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Towards Modeling III-V Compounds

Preliminary Work on InGaN

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Four Topics

1. Developing a Stillinger-Weber InGaN potential;
2. Preliminary simulations of InGaN growth;
3. Introduction to a polymorphic pairstyle in LAMMPS;
4. MD simulations of substitutional diffusion in InGaN.

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Why InGaN as the 1st Case for III-V?

1. Solid-state lighting is currently limited by the "green gap";
2. Increasing In content $In_xGa_{1-x}N$ leads to green light emission;
3. Lattice mismatch defects, phase separation, and piezoelectric/polarization lead to low efficiency for green light emission;
4. MD simulations can help optimize the materials via nanostructuring.

A Stillinger-Weber InGaN potential

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

$$\begin{cases} V_{IJ}^{R}(r_{ij}) - V_{IJ}^{A}(r_{ij}) = A_{IJ}\cdot\varepsilon_{IJ}\cdot\left(\dfrac{\sigma_{IJ}}{r}\right)^{q}\cdot\left[B_{IJ}\left(\dfrac{\sigma_{IJ}}{r}\right)^{p-q} - 1\right]\cdot\exp\left(\dfrac{\sigma_{IJ}}{r - a_{IJ}\cdot\sigma_{IJ}}\right) \\ u_{IJ}(r) = \sqrt{\lambda_{IJ}\cdot\varepsilon_{IJ}}\cdot\exp\left(\dfrac{\gamma_{IJ}\cdot\sigma_{IJ}}{r - a_{IJ}\cdot\sigma_{IJ}}\right) \end{cases}$$

Parameters

pair ij	ε	σ	a	A	B	λ	γ
InIn	2.449833	1.938334	1.622254	7.9170	0.970030	32.5	1.2
GaGa	2.926384	1.759683	1.607120	7.9170	0.995618	32.5	1.2
NN	4.420186	1.726983	1.630012	7.0496	0.969832	32.5	1.2
InN	2.202060	1.852758	1.799906	7.0496	0.761521	32.5	1.2
GaN	2.289660	1.715927	1.799677	7.0496	0.641026	32.5	1.2
InGa	1.984319	1.769153	1.710916	7.0496	0.865982	32.5	1.2

Energies (experimental data from Barin, VCH, 1993)

	In	Ga	N	InN	GaN
prediction	-2.4894	-2.7930	-3.8382	-3.7702	-4.4012
experiment	-2.4894	-2.7930	-3.8382*	-3.7702	-4.4012

Preliminary Simulations of $In_xGa_{1-x}N$ Growth

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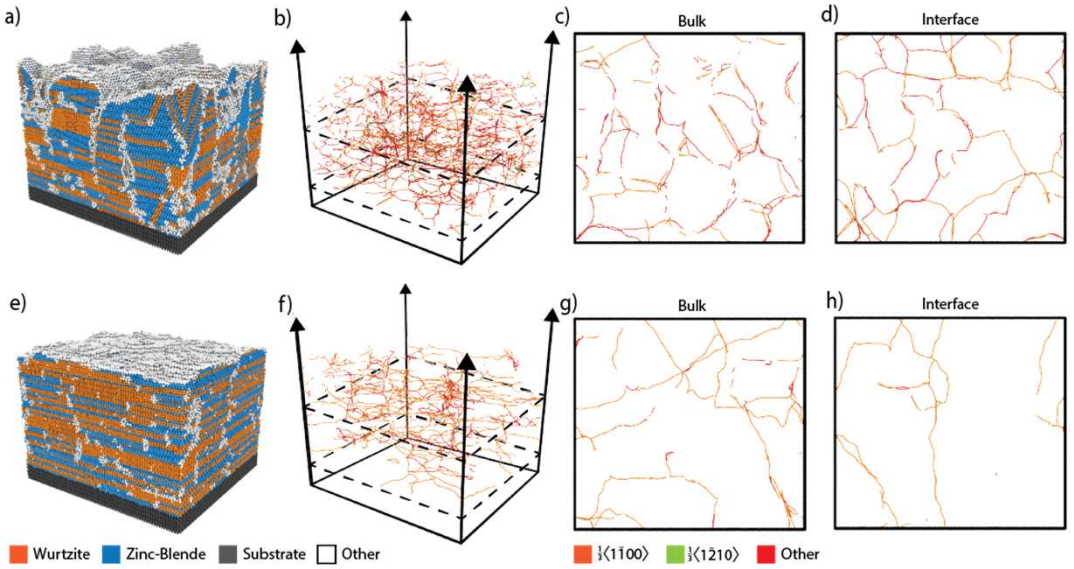
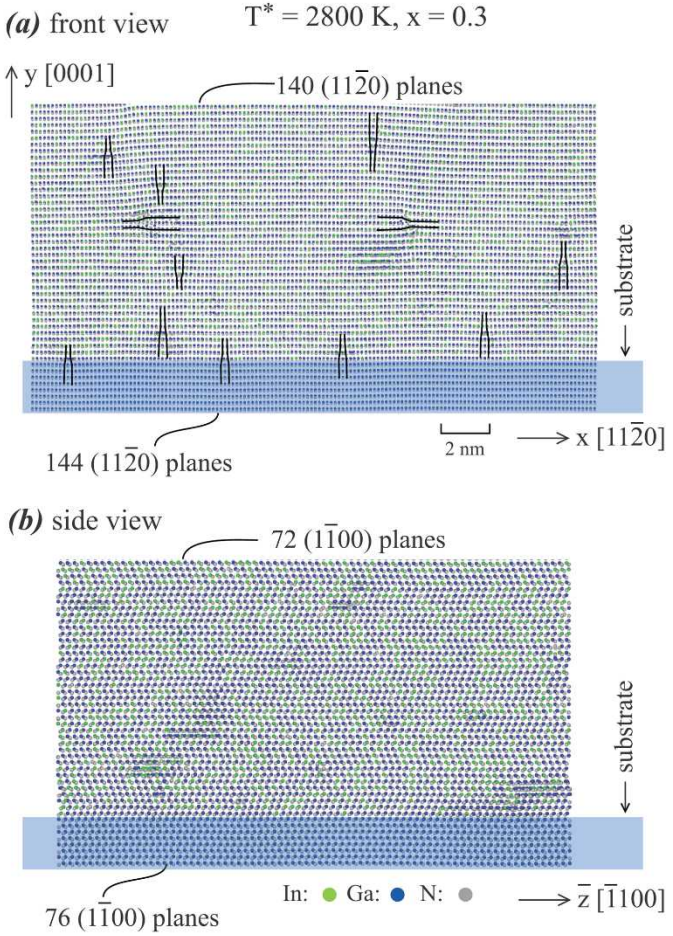
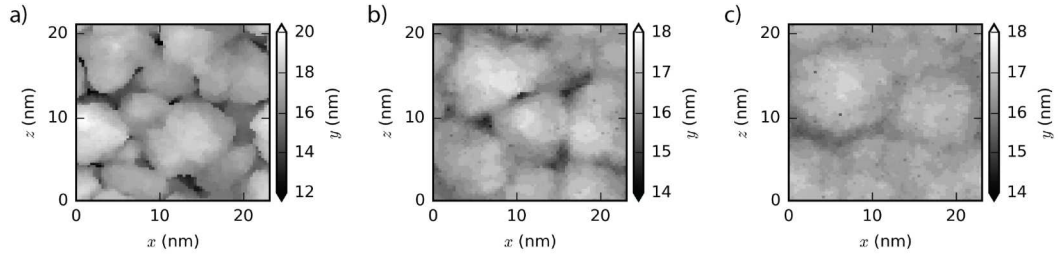
Microstructure Analysis



Dislocation Configuration Analysis



Surface Roughness Analysis



Why SW Potential?

3014 citations as compared to 2103 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.

Issues:

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

F. H. Stillinger and T. A. Weber, Phys. Rev. B 31, 5262 (1985).
J. Tersoff, Phys. Rev. B, 39, 5566 (1989).

SW Potential Improvement

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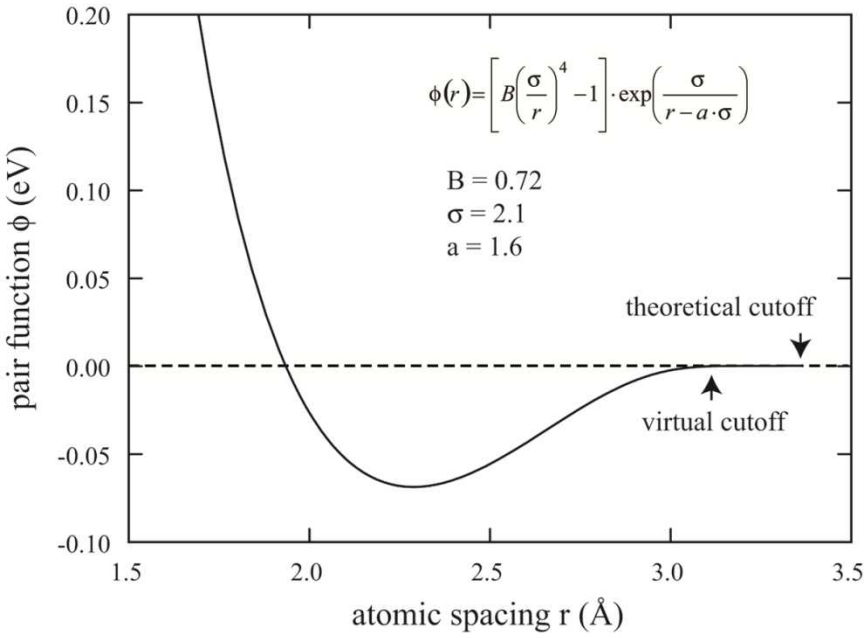
Issue

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 Pairstyle in LAMMPS

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

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}\left(r_{ik}\right)\cdot G_{JIK}\left(\theta_{jik}\right)\cdot P_{IK}\left(\Delta r_{jik}\right)$$

$\Delta r_{jik} = r_{ij} - \xi_{IJ}\cdot r_{ik}$ ξ_{IJ}: parameter

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

$\eta_{ij} = \delta_{ij}$ or $\eta_{ij} = 1- \delta_{ij}$ (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, …)

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

Modified SW Potential

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

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

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}(r_{ik})\cdot G_{JIK}(\theta_{jik})\cdot P_{IK}(\Delta r_{jik})$$

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

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

SW Potential

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

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}\left(r_{ik}\right)\cdot G_{JIK}\left(\theta_{jik}\right)\cdot P_{IK}\left(\Delta r_{jik}\right)$$

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

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

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

Tersoff Potential

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

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}\left(r_{ik}\right)\cdot G_{JIK}\left(\theta_{jik}\right)\cdot P_{IK}\left(\Delta r_{jik}\right)$$

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

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

$$f_{c,IJ}(r) = \begin{cases} 1, & r \le r_{s,IJ} \\ \dfrac{1}{2}+\dfrac{1}{2}\cos\left[\dfrac{\pi(r-r_{s,IJ})}{r_{c,IJ}-r_{s,IJ}}\right], & r_{s,IJ} < r < r_{c,IJ} \\ 0, & r \ge r_{c,IJ} \end{cases}$$

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

Rockett-Tersoff Potential

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

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}\left(r_{ik}\right)\cdot G_{JIK}\left(\theta_{jik}\right)\cdot P_{IK}\left(\Delta r_{jik}\right)$$

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

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

$f_{c,IJ}(r)$ 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

J. Wang, and A. Rockett, Phys. Rev. B 43, 12571 (1991).

EAM Potential

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

$$X_{ij} = \sum_{\substack{k=i_1 \\ k\neq i,j}}^{i_N} W_{IK}\left(r_{ik}\right)\cdot G_{JIK}\left(\theta_{jik}\right)\cdot P_{IK}\left(\Delta r_{jik}\right)$$

$$\begin{cases} \eta_{ij} = 1-\delta_{ij}, \xi_{IJ} = 0 \\ U_{IJ}\left(r\right) = \phi_{IJ}\left(r\right) \\ V_{IJ}\left(r\right) = 1 \\ F_{II}\left(X\right) = -2F_{I}\left(X\right) \\ P_{IK}\left(\Delta r\right) = 1 \\ W_{IK}\left(r\right) = f_{K}\left(r\right) \\ G_{JIK}\left(\theta\right) = 1 \end{cases}$$

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

where $\phi_{IJ}(r)$ is a pair function, $f_J(r)$ is an atomic electron density function, $F_I(X)$ is the embedding energy function, and X is used to represent electron density ($X = \rho$).

M. S. Daw, and M. I. Baskes, Phys. Rev. B, 29, 6443 (1984).

Polymorphic TlBr Potential

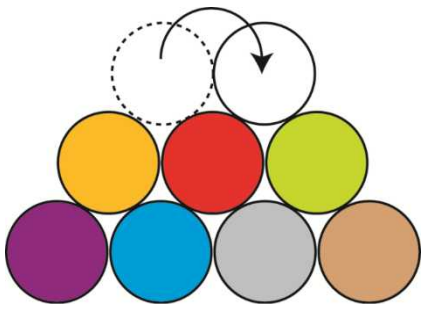
1. The polymorphic pairstyle of a modified SW potential has been successfully applied for TlBr whose crystal structure is B2;
2. Try it out: the polymorphic pairstyle may be faster than sw or tersoff pairstyles.

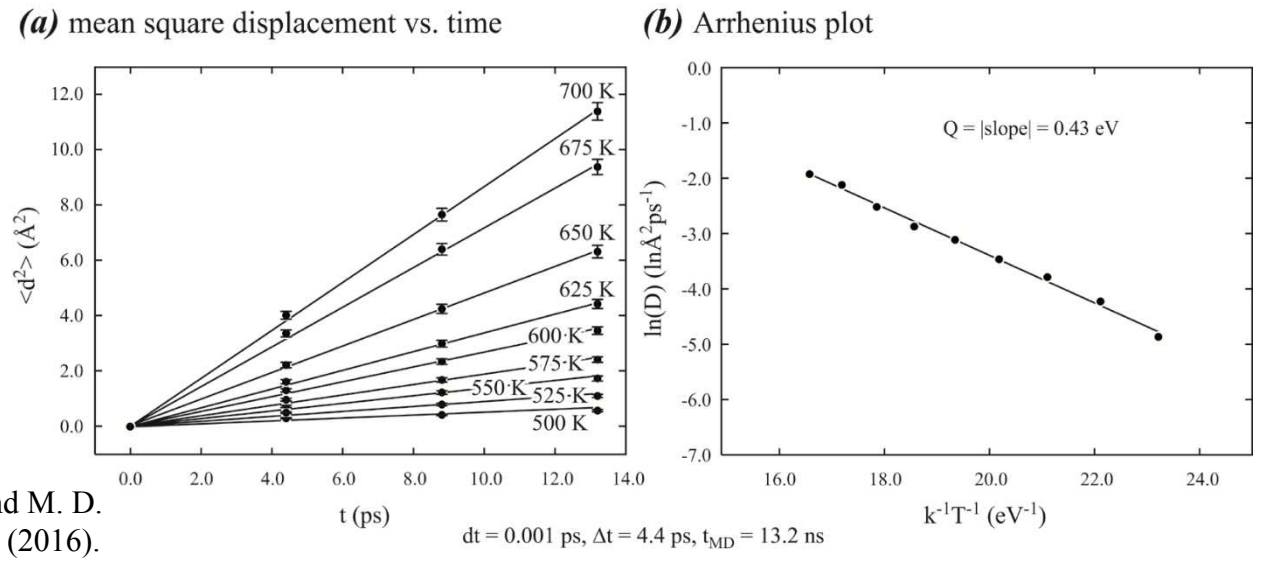
X. W. Zhou, M. E. Foster, R. Jones, P. Yang, H. Fan, and F. P. Doty, J. Mater. Sci. Res., 4, 15 (2015).

MD Simulation of Diffusion

1. Conventionally done at 0 K for atomic jumps;
2. Huge number of atomic jumps with alloys and defects;
3. Unclear about the overall diffusion behavior;
4. No mass effect;
5. Solution: Arrhenius fit to MD diffusivities at different T;
6. Successfully applied for interstitial diffusion of H in Al.

MD Constructed Arrhenius Plot of H in Al

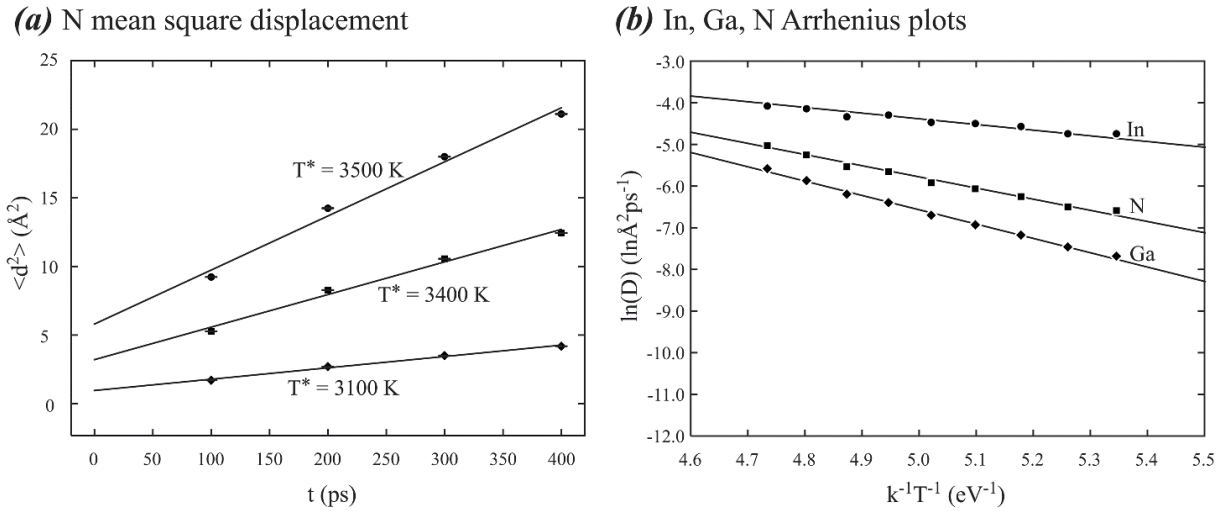




X. W. Zhou, F. El Gabaly, V. Stavila, and M. D. Allendorf, J. Phys. Chem. C, 120, 7500 (2016).

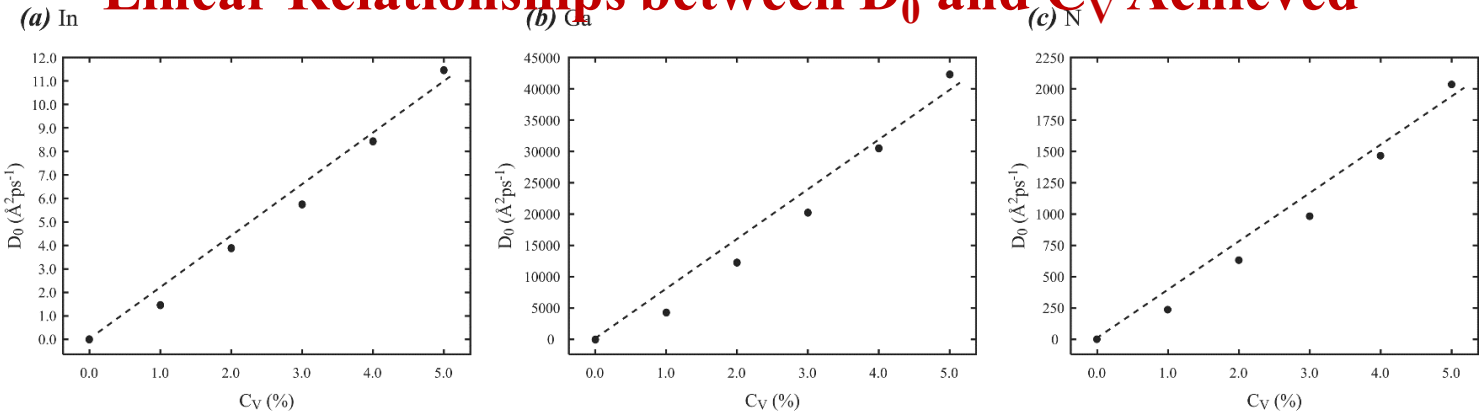
MD Simulation of Substitutional Diffusion in InGaN

MD Constructed Arrhenius Plot of at a Given C_V



t = 1000 ns, Δt = 0.1 ns, Cv = 5%

Linear Relationships between D_0 and C_V Achieved



Long simulation time is the key!

Conclusions

1. Simple SW potential has been developed for InGaN;
2. Preliminary MD simulations of $In_xGa_{1-x}N$ growth already provided understanding of defects;
3. With the polymorphic pairstyle, researchers can now freely modify many potential formats without changing MD codes;
4. MD has become powerful tool to study diffusion regardless complexity of systems.