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

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Li's paper [Phys. Rev. B **85**, 235407 (2012)] presents density functional theory (DFT) results of stress as a function of different strain states. The work of Cooper *et al.* [Phys. Rev. B **87**, 035423 (2013)] performs the same DFT calculations as part of an investigation into the nonlinear elastic properties of MoS_2. Some of the DFT results of Li are substantially different from our recently published paper, Cooper *et al.* [Phys. Rev. B **87**, 035423 (2013)]. Although both papers agree on states of equibiaxial stress, there is substantial disagreement on states of uniaxial tensile stress. In this Comment we show that our DFT computations are properly executed and consistent across three different DFT codes, including the one used by Li.

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Two recent papers by Li [1] and by Cooper *et al.* [2] investigate the mechanical properties of two-dimensional (2D) MoS_2 under conditions of finite strain based upon density functional theory (DFT) calculations. The predicted uniaxial stress at finite strains is different in the two papers. In particular, the uniaxial stress results in Fig. 2 of Li [1] do not agree with the uniaxial stress results in Fig. 5 of Cooper *et al.* [2]. Herein we show that the results of Cooper *et al.* [2] are correct. First, a brief introduction will be given to define precisely all quantities. Subsequently, we present results from three mainstream DFT packages, including the one used by Li [1]. We demonstrate that the results of Cooper *et al.* [2] are robust and that results from all three packages are consistent.

A uniaxial stress state is characterized by the application of stress in one direction while allowing the material to remain stress free in the other two principal directions. In a two-dimensional material, such as MoS_2, only two principal directions are considered, here assigned to be parallel to the zigzag direction (i.e., x_1 axis) and the armchair direction (i.e., x_2 axis). This same convention is used both in Fig. 1 of Li [1] and in Figs. 1 and 2 of Cooper *et al.* [2]. A state of uniaxial tensile stress for 2D MoS_2 in the x_1 direction is defined by stress tensor components $\sigma_{11} > 0$ and $\sigma_{22} = 0$ with corresponding strain tensor components of $\epsilon_{11} > 0$ and $\epsilon_{22} < 0$ given a positive Poisson ratio. The uniaxial tensile stress state in the x_2 direction is defined analogously. An equibiaxial stress state is defined as $\sigma_{11} = \sigma_{22}$ and $\epsilon_{11} = \epsilon_{22}$. The stress measure in a 2D material is defined as force normalized on a per unit length basis. Herein we express the stress as a derived three-dimensional (3D) quantity by normalizing the 2D stress by an effective thickness of the 2D material. We report stress as a 3D quantity to facilitate comparison with Li's [1] results. Thus, engineering stress is defined as $\sigma_{\text{eng}} = F/A_o$, where F is the current force and A_o is the reference cross-sectional area. The corresponding engineering strain is defined as $\epsilon_{\text{eng}} = (L - L_o)/L_o$, where L is the current length and L_o is the original length. True stress is defined as $\sigma_{\text{true}} = F/A$, where A is the current area and is typically plotted against true strain defined as $\epsilon_{\text{true}} = \log(L/L_o)$.

Li [1] uses the QUANTUM ESPRESSO DFT computational package to calculate two uniaxial stress states for 2D MoS_2 (in the zigzag and armchair directions) as well as the equibiaxial stress state, taking the MoS_2 thickness to be 0.6145 nm. The stress measure is erroneously reported to be engineering stress, but the results are in true stress [3], whereas the strain measure is engineering strain. Here we use three different DFT packages (Vienna *ab initio* simulation package (VASP [4–7], QUANTUM ESPRESSO [8], and ABINIT [9]) to calculate the mechanical response of 2D MoS_2 under the same stress states, taking the thickness to be 0.615 nm (the difference in stress arising from assuming a thickness which is 0.0005 nm greater is not perceptible on our plots).

The results of the DFT simulation are expected to be very similar, although there may be small discrepancies due to differences in the nature and degree of discretization of the Kohn-Sham equation (e.g., k points, plane-wave cutoff, etc.), treatment of the core electrons (i.e., psuedopotential choice), and convergence criteria. In this Comment, all three codes utilize the generalized gradient approximation of Perdew *et al.* [10,11] for the exchange-correlation functional.

Our VASP calculations employ the projector augmented-wave (PAW) method [12,13], and the plane-wave cutoff was chosen to be 420 eV, which was found to be converged. The charge self-consistency is terminated when changes in the total energy are less than 10^{-4} eV, and structural minimization is terminated when changes in the energy are less than 10^{-3} eV. A k-point grid of $15 \times 15 \times 2$ was used. When computing the x_1 direction uniaxial stress state the x_2 components of the two lattice vectors are varied until $|\sigma_{22}| \leqslant 0.01$ GPa. The x_2 direction uniaxial stress state is solved analogously. The unstrained unit cell in VASP is found to have dimensions $a_1 = a_2 = 3.183$ Å (unit cell shown in Fig. 1 of Li [1] and Fig. 2 of Cooper *et al.* [2]) with an out-of-plane sulfur ion height of 1.564 Å.

In both QUANTUM ESPRESSO and ABINIT, most aspects of the simulations were equivalent. Troiller-Martins pseudopotentials were used in both codes [14]. A plane-wave cutoff of 420 eV was used in ABINIT, whereas 1361 eV was used in QUANTUM ESPRESSO with both respective values giving converged solutions. The primitive unit cell is doubled to create orthogonal lattice vectors that coincide with principal stress directions to allow systematic variation in the lattice vectors to achieve $|\sigma_{22}| \leqslant 0.01$ GPa for uniaxial stress in

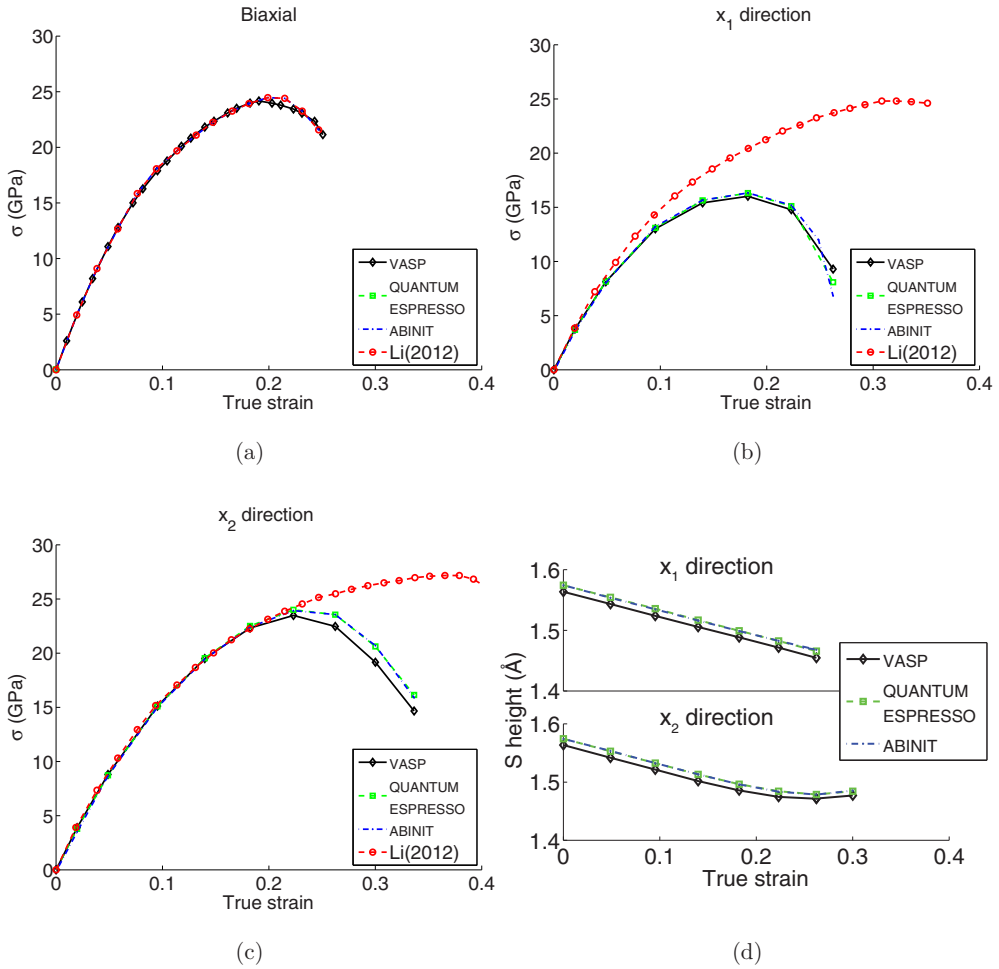

FIG. 1. (Color online) (a) is the biaxial stress state calculated with VASP, QUANTUM ESPRESSO, and ABINIT. (b) and (c) are the uniaxial stress states in the x_1 and x_2 directions, respectively, calculated with the same three DFT codes. The results of Li's [1] uniaxial stress DFT calculations—indicated by red ○'s—are shown for comparison. There is a qualitative and quantitative agreement between the calculations of Li [1] and the calculations of Cooper *et al.* [2] for a biaxial strain state in (a), but there is qualitative disagreement in the x_1 and x_2 directions as seen in (b) and (c). (d) shows the calculated sulfur height as a function of strain for the three DFT codes for the uniaxial stress in the x_1 and x_2 directions in the upper and lower axes, respectively.

the x_1 direction as required by the minimization algorithms within these codes. The biaxial stress state is achieved by applying equal strains in the x_1 and x_2 directions. A k-point grid of $10 \times 10 \times 1$ was used. In QUANTUM ESPRESSO, the self-consistency is terminated when changes in the total energy are less than 13.6×10^{-8} eV, and the structural minimization is terminated when the force is less than 2.571×10^{-2} $\frac{\text{eV}}{\text{Å}}$. In ABINIT, self-consistency was performed such that changes in the total energy are less than 27.2×10^{-7} eV and the structural minimization is terminated when both the force is less than 2.571×10^{-3} $\frac{\text{eV}}{\text{Å}}$ and the change in energy is less than 13.6×10^{-4} eV between structural change steps. In QUANTUM ESPRESSO, the unstrained unit cell is found to be $a_1 = 3.187$ and $a_2 = 5.521$ Å with an out-of-plane sulfur ion height of 1.574 Å. The ABINIT unstrained unit cell is determined to be $a_1 = 3.185$ and $a_2 = 5.517$ Å with an out-of-plane sulfur ion height of 1.574 Å.

Our results from the three DFT packages are compared in Fig. 1. In general, our results are within sufficient agreement. ABINIT and QUANTUM ESPRESSO use the same type of pseudopotential and are therefore nearly indistinguishable in most calculations. Our VASP calculations result in a slightly smaller sulfur height as seen in Fig. 1(d). All codes converge to the same stress until the point of elastic instability as seen in Figs. 1(a)–1(c). The only appreciable difference is an ≈5% difference developing in our VASP results relative to ABINIT/QUANTUM ESPRESSO in the x_2 direction for strains >20%. We presume that this difference can be attributed to the differences in the PAW approach versus the Trouiller-Martins pseudopotential as substantial checks were performed on a k-point plane-wave cutoff and convergence criteria in this region. To summarize, there are no major differences among our calculations with the three different DFT codes.

The uniaxial stress states calculated by Li [1] are not consistent with that of Cooper *et al.* [2]. Li uses the QUANTUM ESPRESSO code with the generalized gradient approximation of Perdew*et al.* [10,11] along with Trouiller-Martins pseudopotentials [1] and a plane-wave cutoff of 100 Ry (i.e., 1360.57 eV). Therefore, there should not be any substantial deviation. Figures 1(a)–1(c) show the direct comparison of

the two calculations. The biaxial stress calculations shown in Fig. 1(a) agree both qualitatively and quantitatively, but there is a qualitative disagreement between the two sets of calculations for the x_1 and x_2 directions as seen in Figs. 1(b) and 1(c) uniaxial stress calculations. We have verified our calculations across three DFT packages and conclude that there is a discrepancy in the paper of Li [1].

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