Comparing the accuracy of Melting Temperature prediction methods for High Entropy Alloys

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Abstract

Refractory complex concentrated alloys (RCCAs) are a relatively new class of materials that can exhibit excellent mechanical properties at high-temperatures, and determining their melting temperature (T_m) is critical to assess their range of operation. Unfortunately, the experimental determination of this property is challenging and computational tools to predict the T_m of RCCAs from first principles are highly desirable. We quantify the uncertainties associated with such predictions for two methods that can be used with density functional theory-based molecular dynamics and apply them to predict the melting temperature of equiatomic NbMoTaW. We find that a combination of free energy calculations of individual phases with a dynamical coexistence method can provide accurate results with the minimum possible computational cost. We predict the melting temperature for the RCCA NbMoTaW to be between 3,000 and 3,100 K.

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1. Introduction

Ni-based superalloys are currently the alloys of choice for high-temperature applications. However, their range of operation is limited by their melting temperatures and capped at approximately 1300K. [1] A search for materials that can operate at even higher temperatures has led to the discovery of refractory complex concentrated alloys (RCCAs). Some RCCAs have high-temperature strength surpassing those of Ni superalloys [2] and these materials are currently being considered for applications as high-temperature load-bearing structures and thermal shielding of interest in aerospace and power generation. [2] Additionally, RCCAs have excellent magnetic properties, irradiation resistance, corrosion resistance, and wear resistance even at high temperatures. [3,4,5,6] Determining the melting temperature (T_m) of these alloys is important to assess their operation range as mechanical strength degradation typically starts at about 0.6 times the melting temperature (T_m). [7] Experimental determination of the melting point for RCCAs is challenging since the high values accelerate oxidation and other unwanted reactions with the crucible and the atmosphere. Hence, theoretical predictions with quantified uncertainties are highly desirable. In this paper, we use a combination of atomistic simulation techniques to predict the melting temperature of equiatomic NbMoTaW RCCA and estimate the uncertainties in the prediction.

Molecular dynamics (MD) can be used to predict melting temperature with a description of atomic interactions as the sole input. The accuracy of these predictions depends both on the specific approach used to determine melting temperatures and the fidelity of the energy expression used to compute interatomic forces. Electronic structure calculations like density functional theory (DFT) provide relatively accurate forces and are applicable to any RCCA, but they are computationally intensive and, hence, limited to relatively small systems. Unfortunately, system size and simulation times achievable via DFT-based MD precludes the use of the most direct and accurate method to determine melting temperatures: the coexistence method that seeks to establish conditions at which liquid and solid phases coexist. [8] Alternatively, melting temperatures can be determined from free energy calculations of the individual phases [9] or the recently proposed solid and liquid in ultra-small coexistence with hovering interfaces (SLUSCHI) method [10]. Both these methods can be used with DFT-based simulations but quantifying the underlying uncertainties is critical to analyze the resulting values. For some alloys, interatomic potentials can provide an energy expression as a function of atomic positions that is computationally inexpensive compared to DFT, enabling large-scale simulations and converged coexistence simulations. Unfortunately, interatomic potentials need to be parameterized for each specific material and are typically less accurate than DFT.

Our goal is to characterize the melting temperature of NbMoTaW RCCAs with quantified uncertainties for which no interatomic potential is available. Thus, we first quantify uncertainties in two possible methods for DFT-based MD melting temperature calculations (free energy calculations using two-phase thermodynamics (2PT) [11] and SLUSCHI [10]) using interatomic potentials for a variety of alloys, for which accurate large-scale coexistence calculations are possible. We then compute the melting temperature of NbMoTaW using both methods and find good agreement within the uncertainties established. The predicted temperature is 3100K with an uncertainty of 200K. The method can be extended to calculate the melting temperature of other unexplored RCCAs. The remainder of the paper is organized as follows: Section 2 first describes the different computational methods to calculate the melting temperature. It further details the DFT calculations for NbMoTaW for the 2PT method and the SLUSCHI method, followed by the simulation details of the 2PT method, the SLUSCHI method, and the large-scale solid-liquid coexistence method for the Ni, Cu, CuNi, and CoCrCuFeNi model systems used for uncertainty quantification. Section 3 benchmarks the results obtained from the different approaches and studies the effect of the system size on the results to obtain the uncertainty quantification. We present the melting temperature results for NbMoTaW using the 2PT method and the SLUSCHI method in Section 4 and predict the melting temperature using the uncertainties established in Section 3. Finally, we present the summary and conclusions in Section 5.

2. Methods

2.1 Calculating melting temperature with MD

Calculation of melting temperatures from first principles using MD simulations requires accurate descriptions of the atomic interactions and possibly large simulation cells (100s of atoms) and long temporal trajectories (10s of picoseconds). The following paragraphs describe the most commonly used approaches.

Heating and cooling method. The most direct approach involves heating a solid until it melts and cooling the liquid until it solidifies. This method results in significant hysteresis due to the lack of nucleation sites and fast cooling/heating rate [12] and will not be considered further.

In the **coexistence method** [13], the solid and liquid exchange energy under constant pressure conditions and stabilize at the melting temperature. This method is considered the gold standard of melting temperature calculations for monoatomic materials as it only assumes classical mechanics in calculating the melting temperature. The drawback is that achieving stable solid-liquid coexistence requires a large cell. [8] Hence, it is relatively easy to calculate it using empirical potentials. However, a lack of good empirical potentials for RCCAs of interest forces us to use ab-initio molecular dynamics (AIMD) methods which are too computationally intensive for this method. Another limitation is the treatment of non-monoatomic systems. Alloys can have incongruous melting over a range of temperatures where the solid and the liquid coexist. Using this method, one can, in principle, find this range. In practice, however, the resulting value is the so-called T_0, the temperature where the free energies of the solid and the liquid with equal composition are equal. This is because the time scales of the simulations are not long enough to allow for changes in composition in the two phases. [14] For the remainder of the paper, we will use T_0 and T_m interchangeably.

The **SLUSCHI** method [10] is an extension of the large-scale coexistence method. As discussed under the coexistence method, the solid-liquid interface is not stable for small cell size and results in it evolving into either a solid or a liquid depending on the initial configuration and velocities, even for the same temperature. The SLUSCHI method first brackets the melting temperature range by calculating the probability of the structure evolving into a solid and a liquid and then uses the same probability statistics to predict the melting temperature. Instead of using a large system where the computation cost grows as a cube of the system size, it uses multiple small systems avoiding the curse of dimensionality. The details of the method can be found in the original paper. [10]

Free energy of individual phases. This method uses free energy calculations of the liquid and solid phases to predict the melting temperature and find the temperature at which they are the same. In the case of alloys with a range of temperatures between the liquidus and solidus, this value is known as T_0 [15] and lies within the range of coexistence temperatures. The challenge is that the entropic contribution to the free energy is not directly available from MD simulations and needs to be approximated or calculated with expensive thermodynamic integration. We obtain the total energy from the MD calculations and use the velocity autocorrelation function (it is an integral of the product of the velocity with a lagged version of itself that determines the correlation between the displacements) to calculate the entropy using the 2PT method [11]. The 2PT method separates the density of states (DoS) into a solid and a gas part to calculate the entropy for the liquid. The solid and the solid part of the liquid are assumed to be harmonic, while the gas part of the liquid is described by the hard-sphere model under pressure.

2.2 Atomic models and atomic interactions

DFT calculations of NbMoTaW using the free energy method. We used a 4x4x4 supercell (128 atoms) with a body-centered cubic (BCC) unit cell for the ab initio molecular dynamics calculations for NbMoTaW. The random structure was generated using the special quasi-random structure method (SQS) [16] as implemented in the alloy-theoretic automated toolkit (ATAT) [17]. The calculations were performed with the Vienna ab-initio simulation package (VASP). [18, 19] We used the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) [20] scheme to calculate the exchange and correlation potential and projector-augmented-wave (PAW) [21] pseudopotentials. We used a Γ-centered k-grid which is sufficient for melting point calculations with an energy cutoff of 350 eV and a timestep of 2 femtoseconds.

The SQS structure was used as the initial solid structure, while the initial liquid structure was generated by melting the SQS structure at 4000 K. Starting from the initial solid and liquid structures, we performed NVE calculations at different temperatures ranging from 2500 K to 3800 K. The lattice parameter was optimized at each temperature with multiple isochoric and adiabatic (NVE ensemble) calculations until the average pressure was under 1 GPa. We used 20 ps of trajectory with the optimized lattice parameter to obtain the velocity autocorrelation function and hence the density of states (DoS) required for the calculation of the entropic contribution to free energies. We separate the DoS into a solid part and a gas part according to the (2PT) method. [11] The quantum harmonic oscillator approximation for the solid and the hard-sphere model approximation method for the gas part is used to obtain the total entropic contribution. [11] We obtain the average internal energy from the AIMD calculation. The free energy at each temperature is determined to get the free energy vs. temperature plot for the solid and the liquid. The intersection of the two curves determines the melting temperature.

DFT calculations for NbMoTaW for the SLUSCHI method. For the SLUSCHI [9] implementation for NbMoTaW in VASP [18, 19], we prepared a 6x3x3 supercell (108 atoms) structure and melted it at a high temperature. After the melting, we did an NVT calculation at 4000K for 10ps and obtained nine different random solid-liquid coexistence structures. Using these random structures, we did an NPT calculation at different temperatures ranging from 2500K to 3500K with 100K differences for 10 ps. Using a similar process as mentioned in the case for SLUSCHI implementation for LAMMPS, we obtain the melting temperature from the enthalpy-temperature curve.

Uncertainty quantification on Ni, Cu, CuNi, and CoCrCuFeNi model systems. We used two system sizes; a 4x4x4 supercell (256 atoms) system similar in unit cell replication to the NbMoTaW system used for the free energy method above and a 10x10x10 supercell (4000 atoms) system similar in the number of atoms used in the large-scale solid-liquid coexistence method (described below) for easy comparison. These systems had a face-centered cubic (FCC) crystal structure and were used for the molecular dynamics calculations for Ni, Cu, CuNi, and CoCrCuFeNi. The random structures for CuNi and CoCrCuFeNi were generated using the SQS method. The classical molecular dynamic calculations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [22] using the Farkas potential [23]. The initial liquid was obtained by melting the initial structure at atmospheric pressure at 3000 K for 100ps, and the initial solid structure was obtained by an NPT simulation at the atmospheric pressure at 500 K. For each temperature, we first cooled or heated the structure at 5K/ps from the initial temperature followed by a 50ps NPT equilibration. The average lattice parameter was used to run an NVE calculation for 90 ps, and the trajectory from the last 40ps was used for the velocity autocorrelation spectrum calculation. The process was repeated 20 different times for each temperature with different velocity seeds for all, in addition to different structures for CuNi and CoCrCuFeNi.

MD calculations for Ni, Cu, CuNi, and CoCrCuFeNi model systems for the SLUSCHI method. For the SLUSCHI [10] implementation for Ni, Cu, CuNi, and CoCrCuFeNi in LAMMPS [22], we prepared a 6x3x3 supercell (108 atoms) structure. We melted one-half of the structure at 3000K for 10ps to obtain a starting structure with solid-liquid coexistence. We then performed an NPT equilibration at atmospheric pressure at different temperatures, 10 times for each temperature, with different starting coexistence structures. At the end of the calculation, we used polyhedral template matching (PTM) to obtain the fraction of solid and liquid and used the last 99.5ps to obtain the mean and the standard deviation of the enthalpy. We obtain the melting temperature by fitting the enthalpy temperature curves.

Large-scale solid-liquid coexistence calculations using MD for the Ni, Cu, CuNi, and CoCrCuFeNi model systems. We used a 16x8x8 supercell (4096 atoms) with an FCC unit cell for the large-scale solid liquid coexistence calculations. The solid and liquid were separately equilibrated at temperatures well below and well above the melting temperature for 10ps using the NPH ensemble followed by 100ps of NPH calculation where the solid and the liquid could exchange energy with each other. PTM analysis of the final structure ensured that the solid and the liquid fractions were at least 0.4 each. Furthermore, the temperature-time curve for the last 50 ps was ensured to be flat (absolute value of the slope < 1) to determine convergence. The average and the standard deviation of the temperature of the last 50ps determine the melting temperature.

3. Verification and uncertainty estimates in melting temperature calculations: role of approach and system size

Ab initio MD simulations are restricted to relatively small simulation cells. Hence, we need to quantify the effects of the approximations made as well as those originating from the system size. To do this, we compare the results for the free energy method (for different sizes) and the SLUSCHI method (small system) against the large-scale solid-liquid coexistence method (the benchmark) for various model systems for which we have interatomic potentials. As described in Section 2, we did this for two single-element FCC metals (Ni and Cu), a binary alloy (CuNi), and a high entropy alloy (CoCuCrFeNi). Figures 1 and 2 show the melting temperature predictions for the single elements, the binary elements, and the HEA. We compare large-scale coexistence with the large and small size free energy. Different starting velocities (drawn stochastically from the Maxwell-Boltzmann distribution) and different starting atomic configurations (where relevant) were used as initial conditions to quantify the variability in the calculation. The results are summarized in Table 1, and the differences are quantified in Table 2.

3.1 Uncertainties introduced by free energy calculations

To isolate the accuracy of the free energy method from size effects, we computed melting temperatures for a similarly sized system as the coexistence benchmark. We find that the large-scale free energy method underpredicts the large-scale coexistence method for all cases, between 4.5% for Ni to 11.6% for CoCrCuFeNi.

As discussed in the methods section, we use the quasiharmonic approximation to calculate the entropy of the crystalline sample. The entropy of the liquid is calculated with the two-phase model [11], where the total density of states is divided into a solid component (treated with the quasiharmonic approximation), and the remaining part is treated as a hard-sphere fluid. The T_m is determined from the intersection of the free energy curves of the solid and the liquid and the free energy curves typically cross at shallow angles. Hence, a small error in the free energy determination results in large errors in the predicted T_m. Thus, we attribute the discrepancy to the hard-sphere model approximation of the *gas* part of the liquid and the underestimation of the melting temperatures to the hard-sphere assumption over-stabilizing the liquid.

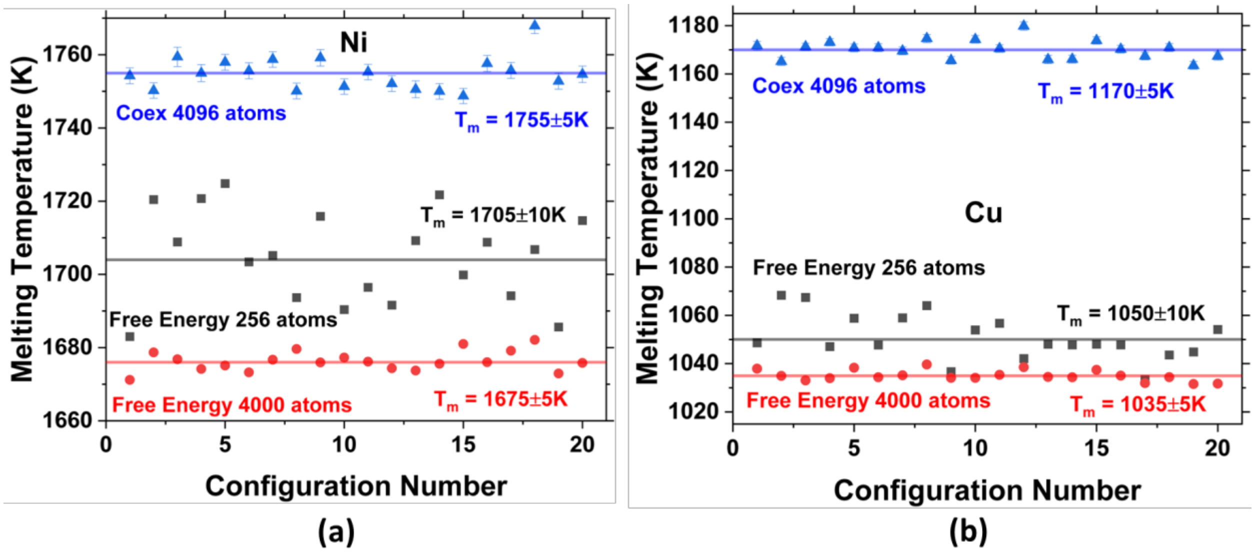
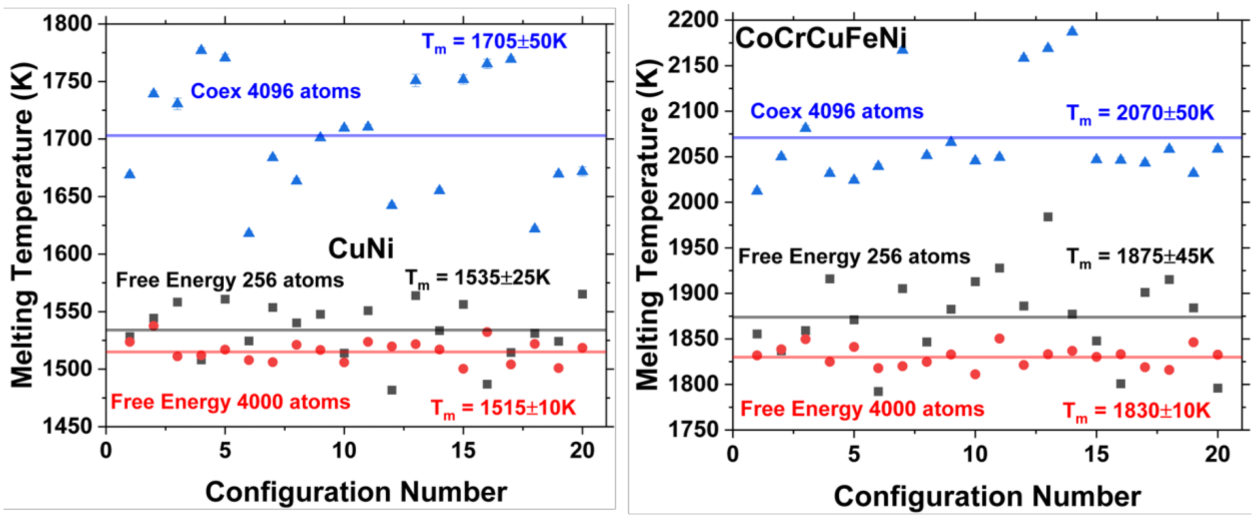


Figure 1 Melting temperature prediction for (a) Ni and (b) Cu using the free energy method compared to the large-scale coexistence method



(a) (b)

Figure 2 Melting temperature prediction for (a) a binary alloy CuNi and (b) a high entropy alloy CoCrCuFeNi using the free energy method compared to the large-scale coexistence method

The small-scale free energy calculations show similar trends to the large-scale counterparts and underpredict the benchmark coexistence method for Ni ~3%), Cu (~10%), CuNi (~10%), and CoCoCrFeNi (~10%). The underestimation of the melting temperature is somewhat less for the smaller systems, by about 25K. A possible explanation for this fact is that for smaller systems, the liquid is more constrained than in larger supercells resulting in increasing energy of the liquid phase. To confirm this, we calculated the difference between the 4000-atoms system and the 256-atoms system over 20 different structures for both solid and liquid. The larger system was always stabilized over the smaller system. But the difference was more marked in the liquid samples. We observed a ~ 3-12 meV/atom stabilization of the liquid over the solid for the metals and the alloys.

We now focus on characterizing the distribution of T_m predictions from the coexistence method as a function of the computational cost in terms of the number of temperatures used in the calculation. We selected n ($2 \le n \le 5$) temperatures from a total of five values around T_m, randomly chose one of the 20 different simulations for the solid and the liquid at each temperature, and calculated the T_m of each set of simulations. All possible combinations of n temperatures were enumerated, and 1000 simulations were sampled for each of these cases. We found T_m by fitting the free energy difference between the solid and the liquid to a line and performed a statistical analysis of the results, see Fig. 3. We find that three temperatures (a total of six simulations) are enough to predict T_m to a reasonable range (200 K) for the single elements and the binary alloy, but we require four points to get a reasonable T_m prediction range for the high entropy alloy.

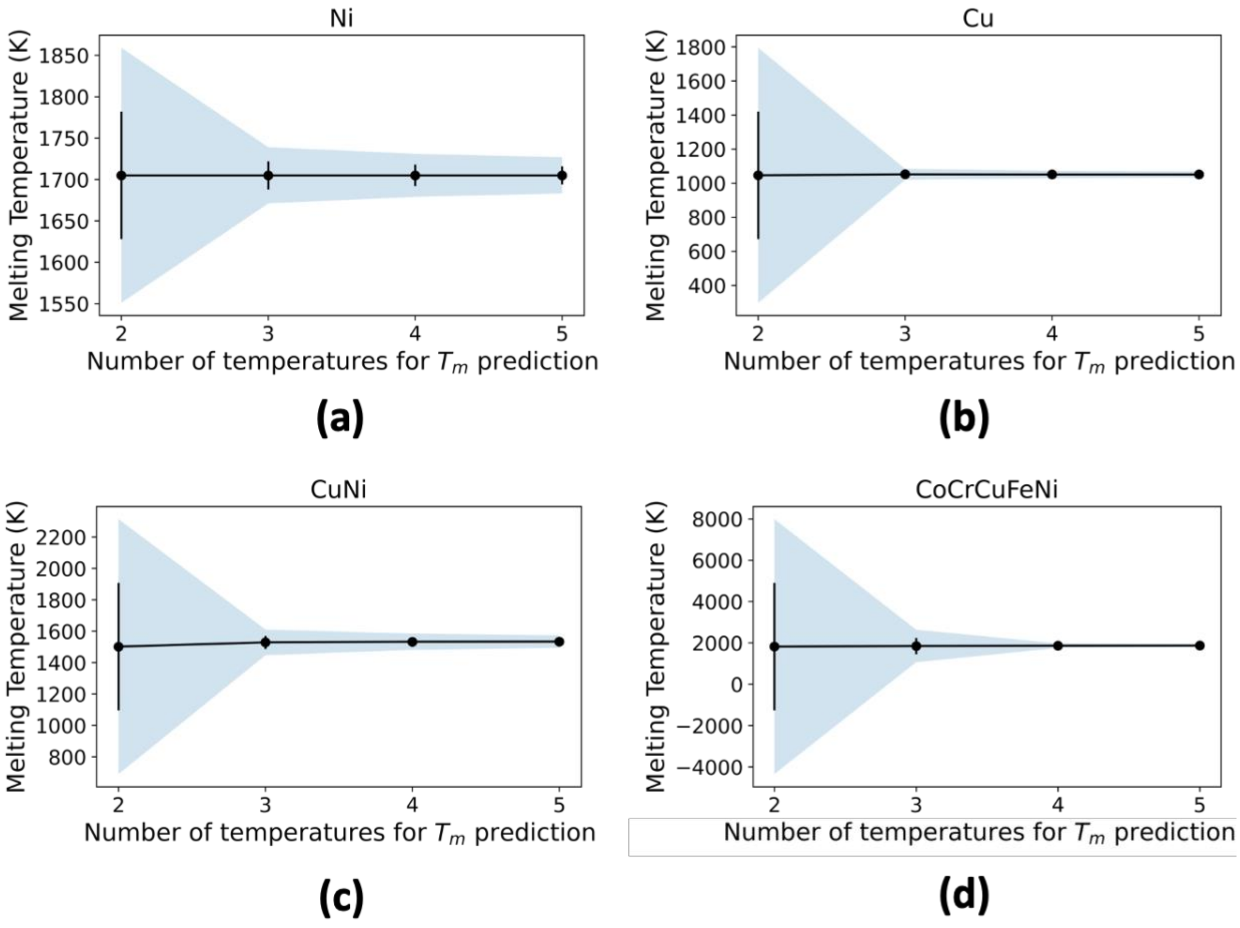


Figure 3 T_m prediction mean, standard deviation and 95% confidence interval for (a) Ni (b) Cu (c) CuNi and (d) CoCrCuFeNi as a function of simulations per Temperature

3.2 Uncertainties in small-scale SLUSCHI calculations

In the small-scale coexistence calculations, temperatures away from T_m result in the system evolving to either a crystal or liquid. For temperatures close to the melting temperature, the system can evolve into a liquid or solid with a temperature-dependent probability. For the single elements (Ni and Cu), this coexistence range is ~200K (see Fig 4(a) 4(b)), whereas, for the alloys (CuNi and CoCrCuFiNi), the range is broader ~400K (Fig 4(c),4(d)). This is because of the larger variability in the composition in alloys with more elements leading to more instability of the small-scale coexistence structure. The small-scale coexistence (SLUSCHI) predictions compare well with the large-scale coexistence and provide the most accurate result with a method applicable to DFT MD. The SLUSCHI method still underpredicts the temperature for Ni (~1%), Cu (~3%), CuNi (~2%), and CoCoCrFeNi (~2%).

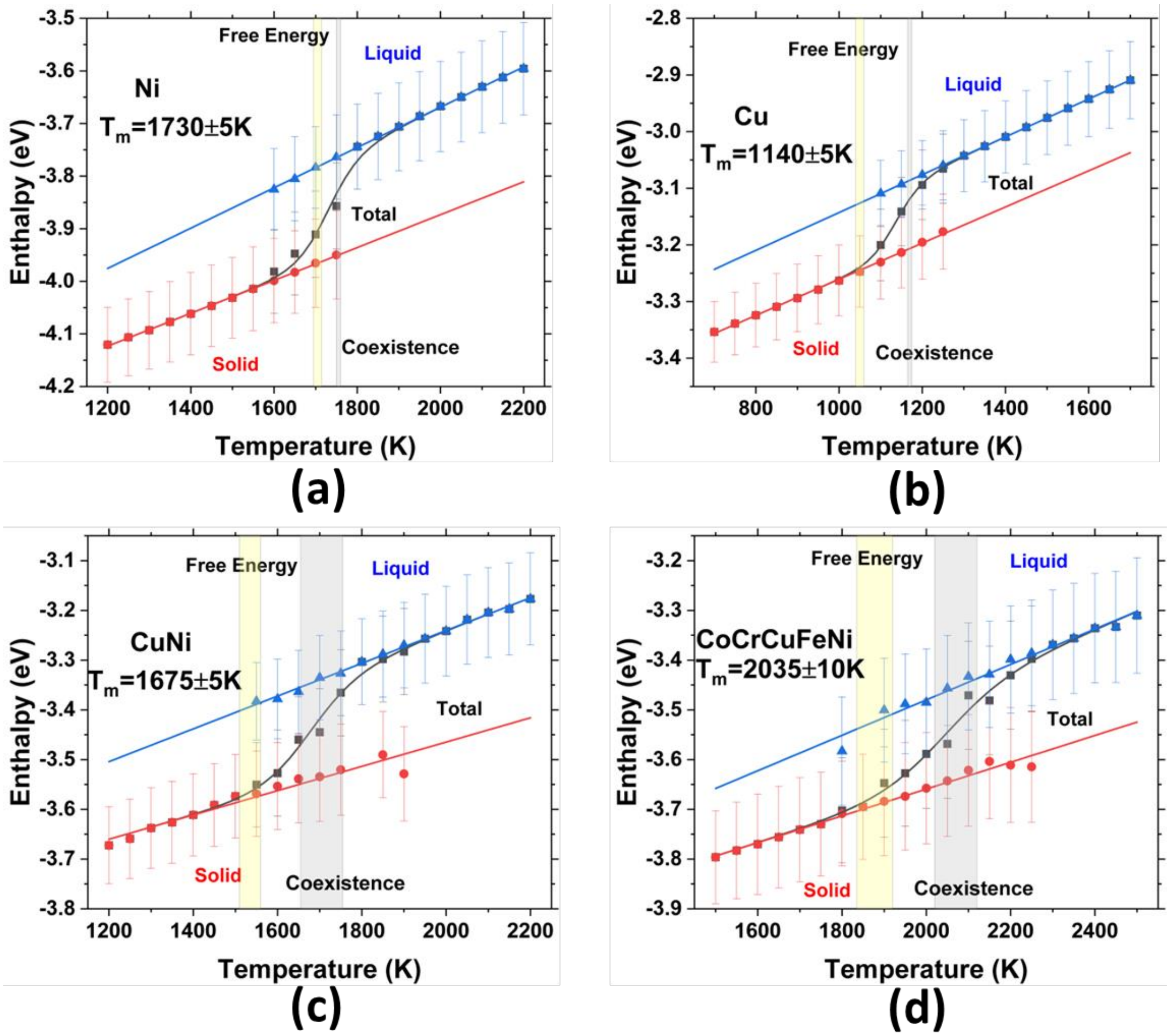


Figure 4 Enthalpy vs temperature for (a) Ni (b) Cu (c) CuNi (d) CoCrCuFeNi for the small-scale coexistence calculation. The shaded regions in each plot represent the melting temperature predictions along with their uncertainties for the free-energy method and the large-scale coexistence method

The results above use 10 independent simulations per temperature. To characterize how the number of simulations per temperature affects the results, we selected 11 temperatures around T_m with 100 K intervals, randomly selected n $(1 \leq n \leq 9)$ simulations per temperature, and calculated the melting temperature. For each n, we performed 1000 random samples and analyzed the distribution of resulting temperatures. Figure 5 shows the mean values, standard deviation, average error from the SLUSCHI fits, and the 95% confidence interval. We find that 5 points are enough to obtain reasonable accuracy and precision with SLUSCHI.

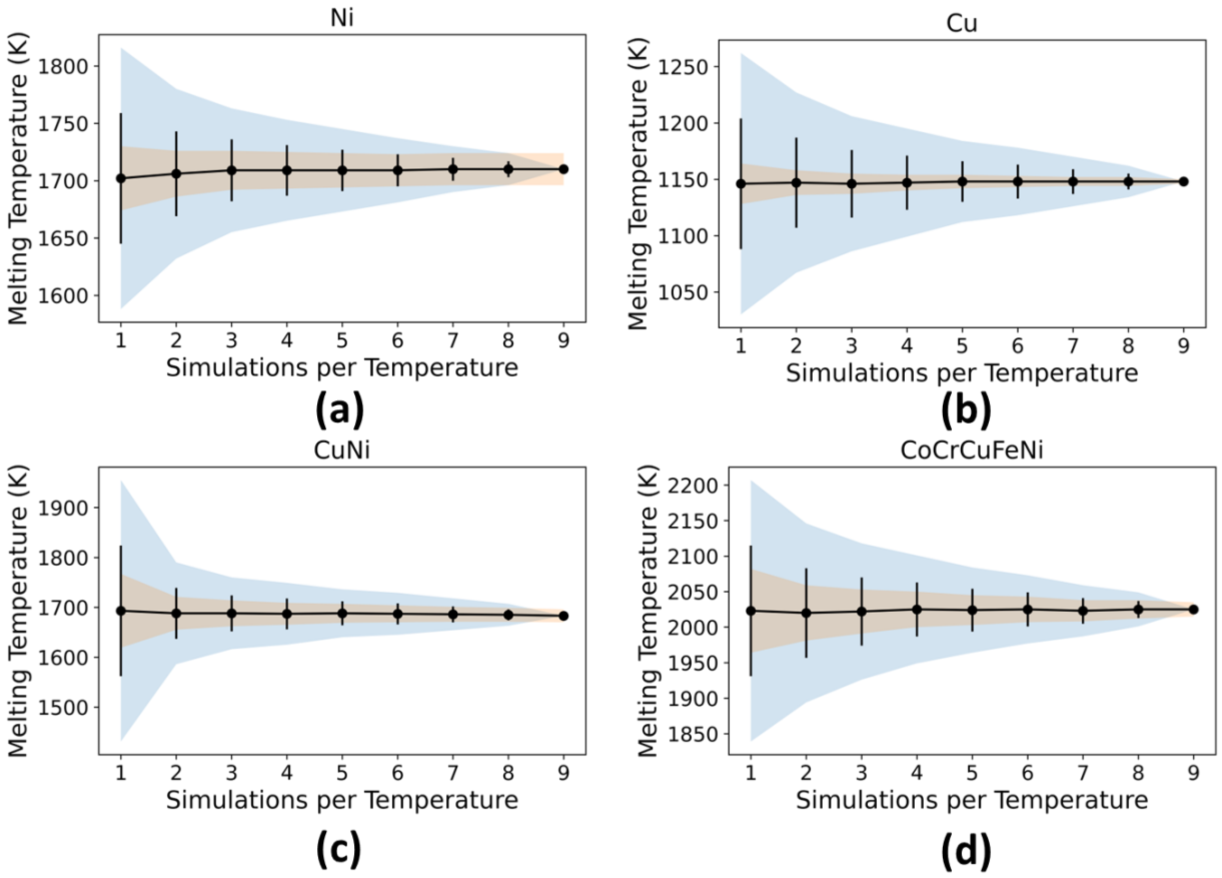


Figure 5 T_m mean, standard deviation, average error from fit (brown), and 95% confidence interval (blue) for (a) Ni, (b) Cu, (c) CuNi, and (d) CoCrCuFeN ias a function of simulations per temperature.

3.3 Uncertainties associated with DFT

DFT provides an ideal combination of accuracy and computational efficiency for many applications in materials science, but it is not without approximations, both numerical and of a fundamental nature [24]. Having quantified the errors associated with the procedure to compute melting temperatures, we can estimate the uncertainties in melting temperatures associated with DFT itself by comparing its predictions to experiments. Melting temperature predictions on Ta have shown that including the core electrons in GGA results in better melting temperature predictions compared to including only the valence electrons. Including the core electrons predicted a melting temperature of 3200K, while including only the valence electrons resulted in a prediction of 2990K, much lower than the experimental melting temperature of 3258K. [10] Another study studied the effect of using GGA vs. LDA on the predicted melting temperature and found that the GGA underpredicts the melting temperature for Al(888K) and Ni(1557K) compared to the experimental melting temperatures (933K and 1728K, respectively), while LDA overpredicts the melting temperature (972K, and 1884K respectively). This is consistent with the fact that the overbinding in GGA leads to increased temperature requirement to melt the system, and the underbinding in LDA requires less temperature for it to turn into a liquid. [25]

4. Ab initio melting temperature of NbMoTaW

4.1 Melting temperature prediction

Equiatomic NbMoTaW has been shown to have exceptional microhardness and desirable high-temperature properties. [26]. Despite the level of interest in this material, its melting temperature is not known experimentally. The melting temperature of high entropy alloys has typically been calculated by a rule of mixtures. Apart from that, the melting temperature has been calculated for the MoRuTaW system using SLUSCHI. [14]

Figure 6(a) shows the free energy as a function of pressure and temperature for the solid and the liquid. The intersection of the free energy surfaces in P-T space represents the melting temperature as a function of pressure, see Fig. 6(a). The pressure dependence of the melting temperature can be obtained independently from the difference in enthalpy and molar volume between the solid and liquid phases using the Clausius-Clapeyron equation $\left(\frac{dT_m}{dP} = \frac{T\Delta V}{\Delta H}\right)$ [27]. The slope obtained from this expression is shown as a red line in Fig. 6(b). We find very good agreement between the slope predicted by the Clausius-Clapeyron expression (61 K/GPa) and the explicit simulations (64 K/GPa). As shown in Figure 6(b), the free energy method based on DFT-GGA MD simulations predicts a T_m of 3290 K at zero pressure. To get a better understanding of the T_m prediction as a function of the number of points used to fit the solid and liquid, we used all calculations at each temperature to obtain the free energy at 0 pressure conditions. We then sampled all possible combinations of n ($2 \leq n \leq 5$) for both solid and liquid for 1000 times at each combination and calculated the T_m. We find that using 2 points gives us a reasonable guess at the T_m range, and using 4 points gives a good T_m prediction.

SLUSCHI calculations with DFT-GGA are shown in Fig. 7(a), we predict a melting temperature of 3000K ±10K. This 10K is from the curve fitting and represents how well the data fits the model to predict T_0 and not the uncertainties in the prediction. We note that the solid-liquid transition is significantly broader (~1000K) compared to the validation sets. The transition happens over ~400K for the single elements and over ~500K for the binary and the HEA. This is a result of the possible random configurations with the increase in the number of elements in the alloy. This adds to the uncertainty in the melting temperature prediction, accounted for in the uncertainty quantification. The red region in Fig. 7(a) represents the T_m prediction from SLUSCHI, including a ~3% uncertainty, and the yellow region represents the T_m prediction from the free energy calculations, including uncertainties. Quite interestingly, the free energy method predicts lower melting temperatures than SLUSCHI in all validation tests except in Ni and the alloy of interest. Considering the uncertainties associated with the methods (summarized in Table 2), we conservatively predict the melting temperature of NbMoTaW to lie between 3,000 and 3,100 K. This uncertainty, associated with the calculation method, is comparable with the intrinsic accuracy of DFT, as discussed in Section 3.3.

We also calculated the T_m prediction as a function of the number of points per temperature in Fig. 7(b). We again find that about 5 points are enough to obtain a good prediction.

4.2 Computational cost and optimal use of free energy and SLUSCHI methods

When comparing the various methods to compute melting temperature, it is important to determine the accuracy and the computational cost associated with them. We established the accuracy in the previous section and found the small-scale coexistence calculation to be more accurate. For each configuration at a given temperature, running a 10 ps MD simulation requires ~1,250 CPU hours ($time(h) \times number\ of\ CPUs$) in a 108-atom system in a NbMoTaW system. From our statistical analysis, we found that we can obtain a reasonable sampling in the SLUSCHI calculations from five different structures for each temperature, which brings the cost per temperature to ~12,500 CPU hours. We used 8 different temperatures to cover the temperature range where the system can evolve to either a solid or a liquid. Assuming that an approximate T_m range is known, the computational cost for the entire SLUSCHI calculation is approximately 50,000 CPU hours (matching closely to the 40,000 CPU hours reported in [9]). In the free energy method, the computational time to obtain the zero-pressure structure and the 20 ps NVT calculation to obtain the entropy using the 2PT method requires approximately ~7,500 CPU hours per temperature. From our statistical analysis, we found that 4 points are enough to get a reasonable estimate even for high entropy alloys. This results in ~30,000 CPU hours, about 60% computational cost of SLUSCHI. However, the accuracy is worse than SLUCHI. In Fig. 6(c), we find that in the free energy method, it is possible to obtain a reasonable T_m range from 3 temperatures for high entropy alloys. Hence, an estimate of the temperature range to be explored can be obtained with a 22,500 CPU hour investment. Hence, an efficient approach would be to use the free energy method to obtain an estimate of the melting temperature and then use this information to establish a set of temperatures for SLUSCHI calculations to get accurate results.

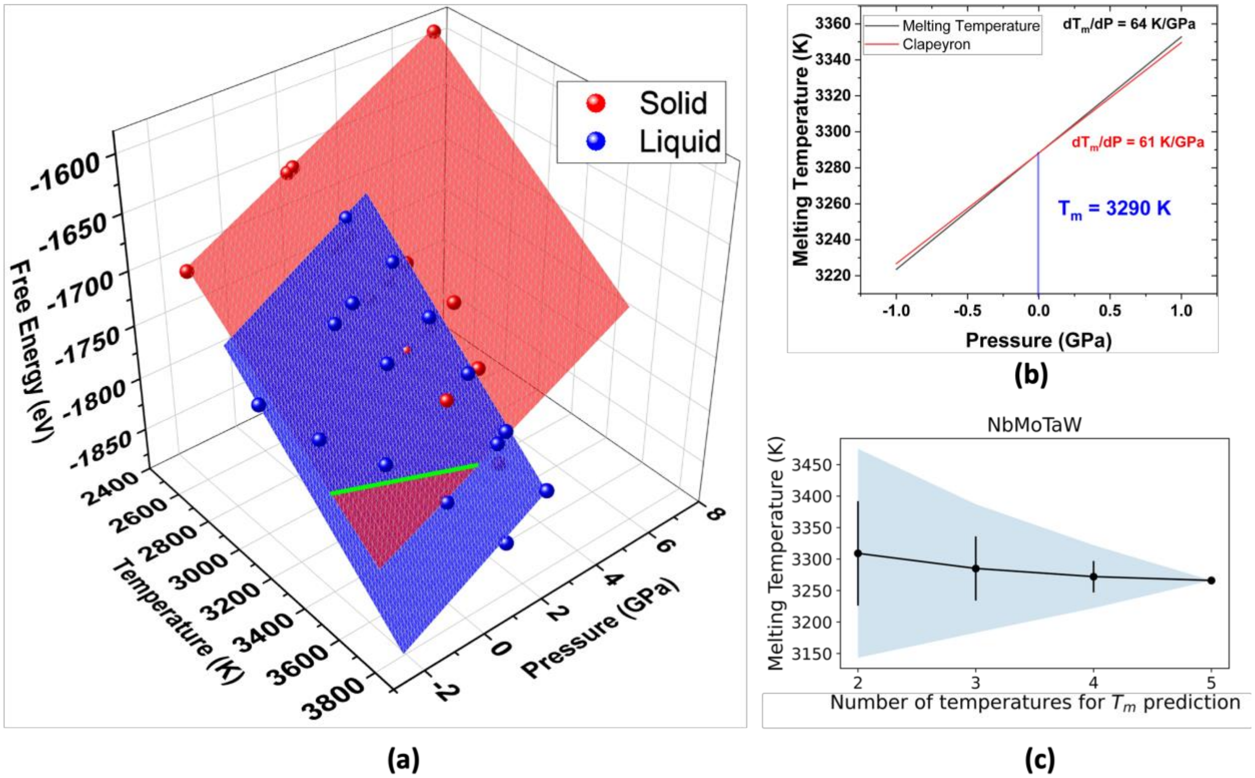
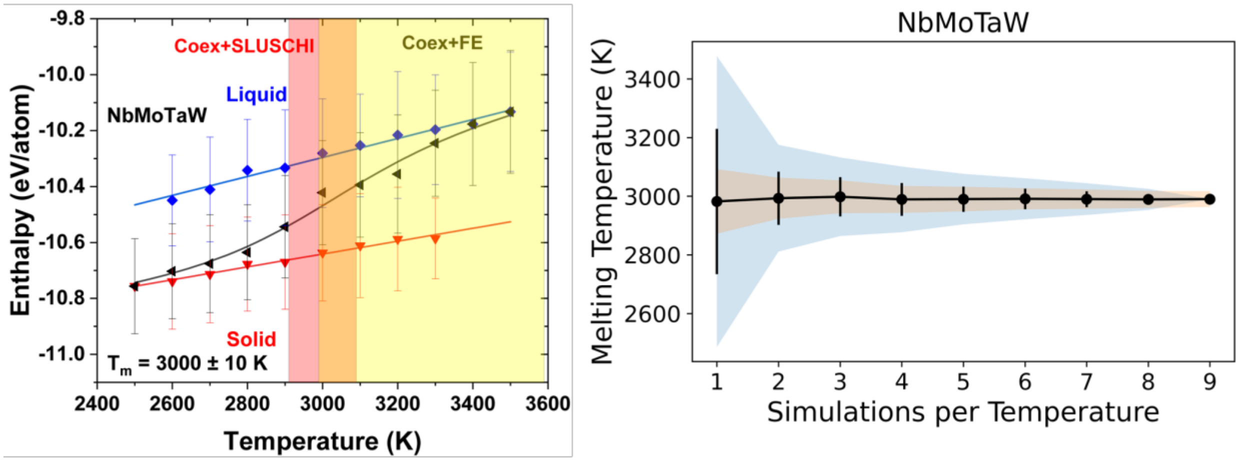


Figure 6 Melting temperature prediction for NbMoTaW using the free energy method. (a) Free energies of the solid and the liquid as a function of pressure and temperature (b) the melting temperature dependence with pressure from the fit in 6(a) compared with that calculated from the Clausius-Clapeyron equation(c) Melting temperature prediction's mean, standard deviation, and the 95% confidence interval with the number of points used to fit the solid and liquid free energy curves.



(a) **(b)**

Figure 7 Melting point prediction for NbMoTaW (a) using the SLUSCHI method. The red region represents the uncertainty in the melting temperature in the SLUSCHI method, while the yellow region represents the uncertainty in the free energy method compared to the large-scale coexistence method as determined from the uncertainty quantification. The orange region is the overlap between the prediction from both the methods with their uncertainties. (b) as a function of the number of simulations per temperature

System	Coexistence	Free Energy	SLUSCHI
Ni	1755±5K (4096atoms)	1705±10K (256atoms) ✱ 1675±5K (4000atoms)	1730±5K (256 atoms) ✤
Cu	1170±5K (4096atoms)	1050±10K (256atoms) ✱ 1035±5K (4000atoms)	1140±5K (256 atoms) ✤

CuNi	1705±50K (4096 atoms)	1535±25K (256 atoms) ✱ 1515±10 K (4000 atoms)	1675±5K (216atoms) ✤
CoCuCrFeNi	2070±50K(4096atoms)	1875±45K (256atoms) ✱ 1830±10K (4000 atoms)	2035±10K (216atoms) ✤
NbMoTaW	-	3290K (108 atoms) †	3000±10K (108 atoms) ✧

Table 1 Comparing the melting temperature predictions from the large-scale coexistence, the free energy, and the small-scale coexistence methods.

✱: Fig. 3; ✤: Fig. 5; †: Fig. 6(c); ✧: Fig. 7(b)

System	**Δ T_m [Coexistence(4096) – Free Energy (256)]**	**Δ T_m [Coexistence(4096) – Free Energy (4000)]**	**Δ T_m [Coexistence(4096) – SLUSCHI (128)]**
Ni	50±15 K	80±10 K	25±10 K
Cu	120±15 K	135±10 K	30±10 K
CuNi	170±75 K	190±60 K	30±55 K
CoCuCrFeNi	195±95 K	240±60 K	35±60 K

Table 2 Difference between the melting temperature prediction from different methods

5 Conclusions

In this work, we quantified the uncertainties associated with the melting temperature calculations that can be used with ab initio or DFT MD simulations. Armed with these uncertainties, we calculated the melting temperature of the equiatomic NbMoTaW system to be between 3,000K and 3,100K. Furthermore, we quantify the errors of the free energy method by comparing it to other melting point determination methods and the effect of simulation cell size and structure variability. Small-scale coexistence calculations are not stable as they can evolve to either solid or liquid with no coexistence. As a result, we need to run extensive calculations to characterize the relative number of times the system ends up as a solid vs. the number of times it ends up as a liquid. Even though the small-scale coexistence method is more accurate than the free energy method, the computational cost of the free energy method will typically be lower. As the computational cost of the small-scale coexistence method can be reduced with a good guess of the temperature range to be explored, the free energy method can be used as a first resort for a rough prediction, followed by a SLUSCHI calculation.

Data availability

The data that supports the findings of this study are available within the article.

Acknowledgments

We acknowledge the support from the US National Science Foundation, DMREF program, under Contract Number 1922316-DMR.

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