Two-dimensional MoS$_2$ electromechanical actuators

Nguyen T Hung©, Ahmad R T Nugraha and Riichiro Saito

Department of Physics, Tohoku University, Sendai 980-8578, Japan

E-mail: nguyen@flex.phys.tohoku.ac.jp

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Abstract

We investigate the electromechanical properties of two-dimensional MoS$_2$ monolayers with 1H, 1T, and 1T$'$ structures as a function of charge doping by using density functional theory. We find isotropic elastic moduli in the 1H and 1T structures, while the 1T$'$ structure exhibits an anisotropic elastic modulus. Moreover, the 1T structure is shown to have a negative Poisson’s ratio, while Poisson’s ratios of the 1H and 1T$'$ are positive. By charge doping, the monolayer MoS$_2$ shows a reversible strain and work density per cycle ranging from $-0.68\%$ to $2.67\%$ and from $4.4$ to $36.9$ MJ m$^{-3}$, respectively, making them suitable for applications in electromechanical actuators. We also examine the stress generated in the MoS$_2$ monolayers and we find that 1T and 1T$'$ MoS$_2$ monolayers have relatively better performance than 1H MoS$_2$ monolayer. We argue that such excellent electromechanical performance originate from the electrical conductivity of the metallic 1T and semimetallic 1T$'$ structures and also from their high Young’s modulus of about 150–200 GPa.

Keywords: electromechanical actuators, two-dimensional MoS$_2$, density functional theory, negative Poisson’s ratio

(Some figures may appear in colour only in the online journal)

1. Introduction

Natural muscle is an example of good-performance actuator with work cycles involving contractions of more than 20%, although the stress generation ability of natural muscle is quite low (0.35 MPa) [1] compared with mechanical machine. Various actuation materials have been studied to replace natural muscle that can directly convert electrical energy into mechanical energy, with wide potential applications in soft robotics, adaptive wings for aircraft, and biometric machines [1]. Some well-known actuation materials, such as carbon nanotubes (CNTs) [2, 3] and graphene [4, 5], were shown to generate larger stress than natural muscle and also larger strain ($\sim1\%$) than ferroelectric materials (0.1–0.2%) due to their high Young’s moduli of about 1 TPa [6, 7]. Recently, Weissmuller et al [8, 9] showed that Au–Pt alloys with a network of nanometer-sized pores are good candidates for the actuation materials because their linear strain reaches $\sim1.3\%$ and work density per cycle is up to 6 MJ m$^{-3}$, which is a performance indicator of the muscle. However, the use of CNTs, graphene, and Au–Pt nanoporous metal as the electromechanical actuator materials are still limited mainly because such actuator materials are expensive and difficult to be synthesized, which also make the development of artificial muscle quite stagnant.

Very recently, Acerce et al [10] obtained a significant performance in the electromechanical actuation of two-dimensional metallic molybdenum disulfide (MoS$_2$) nanosheet. The MoS$_2$ nanosheet is able to generate mechanical stresses of about 17 MPa and strains of about 0.8%, which leads to the work density for freely actuated MoS$_2$ films of about 81 kJ m$^{-3}$. The MoS$_2$ nanosheet actuator is also able to lift more than 150 times its own weight at low voltages $\pm 0.3$ V for hundreds of cycles. High actuation performance of the 1T MoS$_2$ nanosheet originates from the high electrical conductivity of the metallic 1T structure and their elastic modulus of 2.5 GPa. However, such a study is limited to the 1T MoS$_2$ nanosheet (or the multilayer MoS$_2$), while it is known that MoS$_2$ monolayers could have at least three different stable forms (1H, 1T, and 1T$'$ phases) that have been synthesized so far with higher
electrical conductivity and larger surface area than the MoS₂ nanosheet [11–15]. Furthermore, the condition of charge doping that can possibly support for high actuation performance of the monolayer MoS₂ layers is still unclear, both experimentally and theoretically.

With the above backgrounds, it is highly desirable to explore the strain, stress, work density and electronic structure of two-dimensional MoS₂ under the charge doping to understand the best conditions or the best structures for an electromechanical actuator. In this work, by first-principles calculations, we will focus our attention on the electromechanical actuator performance of the 1H, 1T, and 1T’ MoS₂ monolayers as a function of charge doping for both electron and hole doping. As the main highlight of this paper, our calculated results reveal that the 1T and 1T’ MoS₂ monolayers have relatively better performance and a better actuator response than the 1H MoS₂ monolayer. In addition, depending on the structure, we can have either isotropic or anisotropic actuation properties in the MoS₂ monolayers.

2. Method
2.1. Calculation details

In figure 1, we show the 1H, 1T, and 1T’ structures of the monolayer MoS₂. The 1H MoS₂ structure is based on trigonal lattice, where the S atoms are located in a hexagonal close-packed structure while the Mo atoms are sandwiched between two atomic layers of S atoms in a trigonal prismatic geometry. In the cases of 1T MoS₂ and 1T’ MoS₂, the Mo atoms are octahedrally ordered and disordered, respectively, surrounded by the S atoms. The primitive unit cells of the 1H and 1T MoS₂ are hexagonal with the optimized lattice parameters of 3.19 Å and 3.18 Å, respectively, while the unit cell of the 1T’ MoS₂ is rectangular with the optimized lattice parameters \(a = 5.72\, \text{Å}\) and \(b = 3.16\, \text{Å}\) as shown in figure 1. These lattice parameters are consistent with previous theoretical results [16, 17]. Since periodic boundary condition is applied in all models, a vacuum space of 30 Å in the direction perpendicular to the monolayer (z direction) is used in order to avoid virtual interactions between layers.

We perform first-principles calculations to determine the total energy and the electronic structure of monolayer MoS₂ using the Quantum ESPRESSO package [18]. We use pseudopotentials from the Standard Solid-State Pseudopotentials library (accuracy version) [19]. The exchange-correlation energy is evaluated by the general-gradient approximation using the Perdew–Burke–Ernzerhof functional [20]. An energy cut-off of 60 Ry is chosen for the expansion of the plane waves, which is sufficient to obtain convergence of total energy. In our simulation, the k-point grids in the Brillouin zone are employed according to the Monkhorst–Pack scheme [21], where \(k\) is the electron wave vector. We use \(16 \times 16 \times 1, 16 \times 16 \times 1, \) and \(8 \times 16 \times 1\) k-points for the 1H, 1T and 1T’ MoS₂, respectively. To obtain optimized atomic configurations of MoS₂ monolayers, the atomic positions and cell vectors are fully relaxed using the Broyden–Fletcher–Goldfarb–Shanno minimization method [22–25] until all the Hellmann–Feynman forces and all components of the stress are less than \(5 \times 10^{-4}\) Ry a.u.⁻¹ and \(5 \times 10^{-2}\) GPa, respectively.

To discuss the electromechanical actuation of the MoS₂ monolayers, the geometry optimization is then performed for each charge doping from –0.1 to +0.1 electron per atom (e/atom), in which the electron (hole) doping is simulated by adding (removing) electrons to the unit cell with the same amount of uniformly positive (negative) charge in the background so as to keep the charge neutrality.

2.2. In-plane mechanical moduli

In order to obtain mechanical moduli of MoS₂ monolayers, we firstly calculate elastic constants \(C_{ij}\), which are derived from the finite difference approach by using the Thermo-pw code [26]. From the point of view of elasticity theory, it is known that the values of \(C_{ij}\) are related to the equivalent volume of the unit cell. Because a vacuum space is left along the z direction in the unit cell, the calculated \(C_{ij}\) must be rescaled by \(h/d_0\), where \(h\) is the length of the cell along the z axis and \(d_0\) is the effective layer thickness of the monolayer MoS₂. In the present study, we set \(d_0 = 6.145\, \text{Å}\), i.e. one half of the out-of-plane lattice constant of bulk MoS₂ [27]. The angular dependence of the in-plane (xy-plane) Young’s modulus \(Y(\theta)\) and Poisson’s ratio \(\nu(\theta)\) are then expressed as [28]

\[
Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}a^4 + C_{22}b^4 - 2C_{12} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}}} \alpha^2 \beta^2, \tag{1}
\]

and

\[
\nu(\theta) = \frac{C_{12}(\alpha^4 + \beta^4) - (C_{11} + C_{22} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}}) \alpha^2 \beta^2}{C_{11}a^4 + C_{22}b^4 - 2C_{12} - \frac{C_{11}C_{22} - C_{12}^2}{C_{66}}} \alpha^2 \beta^2, \tag{2}
\]

where \(\theta\) is the angle relative to the x direction, \(\alpha = \sin \theta, \beta = \cos \theta,\) and \(C_{ij}\) are the elastic constants obtained from the first-principles calculations. Since monolayer MoS₂ is a two-dimensional structure, there are four independent elastic constants \(C_{11}, C_{22}, C_{12},\) and \(C_{66}\).

2.3. Work-per-cycle analysis

As an important performance indicator for actuation, we adopt the work density per cycle \(W\) of an actuator for discussion of the monolayer MoS₂. We assume that the actuator is a linear elastic solid and the general condition to be considered is illustrated in figure 2. There are three states when the actuator is loaded by a constant tensile force: (1) the material is at zero charge doping \(q = 0\) with an initial length \(L_0\), (2) applying a charge doping \(q \neq 0\) produces a length change \(L_A\) due to the electromechanical actuation process, and (3) applying a force \(F \neq 0\) produces a deformation \(L_B\). According to Hooke’s law, which is generally true at small strains, \(L_A\) and \(L_B\) are given by

\[
L_A = cL_0, \quad L_B = \frac{FL_0}{AY}, \tag{3}
\]
where \( \epsilon \), \( Y \), and \( A \) are, respectively, the strain, Young’s modulus, and cross-sectional area of monolayer MoS\(_2\) after the charge doping has been applied. The work density per cycle that includes steps (1)–(3) as shown in figure 2 is given by [29]

\[
W = \frac{F(L_A - L_B)}{V},
\]  

where \( V = L_0 A \) is the volume. By substituting \( L_A \) and \( L_B \) in equations (3) into (4), \( W \) can be written as

\[
W = \frac{F \epsilon A}{A} - \frac{F^2}{2YA}.
\]  

We can determine the maximum \( W \) from equation (5) by solving \( \frac{dW}{dF} = 0 \). The formula for the maximum work density per cycle is given by

\[
W_{max} = \frac{1}{4} Y \epsilon^2,
\]  

when \( F_{max} = \frac{1}{4} Y \epsilon A \). However, in most of experiments, the work density is often expressed in terms of stored energy density \( W_s \) because it can be compared directly to skeletal muscle and other actuator systems \([9, 30]\). Here, \( W_s \) is defined as the strain energy per unit volume and could be obtained from the linear relation between stress \( \sigma \) and strain \( \epsilon \), i.e. \( \sigma = Y \epsilon \), which then gives the formula of the stored energy density,

\[
W_s = \frac{1}{2} Y \epsilon^2 = 2W_{max}.
\]  

Equation (7) will be used to compare our theoretical results with recent experimental data of MoS\(_2\) electromechanical actuators \([10]\).

3. Results

3.1. Mechanical properties

To discuss the actuator response of the monolayer MoS\(_2\), we firstly check the mechanical moduli at the neutral condition and at the charge doping cases. In figure 3(a), we show the dependences of \( Y \) and \( \nu \) on the direction of monolayer MoS\(_2\) at the neutral condition, i.e. \( q = 0 \). The shape of \( Y \) and \( \nu \) in the polar plot indicates not only the elastic isotropy in the 1H and 1T MoS\(_2\) monolayers, but also the elastic anisotropy in the 1T’ MoS\(_2\) monolayer. The anisotropy of elastic moduli in the 1T’ MoS\(_2\) monolayer originates from the fact that the low-symmetry 1T’ structure is a distorted one from the high-symmetry 1T structure. For comparison, the values of \( C_{ij} \), \( Y \), and \( \nu \) of the 1H, 1T and 1T’ MoS\(_2\) structures are listed in table 1. We can see that \( Y \) is found to be 199 GPa for the 1H MoS\(_2\), which is in good agreement with a previous theoretical result \((Y = 200\,\text{GPa})\) \([13]\). Bertolazzi et al \([14]\) obtained an effective \( Y \) of 270 \( \pm \) 100 GPa for the monolayer MoS\(_2\), while Castellanos-Gomez et al \([15]\) obtained an average \( Y \) of 210–370 GPa for multilayer MoS\(_2\) consisting of 5 to 25 layers. Note that both experiments \([14, 15]\) using an atomic force microscope tip applied on the monolayer or multilayer MoS\(_2\) suspended on the substrate containing an array of circular holes are under biaxial tensile stress. Therefore, the experimental results of biaxial elastic modulus are higher than the theoretical results of uniaxial elastic modulus in this
For all charge doping.

Other 2D materials such as in black phosphorus (\(\nu = -0.267\)) [33]. We expect that exploring 2D materials with a negative Poisson’s ratio could have useful applications, for example, as vanes for aircraft gas turbine engines, sponges, and fasteners [34].

In figure 3(b), we show \(Y\) and \(\nu\) of the monolayer MoS\(_2\) as a function of charge doping, i.e. \(q \neq 0\). For the electron doping (\(q < 0\)), \(Y\) of the 1H and 1T structures is decreased, while \(Y\) of the 1T’ structure is increased. For the hole doping (\(q > 0\) e/atom), \(Y\) of 1T structure is increased, while \(Y\) of the 1H and 1T’ structures decreased. Since the 1H and 1T structures have isotropic Young’s modulus (\(Y_{xx} = Y_{yy}\)), the curve of \(Y_{yy}\) is overlapped by that of \(Y_{xx}\). The maximum \(Y\) of monolayer MoS\(_2\) of about 200 GPa is smaller than that of carbon-based structures (400–1000 GPa) [3, 35], but is comparable to that of stainless steel (192 GPa) [36]. The high \(Y\) values of monolayer MoS\(_2\) are important for artificial muscle applications since it could generate large force per unit area. Moreover, a significant change of \(\nu\) is found in the 1T’ structure from 0.03 to 0.23, as shown in figure 3(b). For the 1H and 1T structures, \(\nu\) increases with increasing \(|q|\) for both electron and hole doping. It should be noted that Poisson’s ratio of the 1T structure becomes positive at \(q = -0.08\) e/atom and at \(q = 0.06\) e/atom for the electron and hole doping, respectively.

### 3.2. Actuator response

In order to study the variation of the structural deformation as a function of charge doping, we define the in-plane strain as

\[
\epsilon_{xx} = \Delta a / a_0, \quad \epsilon_{yy} = \Delta b / b_0, \tag{8}
\]

where \(a_0\) and \(b_0\) are, respectively, the length of the unit cell in the \(x\) and \(y\) directions at geometry optimization for neutral case, and \(\Delta a\) and \(\Delta b\) are the increment (or decrement) of \(a_0\) and \(b_0\), respectively, after the charge doping has been applied. In figure 4, we show the strain for each monolayer MoS\(_2\) as a function of charge doping \(q\) ranging from \(-0.1\) to 0.1 e/atom.

![Figure 4. Strain as function of charge doping per atom of monolayer MoS\(_2\).](image)

present study. We obtained the Young modulus \(Y = 167\) GPa for the 1T MoS\(_2\), while \(Y_{xx} = 189\) GPa and \(Y_{yy} = 150\) GPa for the 1T’ MoS\(_2\).

The values of Poisson’s ratio of the monolayer MoS\(_2\) are unique because the 1T structure exhibits a negative Poisson’s ratio of \(-0.02\), while Poisson’s ratios of the 1H (\(\nu = 0.20\)) and 1T’ MoS\(_2\) (\(\nu_{xx} = 0.18\) and \(\nu_{yy} = 0.14\)) are positive. When a compressive (tensile) strain is acted in one direction, materials tend to expand (contract) in the perpendicular direction, corresponding to the positive Poisson’s ratio for ordinary materials. The opposite is the situation for materials with negative Poisson’s ratio. We note that beside our study, there have been reports that Poisson’s ratio can be negative in other 2D materials such as in black phosphorus (\(\nu = -0.5\)) [31], single-layer graphene ribbons (\(\nu = -1.51\)) [32], and \(\delta\)-phosphorene (\(\nu = -0.267\)) [33].
and are approximately \( \epsilon \) and \( \epsilon \) respectively. We can also say that 1H and 1T MoS\(_2\) monolayers will show an isotropic compression with the maximum strains of 1.78% and 2.25%, respectively. In this present study, the strain magnitude of 0.68% of the 1T MoS\(_2\) by the hole doping is in a good agreement with the experimental data of about 0.15% and 0.68% at \( q = 0.04 \) e/atom and 0.06 e/atom, respectively, as shown in figure 4. On the contrary, the 1T MoS\(_2\) shows an anisotropic behaviour with the expansion strain (\( \epsilon_{xx} = 1.40\% \) at \( q = 0.1 \) e/atom) and the compression strain (\( \epsilon_{yy} = -0.55\% \) at \( q = 0.04 \) e/atom) along the \( x \) and \( y \) directions, respectively. In this present study, the strain magnitude of 0.68% of the 1T MoS\(_2\) by the hole doping is in a good agreement with the experimental data of about 0.6–0.8% [10], hence making them suitable for applications in electromechanical actuators. It should be noted that the work-per-cycle analysis given in section 2.3 is still valid for the hole doping case although the relationship between the strain and the stress becomes nonlinear, as shown in figure 4. The reason is that the relationship between the strain and the stress generated (or the force generated) within small strain (\( \epsilon < 3\% \)) is linear, which is important to justify validity of Hooke’s law.

3.3. Actuator performance

The performance of electromechanical actuators is characterized by the stress \( \sigma \) that is generated. In figure 5(a), we show the stress generated in monolayer MoS\(_2\) as a function of charge doping. In the neutral case, we obtain \( \sigma_{xx} = \sigma_{yy} = 0 \) because \( \epsilon_{xx} = \epsilon_{yy} = 0 \). For the electron doping at \( q = -0.1 \) e/atom, we obtain \( \sigma_{xx} = \sigma_{yy} = 2.72 \) GPa and 3.27 GPa for the 1H and 1T structures, respectively, while \( \sigma_{xx} = 2.06 \) GPa and \( \sigma_{yy} = 4.13 \) GPa for the 1T’ structure. For the hole doping, the maximum stress (\( \sigma_{xx} = \sigma_{yy} = -1.30 \) GPa) is found in the 1T structure at \( q = 0.06 \) e/atom. Our calculated \( \sigma \) ranging from –1.30 to 3.27 GPa for the 1T MoS\(_2\) monolayer is higher than the experimental value for the 1T MoS\(_2\) nanosheet (0.017 GPa) [10] due to its high Young’s modulus (see figure 3(b)) and it is comparable to the carbon nanotube actuators (~3 GPa) [3, 38]. Our results suggest that the electron doping should be good for the actuator application of MoS\(_2\) monolayers.

The performance of electromechanical actuators is characterized by the work density per cycle \( W \) of the monolayer MoS\(_2\) as a function of charge doping. For the 1T MoS\(_2\) monolayer, \( W \) is up to 36.9 MJ m\(^{-3}\) at \( q = -0.1 \) e/atom and 4.4 MJ m\(^{-3}\) at \( q = 0.06 \) e/atom for the electron and hole dopings, respectively, which is more than 100–1000 times that of skeleton muscle (~0.04 MJ m\(^{-3}\)) [1]. These results are much higher than the experimental values for the 1T MoS\(_2\) nanosheet (0.081 MJ m\(^{-3}\)) [10] since \( Y \) (145–193 GPa) of the monolayer MoS\(_2\) is larger than that of the MoS\(_2\) nanosheet (\( Y = 2.5 \pm 0.1 \) GPa) [10]. For the 1H and 1T’ structures, \( W \) at the electron doping case is higher than that of the hole doping case, which
suggest that the electron doping should be good to achieve high-performance electromechanical actuators.

3.4. Electronic properties

To understand the variation of the electronic properties of the monolayer MoS2 under charge doping, finally, we can examine the energy band structures of the monolayer MoS2 within the range of charge doping considered in the present work. In figures 6(a)–(c), we show, respectively, the calculated electronic structures of the 1H, 1T and 1T′ MoS2 along the high-symmetry points of their corresponding Brillouin zone for neutral and charge doping states. From figure 6(a), we can see that in the neutral case, the 1H MoS2 monolayer is an indirect-gap semiconductor (the top of valence band is at the Γ point while the bottom of conduction band is at the K point) with the band gap of about 1.59 eV. The electron (hole) doping does (does not) transform the 1H MoS2 monolayer to a direct-gap semiconductor. The direct (indirect) band-gap of 1H MoS2 monolayer in the case of electron (hole) doping is about 1.25 (1.35) eV. On the other hand, from figures 6(b) and (c), we find that basically in both cases of charge doping and neutral condition, the 1T MoS2 is a metal, while the 1T′ MoS2 is a semimetal, with an exception that the 1T′ MoS2 transforms to a metal by heavy electron doping. A common interesting feature we can see in figures 6(a)–(c) is that the electron doping ‘pull down’ many interlayer bands of the 1H, 1T and 1T′ MoS2, while hole doping do not. Such a phenomenon might contribute to the higher performance of MoS2 electromechanical actuators by the electron doping rather than the hole doping, as shown previously in figures 5(a) and (b).

4. Conclusions

We have performed a first principles theoretical study on the actuator performance and on the electronic structure as a function of charge doping for the 1H, 1T and 1T′ MoS2 monolayers. We find that the work density per cycle and stress generated in 1T and 1T′ MoS2 monolayers are relatively larger than those in 1H MoS2 monolayer. This excellent electromechanical performance originate from the electrical conductivity of the metallic 1T and semimetallic 1T′ structures and their high Young’s modulus of about 150–200 GPa under charge doping. The results obtained also reveal that the 1H and 1T MoS2 show the actuator isotropy, while 1T′ MoS2 shows the actuator anisotropy, which implies that researchers can have more freedom to choose the best MoS2 structures depending on the isotropic or anisotropic electromechanical applications.

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ORCID IDs

Nguyen T Hung @ https://orcid.org/0000-0003-4156-6230

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