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# Dynamical properties of Ag-Cu binary alloy from molecular dynamics simulation

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**Abstract.** Molecular dynamics simulations (MD) of dynamical properties of molten binary Ag-Cu alloy is presented at various temperature above the eutetic temperature. Atoms in the system have been modelled through an interatomic Lennard-Jones potential interaction. The structure, through the effective pair distribution function allows to determine the Enksog collision frequency as well as the coordination of atoms in the first shell. The surface traction, which is the force per unit area between the species shows a long separation oscillation about the value zero, while the collision frequency of pairs of atoms increase with increasing temperature. The adhesion energy between components found to be 3.4178 J/m$^2$. In agreement with theory, we found a decrease in surface tension of Ag-Cu alloy as temperature increases. Separation of atoms pairs in the first shell might be responsible for a non linear relationship found between temperature and coordination number in present calculations.

**PACS.** 61.20.-p Structure of liquids – 61.20.Ja Computer simulation of liquid structure

## 1 Introduction

Generally speaking, binary alloys are important in materials and metallurgical engineering. The study of alloys therefore could be said to be interdisciplinary as it involves both the chemical and physical understanding of microscopic and macroscopic theories. It will therefore, not be an under statement to say that the behaviour of binary alloys at eutetic temperatures and above is a topic of great interest because, there are divergences in many dynamical and structural properties of binary alloys. Therefore, attempts at understanding the behaviours of the dynamical properties at the surface as well as in the bulk alloy are worthy of investing on. Although, the surface and bulk properties of liquid alloys are considered fairly well understood, considerably less emphasis is placed on calculating the properties via dynamical coefficients such as viscosity and diffusion. One reason for that is the difficulty in the determination of these coefficients through standard and well known binary alloys models. For example, recent works [1–5] of the surface and transport properties of liquid alloys made use of quasi-lattice-theory or compound formation model leading to the use of concentration fluctuation $S_{cc}(0)$ in the long wavelength limit in the determination of most properties of the alloys. Simulations studies therefore, are important for our understanding of the relationships between dynamical coefficients and thermophysical properties of binary alloys; of course, this may not be true in the case one is interested in critical dynamics because of phenomenon of slowing down where the dynamics become slower towards the critical point.

In any liquid system, the interactions are essentially a summation of pairwise interactions and higher terms or many-body in nature. One can then model many-body interactions using quantum mechanical theory (QMT), but this approach is computationally expensive and in most cases does not allow for large systems to be studied. However, there exists methods which approximate the QMT approach with effective medium theory [6–9].

Assuming that the interaction between a pair of atoms are independent of any other atoms, then a pairwise potential could be used and the potential energy could then be written in terms of pair distance only. The LJ potential is one class of interactions approximation which is pairwise in nature and computationally convenient and has found widespread use in modelling not only closed shell systems but in metallic and other systems.

In this work, we have used the LJ potential, our study is made feasible by the choice of our model, we modify the energy parameter $\epsilon_{\text{Ag-Cu}}$ so that the reduced interaction energy resulting from lower coordination of atoms at higher temperatures is accounted for. Our work is

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organized in the following manner, in Section 2, we give the details of simulations method used. Section 3 consists of our results and findings with discussions. In Section 4, we give concluding statements.

**Table 1.** The parameters of the Lennard-Jones potential.

| | $\epsilon$ (eV) | $\sigma$ (Å) |
|---|---|---|
| Ag-Ag | 0.3450 | 2.644 |
| Cu-Cu | 0.4096 | 2.338 |
| Ag-Cu | 0.3759 | 2.491 |

## 2 Simulations method and theory

The Ag-Cu alloy used in this work consists of 710 atoms of Ag and 290 atoms of Cu, we have chosen the reduced density of each specie to be 0.48 and 0.32 of Ag and Cu respectively. This is done to coincide with experimental [10] values of ≈28.5 wt. % Cu. Simulation runs were performed at the elevated temperatures between 1153 K and 1193 K with Eutetic temperature $T_{eut}$ of Ag-Cu being 779 K [12]. We have used $T_{eut}$ in the determination of the reduced temperature, since we can define this as a point where the liquid phase borders directly on the solid phase and representing the minimum melting temperature of an alloy. With this in mind we define the reduced temperature $T^*$, as the ratio of the actual temperature $T$ to $T_{eut}$, i.e. $T^* = T/T_{eut}$.

The method of Molecular Dynamics simulation is a technique at the atomic level, where it is possible to predict all the physical properties of a crystalline material. The procedure consists of solving numerical equations of atomic motion using Newton's second law of motion. Initial coordinates of positions and velocities are assumed with boundary conditions specified. This boundary condition is usually periodic (PBC), particles are enclosed in a box and this box is replicated in space by rigid translation in three Cartesian coordinates. The implication of this is that, a particle that leaves a computational box on one side will be replaced by another identical particle from the opposite box. The simulation box is formed from a cube of side $L$ with $L\ X\ L\ XL$ as unit cell volume in which $N$ number of particles are enclosed.

In the present calculations, the simulation box was repeated in space, initial configuration of simple cubic (sc) was assigned to atoms in the system, while velocities of atoms were set to zero. The mass, $m$ of an atom is set to unity for convenience. Interactions beyond distance $r_c = L/2$ are set to zero. In this case $L$ is the length of the simulation box. The following units were used, distance in unit of $\sigma_{\text{Ag-Cu}}$, energy in unit of $\epsilon_{\text{Ag-Cu}}$ and time in unit of $\sigma_{\text{Ag-Cu}}\sqrt{\frac{m}{\epsilon_{\text{Ag-Cu}}}}$. The density is given in unit of $\rho\sigma_{\text{Ag-Cu}}{}^3$. The initial sc configurations were melted by allowing the Newton's equation of motion to heat up the system from the zero velocity configurations and scaling the velocities with the square root of the ratio of the temperature and the motion energy. The Verlet algorithm [11] was used in the integration of the equation of motion with a time step of $\Delta t = 0.004$, where the total number of time steps is above 20 000. We used half of this to perform equilibration to be sure that the systems are well equilibrated. This time step is acceptable as long as the energy and momentum are conserved to desired accuracy and that the time step should always be much "shorter" than any relaxation time observed or expected in the system. The atoms interacted via LJ potential given as:

$$V(r) = 4\epsilon_{\text{Ag-Cu}}\left[\left(\frac{\sigma_{\text{Ag-Cu}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{Ag-Cu}}}{r}\right)^{6}\right] \tag{1}$$

where $\epsilon_{\text{Ag-Cu}}$ is a parameter determining the depth of the potential well or the bond energy and $\sigma_{\text{Ag-Cu}}$ is the length scale parameter that determines the position of the potential minimum. For a binary alloy or any two components system, we can use the additive and the product rules [13]

$$\epsilon_{\text{Ag-Cu}} = \sqrt{\epsilon_{\text{Ag}}\epsilon_{\text{Cu}}}, \qquad \sigma_{\text{Ag-Cu}} = \left(\frac{\sigma_{\text{Ag}} + \sigma_{\text{Cu}}}{2}\right). \tag{2}$$

We have obtained the parameters (given in Tab. 1) $\epsilon_i$ from literature [14] and $\sigma_i$ based on the total energy [15] of a crystal

$$\Phi = \frac{1}{2}4N\epsilon\left[\sum_j\left(\frac{\sigma}{\rho_{ij}r_N}\right)^{12} - \sum_j\left(\frac{\sigma}{\rho_{ij}r_N}\right)\right] \tag{3}$$

and it should be noticed that $\rho_{ij}r_N$ is the distance between a reference atom $i$ and other atom $j$ in terms of the distance of the nearest neighbour. Also, we note that the nearest neighbours will contribute most of this interaction energy so that we can actually say:

$$\Phi = \frac{1}{2}4N\epsilon C_n\left[\left(\frac{\sigma}{r_N}\right)^{12} - \left(\frac{\sigma}{r_N}\right)^{6}\right] \tag{4}$$

where $N$ is the total number of atoms in a system and $C_n$ is the coordination number. The equilibrium $r_N$ for the minimum total energy with respect to the coordination number will then be:

$$\frac{d\Phi}{dr_N} = 0 \tag{5}$$

so that

$$\sigma = r_N 2^{-\frac{1}{6}}. \tag{6}$$

The force of attraction between two atoms may be written as:

$$F = -\frac{dV(r)}{dr} = -24\epsilon_{\text{Ag-Cu}}\left[\frac{\sigma^6_{\text{Ag-Cu}}}{r^7} - \frac{2\sigma^{12}_{\text{Ag-Cu}}}{r^{13}}\right]. \tag{7}$$

In macroscopic systems, we can represent the atomic interactions between atoms by surface tractions [16] and by assuming the surface traction due to the interatomic

Lennard-Jones potential to be in the $z$-direction, then for a LJ potential one can write the surface traction $T_o(z)$

$$\begin{aligned} T_o(z) &= \frac{A}{6\pi z_o^3}\left[\left(\frac{z_o}{z}\right)^3 - \left(\frac{z_o}{z}\right)^9\right] \\ &= \frac{8\Delta\gamma}{3z_o}\left[\left(\frac{z_o}{z}\right)^3 - \left(\frac{z_o}{z}\right)^9\right] \end{aligned} \qquad (8)$$

where $A$ is known as Hamakar constant [17] and is defined as

$$A = 4\epsilon\pi^2\rho_1\rho_2\sigma^6 \qquad (9)$$

where $\rho_1$ and $\rho_2$ are the densities of the atoms in contact. The surfaces of the two atoms are in equilibrium when $T_o = 0$ which means the equilibrium distance $z_o$ is written as

$$z_o = \left(\frac{2}{15}\right)^{\frac{1}{6}}\sigma \qquad (10)$$

we can now define $\Delta\gamma$ of equation (8) as the adhesion energy between the surface of two atoms in contact and it is the work done to move two surfaces from equilibrium separation $z_o$ to infinity

$$\Delta\gamma = \int_{z_o}^{\infty} T_o(z)dz = \frac{A}{16\pi z_o^2} \qquad (11)$$

in the present work, the adhesion energy was calculated to be 3.418 J/m$^2$.

Both the liquid-vapour surface tension $\beta_{lv}$ and viscosity $\eta$ are related by the equation [18]

$$\eta(T) = \frac{16}{15}\beta_{lv}(T)\sqrt{\frac{m}{K_{\mathrm{B}}T}} \qquad (12)$$

where $N_{\mathrm{A}}$, $M$ and $K_{\mathrm{B}}$ are respectively the Avogadro's number, atomic mass and Boltzmann's constant. The Stoke-Einstein relation allows to introduce the Diffusion coefficient through

$$D(T) = K_{\mathrm{B}}T/(6\pi r\eta) \qquad (13)$$

and

$$D(T) = \frac{5K_{\mathrm{B}}T}{32\pi r\beta_{lv}(T)}\sqrt{\frac{K_{\mathrm{B}}T}{m}}. \qquad (14)$$

At each temperature in the simulation, we have calculated the diffusion coefficient from the mean square displacements of the atoms via [20]:

$$D = \lim_{t\to\infty}\frac{\langle x^2(t)\rangle + \langle y^2(t)\rangle + \langle z^2(t)\rangle}{6t}. \qquad (15)$$

This then means that equations (12) and (14) allow to determine the surface tension in liquid systems. From the pair distribution function $g(r)$, it is possible to calculate the coordination number $C_n$ and the Enksog collision frequency, $\tau$ in the first shell. The first shell can be defined in several ways, but we have used the position of first minimum $r_m$ to define the first shell in our calculations [19]

$$C_n = 4\pi\int_0^{r_m}\rho(r)r^2g(r)dr \qquad (16)$$

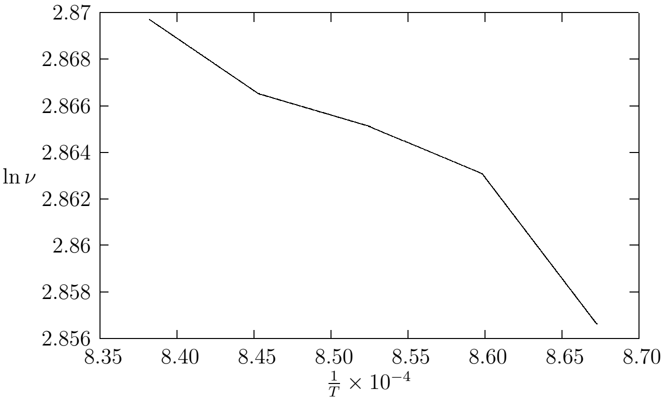

**Fig. 1.** The Collision frequency $\nu$ of atoms in the first shell.

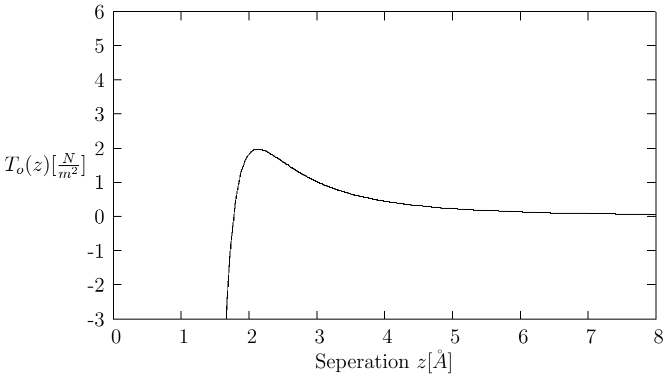

**Fig. 2.** The surface traction in binary Ag-Cu alloy at various temperature.

and

$$\tau = 4\pi\rho r_{max}^2 g(r_{max})\left(\frac{\pi K_{\mathrm{B}}T}{m}\right)^{\frac{1}{2}} \qquad (17)$$

here, $r_{max}$ is the position of first peak in the $g(r)$; for convenience only, $K_{\mathrm{B}}$ and $m$ are set to unity.

## 3 Results and discussion

To mimic experimental conditions [10] in Ag-Cu alloy, we have inserted 29% of Cu specie yielding approximately 0.32 in reduced density. Our results (Fig. 1) show that the pattern of Enksog collision frequency dependence on temperature is such that the natural logarithm of $\nu$ decreases as $1/T$ increases; in other words, Figure 1 depicts the linear increase in Enksog frequency, $\nu$ with increase in temperature at the same density. At low temperature, pairs of atoms bounced into one another, but not as frequently as at higher temperature, although, the increase in very small.

For the Ag-Cu alloy, the surface traction between the species using $z_o = 1.78$ is as shown in Figure 2. It was discovered that the main peak ($\approx z_o * r_{max}$) in the surface traction occurred at $\approx\sigma * r_{min}$ at all temperature suggesting that the surface traction between atoms in the alloy is not temperature dependent. The adhesion energy holding

**Table 2.** Calculated coordination number and collision frequency in the first shell.

| $T$ (K) | $g$ ($r_{min}$) | $g$ ($r_{max}$) | $C_n$ | $\ln \nu$ | $D$ ($10^{-9}$ m$^2$ s$^{-1}$) |
|---|---|---|---|---|---|
| 1153 | 0.6716 | 2.5769 | 8.9359 | 2.8566 | 0.4460 |
| 1163 | 0.6685 | 2.5825 | 8.5363 | 2.8631 | 0.4491 |
| 1173 | 0.6665 | 2.5767 | 8.5111 | 2.8651 | 0.4557 |
| 1183 | 0.6713 | 2.5694 | 8.5721 | 2.8665 | 0.4581 |
| 1193 | 0.6735 | 2.5668 | 8.6008 | 2.8697 | 0.4609 |

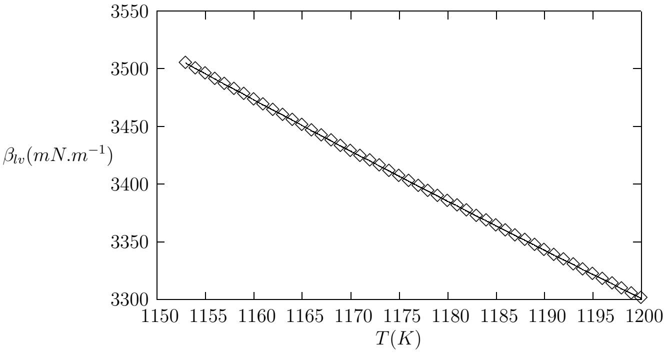

**Fig. 3.** Calculated surface tension in Ag-Cu alloy from Diffusion coefficient.

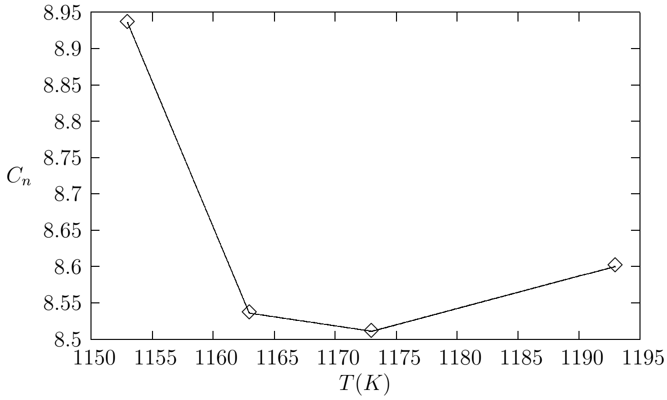

**Fig. 4.** The dependence of $C_n$ on temperature in Ag-Cu binary alloy.

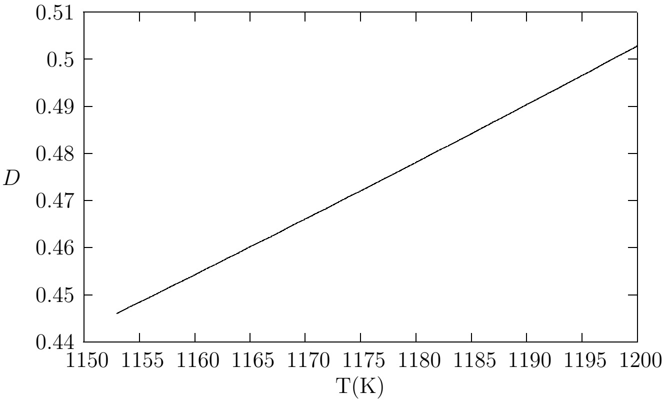

**Fig. 5.** Interdiffusion of species in Ag-Cu binary alloy.

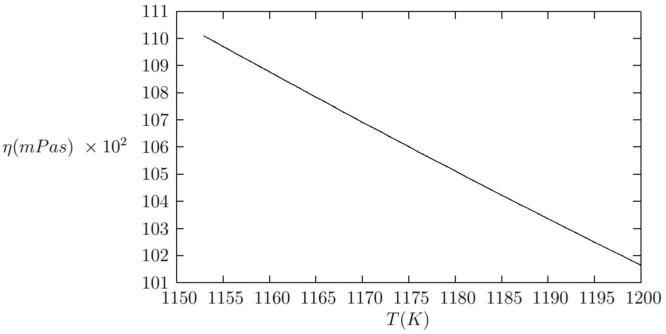

**Fig. 6.** Viscosity of Ag-Cu alloy at 29% Cu as a function of temperature.

atoms together in Ag-Cu was found to be 3.418 J/m$^2$, this is greater than what we discovered if individual species are in contacts with planar surfaces.

The surface tension has been calculated through equation (13). Figure 3 shows the calculated surface tension at various temperature, we see the dependent of $\beta_{lv}$ on $D$, it decreases with increasing temperature. In Figures 5 and 6, we plot the graphs of Diffusion coefficient and viscosity in Ag-Cu alloy respectively. The graphs follow what is expected from theory, i.e. the diffusion coefficient increases while the viscosity decreases with temperature. The number of nearest neighbours calculated in the first shells of $g(r)$ fluctuate about the value of 8.5, we explored the relationship between the temperature and $C_n$ up to the first shell and found a non linear type curve which is given in Figure 6. As temperature increases, pairs of atoms migrate from the first shell which brings about the high Enksog collision frequency and therefore lower coordination. The lower coordination means a reduction in the interaction energy and hence, the need to modify the energy parameter $\epsilon_{\text{Ag-Cu}}$. However, as further increase in temperature occurs, a minimum is reached after which there is an increase in coordination number with increasing temperature. We suspect that as this minimum is reached, there might be a sort of separation or segregation of pairs of atoms which is responsible for the increase in coordination number. This is logical, as a separation of pair of atoms will increase the number of nearest neighbour in the first shell.

## 4 Conclusion

In these studies, we present results of MD simulations using Lennard-Jones potential to model Ag-Cu binary alloy system. The use of Enksog equation allows to determine the collision frequency of atom pairs in the first shell, atoms collide more frequently as temperature increases. In terms of Stoke-Einstein relation, we are able to determine the surface tension between atom species and showed that in Ag-Cu alloy, the surface tension decreases as temperature increase in accordance with theory. The surface traction and adhesion energy were determined based on the overall force between two atoms and the total potential energy. An adhesion energy of 3.4178 $\mathrm{J/m^2}$ was obtained in our calculations. A non linear relationship was obtained between the coordination number and temperature, leading to a possible separations of atoms in the Ag-Cu system at high temperature.

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