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Reply to “Comment on ‘Ideal strength and phonon instability in single-layer MoS_{2}’ ”

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Reply to "Comment on 'Ideal strength and phonon instability in single-layer MoS_2' "

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Abstract

In the comment, Cooper *et. al.* pointed out a disagreement between two recent density functional theory (DFT) studies ([T. Li, Phys. Rev. B 85, 235407 (2012)] and [R.C. Cooper, C. Lee, C.A. Marianetti, X. Wei, J. Hone, and J.W. Kysar, Phys. Rev. B 87, 035423 (2013)]) on the uniaxial tensile stress as a function of the applied strain along the zigzag (x) and armchair (y) directions of single-layer MoS_2. We show here that it is the in-plane atomic relaxation under the applied uniaxial tensile stress, rather than the errors in the execution of DFT calculation, that leads to the discrepancy. Furthermore, through new analysis, we show that our original conclusion that the tensile strength of single layer MoS_2 is dictated by out-of-plane soft-mode phonon instability under the biaxial tension and the uniaxial tension along the armchair direction, is still valid when the in-plane atomic relaxation is considered.

In order to identify the origin for the disagreement in the computed stress state under uniaxial tension of single layer MoS_2 between Cooper *et. al.* [1] and our recent work [2], we carried out further investigation on the uniaxial tension path along the zigzag and armchair directions. The results reported in our recent work [2] were obtained using Quantum Espresso (QE) package, and here we employed VASP [3–5] to crosscheck the results. The DFT calculations were carried out with the Perdew-Burke-Ernzerhof functional [6] and projector augmented wave method [7, 8]. The plane-wave cutoff was set to be 500 eV and a Monkhorst-Pack Kpoint of $15 \times 15 \times 1$ was used to sample the first Brillouin Zone (BZ). We also repeated the calculation of the uniaxial tension along the armchair direction using the QE code, with the parameters identical to those in our original work [2].

As shown in Fig. 1(a & b), the calculated true stress v.s. engineering strain curves along both zigzag (x) and armchair (y) directions based on VASP coincide with those obtained based on the QE code. This demonstrates that the DFT calculations were properly executed in our recent work [2]. To identify the origin of the discrepancy between Cooper *et. al.* and our work, we re-examine the algorithms used for searching the uniaxial stress state for a given tensile strain. We find that while in both studies the orthogonal stresses are relaxed to zero (within a certain numeric tolerance), our previous calculations [2] fixed the Mo and S atoms fractionally with respect to the two in-plane basis vectors of the unit cell, thus leading to a homogeneous in-plane deformation. When atoms are allowed to relax in-plane, we are able to reproduce the results of Cooper *et. al.* [1], as shown in Fig. 1 (a & b).

While the in-plane relaxation of ions plays no role in the bi-axial tension due to the conservation of symmetry, it does affect the computed stresses and the relaxation of the

TABLE I. Comparison of the predicted ideal strengths σ_c, critical engineering strains ε_c, and failure mechanisms of single layer MoS_2 with and without in-plane atomic relaxation

Direction	σ_c (GPa)		ε_c		Failure mechanism	
	unrelaxed	relaxed	unrelaxed	relaxed	unrelaxed	relaxed
Zigzag (x)	24.7[a]	15.6	0.36[a]	0.18	Elastic instability	Elastic instability
Armchair (y)	25.1[a]	24	0.28[a]	0.256	Phonon instability	Phonon instability
Biaxial	23.8[a]	23.8	0.195[a]	0.195	Phonon instability	Phonon instability

[a] From ref. [2]

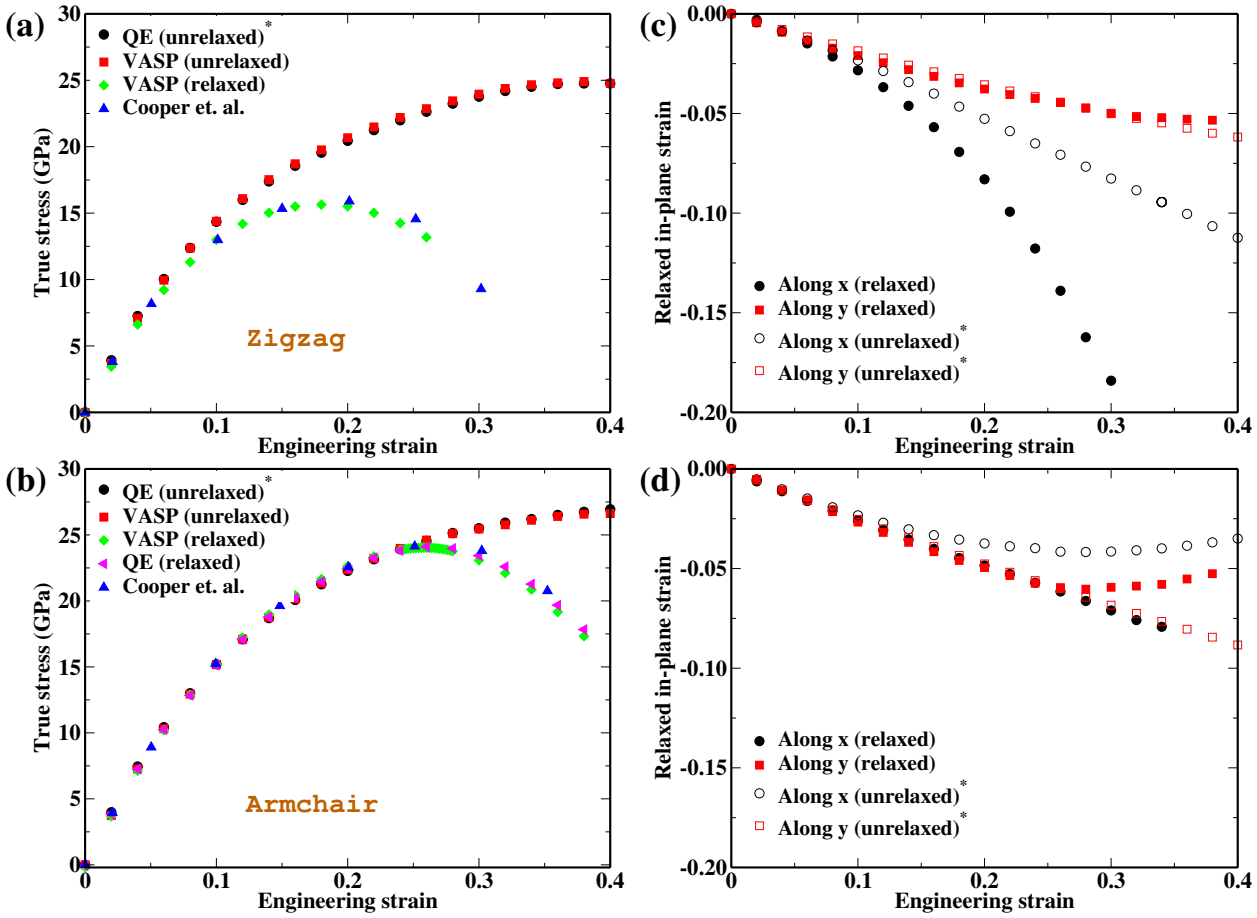

FIG. 1. The effect of in-plane atomic relaxation on the computed uniaxial true stress v.s. engineering strain curves along (a) x or zigzag and, (b) y or armchair directions. * indicates the data extracted from Ref. [2], which were obtained based on QE code and without involving in-plane atomic relaxation. Calculation using VASP (red square) reproduces the same result if atoms are unrelaxed in-plane. When atoms are relaxed laterally, the calculated stresses using VASP (green diamond) and using QE (magenta triangle, in (b)) coincide with those of Cooper *et al* (blue triangles) using QE. The in-plane atomic relaxation also affects (c) the relaxed in-plane strain and (d) the relaxed out-of-plane strain.

unit cell under the uniaxial tension. The maxima of the computed stress are consequently lowered along both uniaxial directions. The predicted ideal tensile strengths, defined as the stress under which the material becomes unstable either elastically or dynamically, are consequently lowered along these two directions. The changes are summarized in Table I. In addition, the variations of the relaxed in-plane and out-of-plane strains with respect to

the applied uniaxial strain are also affected, as shown in Fig. 1(c) and (d).

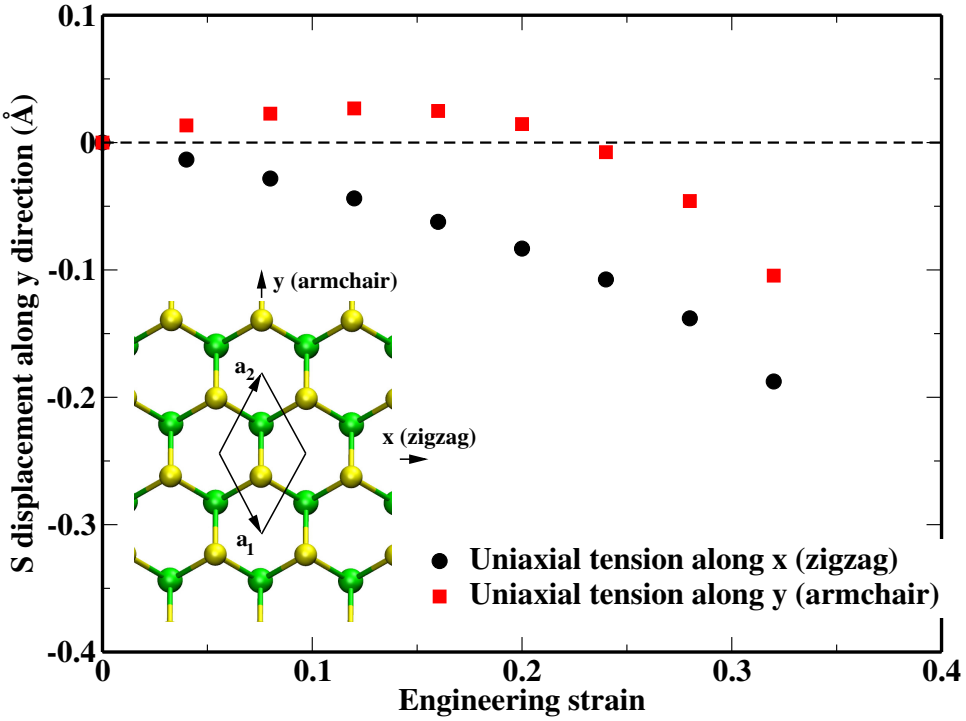

FIG. 2. The displacement of the S atoms along the armchair direction when the in-plane atomic relaxation is applied, with respect to that without the in-plane atomic relaxation. The atomic positions of Mo in the unit cell between the relaxed and the unrelaxed strain paths are matched for comparison. The unit cell of single layer MoS_2 with the two basis vectors $\vec{a}_1$ and $\vec{a}_2$ is shown in the inset. Mo and S atoms are marked by green and yellow, respectively. A negative displacement indicates that the two S atoms (shown as one because one S atom sits on top of the other) within the unit cell move further away from the Mo atom, resulting in a larger Mo-S distance along y, compared to that of the unrelaxed case.

While the in-plane atomic relaxation affects both uniaxial tension paths, Fig. 1 and Table I suggest that it leads to a more notable impact to the stress state under the zigzag uniaxial tension path than the armchair tension path. This can be understood from the displacement of the S atoms along the armchair direction when the in-plane atomic relaxation is applied, with respect to that in the homogeneous deformation. As shown in Fig. 2, while the in-plane internal relaxation only yields very small atomic displacement when the applied strain is below the critical strain ε_c under the armchair uniaxial tension, it results in a more prominent atomic displacement under the zigzag uniaxial tension. In particular, this

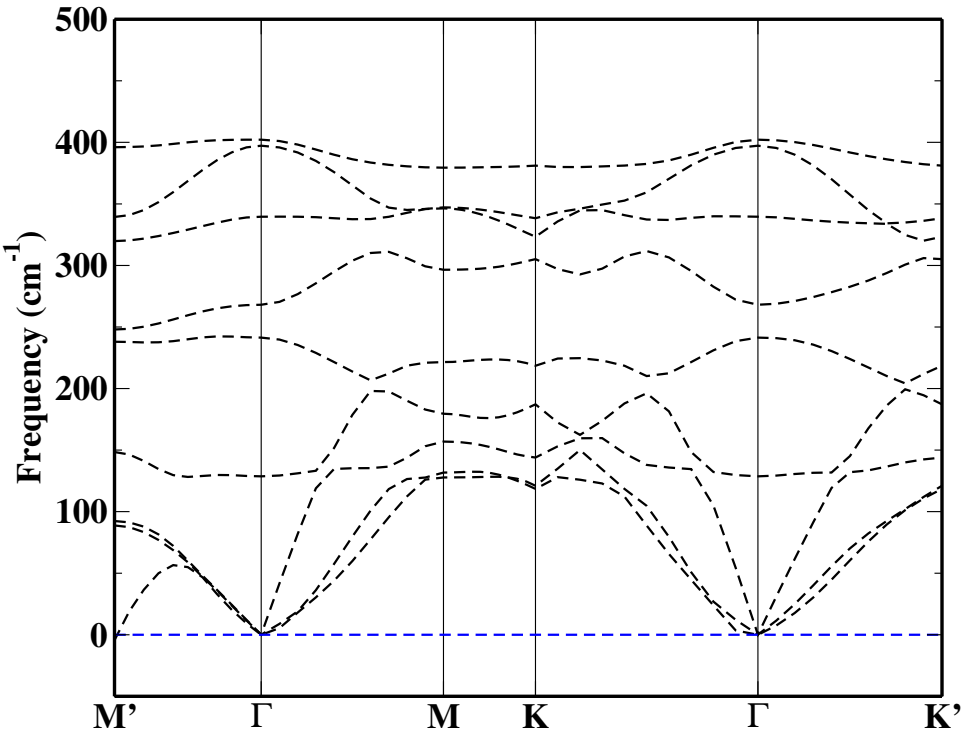

FIG. 3. Calculated phonon dispersion along $M' - \Gamma - M - K - \Gamma - K'$ for single layer MoS_2 under uniaxial tension along the armchair (y) direction at an engineering strain of $\varepsilon_{yy} = 0.256$. The convention of the symmetry points in the first Brillouin Zone is adopted from our previous work [2]. The unstable phonon mode at M' leads to an out-of-plane displacement, which is of the same nature as identified in our previous work [2].

internal relaxation produces a larger Mo-S distance along the armchair direction within the unit cell, thus making the zigzag Mo-S chain more flat than that in the homogeneous in-plane deformation. This is not surprising because the zigzag chains are expected to provide most of the resistance to the tensile load under the zigzag uniaxial tension.

To examine whether the in-plane atomic relaxation affects the identified failure mechanisms of the single layer MoS_2, we computed the phonon dispersion curves near the maximum stress for two uniaxial strain paths. The phonon dispersions were computed using Phonopy code [9] based on the supercell approach, with the force constants calculated by VASP through the Density Functional Perturbation Theory. A $6 \times 6 \times 1$ supercell with a k-point sampling of $5 \times 5 \times 1$ was used to calculate the force constants. As shown in Fig. 3, under the uniaxial tension along the armchair direction, an unstable phonon mode first appears near the boundary M' point of the first Brillouin Zone at $\varepsilon_{yy} = 0.256$, before the

maximum stress is reached at a strain of 0.26. Examination of the corresponding eigenvector of the phonon mode further shows that this unstable phonon bears the same nature, namely, vibration along the out-of-plane direction, as identified previously in the unrelaxed uniaxial tensile path along the armchair direction [2]. On the other hand, the search at the maximum tensile stress along the zigzag direction did not identify any unstable phonon modes, except near the BZ center, which indicates the elastic instability. Therefore it is concluded that the failure mechanisms for all the strain paths considered in our original work remain unchanged when the in-plane atomic relaxation is taken into account.

In conclusion, we identify the in-plane atomic relaxation as the root for the discrepancy between our previous work and Cooper *et. al.* on the reported uniaxial stress-strain curves along the zigzag and armchair directions of single layer MoS_2. While the inclusion of in-plane atomic relaxation does affect the computed maximum stress levels and the structural relaxation along the orthogonal directions, other behaviors reported in our work [2], particularly the main conclusion on the failure mechanisms upon uniaxial tension, remain unchanged.

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