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Melting temperature of tungsten from two *ab initio* approaches

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We have calculated the melting temperature of tungsten by two *ab initio* approaches. The first approach can be divided into two steps. In the first step, we simulate a large coexisting solid and liquid system by the classical embedded-atom method potential and obtain an approximate melting temperature. In the second step, we compute the accurate melting temperature by performing the *ab initio* free-energy corrections. The second approach is to perform a direct *ab initio* molecular-dynamics simulation for the coexisting solid and liquid system using the constant particle number, pressure, and enthalpy ensemble. In the second approach, the simulation is carried out entirely using a density-functional theory Hamiltonian, and no other approximations are imposed. However, the simulation is performed using a relatively small supercell. The results obtained from two *ab initio* approaches can provide a check for each other. Our results show that they are in good agreement with each other and also in reasonably good agreement with the experimental value.

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Computer simulation of solid-liquid equilibrium can be traced back to the 1950s.[1] Thanks to the increasing power of modern supercomputers, it has recently become possible to calculate the melting properties of materials using accurate *ab initio* methods. There are two commonly used computational approaches introduced in previous studies to obtain the melting temperature of a material. The first one is the so-called thermodynamic integration approach.[2–7] In this approach, the Gibbs free energies are calculated *ab initio* for solid and liquid, and the melting transition is determined by the equality of the Gibbs free energies of two phases. The second approach is the direct simulation of the solid-liquid coexistence, i.e., the so-called coexistence approach.[8–18] In this approach, the temperature adjusts spontaneously during the simulation to provide a two-phase equilibrium that satisfies the equality of Gibbs free energies of solid and liquid. In this paper, we use a recently proposed[19–22] hybrid approach combining the above two approaches. An approximate melting temperature is first obtained by coexisting solid and liquid simulation using an empirical potential. Next, the *ab initio* melting temperature is obtained by applying free-energy corrections akin to thermodynamic integration in the limit of small perturbations. This approach has been applied to get the melting properties of Fe,[19] Cu,[20] Ta,[21] and Mo[22] for a wide pressure range. The advantage of this last approach is its moderate computational costs compared with the other two approaches.

As the melting point is a quantity that is very sensitive to small inaccuracies in the Hamiltonian used, the use of accurate *ab initio* methods is desired. However, such methods are computationally demanding, and the accuracy is limited by sampling and system size convergence. The ability to internally check the accuracy of the results is therefore crucial. In the present paper, we employ two *ab initio* approaches, i.e., the free-energy correction approach and the direct molecular-dynamics (MD) coexistence approach, to obtain the melting temperature for W. The melting temperatures obtained from two *ab initio* approaches are consistent with each other. The theoretical result is within an error of 7% of the experimental value, and this discrepancy may be attributed to the limitations of common approximations to density-functional theory.

The free-energy correction approach has been discussed in detail in previous papers.[19–23] In the free-energy correction approach, we first obtain the approximate melting temperature T_m^{ref} by molecular-dynamics simulation of a large coexisting system with 16 384 tungsten atoms (i.e., consisting of $16 \times 16 \times 32$ bcc unit cells), using the embedded-atom method (EAM) reference potential[24] and a constant particle number (N), pressure (P), and enthalpy (H) (NPH) ensemble. Our molecular-dynamics simulation is performed using the large-scale atomic/molecular massively parallel simulator code.[25] 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 expected melting temperature. After this thermalization, the entire system remains in the solid state. Then we fix the atoms in one half of the supercell (along the long axis) and let another half heat to a very high temperature (typically several times the expected melting temperature) to completely melt it. The atoms in this half 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 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 the coexisting solid and liquid state, we calculate the melting temperature by averaging the temperatures for the MD steps through which the system has been in equilibrium.

As was done in several previous papers, we monitor the system throughout by calculating the average number of

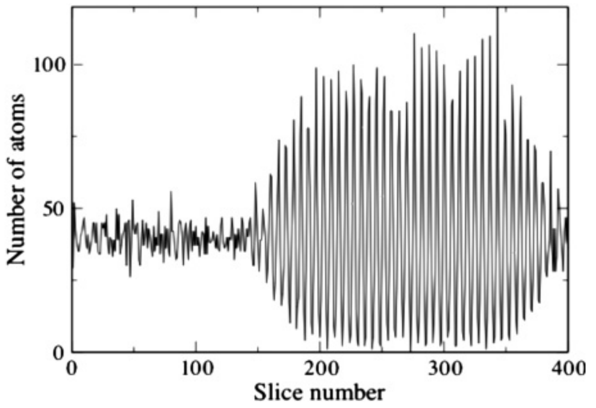

FIG. 1. Density profile in a molecular-dynamics simulation of solid and liquid *W* in coexistence. The supercell is divided into 400 slices of equal thickness parallel to the liquid-solid interface, and the number of atoms in each slice determines the intensity.

density in slices of the supercell taken parallel to the interface between solid and liquid. The density profile for a snapshot at the simulation time of 100 ps is shown in Fig. 1. We can see that the systems are still solid and liquid in coexistence after a long time (100 ps) simulation. On the right half of the supercell, the periodically oscillated density indicates that those atoms are in the form of solid. On the left half of the supercell, they are liquidlike since the density has the form of random fluctuations with a much smaller amplitude compared with that on the right half. The melting temperature is determined by averaging the temperature in the last 30-ps simulation and gives a value of 4637 K. This value is 940 K higher than the experimental value. This might be due to the *W* EAM potential, which was fitted to the zero-temperature material properties. These empirical interatomic potentials fitted to the so-called mechanical properties of the materials usually have no guarantees to give good results for the nonmechanical properties, such as melting temperatures.[31,32]

As the second step of this approach, the *ab initio* melting temperature is computed by correcting the approximate T_m^{ref}. We perform two independent molecular-dynamics simulations for solid and liquid using the reference potential and a small 128-atom supercell. In order to generate the liquid supercell, we fix the supercell at the liquid equilibrium volume and heat it to a temperature several times above the approximate melting temperature. For both molecular-dynamics simulations we employ the constant NVT ensemble. The supercell volume and the simulation temperature are fixed at the corresponding equilibrium volume and temperature at T_m^{ref} during the simulation. We run the simulation for 2 000 000 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. A total of 76 snapshots is taken from each simulation, and we run *ab initio* total-energy calculations for these snapshots using the VASP package.[26,27] We employ the generalized gradient approximation (GGA) for exchange-correlation energy.[28] The projector augmented wave (PAW) pseudopotentials[29,30] are used to describe interactions between ions and valence electrons. The semicore *p* states are treated as valence states. As a test, we keep the semicore frozen and find that there is a change of less than 50 K for the melting temperature. The plane-wave basis cutoff energy is 279 eV. The only Γ point is used for the Brillouin-zone sampling of the supercell with 128 atoms.

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

$$\Delta T_m \approx \frac{\Delta G^{ls}\left(T_m^{\mathrm{ref}}\right)}{S_{\mathrm{ref}}^{ls}}, \qquad (1)$$

where $\Delta G^{ls} = G^{ls}_{\mathrm{AI}} - G^{ls}_{\mathrm{ref}}$. $G^{ls}_{\mathrm{AI}}(P,T) = G^{l}_{\mathrm{AI}}(P,T) - G^{s}_{\mathrm{AI}}(P,T)$ and $G^{ls}_{\mathrm{ref}}(P,T) = G^{l}_{\mathrm{ref}}(P,T) - G^{s}_{\mathrm{ref}}(P,T)$ are the Gibbs free-energy differences between the liquid (l) and solid (s) from the *ab initio* (AI) and the reference potential (ref). The entropy of melting S^{ls}_{ref} is calculated from the relation $T_m^{\mathrm{ref}} S^{ls}_{\mathrm{ref}} = E^{ls}_{\mathrm{ref}} + P V^{ls}_{\mathrm{ref}}$, where the energy difference E^{ls}_{ref} and the volume difference V^{ls}_{ref} on melting are obtained from the reference potential simulations for liquid and solid. P is the pressure. The entropy of melting obtained from the EAM reference potential is 8.89 $\mathrm{J\,mol^{-1}\,K^{-1}}$, compared with the experimental value of 9.62 $\mathrm{J\ mol^{-1}\ K^{-1}}$ and the theoretical value of 8.22 $\mathrm{J\ mol^{-1}\ K^{-1}}$ by the Finnis-Sinclair multibody potential.[32] The equilibrium volumes for solid and liquid are 17.22 and 18.26 Å^3/atom, respectively. For the isothermal-isochoric simulations, we have

$$\Delta G \approx \Delta F - \frac{1}{2}\frac{V \Delta P^2}{K_T}, \qquad (2)$$

where K_T is the isothermal bulk modulus and ΔP is the pressure change when U_{ref} is replaced by U_{AI}. V is the volume, which is kept constant during the simulations. ΔF is given by the following equation:

$$\Delta F \approx \langle \Delta U \rangle_{\mathrm{ref}} - \frac{1}{2k_B T}\langle \delta \Delta U^2 \rangle_{\mathrm{ref}}, \qquad (3)$$

where $\Delta U = U_{\mathrm{AI}} - U_{\mathrm{ref}}$ and $\delta \Delta U = \Delta U - \langle \Delta U \rangle_{\mathrm{ref}}$. k_B is the Boltzmann constant, and T is the simulation temperature. The average is taken for the reference system.

According to Eq. (1), we obtain the first-order correction $\Delta T_m = -1187$ K, so this gives the *ab initio* melting temperature of 3450 K, compared with the experimental value of 3695 K.[33] We find that the pressure change is four or five orders of magnitude smaller than the experimental K_T values, so its contribution to the melting temperature corrections is negligible. The Gibbs free-energy corrections reduce the error in the melting point from 25% to less than 7% of the experimental value, which is a substantial improvement of the accuracy. This remaining discrepancy between the calculated and experimental melting temperatures may be attributed to approximations to density-functional theory itself or to approximations made in computing the corrections to the EAM results (if the EAM potential of *W* differs too much from the *ab initio* Hamiltonian). However, the second problem is unlikely to be significant, because we find that the $\langle (\delta \Delta U)^2 \rangle_{\mathrm{ref}}$ fluctuations for solid and liquid are very small. This indicates two things: first, the bias due to truncating the series [Eq. (3)] is small (the error is less than 1 meV/atom). Second, the statistical fluctuations in estimating the average $\langle (\delta \Delta U) \rangle_{\mathrm{ref}}$ are small as well (the resulting error is of the order of 1 meV/atom). Under the assumption that S^{ls}_{ref} is roughly constant over the temperature range including the raw EAM melting point and the true *ab initio* melting point, the errors caused by truncating the free-energy expansion [Eq. (3)] and by the first-order approximation [Eq. (1)] lead to an error of no more than 100 K (or 3%) on the melting temperature. In contrast, it was found in previous studies that approximations to density-functional theory itself could lead to an error about 13% for Cu.[20] It thus appears unnecessary to develop a more accurate *W* EAM potential for this purpose, which is encouraging, because fitting a potential to mechanical properties alone is considerably easier than including finite temperature data.

In the following, our direct molecular-dynamics coexistence simulation gives a melting temperature that is in excellent agreement with the one given above. This provides further evidence to justify the approximations in the approach, e.g., the number of snapshots, and the truncations of melting temperature corrections.

The direct molecular-dynamics coexistence simulation is performed using a supercell with 448 *W* atoms. 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,[23] and for *W* they vary within 50 K. So we believe that this direct *ab initio* MD simulation can obtain a reasonable melting temperature that is comparable to the one from the free-energy correction approach. We determine the melting temperature at the atmospheric pressure from the *ab initio* simulation with the NPH ensemble, as recently implemented in VASP.[17] As in the coexistence simulations using the classical EAM potentials, the temperature is adjusted spontaneously so that it satisfies the condition of the same free energy for solid and liquid at a given pressure. The initial atomic configuration for *ab initio* MD simulation is an equilibrated snapshot from an EAM reference potential simulation. So initially it contains about half atoms in a solidlike environment and another half in a liquidlike state. The periodic supercell has the dimensions of $13.1 \times 13.1 \times 46.7$Å, i.e., consisting of $4 \times 4 \times 14$ body-centered cells. Again, we use the GGA exchange-correlation functional[28] and the PAW pseudopotential.[29,30] The only Γ k point is used in the simulation, and the energy cutoff is the default value of *W* PAW potential provided in the VASP database. The total energy for each ionic step converges to an accuracy of 10^{-4} eV. The time step in the molecular-dynamics simulation is set to be 3 fs. We run the simulation for a time of 20 ps. With these prescriptions, we estimate that the drift in the enthalpy leads to an effect on the temperature of 1.2 K/ps.

The instantaneous temperatures and volumes versus the simulation time for our direct *ab initio* MD simulation are shown in Fig. 2. It indicates that the simulation has reached the equilibrium state. Figure 3 shows the final atomic configuration for $t = 20$ ps. From the atomic structure, we can see that the system still contains the solid and liquid in coexistence. Figure 2 shows that it does not have any appreciable drift in the instantaneous temperatures and volumes. This indicates that the initial atomic configuration we give based on the EAM potential simulation is close to the *ab initio* equilibrium one. Therefore, we do not need to manually adjust the volume as was done in a previous work.[17] The average temperature is 3465 K from the last 10-ps simulation with a standard deviation of 105 K. There is a difference of a mere 15 K between the results of two *ab initio* approaches, which falls well within the statistical accuracy of the two results, each having a precision of the order of 100 K, in which statistical sampling errors dominate other numerical errors (such as k-point convergence). This provides an independent cross-check for the melting temperature obtained with the free-energy correction approach. (That the 15-K difference happens to be much smaller than statistical error bars is merely fortuitous.) As another example, we find for Ta that there is a difference of 60 K between the melting temperatures by two *ab initio* approaches.[23]

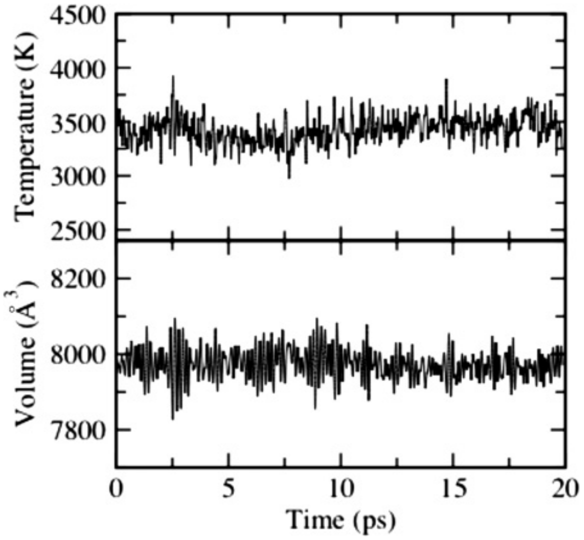

FIG. 2. Time dependence of temperature (upper panel) and volume (lower panel) during a direct *ab initio* simulation of the coexisting solid and liquid *W* using a 448-atom supercell.

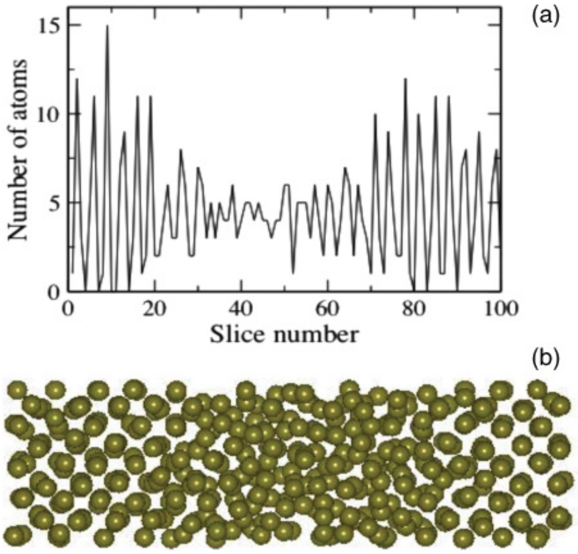

FIG. 3. (Color online) (a) Snapshot of the density profile in *ab initio* molecular-dynamics simulation of the coexisting solid and liquid *W* for time = 20 ps. (b) Final atomic configuration of the simulation corresponding to the density profile snapshot in (a).

In summary, we have calculated the melting temperature of tungsten within the framework of density-functional theory using two *ab initio* approaches. In the first approach, 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 multibody EAM potentials have been employed in our calculations. The calculated 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 temperature is within 7% of the experimental value. The direct *ab initio* molecular-dynamics simulation using the NPH ensemble and a 448-atom supercell obtains a melting temperature that is in excellent agreement with that from the free-energy correction approach. Therefore, two *ab initio* approaches can give a reliable check for the calculation accuracy. The two *ab initio* approaches obtain a consistent result for the melting temperature. However, the free-energy correction approach is about a tenth as computationally demanding as the direct *ab initio* molecular-dynamics simulation approach. Somewhat unexpectedly, we find that the free-energy correction method works well even if the melting point of the reference system differs considerably from the true melting point (in this case, by 940 K or 25%).

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