0,\alpha}, L_\alpha$ are the initial and final dimensions of the sheet in α direction.

By applying lattice dynamics we get their phonon spectra. We use a Langevin thermostat to get these curves at different temperatures following the so-called quasi-harmonic approximation (i.e. assuming that the anharmonicity is restricted to thermal expansion, so that the temperature dependence of the phonon frequencies arises only from the dependence on crystal structure and volume [10]). We have used LAMMPS [12] and our own MD code.

4. Results and discussion

The Hessian of two-dimensional graphene at ground state modeled with REBO can be exactly reproduced with a system of reduced potentials based on four classes of harmonic interactions, as

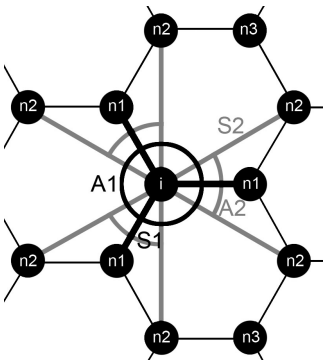

Figure 1. Schematic of the topology of 3+6 harmonic springs, of types S1 (——) and S2 (——), and 3+3 angles, of types A1 (◁) and A2 (◁), that connect atom i to its 1st- and 2nd-order neighbors (n1,n2) in the approximated model.

Table 1. Harmonic springs and angles used in the approximated model

Interaction	Atom/s in interaction (figure 1)	Constant	Equilibrium
Spring 1 (S1)	(i, n1)	$K_1 = 39.76$ eV/ Å^2	$r_{\mathrm{eq},1} = 1.3977$ Å
Spring 2 (S2)	(i, n2)	$K_2 = 1.21$ eV/ Å^2	$r_{\mathrm{eq},2} = 2.4208$ Å
Angle 1 (A1)	(i, n1, n1')	$G_1 = 1.31$ eV	$\theta_{\mathrm{eq},1} = 2\pi/3$
Angle 2 (A2)	(i, n2, n2')	$G_2 = 7.11$ eV	$\theta_{\mathrm{eq},2} = \pi/3$

depicted in figure 1 and detailed in table 1. Accordingly, the phonon dispersion curves obtained with REBO and with the harmonic approximation are indistinguishable at 0 K (figure 2). At nonzero temperatures, these curves change with the former potential, while remaining unchanged with the latter (there is no thermal expansion with harmonic models). Moreover, the mechanical behaviors in tensile tests are the same at small deformations (figure 3).

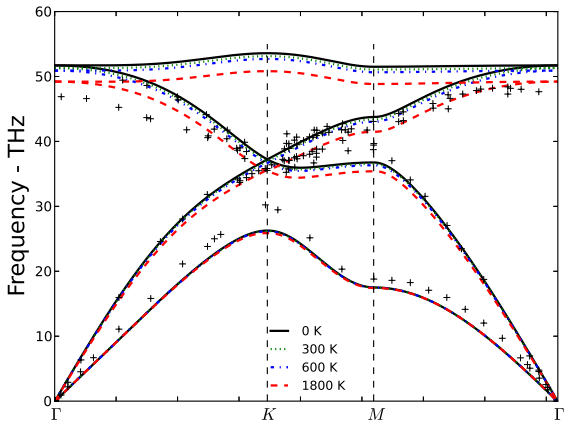

Figure 2. Phonon spectra of graphene obtained with either REBO or a harmonic approximation at $T = 0$ K (——) and with REBO at $T = 300$ (·····), 600 (— · —) and 1800 (– – –) K. Experimental data (+) [13] (included to contextualize the curves).

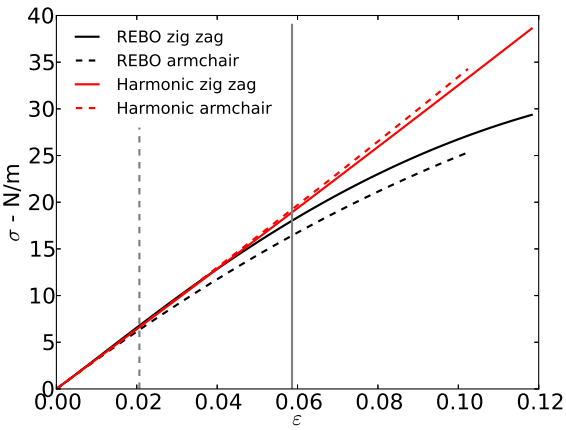

Figure 3. Tensile response of graphene (stress vs. strain) in ziz-zag (——) and arm-chair (– – –) directions obtained from MD simulations with REBO (black) and with a harmonic approximation (red). The vertical lines indicate the strain at which the difference in the stress is larger than 5%.

When atoms move away from their positions in the ground state, the harmonic approximation becomes less and less valid, because of the anharmonic contributions to the reactive potential. It can be due to an increase of the temperature or of the strain, quantities that can be locally estimated around each atom during a simulation, and are therefore suited for constructing indicators for on the fly substitution. The analysis of the bulk behavior far from the ground state enables us to quantify the effects of anharmonicity. For instance, these effects start to be significant for strains between 2% and 6% (see figure 3).

On the other hand, when using a harmonic approximation one has to consider the main macroscopic physical phenomena that originate from anharmonicity and therefore cannot be captured with harmonic approximations. These can be grouped into equilibrium properties (thermal expansion and dependency of elastic constants on temperature and volume) and transport properties (thermal conductivity and almost any of the processes by which the lattice vibrations transmit energy). This is a drawback of the harmonic approximation, which limits the use of the coupling to regions where anharmonicity is small.

Finally, there are various ways of achieving a perfect coupling in the hybrid model to leave the phonon relations unaffected. For instance, the same algebraic methodology explained in section 3 can be used to obtain the spring and angle constants in a representative volume element (RVE) that includes reactive and non-reactive zones. The whole Hessian of this hybrid RVE is the result of the contribution of a reactive and a harmonic part: $\Phi^{\mathrm{HYB}} = \Phi^{\mathrm{HYB(R)}} + \Phi^{\mathrm{HYB(H)}}$. By minimizing the distance $\mathrm{d}\left(\Phi^{\mathrm{REBO}} - \Phi^{\mathrm{HYB(R)}}, \Phi^{\mathrm{HYB(H)}}\right)$, the spring and angles constants of the harmonic part are obtained. The constants near the interface have to be different to those in the pure harmonic zone to guarantee that there are no undesired effects due to the transition between the potentials. However the new values to use there depend on the geometry of the interface in the hybrid RVE. Alternatively, the methodology can be also applied to obtain the set of springs and angles that can substitute a single REBO bond in a full REBO environment. Then, every time a REBO bond is replaced, the corresponding springs and angles are added. Following this approach, a perfect coupling is achieved without prescribing any specific interface, and the substitution can be performed at any time during the simulation, so that the interface can be displaced on the fly. More details on the coupling methodology will be provided in [14].

Acknowledgments

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