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Anharmonic free energy of lattice vibrations in fcc crystals from a mean-field bond lattice (using *ab-initio* potentials)

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Motivation: Anharmonic bond distribution in bulk FCC crystals

- **Free energy** -- key quantity to determine finite temperature material properties

most popular approximation methods →

- Harmonic (HA)
- Quasi-harmonic (QHA)
- Thermodynamic integration (TI)

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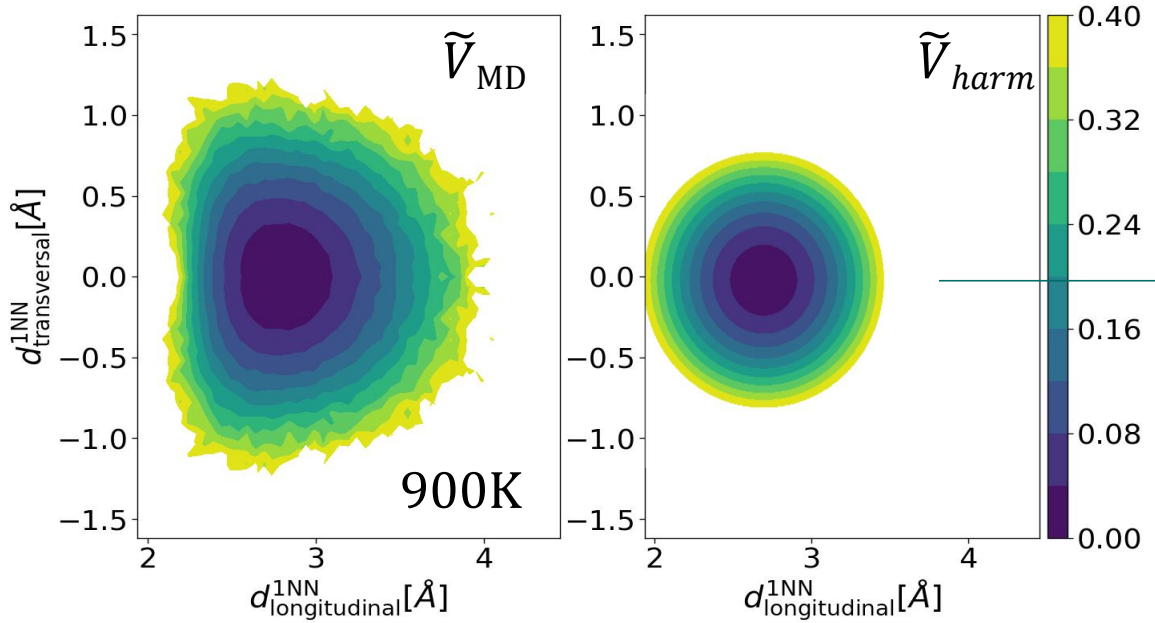
- ***Glensk et al.**** --> Finite temperature **bond density** -- **anharmonic** along the **longitudinal axis**



bond length, $d^{1\mathrm{NN}} = |\mathbf{R}_{\mathrm{l}} - \mathbf{R}_{\mathrm{i}},| \quad \mathrm{l} \in [1, \mathrm{m}]$

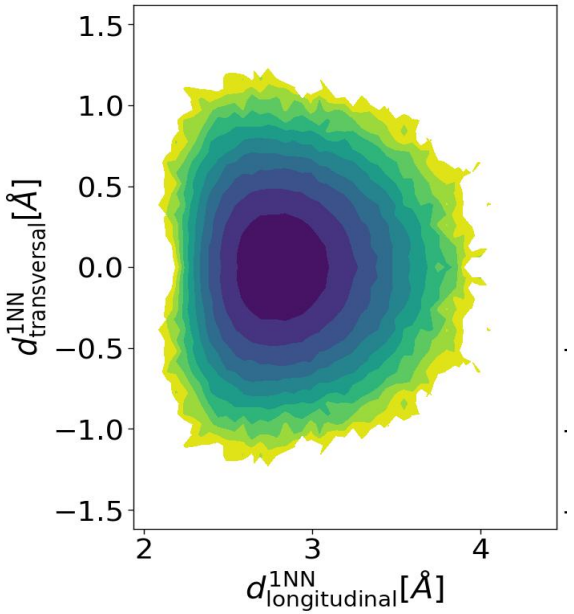
effective potential, $\widetilde{V} = -k_B T ln\rho(d^{1\mathrm{NN}})$

→ HA & QHA cannot reproduce this anharmonic bond density

*Glensk et al., Physical Review Letters 114, 195901 (2015)

Anharmonic bond model: Local approximation (LA)

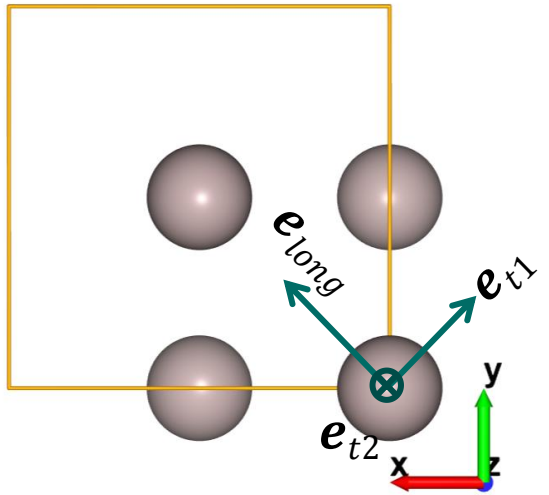
- ***Glensk et al.*** --> simple **anharmonic nearest-neighbor bond model** --> captures bond density anharmonicity



➢perform a few $\mathrm{T} = 0\mathrm{K}$ calculations along $\boldsymbol{e}_{long}$, $\boldsymbol{e}_{t1}$ and $\boldsymbol{e}_{t2}$

➢$F_a(u) = \boldsymbol{F}_{\mathbf{j}}^{0\mathrm{K}}(\mathrm{u}\boldsymbol{e}) \cdot \boldsymbol{e}, \quad V_a(u) = \int_0^u F_a(u')\,du'$

➢$E_{\mathrm{LA}} = \frac{1}{2}\sum_j^N \sum_l^m [V_{long}(u_{lj}) + V_{t1}(u_{t1}) + V_{t2}(u_{t2})]$



✓ meV/atom free energy accuracy to DFT!

✓ better reference for TI than QHA

✖ still requires MD trajectories

Objectives

Build an analytical surrogate model to estimate anharmonic free energy that is

- self-consistent and robust
- requires no MD trajectories
- with a computational cost comparable to the harmonic models
- gives meV/atom free energies compared to DFT TI

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Mean-field bond lattice model*

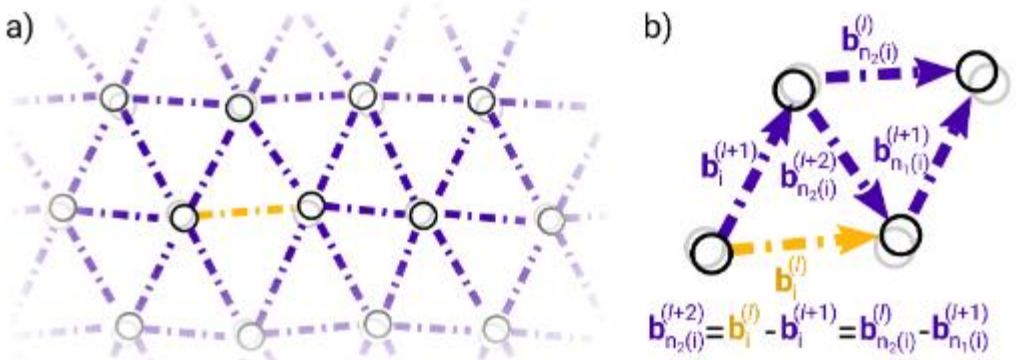
*Swinburne et al., Physical Review B, 102, 100101(R) (2020)

Bond lattice thermodynamics

- Consider a crystal with N atoms with coordinates $\{\mathbf{R}_i\}_{i=1}^{i=N}$

- Each atom has m nearest neighbour bond vectors,

$$\mathbf{b}_i^{(l)} \equiv \mathbf{R}_{l(i)} - \mathbf{R}_i \text{ where l} \in [1, m]$$



- If we impose the following constraint:

$$\mathbf{b}_i^{(l)} - \mathbf{b}_{n_k(i)}^{(l)} = \mathbf{b}_i^{(k)} - \mathbf{b}_{n_l(i)}^{(k)}$$

which enforces zero net displacement, we get a bond lattice

- Total energy $\mathrm{U}(\{\mathbf{b}\}) = \frac{1}{2}\sum_{i=1}^{N}\sum_{l=1}^{m} V_l(\mathbf{b}_i^{(l)})$ where $V_l(\mathbf{b}_i^{(l)})$ is a bonding potential (Morse, EAM etc.)

Bond density for an FCC crystal

- At temperature T, and strain ϵ, the **total energy per atom** is

$$\mathrm{U}(\epsilon, T) = \frac{1}{2}\sum_{l}\int V_l\left(\mathbf{b}^{(l)}\right)\rho_{1,l}\left(\mathbf{b}^{(l)}, \epsilon,\ T\right) d\mathbf{b}$$

where $\rho_{1,l}\left(\mathbf{b}^{(l)}, \epsilon,\ T\right)$ is the bond density and $\widetilde{V} = -\ k_B T ln\rho_{1,l}\left(\mathbf{b}^{(l)}, \epsilon,\ T\right)$ the effective potential

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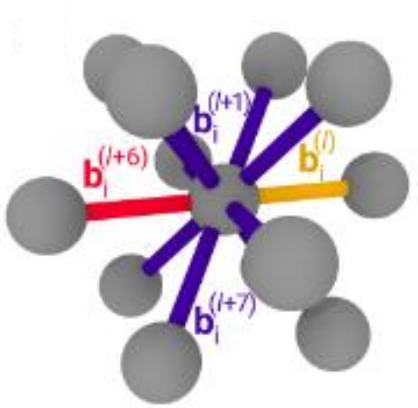

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- For an **FCC crystal**, m=12, all bonds are equivalent $\Rightarrow \mathbf{a}_l^{\epsilon} = \mathbf{G}_{l,k}\mathbf{a}_k^{\epsilon}$

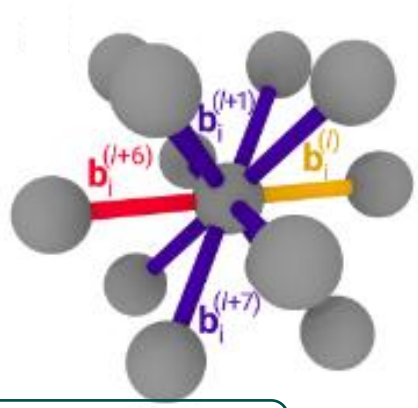
  - $V_l\left(\mathbf{b}^{(l)}\right) = V_1(\mathbf{G}_{1,l}\mathbf{b}^{(l)})$
  - $\rho_{1,l}\left(\mathbf{b}^{(l)}, \epsilon,\ T\right) = \rho_1(\mathbf{G}_{1,l}\mathbf{b}^{(l)},\ \epsilon, T)$

$\mathbf{a}_l$ = primitive lattice vector
$\mathbf{G}_{l,k}$= symmetry operation

and so, $U_{fcc}^{ah}(\epsilon, T) = 6\int V_1(\mathbf{b})\rho_1(\mathbf{b}, \epsilon,\ T)\, d\mathbf{b} - \frac{3}{2}k_{\mathrm{B}}T$ and $F_{fcc}^{ah}(\epsilon, T) = T\int_0^T U^{ah}(\epsilon, T')/(T')^2 dT'$

Mean-field of a bond lattice

- For bonding potential $V_l\left(\mathbf{b}^{(l)}\right) = D\left(1 - \exp\left(-\alpha\left(\mathbf{b}^{(l)} - \mathbf{a}_l\right)\right)\right)$ → **Morse** potential



apply this mean-field approximation: $\mathbf{b}_i^{(l)} - \mathbf{b}_i^{(k)} = \left\langle \mathbf{b}^{(l)} \right\rangle - \left\langle \mathbf{b}^{(k)} \right\rangle = \mathbf{a}_l^{\epsilon} - \mathbf{a}_k^{\epsilon}$

Mean-field effective potential $\widetilde{V}_{mf}(\mathbf{b},\, \epsilon) = \frac{1}{2}\sum_l^m V_l(\mathbf{b} + \mathbf{a}_l^{\epsilon} - \mathbf{a}_1) = \frac{1}{2}\sum_{l=1}^{12} V_l(\boldsymbol{G}_{\mathbf{1},\boldsymbol{l}}(\mathbf{b} + \mathbf{a}_1^{\epsilon}) - \mathbf{a}_1^{\epsilon})$

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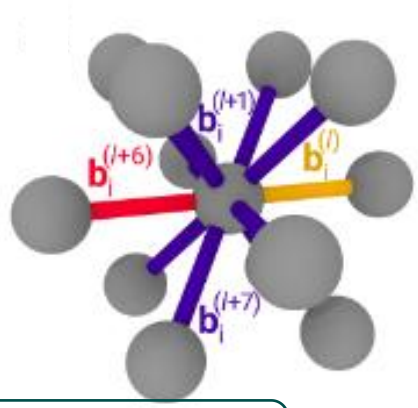

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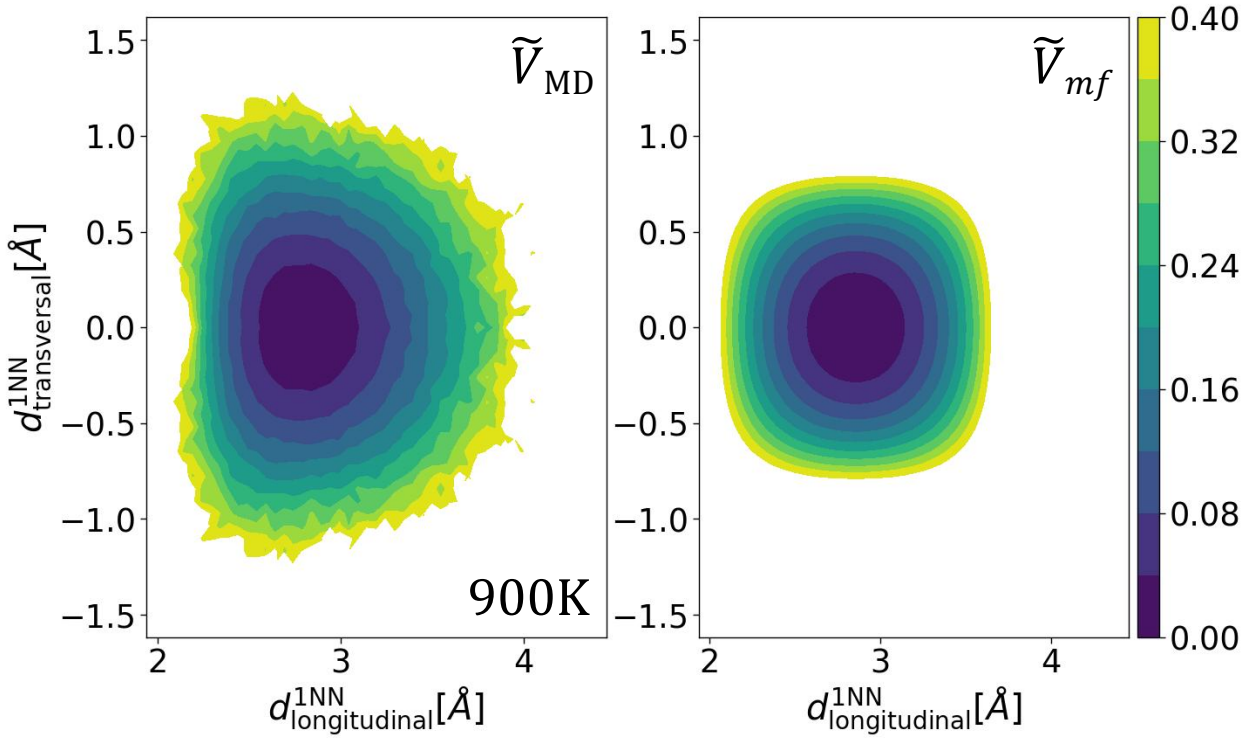
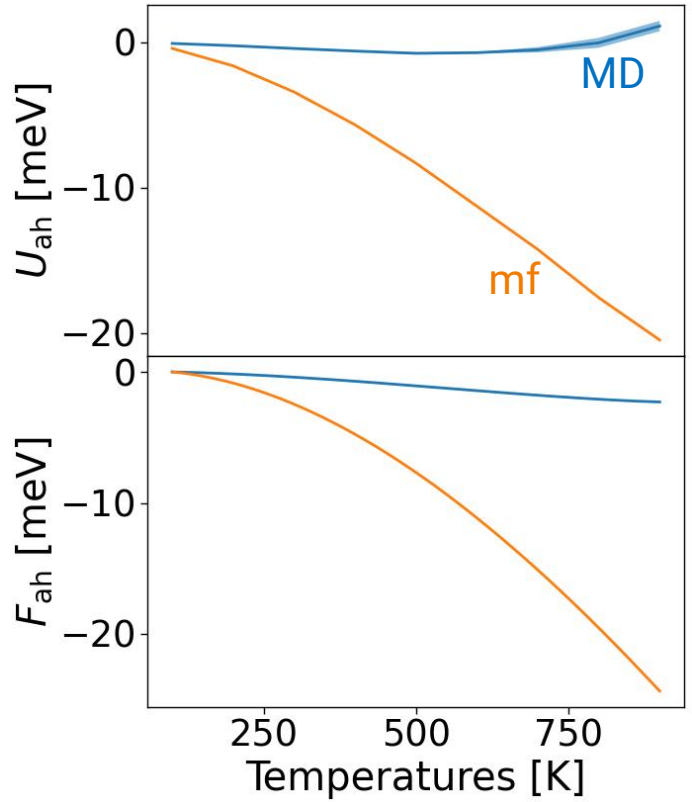
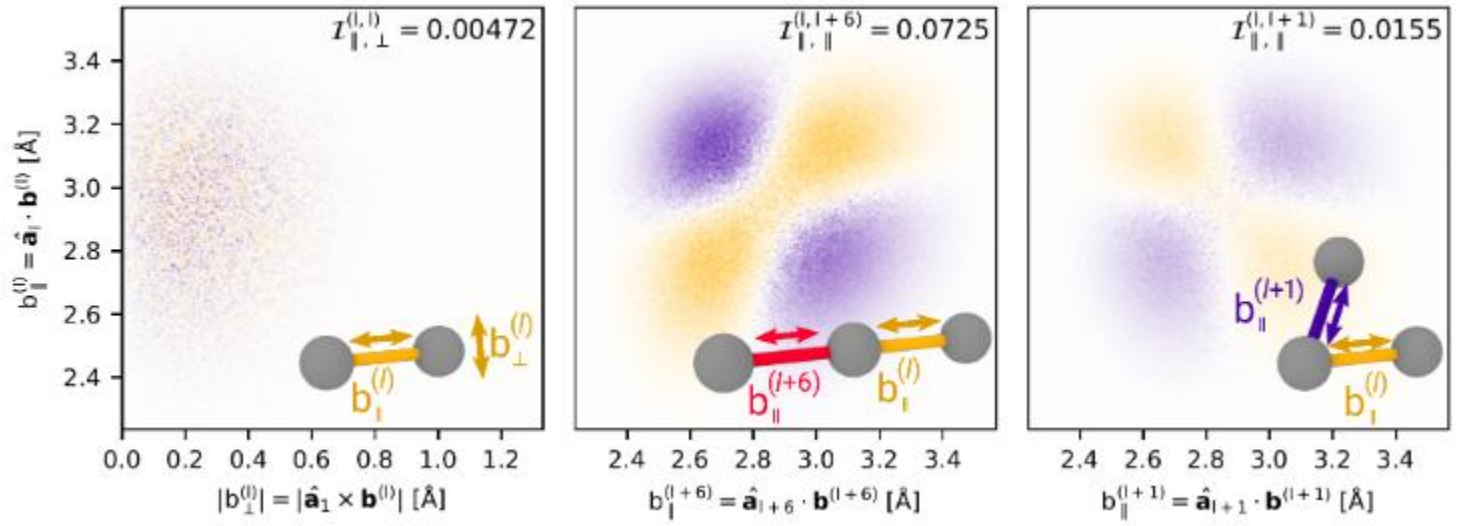


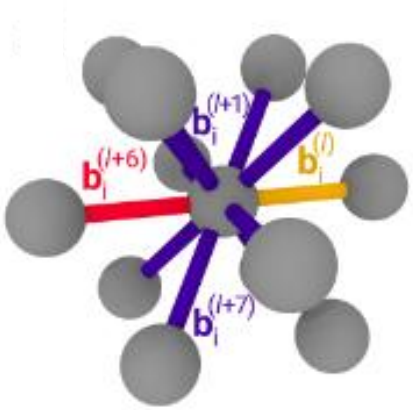


‘Correlated’ mean-field of a bond lattice

Bond pair correlation analysis from the MD run reveals:

- $\mathbf{b}_{\parallel}^{(l)}$, $\mathbf{b}_{\perp}^{(l)}$, are essentially uncorrelated
- $\mathbf{b}_{\parallel}^{(l)}$, $\mathbf{b}_{\parallel}^{(l+6)}$, anti-parallel bond pairs show significantly larger correlation





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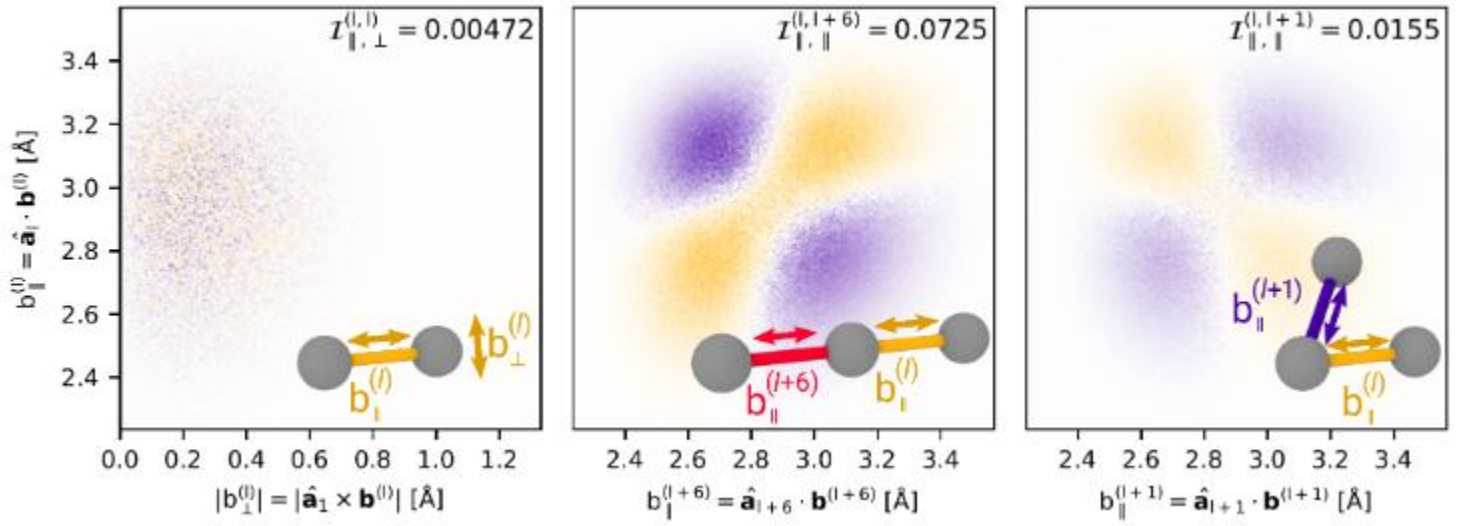

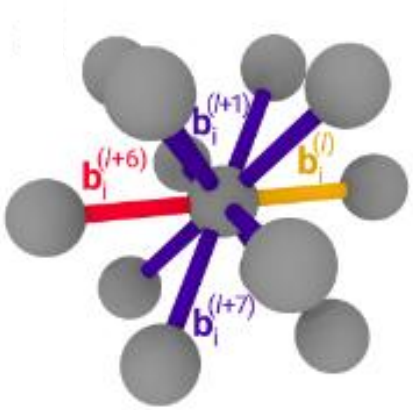

Correlated mean-field approximation: $\mathbf{b}_i^{(l)} - \mathbf{b}_i^{(k)} = \mathbf{a}_l^{\epsilon} - \mathbf{a}_{\mathrm{k}}^{\epsilon}, \quad k \neq l$

‘Correlated’ mean-field model

$$\mathbf{b}_i^{(l)} - \mathbf{b}_i^{(k)} = \mathbf{a}_l^{\epsilon} - \mathbf{a}_{\mathrm{k}}^{\epsilon}, \quad k \neq l$$

constraint that ensures $\langle \boldsymbol{b} \rangle = \boldsymbol{a}_1^{\epsilon}$ at a temperature T

Correlated MF effective potential

$$\widetilde{V}_{mfc}(\mathbf{b}, \epsilon, T) = \widetilde{V}_{mf}(\mathbf{b}, \epsilon) + \frac{1}{2}[V_1(\mathbf{b}) - V_7(\mathbf{b} - 2\mathbf{a}_l^{\epsilon})] + \lambda(\epsilon, T)\hat{\mathbf{a}}_1 \cdot \mathbf{b}$$

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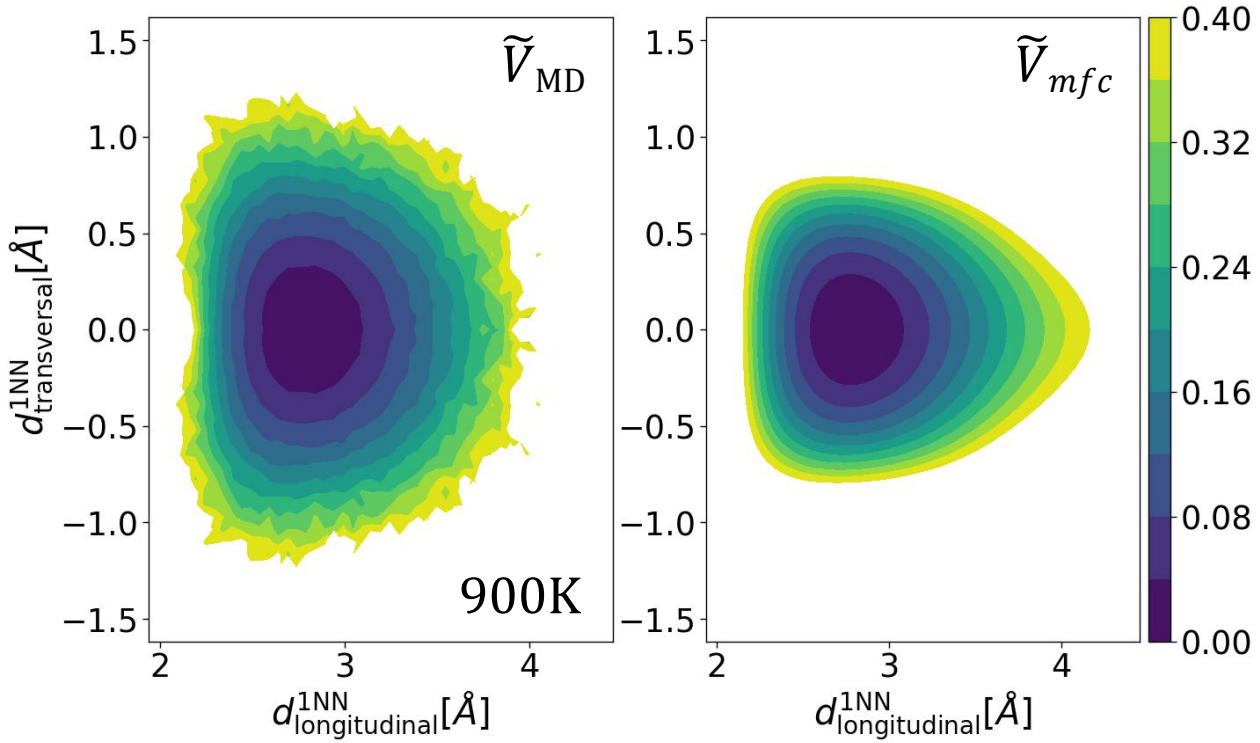

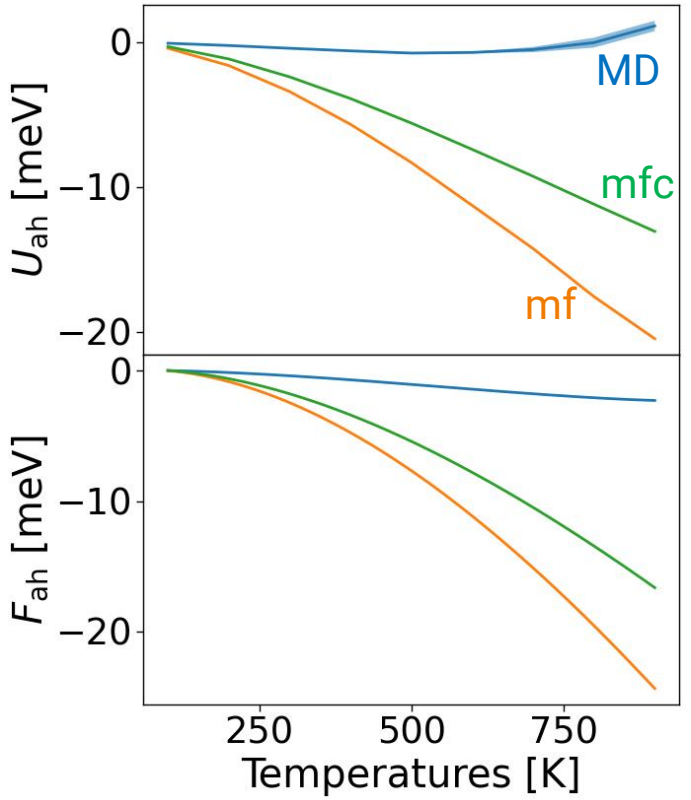

Virial temperature correction

Virial temperature $T_{vir}^{mfc}(T) \equiv \frac{2}{k_B}\int (\mathbf{b}-\mathbf{a}_1^{\epsilon})\cdot\nabla V_1(\mathbf{b})\rho_1^{mfc}(\mathbf{b},\epsilon,T)\cdot d\mathbf{b}$ → $T_{vir}^{mfc}(T)$ may $\neq T$

- optimize an **effective temperature** $\widetilde{T}$: $T_{vir}^{mfc}(\widetilde{T}) = T$
- **virial temperature corrected MFC effective potential** $\widetilde{V}_{mfcv}(\mathbf{b},\ \epsilon, T) = \widetilde{V}_{mfc}(\mathbf{b},\ \epsilon, \widetilde{T})$

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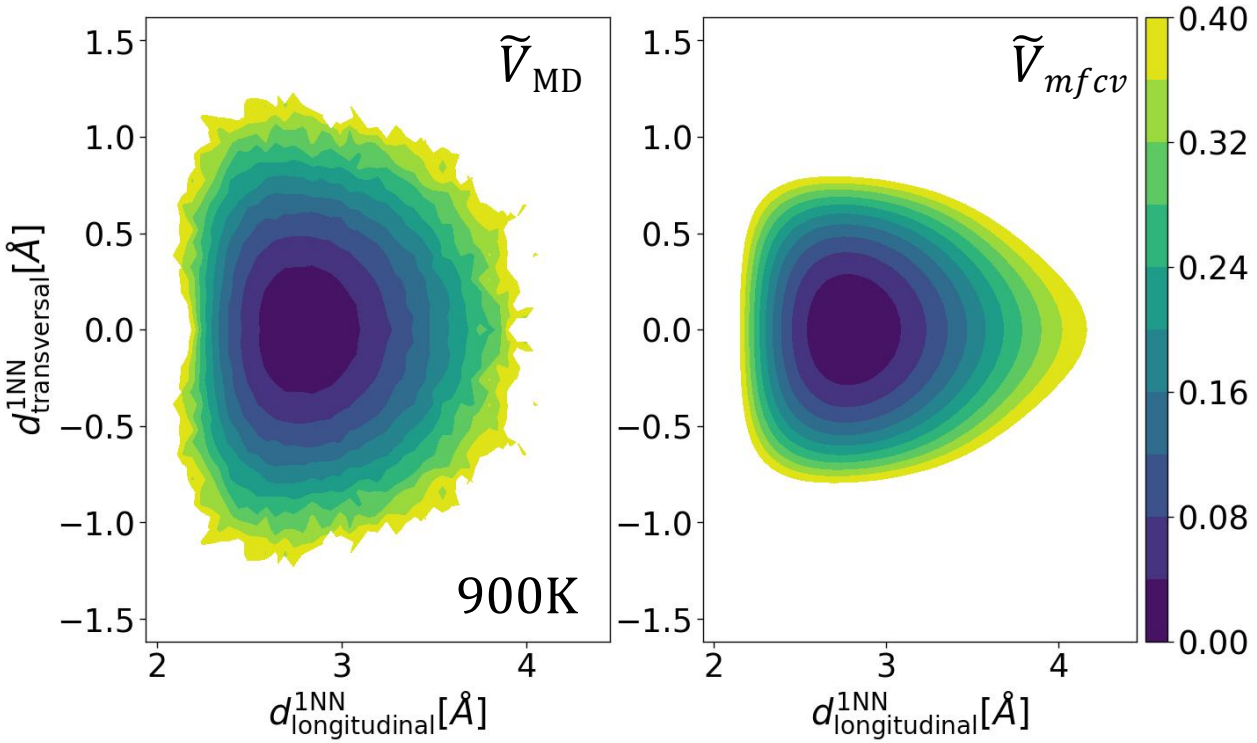
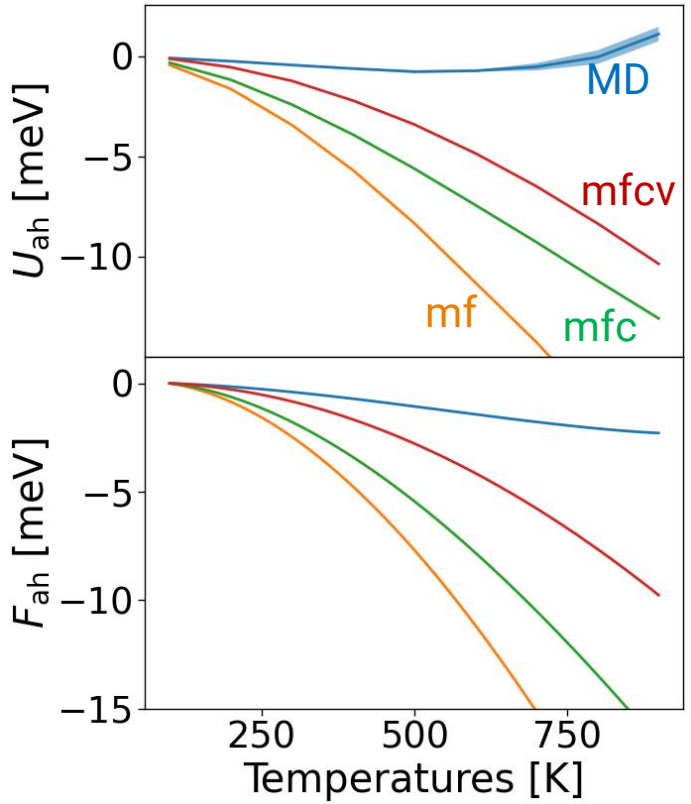




Zero virial pressure -- finite strain

Virial pressure $P_{vir}^{mfc}(T,\epsilon) \equiv \frac{\rho_0}{(1+\epsilon)^d}\left(k_{\mathrm{B}}T + \frac{m}{d}\langle \mathbf{a}_1^{\epsilon} \cdot \boldsymbol{\nabla} V_1 \rangle\right)$

- Further approximate that the model is **formally complete when virial pressure at $\widetilde{T}$ is 0.**
- finite strain mean-field approximation $\mathbf{b}_i^{(l)} - \mathbf{b}_i^{(k)} = (\mathbf{a}_l^{\epsilon} - \mathbf{a}_{\mathrm{k}}^{\epsilon})(1+\alpha),\ \ k \neq l$

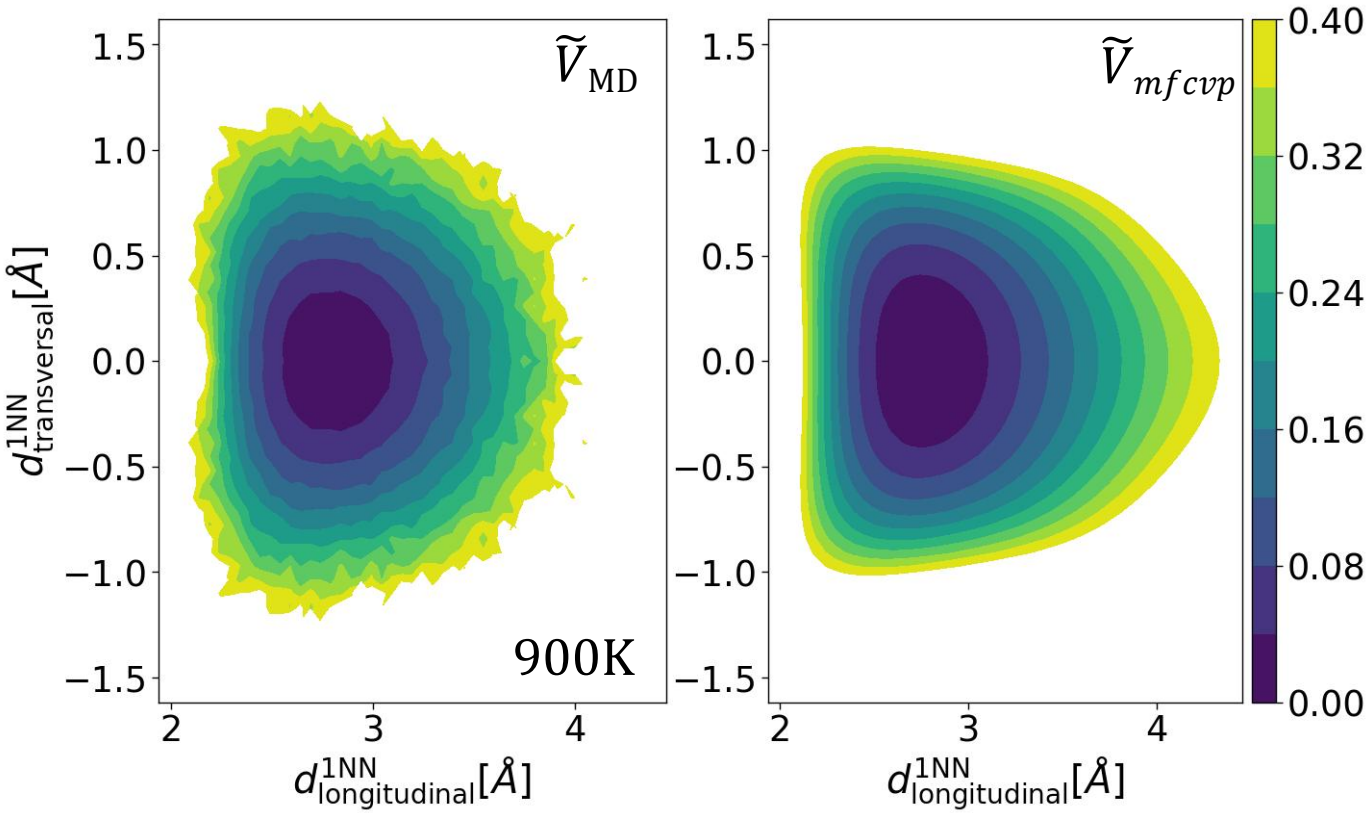
  such that $\alpha(\widetilde{T}) = \epsilon(\widetilde{T})$ when $P_{vir}^{mfc}(\widetilde{T},\epsilon) = 0$
- Mean-field effective potential changes to $\widetilde{V}_{mf}(\mathbf{b},\ \epsilon, \widetilde{T}) = \frac{1}{2}\sum_l^m V_l(\mathbf{b} + (\mathbf{a}_l^{\epsilon} - \mathbf{a}_1)(1+\alpha(\widetilde{T}))$

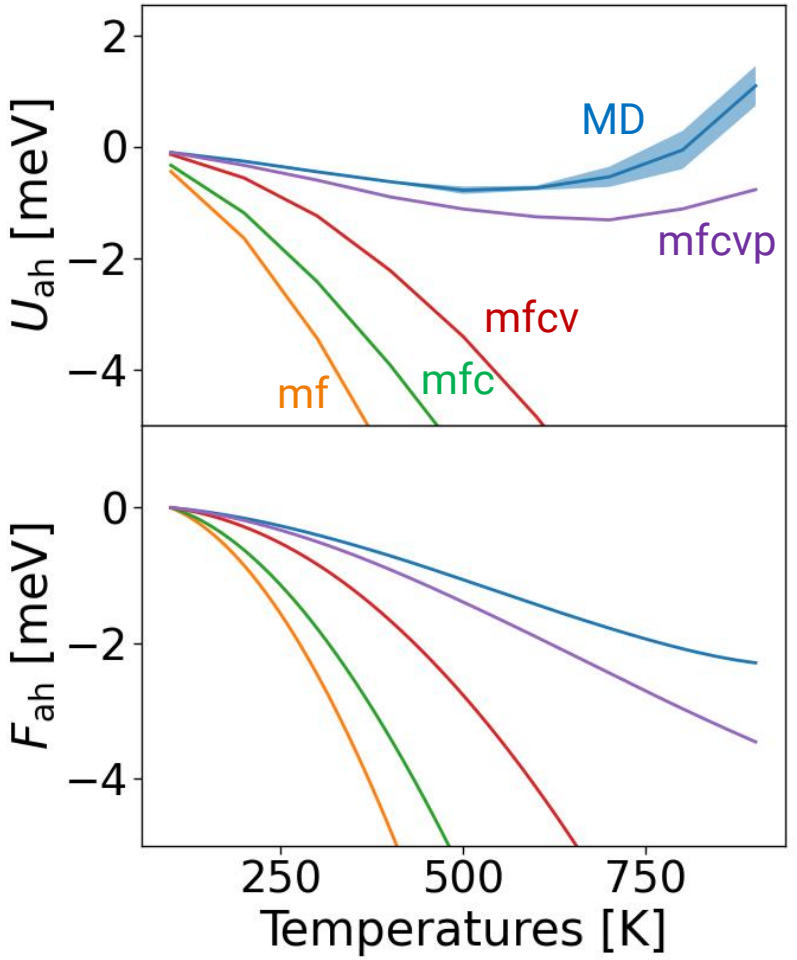
New optimization: for any T, find $\widetilde{T}$, $\alpha(\widetilde{T})$ while ensuring:

- $P_{vir}^{mfc}(\widetilde{T},\epsilon) = 0$
- $T_{vir}^{mfc}(\widetilde{T},\epsilon,\alpha(\widetilde{T})) = T$
- $\alpha(\widetilde{T}) = \epsilon(\widetilde{T})$

Zero virial pressure, temperature corrected model

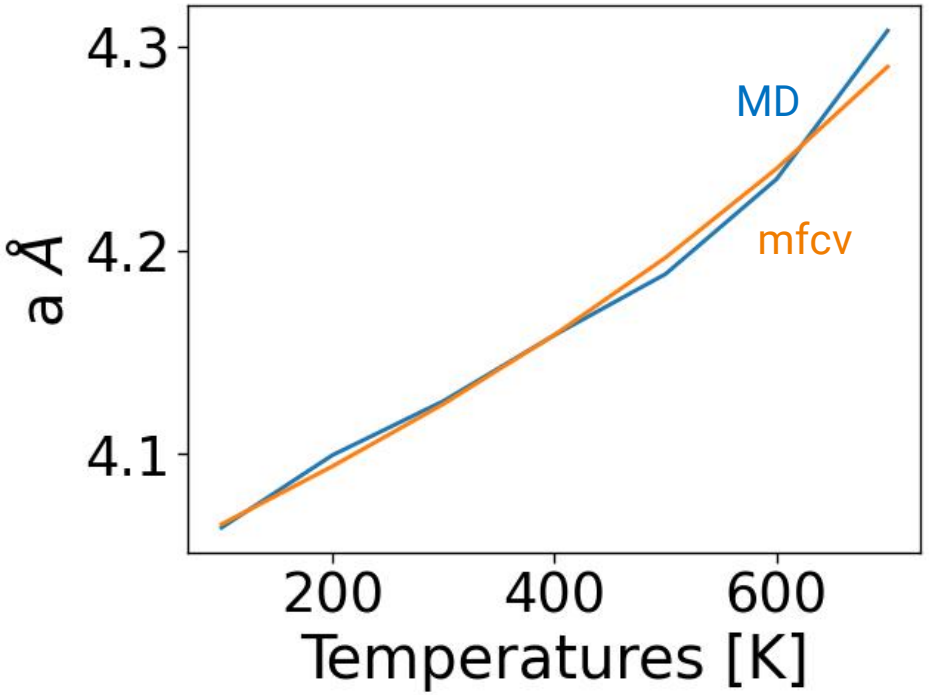
Full virial corrected MFC effective potential: $\widetilde{V}_{mfcvp}(\mathbf{b},\ \epsilon, T) = \widetilde{V}_{mfc}\left(\mathbf{b},\ \epsilon, \widetilde{T}, \alpha(\widetilde{T})\right)$

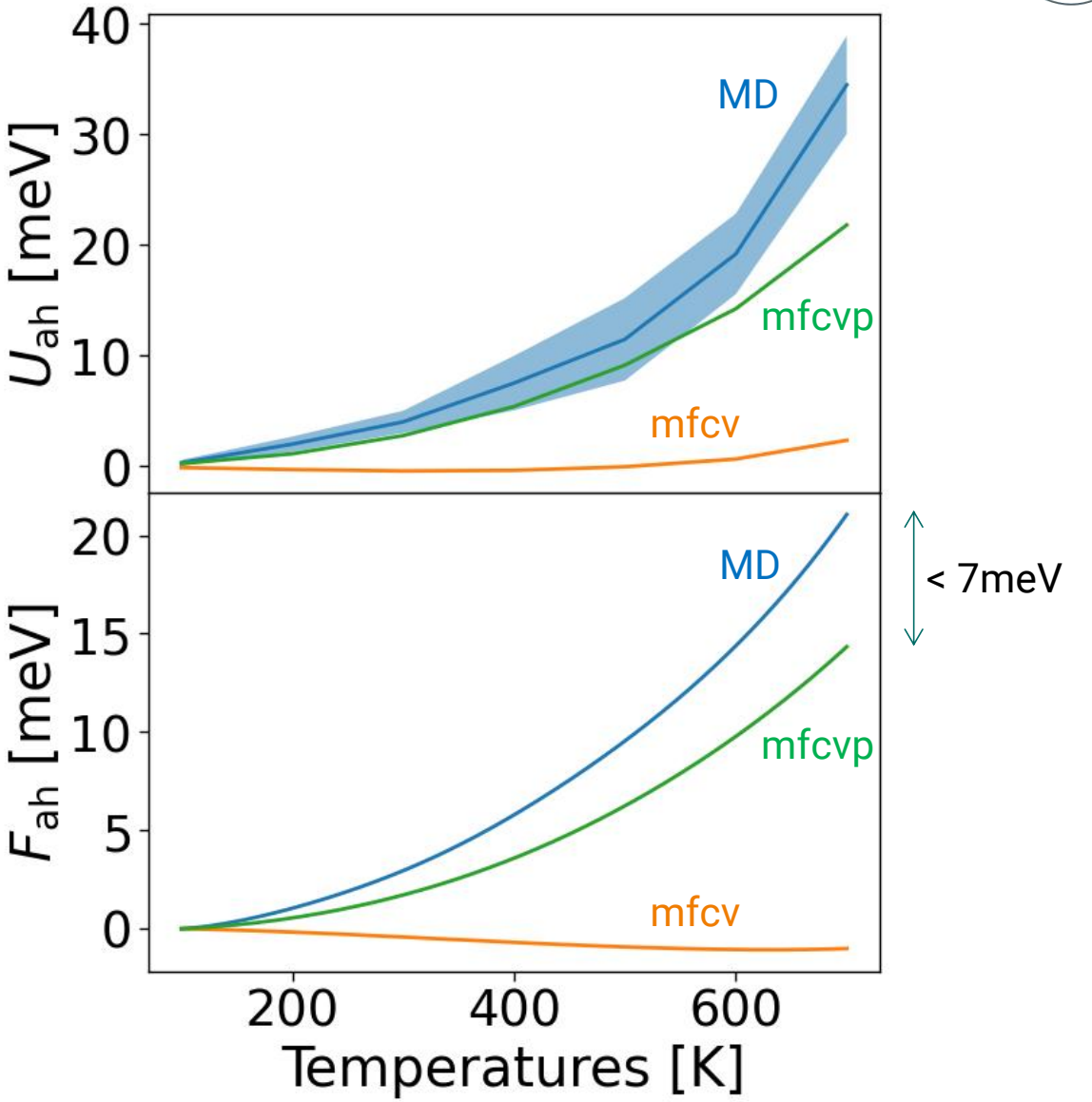




Mean-field bond lattice model vs. zero pressure MD

For $P_{vir}^{mfc}(\widetilde{T}, \epsilon) = 0$,

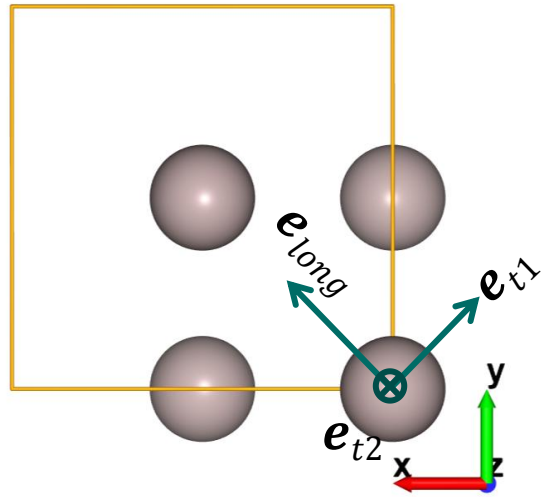




Extension to an *ab-initio* potential

System: PBE Aluminium

Local approximation bonding potential $V_1(\mathbf{b}) = V_{long}(u_{lj}) + V_{t1}(u_{t1}) + V_{t2}(u_{t2})$



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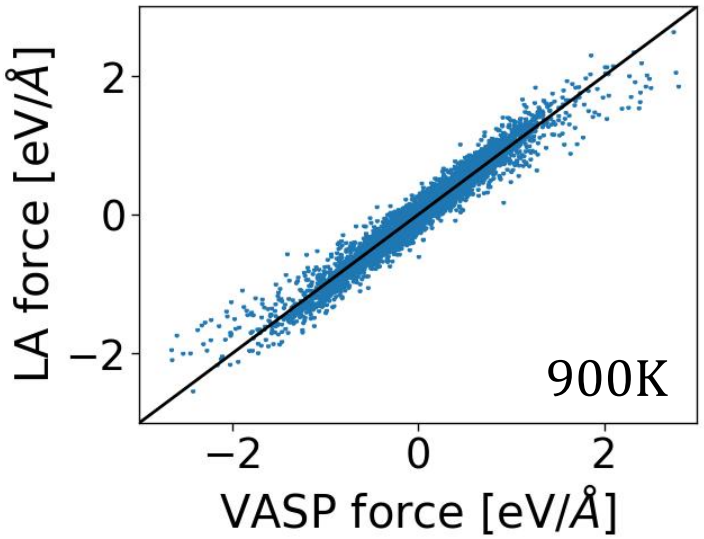
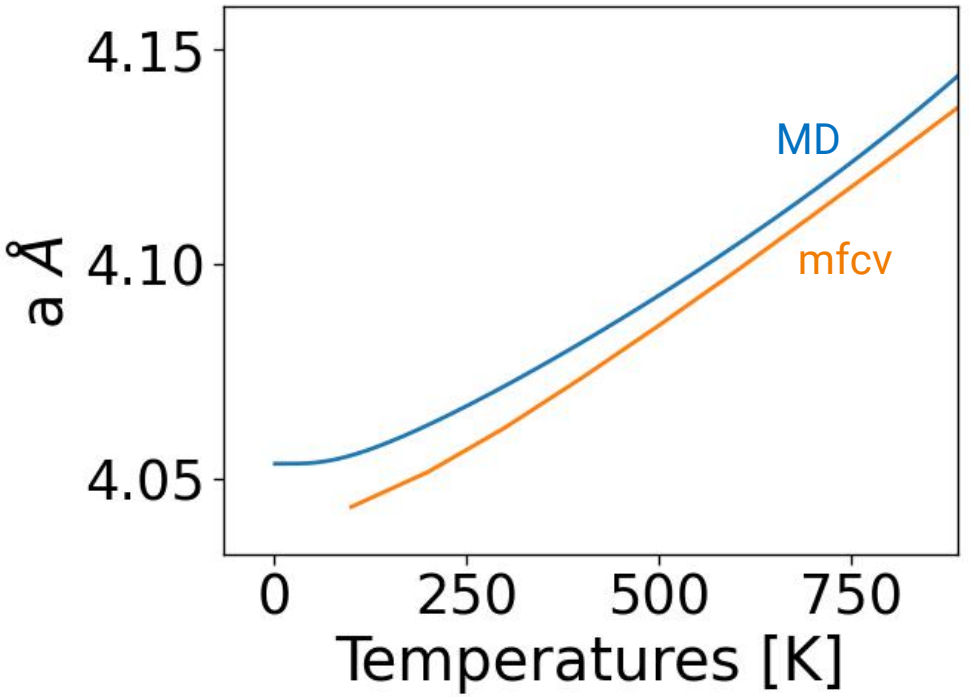
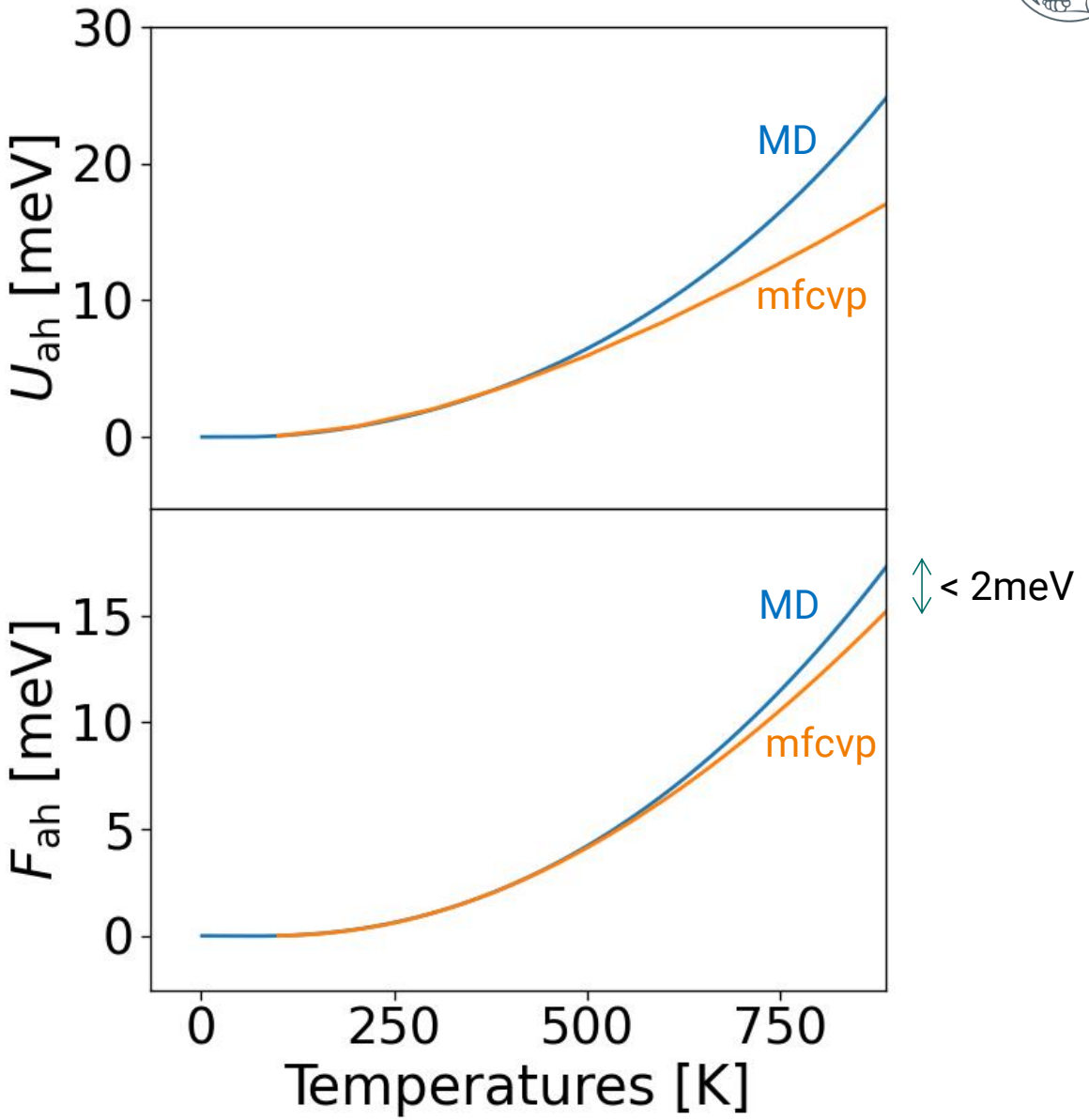
- $F_a(u) = \boldsymbol{F}_{\mathbf{j}}^{0\mathrm{K}}(\mathrm{u}\boldsymbol{e}) \cdot \boldsymbol{e}, \quad V_a(u) = \int_0^u F_a(u')\,du'$



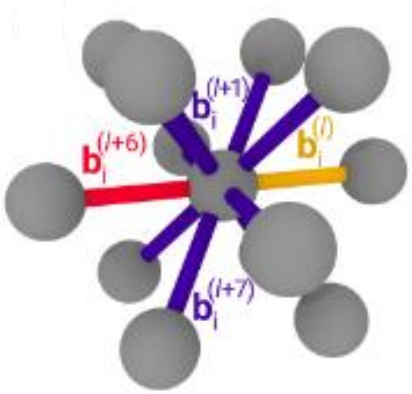
Mean-field bond lattice model vs. TI

For $P_{vir}^{mfc}(\widetilde{T}, \epsilon) = 0$,

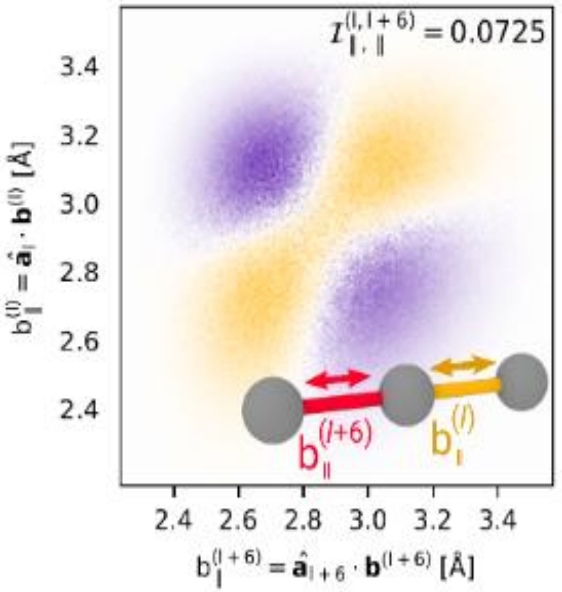




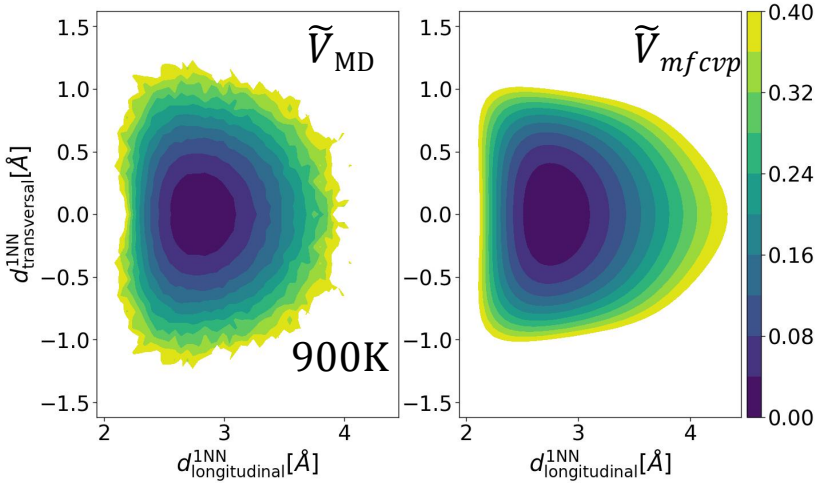
Summary



analytical self-consistent mean-field bond lattice model...

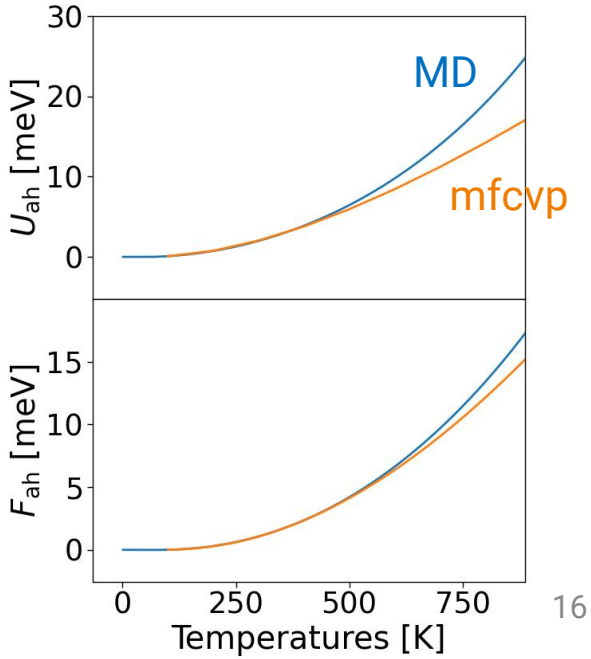


...accounts for bond pair correlations, virial corrections...



...to predict anharmonic bond distribution...

...and the anharmonic free energy



Thank you for your attention!

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