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Ab initio melting curve of copper by the phase coexistence approach

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Ab initio calculations of the melting properties of copper in the pressure range 0–100 GPa are reported. The *ab initio* total energies and ionic forces of systems representing solid and liquid copper are calculated using the projector augmented wave implementation of density functional theory with the generalized gradient approximation for exchange-correlation energy. An initial approximation to the melting curve is obtained using an empirical reference system based on the embedded-atom model, points on the curve being determined by simulations in which solid and liquid coexist. The approximate melting curve so obtained is corrected using calculated free energy differences between the reference and *ab initio* system. It is shown that for system-size errors to be rendered negligible in this scheme, careful tuning of the reference system to reproduce *ab initio* energies is essential. The final melting curve is in satisfactory agreement with extrapolated experimental data available up to 20 GPa, and supports the validity of previous calculations of the melting curve up to 100 GPa.
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I. INTRODUCTION

The last few years have seen a major effort to calculate high-pressure/high-temperature phase diagrams, including melting curves, using *ab initio* methods based on density-functional theory (DFT).[1–5] In the case of melting, this requires accurate *ab initio* calculations on sufficiently large simulated systems representing both the solid and the liquid. For some materials, *ab initio* melting curves are in satisfactory agreement with experimental data; an example is our recent work on aluminum.[5] In other cases, there are disturbingly large disagreements; conflicts between theory and experiment for transition metals are discussed in Refs. 6 and 7, and the case of iron has been controversial.[3,4] These disagreements raise questions about the reliability of both the theoretical and the experimental techniques. In addition, there are sometimes unexpected disagreements between different *ab initio* approaches to the calculation of melting properties, as in recent work on iron.[4,8,9] There thus remains a pressing need for further comparisons both between *ab initio* calculations and experimental data and between different theoretical approaches. To this end, we report here *ab initio* calculations of the melting properties of copper up to 100 GPa, based on the simulation of coexisting solid and liquid phases.

Almost all *ab initio* melting calculations have involved the use of "reference" systems, consisting of empirical total-energy functions designed to mimic the *ab initio* system. The use of reference systems has been essential up to now, because of limitations on the size of system that can be treated by *ab initio* simulations alone. However, the ways in which the reference models have been constructed and applied differ greatly, and the differences certainly account for some of the disagreements between nominally equivalent *ab initio* calculations. One approach is to fit a parametrized reference model to *ab initio* calculations on representative sets of atomic positions in the solid and liquid states, and to calculate melting properties using the reference model.[8–10] Whether the reference melting calculations are done by simulating solid and liquid in coexistence or by computing the solid and liquid Gibbs free energies and requiring them to be equal, system size errors can be effectively eliminated by using very large simulated systems. However, melting results obtained in this way may not be satisfactory, since they depend on the faithfulness with which the reference model mimics the *ab initio* system. To obtain fully *ab initio* results, it is essential to correct for the differences between the reference and *ab initio* total-energy functions.[11]

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The most complete way of going from reference to *ab initio* melting properties is to follow the free-energy route, and to use thermodynamic integration to compute the shifts of solid and liquid free energies due to the differences of reference and *ab initio* total-energy functions.[1,3] If this is done, the choice of reference model has no effect whatever on the final results. Alternatively, if the reference melting properties are obtained by coexistence simulations, then, provided the differences between reference and *ab initio* total-energy functions are small, free energy corrections can again be made to obtain the fully *ab initio* melting properties. In recent work[11] on high-pressure Fe, we demonstrated that the free-energy and coexistence approaches do in practice yield essentially identical results, provided the free energy corrections are included. (We note in parentheses that in very recent work on the melting of aluminum[12] we have shown how reference systems can be completely avoided by direct *ab initio* molecular dynamics simulations on coexisting solid and liquid; however, this direct approach can at present only be used for very simple materials.)

As in our previous work on Fe melting,[4] the present work is based on the projector augmented wave (PAW)[13,14] implementation of DFT. Copper was chosen for this work for several reasons: First, the response of the $Cu\,3d$ electrons must be explicitly included, so that the treatment of Cu melting tests essentially the same techniques that we used for Fe. Second, work on the high-pressure melting of Cu, using input from *ab initio* calculations, has already been reported by two other groups,[10,15] and we regard comparisons with this earlier work as important in establishing the reliability of the different *ab initio* treatments of melting. Third, reference models for solid and liquid Cu are already available.[10] Fourth, experimental data for the melting curve of Cu are available, at least up to moderate pressures.[16] Our calculations employ coexistence simulations to determine the reference melting properties, together with our recent scheme for computing the shift of the melting curve due to free energy corrections.[11] We chose this route in preference to the approach based entirely on free energies because the coexistence route requires considerably less human and computational labor.

In Sec. II, we summarize the methodology we have used, including the techniques for performing reference coexistence simulations and for making free-energy corrections, the *ab initio* methods, the form of the reference model, and our general procedure for fitting the reference model to the *ab initio* results. In presenting our results (Sec. III), we begin by reporting comparisons with experiment for the cold compression curve of the f.c.c. Cu crystal and its phonon dispersion curves, which are useful in assessing the accuracy to be expected of the melting calculations. We then report detailed results of our coexistence calculations, the optimized reference models that we have constructed for different pressure regimes, the free energy corrections, and the comparisons with experiment for the melting curve. Discussion and conclusions are given in Sec. IV.

II. METHODOLOGY

We first outline briefly the overall scheme in which *ab initio* melting properties are calculated by performing coexistence simulations on a reference system and then applying corrections based on the free-energy differences between the reference and *ab initio* systems; for full details, see Ref. 11. We denote by $U_{\rm AI}(\underline{r}_1 \ldots \underline{r}_N)$ and $U_{\rm ref}(\underline{r}_1 \ldots \underline{r}_N)$ the total-energy functions of the *ab initio* and reference systems as a function of ionic positions $\underline{r}_i$. In general, $U_{\rm ref}$ is represented by a parametrized model, which is optimized at each thermodynamic state, as described below, so that $U_{\rm ref}$ reproduces $U_{\rm AI}$ as precisely as possible. At a given pressure, P, the melting temperatures associated with $U_{\rm AI}$ and $U_{\rm ref}$ are denoted by $T_m^{\rm AI}$ and $T_m^{\rm ref}$, respectively. The reference melting temperature $T_m^{\rm ref}$ is determined by coexistence simulations on the reference system (see below), and we then apply corrections to obtain $T_m^{\rm AI}$.

In the present calculations on Cu, we are able to use reference models that mimic the *ab initio* solid and liquid very precisely, so that it suffices to use the lowest-order correction formula:

$$\Delta T_m \equiv T_m^{\rm AI} - T_m^{\rm ref} \approx \frac{\Delta G^{ls}(T_m^{\rm ref})}{S_{\rm ref}^{ls}}. \qquad (1)$$

Here, $S_{\rm ref}^{ls} \equiv S_{\rm ref}^{l} - S_{\rm ref}^{s}$ is the difference between the entropies of the liquid and solid for the coexisting phases of the reference system. The quantity ΔG^{ls} is defined as $G_{\rm AI}^{ls} - G_{\rm ref}^{ls}$ where $G_{\rm AI}^{ls}(P,T) \equiv G_{\rm AI}^{l}(P,T) - G_{\rm AI}^{s}(P,T)$ is the difference of Gibbs free energy of the liquid and solid for the *ab initio* system as function of P and T, and $G_{\rm ref}^{ls}(P,T)$ is the analogous quantity for the reference system. In practice, our simulations are all performed at constant volume and temperature, so that it is more convenient to work with corrections to the Helmholtz free energy. In either solid or liquid, the shift of Gibbs free energy $\Delta G(P,T) \equiv G_{\rm AI}(P,T) - G_{\rm ref}(P,T)$ at constant P and T is related to the corresponding change of Helmholtz free energy $\Delta F(V,T) \equiv F_{\rm AI}(V,T) - F_{\rm ref}(V,T)$ at constant V and T by

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

where K_T is the isothermal incompressibility of the reference model and ΔP is the change of pressure when $U_{\rm ref}$ is replaced by $U_{\rm AI}$ at constant V and T. Finally, the free energy shifts, ΔF, are given by

$$\Delta F = \langle \Delta U \rangle_{\rm ref} - k_{\rm B}T \log\left(\left\langle \exp\left(-\frac{\delta\Delta U}{k_{\rm B}T} \right) \right\rangle_{\rm ref} \right), \qquad (3)$$

where $\Delta U \equiv U_{\rm AI} - U_{\rm ref}$ and $\delta\Delta U = \Delta U - \langle \Delta U \rangle_{\rm ref}$ with the thermal average $(\langle \cdot \rangle_{\rm ref})$ taken in the ensemble generated by the reference system. The second term on the right-hand side of Eq. (3) can be expanded in a Taylor series, and, if the reference system mimics the *ab initio* system closely, ΔF may be evaluated as

$$\Delta F \approx \langle \Delta U \rangle_{\rm ref} - \frac{1}{2k_{\rm B}T}\langle \delta\Delta U^2 \rangle_{\rm ref}, \qquad (4)$$

with the averages taken in the reference ensemble.

The DFT[17] calculations were based on the projector augmented wave (PAW)[13,14] implementation, and were performed using the VASP code.[18] All the main calculations were made using the generalized gradient approximation (GGA) for exchange-correlation energy.[19,20] Although it has been previously found that neither the local-density approximation (LDA) nor the GGA is clearly to be preferred in the calculation of thermal properties of copper,[21] test calculations on the perfect face-centered-cubic (f.c.c.) Cu crystal (see below), in which we compare predictions of the GGA with those of the LDA, indicate that GGA is likely to be more reliable for the treatment of melting properties. The PAW calculations were performed using a cutoff of 273 eV (giving convergence in cohesive energy of the solid to within a few meV) and a core radius of 2.3 a.u. The $3d^{10}4s^1$ states were treated as valence with an Ar-core; we tested the effect of freezing the $3p$ states in the core by performing additional calculations with a PAW potential which explicitly included the $3p$ states. At ~100 GPa, the difference in pressure at a volume of 8.7 Å^3/atom between calculations performed using this pseudopotential and that with $3p$ states treated explicitly (via a Ne$3s^2$-core) was less than 0.5 GPa, which is small for our purposes. Pseudo-partial waves have been constructed following the procedure described by Kresse and Joubert in Ref. 14. Details of the Monkhorst–Pack sets of Brillouin-zone sampling wave vectors will be given when we present the results. Thermal excitation of electrons is fully included in the calculations.[22] For the test calculations on phonon dispersion relations of the perfect Cu crystal, we employed the small-displacement technique, described in detail in Refs. 5 and 24.

The reference system used here is based on the embedded-atom model (EAM), whose total-energy function U_{ref} has the form

$$U_{\text{ref}}=\frac{1}{2}\sum_{i\neq j}\epsilon\left(\frac{a}{r_{ij}}\right)^{n}-\epsilon C\sum_{i}\left[\sum_{j(\neq i)}\left(\frac{a}{r_{ij}}\right)^{m}\right]^{1/2}. \tag{5}$$

As usual, the first term on the right represents an inverse-power repulsive pair potential, while the second term is the sum of embedding energies of the individual ions in the sea of conduction electrons. The model is specified by the characteristic length a, the energy scale ϵ, the dimensionless coefficient C characterizing the strength of the embedding energy, and the embedding and repulsive exponents m and n. We note in passing that the number of independent parameters in this model is four, rather than five, since the parameters a, ϵ, and C occur only in the two combinations ϵa^n and $\epsilon C a^{(1/2m)}$. A total-energy model of this form was used by Belonoshko *et al.*[10] in their earlier calculations on the melting of Cu.

The general question of tuning reference models to mimic *ab initio* total-energy functions has been discussed by many authors (see, e.g., Ref. 4). In the approach to melting employed here, the crucial requirement is that the free energy differences between *ab initio* and reference systems be as small as possible. This requirement has been explored at length in our previous papers.[4,5] We showed there that the essential condition is that the strength of the fluctuations of the energy difference $\Delta U \equiv U_{\text{AI}} - U_{\text{ref}}$ be as small as possible. Specifically, we want to minimize the quantity:

$$\sigma^2 \equiv \langle (\delta\Delta U)^2 \rangle_{\text{ref}}/N, \tag{6}$$

where, as before, $\delta\Delta U = \Delta U - \langle \Delta U \rangle_{\text{ref}}$. In the coexistence approach, it is, of course, vital that this fluctuation strength be small in both the solid and the coexisting liquid. For the embedded-atom reference system used in our initial calculations, the parameters a, ϵ, C, m, and n were set equal to the numerical values proposed by Belonoshko *et al.*[10] However, we found that the fluctuation strength, σ^2, could be significantly reduced by further tuning of these parameters. Furthermore, we found it advantageous to retune the parameters for different thermodynamic states, as described generally later in this section and specifically in Sec. III B.

We conclude this outline of methodology by summarizing the protocols used for the coexistence simulations and for the free-energy corrections. There are a number of different schemes for simulating coexisting solid and liquid, depending on whether the whole system is treated at a constant energy or temperature, and at constant volume or pressure. Provided the different methods are consistently applied, they should all yield the same lines of coexisting thermodynamic states. Here, we perform the reference coexistence simulations at constant N, V, and E as in Ref. 11.

Our practical procedure for the coexistence simulations is as follows. We start with a supercell containing the perfect f.c.c. crystal, and thermalize it at a temperature slightly below the expected melting curve. Under these conditions, the system remains entirely in the solid state. The simulation is then halted, and the positions of the atoms in one half of the cell are held fixed, while the other half is heated to a very high temperature of typically ten times the melting temperature, so that it melts completely. With the fixed atoms still fixed, the molten half is then rethermalized to the expected melting temperature. Finally, the fixed atoms are released, thermal velocities are assigned and the whole system is allowed to evolve freely at constant (N,V,E) for a long time (typically more than 100 ps), so that solid and liquid come into equilibrium. The system is monitored throughout by calculating the average number density in slices of the cell taken parallel to the boundary between solid and liquid. We show in Fig. 1 a typical density profile. This shows that the coexisting phases are straightforward to identify: the presence of the solid is identified by periodic oscillations of the density, while the density of the liquid phase has the form of random fluctuations with a much smaller amplitude. For given settings of the temperatures in this protocol, a certain amount of trial and error is needed to find the overall volume that yields the coexisting solid and liquid in roughly equal amounts. When this is achieved, the overall pressure and temperature in the system give a point on the melting curve.

The choice of the reference system is made through a series of steps. A reference melting point determined by the foregoing protocol is computed first for an initial reference total energy U_{ref}. The initial parameters of U_{ref} were taken from the work of Belonoshko *et al.*[10] on Cu. The next step is now to retune the reference model so as to reduce the fluctuation strength, σ^2, so that the reference system mimics as

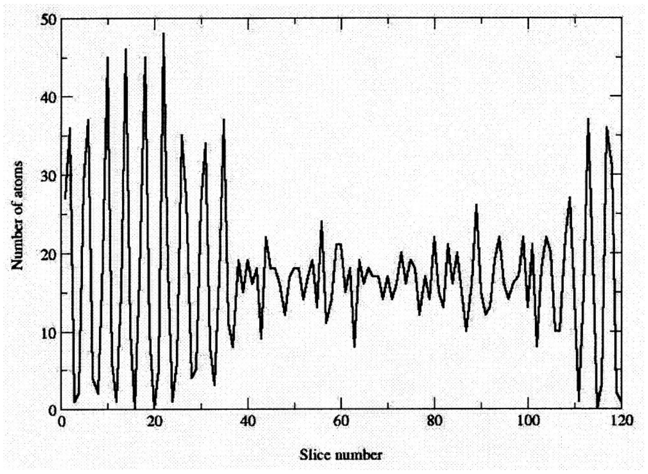

FIG. 1. Density profile in a simulation of solid and liquid copper at zero pressure. The presence of the solid is identified by periodic oscillations of the density, while the density of the liquid phase has the form of random fluctuations with a much smaller amplitude. The simulations were performed on a system of 2016 atoms using the reference potential [Eq. (5)] with parameters tuned to the low pressure regime.

closely as possible the *ab initio* system. To do this, several statistically independent configurations from a long reference simulation (performed using a 64 atom system) are extracted independently from both the solid and liquid at the melting point. The *ab initio* total energy, U_{AI}, is obtained for each configuration, and from this the fluctuation strength is determined via Eq. (6). The reference parameters are then adjusted to minimize σ^2 for the given set of configurations. New simulations are then performed with the reference model thus obtained, independent configurations for the solid and liquid are extracted, the reference parameters are once again tuned to minimize σ^2, and the whole procedure is iterated until σ^2 can be reduced no further. In principle, this tuning of the reference model could be repeated for every required point on the melting curve, but in practice we found it sufficient to use two optimized reference systems: one at low pressure and one at high pressure, as explained in Sec. III B.

As a final step, Eq. (4) is used to compute the free-energy corrections and hence the shifts of melting temperature needed to obtain our best estimate for the *ab initio* melting curve. This is done in the following way: for each pressure, we perform two independent molecular dynamics simulations for the solid and liquid at the appropriate volumes. The temperature is chosen to be the melting temperature of the reference system. The liquid is thermalized using a Nosé thermostat;[23] in order to avoid possible problems associated with slow equilibration, the solid is thermalized using an Andersen thermostat[35] following Ref. 5. The second order approximation [Eq. (4)] is valid for small fluctuations; its validity is confirmed by the evaluation of the full expansion [Eq. (3)] which shows that they differ by only 0–4 meV/atom (see Sec III B). As we shall emphasize in the following section, it is important in this final step to demonstrate that the free-energy corrections are fully converged with respect to the size of simulated system and the k-point sampling used in the calculation of U_{AI}.

TABLE I. The equilibrium volume, V_0, the incompressibility, K, and the derivatives $K' \equiv dK/dP$, and $K'' \equiv d^2K/dP^2$ of f.c.c. Cu from a logarithmic fit to calculated energy–volume data compared with experimental data.

	V_0 (Å^3/atom)	K (GPa)	K'	K'' (GPa^{-1})
GGA Ar-core	12.043(6)	134.721(4)	4.9(1)	−2.7(8)
GGA Ne3s^2-core	12.041(3)	139.190(2)	4.55(5)	0.5(6)
LDA	10.938(2)	182.674(6)	5.10(6)	−3(2)
Experiment (Ref. 26)	11.81	140		

III. RESULTS

A. Tests on perfect crystal

As an initial check on the methodology, we calculated the energy per atom of the perfect f.c.c. Cu crystal as a function of volume. The calculations were performed using a $15\times15\times15$ Monkhorst–Pack[36] set of Brillouin-zone sampling wavevectors (120 k-points in the irreducible wedge), which yielded a precision of better than 1 meV/atom. Calculations were performed at a set of atomic volumes in the range 7–14 Å^3, equivalent to a pressure range of 0–300 GPa. To compare with experiment, we fitted the energy results with a 4th-order logarithmic equation of state,[25] which allows us to extract the zero-pressure volume V_0, and the values at zero-pressure of the incompressibility K_0 and its first and second pressure derivatives. These quantities, calculated with both GGA and LDA, are compared with experimental values in Table I. We note that the LDA calculations significantly underestimate V_0, while GGA slightly overestimates it; K_0 is much better represented by GGA.

Phonon frequencies, determined using the small-displacement technique (details described elsewhere[4,5,24]), were calculated using a 64-atom supercell, with Brillouin-zone sampling performed using a $5\times5\times5$ Monkhorst–Pack grid equivalent to 18 k-points in the irreducible wedge of the cell with the atom displaced; this is based on the extensive cell size and sampling tests carried out in previous work.[5] Test calculations using a variety of atomic displacements showed that phonon frequencies are converged to better than 1% with the displacement of 0.03 Å used for the results reported here. A comparison of calculated frequencies using both GGA and LDA with experimental frequencies[27] is shown in Fig. 2; for completeness, the calculated frequencies are reported both at the experimental equilibrium volume and at the equilibrium volume calculated using, respectively, GGA or LDA.

B. Melting properties

All the simulations of coexisting solid and liquid employed a system of 2016 atoms contained in an orthorhombic supercell (the numbers of conventional f.c.c. cubes of perfect crystal contained in the three edges of this supercell are 6, 6, and 14). This choice of system size is based on the previous work of Belonoshko *et al.*[10] which showed that the size errors in the calculated melting temperature associated with this system are less than ~20 K.

In using the parameters of Belonoshko *et al.*[10] to calculate an initial melting point at P=3.4 GPa, we found the

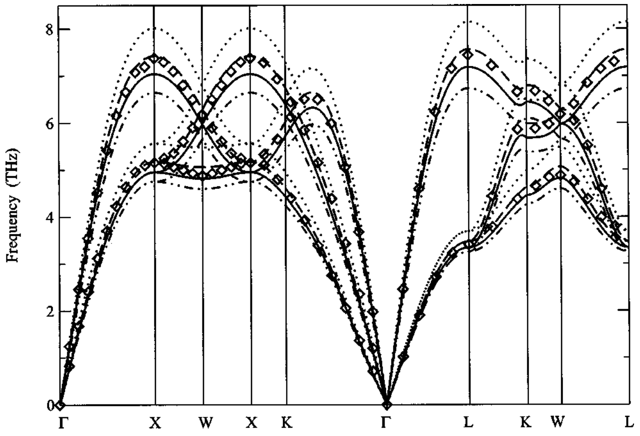

FIG. 2. A comparison of the phonon dispersion curves for Cu from the present calculations with experiments (diamonds, Ref. 27). Solid curve: GGA at the GGA equilibrium volume; dashed curve: GGA at the experimental volume; dotted curve: LDA at the LDA equilibrium volume; dot–dashed curve: LDA at the experimental volume.

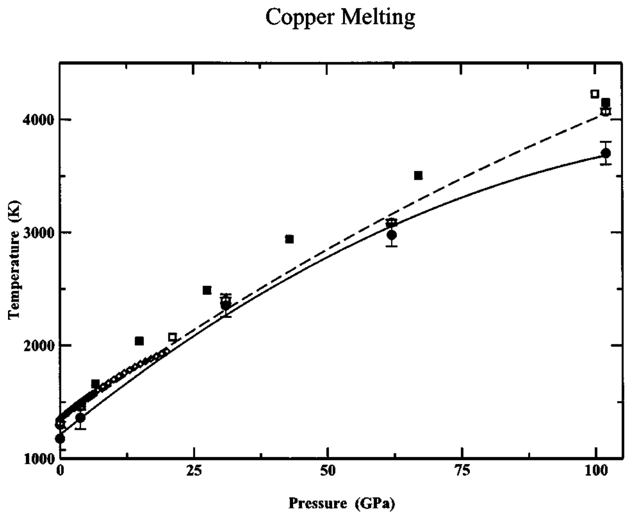

FIG. 3. Calculated *ab initio* melting curve (filled circles and solid line) compared with previous results: filled and unfilled diamonds—experiments and extrapolation of Ref. 16; calculations of Moriarty (Ref. 15) and Belonoshko *et al.* (Ref. 10) are displayed as filled and open squares, respectively. The melting curve from present work calculated from the reference potential is displayed as open circles and a dashed line.

r.m.s. fluctuation strength, σ [Eq. (6)] to be ~50 meV and ΔF as calculated by Eqs. (3) and (4) to differ by 4 meV. By retuning the potential parameters as described in Sec. II, we were able to reduce σ^2 to only 16 meV, and ΔF as defined by Eqs. (3) and (4) were identical.

In order to reduce the fluctuation strength as much as possible over the remainder of the melting curve, we found it essential to retune the reference parameters separately for low and high pressures ($0<P<31\,\text{GPa}$ and $62<P<102\,\text{GPa}$, respectively). The optimized values of the model parameters are reported in Table II. With these parameters, the values of the fluctuation strengths are between 16 and 70 meV at low and high pressures, respectively; Eqs. (3) and (4) differed by between 0 and 3 meV in the low and high pressure regimes, respectively. We note that we would expect greater fluctuations at high pressures due to the dependence of the fluctuations on temperature [Eq. (4)].

The new melting curve obtained with the retuned reference models is reported in Fig. 3. In calculating the free-energy corrections, we have made careful checks on the errors in these corrections due to limitations of system size and of electronic Brillouin-zone sampling in order to determine melting curves with the desired precision (50–100 K). We found that the use of k-points was absolutely essential to ensure the required precision (<5 meV/atom); using the Γ-point only, we found that at least 256 atoms were required to obtain the desired precision in ΔF (a few meV). However, when four k-points were used to sample the cell, a much smaller 64 atom cell was sufficient. In addition to the free energy corrections to the melting curve, we were also able to obtain directly from the *ab initio* calculations the pressure difference between the *ab initio* and reference potential simulations, ΔP. The incompressibility of the solid and liquid at each state point, K_T, are readily calculated in the reference system, enabling us to calculate the correction to the Gibbs free energy via Eq. (2). The entropy difference of melting, $S_l - S_s = (E_l - E_s + P(V_l - V_s))/T$, is also readily calculated in the reference system, where the change in energy, ΔE, is calculated at each state point via separate simulations for the solid and liquid at the melting point. The shifts in melting temperature are then obtained via Eq. (1).

TABLE II. The parameters of the embedded-atom reference model [Eq. (5)] for coexisting solid and liquid Cu, optimized by fitting to *ab initio* calculations in the low and high pressure ranges $0<P<31\,\text{GPa}$ and $62<P<102\,\text{GPa}$. In the fitting procedure, a is fixed at 2.5 Å.

P (GPa)	n	m	ϵ (eV)	a (Å)	C
0–31	8.482	4.692	0.370	2.5	27.561
62–102	8.755	4.743	0.282	2.5	11.290

Our final "best estimate" of the *ab initio* melting curve of Cu is reported in Fig. 3, where we also show the available experimental results,[16] and the earlier theoretical results due to Moriarty *et al.*[15] and Belonoshko *et al.*,[10] which also made use of *ab initio* calculations. Although our use of very large systems ensures that system-size errors are almost negligible for the melting curve of the reference system, there is an uncertainty of ±50 K due to system-size effects on the free-energy correction, ΔF, for the difference between the *ab initio* and reference systems [Eq. (4)]; in addition, there is a statistical uncertainty of ±25 K in ΔF. When combined with the small errors associated with the reference simulations, this gives a technical error on T_m of less than 100 K. A simple quadratic fit has been applied to both melting curves; the fit reproduces the calculated data to within 75 K. The *ab initio* zero pressure melting temperature is 1176(100) K, somewhat lower than the experimental value[26] of 1358 K and that reported using other embedded atom models;[10,29–31] the melting gradient for the *ab initio* melting curve at zero pressure, dT_m/dP, is 38 KGPa^{-1}, in excellent agreement with the experimental value[28] of 36(3) KGPa^{-1}. In contrast to our previous work on aluminum[5] where melting properties were obtained from Gibbs free energies of the solid and liquid, the *ab initio* melting volume is not directly obtainable using this coexistence methodology.

IV. DISCUSSION

The agreement between our calculated melting curve and experimental data is satisfactory, but certainly not perfect. However, we believe that the discrepancies are mainly due to inherent limitations on current approximations for the exchange-correlation energy in DFT. In particular, these discrepancies can be understood by considering the difference between our calculated phonon frequencies and experimental values (Fig. 2). According to the Lindemann criterion, at a given pressure, a crystal will melt when atoms are displaced beyond some fraction of the nearest neighbor distance. This critical displacement is proportional to the melting temperature and also to $\overline{1/\omega^2}$, where ω represents the phonon frequencies, with the average taken over the Brillouin zone. This latter quantity for our calculated phonon frequencies is ~9% lower than that from experiment, and we would therefore expect our calculated value for T_m to be ~9% lower than the experimental value of 1358 K, i.e., ~1235 K; our calculated value for T_m is 1176±100 K which, within error, is in agreement with this estimate. A similar analyis on our previous work on Al[5] suggests the predicted melting temperature in that case should be too low by ~14%; the experimental value for Al melting is 933 K and our predicted value is 786(50) K—16% lower.

The satisfactory agreement with experiment of our predicted melting curve for Cu provides useful evidence for the reliability of current *ab initio* techniques for calculating melting properties. Our calculations also support the validity of previous theoretical work on the melting properties of Cu, some of which made important use of *ab initio* calculations.

In assessing the significance of this work, it is important to note why it represents an advance over previous *ab-initio*-based work on Cu melting. There are two key points: first, the reference models we use were systematically optimized using *ab initio* calculations on both a solid and liquid; second, we have shown the importance of making corrections for the differences between the *ab initio* and reference systems. In early work[32] on the use of *ab initio* calculations to predict melting properties, technical limitations meant that the *ab initio* calculations could be done only on the crystal. A leap of faith was therefore needed in applying the resulting models to solid–liquid coexistence. The present work indicates that these early calculations on Cu were surprisingly successful. Nevertheless, methods based only on *ab initio* information for the crystal lack generality. In particular, one would not expect them to work for materials (Si is an example[33]) for which the ionic and electronic structure of the solid and liquid differ greatly. The recent work of Belonoshko *et al.*[10] on Cu melting made important use of *ab initio* calculations on the liquid in fitting their reference model, but no attempt was made to correct for errors in this fitting, or to characterize these errors quantitatively. The present work indicates that the shift of the melting curve due to the difference between reference and *ab initio* energies cannot generally be ignored.

The present work gives useful insight into the issue of system size errors. In all *ab initio* work using reference models, including our own, size errors are eliminated from the reference calculations by using very large systems. But size errors can still be important in computing the free-energy differences between the *ab initio* and reference systems. In doing this work it has become clear that the two most important controlling factors were (i) the minimization of the fluctuations between the reference and *ab initio* systems (by retuning the reference potential), which enabled us to utilize the truncated second order expansion (and therefore enable much more efficient calculations), and (ii) the use of k-point sampling when calculating the *ab initio* corrections which enabled us to uses a relatively small system size leading to much more efficient calculations.

The success of the present work on Cu lends support to the technical correctness of our earlier *ab initio* work[4,11] on the high-pressure melting of Fe, which employed both coexistence and free-energy methods. But this raises again the controversial question of why apparently reliable *ab initio* calculations, including ours on Fe, yield predictions for melting curves that sometimes differ markedly from the results of static compression experiments at high pressures.[34,7] This problem has already been noted by Moriarty *et al.*[6] who point out that high-pressure static compression melting curves are sometimes in serious conflict with shock data. In view of these unresolved issues, we believe there is now a strong need to extend the current *ab initio* calculations to a much wider range of metals, for which experimental data are becoming available.

In conclusion, the present work gives evidence for the reliability of current *ab initio* techniques for predicting melting properties, but emphasizes the need for careful tuning of the classical reference models generally used in these predictions, using *ab initio* data on both the solid and the liquid. It also emphasizes the need to correct for the inevitable differences between the *ab initio* and reference systems. Although it would appear that the reference potential works very well for copper, such parametrized models cannot be used confidently to predict melting curves where no experimental data exist. *Ab initio* calculations, on the other hand, while not necessarily reproducing the experimental melting curve exactly, have quantifiable errors which can be taken into account; such methods can, therefore, be used to predict melting curves where no experimental data yet exist.

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