

A Genetic Algorithm to Predict the Structures of Interfaces in Multicomponent Systems

Alvin L.-S. Chua,¹ Nicole A. Benedek,^{1,2,*} Lin Chen,¹ Mike W. Finnis,^{1,2} and Adrian P. Sutton^{1,†}

¹*Department of Physics, Imperial College London,
Exhibition Road, London SW7 2AZ, UK.*

²*Department of Materials, Imperial College London,
Exhibition Road, London SW7 2AZ, UK.*

*Current address: Cornell Center for Materials Research, Cornell University, Ithaca, New York 14853, USA.

†Electronic address: a.sutton@imperial.ac.uk

Derivation of the Excess Volume for Non-stoichiometric Grain Boundaries

Consider SrTiO_3 as a pseudo-binary alloy composed of components SrO and TiO_2 . If we hold μ_{TiO_2} constant then the excess volume per unit area of the GB is given by

$$\left(\frac{\partial\sigma}{\partial P}\right)_{T,\mu_{\text{TiO}_2}} = \frac{1}{2A_s} (V_{GB} - N_{\text{SrO}}^{GB} V_{\text{SrTiO}_3}^{\text{bulk}}) \quad (1)$$

where N_{SrO}^{GB} is the number of units of SrO in the simulation cell containing 2 equivalent GBs and $V_{\text{SrTiO}_3}^{\text{bulk}}$ is the volume of one formula unit of bulk SrTiO_3 . Alternatively, if we held μ_{SrO} constant then

$$\left(\frac{\partial\sigma}{\partial P}\right)_{T,\mu_{\text{SrO}}} = \frac{1}{2A_s} (V_{GB} - N_{\text{TiO}_2}^{GB} V_{\text{SrTiO}_3}^{\text{bulk}}). \quad (2)$$

It is only when the GB is *stoichiometric* that these two expressions are equal.

Table S1 shows the excess volume per unit area for each grain boundary considered in the main text.

TABLE S1: Composition and excess volume per unit area for each grain boundary considered in this work. We have calculated the excess volume using both equation 1 (column labelled μ_{TiO_2} constant) and equation 2 (μ_{SrO} constant). All calculations were performed with DFT on supercells containing 120 atoms.

Interface	$A_s\Gamma_{\text{TiO}_2}$	Excess volume per unit area ($\text{\AA}$)	
		μ_{SrO} constant	μ_{TiO_2} constant
$\Sigma 3(111)[\bar{1}10]$, SrO_3 -terminated ¹	0	0.17	0.17
$\Sigma 3(111)[\bar{1}10]$, Ti-terminated	0	0.29	0.29
$\Sigma 3(111)[\bar{1}10]$	-1	1.17	0.05
$\Sigma 3(111)[\bar{1}10]$	1	0.19	1.27
$\Sigma 3(112)[\bar{1}10]$, SrTiO -terminated ¹	0	0.19	0.19
$\Sigma 3(112)[\bar{1}10]$, O_2 -terminated ¹	0	0.43	0.43
$\Sigma 3(112)[\bar{1}10]$	1	0.19	1.77
$\Sigma 3(112)[\bar{1}10]$	2	-0.11	3.04

¹ From Ref. 1.

[1] Benedek, N. A., Chua, A.-L. S., Elsässer, C., Sutton, A. P. & Finnis, M. W. Interatomic potentials for Strontium Titanate: An Assessment of their Transferability and Comparison with Density Functional Theory. *Phys. Rev. B* **78**, 064110 (2008).