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Abstract

Molecular dynamics simulations of bulk copper, gold pure metals and their ordered intermetallics alloys of $Cu_3Au(L1_2)$ and $CuAu_3(L1_2)$ have been carried out between above 0 K and below the their melting points of the materials for predicting their temperature-dependent thermophysical properties. The effects of temperature and concentration on the physical properties such as enthalpy, volume, heat capacity, thermal expansion and density of Cu_xAu_{1-x} are studied. Especially, temperature-dependent polynomial functions of enthalpy, volume and density are obtained. Sutton-Chen (SC) and Quantum Sutton-Chen (Q-SC) many-body potentials are used in the constant enthalpy-constant pressure ensemble (HPN) and constant pressure-constant temperature ensemble (TPN). Three important properties such as the coefficient of thermal volume expansion, heat capcity and density are correctly found to increase with temperature. Q-SC potential parameter results are usually closer to experimental values than the ones predicted from SC potential parameters.

Key Words: Molecular dynamics, Sutton-Chen potential, intermetallic alloys, thermophysical properties.

1. Introduction

The estimation of thermal properties of intermetallic alloys such as enthalpy, volume, density, heat capcity, and volume thermal expansion is very important in the design of components and production of new materials. Intermetallics are compounds that form between metals [1]. The rules of bonding and valence structure of intermetallic are still largely unknown. Intermetallic compounds have structure and properties differing from the constituent metals [2]. These compounds are stable materials which have desired properties. They have also high melting point, low density and good oxidation or corrosion resistance. These properties of the intermetallic alloys motivated many researchers to investigate their fundamental properties [3–8].

As we discussed in the our previous paper [9], Cu-Au intermetallic system is a well-known model binary system for existence of temperature-induced order-disorder transition and capability of the stable long period superlattice structure. In the previous study, we have investigated the temperature and concentration dependence of the the Cu-Au system. Experimental studies of this intermetallic system are sparse in the literature because of their high melting point. In this study, first aim is that temperature and concentration dependence of the thermophysical properties of the Cu-Au system are fitted to any quadratic function to calculate some physical properties such as heat capacity and volume thermal expansion. Second goal is to show the behavior of the these physical properties at desired temperatures below the melting points. This problem is focused in the present work.

Ab initio electronic structure methods are superior and highly accurate, but they can not be efficient as empirical potentials for simulating large system and long times. Parameter-based semiempirical methods such as embedded atom model (EAM) [10], Finnis-Sinclair (FS) [11], Sutton-Chen (SC) [12] potentials, the second moment approximation (SMA) to tight binding (TB) model [13], and the glue model [14], are very efficient to study the properties of the some metals and alloys. The above potentials, while mathematically simple, in many case provide a good description of the bonding and energetics of the metallic system. Therefore, these potentials play an important role to determine the physical properties of the metallic system to the first-principle calculations and simulations.

Sutton and Chen [12] developed a long range potential for ten FCC metals by fitting to the actual material characters such as the lattice constant, cohesive energy and bulk modulus to study the physical properties of these materials. This potential was then extended to the study of binary FCC random alloys by Rafii-Tabar and Sutton [15] without changing available pure elemental parameters. This method was successfully applied to many physical problems [16]. Recently, Çağın and co-workers re-parameterized the Sutton-Chen (SC) potential to improve the temperature dependence of physical properties of FCC metals by fitting to extra physical properties such as phonon frequencies at X point and by taking into account zero point energy (ZPE) [17]. This new version of SC potential is called quantum Sutton-Chen potential (Q-SC). This potential has been used in various applications, ranging from random alloys, glass formation, crystallization, surfaces, clusters, nanowires, and single crystal plasticity of pure metals to transport properties of FCC metals [18–23].

In this study, SC and Q-SC potential parameters of the pure Cu and Au metals are used as interatomic potential parameters to investigate the thermophysical properties of Cu and Au pure metals and ordered Cu-Au alloys, (especially, $Cu_3Au(L1_2)$ and $CuAu_3(L1_2)$). In the present study, we have calculated the enthalpy, volume, density, heat capacity, thermal coefficient of volume expansion by using two set of SC type potentials. The results are compared with experimental and theoretical data available in literature.

This paper has the following structure. Simulation details are presented in Section 2. Section 3 deals with results of computer simulations. The results are compared with the whenever available experimental data and theoretical calculations in the same section.

2. Simulation details

Molecular dynamics simulation is performed in two successive ensembles subject to periodic boundary conditions, that is, constant-enthalpy constant-pressure (HPN), constant-temperature constant-pressure (TPN) ensembles. The simulation procedure followed in this study is described in Refs. [16, 22, 23]. The simulation box is made up of 1372 particles arranged on the FCC structure for the pure Cu and Au, $L1_2$ structure for the Cu_3Au and $CuAu_3$ ordered intermetallic systems. In the case of Cu_3Au, the Au atoms occupy the corner cites, while Cu atoms occupy the face centers of the basis cube, the opposite occurs for $CuAu_3$.

Total potential energy of the pure metals and alloys in Sutton-Chen formalism for the system of N atoms is given as follows [12, 22];

$$U_{tot} = \sum_{i}^{N} U_i = \sum_{i}^{N} \left[\sum_{j \neq i} \epsilon_{ij} \frac{1}{2} (\frac{a_{ij}}{r_{ij}})^{n_{ij}} - c_i \epsilon_{ii} \left(\left(\frac{a_{ij}}{r_{ij}} \right)^{m_{ij}} \right)^{\frac{1}{2}} \right] . \quad (1)$$

The first term in Eq. (1) is a two body repulsive interaction between the atoms i and j, separated by a distance r_{ij}. The second term represents the many-body cohesion term associated with atom i. The square root term introduces a many-body component into the energy summation. The popularity of SC potentials is partly due to the computationally tractable form adopted for the many-body forces. It is the relatively simple analytic form of the potential that enables one to calculate the many physical properties of the materials.

In Eq. (1), r_{ij} is the distance between atoms i and j, a is a length parameter scaling to the lattice spacing of the crystal, c is a dimensionless parameter scaling the attractive terms, ϵ is an energy parameter determined from experiment, and n, m are integer parameters with $n > m$ which determine the range of the

Table 1. Q-SC and SC potential parameters for the Cu and Au pure metals

metal		n	m	ϵ (eV)	c	a(Å)
Cu	Q-SC	10	5	5.7921E-3	84.843	3.6030
	SC	9	6	1.2386E-2	39.755	3.6153
Au	Q-SC	11	8	7.8052E-3	53.581	4.0651
	SC	10	8	1.2794E-2	34.428	4.0783

two components of the potential. The interaction length of potential is taken as two lattice parameters for the efficiency of the computer simulation time. The temperature effects in the simulations are considered by giving an additional length of half the lattice parameter.

The parameters for the ordered CuAu intermetallic alloys are obtained through the following combination rules [18, 22].

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{\frac{1}{2}} , \qquad a_{ij} = \frac{(a_i + a_j)}{2} , \tag{2}$$

$$m_{ij} = \frac{(m_i + m_j)}{2} , \qquad n_{ij} = \frac{(n_i + n_j)}{2} . \tag{3}$$

SC potential and Q-SC potential parameters are given in Table 1 [15, 17]. Specific heat can be determined from the differential of the enthalpy as follows;

$$C_p(T) = \left(\frac{\partial H(T)}{\partial T} \right)_p . \tag{4}$$

Coefficients of thermal volume expansion is calculated by using following expression;

$$\alpha_p(T) = -\frac{1}{V(T)} \left(\frac{\partial V(T)}{\partial T} \right)_p . \tag{5}$$

3. Results

3.1. Enthalpy, Volume and Density

In the following sections, we have presented results of the enthalpy, the volume, and density for the Cu and Au pure metals and their ordered metals calculated from TPN ensemble average over 20000 time steps as a function of temperature up to melting points for two parameter sets of Q-SC and SC. The data given here for enthalpy, volume and density as a function of temperature may be used to calculate the other physical properties such as heat capacity and thermal expansion of the materials considered in this study at elevated temperatures.

3.2. Heat Capacity and Volume Thermal Expansion

The enthalpy of Cu-Au alloys is fitted to a quadratic polynomial by using the data below the melting temperature to analyze the heat capacity as a function of temperature and concentration. The quadratic function form may be chosen as;

$$H(T) = a + b \;\; T + c \;\; T^2 \text{ kJ/mole} . \tag{6}$$

Here T is the temperature. Heat capacity can be found by taking the derivative of the polynomial function of Eq. (6) according to Eq. (4). The resulting C_p should not be extrapolated to $T = 0$ K, as it is derived from $H(T)$ which is fitted to simulation results between 0 K and below the melting temperature for each materials studies here. The coefficients of expression in Eq. (6) calculated from both Q-SC potential and SC potential parameters for the materials considered in this study are given as a function of temperature.

Table 2. Heat capacity of Cu, Au pure metals and their alloys. Heat capacity values of the metals along with whenever available experimental data [24] at 300 K. The unit of the C_p is kJ mole^{-1} K^{-1}. The data in the parenthesis are experimental values. The first line at specific temperatures is Q-SC results and second one is the SC calculations.

Temperature	Cu	Cu_3Au	$CuAu_3$	Au
300	0.026642 (0.024464)	0.025962	0.025418	0.024804 (0.025325)
	0.026038	0.026278	0.026038	0.026050
500	0.027670	0.027270	0.027030	0.026940
	0.028130	0.027730	0.027930	0.028150
700	0.028698	0.028578	0.028642	0.029076
	0.030222	0.029182	0.029822	0.030250
900	0.029726	0.029886	0.030254	0.031212
	0.032314	0.030634	0.031714	0.032350
1100	0.030754	0.031194	0.031866	0.033348
	0.034406	0.032086	0.036606	0.034450

The enthalpy values of Q-SC calculations are;

$$H_{Cu}(T) = -339.58 + 2.51 \times 10^{-02}\ T + 2.57 \times 10^{-06}\ \text{kJ/mole}, \tag{7}$$
$$H_{Cu_3Au}(T) = -346.18 + 2.40 \times 10^{-02}\ T + 3.27 \times 10^{-06}\ T^2\ \text{kJ/mole}, \tag{8}$$
$$H_{CuAu_3}(T) = -360.71 + 2.30 \times 10^{-02}\ T + 4.03 \times 10^{-06}\ T^2\ \text{kJ/mole}, \tag{9}$$
$$H_{Au}(T) = -368.74 + 2.16 \times 10^{-02}\ T + 5.34 \times 10^{-06}\ T^2\ \text{kJ/mole}. \tag{10}$$

The following expressions are the SC parameter set results;

$$H_{Cu}(T) = -337.38 + 2.29 \times 10^{-02}\ T + 5.23 \times 10^{-06}\ T^2\ \text{kJ/mole}, \tag{11}$$
$$H_{Cu_3Au}(T) = -344.57 + 2.41 \times 10^{-02}\ T + 3.63 \times 10^{-06}\ T^2\ \text{kJ/mole}, \tag{12}$$
$$H_{CuAu_3}(T) = -357.33 + 2.32 \times 10^{-02}\ T + 4.73 \times 10^{-06}\ T^2\ \text{kJ/mole}, \tag{13}$$
$$H_{Au}(T) = -364.58 + 2.29 \times 10^{-02}\ T + 5.25 \times 10^{-06}\ T^2\ \text{kJ/mole}. \tag{14}$$

As shown in Table 2, agreement between the simulated results and experimental data given in Ref. [24] is very good. For example the heat capacities of Cu and Au at 300 K for the Q-SC are 0.026642 kJ mole^{-1} K^{-1} and 0.024804 kJ mole^{-1} K^{-1}, respectively. Deviations from the experimental values for Cu and Au are 8.9 % and 2.05 %, respectively. Deviations from experimental data at 300 K for the SC calculation for each materials are acceptable and as temperature increases the values of the heat capacity for both Q-SC and SC sets increase. However, heat capacity of the SC results are generally greater than the values of the Q-SC.

We have also fitted the volume and temperature curve by the same type of quadratic polynomial function as done in the heat capacity to analyze further the volume thermal expansion behavior. The function used in the fitting procedure is;

$$V(T) = a + b\ T + c\ T^2\ \text{nm}^3/\text{mole}. \tag{15}$$

The coefficients in Eq (15) and the values of the volume for Cu, Au metals and their ordered alloys Cu_3Au and $CuAu_3$ are given for both Q-SC and SC parameter sets, respectively;

$$V_{Cu}(T) = 1.16 \times 10^{-02} + 6.64 \times 10^{-07}\ T + 3.65 \times 10^{-10}\ T^2\ \text{nm}^3/\text{mole}, \tag{16}$$
$$V_{Cu_3Au}(T) = 1.30 \times 10^{-02} + 6.49 \times 10^{-07}\ T + 3.74 \times 10^{-10}\ T^2\ \text{nm}^3/\text{mole}, \tag{17}$$

Table 3. Thermal volume expansion coefficients of Cu, Au pure metals and their ordered intermetallic alloys at elevated temperatures. Thermal volume expansion values of the metals along with whenever available experimental data [24, 25]

	$\alpha_p \times 10^{-5}$ (K^{-1})			
Temperature	Cu	Cu_3Au	$CuAu_3$	Au
300	7.445(4.95)	6.602	6.159(4.77)	6.025
	8.182	7.966	8.045	8.161
500	8.544	7.624	7.265	7.336
	9.531	9.132	9.392	9.820
700	9.581	8.598	8.322	8.589
	10.803	10.234	10.662	11.380
900	10.557	9.521	9.325	9.777
	11.990	11.266	11.849	12.832
1100	11.468	10.389	10.270	10.893
	13.088	12.225	12.947	14.168

$$V_{CuAu3}(T) = 1.56 \times 10^{-02} + 6.90 \times 10^{-07}\ T + 4.77 \times 10^{-10}\ T^2\ \mathrm{nm}^3/\mathrm{mole}, \quad (18)$$
$$V_{Au}(T) = 1.68 \times 10^{-02} + 6.67 \times 10^{-07}\ T + 6.01 \times 10^{-10}\ T^2\ \mathrm{nm}^3/\mathrm{mole}. \quad (19)$$

$$V_{Cu}(T) = 1.18 \times 10^{-02} + 7.13 \times 10^{-07}\ T + 4.59 \times 10^{-10}\ T^2\ \mathrm{nm}^3/\mathrm{mole}, \quad (20)$$
$$V_{Cu_3Au}(T) = 1.31 \times 10^{-02} + 8.00 \times 10^{-07}\ T + 4.43 \times 10^{-10}\ T^2\ \mathrm{nm}^3/\mathrm{mole}, \quad (21)$$
$$V_{CuAu3}(T) = 1.58 \times 10^{-02} + 9.32 \times 10^{-07}\ T + 6.10 \times 10^{-10}\ T^2\ \mathrm{nm}^3/\mathrm{mole}, \quad (22)$$
$$V_{Au}(T) = 1.70 \times 10^{-02} + 9.38 \times 10^{-07}\ T + 7.97 \times 10^{-10}\ T^2\ \mathrm{nm}^3/\mathrm{mole}. \quad (23)$$

Thermal volume expansion values for each metallic system calculated from equation 5 at elevated temperatures are presented in Table 3.

The value for copper, 7.445×10^{-05} K^{-1} at 300 K, is in good agreement with the value of 7.19×10^{-05} K^{-1} at 298 K from simulation calculation of Ref. [26]. But the calculated value is greater than the experimental value of 4.95×10^{-05} [26]. Thermal volume expansion coefficients of the pure metals and ordered alloys studied in the present work increase as the temperature goes up.

From the similar way, we can also calculate the density expressions by fitting density and temperature values to any quadratic function to find the temperature dependent behavior of density. Density results calculated from Q-SC and SC potential parameters for each material studied here are given in the following equations, respectively.

$$\rho_{Cu}(T) = 9089.02 - 565.97 \times 10^{-03}\ T - 175.31 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3, \quad (24)$$
$$\rho_{Cu_3Au}(T) = 12416.50 - 671.77 \times 10^{-03}\ T - 238.68 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3, \quad (25)$$
$$\rho_{CuAu3}(T) = 17406.20 - 850.12 \times 10^{-03}\ T - 365.04 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3, \quad (26)$$
$$\rho_{Au}(T) = 19514 - 895.91 \times 10^{-03}\ T - 483.65 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3. \quad (27)$$

$$\rho_{Cu}(T) = 8923.46 - 577.22 \times 10^{-03}\ T - 229.224 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3, \quad (28)$$
$$\rho_{Cu_3Au}(T) = 12233.60 - 784.25 \times 10^{-03}\ T - 274.608 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3, \quad (29)$$
$$\rho_{CuAu3}(T) = 17197.80 - 1073.90 \times 10^{-03}\ T - 460.894 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3, \quad (30)$$
$$\rho_{Au}(T) = 19271.60 - 1162.98 \times 10^{-03}\ T - 628.825 \times 10^{-06}\ T^2\ \mathrm{kg/m}^3. \quad (31)$$

These expressions allow us to calculate density values by putting desired temperatures below the melting points of materials. Experimental values of the density of Cu and Au at 300 K are 8931.7 kg/m^3 and 19300 kg/m^3, respectively [27]. The calculated values of these pure metals are very good for both Q-SC and SC calculations. But, Q-SC parameters produce better results compatible with experimental data. The experimental density value of Cu_3Au at 300 K is 12214.0 kg/m^3. This value is also in agreement with the Q-SC and SC simulation results.

4. Conclusion

We have presented thermophysical properties such as enthalpy, volume, density, heat capacity, and thermal expansion coefficients of Cu, Au pure metals and their Cu_3Au and $CuAu_3$ ordered intermetallics below the their melting points by using Q-SC and SC potential parameter sets. Although potential parameters for the intermetallic systems are derived from elemental parameters by using simple combinations rules, the simulation results are compatible with the experimental and other theoretical results. Each of thermophysical properties of the materials considered in this work is correctly predicted to increase with temperature. The computed values are consistently larger in magnitude than the experimental. The temperature dependence of thermophysical properties for ordered intermetallic alloys below the melting points are presented for the first time.

In this study, Q-SC potential parameters provide fairly accurate temperature dependent properties of both pure elements and ordered systems studied here at low and high temperatures. The results demonstrate the transferability of the Q-SC parameters from low to high temperatures and from elemental to intermetallic alloys. If the potential energy function considered here is fitted to the solid properties of the intermetallic compounds of Cu_3Au, $CuAu_3$ the results may be improved further.

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