



Research paper

Study of bi-dimensional materials using a semi-empirical potential including a torsional term

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ABSTRACT

The static and dynamical properties of graphene, silicene and their fully hydrogenated compounds were studied using a semi-empirical potential of the form proposed by Tersoff with the addition of a torsion-like term. The importance of the torsion term for bi-dimensional silicon compounds is analyzed. Calculated structures are in reasonable agreement with experiments or first principle calculations predicting a flat structure for graphene and a buckled one for silicene, silicane and graphane.

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1. Introduction

Recently, the existence of new two dimensional (2D) materials has been experimentally demonstrated or theoretically predicted on the basis of *ab initio* calculations in different approximations [1–3]. Among them, a set of particular interest for the potential technological applications in electronic devices, is the one constituted by carbon or silicon 2D compounds such as graphene and silicene with varying degrees of hydrogenation. Graphene has been produced by several methods, including exfoliation from bulk graphite, surface segregation and chemical vapor deposition. It has been largely studied by several techniques (see Refs. [1,2] and references there in). The synthesis of epitaxial silicene on silver (1 1 1) surfaces has been confirmed in a few works by some experimental techniques as scanning tunneling microscopy (STM), Raman spectroscopy and low-energy electron diffraction (LEED) [4–11]. In order to study these materials, it results appealing to have simple semiempirical potentials that allow adequately describing structural and dynamical properties. Such simple potentials would enable to study also non periodic structures such as amorphous and nanometric materials, nanoribbons, nanowires, etc. for which a great number of atoms is needed in the simulations. For this

propose several potentials and parametrizations have been proposed: Stillinger-Weber, Tersoff, ReaxFF, etc. [12–14].

Semiempirical potentials of the form proposed by Tersoff have been widely applied in the last three decades [13,15–19]. They have proved to be suitable for describing structures of group IV compounds (C, Si, Ge) and even to predict hypothetical structures subsequently substantiated by more sophisticated *ab-initio* calculations [20]. However, these potentials are not completely satisfactory to describe some dynamical properties and in these cases they yield vibrational frequencies in poor agreement with experiment. To overcome this inadequacy in carbon systems (graphite, diamond, C₆₀ fullerenes, etc.) we have undertaken in a previous paper [21] a reparametrization and a slight modification of Tersoff's potentials with the addition of a torsion-like term. Such a term does not modify the calculated static energy of zinc blende (diamond, silicon, germanium) and planar honeycomb (graphite, graphene) structures, but can supply a contribution for other symmetries, in particular if planarity is broken in honeycomb structures (graphane).

In the case of silicon compounds, Tersoff potential parameters have been refined fitting exclusively the physical properties of crystalline silicon. Although static and dynamical properties are calculated in reasonable agreement with experimental results, recent works have introduced important modifications to the potential in order to improve such results. In particular, Monteverde et al. [22] have included multibond interactions to the 2- and 3-body terms and a volume dependency improving

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the agreement between calculated and experimental phonon dispersion curves. However, this new potential includes several additional parameters.

The recent discovery of new crystalline forms of C and Si, such as graphene, silicene and their hydrogenated compounds, has expanded the spectrum of materials to be studied giving the possibility of testing and/or modifying the potentials.

Tersoff potential predicts planar forms for both, graphene and silicene. It is known that graphene is flat, but planarity is lost with varying degrees of hydrogenation [23]. Silicene, on the other hand, presents a honeycomb buckled structure with or without hydrogen [4,24,25]. This structure consists of two flat triangular parallel networks separated by a distance called buckling parameter. Therefore, the inclusion of a torsion-like term in the original Tersoff silicon potential (in the form previously described for carbon compounds) is explored in the present paper. This term includes a torsion parameter which has been refined by fitting experimental data on structural and dynamical properties of silicon and *ab initio* calculations on silicene. The potential thus modified is applied to the calculation of static and dynamical properties of silicene and its fully hydrogenated form, silicane.

2. Calculation method

Tersoff potential, in its original form, proposes an interaction energy between covalently bonded atoms of the type:

$$E = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (1)$$

with the atom-atom (V_{ij}) potential

$$V_{ij} = f_c(r_{ij}) [V_R(r_{ij}) - b_{ij}^{sym} V_A(r_{ij})] \quad (2)$$

consistent of one repulsive and one attractive term with a cut-off function $f_c(r_{ij})$ that confines the potential in a continuous and derivable way. Although the bond energy V_{ij} has the formal appearance of a pairwise energy, it also depends on the position of all the atoms bonded to i and j ; the factor b_{ij}^{sym} is in fact a three body term.

The detailed expression for V_R , V_A and b_{ij}^{sym} , as well as that for the cut-off function can be found in several papers [13,21].¹ This potential has been reparametrized by Brenner [16,17], keeping its original form but giving a more precise physical meaning to some parameters and hence making them better suited for fitting. As it was said above, we have fitted parameters to give account of structural and dynamical properties of a number of carbon compounds, with the addition of a torsion-like term, giving a new expression for eq. (1):

$$E = \frac{1}{2} \sum_{i \neq j} (V_{ij} + V_{ij}^{tor}) \quad (3)$$

with

$$V_{ij}^{tor} = \tau f_c(r_{ij}) \sum_{(k,l) \neq (i,j)} f_c(r_{ik}) f_c(r_{jl}) T_{kijl} \quad (4)$$

being τ a torsion parameter, and

$$T_{kijl} = \frac{(\vec{r}_{ik} \times \vec{r}_{ij}) \cdot (\vec{r}_{jl} \times \vec{r}_{ji})}{r_{ik} r_{ij} r_{jl} r_{ji}} \quad (5)$$

As mentioned before, this term, which involves four-body interactions, does not contribute to the static cohesive energy of zinc blende and planar honeycomb lattices, as is the case of diamond, graphite and silicon crystals.

In the present work we use parameters given in Ref. [21] for carbon compounds and Tersoff parameters [13] with the addition of the torsion like term for silicon compounds. For the hydrogenated compounds, the corresponding parameters were taken from Ref. [19].

3. Results and discussion

3.1. Torsional term

As it was mentioned, the inclusion of a torsional term in Tersoff potential for silicon compounds is proposed. The effect is first analyzed in crystalline silicon, taking into account a number of available experimental results for structural and dynamical properties.

Using different τ values, root mean square (*rms*) relative deviations on dynamical properties for silicon were calculated by comparing simulated and experimental results.

In the range $-0.20 \text{ eV} < \tau < 0$, no significant changes were found in the *rms* relative deviations. A slight improvement in vibrational frequencies values at the centre (Γ) and at some special points of the Brillouin Zone (BZ) is compensated by a greater discrepancy in the elastic constants values, going from 0 to -0.20 eV τ values. For $\tau < -0.20 \text{ eV}$ and $\tau > 0$ the *rms* relative deviation increases.

In order to find the best τ value, additional information has been considered: the silicene structure found by first principle calculations and experimental results [4,24,25]. This structure would not be flat, but buckled, unlike graphene structure or each graphite sheet.

It was found that for τ values $-0.13 \text{ eV} < \tau < 0$ the minimum energy structure would still be flat. However, for $-0.20 \text{ eV} < \tau < -0.13 \text{ eV}$ this structure becomes buckled. In this range, a quite shallow minimum for *rms* relative deviation was found around $\tau = -0.18 \text{ eV}$. Thus, these τ value was selected as it presents a reasonable agreement for silicene structure and silicon dynamical properties. Table 1 summarizes experimental values and calculated results obtained for crystalline silicon using Tersoff original potentials, with and without torsional term. Tersoff potential with this torsional term was employed to study bi-dimensional carbon and silicon compounds and their full-hydrogenated forms.

3.2. Graphene - graphane

For carbon compounds in three different forms (diamond, graphite and C₆₀ fullerene), the statics and dynamics were studied

Table 1

Calculated and experimental values for silicon primitive cell parameter a (Å), Si-Si bond length $d_{\text{Si-Si}}$ (Å), energy per cell (with two Si atoms) E_{cell} (eV), elastic constants C_{ij} (10^{12} dyn/cm²) and frequencies (cm⁻¹). References between brackets.

	Tersoff	Tersoff + torsional term ($\tau = -0.18 \text{ eV}$)	Experimental
a	3.842	3.842	3.840 [26]
$d_{\text{Si-Si}}$	2.352	2.352	2.351 [26]
E_{cell}	-9.26	-9.26	
C_{11}	1.789	1.789	1.6564 [27]
C_{44}	0.8786	0.7044	0.7951 [27]
C_{12}	0.5366	0.7823	0.6394 [27]
LTO (Γ)	536.4	513.6	519.0 [28], 516.7 [29], 519.0 [30]
TA (X)	230.4	215.3	142.7 [28], 150.0 [29], 151.0 [30]
LA (X)	407.0	407.0	410.0 [29]
TO (X)	497.0	497.8	463.0 [29], 460.0 [30]
TA (L)	156.0	158.7	114.3 [28], 115.0 [29], 113.0 [30]
LA (L)	377.7	344.5	376.7 [29]
LO (L)	439.0	439.0	420.0 [29]
TO (L)	514.9	512.7	490.0 [29], 480.0 [30]

¹ Supplementary material.

Table 2
Structural parameters for graphene and graphane. Values for comparison between brackets.

Material	Cell param. (Å)	d_{C-C} (Å)	d_{C-H} (Å)	Buckling param. Δ (Å)	E_{cell} (eV)
Graphene	$a = b = 2.470$ (2.46 [24,32], 2.45 [31], 2.469 [23])	1.426 (1.42 [24,32], 1.41 [31], 1.426 [23])		0.0 (0.0 [24,23])	–17.12
Graphane	$a = b = 2.504$ (2.54 [24], 2.545 [23], 2.516 [33])	1.521 (1.53 [24], 1.54 [23], 1.52 [33])	1.10 (1.11 [24,23,33])	0.473 (0.46 [24,23])	–21.28

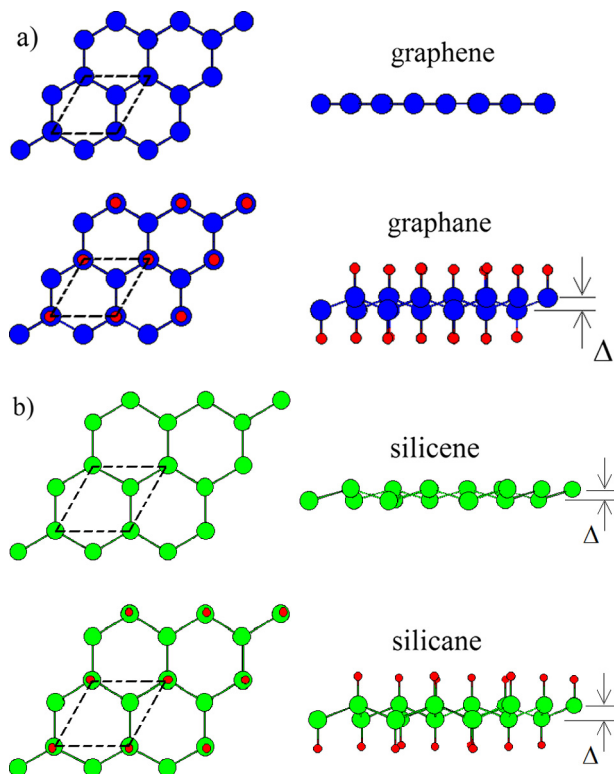


Fig. 1. Top and side view of (a) graphene, and C_2H_2 (graphane); (b) silicene and Si_2H_2 (silicane). Dark blue balls indicate C atoms; green balls indicate Si atoms; red balls indicate H atoms; Δ indicates buckling parameter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in a previous paper [21]. Potential parameters were refined including the torsional term with $\tau = -0.208$ eV. We present here the calculation of static and dynamical properties of graphene and graphane, unknown at that time.

For these compounds, hydrogen parameters were taken from Ref. [19] and were applied according to the usual rule for mixed interactions [13] taking the mix C-H parameter $\chi = 0.89$ [15].

Table 2 shows the resulting structural parameters for graphene and graphane, as illustrated in Fig. 1a. It can be seen that while graphene (as one isolated graphite sheet) is flat, graphane results slightly buckled with a buckling parameter (Fig. 1) $\Delta = 0.473$ Å. Graphene and graphane have hexagonal primitive unit cells with two and four atoms per cell respectively. An excellent agreement between calculated structures and experimental data or first principle calculations is observed, both in the expansion of the cell parameter when graphene is fully hydrogenated, and in the buckling parameter for graphane. As it can be expected the calculated C–C distance, 1.426 Å in graphene and graphite, increases to 1.521 Å in graphane, approaching the distance in diamond [21].

As Tersoff potential is a short range one that describes only covalent bonds, the different graphite planes having a purely Van der Waals interaction are completely uncoupled. As a result, calculated vibrational graphene modes are identical to those found for each graphite plane: one frequency for the in-plane degenerate

mode at 1783 cm^{-1} , and one for the out-of-plane mode at 861 cm^{-1} . Phonon dispersion curves at some special directions of the Brillouin zone ($\Gamma \rightarrow M$, $\Gamma \rightarrow K$ and $\Gamma \rightarrow L$), together with the corresponding density of states are shown in Fig. 2 for graphene and graphane. As can be seen, the absence of imaginary frequencies indicates that both compounds are stable for the applied potential.

Table 3 shows the calculated vibrational optical frequencies at Γ for graphene and graphane, with the inclusion of the torsional term in Tersoff potential. In the case of C_2H_2 (graphane), the primitive unit cell contains two C and two H atoms in a honeycomb buckled structure. The two modes associated to C–H stretchings have frequencies at 2843 and 2814 cm^{-1} for the in-phase and out-of-phase movements respectively. The 1145 cm^{-1} mode is associated to out-of-plane C displacements. The remaining frequencies correspond to three doubly degenerated modes: in-plane C atoms movement (1141 cm^{-1}) and in-phase and out-of-phase C–H bending (1400 and 1403 cm^{-1}). In this work, in-plane and out-of-plane refers to atomic displacements parallel and perpendicular to the flat triangular networks forming the honeycomb structure.

Comparing the frequencies associated with C atoms movements in graphene and graphane, it can be seen that the in-plane frequency is considerably lower in graphane; this is to be expected as C atoms move away from the sp^2 configuration. For the same reason, the loss of planarity, the contrary occurs for the out of plane movements. The frequencies associated to both modes approaches the calculated diamond frequency: 1332 cm^{-1} [21].

3.3. Silicene - silicane

In the case of silicene, Tersoff potential with its original parametrization [13] has been applied with the inclusion of the torsional term with $\tau = -0.18$ eV. In the case of silicane, static and dynamical properties have been calculated using a Si–H mix parameter $\chi = 0.70$ which provides a better agreement on Si–H bond length than the original Tersoff parameter [19].

Table 4 shows the resulting equilibrium structures for pure silicene and silicane. They present a hexagonal primitive cell with two and four atoms per cell respectively. In this case both compounds are non planar with buckling parameters $\Delta = 0.30$ Å for silicene and $\Delta = 0.75$ Å for silicane (Fig. 1b), in good agreement with first principle calculations [24,36,37].

Phonon dispersion curves along some special directions, together with the corresponding density of states for silicene and silicane are shown in Fig. 3, showing the stability of both systems; Table 5 shows the corresponding calculated optical frequencies.

For silicene the calculated vibrational frequencies correspond to one out-of-plane mode at 126 cm^{-1} and two in-plane degenerate modes at 612 cm^{-1} .

For Si_2H_2 (silicane), the primitive cell contains two Si and two H atoms. The two modes associated to the Si–H stretching have frequencies at 2140 cm^{-1} for the out of phase movement and at 2144 cm^{-1} for the in phase one. The out-of-plane displacement of the Si atoms has a frequency of 330 cm^{-1} ; the in-plane movement of Si atoms has a doubly degenerated frequency of 499 cm^{-1} . As in the case of graphene-graphane, these frequencies tend to the calculated triply degenerated silicon frequency (514 cm^{-1}). The remaining frequencies correspond to two doubly

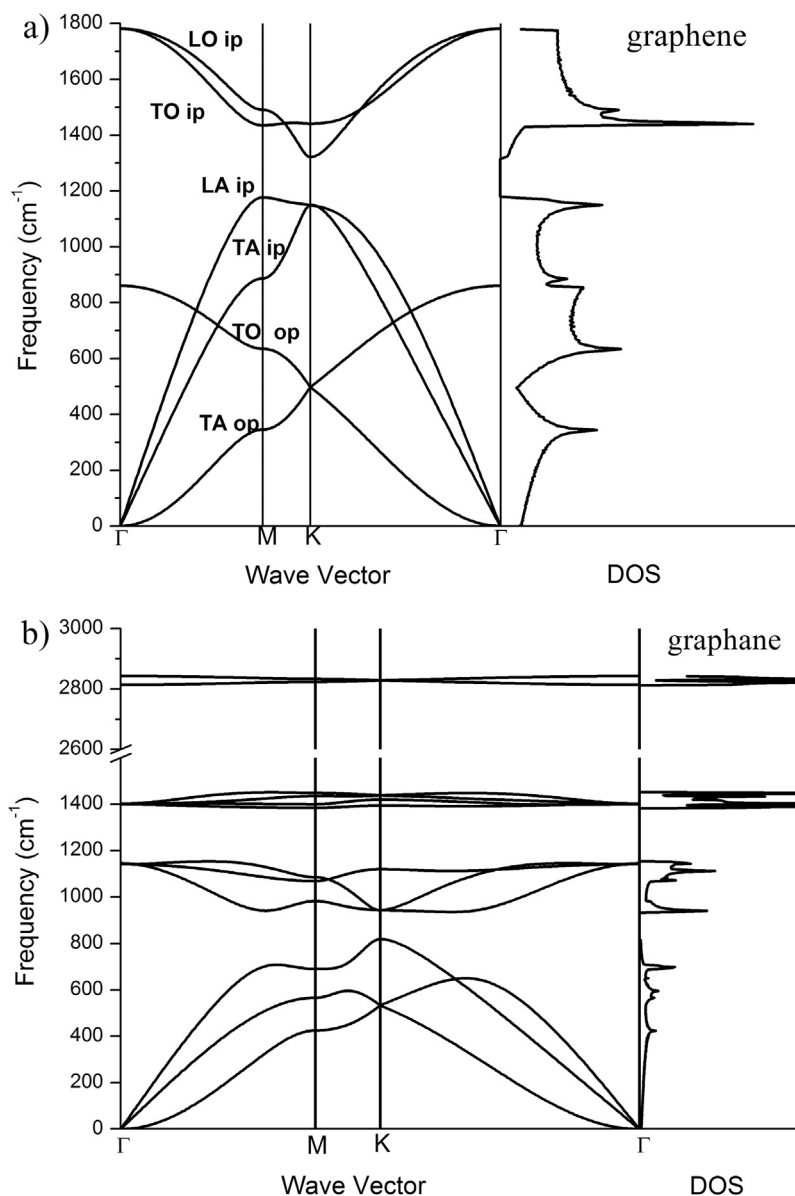


Fig. 2. Phonon dispersion curves and vibrational density of states (DOS) for: (a) graphene; (b) graphane.

Table 3

Calculated optical frequencies for graphene and graphane. Values for comparison between brackets.

Material	Freq. (cm^{-1})	
Graphene	861 (867 [34])	C out of plane
	1783 ^a (1588 [34], 1585 [35])	C in plane
Graphane	1141 ^a	C in plane
	1145	C out of plane
	1400 ^a	C–H bending (in phase)
	1402 ^a	C–H bending (out of phase)
	2814	C–H stretching (out of phase)
	2843	C–H stretching (in phase)

^a Doubly degenerate frequency.

Table 4

Structural parameters for silicene and silicane. Values for comparison between brackets.

Material	Cell param. (Å)	$d_{\text{Si-Si}}$ (Å)	$d_{\text{Si-H}}$ (Å)	Buckling param. Δ (Å)	E_{cell} (eV)
Silicene	3.966 (3.86 [24], 3.82 [31], 3.83 [32])	2.309 (2.28 [24], 2.25 [31,32])		0.300 (0.47 [24], 0.44 [31,32])	–7.83
Silicane	3.864 (3.89 [24], 3.93 [36], 3.78/3.84 [37])	2.354 (2.36 [24], 2.38 [36], 2.31/2.34 [37])	1.45 (1.50 [24], 1.53 [36], 1.51 [37])	0.750 (0.71 [24], 0.72 [36], 0.74 [37])	–12.17

degenerated modes associated with the in phase and out of phase Si–H bending at 646 and 583 cm^{-1} respectively.

4. Conclusions

This work shows the convenience of including in the Tersoff silicon potential a torsional term similar to that previously introduced for carbon compounds [21]. This avoids a full reparametrization of this potential and/or the inclusion of an excessive number of additional parameters in order to find correct structures for the studied 2D compounds. The potentials defined in this way, allow to calculate with reasonable precision the equilib-

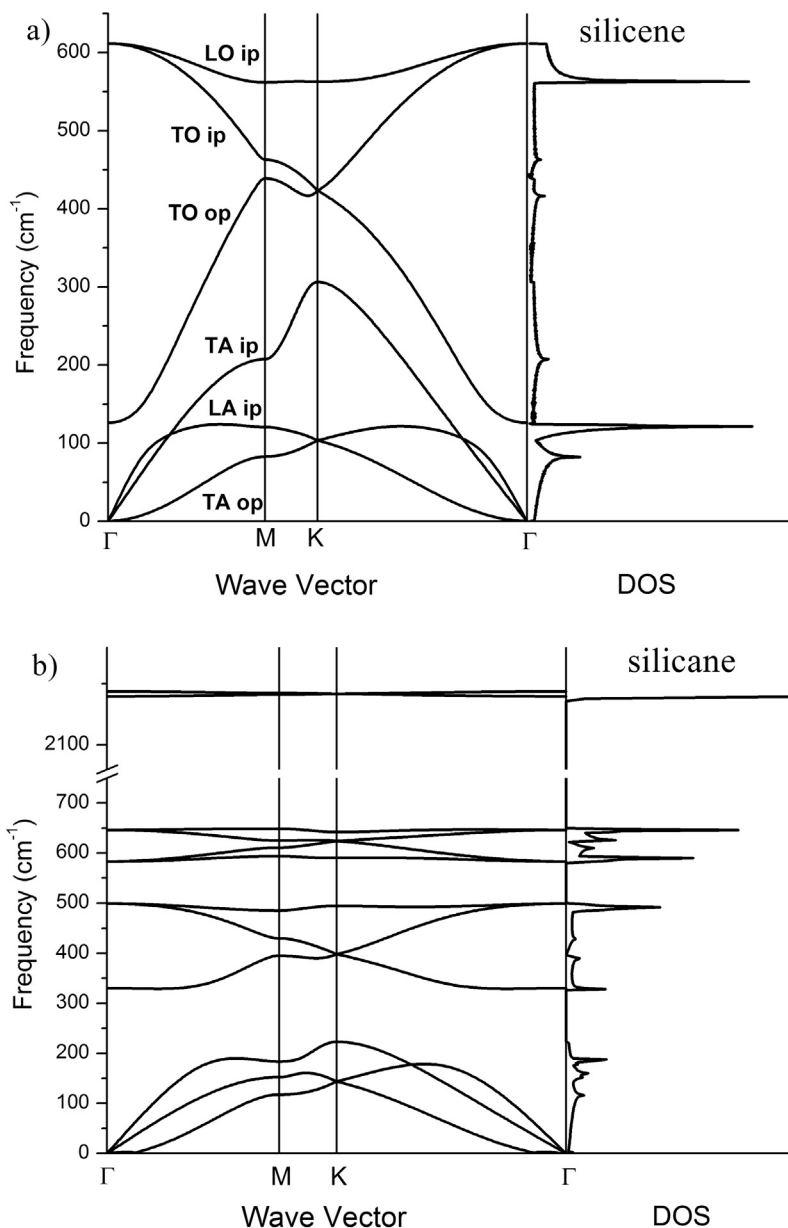


Fig. 3. Phonon dispersion curves and vibrational density of states (DOS) for (a) silicene and (b) silicane.

Table 5

Calculated optical frequencies for silicene and silicane.

Material	Freq. (cm ⁻¹)	
Silicene	126	Si out of plane
	612 ^a	Si in plane
Silicane	330	Si out of plane
	499 ^a	Si in plane
	583 ^a	Si–H bending (out of phase)
	646 ^a	Si–H bending (in phase)
	2140	Si–H stretching (out of phase)
	2144	Si–H stretching (in phase)

^a Doubly degenerate frequency.

rium structures of the materials under study: cell parameters and buckling distances are in good agreement with experiments or first principle calculations. It is found that graphene (as graphite) is flat while the fully hydrogenated form results buckled. Silicene and silicane are both buckled with an appreciable increase in buckling parameter upon hydrogenation.

The results exposed here suggest that Tersoff potential with the inclusion of a torsional-like term would provide an adequate description of structural and dynamical properties of amorphous and nano-crystalline carbon and silicon compounds, where a great number of atoms needs to be involved.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2017.08.040>.

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