Supplementary Information - Thermodynamic stability of β-phases in Zr-Nb alloys

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AIMD simulation parameter convergence was carried out for simulation time, time step and supercell size. Relative uncertainty of these parameters was calculated against a benchmark classical MD simulation of BCC-Zr using potentials by Mendelev and Ackland [1]. The benchmark simulation was run for a 16000 atoms supercell over 20 ps with 1 fs time steps. This would ensure a big enough structure to remove any added finite size effects, while running it long enough for good statistics along with more than adequate sampling rate.

Fig. 1 shows vDOS from different time steps over 20 ps. The plot show that the largest time step value (2 fs) ensures good agreement of the vDOS with the results being quite insensitive to the choice of time step.

Fig. 2a shows the vDOS obtained for the 16000-atom cell over 1, 2, 5, 10 and 20 ps with a 2 fs time step at 600 K. Even the 1 ps run captures the 2 major peaks of the vDOS curve (representing the frequency of most phonons), however, simulation lengths below 10 ps leads to loss of detail in the overall vDOS. This loss of detail is due to the dual effect of shorter VACFs being converted to vDOS (length of VACF is 500 points in the 1 ps run and 10000 points in the 20 ps run) and the dynamics of the system being evaluated over shorter periods of time. Shorter length of data in the time domain results in poor resolution of the FFT signal. One possible way to increase resolution from shorter VACFs is to pad them with zeros to obtain the same number of points as the longest VACFs. This results in more frequency bins that are more closely spaced in frequency. Statistically, the higher density of FFT result bins would probably ensure that the peak magnitude bin is closer to the frequency of a random isolated input frequency sinusoid (without further interpolation). Essentially, padding with zeros before taking a FFT is a computationally efficient method of interpolating a large number of points. However this doesn't buy any more

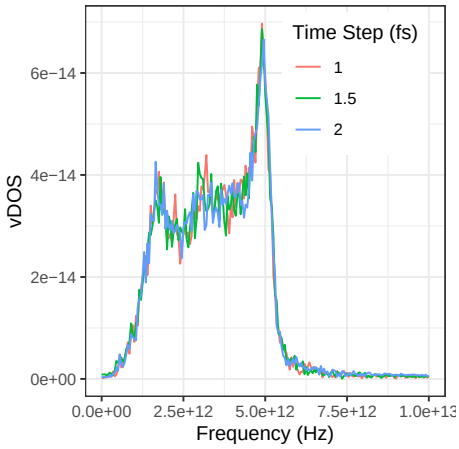
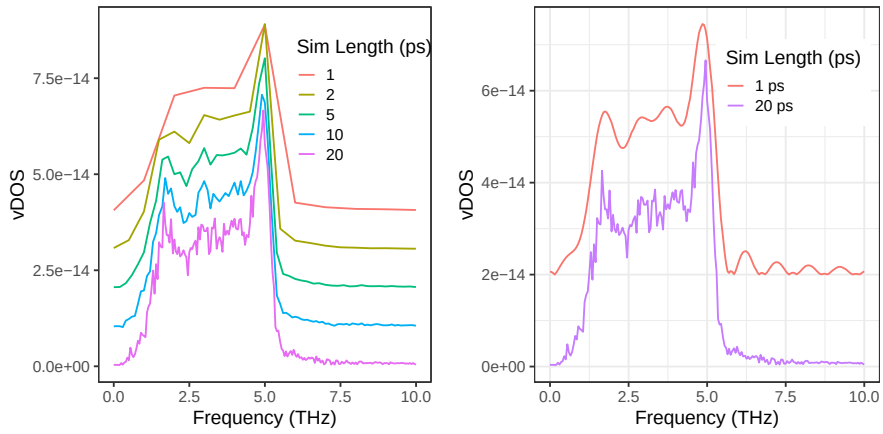


Figure 1: vDOS obtained over 20 ps run with time steps of 1, 1.5 and 2 fs.

true resolution. This leads to loss of information of number of states at each energy level that is available to be occupied by phonons, which will result in inaccuracies while calculating F_{vib}. This has been shown in fig. 2b, where the VACF of the 1 ps simulation was padded with zeros to make it the same length as the VACF of the 20 ps simulation before taking its FFT. Padding the 1 ps simulation VACF also introduces artefacts in the vDOS with equal size to features of the vDOS. This is best viewed by looking at the noise introduced at high frequencies in 1 ps simulation vDOS, which is comparable to the humps at 2.5-5 THz. As expected, the simulation run over the longest time has the most number of points in the time domain and therefore, the most detail in the vDOS curve, which would ensure most accurate results.

Fig. 3 shows the vibrational free energy results for all time steps over different simulation lengths. It is evident that the results for 2 fs time step (in 20 ps simulation length) converge to the most accurate 1 fs time step results over the same simulation length. Therefore, the parameters were finalised to 2 ps time step and 20 ps simulation length to ensure a good balance between computational resources requirements and accuracy of results.

It is important to estimate the finite size effects on varying supercell sizes, as it is favourable to use the smallest possible supercell for the computationally expensive AIMD simulations to maximise simulation length, without losing much accuracy. The basic quantity being solved for while performing phonon calculations is the force constants matrix. Therefore, we need a large enough supercell to capture most of the zero interaction entries in the force constants matrix, or in other words, a supercell big enough to capture negligible interaction between 2 distant atoms and ensure that the force between 2 faraway atoms falls off faster than $1/r^2$. Once enough interactions between atoms are captured, the forces obtained give an accurate representation of the velocities of atoms at each step. This results in accurate VACF and vDOS calculations.



(a) (b)

Figure 2: (a) vDOS comparison between different simulation lengths for BCC-Zr at 600 K. (b) vDOS comparison between 1 ps and 20 ps simulations with 1 ps vDOS obtained from VACF padded with zeros to make it the same length as 20 ps vDOS. vDOS have been offset by multiples of 2×10^{-4} in order to aid clarity.

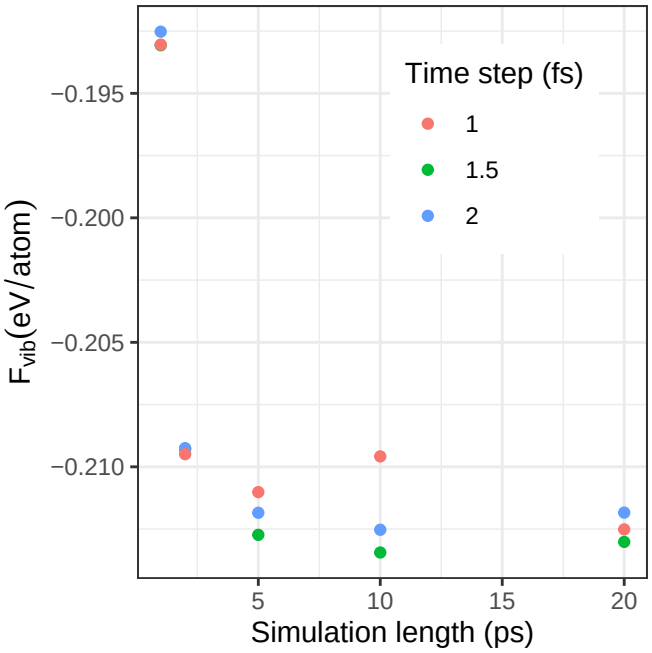
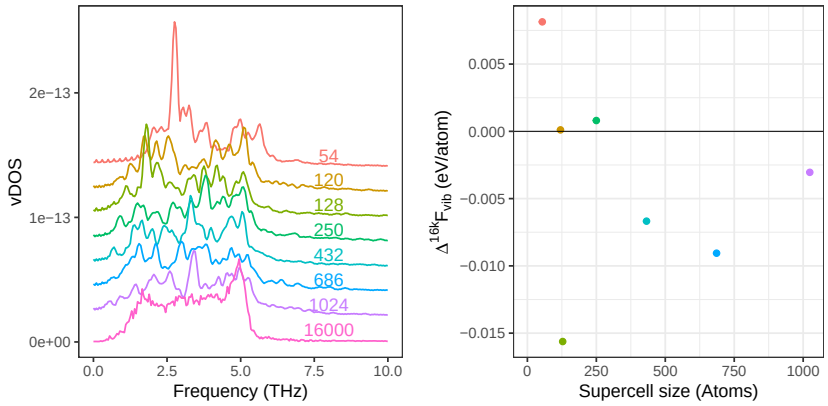


Figure 3: Vibrational free energy convergence to the most accurate time step (1 fs) over a 20 ps simulation.

Fig. 4a shows the vDOS obtained for all the supercell sizes considered. As can be seen, there are additional peaks at lower frequencies in the small supercell structures. This can be attributed to the small supercell size strongly influencing long wavelength phonons and consequently overestimating the correlation effects in atomic motion.

Fig. 4b shows absolute difference between the vibrational free energy from the benchmark supercell and the other supercells ($\Delta^{16k}F_{vib}$). An anisotropic supercell (3×4×5 - 120 atoms) provides more accurate results than an isotropic 4×4×4 supercell of comparable size (128 atoms), while providing comparable results to the much more computationally taxing 5×5×5 supercell containing 250 atoms. This improved accuracy of anisotropic cells may be due to the increased (and different) phonon interactions captured in 2 dimensions due to the increased (and different) length in these 2 dimensions. Box size limits the maximum phonon wavelength and thus the minimum phonon frequency. Consequently, the number of permitted wavelengths for low frequency phonons is finite and increasingly sparse in smaller boxes. This can also explain the increasing fluctuations observed in fig. 4a at lower frequencies with decreasing supercell size. Moreover, only the effect of longer wavelength phonons that are commensurate with the box size are captured. Using different box lengths in all 3 dimensions allows the capture of different wavelength phonons. The choice of this 3×4×5 supercell is based on it being a good balance between computational requirements and accuracy.



(a) (b)

Figure 4: (a) Comparison of vDOS obtained from different supercell sizes (denoted by label on each vDOS), (b) $\Delta^{16k}F_{vib}$ obtained at 600 K as difference between F_{vib} obtained from 16000 atoms supercell and smaller supercell sizes.

Fig 5 shows the Helmholtz vibrational free energy at 50 K increments between 50 K and 1200 K for all volumes simulated using AIMD. As can be seen, the Helmholtz free energy reduces with increasing temperature at the same volume, with a much steeper decrease observed after room temperature $\sim$ 293 K.

Similar trend was observed in the F_{vib} obtained from similar thermodynamic integration for BCC-CrN [2].

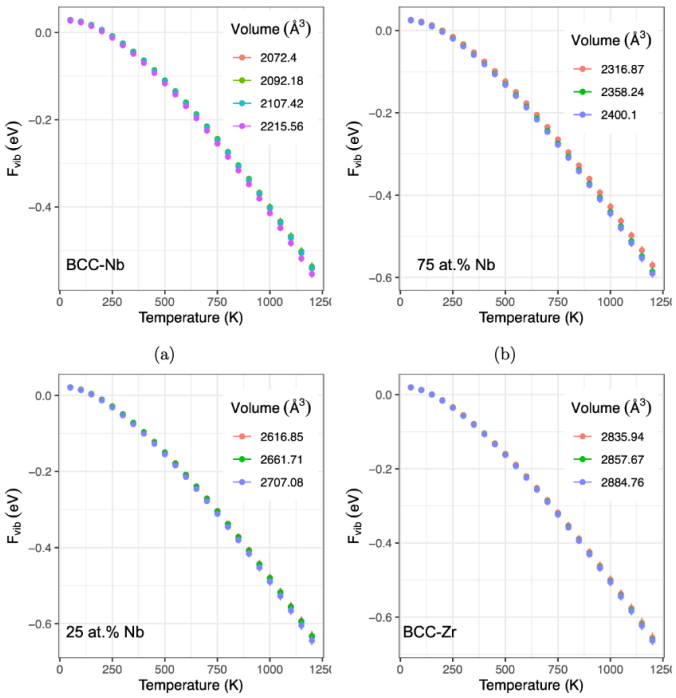


Figure 5: Helmholtz free energy between 600 and 1200 K obtained by integrating vDOS obtained at 600 K using AIMD for a)BCC-Nb, b) 75 at.% Nb, c)25 at.% Nb and 1200 K for d)BCC-Zr

References

1. Mendelev, M. I. & Ackland, G. J. Development of an interatomic potential for the simulation of phase transformations in zirconium. *Philosophical Magazine Letters* **87,** 349–359 (2007).

2. Shulumba, N., Alling, B., Hellman, O., Mozafari, E., Steneteg, P., Odén, M. & Abrikosov, I. A. Vibrational free energy and phase stability of paramagnetic and antiferromagnetic CrN from ab initio molecular dynamics. *Physical Review B - Condensed Matter and Materials Physics* **89** (2014).