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# Molecular-dynamics studies of the thermal properties of the solid and liquid fcc metals Ag, Au, Cu, and Ni using many-body interactions

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Molecular-dynamics (MD) simulations of pure Ag, Au, Cu, and Ni are reported. The *NPT* (isobaric-isothermal) MD method is used in order to reveal the behavior of these metals at various temperatures in the solid as well as in the liquid state. According to the embedded-atom method [M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984)] the interactions in metals are assumed to be composed of the pair component (caused by cores overlapping) and the cohesive many-body term (gluing term). The scheme for the empirical *N*-body potentials derivation proposed by Ackland *et al.* [G. J. Ackland, G. Tichy, V. Vitek, and M. W. Finnis, Philos. Mag A **56**, 735 (1987)] is used. The potential parameters have been derived exclusively on the basis of the room-temperature properties (the equilibrium lattice constant, elastic constants, the cohesive energy, the stacking-fault energy, the unrelaxed vacancy-formation energy, and the volume-pressure dependency). The various quantities describing the temperature-dependent behavior of the simulated systems (thermal-expansion coefficients of solids and liquids, specific heats of solids and liquids, the volume change on melting, and the enthalpy of melting) as well as the radial distribution functions at various temperatures are derived. Generally, satisfactory agreement with the experimental data is achieved.

## I. INTRODUCTION

There are some basic objections against the use of pair potentials for the metallic systems. Any pure pairwise-potential model gives, for example, the Cauchy relation between the elastic constants $C_{12}=C_{44}$, which is seldom the case in real metals (for Ag, $C_{12}/C_{44}\approx 2$; for Au, 3.7; for Cu, 1.6; and for Ni, 1.15). The pair models also fail when describing surface properties (e.g., surface relaxation) or defects. In general, the pure pairwise-potential models do not work properly when the local environment differs from the uniform bulk. The most important failures of the two-body models are summarized in, e.g., Ref. 1.

An original and alternative approach, being a significant improvement over the pair potentials, was proposed by Daw and Baskes[2,3] and Finnis and Sinclair.[4] Daw and Baskes' method, called the embedded-atom method (EAM), has been successfully applied to many problems, e.g., studies of surfaces,[3] liquid metals,[5] alloys,[6,7] grain boundaries,[8] or melting processes.[9]

The scheme for empirical *N*-body potentials derivation for metallic systems put forward by Finnis and Sinclair[4] for the bcc metals and later developed by Ackland *et al.*[10] for the fcc metals can be regarded as a version of the EAM. This scheme has been also successfully applied for studies of surfaces,[11] vacancies,[12] interstitials,[13] or diffusion.[14] The potentials of Ackland *et al.*[10] have already been used in molecular-dynamics (MD) simulations of pure copper.[15] In the present study the potentials proposed by Ackland *et al.*[10] are used, not the functions of Foiles *et al.*,[16] just because of a computational convenience.[17]

The main purpose of the present paper is to simulate behavior of pure silver, gold, copper, and nickel over a wide temperature range using the many-body interactions. Both the solid and the liquid states are simulated. The majority of the results concerning copper has already been published,[15] but an additional analysis is carried out.

The main question is whether the above potentials, derived on the basis of exclusively one temperature property of the solid phase, could describe correctly the temperature-dependent behavior of the solid and liquid metals. The molecular-dynamics studies result in various quantities describing the temperature-dependent behavior of the analyzed systems. The radial distribution functions of the solid and liquid phase are also derived providing structural information about the phases and about the melting phenomenon. Temperatures of the solid-liquid transition are estimated. They must not be, however, interpreted as the real melting temperatures of the systems, but rather as the temperatures of the mechanical instability of the infinite single crystal. Melting has recently been very intensively studied using the MD technique.[9,15,18–22] In Refs. 9 and 18 it is shown that the lattice collapses at temperatures of the mechanical instability given by the Born criterion. In other words, the upper limit of superheating, when three-dimensional periodic boundary conditions are used, is at a point in which the lattice loses its mechanical stability.

In order to simulate the ordinary experimental conditions (constant pressure) the *NPT* MD method is used. This method allows the volume of the simulated system to change; in this way the thermal expansions and the volume change on melting can be easily estimated.

## II. INTERACTIONS

The total energy $U$ of a system is approximated by[3,4]

$$U=\tfrac{1}{2}\sum_i \sum_j{}' u(R_{ij})-\sum_i f(k_i) , \tag{1}$$

where $i,j$ denotes atoms, $R_{ij}$ is distance between atoms $i$ and $j$, $u$ the pair potential, $f$ the embedding function, and $k_i=\sum_j \phi(R_{ij})$.

The energy composes of the standard pair term [the first component in (1)] and of the many-body term (the second one). The first term (mainly repulsive) is due to the cores overlapping and the second describes the cohesive effect of the conducting electrons. An interpretation of $k_i$ is different in Refs. 3 and 4. According to Daw and Baskes[3] $k_i$ is an electron density at atom $i$ due to the remaining atoms while Finnis and Sinclair[4] identify $k_i$ with the second moment of the density of states. Although the physical interpretation is different, in both cases the formula (1) can be written.

If the Hamiltonian (1) is derived from the first principles, the distinction between the repulsive pair potential and the cohesive many-body term is quite clear. When dealing, however, with such a Hamiltonian in practice no such distinction exists. The functions in (1) can be replaced by[1]

$$u(r) \rightarrow u(r)+2\lambda\phi(r) \,,$$

$$f(k) \rightarrow f(k)+\lambda k \,, \tag{2}$$

where $\lambda$ is an arbitrary real number. After such a transformation the energy of the system remains unchanged. The $N$-body model given by (1) is invariant to the above transformation. So no physical meaning should be attached to $u$, $\phi$, or $f$ separately.

When considering the formula (1) the force acting between particles $i$ and $j$ is the same as for the effective potential given by

$$u_{\mathrm{eff},ij}(R_{ij})=u(R_{ij})-[f'(k_i)+f'(k_j)]\phi(R_{ij}) \tag{3}$$

provided that the second- and higher-order derivatives of $f$ are neglected (the second-order derivative is essential for the Cauchy discrepancy $C_{12}-C_{44}$).

In general, this effective potential depends on the local configuration and changes from one pair of atoms to another. Only for the ideal periodic fcc structure (without any displacement from the lattice sites) the effective potential is the same for all pairs of the atoms in the system. This potential does not change after the transformation given by (2). From (2) it can also be concluded that the case, when $f$ is the linear function of $K$, is equivalent to the pure pair model.

After[10] the functions $u$ and $\phi$ are assumed to be sums of the third-order polynomials and $f(k)=\sqrt{k}$. The form of function $f$ (the square root) is discussed in Ref. 10 but it is rather an arbitrary choice when treating the fcc metals; on the other hand the functions derived by Ref. 16 can be quite well approximated by the square root.

The potentials parameters are derived on the basis of the following: lattice constant, cohesive energy, elastic constants ($C_{11}$, $C_{12}$, and $C_{44}$), vacancy formation energy, stacking-fault energy, and the volume-pressure dependencies [except Ni (Ref. 17)]. The lattice constant is the less important parameter (when treating pure metals) because it only provides the length unit.

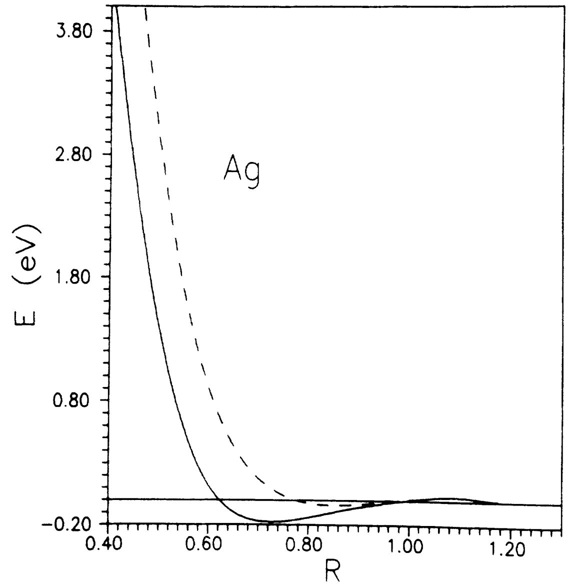

FIG. 1. Pair potential (— — —) and the effective pair potential in the ideal fcc (——) for silver.

No temperature dependency of these quantities is taken into account when deriving potential parameters. The procedure is described in Ref. 10 and values of the experimental quantities and the potential parameters are also presented there.[23] Shown in Fig. 1 is an example of the pair potential and the effective pair potential for the pure fcc structure of Ag calculated according to the formula (3).

In all the simulations it is assumed that the potentials are temperature and structure independent. It means that the same functions describe the interactions at any temperature in the solid as well as in the liquid state. This approximation is commonly accepted and is also justified by Foiles[5] studies of the liquid metals using the EAM method. Even in the very recent paper Sutton,[24] when analyzing the temperature dependence of interatomic forces, assumes that the potentials themselves are temperature independent. It is also assumed that all quantum effects are included in formula (1) and all further calculations are purely classical.

## III. MOLECULAR-DYNAMICS METHOD

When analyzing the system at various temperatures the usual experimental conditions are generated by the *NPT* method (with constant temperature and constant pressure). In this way the thermal expansion and the volume change on melting can be taken into account.

Anderson's method[25] of the constant-pressure molecular dynamics, in which computational cell size (and in a consequence the lattice constant) is an additional dynamic variable, is applied.

Two ways of keeping temperature constant are used. The simplest method of velocities scaling (being a very rough approximation of a canonical ensemble) and the Nosé method[26] with an additional degree of freedom corresponding to time scaling. The second method is well justified and gives proper canonical distribution in phase space but is more complicated. The results using both methods are very similar, so usually the first method was applied (especially during the equalibrization). More details concerning the MD method used in the present study (including equations of motion) are published elsewhere.[15]

It should be stressed that, while formula (1) gives a much more accurate description of the metallic systems, the equations of motion, in comparison with the pure pair wise-potential models, are not much more complicated and the increase in computer time is quite small (additional summations are carried out at any iteration step).

The Ackland's scheme[10] gives potentials approaching zero continuously. There are no cutoff radii. It is a great advantage of the above scheme from the point of view of physical interpretation (otherwise the derivative is infinitive at cutoff radius) as well as computational convenience.

## IV. CALCULATIONS

The equations of motion are integrated using the modified "leap-frog" algorithm. Trajectories of 256 (sometimes 864) particles with the mass equal to the mass of the investigated element are calculated using the three-dimensional (3D) cubic periodic boundary conditions. The lattice constant for crystal or a specific volume for liquid at each temperature are determined using Anderson's constant-pressure method. For any ele-

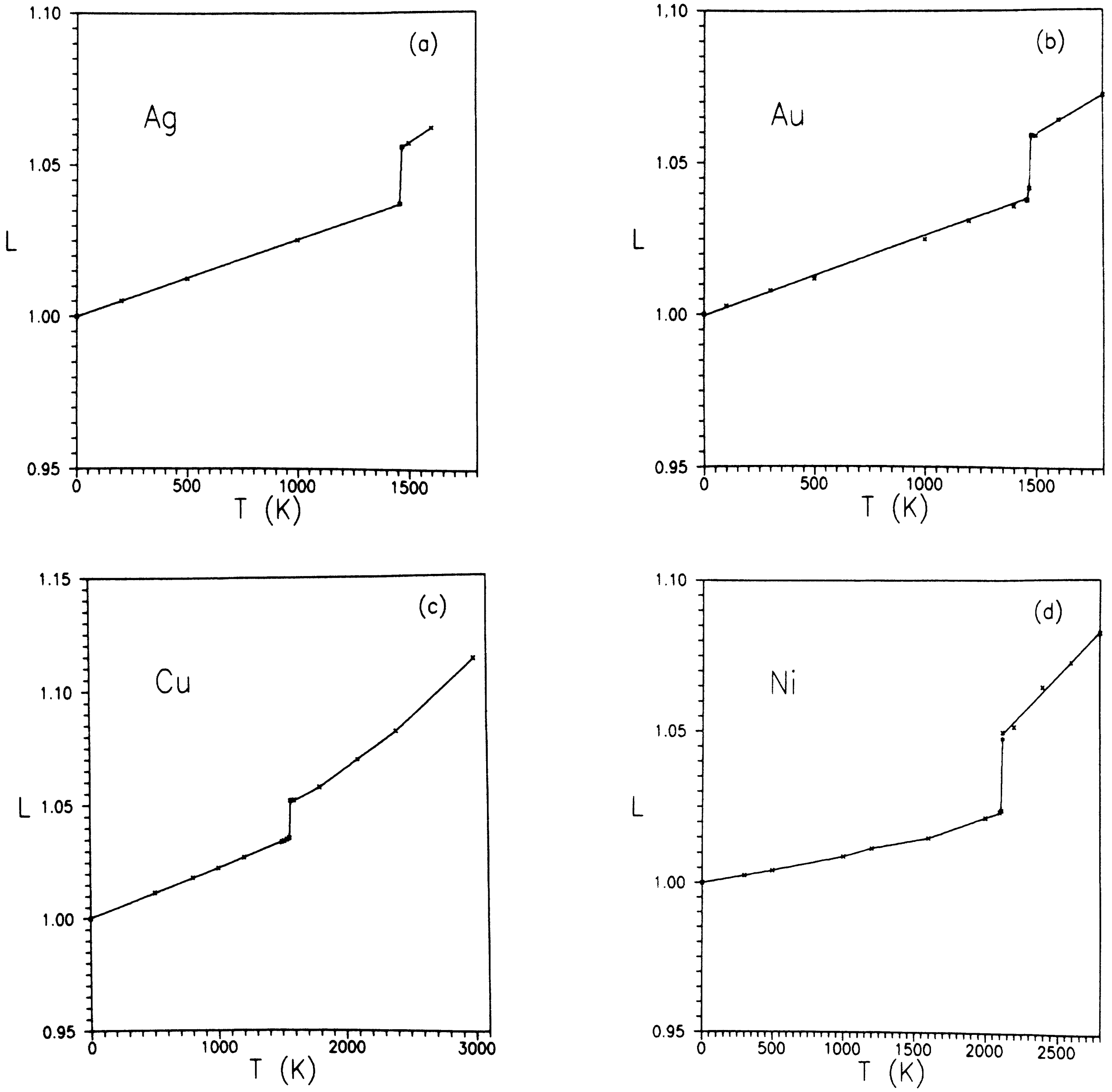

FIG. 2. Lattice constant dependencies on temperature

ment the MD simulations are carried out at various (at least 15) temperatures. At any temperature the initial configuration has the pure fcc structure with the random velocity distribution corresponding to the required temperature. After the preliminary equilibration (about 1000 iterations) the time averages of the various quantities (the internal energy, the lattice constant, the radial distribution function) are calculated over 5000–20 000 steps. The iteration step is equal $10^{-14}$ s. All simulations are carried out under atmospheric pressure.

## V. RESULTS

There is no difference in the results of 256 and 864 particles simulations except fluctuations. Only at few selected temperatures the 864 particles system has been simulated.

After about 50 steps at any temperature, the lattice constant and the internal energy reach their equilibrium values around which they later oscillate. Of course it is only the gross adjustment; it is too short a time, e.g., for density fluctuations to percolate through the system.

The normalized to 0-K lattice constant dependencies on temperature are shown in Fig. 2 and the internal energy (per atom) versus temperature curves are presented in Fig. 3. The radial distribution functions at selected temperatures are shown in Fig. 4. The well-marked structural transformation from the solid phase to liquid phase is visible for any element. It corresponds to the rapid change in the volume, the internal energy, and the radial

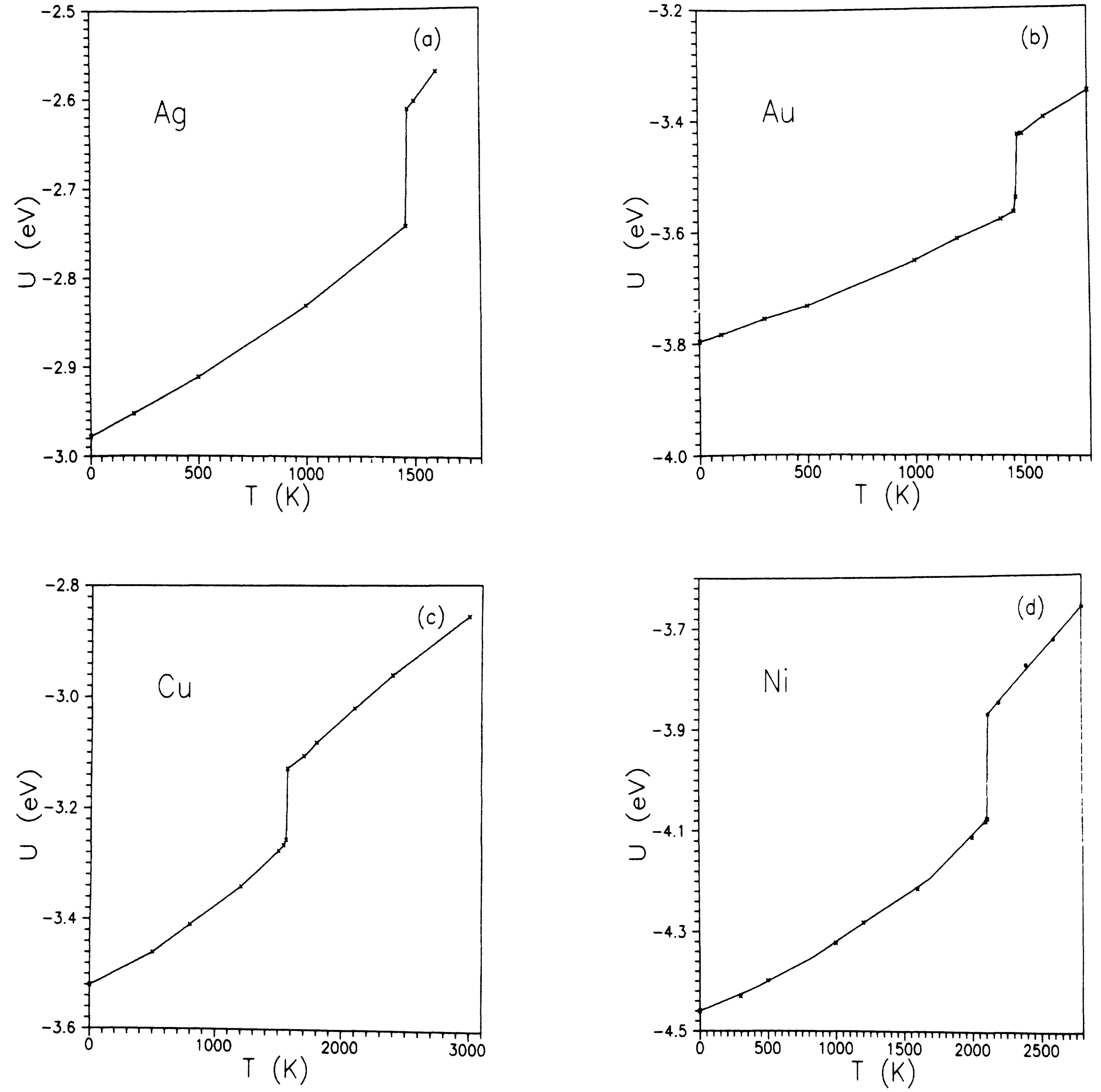

FIG. 3. Internal energy dependencies on temperature.

distribution functions (the peaks corresponding to second and fifth coordination zones disappear). From the above curves the thermal-expansion coefficients ($\alpha_{ls}$ linear for solid and $\alpha_{vl}$ volume for liquid), the volume change on melting ($\Delta V$), the enthalpy of melting ($\Delta H_m$), the temperature of solid to liquid transformation ($T_s$), and the specific heats for solid ($C_{ps}$) (at 1000 K) and liquid ($C_{pl}$) (just above melting) can be estimated. The temperature $T_s$ is well defined. It means that, for example, copper at temperature 1570 K melts after a few iteration steps and at 1560 K it remains solid even during long simulations (40 000 iterations); quantities like the lattice constant or the internal energy oscillates about the means without any steady drift.

All the above-mentioned quantities, together with the available experimental data, are listed in Table I. The positions $r_0$ of the first peak of $g(r)$ and values of $g(r_0)$ just above the melting point are also shown. These two values provide some quantitative description of the liquid state.

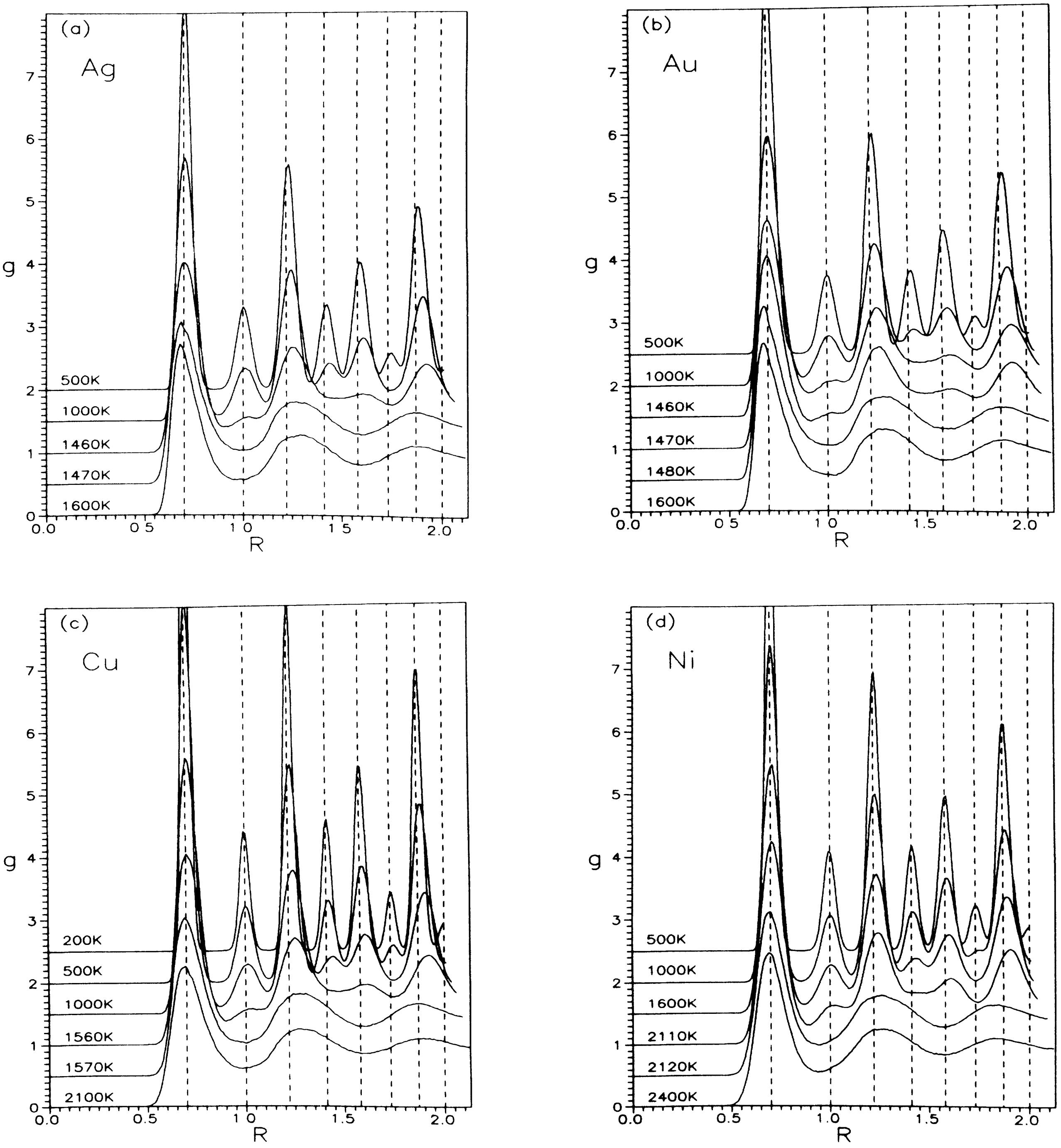

FIG. 4. Radial distribution function at various temperatures. Dotted lines denote coordination zones for ideal fcc at 0 K. The $g$ coordinates correspond to the lowest plot. The remaining plots are shifted up by 0.5 relative to a previous curve.

TABLE I. Simulated and experimental data for silver, gold, nickel, and copper (see text for symbols).

| | Ag | | Au | | Cu | | Ni | |
|---|---|---|---|---|---|---|---|---|
| | expt. | MD | expt. | MD | expt. | MD | expt. | MD |
| $\alpha_{ls}$ ($10^{-6}$ $K^{-1}$) | $19.1^c$ | 25 | $14.1^c$ | 26 | $17.0^c$ | 22 | $13.3^c$ | 10.5 |
| $\alpha_{vl}$ ($10^{-4}$ $K^{-1}$) | $0.98^d$ | 1.2 | $0.69^d$<br>$0.98^d$ | 1.3 | $1.0^d$ | 1.0 | $1.51^d$ | 1.5 |
| $T_s$ (K) | $1234^c$ | 1465 | $1336^c$ | 1475 | $1356^c$ | 1565 | $1728^c$ | 2115 |
| $\beta^a$ | 1.19 | | 1.10 | | 1.15 | | 1.22 | |
| $\Delta V_m$ (%) | $3.8^c$<br>$3.51^d$ | 5.3 | $5.1^c$<br>$5.5^d$ | 6.1 | $4.2^c$<br>$3.96^d$ | 4.4 | $4.5^c$<br>$6.3^d$ | 7.4 |
| $\Delta H$ (kJ/mol) | $11.1^{d,c}$ | 12.3 | $12.8^{d,c}$ | 13.2 | $13.0^{d,c}$ | 13.0 | $17.2^{d,c}$ | 19.2 |
| $r_m{}^b$ | $0.694^d$ | 0.69 | $0.689^d$ | 0.68 | $0.696^d$ | 0.70 | $0.701^d$ | 0.70 |
| $g(r_m)$ | $2.58^d$ | 2.70 | $2.77^d$ | 2.75 | $2.76^d$ | 2.50 | $2.36^d$ | 2.60 |
| $C_{ps}$ (kJ/mol K) | $29.9^e$ | 29.3 | $28.6^e$ | 27.6 | $28.7^e$ | 29.9 | $33.0^e$ | 31.6 |
| $C_{pl}$ (kJ/mol K) | $33.5^e$ | 39.1 | $33.4^e$ | 36.7 | $32.7^e$ | 32.5 | $43.16^e$ | 42.3 |

[a] $\beta = T_s$ (MD)/$T_m$ (expt).

[b] Lattice constant at 0 K is used as a length unit.

[c] Reference 28.

[d] Reference 27.

[e] Reference 29.

## VI. DISCUSSION

The agreement between the simulated and the experimental data (Table I) is quite reasonable. The main disagreement concerns estimated temperature $T_s$ of solid-liquid transition. In any case MD simulations predict the temperature too (at least 10%) high. It is due to lack of a surface in the simulations (3D periodic boundary conditions generate an infinitive single crystal). As it has been already discussed in the Introduction, the estimated temperature should be treated as the temperature of the mechanical instability of an infinitive single crystal. The influence of a free surface, a grain boundary, and a void on melting is analyzed in Refs. 9 and 18. Resulting from MD studies, superheating above the thermodynamic melting point $T_m$ (defined as the temperature at which the free energies of the liquid and the solid are equal) can be a significant fraction of $T_m$.[18] In Ref. 9 authors also carried out rather complicated calculations of the free energy of the solid and the liquid phase which made it possible to determine the $T_m$. Adopted from Ref. 19, the scheme is complicated and the labor consuming and requires some additional approximations. It has not been applied here because the melting phenomenon itself is not the only one task of the paper but the paper is focused on the simulation of a variety of the temperature-dependent properties of the metallic systems. The simulation of systems with surface is in progress[30] and indicates that if the surface is taken into account (via 2D periodic boundary conditions) the simulated superheating is reduced. Similar MD studies of a system of Lennard-Jones particles with 3D periodic boundary conditions revealed 15% superheating.[22] Authors carried out over 200 000 iterations in order to melt the superheated Lennard-Jones crystal (with 3D periodic boundary conditions) without any effect. It has also been experimentally shown that when the surface influence is reduced the metal (silver) can be superheated.[31]

Figure 4 gives some information about structure evolution with increasing temperature. At low temperatures there are peaks at ideal fcc positions (dotted lines in Fig. 4). With increasing temperatures peaks are becoming lower and wider. They are slightly shifted towards longer distances. This effect of thermal expansion is not visible for the first peak. It is probably due to the fact that with increasing temperature atoms are more probable to penetrate smaller interatomic distances. It can be noticed that with increasing temperature the value of $r$ for which $g(r) \neq 0$ decreases. The effect of thermal expansion is, however, very easy to be seen from the shift of second and third peak positions. At temperatures much lower than the melting temperature (below 1000 K for Ag, Au, and Cu; below 1600 K for Ni) the sixth peak disappears. Just below melting point the fourth peak is not visible as well, but the second and fifth peaks provide a way to the localization of the melting point. Their existence seems to be the clear indicator of the existence of crystal structure. Eventually, above melting point, an ordinary liquid structure is attained.

The structures of the liquids just above melting point agree quite well with experimental data (the height and the position of the first peak in the radial distribution function).

In Table I some further disagreements can be found (e.g., the expansion coefficient for solid gold or heat of melting and volume change on melting for silver). It is very difficult to find any reasonable explanation. For example, the thermal-expansion coefficient for Au, resulting from simulations, is about two times too big. On the other hand, taking into account very similar behavior of silver and gold, the much smaller experimental value of alpha for Au is difficult to explain. In general, however, the agreement is quite good, much better than what should be expected. The correct description of the high-temperature behavior is very promising. The specific heats of the solid and liquid metals agree very well (except liquid silver) with experimental data. The fact that the applied potentials describes properties of the liquid metals quite well gives very strong support for the hypothesis that these potentials work properly at high temperatures as well.

The reasonable values of the simulated melting temperatures might have been expected because of well-known correlations between the cohesive energy and the melting temperature.[27] The cohesive energy itself is used as the input data for the procedure of potentials parameters derivation. There are also some other rules[27] correlating various quantities but they are purely phenomenological. There is no obvious reason that other properties like the volume change on melting, the expansion coefficients, the heat of melting, or the specific heats should be estimated correctly by the simulations.

## VII. CONCLUSIONS

Presented in this paper simulations can be treated as a test of applicability of formula (1) and the potentials of Ackland *et al.*[10] over a wide temperature range for a description of solid and liquid metals.

The major conclusion from this work is that potentials based on EAM, derived on the basis of only one temperature property, are capable of providing a quite good description of the temperature-dependent behavior of the metallic systems over a wide temperature range. The same potentials can be used for crystals and liquids, despite the very different local configurations.

Taking into account the other successes of the *N*-body potentials (see the Introduction), this method seems to give quite an accurate description of the metallic systems and at the same time it is only slightly more complicated than the standard pair approach, therefore it can strongly be recommended for the computer studies of such systems.

The above-mentioned differences between simulated and experimental data can be used in a procedure of refining the potentials of Ackland *et al.*, e.g., they can be used to find the set of the potential parameters describing more correctly the constant temperature as well as the temperature-dependent properties.

Finally, the paper illustrates the usefulness of the *NPT* molecular-dynamics technique for the studies of the temperature-dependent behavior and phase transitions.

## ACKNOWLEDGMENTS

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