

Cite this: *Phys. Chem. Chem. Phys.*, 2012, **14**, 1529–1534

www.rsc.org/pccp

PAPER

Ab initio calculations of the melting temperatures of refractory bcc metals

L. G. Wang^{*ab} and A. van de Walle^{ac}

Received 25th September 2011, Accepted 21st November 2011

DOI: 10.1039/c1cp23036k

We present *ab initio* calculations of the melting temperatures for bcc metals Nb, Ta and W. The calculations combine phase coexistence molecular dynamics (MD) simulations using classical embedded-atom method potentials and *ab initio* density functional theory free energy corrections. The calculated melting temperatures for Nb, Ta and W are, respectively, within 3%, 4%, and 7% of the experimental values. We compare the melting temperatures to those obtained from direct *ab initio* molecular dynamics simulations and see if they are in excellent agreement with each other. The small remaining discrepancies with experiment are thus likely due to inherent limitations associated with exchange–correlation energy approximations within density-functional theory.

I. Introduction

High-performance refractory materials attract much attention because of their many technological applications, such as in gas turbine engines, components of rocket thrusters, shields *etc.* However, the reliable determination of the melting properties of extremely high melting-point materials *via* experimental means is challenging. It requires some special techniques, such as aerodynamic levitation and laser heating^{1,2} or diamond-anvil cell experiments, to be performed. Such experiments would be difficult to undertake on a large scale, for instance, to systematically search for novel refractory materials.

In this paper, we investigate the accuracy and feasibility of a computational approach to this problem. The key questions are: (i) are density functional calculations sufficiently accurate? (ii) Can computational costs be kept under control without sacrificing accuracy? (iii) Can the process be automated for the purpose of screening candidate refractory materials?

The paper is organized as follows. In Section II, we overview some of the existing methods available to calculate melting points and motivate our selection of method. We then give the main technical details of our calculations. We describe the techniques for performing the coexisting solid and liquid simulation and the free energy corrections for the melting temperature. The calculated results are presented and discussed in Section III. We summarize the present work in Section IV.

II. Methodology

A. Overview of existing methods

There are a few approaches that are generally used to compute the melting temperature of a material. In the so-called thermodynamic integration approach,^{3–8} the free energy differences of solid and liquid phases with respect to a reference system (such as an ideal gas) whose free energy is known or easily calculated are calculated by thermodynamic integration along a path joining the Hamiltonian of the reference system and the *ab initio* Hamiltonian. The melting temperature is then determined by the equality of the Gibbs free energies of the solid and liquid phases. This approach can be very computationally demanding if the reference systems are not well chosen. A second approach to determine the melting temperature is to simulate the system containing liquid and solid phases in coexistence.^{9–19} Because there is no need to nucleate the solid or liquid phase the system can spontaneously adjust its temperature so that it satisfies the equality of Gibbs free energies of solid and liquid phases. Such two-phase equilibria are stable if the calculations are performed using the NVT or NPH ensembles. Since such a simulation of solid and liquid phases in coexistence requires a large supercell with a few hundreds or thousands of atoms, it is thus very expensive to do direct first-principles molecular dynamics simulations. So this is commonly done by classical molecular dynamics simulations with empirical potentials, which are fitted to *ab initio* data and/or experimental values. The problem for classical MD simulations is the reliability and transferability of the empirical potentials. Empirical interatomic potentials, most commonly fitted to the so-called mechanical properties of the materials, usually provide no guarantee to give good results for the nonmechanical properties, such as melting temperatures.^{20,21}

^a Division of Engineering and Applied Sciences, California Institute of Technology, Pasadena, California 91125, USA.

E-mail: lgwang@caltech.edu

^b Power Environmental Energy Research Institute, Covina, CA 91722, USA

^c School of Engineering, Brown University, Providence, RI 02912, USA

Alfè *et al.*^{22–25} used a method that combines the above two approaches to investigate the melting properties of some metals. In this approach, one first obtains an approximate melting temperature by a solid/liquid coexistence simulation using empirical potentials. Next, using the classical potential as a reference system, the *ab initio* melting temperature is obtained *via* a perturbative treatment of the solid and liquid free energies akin to thermodynamic integration in the limit of two very similar systems. This approach has been successfully applied to get the melting temperatures of Fe,²² Cu,²³ Ta²⁴ and Mo²⁵ in a wide pressure range. For Fe at a pressure of 330 Gpa (close to the pressure at the boundary between the Earth's solid inner core and liquid outer core), the authors found that this approach gives a melting temperature in excellent agreement with the one by the thermodynamic integration approach.²² For Ta and Mo, the authors obtained 3270 K and 2894 K, respectively, at zero pressure which are in excellent agreement with the experimental values. For Cu, the *ab initio* melting temperature of 1176 K at zero pressure by this approach is about 13% below the experimental value.

In the present paper, we follow the latter approach, and demonstrate that it generally provides good accuracy at a very manageable computational cost. Since our ultimate goal is to automate the screening of numerous candidate refractory materials, we are especially interested to see if the method remains robust as the accuracy of the classical potential used decreases. If less accurate classical potentials are sufficient, their construction could, in principle, be more easily automated.

B. Reference potential simulations of the coexisting solid–liquid system

The coexisting solid and liquid simulation is done with an embedded-atom method potential.^{26,27} The total energy E_{tot} of the system is given by

$$E_{\text{tot}} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i \neq j} V(r_{ij}), \quad (1)$$

$$\rho_i = \sum_j \phi(r_{ij}), \quad (2)$$

where $F(\rho)$ is the embedding function, and $V(r_{ij})$ is the pair potential between atoms i and j separated by r_{ij} . $\phi(r_{ij})$ is the electron-density contribution from atom j to atom i . The total electron density ρ_i at an atom position i is a linear superposition of electron-density contributions from the neighboring atoms within the cutoff distance. In eqn (1), the summations run over all atoms in the system. The multi-body nature of the EAM potential is a result of the embedding energy term.

For bcc metals Nb, Ta and W, a number of authors have developed the empirical potentials.^{28–32} For Nb and Ta, we use the potentials fitted by the force-matching method.^{29,30} The potentials were fitted to a database of the forces, energies, and stresses obtained from *ab initio* molecular dynamics simulations at various temperatures and under various strain conditions. As we will see below these potentials can predict excellent melting temperatures for Nb and Ta compared to the experimental values. For W, we use the EAM potential developed by Zhou *et al.*³¹ The potential was fitted to some basic material properties (such as lattice constant, elastic constant, bulk modulus,

vacancy formation energy, *etc.*) at zero temperature. Since the fitting does not include any structures and properties at non-zero temperatures, this potential does not work very well for predicting the melting temperature. At the same time, if accurate results can be obtained with such a potential, this would demonstrate that the accuracy requirements of the potential are relatively easy to meet.

In order to get the melting temperature using the reference potentials we perform the molecular dynamics simulations of constant enthalpy and constant pressure (NPH) ensemble using a coexisting solid and liquid supercell. The supercell is periodic and consists of 16 384 atoms (*i.e.*, consisting of $16 \times 16 \times 32$ bcc unit cells). Our MD simulations are performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) code.³³ The advantage to include the solid and liquid phases in coexistence is that this method avoids the hysteresis caused by the phase nucleation, and the system can spontaneously adjust its temperature to satisfy the equality of Gibbs free energies of solid and liquid phases. If the initial temperature is slightly above the melting temperature, the solid starts to melt, thus reducing the system temperature until it reaches the melting temperature, and *vice versa* if the initial temperature is below the melting temperature. (Of course, if the initial given temperature is too high or low the system may not be large enough to compensate and will completely melt or solidify.) An alternative method to obtain the melting temperature is to perform the simulation of constant volume and constant energy (NVE) ensemble as done in previous works.^{22–25} However, this involves a careful adjustment of the volume in order for the equilibrated system to have the desired pressure.

Our coexistence simulation is carried out *via* the following procedure. We first obtain a very rough estimation of the expected melting temperature by rapidly heating the system (initialized in the crystalline state) until melting is observed. Next, we generate a supercell by cutting it out of an infinite perfect bcc crystal at the equilibrium lattice constant obtained by the reference potential. The supercell is thermalized at a temperature slightly below the previously estimated expected melting temperature. After this thermalization the entire system remains in the solid state. If the system is melted, this means that the thermalization temperature is too high, we have to restart the thermalization at a lower temperature. Then we fix the atoms in one half of the supercell (along the long axis) and let another half to heat to a very high temperature (typically several times the expected melting temperature) to completely melt it. The atoms in this half of the supercell are rethermalized at the expected melting temperature with the fixed half held fixed. Finally, all atoms in the system are allowed to evolve freely at constant enthalpy and constant pressure (NPH) for a simulation time of 100 ps. In our simulation, we fix the pressure at the atmospheric pressure. The temperature and volume are monitored in order to check whether the system reaches the equilibrium. If the system stays in a state of coexistence between solid and liquid, we calculate the melting temperature by averaging the temperatures over the MD steps that the system has been in equilibrium.

C. *Ab initio* free energy corrections

The melting temperature of a material predicted by the coexistence simulation with a reference potential can deviate significantly from

the experimental value.^{20,21} For example, in the case of W the melting temperature obtained in the coexistence simulation is about 940 K too high, relative to the experimental value. So there is no guarantee of accurately predicting the melting temperature of a material within a reasonable accuracy using such reference potentials. *Ab initio* calculations within the framework of density-functional theory (DFT)^{34–38} are considered to be most reliable. Therefore, it is desirable to calculate the melting temperature of a material within the *ab initio* or DFT accuracy. We will follow the approach developed by Alfè *et al.*^{22–25} to correct the melting temperature to the *ab initio* or DFT accuracy.

The difference in melting temperature between the reference potential and the *ab initio* is given, to the first order, by

$$\Delta T_m \approx \frac{\Delta G^{\text{ls}}(T_m^{\text{ref}})}{S_{\text{ref}}^{\text{ls}}}, \quad (3)$$

where $\Delta G^{\text{ls}} = G_{\text{AI}}^{\text{ls}} - G_{\text{ref}}^{\text{ls}}$. $G_{\text{AI}}^{\text{ls}}(P, T) = G_{\text{AI}}^{\text{l}}(P, T) - G_{\text{AI}}^{\text{s}}(P, T)$ and $G_{\text{ref}}^{\text{ls}}(P, T) = G_{\text{ref}}^{\text{l}}(P, T) - G_{\text{ref}}^{\text{s}}(P, T)$ are the Gibbs free energy differences between the liquid (l) and solid (s) phases from *ab initio* (AI) and reference potentials (ref). The entropy of melting $S_{\text{ref}}^{\text{ls}}$ is calculated from the relation $T_m^{\text{ref}} S_{\text{ref}}^{\text{ls}} = E_{\text{ref}}^{\text{ls}} + pV_{\text{ref}}^{\text{ls}}$, where the energy difference $E_{\text{ref}}^{\text{ls}}$ and the volume difference $V_{\text{ref}}^{\text{ls}}$ on melting are obtained by the two separate simulations of liquid and solid phases, while p is the pressure. Following the previous works by Alfè *et al.*,^{22–25} for the isothermal–isochoric simulations the Gibbs free energy shifts for liquid and solid phases can be evaluated by

$$\Delta G = \Delta F - \frac{1}{2} \frac{V \Delta P^2}{K_T}, \quad (4)$$

where K_T is the isothermal bulk modulus, and ΔP is the pressure change. V is the volume which is kept constant during the simulations. ΔF is given by the following equation.

$$\Delta F \approx \langle \Delta U \rangle_{\text{ref}} - \frac{1}{2k_B T} \langle \delta \Delta U^2 \rangle_{\text{ref}}, \quad (5)$$

where $\Delta U = U_{\text{AI}} - U_{\text{ref}}$ and $\delta \Delta U = \Delta U - \langle \Delta U \rangle_{\text{ref}}$. k_B is the Boltzmann's constant, and T is the simulation temperature. The average is taken for the reference system.

Our *ab initio* calculations are performed within the density-functional theory framework as implemented in Vienna *Ab-initio* Simulation Package (VASP) codes.^{39,40} We employ the generalized gradient approximation (GGA) for exchange–correlation energy.⁴¹ The projector augmented wave (PAW) pseudopotentials^{42,43} are used to describe interactions between ions and valence electrons. The semi-core p states are treated as valence states. For W, as a test we keep the semi-core frozen and find that there is a change of less than 50 K for the melting temperature. The cutoff energies are 261 eV for Nb, 280 eV for Ta and 279 eV for W. Only the Γ -point is used for the Brillouin-zone sampling of the supercell with 128 atoms.

III. Results and discussion

In Fig. 1, we show an example of our MD coexistence simulations for Ta. The time evolution of temperature and volume is plotted in Fig. 1, and the results indicate that the simulation has reached the equilibrium state. As it is done in several previous papers,^{22–25} we monitor the system throughout by calculating the average

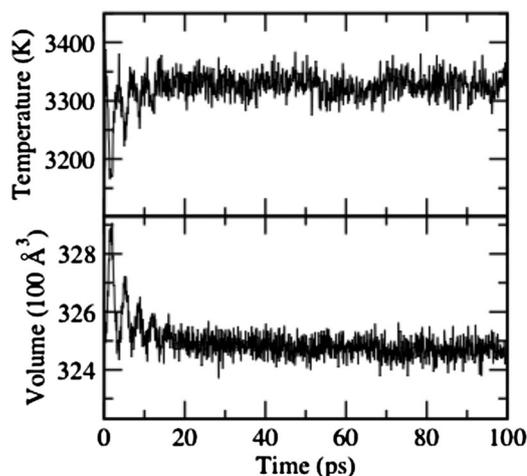


Fig. 1 Temperature (upper panel) and volume (lower panel) for a coexistence simulation of Ta using the EAM reference potential.

number of density in slices of the supercell taken parallel to the interface between solid and liquid phases. The density profiles of Nb, Ta and W for the snapshots at the simulation time of 100 ps are shown in Fig. 2. We can see that the systems still contain solid and liquid phases in coexistence after a long time (100 ps) simulation. On the right half of the supercell, the periodically oscillated density indicates those atoms that are in the form of solid. On the left half of the supercell they are liquid-like since the density has the form of random fluctuations with a much smaller amplitude compared to that on the right half. We determine the melting temperature from the average temperature in the last 30 ps simulation. The melting temperatures for Nb, Ta and W obtained by the two-phase coexistence simulations are given in Table 1. For Ta and Nb, the melting temperatures obtained by these MD simulations are very close to the experimental values; they are 3332 K and 2702 K

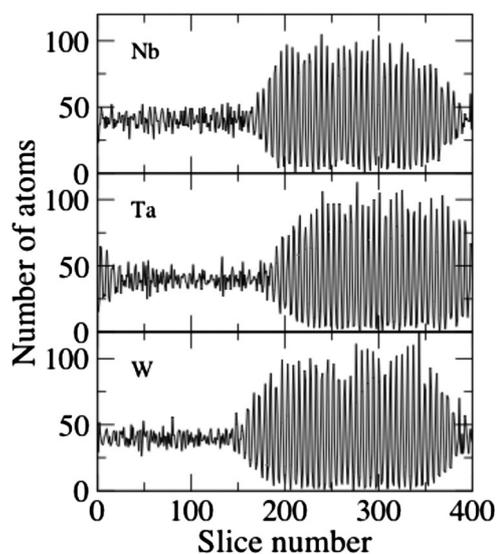


Fig. 2 Density profiles in the coexisting solid and liquid simulations for Nb, Ta and W. The supercell is divided into 400 slices of equal thickness parallel to the liquid–solid interface, and the number of atoms in each slice determines the intensity.

Table 1 Melting temperature, entropy difference, and volumes for the solid and liquid phases determined by the simulations using reference potentials. They are given in the units of K, $\text{J mol}^{-1} \text{K}^{-1}$, and \AA^3 per atom, respectively. The entropy difference and the volumes for the solid and liquid phases are obtained at their T_m temperatures. The experimental melting temperatures⁴⁴ are also presented for comparison

	$S_{\text{ref}}^{\text{ls}}$	$V_{\text{ref}}^{\text{solid}}$	$V_{\text{ref}}^{\text{liquid}}$	T_m	T_m^{exp}
Nb	8.75	19.57	20.25	2702	2720
Ta	10.04	19.17	20.54	3332	3290
W	8.89	17.22	18.26	4637	3695

compared to the experimental values⁴⁴ of 3290 K and 2750 K, respectively. As it is mentioned above, the EAM potentials for Ta and Nb were fitted to the forces, energies, and stresses from some *ab initio* MD snapshots at zero and non-zero temperatures. Therefore, this might explain why we get a good agreement for Ta and Nb. This also indicates that it is important to include some properties (such as forces) at non-zero temperatures into the potential fitting. However, for W the EAM potential was fitted to the zero-temperature material properties (such as lattice constant, elastic constant, bulk modulus, and vacancy formation energy, *etc.*). It is not surprising that we get a poor agreement on the melting temperature compared to the experimental value. In Table 1, we also present the entropy difference between liquid and solid phases, and their equilibrium volumes at the T_m temperatures.

The *ab initio* melting temperatures for Nb, Ta and W are computed by correcting T_m obtained in the coexistence simulations using the reference potentials. For each metal we perform two independent molecular dynamics simulations using the reference potential. The simulation is done for the solid (or liquid) phase using a supercell with 128 metal atoms and the constant NVT ensemble. The supercell volume and the simulation temperature are fixed at the corresponding equilibrium volume and T_m during the simulation. We run the simulation for 2 million steps (*i.e.* a simulation time of 200 ps). We take each snapshot from the simulation every 20 000 MD steps with the first one taken at the 500 000 MD step. This ensures that the snapshots we take are not correlated with each other. Totally 76 snapshots are taken from each simulation, and we run *ab initio* total energy calculations for these snapshots using the VASP package.^{39,40} The results for $\langle \Delta U \rangle_{\text{ref}}$ and $\langle \delta \Delta U^2 \rangle_{\text{ref}}$ per atom are reported in Table 2. Fig. 3 shows $\langle \Delta U \rangle_{\text{ref}}$ as a function of the number of snapshots for Ta. We see that the $\langle \Delta U \rangle_{\text{ref}}$ difference between the liquid and solid phases varies less than 5 meV per atom when the number of snapshots is larger than 50. According to eqn (3) and the values in Table 2, we can calculate the corrections for T_m . The computed

ab initio melting temperatures are given in Table 2. Since the pressure changes are 4 or 5 orders of magnitude smaller than the experimental K_T values, their contributions to the melting temperature corrections are negligible. We see that the *ab initio* melting temperatures are within the errors of 3%, 4%, and 7% of the experimental values for Nb, Ta and W, respectively. Although for Nb and Ta the melting temperatures after corrections are slightly worse than those uncorrected results, the agreement between our *ab initio* results and the experimental data is satisfactory. Our melting temperature for Ta is about 100 K lower than the result obtained in ref. 24 at zero pressure, but falls in the error bar of the calculations. For W, the Gibbs free energy corrections reduce the error from 25% to less than 7%, which is a substantial improvement of the accuracy.

This remaining discrepancy between the calculated and experimental melting temperatures may be attributed to the inherent limitations of density-functional theory and/or the DFT calculation convergences or to approximations made in computing the corrections to the reference potential results. For the latter we especially pay our attention to the W case since there exists the largest difference between the EAM potential and the *ab initio* Hamiltonian. There are mainly three sources of errors stemming from the approximations made in correcting the reference potential melting temperature. The first two errors in correcting the reference potential melting temperature are caused by truncating the free energy expansion (eqn (5)) and the first order approximation we use in eqn (3). Therefore, for this approach it is essential to have the ΔU fluctuations as small as possible. From Table 2, we can see that the $\langle (\delta \Delta U)^2 \rangle_{\text{ref}}$ fluctuations for solid and liquid phases are already very small. This indicates that the EAM potentials should be able to mimic the *ab initio* systems reasonably well. Using the exact form of eqn (5) (*i.e.* eqn (3) in ref. 23) we show that the free energy expansion truncation causes an error < 10 K. It is difficult to compute the higher order corrections to the melting temperature without rather extensive free-energy calculations.²² We estimate the ratio between the second order correction and the first order correction (eqn (7) in ref. 22) using the constant-pressure heat capacities for liquid and solid phases obtained from the reference potentials. We only consider the first term on the right side of the equation, and ignore the term of the shift of entropy of fusion since it is difficult to compute. We expect that it might have a similar contribution as the first term. The second order correction to the melting temperature is found to be about 1–4% of the first order correction ΔT_m , which is a few K for Ta and Nb and less than 50 K for W. A third source of error is that we approximate $S_{\text{ref}}^{\text{ls}}$ as a constant over the temperature range including the raw EAM melting temperature and the true

Table 2 Thermal averages of the difference ΔU between the *ab initio* and reference energies and the squared fluctuation $\delta \Delta U$. Δp is the change of pressure when U_{AI} replaces U_{ref} at constant V and T ($V = V_{\text{ref}}^{\text{solid}}$ or $V_{\text{ref}}^{\text{liquid}}$ and $T = T_m$ given in Table 1). The *ab initio* melting temperature T_m^{AI} is calculated according to eqn (3). All energies are given in eV, and pressure in kb, and melting temperature in K. N is the number of atoms in the supercell

	$\langle \Delta U \rangle_{\text{ref}}/N$		$\frac{1}{2k_B T} \langle (\delta \Delta U)^2 \rangle_{\text{ref}}/N$		$\langle \Delta p \rangle$		T_m^{AI}	$\frac{ T_m^{\text{AI}} - T_m^{\text{exp}} }{T_m^{\text{exp}}} \%$
	Liquid	Solid	Liquid	Solid	Liquid	Solid		
Nb	-3.3749	-3.3833	0.0015	0.0016	4.3	3.5	2794	2.7
Ta	-4.4349	-4.4178	0.0019	0.0020	-21.4	8.3	3170	3.6
W	-5.2414	-5.1321	0.0035	0.0031	-0.7	24.4	3450	6.6

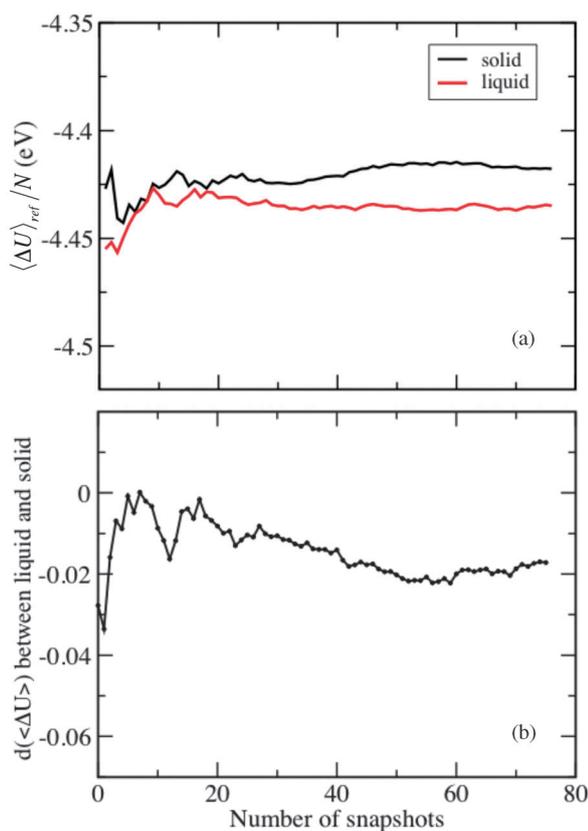


Fig. 3 (a) Thermal averages of the difference $\Delta U = U_{AI} - U_{ref}$ of *ab initio* and reference energies for solid and liquid phases as a function of the number of snapshots. (b) The difference $\langle \Delta U \rangle$ between the liquid and solid phases.

ab initio one. Actually, it can be expressed as a linear function of temperature for the temperature range we are interested in, and we find that $S_{ref}^{ls} \propto 0.00182 T$ for W. If we use the averaging S_{ref}^{ls} for W this can change the melting temperature by about 80 K. For Nb and Ta, the changes are less than 20 K. On the other hand, it was previously found that density-functional theory itself could lead to an error of about 13% for Cu.²³ Here we have not tried to further refine the W potential and figure out what is the reason to lead to the difference between the calculated and experimental melting temperatures. We also notice that as estimated in the previous works^{22,24} there is an uncertainty of about 100 K for the melting temperatures reported here caused by some factors, such as the k-point mesh in our *ab initio* calculations and the number of snapshots, *etc.* If adding up all these errors this makes the experimental values within the error bar of this theoretical method. However, as shown below the melting temperatures obtained by the free energy correction approach are in excellent agreement with the results obtained from the direct *ab initio* MD coexistence simulations. This provides further evidence to justify the approximations in the free energy correction approach.

We compare the melting temperatures of Ta and W to those results obtained from the direct *ab initio* MD coexistence simulations.⁴⁵ The direct *ab initio* molecular dynamics coexistence simulations are performed using a supercell with 448 W atoms and the constant NPH ensemble, as recently implemented

in VASP.¹⁸ Although the supercell is relatively small, using the EAM reference potential we have shown that the melting temperatures for Ta vary within 40 K for the supercell sizes from 448 to 16 384 atoms, and for W they vary within 50 K.⁴⁵ So we believe that the direct *ab initio* MD simulations can obtain the melting temperatures, which are comparable to those from the free energy correction approach. The direct *ab initio* MD coexistence simulations give the melting temperatures of 3110 K and 3465 K for Ta and W (with a standard deviation of ~ 100 K), respectively. They are 60 K and 15 K different from those obtained by the free energy correction approach. These results fall well within the statistical accuracy of the two results, thus providing an independent cross check for the melting temperature obtained with the free energy correction approach. The excellent agreement for the melting temperatures by two *ab initio* approaches leads us to attribute the remaining discrepancies between the calculated results and the experimental values to the inherent limitations of density-functional theory.

IV. Summary

We have calculated the melting temperatures of bcc metals Nb, Ta and W within the framework of density-functional theory. The melting temperatures are calculated in two steps. The first step is to perform a coexisting solid and liquid simulation of a large supercell (including 16 384 metal atoms) by using a reference potential. Given that the reference potential can mimic the *ab initio* systems reasonably well, in the second step the free energy corrections can be made to obtain the fully *ab initio* melting temperature of the material. The multi-body EAM potentials have been employed in our calculations. The calculated free energy differences between the references and the *ab initio* and the free energy difference fluctuations show that the potentials can describe the solid and liquid systems reasonably well. For *ab initio* calculations, we have performed the calculations using the projector augmented wave pseudopotentials and the generalized gradient approximation for exchange–correlation energy. The calculated melting temperatures are within an error of 3%, 4%, and 7% compared to the experimental data for Nb, Ta and W, respectively. The results for W are especially instructive from a methodological point of view, as they show that the free energy correction method is still very effective, even when using a relatively inaccurate (but simpler to construct) reference potential. This was not obvious at the onset, given the perturbative nature of the method. The results obtained from the direct *ab initio* MD coexistence simulations are in excellent agreement with those by the free energy correction approach, thus providing an independent validation of the approximations included in the approach. The remaining discrepancies between the calculated results and the experimental values may be attributed to the inherent limitations of density-functional theory.

The authors thank Prof. Dario Alfè at University College London for providing us their NPH molecular dynamics simulation codes used in ref. 18. Discussions with Qijun Hong, Ljubomir Miljadic, and Pratyush Tiwary are gratefully acknowledged. This research was supported by NSF through TeraGrid resources provided by NCSA and TACC under grant DMR050013N and by ONR under grant N00014-11-1-0261.

References

- 1 P. F. Paradis, F. Babin and J. M. Gagne, *Rev. Sci. Instrum.*, 1996, **67**, 262.
- 2 Y. Arai, P. F. Paradis, T. Aoyama, T. Ishikawa and S. Yoda, *Rev. Sci. Instrum.*, 2003, **74**, 1057.
- 3 O. Sugino and R. Car, *Phys. Rev. Lett.*, 1995, **74**, 1823.
- 4 D. Frenkel and B. Smit, *Understanding Molecular Simulation from Algorithms to Applications*, Academic Press, San Diego, 2002.
- 5 G. A. de Wijs, G. Kresse and M. J. Gillan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **57**, 8223.
- 6 D. Alfè, M. J. Gillan and G. D. Price, *Nature (London, U. K.)*, 1999, **401**, 462.
- 7 D. Alfè, G. D. Price and M. J. Gillan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 045123.
- 8 X. Wang, S. Scandolo and R. Car, *Phys. Rev. Lett.*, 2005, **95**, 185701.
- 9 J. R. Morris, C. Z. Wang, K. M. Ho and C. T. Chan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 3109.
- 10 S. Yoo, X. C. Zeng and J. R. Morris, *J. Chem. Phys.*, 2004, **120**, 1654.
- 11 J. Wang, S. Yoo, J. Bai, J. R. Morris and X. C. Zeng, *J. Chem. Phys.*, 2005, **123**, 36101.
- 12 S. Yoo, X. C. Zeng and S. S. Xantheas, *J. Chem. Phys.*, 2009, **130**, 221102.
- 13 G. R. Fernández, J. L. F. Abascal and C. Vega, *J. Chem. Phys.*, 2006, **124**, 144506.
- 14 E. Schwegler, M. Sharma, F. Gygi and G. Galli, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 14779.
- 15 D. Alfè, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 060101.
- 16 D. Alfè, *Phys. Rev. Lett.*, 2005, **94**, 235701.
- 17 D. Alfè, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **68**, 64423.
- 18 E. R. Hernández, A. Rodríguez-Prieto, A. Bergara and D. Alfè, *Phys. Rev. Lett.*, 2010, **104**, 185701.
- 19 S. Yoo, S. S. Xantheas and X. C. Zeng, *Chem. Phys. Lett.*, 2009, **481**, 88.
- 20 J. B. Sturgeon and B. B. Laird, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **62**, 14720.
- 21 S. Ryu and W. Cai, *Model. Simul. Mater. Sci. Eng.*, 2008, **16**, 085005.
- 22 D. Alfè, M. J. Gillan and G. D. Price, *J. Chem. Phys.*, 2002, **116**, 6170.
- 23 L. Vočadlo, D. Alfè, G. D. Price and M. J. Gillan, *J. Chem. Phys.*, 2004, **120**, 2872.
- 24 S. Taioli, C. Cazorla, M. J. Gillan and D. Alfè, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 214103.
- 25 C. Cazorla, S. Taioli, M. J. Gillan and D. Alfè, *J. Chem. Phys.*, 2007, **126**, 194502.
- 26 M. S. Daw and M. I. Baskes, *Phys. Rev. Lett.*, 1983, **50**, 1285.
- 27 M. S. Daw and M. I. Baskes, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1984, **29**, 6443.
- 28 G. J. Ackland and R. Thetford, *Philos. Mag. A*, 1987, **56**, 15.
- 29 M. R. Fellingner, H. Park and J. W. Wilkins, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 144119.
- 30 Y. Li, D. J. Siegel, J. B. Adams and X. Y. Liu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **67**, 125101.
- 31 X. W. Zhou, R. A. Johnson and H. N. G. Wadley, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **69**, 144113.
- 32 A. Hashibon, A. Y. Lozovoi, Y. Mishin, C. Elsasser and P. Gumbsch, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 094131.
- 33 S. J. Plimpton, *J. Comput. Phys.*, 1995, **117**, 1; see also their webpage <http://lammps.sandia.gov>.
- 34 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
- 35 W. Kohn and L. Sham, *Phys. Rev.*, 1965, **140**, A1133.
- 36 R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.*, 1989, **61**, 689.
- 37 M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.*, 1992, **64**, 1045.
- 38 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
- 39 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **48**, 13115.
- 40 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.
- 41 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 42 P. E. Blochl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
- 43 G. Kresse and J. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 44 D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 86th edn, 2005.
- 45 L. G. Wang and A. van de Walle, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 092102.