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Temperature-dependence of phonons, solid state properties and liquid structure of noble metals: A comparison of pair-potentials

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ABSTRACT

Two groups of effective pair-potentials are studied from the viewpoint of their suitability in being able to describe solid state properties and liquid state structure of noble metals Cu, Ag and Au over a wide temperature range. Since the effective pair-potentials are usually empirical in nature, with parameters obtained by fitting to some reference state properties, the objective of the present study is to determine whether a particular parametrization scheme has any definite advantage over another. We consider Morse potentials with parameters determined by equilibrium lattice parameter, cohesive/sublimation energies as well as bulk modulus values of the solid at low/room temperatures. The other group of potentials considered is Erkoç potentials, where the parameters were determined first by studying dimers and further modified using bulk stability condition and bulk cohesive energy values. The potentials were then used to study the energetics of microclusters containing 3–7 atoms. Quasiharmonic results for the solid obtained at different temperatures and Monte Carlo simulation for the liquid state show that phonon spectra, thermal expansion, temperature-dependence of specific heats and liquid structure are much better described by the latter group. The first group of potentials may have an advantage in reproducing the temperature-dependence of elastic constants and bulk moduli, since they are based on room temperature values of these properties, which show only weak temperature-dependence in general for all metals. It is argued that potentials based on parameters fitted to the properties at a single volume are less versatile in capturing the temperature-dependence of various thermodynamic properties over a wide range. Potentials capable of reproducing the energetics of clusters of different co-ordination numbers and volumes per atom may fare better in this regard.

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1. Introduction

Despite much progress in *ab initio* electronic structure-based calculations of solid state properties, results of effective pair-potential studies still hold merit because of their simplicity as well as considerably less demand on computational efforts and resources. For metals, such potentials are useful because of the associated ease of implementation and for developing an understanding of trends within certain groups, such as transition and noble metals, and their alloys. In addition, they provide a relatively easy way to study systems without periodicity such as clusters, liquids and amorphous solids, and systems with broken periodicity such as surfaces and interfaces. Of course, pair-potential models have some well-known deficiencies. For example, they are unable to distinguish between vacancy formation and cohesive energies [1], and yield identical values for the elastic constants C_{12} and C_{44} for cubic lattices [2]. Attempts to go beyond pair potentials, apart from embarking on full *ab initio* electronic structure-based calculations [3], involve an embedded atom model (EAM) [4] and similar methods [5,6], where the total energy of the static solid is expressed as a sum of pair-potentials plus an empirical volume/density-dependent term or an electronic band (bond) energy term [7]. However, in terms of their implementation these are still empirical or at best semi-empirical methods, and the issue of fitting parameters of such schemes to some chosen reference state properties still remains to be addressed.

In this work we consider two groups of pair-potentials and study their effectiveness in describing the solid state properties and the liquid structure of noble metals Cu, Ag and Au. One group of potentials is the Morse potential with parameters fitted to solid state properties: cohesive (sublimation) or vacancy formation energies, isothermal bulk modulus and equilibrium lattice parameter [8–10]. The other set of potentials used is one that was developed by Erkoç [11]. The starting point in developing this set of potentials was not the solid state properties, but the properties of the dimer. Even though this potential has a larger number of parameters than Morse, the key point is that the potential is tested not only for the bulk solid but also for dimers as well as some

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microclusters. Hence, it is of interest to explore to what extent this potential is capable of reproducing bulk solid and liquid state properties and compare the results with potentials strictly based on solid state properties.

We compute the phonon spectra and carry out quasiharmonic calculations to study the temperature-dependence of the lattice parameter (thermal expansion coefficient), specific heats at constant pressure and volume C_p and C_v, isothermal and adiabatic bulk moduli B_T and B_S as a function of temperature. For the electronic part of the specific heat we use the tight-binding linear muffin-tin orbital (TB-LMTO) [12] scheme to compute the electronic density of states at the Fermi level as a function of the lattice parameter and use the independent quasiparticle result. To study the liquid structure at different temperatures we use Monte Carlo simulation and the standard Metropolis [13] sampling scheme.

The remainder of this paper is divided into the following sections: In Section 2 we provide details of the potentials used. In Section 3 we discuss the calculation of the solid state properties and the comparison with experimental results. In Section 4 we discuss the liquid structure as revealed by the pair distribution function, comparing the computed results with those obtained from diffraction experiments at different temperatures. A summary of results and conclusions are presented in Section 5.

2. Pair-potentials

The Morse potential is well-known and has the form

$$V(r_{ij}) = D\left[e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)}\right]. \tag{1}$$

This three-parameter (D, α and r_0) potential has been used widely in the calculation of solids as well as molecules. Like Lennard–Jones, it is one of the potentials that have shown some success in describing properties of molecules and solids with a minimal set of parameters. Cotterill and Doyama [8–10] used experimental values of cohesive energy, lattice parameter and bulk modulus to obtain the three parameters for some fcc and bcc metals. In an alternate scheme they replaced cohesive energy with vacancy formation energy to fit the parameters. In addition, the fit was performed in some cases for different numbers of neighbor cells, from nearest neighbors to 12 cells of neighbors. The parameters obtained for various cases are shown in Table 1. Note that Cotterill and Doyama [8] did not consider the case of Ag in their work. The Morse potential for Ag used by us is taken from the work of Flahive and Graham [9], which is based on the cohesive energy, and is considered in the list of potentials discussed by Erkoç in a monograph edited by Stauffer [10]. Morse potential based on vacancy formation energy for Ag is thus not included in our study.

Table 1
Parameters for the Morse potential. For copper and gold, letters in parentheses beside the element names indicate whether cohesive (coh) or vacancy (vac) formation energy was used in the fitting. The numbers within these parentheses indicate the number of neighbor cells used in the calculation of the parameters. The parameters for copper and gold are from Cotterill and Doyama [8] and those for silver are from Flahive and Graham [9,10], based on cohesive energy, lattice parameter and bulk modulus. Six neighbor shells were used in our calculations involving silver. Going beyond six shells did not change the results to any noticeable degree.

Metal	D (eV)	α(Å^{-1})	r_0 (Å)
Cu (coh,1)	0.58922	1.35438	2.54756
Cu (coh,6)	0.32688	1.27234	2.89360
Cu (coh,12)	0.32365	1.29415	2.91331
Cu (vac,1)	0.19500	2.342508	2.547564
Cu (vac,6)	0.170073	2.321248	2.592091
Cu (vac,12)	0.170002	2.321628	2.592351
Au (coh,1)	0.603392	1.481405	2.874127
Au (coh,6)	0.420915	1.439041	3.065135
Au (coh,12)	0.418841	1.444322	3.071131
Au (vac,1)	0.163333	2.847319	2.874127
Au (vac,6)	0.156342	2.839503	2.885484
Au (vac,12)	0.156340	2.839513	2.885490
Ag	0.3294	1.3939	3.096

The Erkoç potential [11], based on energies of dimers and some consideration of the bulk properties of the solid, contains eight parameters in general. In this scheme the total interaction energy has the form

$$\Phi = D_{21}\phi_{21} + D_{22}\phi_{22};$$
$$\phi_{2n} = \sum_{i<j} V_{ij}^{(2n)}, \quad n = 1, 2$$
$$V_{ij}^{(2n)} = A_n\left(1/r_{ij}^{\lambda_n}\right)e^{-\alpha_n r_{ij}^2}; \quad n = 1, 2 \tag{2}$$

The pair-potential function is given by the sum

$$V_{ij} = V_{ij}^{(21)} + V_{ij}^{(22)}$$

In the parametrization procedure of Erkoç [11] the first six parameters of the set $(A_1, \lambda_1, \alpha_1, A_2, \lambda_2, \alpha_2, D_{21}, D_{22})$ were determined by using dimer data. The remaining two parameters (D_{21}, D_{22}) were determined using bulk stability condition and bulk cohesive energy value. This potential was then applied to study clusters of 3–7 atoms. If one takes $D_{21} = D_{22} = 1$, then the potential represents dimer interaction. If the determined values of (D_{21}, D_{22}) are used then the potential represents the effective pair-potential for bulk. If one considers the product $A_n D_{2n}, n = 1, 2$ as a single parameter then the pair-potential can be thought of as a six-parameter potential. The values of the various parameters for this potential are provided in Table 2. The Morse and Erkoç potentials used in this work are shown in Fig. 1.

3. Solid state properties

3.1. Phonons

The phonon spectra were calculated by diagonalizing the dynamical matrix, obtained from the Fourier transform of the force constant tensor $\mathbf{\Phi}_{ij}(l, m)$ given by

$$\mathbf{\Phi}_{ij}(l, m) = \frac{\partial^2 E_{tot}}{\partial R^i(l)\partial R^j(m)}, \tag{3}$$

where i, j are the labels of the atoms and l, m refer to Cartesian components of the position vectors of these atoms. E_{tot} is the total static energy per atom of the solid given by

$$E_{tot} = \frac{1}{2}\sum_{\substack{i,j \\ (i \neq j)}} V(R_{ij}), \tag{4}$$

The frequency vs. wave vector dispersion of the phonons in various symmetry directions for fcc Cu, Ag and Au at equilibrium lattice parameters are shown in Fig. 2 and compared with the

Table 2
Parameters for the Erkoç [11] potential. Six shells of neighbors were used in the calculation.

Parameter	Cu	Ag	Au
A_1	110.766008	220.262366	345.923364
λ_1	2.09045946	1.72376253	1.04289230
α_1	0.394142248	0.673011507	0.750775965
D_{21}	0.436092895	1.00610152	0.888911352
A_2	−46.1649783	−26.0811795	−38.9245908
λ_2	1.49853083	1.81484791	1.05974062
α_2	0.2072255507	0.120620395	0.229377368
D_{22}	0.245082238	0.221234242	0.254280292

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