Parametrization of Stillinger–Weber potential based on valence force field model: application to single-layer MoS$_2$ and black phosphorus

Jin-Wu Jiang

Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, People’s Republic of China
Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai University, Shanghai 200072, People’s Republic of China
E-mail: jiangjinwu@shu.edu.cn and jwjiang5918@hotmail.com

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Abstract

We propose parametrizing the Stillinger–Weber potential for covalent materials starting from the valence force-field model. All geometrical parameters in the Stillinger–Weber potential are determined analytically according to the equilibrium condition for each individual potential term, while the energy parameters are derived from the valence force-field model. This parametrization approach transfers the accuracy of the valence force field model to the Stillinger–Weber potential. Furthermore, the resulting Stillinger–Weber potential supports stable molecular dynamics simulations, as each potential term is at an energy-minimum state separately at the equilibrium configuration. We employ this procedure to parametrize Stillinger–Weber potentials for single-layer MoS$_2$ and black phosphorous. The obtained Stillinger–Weber potentials predict an accurate phonon spectrum and mechanical behaviors. We also provide input scripts of these Stillinger–Weber potentials used by publicly available simulation packages including GULP and LAMMPS.

Keywords: MoS$_2$, black phosphorus, Stillinger–Weber potential, molecular dynamics simulation

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

1. Introduction

The atomic interaction is a fundamental ingredient for numerical investigation of nearly all physical or mechanical processes. For instance, in molecular dynamics (MD) simulations, the atomic interaction provides the retracting force for each atom in the Newton’s equation. There have been huge numbers of available potential models for the atomic interaction within different materials. For the covalent material, some representative potential models are shown in figure 1 in the order of their simulation cost; i.e., the valence-force field (VFF) model, the Stillinger–Weber (SW) potential, Tersoff potential, Brenner potential, and ab initio approaches. These potentials (or approaches) are able to describe the bond-stretching and angle-bending motions, which are two dominant motion styles in covalent materials. The bond-twisting motion can also be treated by these potentials, although the twisting energy is usually very small.

The VFF model is a linear model, and is suitable for analytic derivation of many elastic quantities, so this model requires only limited computation cost. As an advantage of the VFF model, its parameters can be determined with high accuracy by fitting directly to some observable elastic quantities. As a result, the VFF model was very popular for covalent materials, especially before the 1980s, when the central processing unit speed was very low. Consequently, the
VFF model for most covalent materials was well developed. For instance, the VFF model for MoS$_2$ was proposed in 1975 [1], while the VFF model for black phosphorus (BP) was proposed in 1982 [2], and the VFF model for graphene was developed in 1990 by Aizawa et al [3]. These VFF models have been useful for the study of many elastic properties in these quasi-two-dimensional nano-materials in recent years, especially during the gold rush of graphene in the past decade.

While the VFF model is beneficial for the fastest numerical simulation, its strong limitation is the absence of a nonlinear effect. Due to this limitation, the VFF model is not applicable to nonlinear phenomena, for which other potential models with nonlinear components are required. The ab initio approach is accurate and applicable to nonlinear phenomena, but it requires the most expensive simulation cost, due to the solution of the full quantum electronic problem. However, this approach desires the most expensive simulation resources. As a result, the ab initio approach usually cannot simulate more than around a few thousand atoms, which poses serious limitations for comparisons to experimental studies.

We are now aware that the VFF model is the cheapest in computation cost, but it only works for elastic properties. On the other hand, the ab initio approach can simulate nearly all physical processes with high accuracy, but it requires the most expensive computation cost. Hence, the bridging between these two extreme cases is of practical significance, since lots of studies prefer efficient simulation with reasonable accuracy for the nonlinear treatment. There have been several potential forms to fill this bridging domain, including SW potential [4–6], Tersoff potential [7–13], and Brenner potential [14–16]. All of these potential forms comprise reasonably accurate nonlinear effects, and are particularly suitable for MD simulations.

Among these potentials, the SW potential is one of the simplest potential forms with nonlinear effects included [4]. An advanced feature for the SW potential is that it includes the nonlinear effect, and keeps the numerical simulation at a very fast level. As a result, the SW potential has been widely used in the numerical simulation community. The SW potential was originally proposed by Stillinger and Weber to describe the interaction in solid and liquid forms of silicon, and it has been used in other covalent materials like single-layer MoS$_2$ (SLMoS$_2$) [5] and single-layer BP (SLBP) [6].

For chemically different materials, the SW potential form remains unchanged, but all parameters need to be determined properly. In all present works, the parametrization of the SW potential (and also Brenner and Tersoff potentials) is done by fitting to some experimentally known quantities like the Young’s modulus, phonon spectrum, cohesion energy, etc. Actually, from the above discussion, we have learned that most covalent materials already have an accurate VFF model, which can describe linear properties accurately. Such an attractive essence should be helpful for the parametrization of atomic potentials like the SW potential, Tersoff potential, and Brenner potential. However, to date, the accuracy of the VFF model was not transferred to other atomic potentials during their parametrization process. The present work takes the SW potential as an example to demonstrate the relationship between the VFF model and the SW potential. In doing so, we illustrate that the SW potential parameters can be analytically parametrized based on the VFF model.

In this paper, we propose a parametrization procedure for the development of SW potentials based on the VFF model. All SW geometrical parameters are determined according to the equilibrium condition for each SW term, while the SW energy parameters are derived from the VFF model analytically. This parametrization procedure is employed to develop the SW potentials for SLMoS$_2$ and SLBP, which provide an accurate phonon spectrum and mechanical behaviors.

The present paper is organized as follows. In section 2, we present details about the parametrization of the SW potential based on the VFF model. The parametrization procedure is applied to develop the SW potential for SLMoS$_2$ in section 3. Section 4 is devoted to the analytic parametrization of the SW potential for the SLBP. The paper ends with a brief summary in section 5.

2. VFF model and SW potential

For most covalent bonding materials, the bond-stretching and the angle-bending are two typical motion styles, as shown in figure 2. The corresponding interactions can be described by the VFF model in the linear regime for small bond variation $\Delta r$ and angle variation $\Delta \theta$.

$$V_r = \frac{1}{2} K_r (\Delta r)^2,$$

(1)

$$V_\theta = \frac{1}{2} K_\theta d_2 (\Delta \theta)^2,$$

(2)

where $K_r$ and $K_\theta$ are two VFF parameters. The $V_r$ term is the potential that captures a variation in the bond length $\Delta r$. The $V_\theta$ is for the potential corresponding to the variation of the angle $\Delta \theta$, where the angle $\theta$ is formed by two bonds of length $d_1$ and $d_2$.

Besides the VFF model, the SW potential is another useful potential for these two typical interactions in figure 2. There are
two-body and three-body interactions in the SW potential,
\[ V_2 = \alpha \rho \left( \frac{d}{r_{\text{max}}^3} \right) \left( \frac{B}{r^4} - 1 \right), \]  
(3)

where \( V_2 \) corresponds to the bond-stretching and \( V_3 \) associates with the angle-bending. The cutoffs \( r_{\text{max}}, \ r_{\text{max}12}, \) and \( r_{\text{max}13} \) are geometrically determined by the material’s structure. There are five unknown geometrical parameters, i.e., \( \rho \) and \( B \) in the two-body SW term and \( \rho_1, \ \rho_2, \) and \( \theta_0 \) in the three-body SW term, and two energy parameters \( A \) and \( K. \)

Let us assume that the material’s structure (bond length \( d \) and angle \( \theta_0 \)) has been identified via experiments or other accurate theoretical methods. Using this knowledge, we can determine geometrical parameters in the SW potential. First of all, it is reasonable to require that all bonds are at their equilibrium length and all angles are at their equilibrium angle value in the equilibrium configuration. That is, we have the equilibrium condition, \( \frac{\partial V}{\partial r} |_{r=d} = 0 \) and \( \frac{\partial V}{\partial \theta} |_{\theta=\theta_0} = 0, \) for each bond and each angle individually. From \( \frac{\partial V}{\partial r} |_{r=d} = 0, \) we obtain the following constraint for parameters \( \rho \) and \( B \) in \( V_2, \)

\[ \rho = \left( \frac{d}{r_{\text{max}}} \right)^2 \left( \frac{B}{d^4} - 1 \right), \]  
(5)

where \( d \) is the equilibrium bond length from experiments. Hence, there is only one free geometrical parameter left in \( V_2. \) In other words, equation (5) ensures that the bond has an equilibrium length of \( d \) and the \( V_2 \) interaction for this bond is at the energy minimum state at the equilibrium configuration.

The three-body \( V_3 \) term shown in equation (4) ensures \( \frac{\partial V}{\partial \theta} = 0 \) explicitly, so we have no constraint on geometrical parameters for the three-body term. In fact, there is no free geometrical parameter in \( V_3, \) because the angle \( \theta_0 \) is from the experiment, while \( \rho_1 \) and \( \rho_2 \) have been determined by equation (5).

The energy parameters \( A \) and \( K \) in the SW potential can be derived from the VFF model by equating the force constants from the SW potential and the force constants in the VFF model. More specifically, we have \( \frac{\partial^2 V}{\partial \theta^2} |_{\theta=\theta_0} = K_\theta d_1 d_2 \) at the equilibrium structure, leading to,

\[ A = \frac{K_\theta d_1 d_2}{\alpha e \left( r/d - r_{\text{max}} \right)^2}, \]  
(6)

\[ K = \frac{K_\theta d_1 d_2}{2 \sin^2 \theta_0 \left( r_1 d_1 + r_2 d_2 \right)}, \]  
(7)

where the coefficient \( \alpha \) in equation (6) is,

\[ \alpha = \left( \frac{\rho}{\left( d - r_{\text{max}} \right)^2} \right)^2 \left( \frac{B}{d^4} - 1 \right) + \frac{2 \rho}{\left( d - r_{\text{max}} \right)^3} \left( \frac{B}{d^4} - 1 \right) + \frac{\rho}{\left( d - r_{\text{max}} \right)^2} \left( \frac{8B}{d^6} + \frac{20B}{d^8} \right). \]  
(8)

The bond length of the arms for the angle are \( d_1 \) and \( d_2, \) which are from experiments or other theoretical calculations. As a result, energy parameters in the SW potential are analytically related to the energy parameters in the VFF model.

We summarize the key steps in the above analytic parametrization of the SW potential. In the SW potential, the bond-stretching interaction is described by equation (3), and the angle-bending interaction is described by equation (4). The potential parameters are determined in three steps. The first, the interaction cutoffs \( \left( r_{\text{max}}, \ r_{\text{max}12}, \right. \) and \( \left. r_{\text{max}13} \right) \) are determined geometrically by the equilibrium configuration of the material. The bond length \( d, \ d_1, \) and \( d_2 \) and the angle \( \theta_0 \) are also from the experiment or other theoretical calculations. Second, geometrical parameters \( \rho \) in the two-body term and \( \rho_1 \) and \( \rho_2 \) in the three-body term are determined by equation (5) by assuming that each two-body SW term is at equilibrium separately. Third, energy parameters \( A \) and \( K \) are determined by equations (6) and (7), based on the VFF model.
B < d^4, so that ρ > 0. We will explain in the next two sections that parameter B is related to the nonlinear mechanical process and should be fixed according to a nonlinear quantity.

Before further processing, we note some advantages for the SW potential derived in this approach. First, such as SW potential has fully inherited the accuracy of the VFF model, so it provides accurate description for linear properties that can be accurately described by the VFF model. Second, the equilibrium structure has been pre-built-in during the derivation, as shown by equation (5), so this SW potential allows an accurate relaxed configuration intrinsically. Third, each two-body and three-body term in the SW potential is fully relaxed separately at the equilibrium configuration; i.e., all bonds and angles are relaxed individually at the relaxed configuration. Hence, the SW potential will be extremely stable during MD simulations. Fourth, the SW potential includes nonlinear effects through the nonlinear forms of both two-body and three-body terms, as shown in equations (3) and (4), so the SW potential is able to provide nonlinear properties, e.g., via performing MD simulations.

### 3. SW potential for MoS2

As an example, we apply the above parametrization procedure to develop the SW potential for SLMoS2 in this section. We use the equilibrium structure for SLMoS2 from the first-principles calculations, as shown in figure 3. The bond length between neighboring Mo and S atoms is d = 2.382 Å, and the angles are \( \theta = \angle \text{SMoS} = 80.581^\circ \) and \( \psi = \angle \text{MoSMo} = 80.581^\circ \).

The VFF model for SLMoS2 is from reference [1], which is able to describe the phonon spectrum and the sound velocity accurately. We have listed the first three leading force constants for SLMoS2 in table 1, neglecting other weak interaction terms.

#### Table 1. The VFF model parameters for SLMoS2 from reference [1].

| \( K_e \left( \frac{eV}{Å} \right) \) | \( K_\rho \left( \frac{eV}{Å^4} \right) \) | \( K_\psi \left( \frac{eV}{Å^4} \right) \) |
|---|---|---|
| 8.640 | 0.937 | 0.862 |

The bond-stretching term is \( V_e = \frac{k_e}{2}(\Delta d)^2 \) with \( \Delta d \) as the length variation of Mo–S bond (e.g., Mo1–S1). The angle-bending term is \( V_\psi = \frac{k_\psi}{2}(\Delta \psi)^2 \) for angle Mo–S–S with Mo as the apex (e.g., \( \angle \text{SMoMo} \)), and \( V_\rho = \frac{k_\rho}{2}(\Delta \rho)^2 \) for angle S–Mo–Mo with S as the apex (e.g., \( \angle \text{MoSMo} \)).

Using equations (5)–(7), we obtain the SW potential parameters for SLMoS2 used by GULP [19], as listed in tables 2 and 3. We have found in section 2 that parameter B cannot be determined by the linear VFF model, because B corresponds to the nonlinear mechanical behavior. In other words, parameter B has no effect on linear properties. For instance, we compute the phonon spectrum for the SLMoS2 using two different sets of the SW potential with \( B = 0.1d^4 \) and \( B = 0.552d^4 \). Although these two SW potential sets look completely different, figure 4 shows that the phonon spectrum corresponding to different parameter B are exactly the same.

To fix parameter B, a nonlinear quantity is needed. Figure 5 clearly demonstrates that parameter B has a strong effect on the nonlinear mechanical behavior of the stress-strain relation during the tension of a SLMoS2 of dimensions 27.0 × 28.1 Å at 1.0 K. The stress (\( \sigma \)) is fitted as a function of strain (\( \epsilon \)), \( \sigma = E\epsilon + \frac{1}{2}D\epsilon^2 \), with E as the Young’s modulus and D as the third-order elastic constant (TOEC). The left top inset in figure 5 shows that the parameter B has no effect on another elastic property, the Young’s modulus. Figure 5 right bottom inset shows the relationship between B and parameter D. Using the first-principles result [17], \( D = -899.8 \) GPa, we can fix the parameter B = 0.552d^4.

The SW potential parameters for SLMoS2 used by LAMMPS [18] are listed in table 4. The potential script for LAMMPS can be found in the supplemental material (available at stacks.iop.org/nano/26/315706/mmedia). We use LAMMPS to perform MD simulations for the mechanical behavior of the SLMoS2 under uniaxial tension at 1.0 K and 300.0 K. Figure 6 shows the stress-strain curve during the tension of a SLMoS2 of dimension 27.0 × 28.1 Å. Periodic boundary conditions are applied in both the armchair and zigzag directions. The structure is thermalized to the thermal steady state with the NPT (constant particle number, constant pressure, and constant temperature) ensemble for 100 ps by the Nosé–Hoover [20, 21] approach. After thermalization, the MoS2 is stretched in one direction at a strain rate of \( 10^8 \) s\(^{-1} \), while the stress in the lateral direction is allowed to be relaxed to be zero. We have used the inter-layer space in bulk MoS2, 6.092 Å, as the thickness of the SLMoS2 in the computation of the strain energy density.

#### Table 2. Two-body (bond-stretching) SW potential parameters for SLMoS2 used by GULP. The expression is \( V_e = A \left( \frac{\rho}{\rho_{\text{max}} - \rho_{\min}} \right)^3 \) (\( B/\rho^4 - 1 \)).

| A (eV) | B (Å^4) | \( r_{\text{min}} \) (Å) | \( r_{\text{max}} \) (Å) |
|---|---|---|---|
| Mo-S | 6.918 | 1.252 | 17.771 | 0.0 | 3.16 |

The bond-stretching term is \( V_e = \frac{k_e}{2}(\Delta d)^2 \) with \( \Delta d \) as the length variation of Mo–S bond (e.g., Mo1–S1). The angle-bending term is \( V_\psi = \frac{k_\psi}{2}(\Delta \psi)^2 \) for angle Mo–S–S with Mo as the apex (e.g., \( \angle \text{SMoMo} \)), and \( V_\rho = \frac{k_\rho}{2}(\Delta \rho)^2 \) for angle S–Mo–Mo with S as the apex (e.g., \( \angle \text{MoSMo} \)).

Using equations (5)–(7), we obtain the SW potential parameters for SLMoS2 used by GULP [19], as listed in tables 2 and 3. We have found in section 2 that parameter B cannot be determined by the linear VFF model, because B corresponds to the nonlinear mechanical behavior. In other words, parameter B has no effect on linear properties. For instance, we compute the phonon spectrum for the SLMoS2 using two different sets of the SW potential with \( B = 0.1d^4 \) and \( B = 0.552d^4 \). Although these two SW potential sets look completely different, figure 4 shows that the phonon spectrum corresponding to different parameter B are exactly the same.

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Table 3. Three-body (angle-bending) SW potential parameters for SLMoS2 used by GULP. The expression is $V_i = K\left(\rho_{\ell 2}/\rho_{\ell 2}^{\max 12} + \rho_{\ell 3}/\rho_{\ell 3}^{\max 13}\right)\left(\cos \theta - \cos \theta_0\right)^2$. Mo–S–S indicates the bending energy for the angle with Mo as the apex.

| $K$ (eV) | $\theta_0$ (degree) | $\rho_{\ell 2}$ (Å) | $\rho_{\ell 3}$ (Å) | $r_{\min 12}$ (Å) | $r_{\max 12}$ (Å) | $r_{\min 13}$ (Å) | $r_{\max 13}$ (Å) | $r_{\min 23}$ (Å) | $r_{\max 23}$ (Å) |
|----------|---------------------|---------------------|---------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Mo–S–S   | 67.883              | 81.788              | 1.252               | 1.252             | 0.0               | 3.16              | 0.0               | 3.16              | 0.0               | 3.78              |
| S–Mo–Mo  | 62.449              | 81.788              | 1.252               | 1.252             | 0.0               | 3.16              | 0.0               | 3.16              | 0.0               | 4.27              |

Figure 4. Phonon spectrum for SLMoS2 along the $\Gamma M$ direction in the Brillouin zone. The results from the SW potential (lines) are compared with the experiment data (pentagons) from reference [1]. Parameter $B$ has no effect on the phonon spectrum.

Figure 5. The effect of parameter $B$ on the stress–strain relation for SLMoS2 of dimension 27.0 × 28.1 Å along the armchair direction at 1.0 K. The stress–strain curve is fitted to function $\sigma = Ee + \frac{1}{2}De^2$, with $E$ as the Young’s modulus and $D$ as the TOEC. The left top inset shows that the parameter $B$ has no effect on the elastic property, Young’s modulus, while the right bottom inset shows that parameter $B$ dominates the nonlinear quantity, TOEC, which is fitted by function $D = -2953.8B^2$. The blue circle in the right bottom inset represents $D = -899.8$ GPa from the first-principles calculation [17], which fixes parameter $B = 0.552d^4$ for the SW potential.

In figure 6, from the curve in the linear region, $e \in [0, 0.01]$, we get the Young’s modulus of SLMoS2 around 165.7 GPa and 167.0 GPa in the armchair and zigzag directions, respectively. The shear modulus and Poisson’s ratio can also be obtained in this linear regime. It is obvious that the Young’s modulus is isotropic for SLMoS2 due to the three-fold rotational symmetry in this quasi-hexagonal lattice structure [22]. Recent experiments have measured the effective Young’s modulus to be $E = 120 \pm 30$ Nm$^{-1}$ [17, 23], or $E = 180 \pm 60$ Nm$^{-1}$ [24]. These values correspond to an in-plane Young’s modulus of 198.6 ± 49.7 GPa or 297.9 ± 99.3 GPa, considering the thickness of 6.092 Å. Our theoretical values are quite close to the first experiment. The TOEC in the zigzag direction is larger than that in the armchair direction, which agrees with the first-principles calculations [17]. The SLMoS2 yields at smaller strain at 300 K than 1.0 K for both the armchair and zigzag directions.

In 2013, the author parametrized with collaborators an SW potential set (SW2015-MoS2) for the SLMoS2 by fitting parameters to the experimental phonon spectrum [5]. The present SW potential (SW2015-MoS2) has fewer interaction components than the SW2013-MoS2 potential. However, the phonon spectrum from the SW2015-MoS2 potential can be as accurate as the SW2013-MoS2 potential, because the present parametrization procedure transfers the accuracy of the VFF model to the SW potential. Furthermore, each interaction component in the present SW2015-MoS2 potential is at equilibrium invidually, which is more strict than the SW2013-MoS2 potential, in which the equilibrium condition is satisfied overall among all interaction components. As a result, the SW2015-MoS2 potential is more stable for MD simulations.

4. SW potential for SLBP

As another example, we apply the parametrization procedure to develop the SW potential for SLBP in this section. The structure for SLBP shown in figure 7 has been identified by experiment [27]. P atoms are divided into the top group (including atoms 1, 2, and 3) and the bottom group (including atoms 4, 5, and 6). There are two bond lengths, i.e., the intra-group bond (e.g., bond 1–2) $d_1 = 2.224$ Å and the inter-group bond (e.g., bond 1–4) $d_2 = 2.444$ Å. These two bond lengths are very close to each other, so it can be assumed that both bonds have the same length of $d = 2.224$ Å. The intra-group angle (e.g., $\angle 213$) is $\theta = 96.359^\circ$ and the inter-group angle (e.g., $\angle 314$) is $\psi = 102.09^\circ$.

Table 5 lists the VFF model parameters for SLBP from reference [2]. The bond-stretching potential between two neighboring P atoms is $V_i = \frac{K_i}{3}(\Delta d)^3$. We note that the intra-group bond and the inter-group bond essentially have the same stretching parameter [2]. As a result, there is only one VFF model parameter for bond-stretching potential. The angle-bending potential is $V_0 = \frac{K_t}{2}(\Delta \theta)^2$ for the intra-group
The two-body potential expression is 
\[ V_2 = eA \left( B_1 \sigma \sigma - \sigma \sigma \right)^2 e^{\delta \left( \cos \theta - \cos \theta_0 \right)^2} \].

The three-body potential expression is 
\[ V_3 = eA \left( B_1 \sigma \sigma - \sigma \sigma \right)^2 e^{\delta \left( \cos \theta - \cos \theta_0 \right)^2} \].

The quantity ‘tol’ in the last column is a controlling parameter in LAMMPS.

| Group 1 | Group 2 | Parameter 1 | Parameter 2 | Parameter 3 |
|---------|---------|-------------|-------------|-------------|
| Mo–S–S  | 1.000   | 1.252       | 25.23       | 67.883      |
| S–Mo–Mo | 1.000   | 1.252       | 25.23       | 64.249      |

The VFF model parameters for SLBP from reference [2].

| Parameter | Value 1 | Value 2 | Value 3 |
|-----------|---------|---------|---------|
| \( K_v \) | 7.578   | 0.818   | 0.710   |

Using equations (5)–(7), we obtain the SW potential parameters for SLBP used by GULP [19] as shown in tables 6 and 7. The determination of \( B \) is illustrated in figure 8. Parameter \( B \) has no effect on the elastic property, the Young’s modulus, as shown by the left top inset in figure 8. However, the parameter \( B \) has a strong effect on the nonlinear quantity, TOEC, which can be fitted to the function \( D = -13.8 - 227.1B^2 \). Using this relationship between the TOEC and parameter \( B \), we obtain the parameter \( B = 0.584d^4 \) corresponding to \( D = -91.3 \) GPa from the first-principles calculations [25]. We note that \( D = -13.8 \neq 0 \) even for \( B = 0 \), as shown in the right bottom inset of figure 8. For \( B = 0 \), the only nonzero SW potential term is \( V_3 = K \left( \cos \theta - \cos \theta_0 \right)^2 \), so the nonzero residue, \( D = -13.8 \) GPa, originates from the nonlinear effect purely contributed by the angle-bending interaction. This is different from the SLMoS2 results shown in the right bottom inset in figure 6, where \( D = 0 \) at \( B = 0 \). This difference can be attributed to the different space groups for SLBP (C\( \text{\_2h} \)) and SLMoS2 (D\( \text{\_3h} \)). As a restriction of the three-fold symmetry in the SLMoS2, the overall nonlinear effect from the angle-bending vanishes.

The phonon spectrum for the SLBP from the SW potential is shown in figure 9. The results from the SW potential agrees quite well with the first-principles calculations [26].

The SW potential parameters for SLBP used by LAMMPS [18] are listed in table 8. The potential script for LAMMPS can be found in the supplemental material. We use LAMMPS to perform MD simulations for the tensile behavior for the SLBP of dimension 26.3 \( \times \) 29.8 Å at 1.0 K and 300.0 K. Figure 10 shows the stress-strain curves during the tensile deformation of the SLBP along the armchair direction and the zigzag direction. Periodic boundary conditions are applied in both the armchair and zigzag directions. The structure is thermalized to the thermal steady state with the NPT (constant particle number, constant pressure, and constant temperature) ensemble for 100 ps by the Nosé-Hoover [20, 21] approach. After thermalization, the SLBP is stretched in one direction at a strain rate of 10\(^8\) s\(^{-1}\), and the stress in the lateral direction is allowed to be fully relaxed. We have used the inter-layer space of 5.24 Å as the thickness of the SLBP in the computation of the strain energy density.

In figure 10, from the stress-strain curve in the strain range [0, 0.01], we obtain the Young’s modulus 33.5 GPa and
105.5 GPa in the armchair and zigzag directions, respectively. These values are close to the previously reported \textit{ab initio} results, e.g., 28.9 Nm$^{-1}$ in the armchair direction and 101.6 Nm$^{-1}$ in the zigzag direction from reference [28]. The SLBP yields at a smaller strain at 300 K than 1.0 K for both armchair and zigzag directions.

In a recent work, the author parametrized with collaborators an SW potential set (SW2013-BP) for the SLBP by fitting parameters to the phonon spectrum from \textit{ab initio} calculations [6]. The present SW potential (SW2015-BP) has fewer interaction components than the SW2013-BP potential. However, the phonon spectrum from the SW2015-BP potential can be as accurate as the SW2013-BP potential, because the present parametrization procedure transfers the accuracy of the VFF model to the SW potential. Furthermore, each interaction component in the present SW2015-BP potential is at equilibrium individually, which is more strict than the SW2013-BP potential, in which the equilibrium condition is satisfied overall among all interaction components. As a result, the SW2015-BP potential is more stable for MD simulations.

As a final note, this work proposes a method to develop the SW potential based on the VFF model and applies this parametrization approach to SLMoS2 and SLBP. The parametrization procedure, represented in section 2, is actually applicable to the development of other atomic potentials for a wide range of covalent materials. It is quite obvious that the SW potential for other covalent materials can also be developed analogously.

An important technical note: for the simulation of SLMoS2 by LAMMPS, one needs to recompile the LAMMPS package with our modified source file, \texttt{pair\_sw\_cpp}, in the supplemental material. This helps to exclude angle-bending for angles like $\angle$S$_{3}$M$_{2}$S$_{4}$ in figure 3, which is not considered in the present work. However, for the simulation of SLBP using LAMMPS, one must use the original LAMMPS package; i.e., use the original source file, \texttt{pair\_sw\_cpp}.

5. Conclusion

In conclusion, we have proposed an approach to determine the SW potential parameters based on the valence force-field model. The SW potential developed following this approach inherits the accuracy of the VFF model in the description of

| $K$ (eV) | $\theta_0$ (degree) | $\rho_1$ (Å) | $\rho_2$ (Å) | $r_{\text{min}}$12 (Å) | $r_{\text{max}}$12 (Å) | $r_{\text{min}}$13 (Å) | $r_{\text{max}}$13 (Å) | $r_{\text{min}}$23 (Å) | $r_{\text{max}}$23 (Å) |
|----------|------------------|-------------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Pt–Pt–Pt | 35.701           | 96.359      | 0.809       | 0.809             | 0.0               | 2.79              | 0.0               | 2.79              | 0.0               |
| Pb–Pb–Pb | 35.701           | 96.359      | 0.809       | 0.809             | 0.0               | 2.79              | 0.0               | 2.79              | 0.0               |
| Pt–Pt–Pb | 32.006           | 102.094     | 0.809       | 0.809             | 0.0               | 2.79              | 0.0               | 2.79              | 0.0               |
| Pb–Pb–Pt | 32.006           | 102.094     | 0.809       | 0.809             | 0.0               | 2.79              | 0.0               | 2.79              | 0.0               |

Table 7. Three-body (angle-bending) SW potential parameters for SLBP used by GULP. The expression is $V_i = K \left( \rho_i / \rho_{\text{max}} \right)^2 \left( \rho_i / \rho_{\text{max}} \right)^2 \left( \cos \theta_i - \cos \theta_0 \right)^2$. The first two lines are for intra-group angles. The last two lines are for inter-group angles.
linear physical properties. Furthermore, the accurate equilibrium structure information is pre-built-in, and this potential is very suitable for stable MD simulations. Finally, the SW potential can be easily used in many available MD simulation packages such as GULP and LAMMPS. As two examples, we apply this parametrization technique to develop the SW potential for SLMoS2 and SLBP, which are found to provide accurate phonon spectrum and mechanical properties.

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