Large-scale atomistic simulations using the reactive empirical bond order force field approach is implemented to investigate thermal and mechanical properties of single-layer (SL) and multi-layer (ML) molybdenum disulfide (MoS$_2$). The amplitude of the intrinsic ripples of SL-MoS$_2$ are found to be smaller than those exhibited by graphene (GE). Furthermore, because of the van der Waals interaction between layers, the out-of-plane thermal fluctuations of ML-MoS$_2$ decreases rapidly with increasing number of layers. This trend is confirmed by the buckling transition due to uniaxial stress which occurs for a significantly larger applied tension as compared to graphene. For SL-MoS$_2$, the melting temperature is estimated to be 3700 K which occurs through dimerization followed by the formation of small molecules consisting of 2 to 5 atoms. When different types of vacancies are inserted in the SL-MoS$_2$ it results in a decrease of both the melting temperature as well as the stiffness.

PACS numbers: 68.60.Dv, 62.20.-x

I. INTRODUCTION

Two-dimensional (2D) transition-metal dichalcogenides (TMDCs) have attracted a lot of attention due to the wide range of electronic phases that they can exhibit, ranging from metallic\cite{1,2} semiconductor\cite{3,4,5} to superconductor\cite{6}. Recently, a lot of research efforts were devoted to MoS$_2$ due to its wide availability in nature as molybdenite and its promising semiconducting characteristics (in contrast to graphene which has a zero band gap). Bulk MoS$_2$ has an indirect bandgap\cite{7} whereas its single-layer has a direct bandgap\cite{8} and exhibits photoluminescence\cite{9} which is advantage for optoelectronic applications. While it is known that the band gap can be tuned by lattice deformations\cite{10}, the microscopic details of MoS$_2$ under applied strain are still not well understood.

The phonon spectrum of MoS$_2$ is very different from that of graphene resulting in distinct structural and thermal properties, e.g. the well known negative thermal expansion of graphene is not observed in MoS$_2$\cite{11}. There is also an energy gap of $\sim 50$ cm$^{-1}$ in the phonon spectrum of MoS$_2$ which separates optical and acoustic phonon bands. The knowledge of the thermo-mechanical properties of MoS$_2$ is crucial for the enhancement of the performance of devices made of MoS$_2$. The role of defects on the physical properties of monolayer MoS$_2$ is also important because most of the 2D materials contain vacancies, which are generated during the growth process\cite{12,13} or by ballistic displacements during imaging such as electron irradiation, due to chemical etching and electron excitations in high resolution transmission electron microscopy\cite{14,15}. Recently, Zhou et al.\cite{16} found six types of point defects in monolayer MoS$_2$ grown by chemical vapor deposition: i) monosulfur vacancy ($V_{S_2}$), ii) disulfur vacancy ($V_{S_2}$), iii) vacancy complex of Mo and nearby three sulfurs ($V_{MoS_3}$), iv) vacancy complex of Mo nearby three disulfur pairs ($V_{MoS_6}$), and v) antisite defects where a Mo atom substitutes a S$_2$ column ($MoS_2$), or vi) a S$_2$ column substituting a Mo atom ($S_2Mo$).

In our previous studies we investigated the thermo-mechanical properties of different 2D-materials, e.g. graphene (GE), hexagonal boron-nitride (h-BN) and...
their functionalized structures. Here we report on the thermo-mechanical properties of single and multi-layer MoS$_2$. Due to the S-Mo-S sandwich structure, we found exceptional mechanical stability and a lower thermal excited rippling behavior as compared to graphene. Similarly, the melting of MoS$_2$ occurs also at a lower temperature and exhibits different microscopical characteristics such as the formation of small molecules.

The paper is organized as follows. Details of the MD simulation and a description of the modified Lindemann parameter used to detect the melting transition are described in Sec. II. Then, in Sec. III we present results for the thermal ripples and we compare them with those of GE. In Sec. IV we obtain the buckling transition for applied stress in the zig-zag and arm-chair directions. We discuss the melting behavior of MoS$_2$ together with the effect of several kinds of vacancies on it in Sec. V. Finally, in Sec. VI we present the conclusions of our work.

II. SIMULATION METHOD

A proper interatomic potential function which is capable of describing accurately the interactions in the material system is of crucial importance. Recently, a new approach based on bond-order potentials emerged that depend on the local chemical environment in reactive simulations which capture bond formation and breaking, saturated and unsaturated bonds, dangling and radical bonds, as well as single, double or triple bonds. Liang et al. presented an interatomic potential for Mo-S systems which contains a many-body reactive empirical bond-order (REBO) potential with a two-body Lennard-Jones (LJ) potential. The REBO potential was chosen because it allows for bond breaking and bond formation during simulation. The parameterized many-body Mo-S potential energy focuses primarily on the structural and elastic properties of MoS$_2$ maintaining its transferability to other systems such as pure Mo structures, low coordinated S, and some other binary structures.

The Mo-S many-body empirical potential has the following analytical form:

$$E_b = \frac{1}{2} \sum_i \sum_{j(>i)} [V^R(r_{ij}) - b_{ij}V^A(r_{ij})].$$

(1)

Here $E_b$ is the total binding energy, $V^R(r_{ij})$ and $V^A(r_{ij})$ are a repulsive and an attractive term, respectively, with $r_{ij}$ the distance between atoms $i$ and $j$, given by

$$V^R(r) = f^C(r)(1 + Q/r)Ae^{-\alpha r},$$

(2)

$$V^A(r) = f^C(r)\sum_{n=1}^{3} B_n e^{-\beta r},$$

(3)

where the cut-off function $f^C(r)$ is taken from the switching cutoff scheme. The values for all the parameters used in our calculation for the Mo-S potential can be found in Refs. and are therefore not listed here. Alternatively, it is also possible to use its competitor, the Stillinger-Weber potential, to model the interaction between Mo-Mo, Mo-Mo and S-S.

The mutual interaction between different S-Mo-S tri-layers is a van der Waals (vdW) attraction between the S atoms which we describe by the well-known Lennard-Jones potential,

$$E_{LJ}(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^12 - \left( \frac{\sigma}{r} \right)^6,$$

(4)

where $r$ is the interatomic distance between S-S atoms, $\sigma = 3.3$ Å and $\epsilon = 6.93$ meV. The 12-6 Lennard-Jones potential parameters are used for the S-S interaction such that the elastic constant $c_{13}$ of MoS$_2$ bulk is correctly reproduced.

In the next section we study the thermal rippling, the mechanical properties and the melting of a single- and bilayer of MoS$_2$ using large scale atomistic simulations with the above potentials. The Mo-S parameters were implemented in the large-scale atomic/molecular massively parallel simulator package LAMMPS.

To account for the melting transition we analyzed the variation of the total potential energy $E_T$ per atom with temperature identifying partial contributions from Mo-atoms ($E_{Mo}$) and S-atoms ($E_S$). The Lindemann criterion which states that the system is melted when the root-mean-square (rms) value of the atomic displacement is of the order of a tenth of the lattice constant, was used to characterize the ordered state by considering the modified parameter $\gamma$, used previously for 2D systems, and defined as

$$\gamma = \frac{1}{a^2}(|r_i - \frac{1}{n} \sum_j r_j|^2),$$

(5)

where $a = 1/\sqrt{\pi\rho_0}$, $\rho_0$ is the 2D particle density at $T=0$ K, $n$ is the number of nearest-neighbor atoms, $r_i$ is the position of the $i^{th}$ atom and the sum over $j$ runs over the nearest-neighbor atoms. Here, $i$ and $j$ were restricted to run only over Mo-atoms.

III. INTRINSIC RIPPLES

In order to study the thermal stability of MoS$_2$ we considered a square shaped computational unit cell of MoS$_2$ ($l_x=260$ Å , $l_y=280$ Å) with both arm-chair and zig-zag edges in the $x$ and $y$ directions with a total number of $N = 25920$ atoms in the single layer and $N = 51840$ atoms in the bilayer MoS$_2$. In our simulation we adopted periodic boundary conditions and employed the NPT ensemble with $P=0$ using the Nosé-Hoover thermostat and varied the temperature from 10 K to 900 K.
In Fig. 2(a) we show the evolution with temperature of the average value of the height fluctuations $\langle h^2 \rangle$ where $h$ refers to the height of the Mo atoms with respect to the center of mass of the central Mo-layer. For comparison we have added here the results of single layer graphene (circles) of comparable system size. Notice that in the whole temperature range $\langle h^2 \rangle$ for single layer MoS$_2$ is smaller than that of graphene. This result agrees with the estimated mechanical properties of these materials where MoS$_2$ is expected to be more rigid.$^{23}$ Notice that while the distance between the Mo atoms in the Mo-layer is larger than that of the C atoms in graphene, it is the Mo-S interaction that suppresses the height fluctuations of the Mo atoms in MoS$_2$.

When a second layer of MoS$_2$ is added to form bi-layer MoS$_2$, $\langle h^2 \rangle$ is strongly reduced. This effect, due to the S-S van der Waals type-interaction acting between the S-layers, is fundamentally different from the Mo-S interaction. The temperature-dependence of the intra-layer Mo-S and inter-layer S-S (for bi-layer MoS$_2$) distances are shown in Figs. 2(b) and (c), respectively. Notice that the distance Mo-S in bilayer MoS$_2$ is slightly larger than that of the single layer and that there exists a small difference between the S atoms from the inner and the outer side which are more free to move.

The most adequate theory which allows to analyze in more depth the behavior of the intrinsic ripples is the elastic theory of continuum membranes.$^{25}$ Its usage permits the detection of ripples with particular wavelengths and also an estimation of the anharmonic interactions in the system. The key-quantity which characterizes the behavior of the out-of-plane thermal fluctuations is the height-height correlation function which in the harmonic limit has the following power law behaviour $H(q) = \langle h(q)^2 \rangle \approx q^{-4}$. The out-of-plane displacements of Mo atoms was analyzed by calculating $H(q)$ from our molecular dynamics simulation by following the same procedure as explained in our previous work.$^{21,22}$

In Fig. 3 we show $H(q)$ at 300 K, 500 K, and 700 K for single layer MoS$_2$. The results are shifted for a better comparison. The dashed-lines correspond to the harmonic behavior and the peaked-structures at large wavelengths are the Bragg peaks of the crystalline lattice of the Mo-layer. In all the cases $H(q)$ follows closely the $q^{-4}$ law. In the long-wavelength regime, however, a larger fluctuation of the points together with a deviation from the harmonic curve is observed.

In the case of GE, the stability of the membrane has been ascribed to the anharmonic coupling between the in-plane and out-of-plane modes which renormalizes the long wavelength ripples and prevents the occurrence of the crumpling transition.$^{26,27}$ In Fig. 3(b) we show $H(q)$ for GE together with the one obtained for MoS$_2$, at 500 K. While $H(q)$ in GE exhibits the expected deviation from the $q^{-4}$ harmonic scaling due to the anharmonic interactions at small $q$, in MoS$_2$ a larger fluctuation in the simulation results is present. However, in the long-wavelength regime a deviation from the harmonic law still exist and it appears to be larger than that in GE. This result is consistent with the lower value of $\langle h^2 \rangle$ reported in Fig. 2(a) which is a consequence of the reduction in long-wavelength ripples.

The origin of the breakdown of the harmonic behavior in MoS$_2$ is very different from the one in GE. Because of the layered structure of MoS$_2$, its phonon modes and lattice vibration are different from those in single layer graphene. The internal modes (due to the vibration of the Mo-S bonds) are activated with lower energy with respect to e.g. the C-C bonds in graphene. The latter is more susceptible to temperature making it a more floppy material. This can be seen also from the results of next section where we investigate the buckling transition. Therefore, we expect less coupling between out-of-plane and in-plane modes in MoS$_2$ as compared to graphene.

**IV. BUCKLING TRANSITION**

The specific crystal structure of MoS$_2$ influences its response to external stress. Here we investigate the ef-
Fig. 4: (Color online) Variation of \(\langle h^2 \rangle\) in SL-MoS\(_2\) with applied uniaxial stress along (a) arm-chair and (b) zig-zag directions. For comparison purposes we show also the corresponding results for graphene. (c) \(\langle h^2 \rangle\) of single-, bi-, tri- and four-layer MoS\(_2\) versus uniaxial strain. (d) Variation of the total energy with uniaxial strain for MoS\(_2\) along arm-chair (blue) and zig-zag (red) directions.

Fig. 5: (Color online) (a) perpendicular (b) parallel vacancy lines with applied uniaxial stress along zig-zag direction. Various models for the lines (c) single vacancy line, (d) two neighboring vacancy lines in the same S layer (e) two vacancy lines coinciding in top and bottom layers, and (f) two vacancy in staggered configuration.

Fig. 6: (Color online) Variation of \(\langle h^2 \rangle\) in SL-MoS\(_2\) for perpendicular and parallel vacancy lines with applied uniaxial stress along zig-zag direction.

Figure 4(a) shows the variation of \(\langle h^2 \rangle\) with applied uniaxial strain which was determined using \(\epsilon = \mu t/l\) where \(t\) is the time (after starting the compression) and \(l\) is the initial length in the direction of the compression. The buckling transition occurs for 0.60% strain, which is about seven times larger than GE (0.09%) when the stress is applied along the zig-zag direction and 0.80% which is about five times larger than the one for GE (0.16%) when uniaxial stress is applied along the arm-chair direction. Notice that the buckling transition in MoS\(_2\) is sharper than in GE which is attributed to the sandwich structure of MoS\(_2\).

The different responses of multilayer MoS\(_2\) on the applied uniaxial stress are displayed in Fig. 4(c). Here MoS\(_2\) flakes with dimension \(l_x \times l_y = 14 \times 14\) nm\(^2\) are considered. It is clear that the single layer becomes buckled at smaller strains as compared to the cases of bi-, tri- and four-layer for which the buckling transition takes place at 1.5%, 1.8% and 1.85%, respectively. In particular, tri- and four-layer are close to each other and therefore they...
approach the limit of bulk MoS$_2$.

Uniaxial stress simulations can also be used to estimate the Young’s modulus. The results for applied stress in the longitudinal (arm-chair direction) and lateral (zig-zag direction) directions are shown in Fig. 4(d). The Young’s modulus is found by fitting the total energy (per area) to the quadratic function:

$$E_T = E_0 + \frac{1}{2} Y \varepsilon^2,$$

where $Y$ is the Young’s modulus of the system. Using aforementioned fitting process, $Y$ is calculated for a flake with arm-chair and zig-zag MoS$_2$, to be 149 N/m and 148 N/m respectively, which are values between the recent DFT results $^{11,12}$ 130 N/m and the experimental value 180±60 N/m. Notice that the Young’s modulus of graphene is 340 N/m which is 2.25 times larger than that of MoS$_2$.

Notice that since graphene is one-atomic-thick structure it is extremely soft in the out-of-plane direction. The latter results in much lower bending modulus than MoS$_2$. This is the reason for higher $<h^2>$ in Fig. 2(a) for graphene with respect to MoS$_2$. However the in-plane stiffness of graphene because of strong in-plane sp$^2$ bonds is expected to be much larger than MoS$_2$.

We also studied the effect of vacancies on the buckling transition. Notice that vacancies alter the structure of MoS$_2$ and change the internal bonds between atoms. This results in a change of the response of the system to any external force simply because the stiffness of the system is reduced even for a few vacancies. Recently, Komsa et al. $^{13}$ studied sulfur vacancies in monolayer MoS$_2$ under electron irradiation using high-resolution transmission electron microscopy. These single vacancies are mobile under the electron beam and tends to agglomerate into lines, where the direction of line defects is sensitive to applied uniaxial stress. Figs. 5(a,b) present the vacancy lines perpendicular and parallel to the applied uniaxial stress, respectively. The buckling transition for staggered double vacancy lines (which are more favorable in experiments) perpendicular and parallel to the applied stress occurs for 0.4% and 0.6% strain (see Fig. 6) where later is close to the pristine system.

V. MELTING BEHAVIOR

We investigate now the microscopical characteristics of the melting process of a single layer MoS$_2$. Due to the large simulation time for each temperature we considered here a smaller square shaped computational unit cell having $N=7290$ (Mo=2430 and S=4860) atoms. The simulations were performed in the NPT (P=0) ensemble with periodic boundary conditions. Temperature was maintained by the Nosé-Hoover thermostat and the MD time-step was taken to be 0.1 fs.

We first analyze the case of single layer MoS$_2$ and keep separately track of the Mo and S potential energy contribution. In Fig. 7 we show two snap shots of the system before (a) and during (b) melting. The melting temperature $T_m=3700$ K is confirmed by the Lindemann parameter $\gamma$ (Fig. 7(c)) for only the Mo atoms and their nearest neighbors. $\gamma$ increases linearly as temperature increases and diverges at melting. Figures 8(a,b) show the variation of the potential energy per atom with time for Mo and S atoms, i.e. $E_{Mo}$ and $E_{S}$ respectively, at 3600 K and 3700 K. The sharp increase (decrease) in $E_{Mo}$ ($E_{S}$) is a signature of melting at $T_m \sim 3700$ K. After melting, the Mo-atoms remain bonded to the S-atoms and form small molecules which is the reason for the observed increase and decrease of the energy in Figs. 8(a,b). The larger reduction in $E_{S}$ indicates that the S atoms prefer to be bonded to the Mo atoms rather than to result in free S atoms.

The radial distribution function (rdf) of Mo-Mo shows that before melting there is a sharp peak around 3.2 Å that after melting is shifted to the range 2.1Å-2.5Å which is the distance between Mo-atoms in small MoS clusters (see Fig. 8(c)). However, the Mo-S rdf in Fig. 8(d) shows that after melting there are only two peaks around 2.2 Å and 3.2 Å which are due to the formation of Mo-S and Mo-S$_2$ clusters. In contrast to graphene, where after melting the sample turns into random chains of carbon, SL-MoS$_2$ transits to a phase consisting of MoS$_X$ clusters. Thus at melting, atoms fluctuate around their equilibrium position, the inter-atomic Mo-Mo bonds are broken and Mo becomes free and forms clusters with S atoms.

Previously it was found in the presence of helium gas at 1 bar pressure that the melting of bulk MoS$_2$ occurred around 1853-1895 K depending on the rate of heating. It was found that at high heating rate MoS$_2$ began to decompose into Mo$_3$S and sulfur gas starting from the solid phase. At lower rates the evaporation losses increased markedly and MoS$_2$ was converted into the solid Mo$_3$S$_3$ and Mo gas which is a mixture composed of variable amounts of the phases identified chemically and structurally. It was shown that the helium gas pressure had an influence on the melting temperature. Our results show almost a factor of two higher melting temperature. The reasons for this substantial larger melting temperature may be the presence of helium gas in the experiment, the presence of defects (see Fig. 9), dislocations in experimental sample, and the weak vdW interaction between layers. Recently, using high resolution electron microscopy imaging the atomic structure and morphology of grain boundaries in MoS$_2$ have been reported. As we show in Fig. 9 any kind of vacancy in the system reduces the melting temperature. In multilayer MoS$_2$ the melting starts at the outer layer also known as "surface melting", while in single layer the melting occurs when the bonds between Mo and S are broken. We also calculated the melting of bi-layer and tri-layer MoS$_2$ and found a similar melting temperature as for single layer MoS$_2$. Nevertheless, the melting problem of MoS$_2$ should be studied systematically by performing tests using dif-
different potentials as well as studying the size effect. We emphasize that using any bond order type potential, the same order of melting temperature is found which is not expected to be responsible for the factor of two difference in melting temperature between bulk and SL-MoS$_2$. It is also important to note that the time scale in our MD simulation is restricted to maximum nano-seconds which will lead to an overestimation of the melting temperature, while a real melting phenomena occurs in seconds.

It is worthwhile to study the effect of atomic vacancies in MoS$_2$ on the melting temperature. We performed several simulations for MoS$_2$ with different percentage of vacancies (Mo, S, S$_2$) randomly distributed along the sample. The presence of atomic defects in the MoS$_2$ sheet makes it less stiff and consequently results in a lowering of the melting temperature as can be observed in Fig. 9. It is clear that monosulfur vacancies (V$_S$), which is usually observed in experiments due to its lower formation energy, has little impact on the melting in comparison to disulfur vacancies (V$_{S_2}$) and V$_{Mo}$. We can conclude that the presence of V$_{Mo}$ type defects makes MoS$_2$ thermally more unstable than the other type of vacancies. Therefore missing either Mo or S atoms reduces the melting temperature significantly. This may only indicate that the experimental sample in Ref. [50] is not perfect.

VI. CONCLUSION

Different thermal and mechanical properties of multilayer MoS$_2$ were investigated using atomistic simulations. The melting temperature of MoS$_2$ was found to be very weakly dependent of the number of layers and is lower than the one for graphene. MoS$_2$ transits quickly to a phase with MoS$_X$ clusters without the appearance of random coils unlike graphene and graphite. The buckling transition in MoS$_2$ under uniaxial compression is inde-
dependent of the direction of the applied stress which is also different from graphene. We found that the sandwich structure of MoS$_2$ makes it a less stiff material with respect to graphene and it was found to affect different physical properties. MoS$_2$ is more sensitive to temperature and less energy is needed to excite vibrational modes. The buckling transition is sharper as compared to that of graphene and occurs at substantially larger values of strain. We found that perfect MoS$_2$ has a higher melting temperature than those systems with defects. The melting temperature of MoS$_2$ has a higher melting temperature than those systems with defects. This work is supported by the ESF-Eurographene project CONGRAN, the Flemish Science Foundation (FWO-Vl) and the Methusalem Foundation of the Flemish Government. We acknowledge funding from the FWO (Belgium)-MINCyT (Argentina) collaborative research project. We would like to acknowledge Douglas E. Spearot for giving us the implemented parameters of MoS$_2$ in LAMMPS.

VII. ACKNOWLEDGMENTS

This work is supported by the ESF-Eurographene project CONGRAN, the Flemish Science Foundation (FWO-Vl) and the Methusalem Foundation of the Flemish Government. We acknowledge funding from the FWO (Belgium)-MINCyT (Argentina) collaborative research project. We would like to acknowledge Douglas E. Spearot for giving us the implemented parameters of MoS$_2$ in LAMMPS.
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