Edge eigen-stress and eigen-displacement of armchair molybdenum disulfide nanoribbons

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ABSTRACT

Edge effects on mechanical properties of armchair molybdenum disulfide nanoribbons were investigated using first principles calculations. The edge eigen-stress model was applied to explain the relaxation process of forming molybdenum disulfide nanoribbon. Edge effects on surface atoms fluctuation degree were obtained from each fully relaxed nanoribbon with different width. Changes of the relaxed armchair molybdenum disulfide nanoribbons structure can be expressed using hexagonal perimeters pattern. Based on the thickness change, relaxed armchair molybdenum disulfide nanoribbons tensile/compression tests were simulated, providing intrinsic edge elastic parameters, such as eigen-stress, Young’s modulus and Poisson’s ratio.

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1. Introduction

Molybdenum disulfide (MoS2) belongs to two-dimensional (2D) transition metal dichalcogenides [1]. Single layer MoS2 is constructed by graphene-like hexagonal arrangement of Mo and S atoms stacked together to form S–Mo–S sandwiches. Recently, single layer MoS2 captured researchers’ interest due to its prominent mechanical [2–4], electronic [5], thermal [6], and optoelectronic [7] properties.

MoS2 nanoribbons (MoS2 NRs) are MoS2 strips with ultra-narrow width, obtained using electrochemical methods [8]. Based on their edge configuration, MoS2 NRs are classified as armchair MoS2 nanoribbons (AMoS2 NRs) and zigzag MoS2 nanoribbons (ZMoS2 NRs). For armchair graphene ribbons (AGNRs), unique mechanical properties were found where AGNRs exhibited three periodicities in the nominal Young’s modulus and Poisson’s ratio [25]. Considering their band gap [9], intrinsic carrier mobility [10] and binding energy [11], AMoS2 NRs exhibit oscillating width-dependent behavior. The authors wanted to figure out whether AMoS2 NRs exhibit three periodicities in the nominal Young’s modulus and Poisson’s ratio, and further investigate the reasons. The elastic modulus [10–12], edge energy density [13,14] and edge stress [13,15] have been obtained for MoS2 NRs considered as 2D structures, i.e., without taking into account the influence of MoS2 NRs thickness. However, the thickness of MoS2 NRs varies with the width change. Hence, it is important to accurately determine the edge properties by taking into consideration the thickness change. Intrinsic edge parameters effects on mechanical properties, surface atoms fluctuation degree, edge eigen-stress and Poisson’s ratio need to be investigated.

By taking the stress-free monolayer MoS2 sheet as a reference, an AMoS2 NR can be created from it. A newly formed AMoS2 NR, with the lattice constant of the stress-free monolayer MoS2 sheet, has substantially higher excess energy, and the free-edges (S–Mo–S sandwich structure) of the AMoS2 NR are formed with eigen-stress [16]. The newly formed AMoS2 NR relaxes unavoidably to reduce the excess energy and the edge eigen-stress. This relaxation causes initial deformation and relaxation-induced strain in the AMoS2 NR along the length and thickness directions.

In the present study, AMoS2 NRs were allowed to relax in two steps of normal relaxation and parallel relaxation, so that the change in the excess energy could be systematically studied. The surface atoms fluctuation degree was obtained from the changes of atomic positions at two layers of sulfur atoms. Perimeters of each hexagon ring in the relaxed AMoS2 NRs are given to investigate the structure change. The nominal Young’s modulus and Poisson’s ratio were determined by performing tensile/compressive tests on the relaxed AMoS2 NRs to extract the edge eigen-stress, edge Young’s modulus and Poisson’s ratio.

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The dimensions changes to \( L^{\text{ini}} \times W^{\text{ini}} \times T^{\text{ini}} \) with \( L^{\text{ini}} = L_0 + \Delta L, W^{\text{ini}} = W_0 + 2p_0 + \Delta W \) and \( T^{\text{ini}} = T_0 + \Delta T \), where \( p_0 \) is the edge eigen-displacement [22] and the change of width \( \Delta W \) and thickness \( \Delta T \) are caused by the Poisson’s ratio effect. Relaxation causes initial deformation, and the relaxation-induced strain along the AMoS2 NRs length and thickness directions are called the initial strain. The initial strain along the length and thickness directions is calculated as \( \varepsilon^{\text{ini}}_l = (L^{\text{ini}} - L_0) / L_0 \) and \( \varepsilon^{\text{ini}}_t = (T^{\text{ini}} - T_0) / T_0 \).

In equilibrium, zero total force along the length direction must be satisfied along any lateral section perpendicular to the length, and the traction-free boundary conditions must be met along the AMoS2 NR edges. The initial edge stress and core stress after parallel relaxation were calculated as \( \sigma^{\text{ini}}_e = \sigma^{\text{ini}}_0 + Y_c \varepsilon^{\text{ini}}_l \) and \( \sigma^{\text{ini}}_c = Y_c \varepsilon^{\text{ini}}_t \), respectively. The self-balanced force requires

\[
2F^{\text{ini}}_e + T^{\text{ini}}_c = 0
\]

where \( F^{\text{ini}}_e = T^{\text{ini}}(\sigma^{\text{ini}}_0 + Y_c \varepsilon^{\text{ini}}_l) \) and \( T^{\text{ini}}_c = W^{\text{ini}}T^{\text{ini}}(Y_c \varepsilon^{\text{ini}}_t) \) denote the edge force and the core force, which includes the surface force of the two surfaces (S atomic layer) and the core force (Mo atomic layer) per unit length, respectively.

4. Results and discussion

Fig. 2(b) shows that the initial strain along the length direction increases as the width increases, whereas the initial strain along the thickness direction decreases with the width. As the dimensions change, the structures also change.

The edge effect on surface atoms fluctuation degree \( R_0 \) of each fully relaxed AMoS2 NR with different width was proposed to reflect the fluctuations of atomic layers at zero temperature. It was calculated using

\[
R_0 = \frac{1}{n_s} \sum_{i=1}^{n_s} |zk^{\text{ini}}_{\text{top}} - z^{\text{ini}}_{\text{top}}| + |zk^{\text{ini}}_{\text{bottom}} - z^{\text{ini}}_{\text{bottom}}|
\]

where \( n_s \) is the total number of sulfur atoms in AMoS2 NRs, \( z^{\text{ini}}_{\text{top}} \) and \( z^{\text{ini}}_{\text{bottom}} \) denote the sulfur atomic coordinate value along the thickness direction of the AMoS2 NR's top-layer, AMoS2 NR's bottom-layer, sheet's top-layer, and sheet's bottom-layer, respectively. Fig. 2(a) shows that the AMoS2 NR surface atoms fluctuation degree increases as the width decreases. In this case, the change of thickness \( \Delta T \) is determined by \( \Delta T = \varepsilon^{\text{ini}}_t = \Delta L / T_0 \) in consideration of the uneven surface, where \( \varepsilon^{\text{ini}}_t \) and \( \varepsilon^{\text{ini}}_l \) denote the arithmetic mean distance between the top layer and the bottom layer in AMoS2 NRs and stress-free MoS2 parent sheet, respectively.

The latest study [25] shows that the armchair graphene nanoribbons (AG NRs) with similar honeycomb-like structure to AMoS2 NRs exhibit three periodicities in the nominal Young’s modulus and Poisson’s ratio. Investigations of the Young’s modulus and Poisson’s ratio of AMoS2 NRs are reported later in the paper. The phenomenon of the width-dependent elastic properties and perimeter patterns with a periodicity of three depends on the nature of the edge, which can be explained by the Clar sextets [26]. The Clar sextets defined as six \( \pi \)-electrons localized in a single hexagons ring separated from adjacent rings by C–C single bonds. Corresponding relationships were found between the hexagon perimeters pattern and the Clar sextets in AG NRs [28]. Without the Clar sextets, AMoS2 NRs exhibit different hexagon perimeters pattern. Fig. 3 shows the hexagon “perimeters” (six sides are not in the same plane) of each relaxed AMoS2 NRs with width \( N_w \) ranging from 8 to 15. In contrast to the AG NRs, the perimeter patterns of the AMoS2 NRs show different variation rules. For the AMoS2 NRs with \( 3n + 1 \) and \( 3n - 1 \) width, no obvious arrangement rule was observed. According to the structural symmetry, AMoS2 NRs were classified by central \( (N_w = 2k) \) and mirror \( (N_w = 2k + 1) \) symmetry. As the width increases, the value of the hexagonal perimeter approaches the infinite MoS2 sheet value.
The infinite MoS2 sheets and MoS2 NRs are usually treated as a 2D structure to extract their mechanical parameters [3]. However, Fig. 2(b) indicated that around 0.03–0.05% tensile strain forms in the thickness direction of the AMoS2 NRs during relaxation and deformation, and changes with the width. Hence, AMoS2 NR is treated as a composite of a geometrical 3D core and two 2D edges to extract its energy change during relaxation, and its mechanical parameters, such as eigen-stress, Young’s modulus and Poisson’s ratio.

The energy of an AMoS2 NR without relaxation is calculated from $E^{\text{ini}} = E_0 + E^{\text{exc}}_{\text{ini}}$, where $E_0$ and $E^{\text{exc}}_{\text{ini}}$ represent the reference energy of the stress-free monolayer MoS2 sheet and the unrelaxed excess energy, respectively. $E^{\text{exc}}_{\text{ini}}$ includes two parts: chemical energy formed due to broken chemical bonds of the edge atoms during the formation of the two nanoribbon edges, and the strain energy of the thickness formed due to transformation from the edge atoms. Thus, the unrelaxed edge energy density is given by $E^{\text{exc}}_{\text{ini}} = E^{\text{exc}}_{\text{ini}}/2L_0 T_0$, where $T_0$ denotes the thickness of the AMoS2 NRs, which changes with the AMoS2 NRs width. After normal relaxation, the potential energy decreases from $E^{\text{unr}}$ to $E \doteq E_0 + E^{\text{exc}}_{\text{ini}}$, where $E^{\text{exc}}_{\text{ini}}$ denotes the excess energy after normal relaxation, and the edge energy density decreases to $\rho \doteq E^{\text{exc}}_{\text{ini}}/2L_0 T_0$. Parallel relaxation further reduces potential energy to $E^{\text{ini}} = E_0 + E^{\text{exc}}_{\text{ini}}$, where $E^{\text{exc}}_{\text{ini}}$ denotes the total excess energy relative to the stress-free monolayer MoS2 sheet. Due to the initial deformation, the total excess energy $E^{\text{exc}}_{\text{ini}}$ contains two parts: the core strain energy $E^{\text{ini}}_{\text{exc}(c)}$, which is equivalent to the strain energy of the sheet counterpart by the relaxation-induced initial deformation and the excess energy attributed to the edge $E^{\text{ini}}_{\text{exc}(e)}$. The core strain energy $E^{\text{ini}}_{\text{exc}(c)}$ is determined as $E^{\text{ini}}_{\text{exc}(c)} = (L^{\text{ini}} W^{\text{ini}} A^{\text{ini}}) Y_L s^{\text{ini}}_L^2$, where $s^{\text{ini}}_L$ denotes the initial strain of the cores along the length and $Y_L$ denotes the 3D bulk Young’s modulus. Hence, the edge energy density $\rho^{\text{ini}}_{(e+c)}$ is calculated from $\rho^{\text{ini}}_{(e+c)} = E^{\text{ini}}_{\text{exc}(e+c)}/(2L^{\text{ini}} T^{\text{ini}})$ and the edge energy density $\rho^{\text{ini}}_{e}$ can be obtained as $\rho^{\text{ini}}_{e} = E^{\text{ini}}_{\text{exc}(e)}/(2L^{\text{ini}} T^{\text{ini}})$. This indicates that under the fully relaxed state in Fig. 2(c), the edge energy density is almost constant when the width index $N > 8$, and slightly lower than the excess energy density. If the AMoS2 NR is treated as a 2D structure, the corresponding edge energy density above can be defined as $\gamma^{\text{ext}} = E^{\text{ext}}_{\text{ini}}/2L_0$, $\gamma^{\perp} = E^{\perp}_{\text{ini}}/2L_0$, $\gamma^{\text{ini}}_{(e+c)} = E^{\text{ini}}_{\text{exc}(e+c)}/2L^{\text{ini}} T^{\text{ini}}$, and $\gamma^{\text{ini}}_{e} = E^{\text{ini}}_{\text{exc}(e)}/2L^{\text{ini}} T^{\text{ini}}$, respectively. This indicates in Fig. 2(d) that $\gamma^{\text{ext}}$ and $\gamma^{\perp}$ increase and $\gamma^{\text{ini}}_{(e+c)}$ decreases with the thickness if the change of the AMoS2 NR thickness during relaxation and deformation is not taken into account. The 2D edge energy density $\gamma^{\text{ini}}_{e}$ is almost constant with the increase of the AMoS2 NRs width.

The simulated uniaxial compression/tensile tests were conducted on the relaxed AMoS2 NRs and monolayer MoS2 sheet. A range of 0% to 1% (−1%) uniaxial strain was implemented to adjust the periodic length $L$ with an increment (or decrement).

Fig. 2. (a) The surface atoms fluctuation degree; (b) the initial strain; (c) 3D and (d) 2D edge energy densities of AMoS2 NRs as functions of the width index.

Fig. 3. Hexagon perimeters of each of AMoS2 NRs with width $N$ ranging from 8 to 15.
Table 1
Core and edge Young’s modulus, width and thickness directional Poisson’s ratio, and eigen-stress of AMoS2 NRs.

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio (width)</th>
<th>Poisson’s ratio (thickness)</th>
<th>Eigen-stress (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>3D: 187.29</td>
<td>0.25</td>
<td>0.11</td>
<td>−0.32</td>
</tr>
<tr>
<td></td>
<td>2D: 121.74</td>
<td>0.25</td>
<td>0.75</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Core: −29.61</td>
<td>Edge: −19.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Diagram](image)

Fig. 4. (a) The uniaxial Young’s modulus and (b) Poisson’s ratio of the AMoS2 NRs versus width.

Table 1 shows the 3D and 2D nominal Young’s modulus values of AMoS2 NRs. The Young’s modulus of AMoS2 NRs exhibits width-dependent behavior, i.e., larger width corresponds to higher nominal Young’s modulus. The nominal uniaxial Young’s modulus is expressed as

\[
Y^*_{3D} = Y^*_{3D} + \frac{2Y^*_{3D}}{W}
\]

(2)

\[
Y^*_{2D} = Y^*_{2D} + \frac{2Y^*_{2D}}{W}
\]

(3)

Both the 3D and 2D edge Young’s moduli were calculated by fitting the nominal Young’s modulus to the width of the AMoS2 NRs, and the value of the core Young’s modulus is equal to that of the MoS2 sheet, as listed in Table 1. The negative edge Young’s modulus suggests that the nominal uniaxial Young’s modulus is lower than the core Young’s modulus.

When uniaxial strain \( \varepsilon^*_{3D} \) is applied along the length direction, there is a strain \( \varepsilon^*_{W} \) along the width direction and \( \varepsilon^*_{T} \) along the thickness direction. The perpendicular strains \( \varepsilon^*_{W} \) and \( \varepsilon^*_{T} \) were available in the simulations, enabling the determination of the width direction nominal Poisson’s ratio \( v^*_{W} = -\varepsilon^*_{W}/\varepsilon^*_{T} \) and the thickness direction nominal Poisson’s ratio \( v^*_{T} = -\varepsilon^*_{T}/\varepsilon^*_{W} \), for each AMoS2 NR. Fig. 4(b) shows both the width and thickness directions nominal Poisson’s ratio versus the width, indicating that the width direction nominal Poisson’s ratio decreased as the width increased, and the thickness direction nominal Poisson’s ratio increased as the width increased. Following the edge eigen-displacement model [24] the nominal Poisson’s ratios were expressed as

\[
v^*_{W} = v^c_{W} + \frac{2v^c_{W}}{W}
\]

(4)

\[
v^*_{T} = v^c_{T} + \frac{2v^c_{T}}{W}
\]

(5)

where \( v^c_{W} \), \( v^c_{T} \), and \( v^c_{W} \) are the core, width edge and thickness edge Poisson’s ratios, respectively. The edge Poisson’s ratios, which represent the excess Poisson’s ratio induced by the presence of an edge, are listed in Table 1. The positive value for the width direction Poisson’s ratio suggests that the nominal Poisson’s ratio decreased as the width increased and was larger than the monolayer sheet width direction Poisson’s ratio. The negative value for the thickness direction Poisson’s ratio suggests that the nominal Poisson’s ratio increased with the width and was smaller than the monolayer sheet thickness direction Poisson’s ratio. Periodically modulated width-dependent Young’s modulus and Poisson’s ratio of AMoS2 NRs were not observed. The results show that the phenomenon of the width-dependent elastic properties with periodicity of three depends on the nature of the edge, which is not mainly caused by the unique honeycomb-like structure in armchair ribbons. Compared with the AG NRs, calculation results in this study indicate that the Clar sextets play the key role in the periodically modulated width-dependent behavior.

From Equation (2) and (3) and using Equation (1), the length directional initial strain is treated as a function of the width, which takes the form

\[
\varepsilon^{ini}_{3D} = \frac{-2\sigma^{ini}_{0-3D}}{W(Y^*_{3D} + \frac{2Y^*_{3D}}{W})} = \frac{-2\sigma^{ini}_{0-3D}}{WY^*_{3D}^{3D}}
\]

(6)

\[
\varepsilon^{ini}_{2D} = \frac{-2\sigma^{ini}_{0-2D}}{W(Y^*_{2D} + \frac{2Y^*_{2D}}{W})} = \frac{-2\sigma^{ini}_{0-2D}}{WY^*_{2D}^{2D}}
\]

(7)

The 3D and 2D edge eigen-stresses, listed in Table 1, were determined by fitting the calculated initial strain versus the reciprocal of the product of the width and the nominal Young’s modulus. The positive edge eigen-stress suggests that the edges of AMoS2 NRs are stretched when constructed with the monolayer MoS2 sheet lattice constant without any deformation. To release the tensile edge eigen-stress, compressive initial strains must be induced during relaxation.

5. Conclusions

In conclusion, energies and mechanical properties of the AMoS2 NR with bare edges dimensions changed after normal relaxation...
and parallel relaxation. As the width increased, the initial strain along the length increased, and the initial strain along the thickness, the surface atoms fluctuation degree and the edge energy density of the relaxed AMoS2 NRs decreased. The structure change of the relaxed AMoS2 NRs with bare edges was expressed by the perimeter patterns, which were divided into two periodic groups. Tensile/compressive tests were conducted on the relaxed AMoS2 NRs to determine the nominal elastic constants. Nominal Young’s modulus and nominal Poisson’s ratio also illustrated width-dependent behavior, i.e., larger width corresponded to higher nominal Young’s modulus, higher nominal Poisson’s ratio along the thickness direction, and smaller nominal Poisson’s ratio along the width. The edge Young’s modulus and Poisson’s ratio were calculated based on the edge eigen-stress and eigen-displacement models. The results obtained herein are helpful to aid MoS2 nanoribbons-based devices design.

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