MonteCarlo Simulations of Carbon-based Structures Based on an Extended Brenner Potential.

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ABSTRACT

Extended grand-canonical off-lattice Monte Carlo simulations of the (100) and (111) diamond surfaces have shown that the Brenner potential is extremely accurate in describing the structural properties at surfaces, supporting the recent predictions of new meta-stable reconstructions of diamond(111) very close in energy to the (2×1) (π-bonded) chain reconstruction but with surface atoms in three-fold graphite-like bonding.

The Brenner potential, however, cannot describe weak long-range interactions, such as the interplanar interactions in graphite. Here we suggest an extension of the Brenner potential beyond its cut-off radius of 2 Å of importance to describe the process of graphitization as well as (nested) fullerene-like carbon structures. Preliminary results for the graphitization at (111) surfaces are presented.

Keywords: Carbon, diamond, fullerenes, Brenner potential, graphitization

1 INTRODUCTION

Since the discovery of fullerenes and nanotubes, a wealth of new carbon structures from carbon onions [1] to peapods [2] and fishbone [3] has been synthesized. However the conditions for the growth and synthesis of these structures as well as their relative stability are still largely unknown. A closely related problem is represented by the process of graphitization at the diamond surface which is known to occur at high temperatures with transformation paths still under debate [4]. One has to realize that both diamond and the new fullerene-like forms of carbon are metastable states with respect to graphite and as such their study represents a challenge for most theoretical and numerical approaches.

Beside the fundamental interest, understanding the structure and transformation of carbon under different conditions is technologically relevant for coatings, growth and machining of diamond and new superhard materials. It is noteworthy how many open questions exist and how many unexpected results have recently come out for this elemental material. It is therefore important to develop predictive schemes to treat diamond, graphite and mixed bonding with approaches able to deal with large structures which are beyond the possibility of ab initio calculations.

Our approach is based on the use of a state of the art phenomenological potential due to Brenner [5] which is detailed enough to describe both types of bonding and simple enough to deal with very large samples.

Tersoff had previously proposed effective many body empirical potential for all group IV elements in which the potential energy of the system is written as a sum of effective pair terms for each bond, the energetics of which depends on the local environment (bond order). These potentials are very accurate for Si and Ge, also as far as interface properties are concerned, but less reliable for C. In fact, the Tersoff potential for C [6], which has been fit to the bulk properties of both diamond and graphite, does not distinguish the chemical character of the bond. This shortcoming turns out to be particularly serious when dealing with structures presenting both types of bonding. For instance, this potential predicts the diamond(111) surface to be unreconstructed [5, 7] against the experimental evidence of the (2×1) Pandey chain reconstruction [8] analogous to that of Si(111).

Brenner [5] has re-parametrized the Tersoff potential and added nonlocal terms to properly account for the bond modifications induced by a change of bonding of neighboring atoms. The major improvement with respect to Tersoff is due to the fact that the bond energy takes into account the local environment via a many body term which depends not only on bond length and angle but also on the coordination of the atoms making the bond and of their nearest neighbor.

We have demonstrated, by extended grand-canonical Monte Carlo simulations, the very high accuracy of the empirical many-body Brenner potential for carbon structures by a detailed comparison of its structural predictions with those of *ab-initio* studies for known reconstruction of the diamond (100) and (111) surfaces [9,10]. In addition to the minimal energy unbuckled undimerized Pandey (2×1) (π-bonded) chain reconstruction we find three new meta-stable states, very near in energy, with surface atoms in three-fold graphite-like bonding [9]. The absence of consensus on the structural details and electronic structure of the clean (111) surface might be related to these surface structures, which are peculiar of carbon and have never been considered so far.

The short range interactions, which are well accounted for by Brenner, are not the only important term when dealing with graphite-like, almost planar, structures. With a cut off of 2 Å Brenner cannot describe interplanar forces in graphite and related structures. The relative stability of single-shell versus nested fullerenes for instance seems to be driven by long-range non-bonded interactions [11]. Therefore extensions of the Brenner potential beyond its cut off radius have been proposed [12, 13]. Sinnott et al. suggested an efficient scheme based on a simple, long-range pair potential, which is switched off at shorter distances, where the Brenner potential acts. However, this potential yields an unphysical minimum around 2 Å. Che et al. have proposed a more complicated three-body scheme of joining the short- and long-range part of the potential, which is much less efficient for computer implementation.

Here we propose a new parametrization to extend the Brenner potential to include non-bonded long range interactions. While keeping the simple and computationally efficient pair-wise form of the long-range potential of Ref. [12] it reproduces accurately interplanar distances and energetics of graphite.

In Section II we describe the new potential energy term and its implementation and compare it to the previous schemes [12, 13]. In Section III we show preliminary results for the graphitization of the (111) surface in a wedge geometry. Finally in Section IV we give summary and conclusions.

2 Long range potential terms

Following Refs. [12, 13], we write the long-range potential energy term due to non-bonded (NB) interactions $E_{\rm NB}$ as sum of pair-wise contributions

$$E_{\rm NB} = \frac{1}{2}\sum_{i,j} V_{\rm NB}(r_{i,j}),$$

where $r_{i,j}$ is the distance between atoms i and j. The form of $V_{\rm NB}(r_{i,j})$ assumed by Sinnott *et al.* is shown in Fig. 1.

It is zero at distances smaller than $r_1 = 2.3$ Å and larger than the long-range cut off distance $r_3 = 10$ Å. At $r_{i,j}$ between $r_2 = 3.4$ Å and r_3 the Lennard-Johns (L-J) 12-6 potential is used whereas, between r_1 and r_2, a smooth cubic interpolation is exploited.

In Fig. 2 we show the long-range interplanar energy $E_{\rm NB}$ per atom as a function of the inter-planar distance in graphite. Only the long-range part of the potential for pairs belonging to different graphite sheets is taken into account and the in-plane interactions are not included in Fig. 2. One can immediately see that besides the minimum at ~ 3.4 Å , representing the equilibrium interplanar distance of graphite, an additional, unphysical, deeper energy minimum is found at smaller distances

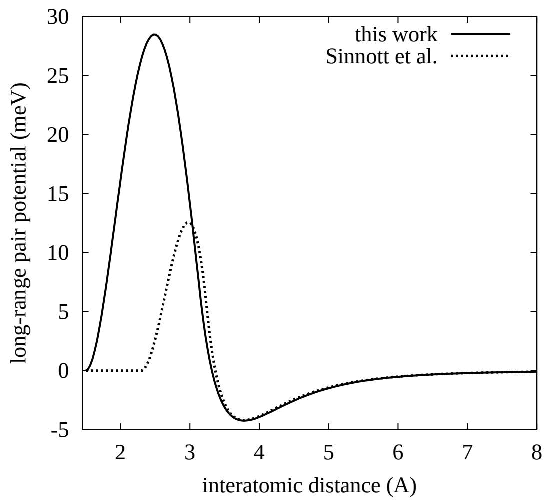

Figure 1: Long range non-bonded potential energy $V_{\rm NB}$ of Ref. [12] compared to the one proposed in this work.

($r \sim 2$ Å), before the short-range part of the Brenner potential is switched on. The reduction of $E_{\rm NB}$ upon reduction of the interplanar distances is caused by the attraction between atom pairs separated by $r_{i,j} > 3.8$ Å *and* by $2.3 < r_{i,j} < 3$ Å.

In order to avoid this spurious energy minimum one has to shift the second attracting region in the pair interaction energy closer to 2 Å, the cut off distance of the stronger, short-range, part of the potential. In other words, the maximum of the non-bonded potential shown in Fig. 1 has to be shifted to the left. For this purpose we have changed the long-range potential of Sinnott in several aspects. First of all, we have chosen other values of $r_1 = 1.5$ Å and $r_2 = 3.15$ Å to connect the long range part to the short range Brenner potential, the most significant change being the reduction of r_1. Secondly, we have replaced the L-J form of $V_{\rm NB}$ for $r_2 < r_{i,j} < r_3$ by an exp-6 potential [14] of the form:

$$V_{\rm NB}(r) = b\exp(-c_0 r) - \epsilon\left(\frac{\sigma}{r}\right)^6 - V_{\rm shift}, \quad r_2 < r < r_3$$

where $c_0 = 3.2$ Å^{-1} (from Ref. [14]), $\sigma = 3.37$ Å and $\epsilon = 16.815$ meV [15]. This replacement preserves the form of the tail beyond 4 Å while making the potential slightly less steep on the left-hand side of the minimum. The parameter $b = 3\epsilon\exp(c_0 r_0)/(c_0 r_0)$, where $r_0 = \sigma(2)^{(1/6)}$ is chosen as to have the minimum of $V_{\rm NB}(r)$ at r_0. $V_{\rm shift}$ is introduced to avoid a discontinuity at the cut-off distance r_3.

Following Sinnott *et al.*, at $r < r_2$ the long-range potential is smoothly switched off. For $r < r_1$ $V_{\rm NB}(r)$ is set to the small constant value $-V_{\rm shift}$. In the range $r_1 < r < r_2$ the potential $V_{\rm NB}(r)$ is interpolated by a fourth-order polynomial

$$V_{\rm NB}(r) = a_4(r-r_1)^4 + a_3(r-r_1)^3 + a_2(r-r_1)^2 - V_{\rm shift},$$

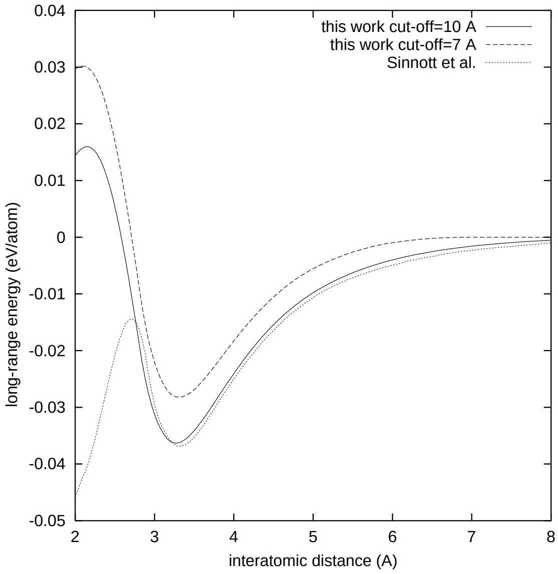

Figure 2: Long-range interplanar energy E_{NB} per atom as a function of the inter-planar distance in graphite

where a_n, $n = 2 \ldots 4$ are chosen to avoid discountinuity in $V\mathrm{NB}(r)$ and its derivative at $r = r_2$ (note that the chosen form of the polynomial automatically leads to a smooth behavior at $r = r_1$). An additional condition to choose the a_n coefficients is to require that the maximum of the polynomial is reached at $r = r_1 + \alpha(r_2 - r_1)$. The choice of a higher-order polynomial (compared to Sinnott et al.) allows to modify the shape of the potential at r between r_1 and r_2 and to shift the position of the maximum to smaller $r_{i,j}$. The parameter α can be chosen between 0.5 and 1.0 and we have used $\alpha = 0.6$ in our simulations. The resulting values are: $a_2 = 0.114212$, $a_3 = -0.113328$, $a_4 = 0.0275889$.

Our potential $V_{\mathrm{NB}}(r)$ is compared to that of Sinnott *et al.* [12] in Fig. 1 and the resulting E_{NB} per atom in Fig. 2. Here we have shown the results for two values of the cut-off distance r_3, namely $r_3 = 10$ Å as in Sinnott et al. [12] and $r_3 = 7$ Å. One can see that in both cases the unphysical minimum has disappeared although a small plateau at interatomic distances ~ 2 Å is still present. The latter does not agree with the results of *ab-initio* calculations [16] but we did not find a way to overcome it within the chosen functional form of the non-bonded energy. For bulk diamond, graphite and nanostructures our parametrization leads to a small positive contribution of E_{NB} to the total energy. The bulk lattice constants are negligibly affected. This potential can thus be used also in disordered structures without favoring interatomic distances which are neither those of diamond nor those of graphite. In our implementation we have chosen to use the cut off of 7 Å which is much faster in computation. With this value we get a more precise value of the minimum at the correct interplanar

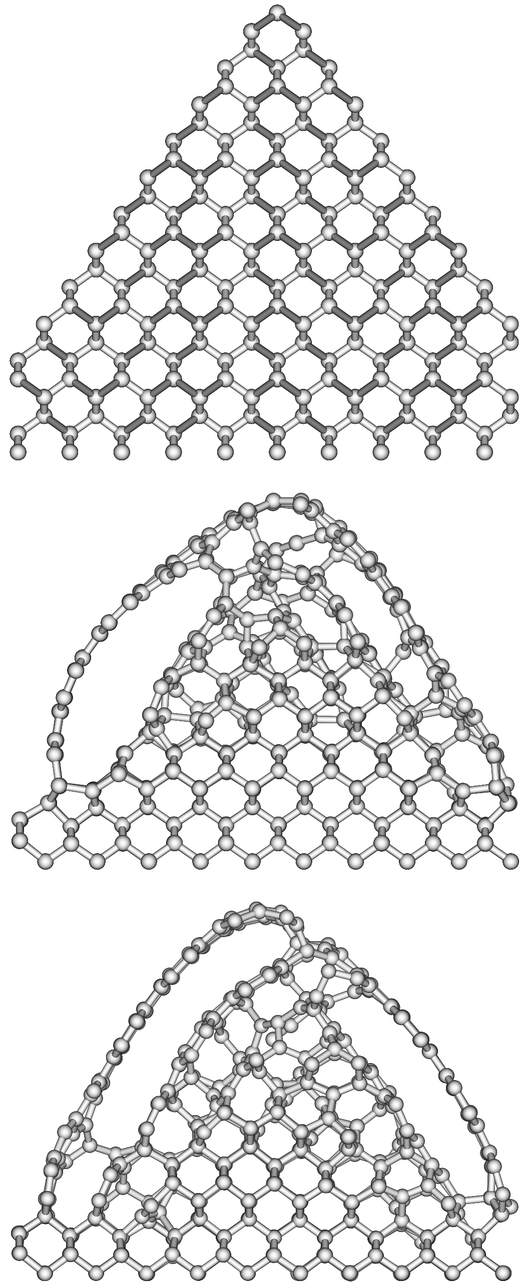

Figure 3: Top: original sample, with 676 atoms. The vertical direction is along (100), the groove is along (110) and the lateral surfaces are (111). The thickness of the grove is is $2\sqrt{2}a$, where a=3.567 Å is the cube size of the bulk diamond lattice (four periods of the lattice along the (110) direction)and periodic boundary conditions are imposed. The four bottom layers are kept fixed during the simulation. Middle) Structure after the grand canonical MC annealing up to 800 K without including long range interactions. Bottom) Same as middle panel but with long-range interactions. Three atomic layers at the bottom are removed in the middle and bottom panels for clarity.

spacing, 3.35 Å against 3.27 Å obtained with $r_3 = 10$ Å and a shallower minimum which compares better to the value used by Che et al. in Ref. [13].

We have also addressed the question of whether also the right stacking ABAB of the graphite planes can be reproduced. With both values of the cut-off, however, we find a negligible difference (< 0.1 meV) between the stacking ABAB and ABC whereas the stacking AAA is at least 10meV higher in energy.

3 Graphitization of the (111) surface

The pioneering work of Davies and Evans [17] has clarified the surface-induced nature of the process of graphitization of diamond, known to occur at ambient pressure and high temperature since 1920. The mechanisms and transformation paths for this process have been and still are subject of intensive studies over the years [4]. Although this phenomenon remains controversial, general consensus exists on the fact that graphitization proceeds from puckered (111) diamond planes. One of the questions which remains open and which we address here is whether, once started, graphitization proceeds into the bulk or remains limited to a finite region below the surface. Recent observation of the diamond graphite interface, obtained by High Resolution Electron Microscopy [18], have led the authors to make the hypothesis that a strained graphite layer might act as a seal to prevent further transformation to graphite. To this purpose we have performed grand canonical Monte Carlo simulations starting with the structure shown in the top panel of Fig. 3, a diamond wedge with a groove along (110) and with (111) lateral surfaces. This structure is meant to model a puckered (111) surface. We have performed a long annealing cycle, bringing the temperature up to 800K and back to zero. The minimized structures obtained by the Brenner potential alone or supplemented by our long range potential V_{NB} are shown in the middle and bottom panels of Fig. 3 respectively. The total number of 676 atoms in the starting structure reduces during the grand canonical simulation to 664 and 657 respectively. One can see a well developed graphitic layer forming in both simulations. Although less evident from the figure, underneath the most external layer other portions of graphitic planes have formed. Conversely, the central part at the bottom remains ordered as diamond. There are several differences between the two simulations with and without long range interactions. When V_{NB} is includes, a rather symmetric structure forms on both sides of the wedge and the graphitic planes remain at a distance of ~ 2.9 Å from the planes underneath. Without V_{NB} instead the structures is more disordered and the left external plane is at larger distances, well beyond the range of the potential. In both case the external graphitic layers show a regular hexagonal lattice with interatomic distances intermediate between diamond and graphite. Our results support the conjecture of Ref. [18] in that indeed strained graphitic layers form at non-flat (111) surfaces without proceeding into the bulk at least at the temperatures considered. This conclusion is also supported by simulations on larger samples which are in progress.

In summary, we have proposed an extension of the Brenner potential to include non bonded interactions and we have shown results for the graphitization of (111) surfaces. This phenomenological potential can be used to study situations where both diamond and graphitic bonding is present and interaction between graphitic planes are important. Its use in off-lattice grand canonical MC simulations such as the one presented here can help advancing our understanding of the fascinating structural properties of carbon.

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