

ARTICLES

Quasi *ab initio* molecular dynamic study of Cu melting

A. B. Belonoshko, R. Ahuja, O. Eriksson, and B. Johansson

Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

(Received 22 April 1999)

We have investigated the melting of Cu theoretically by means of a molecular dynamic method employing the Sutton-Chen model for the interatomic interaction. This interaction has been fitted to reproduce results from first-principles self-consistent total-energy calculations within the local-density approximation using the full-potential linear-muffin-tin-orbital method for the bcc, fcc, hcp, and liquid configurations. No experimental data were used to tune the potential. A large number of properties including equation of state, melting temperature, high-pressure melting curve, change of volume and entropy at melting, liquid structure, diffusion coefficient in liquid, and vacancy formation energy are all in good agreement with experimental data. Inclusion of the full potential energy of a liquid configuration in the fitting procedure is critical for obtaining good agreement with experiment. Different ways to calculate the melting transition are shown to produce very different results. The use of a large number of particles in combination with the solid-liquid interface as an initial configuration in the simulation is essential in order to obtain the correct melting temperatures.

I. INTRODUCTION

Ab initio calculations are very time consuming, because computational work scales as the third (or worse) power of the number of atoms (N). Therefore, in these calculations N is normally restricted to be less than 100 atoms. This is not always sufficient. For example, atomistic simulation of a melting transition requires at least several hundred atoms.¹⁻³ Another example⁴ shows that even a system of 576 atoms (supercell of $4 \times 4 \times 3$ MgSiO₃-perovskite unit cells) is not sufficient for a correct calculation of temperature-dependent thermodynamic properties. An obvious solution would be to introduce a model that could establish a relationship between a particular configuration of atoms and its energy. If such a model allows a sufficiently precise energy calculation to be made for any possible configuration, which is in agreement with first-principles calculations, then the use of such a model in molecular dynamic (MD) simulations should produce the same results as *ab initio* MD simulation. This approach does not consider any effects related to temperature-dependent changes of the electron density and the basic assumption is that the configurational energy (E_{conf}) depends on the atomic positions only, which is not always true. However, at moderate temperatures the error is small.

Normally, models of interatomic interaction are parametrized to fit experimental data only⁵⁻⁷ or, more recently, experimental data combined with results from *ab initio* calculations.⁸ The experimental data are not always available and theoretical results are often different from the experimental ones. For this reason it is interesting to test the possibility to use a simple model that is exclusively fitted to *ab initio* data. A similar approach was already applied to Al.⁹ However, the model included a significant number of parameters. With the development of reliable first-principles methods such data can today always be made available. If the

model would be successful in MD simulations then this would provide a simple way for studying any substance without referring to experimental data. Furthermore, the restriction on N can be significantly extended, allowing simulations of systems larger by a factor of 10^6 than in *ab initio* MD simulations. As a test of this approach, we have chosen copper and the Sutton-Chen^{6,7} model for the interatomic interaction, which is probably the simplest among embedded-atom-type models.⁵

In the present paper, we first describe how the data for Cu were calculated and the procedure for our parametrization. This is followed by a description of our MD simulations. Next, MD simulated data are compared with experiment and also with previous simulations. The advantages and shortcomings of such an approach are discussed.

II. FPLMTO CALCULATIONS AND PARAMETRIZATION OF THE SUTTON-CHEN MODEL

The introduction of embedded-atom-type models⁵ for the energy of N metal atoms has allowed for a dramatic improvement and considerably expand the possibilities of using atomistic simulations for metals. Though justifications behind these models are somewhat different, the resulting forms are virtually identical for the pure elements¹⁰ and are as follows:

$$E_{conf} = \sum_{i=1}^N E_i, \quad (1)$$

where

$$E_i = \frac{1}{2} \sum_{j=1, j \neq i}^N \phi(r_{ij}) + F(\rho_i) \quad (2)$$

with

$$\rho_i = \sum_{j=1, j \neq i}^n \rho(r_{ij}). \quad (3)$$

Here E_i is the energy of atom i , ϕ is the pairwise interaction between atoms i and j , r_{ij} is the distance between them, $F(\rho)$ is the embedding function, and ρ is another pairwise interaction leading to the density term ρ_i .

There are two features common for all these models. First, the expression for the energy includes a volume-dependent $F(\rho)$ term and pair-interaction $[\phi(r)]$ term. Second, these models are semiempirical ones and have to be parametrized or fitted to some data. Because there is no ‘‘magic’’ function that could describe all the variety of the atomic configurations, the choice of the data to be fitted is the most important and crucial step. For example, it was noted that some simulations⁵ have been more successful than others because the most relevant data were included in the fitted set. If the purpose is to study the phase diagram of a particular system it is necessary to compose the data set including E - V dependence for all possible solid and liquid phases for a wide range of densities. The data for the solid phases are readily available from first-principles calculations. As for the liquid the situation is more complicated. Experiment sometimes provides us with a structure factor of a liquid, which, however, is not sufficient as an input for the *ab initio* code. The necessary information is contained in the coordinates of atoms. MD simulation can provide those coordinates if the interatomic potential is known — but this potential has to be fitted to the results of *ab initio* calculations. The solution to this problem is (1) to fit the potential to the energy (E)-volume (V) data for solid phases, (2) calculate with MD simulation the atomic coordinates of the liquid, (3) calculate E - V data for liquid, (4) refit the potential again. This might require several iterations and the iterative process converges to the potential, which is consistent with the *ab initio* data. We have to emphasize that the inclusion of data for the liquid in the total data set to be fitted is straightforward when using *ab initio* calculations, while it requires simplifying assumptions when other methods are used.

In order to study the electronic structure of Cu we have used the full-potential linear-muffin-tin-orbital (FPLMTO) method.¹¹ The calculations were based on the local-density approximation and we used the Hedin-Lundqvist¹² parametrization for the exchange and correlation potential. Basis functions, electron densities, and potentials were calculated without any geometrical approximation.¹¹ These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $l_{max}=8$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region. The muffin-tin sphere occupied approximately 50% of the unit cell. The radial basis functions within the muffin-tin spheres are linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site and principal as well as orbital atomic quantum numbers, whereas outside the spheres the basis functions are combinations of Neuman or Hankel functions.^{13,14} In the calculations reported here, we made use of pseudocore $3p$ and valence band $4s$, $4p$, and $3d$ basis functions with corresponding two sets of energy parameters, one appropriate for the semicore $3p$ states, and the other appropriate for the valence states. The resulting

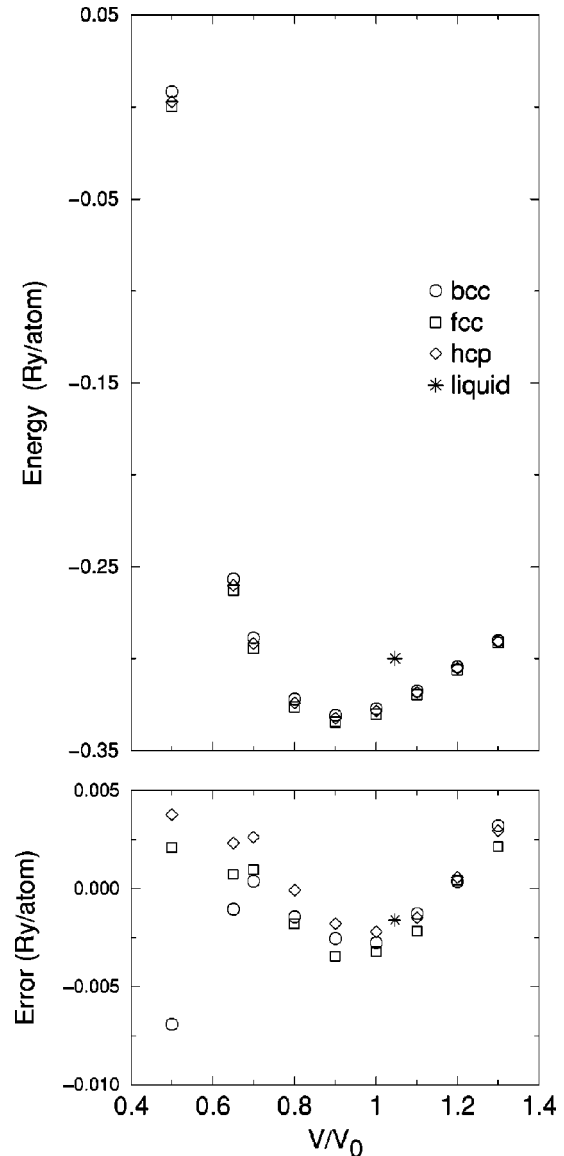


FIG. 1. The calculated FPLMTO energies for four different structures as a function of volume V/V_0 ($V_0=12.1 \text{ \AA}^3$) (upper part). The differences between the FPLMTO energy and the corresponding fitted energies are shown in the lower part.

basis formed a single, fully hybridizing basis set. For sampling the irreducible wedge of the Brillouin zone we used the special k -point method.¹⁵ In order to speed up the convergence we have associated each calculated eigenvalue with a Gaussian broadening of width 20 mRy.

The obtained data for the E - V relations for three phases with bcc, fcc, and hcp structures (Fig. 1) were fitted using the relations (1)–(3), where the particular form of the functions ϕ , ρ_i , and $F(\rho)$ were as follows:

$$\phi(r_{ij}) = \epsilon \left(\frac{a}{r_{ij}} \right)^n, \quad (4)$$

$$\rho(r_{ij}) = \left(\frac{a}{r_{ij}} \right)^m, \quad (5)$$

TABLE I. Parameters of the Sutton-Chen potential [Eqs. (1)–(6)].

Source	n	m	ϵ (eV)	a (Å)	C
Sutton and Chen	9.0	6.0	0.0126	3.612	39.765
Fitted to solid phases	7.613	6.478	0.0307	3.583	20.273
Fitted to solid and liquid phases	9.05	5.005	0.0225	3.270	33.17

^aReferences 7 and 37.

$$F(\rho_i) = -\epsilon C \sum_{i=1}^N \sqrt{\rho_i}, \quad (6)$$

using the algorithm of Nelder and Mead.¹⁶ The resulting function with parameters given in Table I (second line) was used to calculate the coordinates of 32 Cu atoms in the liquid phase. One of the liquid configurations obtained from the MD simulation (for technical details see below) was then calculated with the FPLMTO method. It was found that the FPLMTO and MD energies were different by approximately 1 eV/atom. Therefore, for the functions (1)–(6) to be consistent with the FPLMTO they had to be refitted. The FPLMTO energy of the liquid configuration was then included as an additional point in the E - V set. After that the functions (1)–(6) were fitted again to match the new (27 solid and 1 liquid points) E - V set. The results of the fit are shown in Fig. 1. The parameters are given in Table I. Thus, the first iteration was completed. Because the errors of the fit were insignificant, we decided that no further iterations were necessary. The errors of fit for solid phases are about the same before and after inclusion of the liquid data in the fitting procedure. It should be noted that it is not feasible to completely check the self-consistency, i.e., to ensure that both FPLMTO and Eqs. (1)–(6) produce the same energy for any atomic configuration for one simple reason — there is an infinite number of such configurations. Still, the fit is statistically well defined because with four independent parameters we succeeded to fit 28 E - V points. The rule of thumb in fitting says that the number of parameters should not be more than the square root of the number of fitted points. This rule comes from the requirement that a number of degrees of freedom should be of the same order as number of fitted points to lower the probability of accepting a wrong hypothesis.¹⁷ The errors of the fit are small and do not influence the resulting relative stability of the solid phases. According to the models (1)–(6) the fcc phase is the most stable one, with the hcp phase very close to fcc. The bcc phase is the most unstable phase at $T=0$ K.

III. MOLECULAR DYNAMIC SIMULATION

A. Technical details

A description of the molecular dynamic method can be found elsewhere.¹⁸ Most of the simulations were performed using the package DL_POLY version 2.0.¹⁹ To ensure the reliability of our results, some of the simulations were duplicated using our MD code and no relevant difference was found. Simulations in constant volume and energy (NVE) and constant temperature and pressure (NTP) ensembles were performed. The results of MD simulations at constant

volume and energy (NVE ensemble) with the chosen model of interatomic interaction depend on, apart from the initial arrangement of atoms, number of time steps ($n_{time\ steps}$), size of the time step (Δt), number of atoms (N), and cutoff (r_{cutoff}) of the interatomic potential. In addition to that, the simulations at constant pressure (P) and temperature (T) (NTP ensemble) can be also affected by the specified time constants for temperature (τ_T) and pressure (τ_P) fluctuations. Therefore, the influence of these parameters was carefully studied by carrying out test runs at various T and P . It was found that correct results can normally be obtained with $N > 500$, $n_{time\ steps} = 10\,000$, $\Delta t = 0.003$ psec, $r_{cutoff} = 6$ Å, $\tau_T = 0.2$ psec, and $\tau_P = 0.5$ psec. These values were normally used unless it was specifically intended to study the behavior of, for example, a small system. The assumption of a mean-field distribution of the density was applied for calculations of energy and forces at $r > r_{cutoff} = 6$ Å, because the cutoff was abrupt. The initial configuration for all runs, except those for the calculation of the melting temperatures and the vacancy energy, was an ideal fcc lattice. For the calculation of the vacancy-formation energy, one atom was taken out from the ideal fcc lattice.

The initial configuration for simulation of melting was prepared in the following manner. First, the fcc lattice was generated by translating the unit cell five times in the x and y directions and 10 times in the z direction. Second, the MD run with half of the atoms as frozen was carried out at $T = 2500$ K and $P = 1$ bar. As a result a supercell that contained a crystal and a liquid phase with a common interface was obtained. This supercell was then used as an initial configuration for further simulation of melting and solidification in the NTP ensemble. The method has been demonstrated^{1–3,20} to provide the true melting temperature for the chosen model of interatomic interaction.

B. Pressure-temperature equation of state

To assess the quality of the models (1)–(6) by comparison with experimental data and previous simulations we have performed MD simulations for temperatures up to 1400 K and for pressures up to 2 Mbar. In agreement with our FPLMTO calculations and experiment^{21–23} no phase transitions were found and the fcc phase remained stable at all P and T . Both FPLMTO and the MD simulation underestimate the lattice constant at ambient P (see Table II). The calculated P - V equation of state (EOS) (Fig. 2) is somewhat different from the experimental one with the MD EOS being less compressible than real Cu. We have calculated the volumes of Cu at a pressure of 1 bar at T from 200 K to 1400 K. From these volumes the linear coefficient of thermal expansion was calculated and the comparison with experiment is shown in Fig. 3. The calculated coefficient is about 20%

TABLE II. Some calculated and experimental values. L , lattice constant, Å; E_v , energy of vacancy formation, eV; V_{liquid} , volume of liquid at the fusion and pressure 1 bar, cm³/mol; ΔS_f , entropy of fusion, cal/mol deg; ΔV_f , volume change of fusion, cm³/mol; dT/dP , gradient of melting curve, deg/kbar; $(\partial V/\partial T)_P$, thermal expansivity of liquid at 1 bar, cm³/mol deg; D_{1423} , coefficient of diffusion in liquid, Å² ps⁻¹.

Value	Calculated	Experiment
L	3.534	3.61 ^a
E_v	1.42	1.09-1.4 ^{b,c}
V_{liquid}	7.529	7.951 ± 11 ^d
ΔS_f	2.55	2.3 ± 0.1 ^e
ΔV_f	0.386	0.350 ± 11 ^{d,f}
dT/dP	3.67	3.65 ± 0.27 ^g
$(\partial V/\partial T)_P$	0.00098	~0.00079 ^d
D_{1423}	0.368	0.471, ^h 0.303 ⁱ

^aReference 21.

^bReference 26.

^cReference 27.

^dReference 38.

^eReference 39.

^fReference 40.

^gReference 31.

^hReference 41.

ⁱReference 42.

larger than the experimental one. However, the temperature trend is remarkably similar to the experimental data. It is not always possible to reproduce experimental temperature dependence of thermal expansion.²⁴ Before it has been noted²⁵ that the coefficient of thermal expansion predicted by the Finnis-Sinclair interactions was very poor and in some cases (for bcc metals) even negative.⁵ The agreement in the present study demonstrates that that disagreement is not due to the deficiencies in the functional form of Sutton-Chen potential but rather due to the set of data that was chosen for the parametrization of the potential.

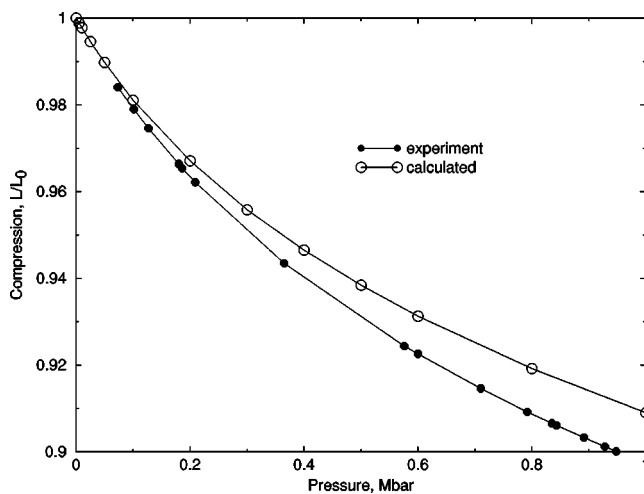


FIG. 2. The MD and experimental (Refs. 21–23) relative change of lattice constant against pressure. The maximum error in lattice constant is about 1.1% at a pressure of 1 Mbar. The MD and FPLMTO equation of states are nearly identical (the volumes at a pressure of 1 Mbar are 8.29 and 8.32 Å³/atom, respectively).

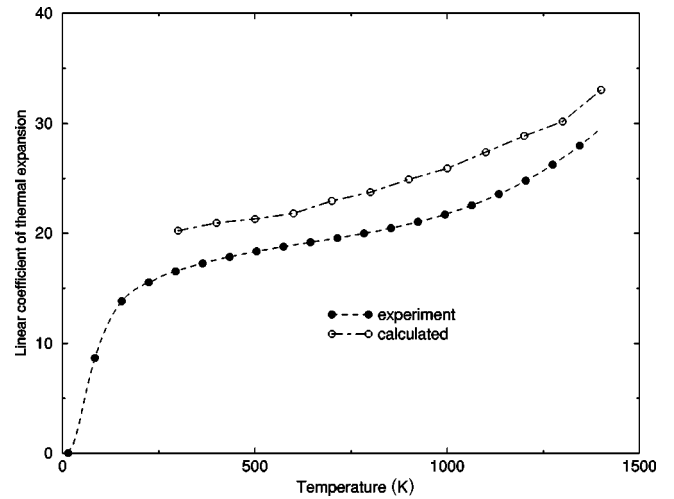


FIG. 3. The MD linear coefficient of thermal expansion $(1/L)(dL/dT) \times 10^6$ K, where L is the lattice constant (the derivative was calculated numerically as a central derivative with a temperature step of 100 K) and experimental (Refs. 43 and 44) linear coefficient of thermal expansion. Though the MD thermal expansion is somewhat higher than the experimental one, the trends are very similar.

The ability of the EAM potential to correctly describe the energy of structures different from the ideal crystal is a good test because this is one of the reasons for introducing the EAM instead of pair-interaction models. We calculated the energy needed to create a point vacancy by deleting one atom from ideal fcc lattice and comparing energies of the ideal structure and the one containing vacancy structure. The results are given in Table II. The error is within the range of different experimental determinations.^{26,27} This is quite remarkable because normally EAM functions are fitted to reproduce the vacancy formation energy,⁵ while here we did not use any data on the vacancy formation energy for fitting the potential.

C. Melting and properties of liquid phase

The melting/freezing was simulated as described above. All MD runs for calculating true T_m of our model were starting from the same initial configuration prepared as described in the Sec. II. These simulations are denoted further as “ $N+N$ ” where N indicates the number of particles in liquid and solid parts of a supercell. Sometimes the method “heat-until-it-melts” is used instead of calculating melting temperatures. The former will be denoted further as “ N ” where N is the number of particles in supercell arranged in perfect fcc lattice. The method “heat-until-it-melts” was used for the purpose of comparison only, to demonstrate that this method produces quite incorrect results. The phase transition was detected by discontinuous changes of the volume and the diffusion coefficient, structure, and animation of time history of atomic positions. The change of volume with temperature at the pressure 1 bar is shown in Fig. 4 (indicated in the legend as 500+500). The size “500+500” is sufficient for calculating melting temperature. This was checked by simulations using supercells “108+108,” “256+256,” and “864+864.” While T_m of the supercell “108+108” was different from the T_m of the supercell “500+500” by 60 K,

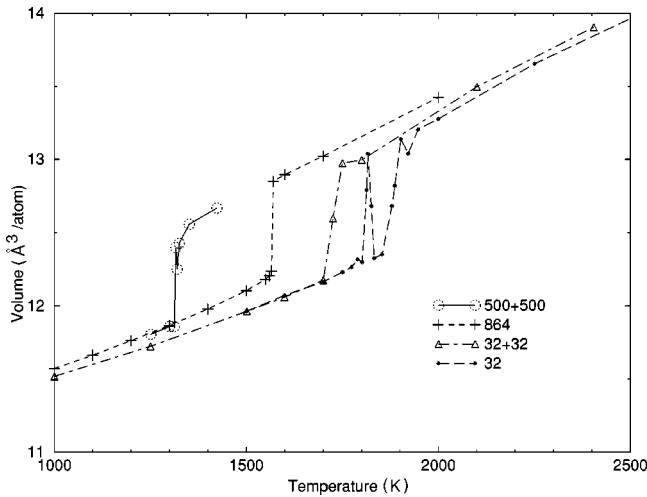


FIG. 4. The MD volume change for different supercells as a function of temperature at ambient pressure. Volumes calculated using two-phase simulations are denoted as $N+N$. The points denoted as a single “ N ” are results of a conventional simulation of the kind “heat-until-it-melts.” The details of simulations are described in the text.

the cells “256+256,” “500+500,” and “864+864” melted within 20 K interval. The dependence of melting temperature on the number of atoms follows the dependence of mean-square displacement on the number of atoms.²⁸ As the system is finite, the temperature of the phase transition cannot be located exactly. The highest T at which the system freezes is equal 1316 K. At $T > 1340$ K the calculated volumes clearly belongs to the liquid branch (compare with the simulations with 864 atoms). As one can see there is a very narrow uncertainty in temperature, therefore the position of the melting/freezing transition can be located rather precisely.

The melting/freezing was simulated at several pressures and the resulting PT copper melting curve is shown in Fig. 5. The calculated and experimental PT melting curves are very close. To the authors’ knowledge there are only two

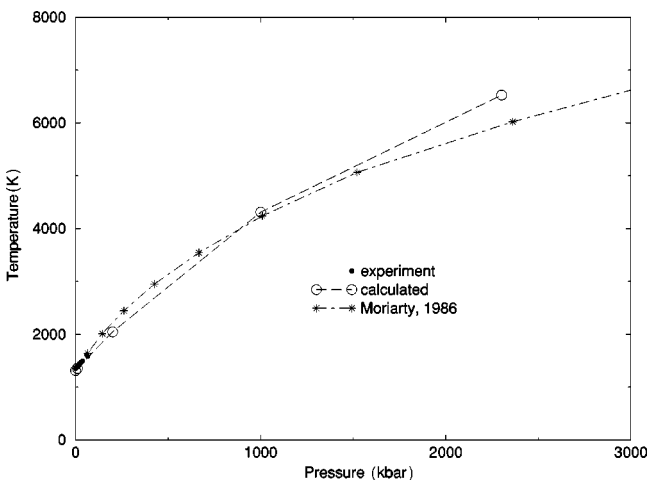


FIG. 5. The simulated melting curve compared with experimental data (Refs. 31,33,32) (up to 65 kbar) and calculated by Moriarty (Ref. 29). Our melting curve and that by Moriarty are very close, which lend support to both of them.

previous theoretical determinations of the copper PT melting curve.^{29,30} The calculations by McQueen *et al.*³⁰ give lower melting temperatures than our curve. This is probably because their calculations are based on insufficient experimental data (even the initial gradient of their melting curve is lower than experiment.^{31–33} The curve by Moriarty²⁹ is very close to ours. Since these curves are calculated using quite different methods we believe that the coincidence is not fortuitous and the calculated curve is likely to be a reliable prediction. This is also supported by the well-reproduced experimental data at lower pressures concerning the melting/freezing transition and properties of liquid Cu (see Table II and Fig. 6).

IV. DISCUSSION

The room pressure melting temperature of Cu was very precisely (1340 K) calculated by Foiles and Adams.³⁴ In contrast, the Sutton-Chen potential (Table I, first line) gives T_m by about 300 K lower than the experimental value (1358 K). When the potential in this work is fitted to only the properties of the solid phases (Table I, second line), it gives T_m about 800 K. Because the functional form of all these potentials is close and for the latter two is identical, it is clear that the choice of the data for fitting is the most important step. Calculation of melting is in some respect equivalent to an extrapolation of low-temperature data used for the fitting to high temperature. If additional data on the melt are included in the fitting then we are dealing with interpolation rather than extrapolation. As is well known, an interpolation is a more precise procedure. *Ab initio* calculations provide the way to establish a relation between a liquidlike configuration of atoms and their energy. There is no other way to do this. On the other hand, such information is sufficient to make it possible to calculate properties of the solid and liquid phases in good agreement with experiment. Figure 4 shows that a large number of particles (compare the two curves “500+500” and “32+32”) as well as a correct procedure (compare the two curves 500+500 and 864) for simulating a melting transition are critical for a correct calculation of T_m . At extreme cases the error can be as large as 600 K [about 1300 K for two-phase simulation with 1000 atoms and about 1900 K for one-phase simulation (“32” in Fig. 4) with 32 atoms]. This is almost about half of the true value for T_m . At a pressure of 2.3 Mbar the difference is close to 2000 K. Recently, the melting of Al was simulated using *ab initio* MD and a unit cell with 64 atoms.³⁵ Melting was determined as the point where the Gibbs free energy of the liquid and the solid are equal. This method is equivalent to a two-phase simulation (or “64+64,” as it could be marked in Fig. 4). Such a simulation, assuming that the interaction model is perfect, should produce overheating (in the case of Cu about 200–300 K), because 64 atoms might not be sufficient to calculate the heat capacity of a solid correctly.^{4,36} Therefore, the obtained agreement between calculated (890 K) and experimental (933 K) melting temperatures suggests that possibly the energies of the solid and/or liquid phase(s) have not been correctly calculated. Any simulation of melting must involve at least a few hundred particles (the precise number depends on the particular system). Therefore, one can disregard all simulations where the number of atoms is small and

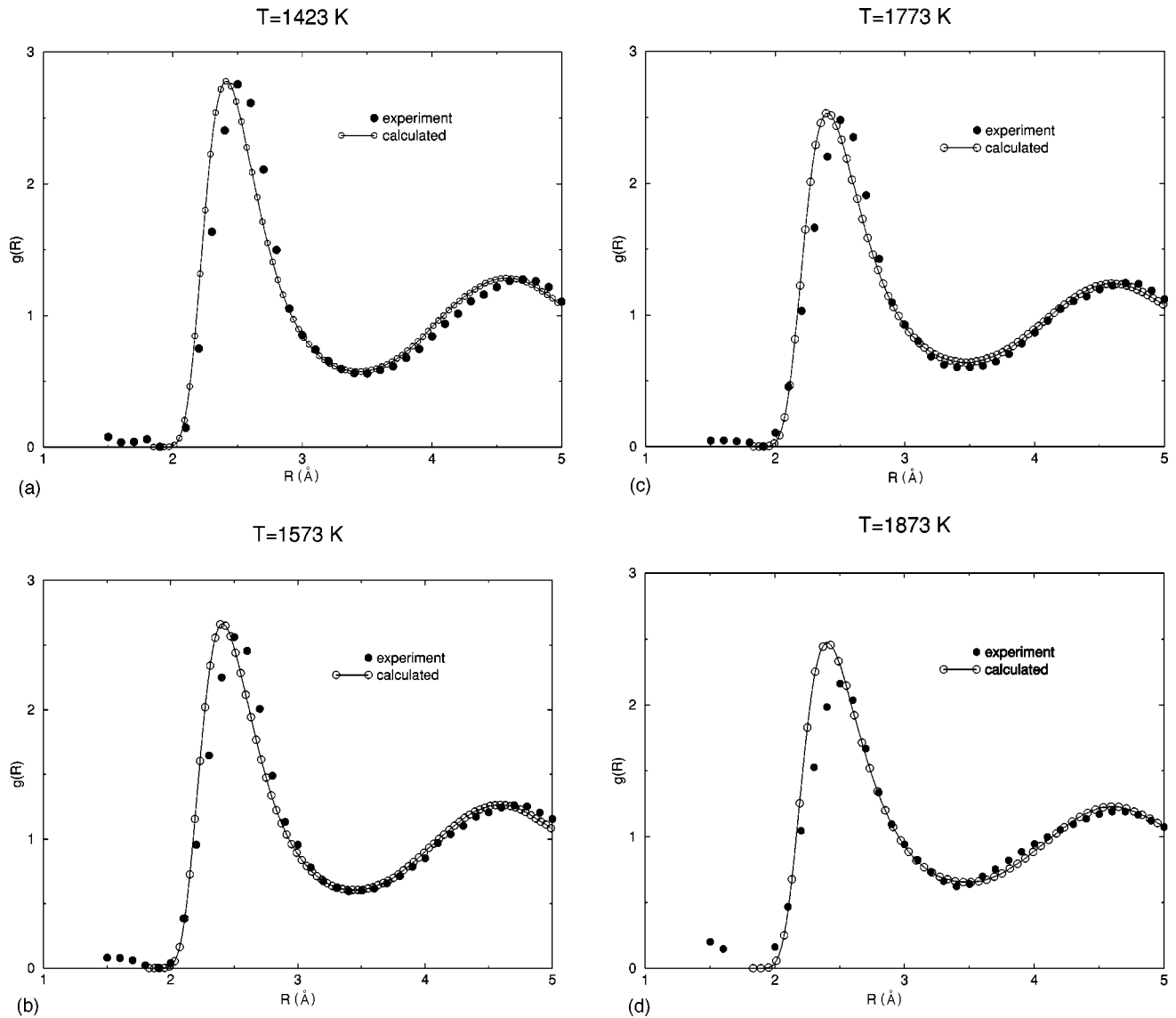


FIG. 6. Radial distribution functions (RDF) calculated at four different temperatures [(a) $T = 1423$ K, (b) $T = 1573$ K, (c) $T = 1773$ K, and (d) $T = 1873$ K] and compared with experimental data (Ref. 45). There is a very good agreement at all temperatures except for $T = 1873$ K. The calculated RDF's are slightly shifted to shorter distances relative to the experimental RDF's. This is because FPLMTO volumes are somewhat smaller than the experimental volume. The corresponding particle densities are 0.0755, 0.0745, 0.0728, 0.0722 [experimental (Ref. 45)] and 0.0789, 0.0777, 0.0762, 0.0754 (calculated). The experimental and calculated particle density changes in this range of temperatures are 0.033 and 0.035, correspondingly.

the size dependence of results have not been checked, unless one is satisfied with a precision of about 50%. If the melting temperature is not determined correctly and instead the temperature of thermal instability is erroneously accepted as T_m , then there is a danger that all phenomena calculated between the true T_m and the erroneous T_m , which normally would be classified as artifacts in the range of a metastable solid phase, can be regarded as real. This temperature range can in fact be very large, in the case of Cu it is about 600 K at ambient pressure and about 2000 K at a pressure of 2.3 Mbar. This interval increases as pressure increases.

The present approach cannot be better than the quality of the data from first-principles calculations. If for some reason results of the first-principles calculations are different from experiment then there is no way in the frame of the presented approach to reach an agreement between MD simulations and experiment.

V. CONCLUSIONS

The present study introduces a robust way to parametrize the EAM model for studying the melting transition of Cu and properties of liquid Cu. A similar procedure has now also been applied to Pd and it works as well as for Cu. It might sound trivial, but we want to emphasize that if the intention is to study melting, the model parameters should be fitted both to properties of the solid and the liquid phases. *Ab initio* calculations, in particular the FPLMTO method, are able to provide such data on both phases with a sufficient precision for the fitting of the potential. MD simulations using that potential reproduce experimental data of Cu in a successful way. The present approach has the potential to be used on any system, enabling detailed and accurate simulations with large number of atoms and in agreement with first-principles calculations.

ACKNOWLEDGMENTS

A.B.B. is thankful to W. Smith for the DL_POLY software package. J. Moriarty provided us with his tabulated Cu melt-

ing curve. Discussions with P. Korzhavyi and I. Abrikosov are appreciated. The help of B. Holm was very valuable. We are grateful to Naturvetenskap Forsknings Rådet and Swedish Material Consortium No. 9 for financial support.

- ¹A.B. Belonoshko, *Geochim. Cosmochim. Acta* **58**, 4039 (1994).
- ²A.B. Belonoshko, *Phys. Chem. Miner.* **25**, 138 (1998).
- ³R. Ahuja, A.B. Belonoshko, and B. Johansson, *Phys. Rev. E* **57**, 1673 (1998).
- ⁴B. Winkler and M.T. Dove, *Phys. Chem. Miner.* **18**, 407 (1992).
- ⁵M.S. Daw, S.M. Foiles, and M.I. Baskes, *Mater. Sci. Rep.* **9**, 251 (1993).
- ⁶M.W. Finnis and J.E. Sinclair, *Philos. Mag. A* **50**, 45 (1984).
- ⁷A.P. Sutton and J. Chen, *Philos. Mag. Lett.* **61**, 139 (1990).
- ⁸Y. Mishin, D. Farkas, M.J. Mehl, and D.A. Papaconstantopoulos, *Phys. Rev. B* **59**, 3393 (1999).
- ⁹F. Ercolessi and J.B. Adams, *Europhys. Lett.* **26**, 583 (1994).
- ¹⁰A.F. Voter, in *Intermetallic Compounds*, edited by J. H. Westbrook and R.L. Fleischer (Wiley, New York, 1994), Chap. 4, p. 77.
- ¹¹J.M. Wills (unpublished); J.M. Wills and B.R. Cooper, *Phys. Rev. B* **36**, 3809 (1987); D.L. Price and B.R. Cooper, *ibid.* **39**, 4945 (1989).
- ¹²L. Hedin and B.I. Lundqvist, *J. Phys. C* **4**, 2064 (1971).
- ¹³O.K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
- ¹⁴H.L. Skriver, *The LMTO Method* (Springer, Berlin, 1984).
- ¹⁵D.J. Chadi and M.L. Cohen, *Phys. Rev. B* **8**, 5747 (1973); S. Froyen, *ibid.* **39**, 3168 (1989).
- ¹⁶W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in FORTRAN* (Cambridge University Press, Cambridge, 1992), p. 402.
- ¹⁷G.A. Korn and T.M. Korn, *Mathematical Handbook for Scientists and Engineers*, 2nd ed. (McGraw-Hill, New York, 1968), p. 650.
- ¹⁸M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- ¹⁹T.R. Forester and W. Smith, *The DL_POLY_2.0 User Manual* (CCLRC, Daresbury Laboratory, Daresbury, Warrington, England, 1998).
- ²⁰J.R. Morris, C.Z. Wang, K.M. Ho, and C.T. Chan, *Phys. Rev. B* **49**, 3109 (1994).
- ²¹H.K. Mao, P.M. Bell, J.W. Shaner, and D.J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
- ²²J. Xu, H.K. Mao, and P.M. Bell, *High Temp.-High Press.* **16**, 495 (1984).
- ²³P.M. Bell, J. Xu, and H.K. Mao, in *Shock Waves in Condensed Matter*, edited by Y.M. Gupta (Plenum, New York, 1986), p. 125.
- ²⁴J. Mei, J.W. Davenport, and G.W. Fernando, *Phys. Rev. B* **43**, 4653 (1991).
- ²⁵S.M. Foiles and M.S. Daw, *Phys. Rev. B* **38**, 12 643 (1988).
- ²⁶P. Ehrhart, P. Jung, H. Schultz, and H. Ullmaier, in *Atomic Defects in Metals*, edited by H. Ullmaier, Landolt-Börnstein, New Series, Group III, Vol. 25 (Springer-Verlag, Berlin, 1991).
- ²⁷P.A. Korzhavyi, I.A. Abrikosov, and B. Johansson, *Phys. Rev. B* **59**, 11693 (1999).
- ²⁸A.B. Belonoshko, *Science* **278**, 1475 (1997).
- ²⁹J.A. Moriarty, in *Shock Waves in Condensed Matter*, edited by Y.M. Gupta (Plenum Press, New York, 1986), p. 101.
- ³⁰R.G. McQueen, W.J. Carter, J.N. Fritz, and S.P. Marsh, in *Accurate Characterization of High Pressure Environment*, edited by E.C. Lloyd, U.S. National Bureau of Standards Special Publication No. 326 (U.S. GPO, Washington, D.C., 1971), p. 219.
- ³¹L.H. Cohen, W. Klement, Jr., and G.C. Kennedy, *Phys. Rev.* **145**, 519 (1966).
- ³²N.R. Mitra, D.L. Decker, and H.B. Vanfleet, *Phys. Rev.* **161**, 613 (1967).
- ³³J. Akella and G.C. Kennedy, *J. Geophys. Res.* **76**, 4969 (1971).
- ³⁴S.M. Foiles and J.B. Adams, *Phys. Rev. B* **40**, 5909 (1989).
- ³⁵G.A. de Wijs, G. Kresse, and M.J. Gillan, *Phys. Rev. B* **57**, 8223 (1998).
- ³⁶A. Pasquarello, K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 1982 (1992).
- ³⁷B.D. Todd and R.M. Lynden-Bell, *Surf. Sci.* **281**, 191 (1993).
- ³⁸J.A. Cahill and A.D. Kirshenbaum, *J. Phys. C* **66**, 1080 (1962).
- ³⁹R. Hultgren, R.L. Orr, P.D. Anderson, and K.K. Kelley, *Selected Values for the Thermodynamic Properties of Metals and Alloys* (Wiley, New York, 1963).
- ⁴⁰R.O. Simmons and R.W. Baluffi, *Phys. Rev.* **119**, 600 (1960).
- ⁴¹M. Shimoji and T. Itami, *Atomic Transport in Liquid Metals* (Trans Tech, Zurich, Switzerland, 1986).
- ⁴²M.M.G. Alemany, C. Rey, and L.J. Gallego, *J. Phys. Chem.* **109**, 575 (1998).
- ⁴³T.A. Hahn, *J. Appl. Phys.* **41**, 5096 (1970).
- ⁴⁴J.W. Harrison, *J. Phys. E* **9**, 545 (1976).
- ⁴⁵Y. Waseda, *The Structure of Non-Crystalline Materials, Liquids and Amorphous Solids* (McGraw-Hill, New York, 1980).