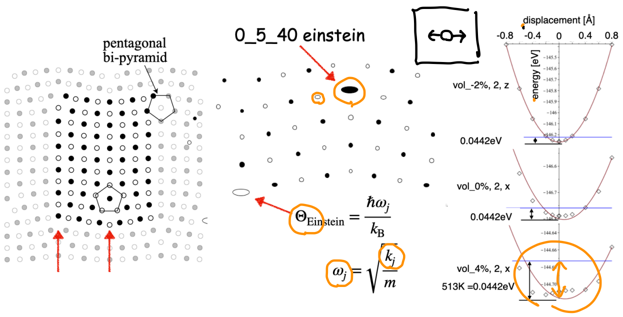


$dE = E_d - nE_0$

$dF(T) = F_d(T) - nF(T)$

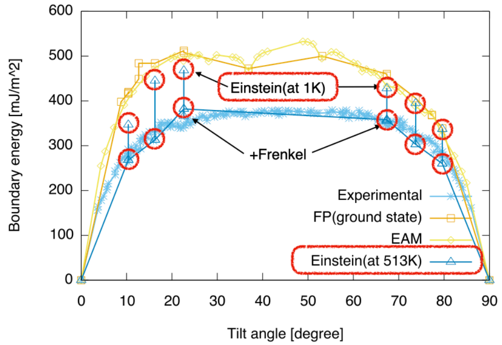
$F = E_0 + F_{Einstein} + F_{Frenkel}$

調和　非 ~0 (513K)

問題
① 他？欠陥
② 非調和
③ FP

Finite Temp VASP Al<100> tilt GB

“Finite-temperature first-principles calculations of Al⟨100⟩ symmetric tilt grain-boundary energy”

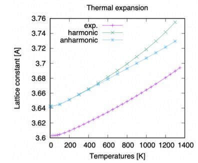


S. R. Nishitani, Phil. Mag., vol. 101, pp. 622–42, 2021, (https://doi.org/10.1080/14786435.2020.1855371).

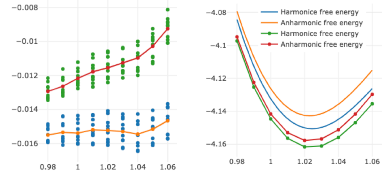
- Analytical/numerical anharmonic free energy of pure Cu or Al system
- Conclusions
  - VuVanHung’s Moment method
    - Thermal expansion
      - Cu (x), Al (o)
  - Frenkel Integration
    - $F_{\rm Frenkel} \neq F_{\rm moment}$
    - $F_{\rm VASP} = F_{\rm moment} + \int \frac{dE}{d\lambda} d\lambda \neq F_{\rm Einstein} + F_{\rm Frenkel\ Integral}$

物理学会(2022-09-15)
領域10

Cu 完全結晶の解析的・数値的 非調和 自由エネルギー



関西学院大学・工学部・西谷滋人



Al

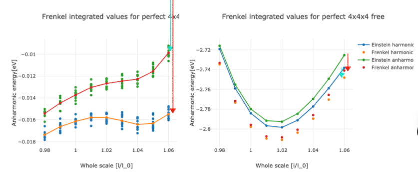
$E_{\rm moment} = E_{\rm Einstein} + E_{\rm higher\ order}$

$E_{\rm total} = \lambda E_{\rm VASP} + (1-\lambda) E_{\rm Einstein}$　　$E_{\rm total} = \lambda E_{\rm VASP} + (1-\lambda) E_{\rm moment}$

$\frac{\partial E}{\partial \lambda} = E_{\rm VASP} - E_{\rm Einstein}$　　$\frac{\partial E}{\partial \lambda} = E_{\rm VASP} - E_{\rm moment}$

$F_{\rm VASP} = F_{\rm Einstein} + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial E}{\partial \lambda} \right\rangle d\lambda$　　$F_{\rm VASP} = F_{\rm moment} + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial E}{\partial \lambda} \right\rangle d\lambda$

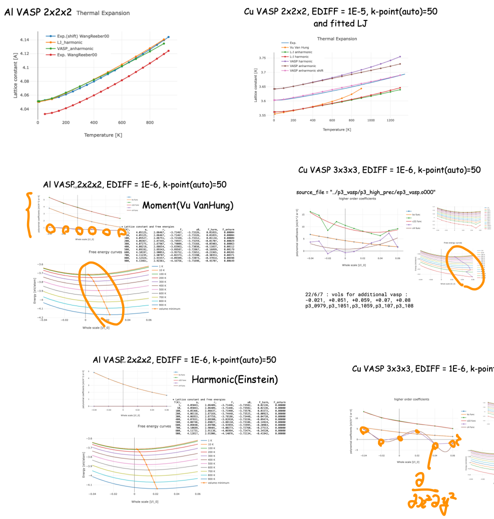
Skipped



Cu

Static/Analytical Moment method

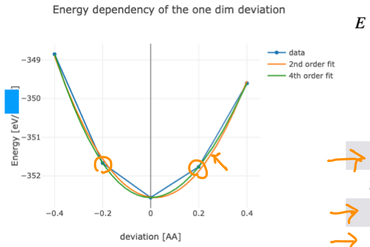
- thermal expansion
  - Al
  - Cu



outline

- Finite Temperature First Principles Calculations
  - Al <100> symmetric tilt boundary energy
- How to include anharmonicity
  - analytical : SMM (Statistical Moment Method)
  - numerical : Frenkel (Monte Carlo based Thermodynamic Integration)
- Al and Cu system
- VASP vs fitted LJ (2nd NN)

SMM (Statistical Moment Method)



$$E = E_0 + \frac{\partial E}{\partial x_i}dx_i + \frac{\partial^2 E}{\partial x_i^2}dx_i^2 + \frac{\partial^3 E}{\partial x_i^3}dx_i^3 + \frac{\partial^4 E}{\partial x_i^4}dx_i^4$$

0th	-352.5518	-352.5603
1st	-0.8025	-0.0067
2nd	20.7770	21.2321
3rd	0.0	-5.8513
4th	0.0	-2.5690

N. Tan, V. V. Hung, “Investigation of the Thermodynamic Properties of Anharmonic Crystals by the Momentum Method”, Phys. Stat. Sol. (B), vol. 149, pp.511–519, 1988.

$$F_{\rm anharm} \approx E_0 + F_{\rm harm} + 3\left\{\frac{\theta^2}{k^2}\left[\gamma_2 x^2 \coth^2 x - \frac{2\gamma_1}{3}\left(1+\frac{x\coth x}{2}\right)\right] + \frac{2\theta^3}{k^4}\left[\frac{4}{3}\gamma_2^2 x\coth x\left(1+\frac{x\coth x}{2}\right) - 2(\gamma_1^2+2\gamma_1\gamma_2)\left(1+\frac{x\coth x}{2}\right)(1+x\coth x)\right]\right\},$$

$\theta = k_B T, x = \frac{\hbar\omega}{2\theta}$

$$E_0 \equiv \sum_j \varphi(|a_j|),$$

$$F_{\rm harm} = \theta[x + \log(1-e^{-2x})],$$

$$k = \frac{1}{2}\sum_j\left(\frac{\partial^2\varphi_{j0}}{\partial u_j^2}\right) = m\omega^2$$

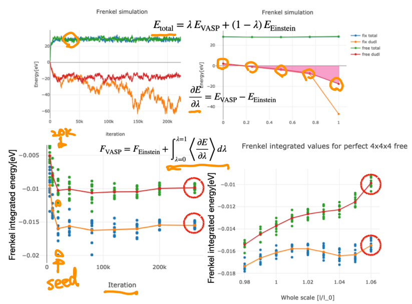
$$\gamma_1 = \frac{1}{48}\sum_j\frac{\partial^4\varphi_{j0}}{\partial u_{j\beta}^4}, \gamma_2 = \frac{6}{48}\sum_j\frac{\partial^4\varphi_{j0}}{\partial u_{j\alpha}^2\partial u_{j\beta}^2}$$

$$E_{\rm higher}(l') = E_0(l') + \sum_{[k,l,m]} k_{klm}(l')\delta x^k \times \delta y^l \times \delta z^m$$

PAW - PBE

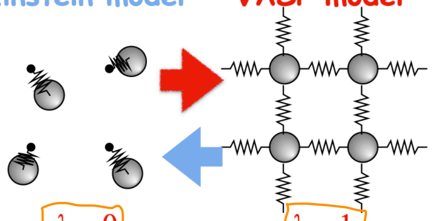
TABLE I. Higher order coefficients of the energy potential.

indexes	analytical	numerical p4 dev.=0.04	numerical p4 dev.=0.10	harmonic	VASP(2x2x2) dev.=0.04	VASP(2x2x2) dev.=0.10	VASP(3x3x3) dev.=0.10
0 [0 0 0]	-2.47840	-2.47840	-2.47840	-3.72303	-3.69879	[illegible]	
1 [2 0 0]	6.60522	6.60496	6.60288	6.66320	3.30538	3.37042	4.26487
2 [0 2 0]	6.60522	6.60496	6.60288	6.66320	3.33010	3.35011	4.27330
3 [0 0 2]	6.60522	6.60496	6.60288	6.66320	3.39418	3.35422	4.28811
4 [0 1 1]		1.720e-12	2.842e-13		[illegible]	[illegible]	[illegible]
5 [1 1 0]		1.600e-11	-1.125e-12		-0.02505	-0.01058	0.00217
6 [1 0 1]		1.720e-12	8.527e-13		0.03010	0.01165	-0.00154
7 [3 0 0]		-2.852e-09	-1.218e-10		-0.05000	0.00020	0.00054
8 [0 3 0]		-1.158e-09	-5.801e-11		-0.25417	-0.00222	0.00374
9 [0 0 3]		-2.147e-09	2.404e-11		0.25833	-0.00588	0.02284
10 [1 1 1]		-2.224e-26	-8.807e-12		-0.04375	0.00024	0.00056
11 [2 2 0]	29.14519	29.23755	29.34441		53.12500	9.96245	10.62694
12 [2 0 2]	29.14519	29.23755	29.34441		46.30102	9.91347	10.73143
13 [0 2 2]	29.14519	29.23755	29.34441		[illegible]	[illegible]	[illegible]
14 [4 0 0]	6.35142	6.51689	6.84933		-3.54167	0.30400	-0.56800
15 [0 4 0]	6.35142	6.51690	6.84933		-14.47916	2.01067	-1.22133
16 [0 0 4]	6.35142	6.51689	6.84933		47.29167	1.58400	-2.62133
standard dev.		0.000000	0.000014		[illegible]	[illegible]	0.000031



Dynamic/Numerical

- Frenkel(MC-TI)



$$F_i = E_i^0 - k_B T \ln Z_i = E_i^0 - k_B T \sum_{j=x,y,z} \ln\left(\frac{\exp(-\hbar\omega_j/2k_BT)}{1-\exp(-\hbar\omega_j/k_BT)}\right)$$

$$E_{\rm total} = \lambda E_{\rm VASP} + (1-\lambda) E_{\rm Einstein}$$

$$\frac{\partial E}{\partial \lambda} = E_{\rm VASP} - E_{\rm Einstein}$$

$$F_{\rm VASP} = F_{\rm Einstein} + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial E}{\partial \lambda} \right\rangle d\lambda$$