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Reconstructions of diamond (100) and (111) surfaces: Accuracy of the Brenner potential

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February 1, 2008

Abstract

We present a detailed comparison of the structural predictions of the effective many-body Brenner potential with those of *ab-initio* studies for known reconstructions of diamond (100) and (111) surfaces. These results suggest high reliability of the Brenner potential for dealing with carbon-based structures where different types of bonding are present at the same time.

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1 Introduction

Carbon-based structures are of a great current interest [1–4]. The challenge of these systems from the fundamental point of view is related to the interplay between different types of atom bonding, leading to a uniquely large variety of structural phases formed by a single element, such as diamond and graphite, single- and multi-shell fullerenes and nanotubes [1] and other structures [2] with many peculiar properties. To study the elastic properties and fracture of these structures and their mixtures, the transformation paths between them [3, 4], etc. it is important to develop predictive schemes based on simplified empirical potentials, which allow large-scale simulations of complex structures with mixed atomic bonding, which are often beyond the possibilities of *ab-initio* calculations. Effective many-body empirical potentials have proven to be useful and predictive for a number of materials [5–7]. The potentials developed by Tersoff [5] for group IV elements are very accurate for Si and Ge, also as far as interface properties are concerned, but less reliable for C.

Carbon is particularly difficult for an empirical scheme due to the large variety of different types of C–C bonding with very different energetics and bond lengths d_{CC} . For example, for a single C–C bond in diamond $d_{CC} = 1.54$ Å, for a conjugated bond in graphite $d_{CC} = 1.42$ Å and for a double bond in $H_2C=CH_2$ $d_{CC} = 1.34$ Å. The Tersoff potential, which has been fit to the bulk properties of both diamond and graphite, does not, however, distinguish the chemical character of the bond. At diamond surfaces, different types of bonding are present at the same time, leading to poor results of the Tersoff potential for the surface reconstructions as we show in detail in this work.

Brenner [7] has re-parametrised the Tersoff potential and added nonlocal terms to properly account for the bond modifications induced by a change of bonding of neighbouring atoms. As in the Tersoff scheme, 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 of Tersoff) and, in addition, on the chemical character of the bond (single, double, triple or conjugated) derived by evaluating the number of neighbours for the atoms forming the bond and all their nearest neighbours.

Diamond surfaces are an example of a rather simple system, where the interplay between different types of carbon bonding becomes important. Numerous calculations exploiting various *ab-initio* approaches and extensive experimental data are available, making the diamond surfaces an important check point to verify the accuracy and predictive power of empirical schemes. The Tersoff potential for C yields the unreconstructed (111) (1×1) surface as the most stable against the experimental evidence of the (2×1) Pandey chain reconstruction [8] analogous to that of Si(111). For the (001) face it strongly favours an asymmetric re-arrangement of carbon atoms beneath the row of unbuckled dimers [9]. In the present work we compare in detail the predictions of the Brenner and Tersoff potentials with results of *ab-initio* calculations for known reconstructions of the diamond(100) and (111) surfaces. Our results reveal high quantitative accuracy of the Brenner potential. Since the parameters are fit to the *bulk* properties of

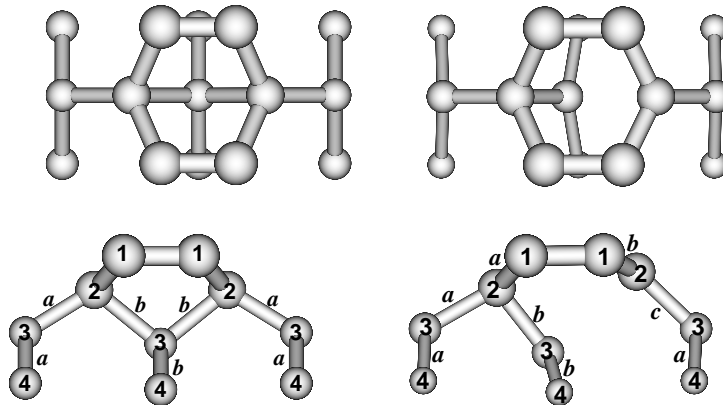


Figure 1: Unit cell of (left) the symmetric (2×1) and (right) the asymmetric $(2 \times 1)a$ reconstructions of diamond(100) after MC energy minimisation with the Brenner potential. The top and bottom panels show the top (100) and the side (011) views. The numbers on the atoms denote the atomic layer they belong to. Inequivalent bonds between two atomic layers are labelled with letters a , b and c .

diamond and graphite and to properties of various hydrocarbon molecules, the high accuracy at the *surface* suggests a high predictive power of the potential at short distances. With further modifications to include also long-range interactions (beyond 2 \AA , the cut-off of the potential) [10, 11], which are now under development [12], the Brenner potential promises to become a powerful tool to investigate carbon-based structures on a large scale.

2 (100) surface

Our previous study [9] of the diamond(100) surface with the Tersoff potential has suggested a new reconstruction with a strongly asymmetric rearrangement of atoms in deeper layers. These predictions have now been verified using the off-lattice Monte Carlo (MC) technique with the Brenner potential. We have confirmed that both the symmetric (2×1) and asymmetric $(2 \times 1)a$ (where ‘a’ stands for ‘asymmetric’) structures shown in Fig. 1 correspond to local energy minima. However, the energies for the two reconstructions given by the Brenner potential are found in a reversed order compared to the prediction of the Tersoff potential. Relative to the energy of the relaxed (1×1) ideal diamond (100) surface, the energy gain is found with the Brenner potential to be 5.40 and 4.19 eV per surface dimer for the (2×1) and $(2 \times 1)a$ structures, respectively. For comparison, the Tersoff predictions were 0.26 and 1.55 eV, respectively [9].

The length of the bonds between atoms in the top four layers are given for the two structures in Table 1. For comparison, we also give the results obtained with the Tersoff potential [9] and those found in *ab-initio* calculations [13]. Note

Table 1: Bond lengths for the dimerised symmetric (2×1) and asymmetric (2×1)a reconstructions (given in Å). The bond between an atom in the N th layer and one in the M th layer is labelled by NM . Whenever more than one nonequivalent bond is present, they are labelled by a , b and c in Fig. 1 and are displayed in the table in this order. For completeness, we show the bond length as given by *ab-initio* calculations [13], the Brenner [this work] and Tersoff [9] empirical potentials as well as the corresponding bulk diamond bond lengths.

bond	<i>ab-initio</i> [13]	Brenner [this work]			Tersoff [9]	
	(2×1)	(2×1)	(2 × 1)a		(2×1)	(2×1)a
11	1.37	1.3807	1.4370		1.542	1.487
12	1.50	1.5096	1.4937, 1.4318		1.515	1.496, 1.565
23	1.55, 1.57	1.5059, 1.5905	1.5339, 1.5287, 1.5321		1.524, 1.579	1.541, 1.489, 1.506
34	1.56, 1.50	1.5670, 1.5140	1.5856, 1.4739		1.570, 1.521	1.582, 1.477
bulk	1.53	1.5407			1.5445	

that, from the chemical point of view, each surface atom at the bulk-terminated surface has two un-paired electrons (two dangling bonds). Therefore, the dimer bond (bond 11 in Table 1) in the symmetric (2×1) surface structure has the character of a double-bond. The Brenner potential correctly reproduces the length of the bond 11, which is much shorter than both the single C–C bond in diamond and the conjugated bond in graphite, but rather close to the length of a double bond. It quantitatively agrees with the dimer bond length of 1.37 Å for the (2×1) diamond(100) surface found in *ab-initio* calculations [13–15]. Conversely, the Tersoff potential, which does not include the nonlocal terms, predicts very different length of the dimer bond; it also gives much smaller reconstruction energy for both structures since the chemical character of stronger double and conjugated bonds is not accounted for. With the Brenner potential, in the asymmetric (2×1)a structure, the bond 11 is elongated up to 1.437 Å (close to the graphite value) since it becomes a member of a conjugated (π -bonded) system. Note that the bond 12*b*, which also connects three-fold coordinated atoms, has a very similar length.

Examination of the first two columns in Table 1 reveals the high accuracy of the predictions of the Brenner potential for the bond lengths of the symmetric (2×1) diamond(100) reconstruction. Except a slightly higher difference of the length of the bonds 23*a* and 23*b*, our results agree with the *ab-initio* results [13] within 0.01 Å accuracy. Note that the *ab-initio* approach of Ref. [13] underestimates the bulk bond length by 0.01 Å with respect to the experimentally-determined value. In contrast to the surprisingly good quantitative agreement of the structural data, the reconstruction energy is different. The value of 5.40 eV/dimer as given by the Brenner potential is found between the *ab-initio* values (3.02 [13], 3.36 [14] and 3.52 [15] eV/dimer) and the reconstruction energy given by the semi-empirical SLAB-MINDO scheme (7.86 eV/dimer [16]).

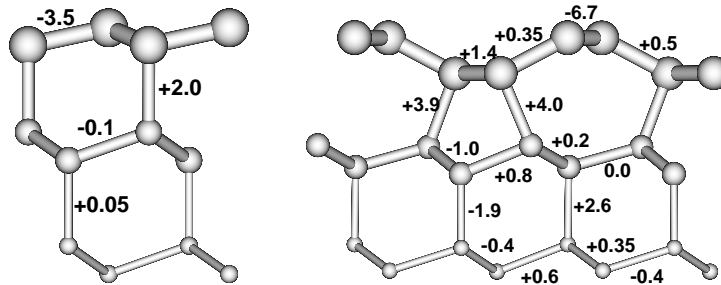


Figure 2: Side ($\bar{1}10$) views of (left) the relaxed (1×1) and (right) the Pandey (2×1) reconstruction of the (111) surface along with the bond lengths shifts relative to the bulk value as given by the Brenner potential.

3 (111) surface

We do not consider the Tersoff potential here since it gives the unreconstructed (1×1) surface as the minimum energy structure. Fig. 2 shows the relaxed (1×1) and the (2×1) Pandey chain reconstructions of the diamond(111) surface as given by the Brenner potential. In brief, the most important changes of the bond lengths as compared to the bulk value are as follows. For the relaxed (1×1) structure: (i) the contraction of the bond within the first bilayer by -3.5% agrees with *ab-initio* values of -3.1% [17], -4.0% [18] and -4.2% [19]; (ii) the elongation of the bond between the first and second bilayer by $+2.0\%$ agrees with $+2.1\%$ of Ref. [17] but seems underestimated compared to $+8.7\%$ and $+9\%$ of Refs. [18, 19]. In the (2×1) Pandey reconstruction: (iii) the π -bonded upper chain bond length of 1.437 \AA (-6.7%) well compares to *ab-initio* values of 1.47 \AA (-4.4%) [17], 1.44 \AA [20] and 1.43 \AA (-6.5%) [19]; (iv) the lower chain elongation by $+1.4\%$ is close to $+0.7\%$ [17] and $+0.9\%$ [19]; (v) the stretch of the bonds between the first and second bilayers by $+3.9\%$ and $+4.0\%$ seems to be underestimated with respect to the *ab-initio* values of $+8.1\%$ [17], $+8\%$ [20], $+4.5\%$ and $+6.6\%$ [19]. Further comparison with the results of Refs. [17–20] shows that all other bond shifts agree with the *ab-initio* calculations within $\sim 1\%$. Therefore, except a tendency to underestimate the elongation of the bonds between the top and second bilayer, our structural results for diamond(111) agree remarkably well with *ab-initio* predictions [17–20].

Relative to the energy of the bulk-terminated diamond(111), we find energy gains per 1×1 unit cell of 0.244 eV for the (1×1) structure (cf 0.37 eV [17] and 0.57 eV [19]) and 1.102 eV for the Pandey reconstruction (cf 0.47 eV [17] and 1.40 eV [19]).

We note that there is a long-standing debate on the structural and electronic properties of the diamond(111) surface. An important issue is whether this surface is metallic or semiconducting. In most calculations [17, 19] the band of surface states is metallic whereas experimentally the highest occupied state is at least 0.5 eV below the Fermi level [21]. Dimerisation along the π -bonded chain

could open the surface gap but only one total-energy calculation obtains slightly dimerised chains yielding a 0.3 eV gap [20] in the surface band. Experimentally, recent X-ray data [22] does not show any dimerisation but favour the (2×1) reconstruction accompanied by a strong tilt of the π -bonded chains, similar to the (2×1) reconstruction of Si(111) and Ge(111). The tilt is however not confirmed by theoretical studies [17, 19, 20].

Neither dimerisation nor buckling of the π chain is found in our results for the Pandey reconstruction in agreement to most *ab-initio* results. However, our recent MC study [23] of the structure of diamond(111) based on the Brenner potential has shown that, in addition to the stable (2×1) Pandey chain reconstruction, there exist additional meta-stable states, specific for carbon, with all surface atoms in three-fold graphite-like bonding. Since the energy of these metastable states is very close to the one of the Pandey (2×1) , these structures can coexist with the Pandey structure at a real surface. Moreover, due to symmetry breaking induced by a strong dimerisation of the lower (4-fold coordinated) atomic chain in the first bilayer, the meta-stable reconstruction is likely to exhibit semiconducting behaviour. Although the new structures and their surface electronic properties ought to be checked in *ab-initio* studies, the high accuracy of the Brenner potential demonstrated in this work strongly supports this prediction.

4 Conclusion

We have performed off-lattice Monte Carlo study of the (100) and (111) diamond surfaces with the empirical many-body Brenner potential [7] and compared the results in detail with those obtained with the Tersoff potential [9] and with *ab-initio* approaches [13–15, 17–19]. We find that the Brenner potential is extremely accurate in describing the structural properties at surfaces, supporting the recent predictions [23] of new meta-stable reconstructions of diamond(111). On the other hand, the Tersoff potential [5], which does not distinguish the chemical character of the bond, turns out to give a poor description of surface properties.

The Brenner potential, however, cannot describe weaker long-range interactions, such as the interplanar interactions in graphite due to the cut-off at 2 Å. This is the most serious limitation to be overcome. Recently, further modifications of the Brenner potential to include also long-range interactions beyond 2 Å are being proposed [10–12]. Given the high accuracy of the short-range part, the modified Brenner potential [10–12] promises to become a powerful tool to investigate carbon-based structures on a large scale.

Acknowledgements We would like to thank Daniele Passerone, Furio Ercolessi and Erio Tosatti for their help in implementing the off-lattice grand canonical Monte Carlo code. Valuable discussions with Elias Vlieg, Frank van Bouwelen, Rob de Groot, Hans ter Meulen, Willem van Enkevort and John Schermer are acknowledged.

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