



Stillinger-Weber (SW) Potential and Its Polymorphic Extension

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Why SW Potential?

2877 citations as compared to 1986 for Tersoff potential

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V_{IJ}^R(r_{ij}) - V_{IJ}^A(r_{ij}) + u_{IJ}(r_{ij}) \sum_{k \neq i, j} u_{IK}(r_{ik}) \left(\cos \theta_{jik} + \frac{1}{3} \right)^2 \right]$$

1. SW potentials are very easy to parameterize;
2. The difficulty of potential parameterization is to ensure the lowest energy for the equilibrium phase as compared to ANY OTHER configurations;
3. MD simulations of crystalline growth or crystallization from melt can be used to determine if a potential captures the equilibrium phase
4. Using an angular term to penalize non-tetrahedral bond angles, SW potentials easily ensure the lowest energy for the diamond-cubic or zinc-blende structure;

F. H. Stillinger and T. A. Weber, Phys. Rev. B 31, 5262 (1985).

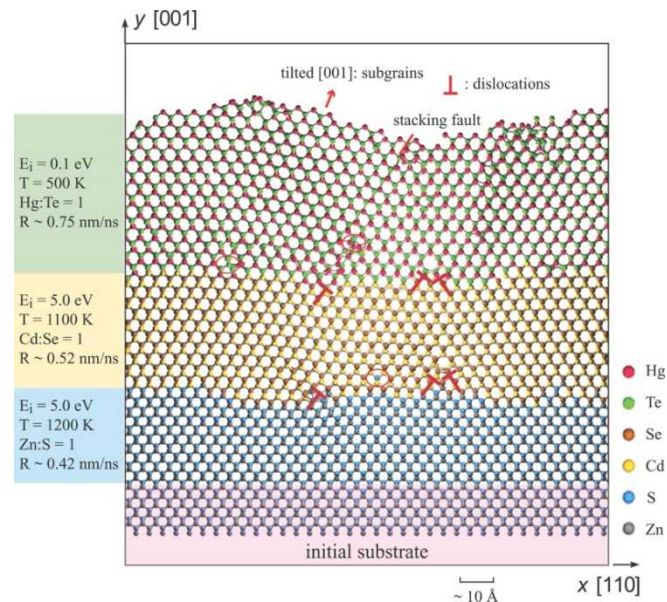
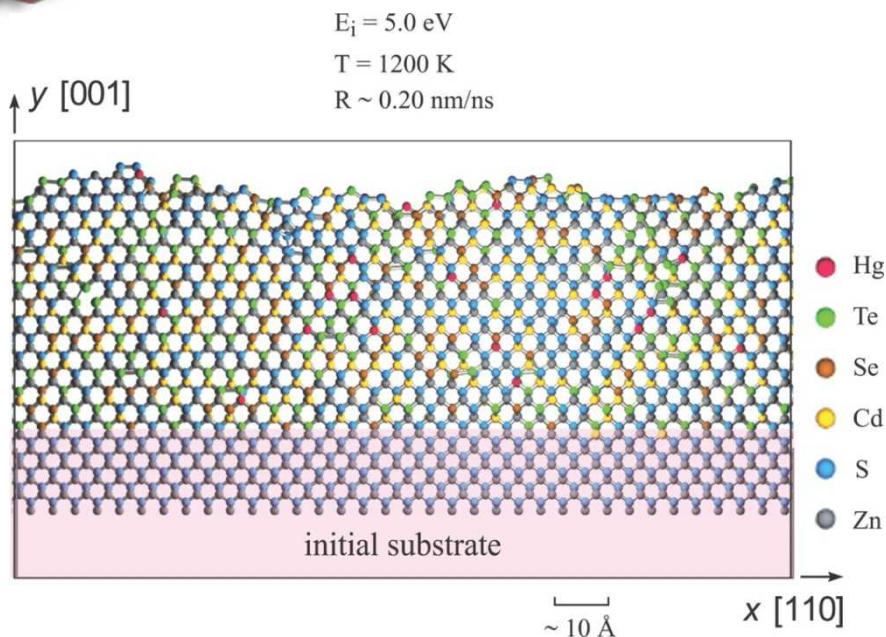
J. Tersoff, Phys. Rev. B, 39, 5566 (1989).

A Zn-Cd-Hg-S-Se-Te SW Potential

Material	Structure		Ω		E_c		B		C'			C_{44}^*		
	Exp.	Model	Exp. ^a	Cal.	Exp. ^b	Cal.	Exp. ^c	Cal.	Exp. ^c	Cal.	Cal. ^d	Exp. ^c	Cal.	Cal. ^d
Zn	hcp	fcc/hcp	16.1	16.1	-1.33	-1.33	0.49	2.60						
Cd	hcp	fcc/hcp	23.1	23.1	-1.13	-1.13	0.39	1.55						
Hg	liquid	fcc	24.6	24.6	-0.61	-0.61	0.16	1.24						
S	orth	fcc	25.7	25.7	-2.85	-2.85	0.13	3.85						
Se	A8	fcc	27.4	27.4	-2.41	-2.41	0.05	2.75						
Te	A8	fcc	34.0	34.0	-2.17	-2.17	0.41	1.88						
ZnS	zb	zb	19.7	19.7	-3.08	-3.08	0.49	0.49	0.12	0.12	0.12	0.29	0.55	0.54
ZnSe	zb	zb	22.8	22.8	-2.69	-2.69	0.39	0.39	0.11	0.14	0.11	0.26	0.45	0.44
ZnTe	zb	zb	28.4	28.4	-2.36	-2.36	0.32	0.32	0.10	0.10	0.09	0.20	0.36	0.36
CdS	wz	zb/wz	24.8	24.8	-2.76	-2.76	0.38	0.38	0.08	0.22	0.08	0.15	0.43	0.40
CdSe	zb	zb	27.7	27.7	-2.52	-2.52	0.33	0.33	0.06	0.16	0.06	0.14	0.37	0.35
CdTe	zb	zb	34.0	34.0	-2.18	-2.18	0.27	0.27	0.05	0.10	0.05	0.13	0.29	0.28
HgS	zb	zb	25.1	25.1	-2.00	-2.00	0.43	0.43	0.06	0.11	0.06	0.17	0.45	0.44
HgSe	zb	zb	28.2	28.2	-1.74	-1.74	0.32	0.32	0.05	0.09	0.05	0.14	0.34	0.33
HgTe	zb	zb	33.7	33.7	-1.55	-1.55	0.26	0.26	0.05	0.07	0.05	0.13	0.28	0.28

1. Captures equilibrium compound phases;
2. Captures model elemental phases;
3. Reproduces experimental energy, atomic volume, and bulk modulus of compounds;
4. Reproduces experimental energy and atomic volume of elements.

Growth Simulation Validation



1. Crystalline growth simulations achieved for both $(\text{Cd}_{0.28}\text{Zn}_{0.68}\text{Hg}_{0.04})(\text{Te}_{0.20}\text{Se}_{0.18}\text{S}_{0.62})$ films and ZnS/CdSe/HgTe multilayers;
2. The lowest energy for the equilibrium compound phases and energy transferability between compounds, alloys, and elements validated;
3. Robust application for many problems, especially microstructure prediction in semiconductor device structures.

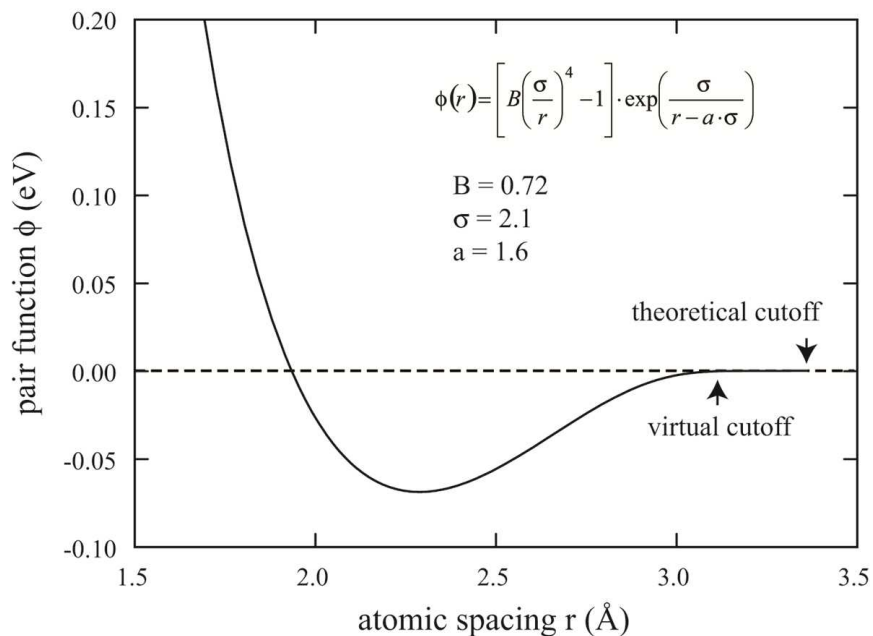
Issues:

1. Designed only for diamond-cubic, zinc-blende crystals;
2. Can be extended for fcc elements, but elastic constants are too high.

SW Potential Improvement

Issue

High elastic constants for fcc elements are due to nearest neighbor, smooth cutoff



Solution

Morse potential function + longer cutoff for similar species (nearest neighbor cutoff only required for dissimilar species)

Issue

Limitation to crystals are due to angular function penalizing only tetrahedral angle

$$\left(\cos \theta_{jik} + \frac{1}{3} \right)^2$$

Solution

More general angular function

Hurdle to LAMMPS Users

Any modifications of interatomic potentials require new pair styles

Note:

Tersoff potentials have also been modified to improve property prediction:

1. J. Wang, and A. Rockett, Phys. Rev. B 43, 12571 (1991)
2. X. W. Zhou, and R. E. Jones, Modelling Simul. Mater. Sci. Eng., 19, 025004 (2011).

Polymorphic Potential Model

$$E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left[(1 - \delta_{ij}) \cdot U_{IJ}(r_{ij}) - (1 - \eta_{ij}) \cdot F_{IJ}(X_{ij}) \cdot V_{IJ}(r_{ij}) \right]$$

$$X_{ij} = \sum_{\substack{k=1 \\ k \neq i, j}}^{i_N} W_{IK}(r_{ik}) \cdot G_{JIK}(\theta_{jik}) \cdot P_{IK}(\Delta r_{jik})$$

$$\Delta \mathbf{r}_{jik} = \mathbf{r}_{ij} - \xi_{IJ} \cdot \mathbf{r}_{ik} \quad \xi_{IJ}: \text{parameter}$$

$$\delta_{ij} = 1 \text{ (} i = j \text{) or } 0 \text{ (} i \neq j \text{)}$$

$$\eta_{ij} = \delta_{ij} \text{ or } \eta_{ij} = 1 - \delta_{ij} \text{ (depending on potential type)}$$

The potential is fully defined by indicators η_{ij} and ξ_{IJ} , and the six functions $U_{IJ}(r)$, $V_{IJ}(r)$, $P_{IJ}(\Delta r)$, $W_{IJ}(r)$, $F_{IJ}(X)$, and $G_{JIK}(\theta)$ (for all the species $I, J, K = 1, 2, \dots$)

Modified SW Potential

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V_{IJ}^R(r_{ij}) - V_{IJ}^A(r_{ij}) + u_{IJ}(r_{ij}) \sum_{k \neq i, j} u_{IK}(r_{ik}) \cdot g_{JIK}(\theta_{jik}) \right]$$

The polymorphic potential reduces to any modified SW potential shown above, if user use this polymorphic tabulation:

$$\left\{ \begin{array}{l} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = V_{IJ}^R(r) - V_{IJ}^A(r) \\ V_{IJ}(r) = u_{IJ}(r) \\ F_{IJ}(X) = -X \\ P_{IJ}(\Delta r) = 1 \\ W_{IJ}(r) = u_{IJ}(r) \\ G_{JIK}(\theta) = g_{JIK}(\theta) \end{array} \right.$$

SW Potential

The polymorphic potential reduces to original SW potential if user use this polymorphic tabulation:

$$\left\{ \begin{array}{l} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = A_{IJ} \cdot \varepsilon_{IJ} \cdot \left(\frac{\sigma_{IJ}}{r} \right)^q \cdot \left[B_{IJ} \left(\frac{\sigma_{IJ}}{r} \right)^{p-q} - 1 \right] \cdot \exp \left(\frac{\sigma_{IJ}}{r - a_{IJ} \cdot \sigma_{IJ}} \right) \\ V_{IJ}(r) = \sqrt{\lambda_{IJ} \cdot \varepsilon_{IJ}} \cdot \exp \left(\frac{\gamma_{IJ} \cdot \sigma_{IJ}}{r - a_{IJ} \cdot \sigma_{IJ}} \right) \\ F_{IJ}(X) = -X \\ P_{IJ}(\Delta r) = 1 \\ W_{IJ}(r) = \sqrt{\lambda_{IJ} \cdot \varepsilon_{IJ}} \cdot \exp \left(\frac{\gamma_{IJ} \cdot \sigma_{IJ}}{r - a_{IJ} \cdot \sigma_{IJ}} \right) \\ G_{JIK}(\theta) = \left(\cos \theta + \frac{1}{3} \right)^2 \end{array} \right.$$

F. H. Stillinger and T. A. Weber, Phys. Rev. B 31, 5262 (1985).

Tersoff Potential

The polymorphic potential reduces to original Tersoff potential if user use this polymorphic tabulation:

$$\left\{ \begin{array}{l} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 1 \\ U_{IJ}(r) = \frac{D_{e,IJ}}{S_{IJ} - 1} \exp\left[-\beta_{IJ} \sqrt{2S_{IJ}}(r - r_{e,IJ})\right] \cdot f_{c,IJ}(r) \\ V_{IJ}(r) = \frac{S_{IJ} \cdot D_{e,IJ}}{S_{IJ} - 1} \exp\left[-\beta_{IJ} \sqrt{\frac{2}{S_{IJ}}}(r - r_{e,IJ})\right] \cdot f_{c,IJ}(r) \\ F_{IJ}(X) = (1 + X)^{-\frac{1}{2}} \\ P_{IK}(\Delta r) = \exp[2\mu_{IK} \cdot \Delta r] \\ W_{IK}(r) = f_{c,IK}(r) \\ G_{JIK}(\theta) = \gamma_{IK} \left[1 + \frac{c_{IK}^2}{d_{IK}^2} - \frac{c_{IK}^2}{d_{IK}^2 + (h_{IK} + \cos\theta)^2} \right] \end{array} \right. \quad f_{c,IJ}(r) = \begin{cases} 1, & r \leq r_{s,IJ} \\ \frac{1}{2} + \frac{1}{2} \cos\left[\frac{\pi(r - r_{s,IJ})}{r_{c,IJ} - r_{s,IJ}}\right], & r_{s,IJ} < r < r_{c,IJ} \\ 0, & r \geq r_{c,IJ} \end{cases}$$

J. Tersoff, Phys. Rev. B, 39, 5566 (1989).

Rockett-Tersoff Potential

The polymorphic potential reduces to Rockett-Tersoff potential if user use this polymorphic tabulation:

$$\left\{ \begin{array}{l} \eta_{ij} = \delta_{ij}, \xi_{IJ} = 1 \\ U_{IJ}(r) = \begin{cases} A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r), & r \leq r_{s,1,IJ} \\ A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r) \cdot f_{c,1,IJ}(r), & r_{s,1,IJ} < r < r_{c,1,IJ} \\ 0, & r \geq r_{c,1,IJ} \end{cases} \\ V_{IJ}(r) = \begin{cases} B_{IJ} \cdot \exp(-\lambda_{2,IJ} \cdot r) \cdot f_{c,IJ}(r), & r \leq r_{s,1,IJ} \\ B_{IJ} \cdot \exp(-\lambda_{2,IJ} \cdot r) \cdot f_{c,IJ}(r) + A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r) \cdot [1 - f_{c,1,IJ}(r)], & r_{s,1,IJ} < r < r_{c,1,IJ} \\ B_{IJ} \cdot \exp(-\lambda_{2,IJ} \cdot r) \cdot f_{c,IJ}(r) + A_{IJ} \cdot \exp(-\lambda_{1,IJ} \cdot r) \cdot f_{c,IJ}(r), & r \geq r_{c,1,IJ} \end{cases} \\ F_{IJ}(X) = \left[1 + (\beta_{IJ} \cdot X)^{n_{IJ}} \right]^{-\frac{1}{2n_{IJ}}} \\ P_{IK}(\Delta r) = \exp[\lambda_{3,IK} \cdot \Delta r^3] \\ W_{IK}(r) = f_{c,IK}(r) \\ G_{JK}(\theta) = 1 + \frac{c_{IK}^2}{d_{IK}^2} - \frac{c_{IK}^2}{d_{IK}^2 + (h_{IK} + \cos \theta)^2} \end{array} \right.$$

$f_{c,IJ}(r)$ and $f_{c,1,IJ}(r)$ are two cutoff functions operating at different cutoff ranges, but their format is the same as that in Tersoff potential

EAM Potential

The polymorphic potential reduces to embedded-atom method potential if user use this polymorphic tabulation:

$$\left\{ \begin{array}{l} \eta_{ij} = 1 - \delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}(r) = \phi_{IJ}(r) \\ V_{IJ}(r) = 1 \\ F_{II}(X) = -2F_I(X) \\ P_{IK}(\Delta r) = 1 \\ W_{IK}(r) = f_K(r) \\ G_{JIK}(\theta) = 1 \end{array} \right. \quad \begin{array}{l} \text{where } \phi_{IJ}(r) \text{ is a pair function, } f_J(r) \text{ is} \\ \text{an atomic electron density function,} \\ F_I(X) \text{ is the embedding energy} \\ \text{function, and } X \text{ is used to represent} \\ \text{electron density } (X = \rho). \end{array}$$

Polymorphic TlBr Potential

X. W. Zhou, M. E. Foster, R. Jones, P. Yang, H. Fan, and F. P. Doty, J. Mater. Sci. Res., 4, 15 (2015).

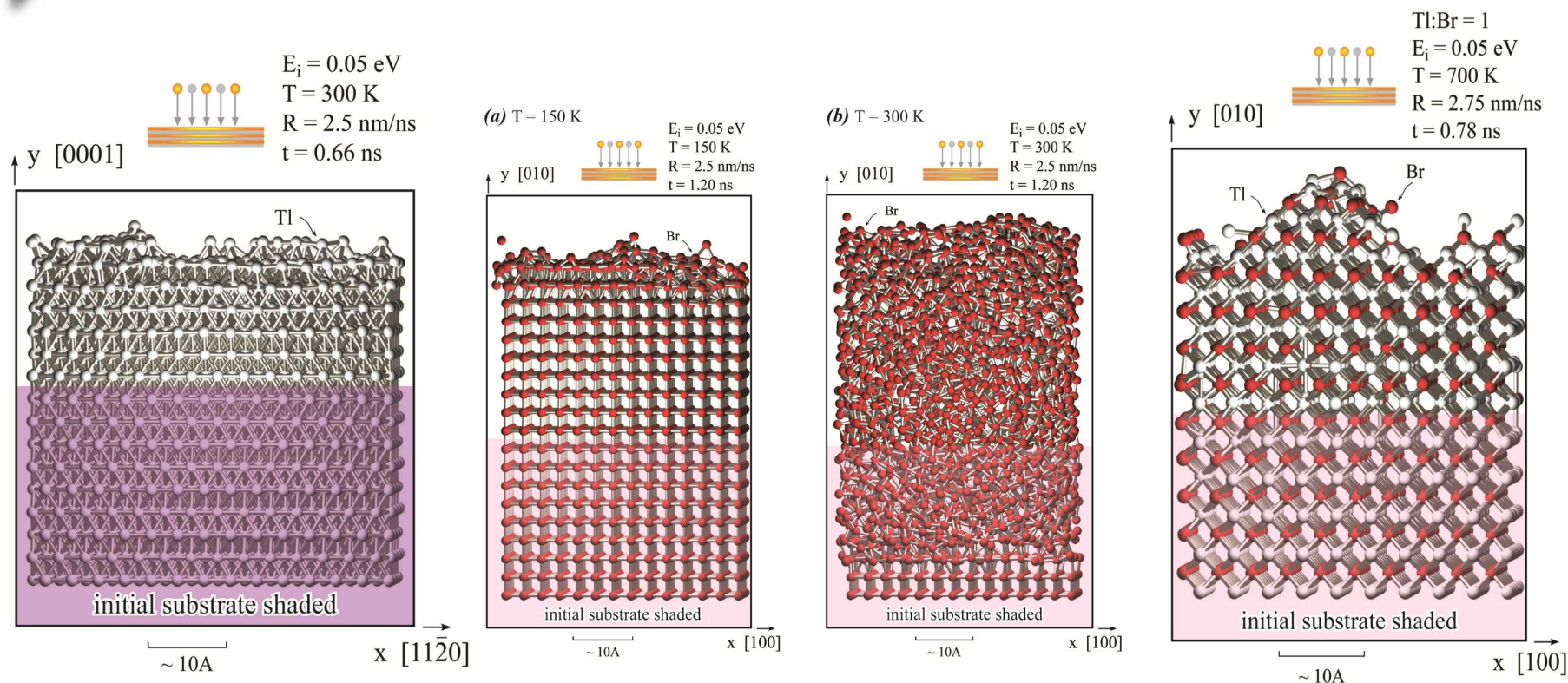
material	structure	MSW			DFT			Exp.		
		a	c	E _c	a	c	E _c	a [25]	c [25]	E _c [26]
Tl	dc	7.180	-----	-0.999	-----	-----	-----	-----	-----	-----
	sc	3.012	-----	-1.800	-----	-----	-----	-----	-----	-----
	bcc	3.854	-----	-1.805	3.868	-----	-2.368	-----	-----	-----
	fcc	4.825	-----	-1.848	4.873	-----	-2.340	-----	-----	-----
	hcp	3.408	5.582	-1.850	3.500	5.581	-2.399	3.450	5.520	-1.850
Br	dc	6.591	-----	-0.731	6.898	-----	-0.961	-----	-----	-----
	fcc	4.878	-----	-0.748	4.464	-----	-1.123	-----	-----	-----
	bcc	3.847	-----	-0.780	3.703	-----	-1.160	-----	-----	-----
	hcp	3.328	5.743	-0.787	-----	-----	-----	-----	-----	-----
	sc	3.004	-----	-0.827	3.006	-----	-1.218	-----	-----	-1.134 [*]
TlBr	wz	4.877	7.964	-1.657	-----	-----	-----	-----	-----	-----
	zb	6.897	-----	-1.657	-----	-----	-----	-----	-----	-----
	NaCl	6.197	-----	-2.239	6.622	-----	-2.866	-----	-----	-----
	CsCl	3.985	-----	-2.389	3.959	-----	-2.881	3.985	-----	-2.389

*: Br-sc is the lowest energy lattice in models. No experimental data is available for the metastable Br-sc phase. Instead, we list the experimental cohesive energy of the lowest energy phase (Br₂-liquid) as a reference.

structure	method	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	B	T _m
Tl (hcp)	MSW	0.240	0.140	0.137	0.242	0.053	0.133	691
	Exp. [27,37]	0.277	0.235	0.187	0.376	0.055	0.239	577
TlBr (CsCl)	MSW	0.275	0.104	0.104	0.275	0.067	0.161	1442
	Exp. [28,38]	0.275	0.104	0.104	0.275	0.067	0.161	753

Growth Simulation Validation

X. W. Zhou, M. E. Foster, R. Jones, P. Yang, H. Fan, and F. P. Doty, J. Mater. Sci. Res., 4, 15 (2015).



Successful growth simulations of Tl, Br, and TlBr validated that the modified SW potential using the polymorphic implementation captures the experimental or model equilibrium phases

Conclusions

1. Simple SW potential enables a rapid parameterization for systems involving many elements;
2. Capturing the correct energy transferability between elements, alloys, and compounds produces robust MD models to enable challenging growth simulations;
3. Conventional SW potentials overestimate elastic constants of elements and are limited to tetrahedral crystals;
4. A modified SW potential can overcome the problems of old SW potential.
5. A polymorphic pair style implemented in LAMMPS allows potentials to be modified without changing the LAMMPS;
6. These new approaches lead to a TlBr model with the CsCl type of compound crystal and simple-cubic type of elemental crystal.