

Derivation of a Force Field for Computer Simulations of Multi-Walled Nanotubes using genetic algorithm. I. Tungsten Disulfide

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Supplementary Material

The SWMBL-C model explicitly considers the partially ionic character of atoms in the WS₂ systems. The Coulomb contribution to the SWMBL-C force field is determined by the partial charges on atoms of bulk WS₂ crystal $q_W=1.08 e$, $q_S=-0.54 e$ calculated by the DFT method using the Mulliken population analysis. The Morse function formally corresponds to the energy of stretching W-S and W-W covalent interactions inside the WS₂ monolayer:

$$V_M(r_{ij}) = D_e \left[\left(1 - \exp \left(-\alpha(r_{ij} - r_0) \right) \right)^2 - 1 \right], \quad (1)$$

where r_{ij} is a distance between atoms i and j ; D_e , α and r_0 are empirical parameters. The repulsive and attractive (van der Waals) interactions between the two different sulfur atoms are calculated using Buckingham term:

$$V_B(r_{ij}) = A \exp \left(-\frac{r_{ij}}{\rho} \right) - \frac{C_6}{r_{ij}^6}, \quad (2)$$

where A , ρ and C_6 are empirical parameters. The three-body Stillinger-Weber (SW) term considers the interactions which result in bending of the angles $\angle WSW$:

$$V_3^{SW}(r_{ij}, r_{ik}, \theta_{ijk}) = K \exp[\rho_1/(r_{ij} - r_{maxij}) + \rho_2/(r_{ik} - r_{maxik})] (\cos \theta_{ijk} - \cos \theta_0)^2, \quad (3)$$

where K , ρ_1 , ρ_2 , r_{maxij} , r_{maxik} , θ_0 are the empirical parameters. θ_{ijk} is the valence angle formed by W_j , S_i and W_k atoms. Here a sulfur atom S_i is placed at the apex. The Linear-three-body (LTB) potential reflects the angular dependence of the energy for bond angles $\angle SWS$ close to 0° , 90° , or 180° :

$$V_3^{LTB}(\theta_{ijk}) = k[1 + \cos(4\theta_{ijk})], \quad (4)$$

where k is the empirical parameter, θ_{ijk} is the valence angle formed by S_j , W_i and S_k atoms. Here a tungsten atom W_i is placed at the apex.

Finally, the total potential energy in the proposed force field is presented as follows:

$$V = \sum_{i < j} q_i q_j / r_{ij} + \sum_{S_i S_j} V_B(r_{ij}) + \sum_{W_i S_j} V_M(r_{ij}) + \sum_{W_i W_j} V_M(r_{ij}) + \\ + \sum_{S_i W_j W_k} V_3^{SW}(r_{ij}, r_{ik}, \theta_{ijk}) + \sum_{W_i S_j S_k} V_3^{LTB}(\theta_{ijk}). \quad (5)$$

In Table S1 the SWMBL-C optimized parameters obtained from genetic algorithm are listed.

Table S1. The SWMBL-C force field parameters (All distances are in Å).

<i>Two-body Morse potential (see Eq. (1))</i>										
Atoms	D_e , eV	α , Å ⁻¹			r_0			$r_{\max}$		
W–W	3.299924	1.261773			2.248142			15.0		
W–S	0.259415	2.907724			2.524197			15.0		
<i>Two-body Buckingham potential (see Eq. (2))</i>										
Atoms	A , eV	ρ , Å			C_6 , eV·Å ⁶			$r_{\max}$		
S–S	10419.081	0.294982			99.742365			15.0		
<i>Three-body SW potential (see Eq. (3))</i>										
Atoms	K , eV	θ_0 , degree	ρ_1 , Å	ρ_2 , Å	$r_{\min 12}$	$r_{\max 12}$	$r_{\min 13}$	$r_{\max 13}$	$r_{\min 23}$	$r_{\max 23}$
S–W–W	3.619232	84.165491	0.234068	0.234068	0	3.16	0	3.16	0	4.3
<i>Three-body LTB potential (see Eq. (4))</i>										
Atoms	k , eV	$r_{\max 12}$			$r_{\max 13}$			$r_{\max 23}$		
W–S–S	0.096840	3.16			3.16			5.00		

The relative stability of 3R- and 1T-phases is determined by a difference between the total lattice energy of each phase and 2H–WS₂ one, ΔE_{3R-2H} and ΔE_{1T-2H} , as written below:

$$\Delta E_{3R-2H} = E_{3R}/n_{3R} - E_{2H}/n_{2H}, \quad (6)$$

where E_{3R} is the total lattice energy of 3R–WS₂ and E_{2H} is the total lattice energy of 2H–WS₂; n_{3R} and n_{2H} are the numbers of formula units per unit cell of the corresponding polytypes. The relative stability of a monolayer and nanotubes can be determined by the formation energy E_{form} calculated with respect to the most stable bulk phase:

$$\Delta E_{\text{form}} = E_{\text{ml}}/n_{\text{ml}} - E_{\text{bulk}}/n_{\text{bulk}}, \quad (7)$$

where E is the total energy and n is a number of formula units per unit cell of the monolayer (ml) or bulk 2H–WS₂ crystal (bulk). The other quantity, the strain energy E_{str} , is the measure of the nanotube (NT) stability with respect to (infinite) monolayer:

$$\Delta E_{\text{str}} = E_{\text{NT}}/n_{\text{NT}} - E_{\text{ml}}/n_{\text{ml}}, \quad (8)$$

where E is the total energy and n is a number of formula units per unit cell of a nanotube or monolayer.

In Tables S2 and S3 the ability of the SWMBL-C potential to reproduce the properties of the WS₂ systems from the training database is demonstrated.

Table S2. Comparison of the properties of WS₂ 2H and 3R bulk phases, monolayer and nanotubes (12, 12), (6, 6), measured experimentally or calculated by DFT method with the results of modeling by molecular mechanics using the proposed force field. $\Delta_i = 100 \times \text{abs}((x_i^{\text{calc.}} - x_i^{\text{exp.}})/x_i^{\text{exp.}})$; $\bar{\Delta} = \sum_i^n \Delta_i/n$

Property	Experiment	Force field, present work
<i>Phase 2H</i>		
Lattice constants (Å):		
<i>a</i>	3.153 [1]	3.161
<i>c</i>	12.323 [1]	12.327
$\bar{\Delta}$, %		0.14
Elastic constants (GPa):		
<i>c</i> ₁₁	158 [2]	204
<i>c</i> ₃₃	60 [2]	75
<i>c</i> ₄₄	16 [2]	12
$\bar{\Delta}$, %		26
<i>B</i> , bulk modulus, GPa	44 [DFT]	71
$\bar{\Delta}$, %		61
Young's modulus, GPa (<i>x, y</i>)	272±18 [3], 150 [4]	171
$\bar{\Delta}$, %		7
<i>Phase 3R</i>		
Lattice constants (Å):		
<i>a</i>	3.158 [1]	3.161
<i>c</i>	18.49 [1]	18.50
$\bar{\Delta}$, %		0.07
ΔE_{3R-2H}^a , kJ·mol ⁻¹	0.21 [DFT]	0.08
$\bar{\Delta}$, %		62
<i>Phase 1T</i>		
Lattice constants (Å):		
<i>a</i>	3.174 [DFT]	3.139
<i>c</i>	6.281 [DFT]	6.199
$\bar{\Delta}$, %		1.2
ΔE_{1T-2H} , kJ·mol ⁻¹ (see Eq. (6))	109.7 [DFT]	97.7
$\bar{\Delta}$, %		11
<i>Monolayer</i>		
<i>a</i> , Å	3.161 [DFT]	3.157
<i>b</i> , Å	3.161 [DFT]	3.157
$\bar{\Delta}$, %		0.13
<i>E</i> _{form, ml-2H} , kJ·mol ⁻¹ (see Eq. (7))	22.6 [DFT]	24.2
$\bar{\Delta}$, %		7
<i>SW nanotube (12, 0)</i>		
<i>a</i> , Å	5.365 [DFT]	5.269
<i>D</i> , Å	13.2 [DFT]	13.9
$\bar{\Delta}$, %		3.5
<i>E</i> _{str} , kJ·mol ⁻¹ (see Eq. (8))	111.2 [DFT]	107.0
$\bar{\Delta}$, %		4
<i>SW nanotube (6, 6)</i>		
<i>a</i> , Å	3.194 [DFT]	3.239
<i>D</i> , Å	11.4 [DFT]	12.0
$\bar{\Delta}$, %		33
<i>E</i> _{str} ^c , kJ·mol ⁻¹	145.5 [DFT]	144.1
$\bar{\Delta}$, %		1

Table S3. Comparison of the phonon frequencies (cm^{-1}) at the Γ point of the Brillouin zone for the $2H\text{-WS}_2$ crystal, measured experimentally and calculated by DFT method, with the results of modeling by the molecular mechanics using the proposed force field.

$$\Delta_i = \text{abs}(v_i^{\text{calc.}} - v_i^{\text{exp.}}); \bar{\Delta} = \sum_i^n \Delta_i / n.$$

i	Phonon mode	experiment [2]	Force field, present work	$v_i^{\text{calc.}} - v_i^{\text{exp.}}$	DFT calculation	$v_i^{\text{calc.}} - v_i^{\text{exp.}}$
1	A_{2u}	0.0	0.0	0	0.0	0
2, 3	E_{1u}	0.0	0.0	0	0.0	0
4, 5	E_{2g}	27	22	5	25	2
6	B_{1g}	(45) ^a	54	9	45	0
7, 8	E_{2u}	(306) ^a	288	18	313	7
9, 10	E_{1g}	306	291	15	315	9
11, 12	E_{1u}	356	357	1	379	23
13, 14	E_{2g}	356	359	3	379	23
15	B_{2u}	(420) ^a	426	6	441	21
16	A_{1g}	421	446	25	449	28
17	A_{2u}	435	465	30	466	31
18	B_{1g}	(436) ^a	465	29	473	37
$\bar{\Delta}, \text{cm}^{-1}$			7		5	

^aValence force field estimation for frequencies of the silent modes.

Cross-sections of the five-walled NTs with armchair and zigzag chirality we demonstrate in Fig. S1 and S2, respectively. About 14 facets of the NT with armchair chirality can be distinguished in Fig. S1.

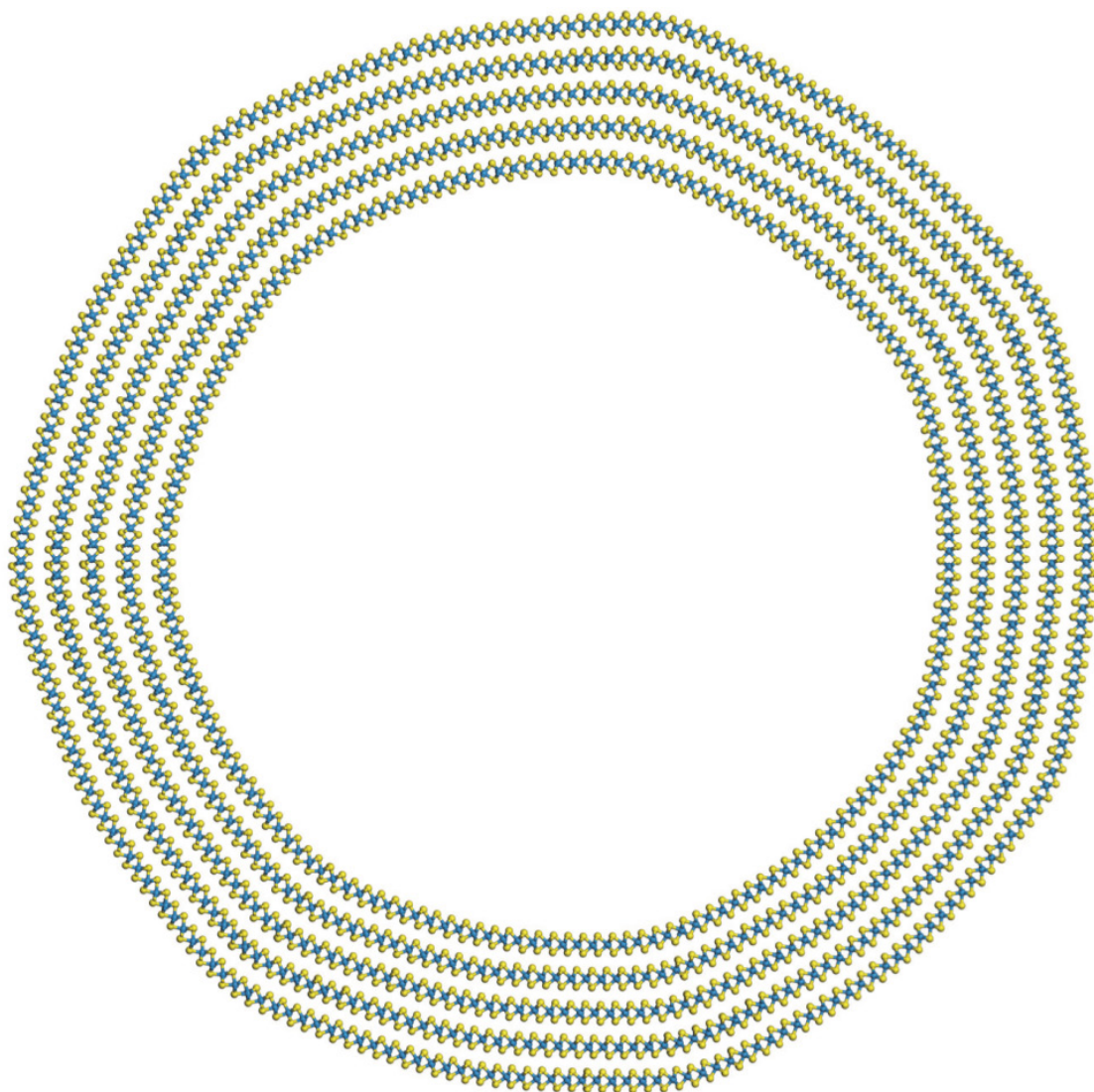


Figure S1. Cross-sectional view of the force-field optimized structure of a WS₂ 5-walled NT (82,82)@(89,89)@(96,96)@(103,103)@(110,110) with armchair chirality. Yellow spheres are S atoms; blue spheres are W atoms.

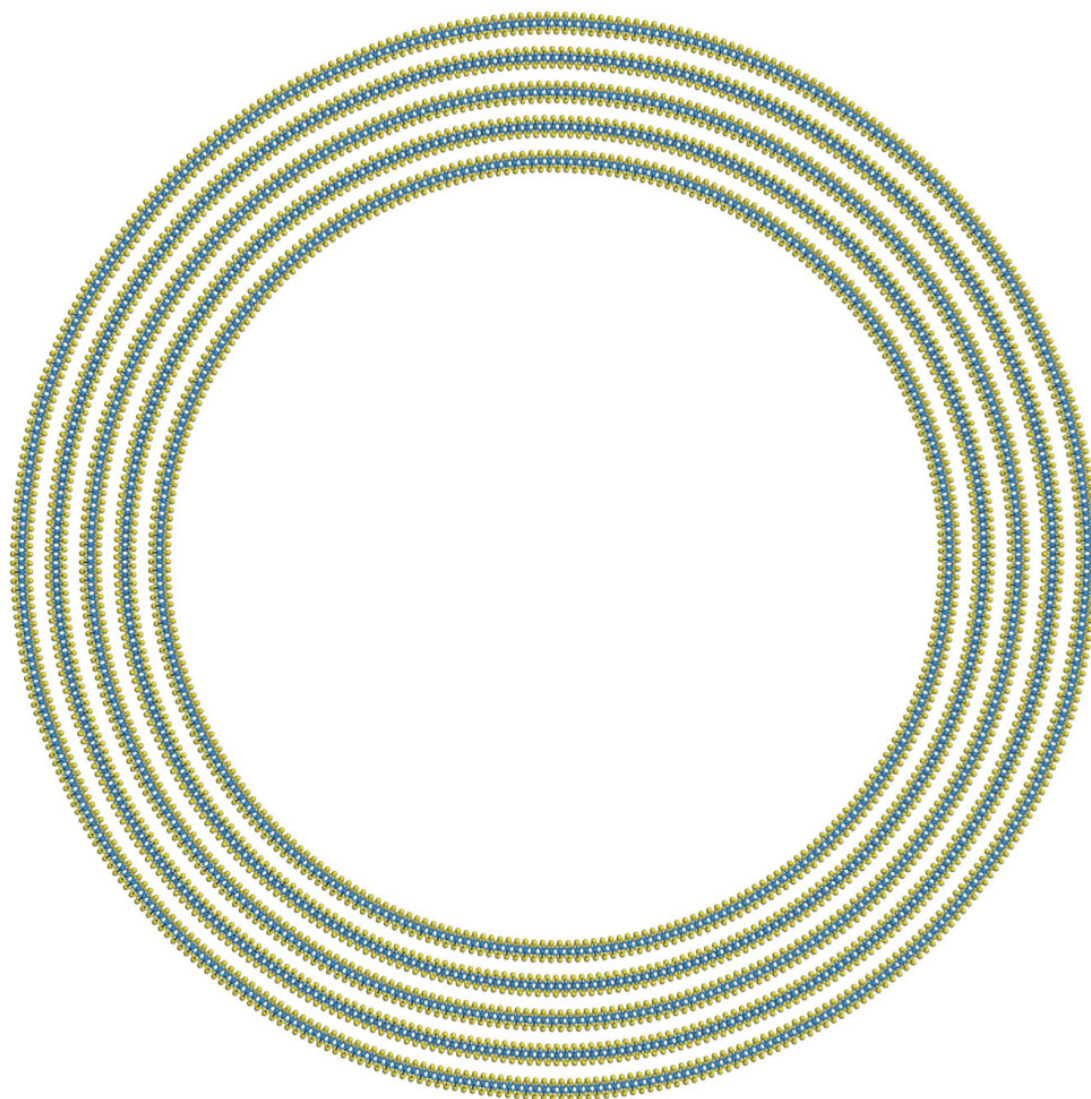


Figure S2. Cross-sectional view of the force-field optimized structure of a WS₂ 5-walled NT (142,0)@(154,0)@(166,0)@(178,0)@(190,0) with zigzag chirality. Yellow spheres are S atoms; blue spheres are W atoms.

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