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# Structural, mechanical and thermodynamical properties of silver amalgam filler: A Monte Carlo simulation study

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ABSTRACT

In this work Canonical Monte Carlo (CMC) simulations were carried out to investigate structural, thermodynamics and mechanical properties of silver alloy (Ag–Cu) dissolved in mercury metal, which is known as silver amalgam for dental filler.

All metal–metal interactions were modeled by Lennard-Jones (LJ) potential function. The pair correlation functions were used to shed light on the interparticle correlation in the amalgamation process, interactions, and topological structure of Ag–Cu solid in the mercury solvent. The simulated solvation process of the alloy in Hg extensively manifests the amalgamation mechanism. Thermodynamic and thermomechanical properties such as heat capacity, isothermal compressibility and bulk modulus of elasticity were calculated. Importantly, the isothermal compressibility of Ag–Cu amalgam was found to be higher than pure mercury itself, which can be attributed to voids generated due to amalgamation based on predictions of the approximation statistical mechanical models and empirical relation. This result is not verified by Virial theorem and lower isothermal compressibility resulted, which coincides with experimental values of real (dental) amalgam. The simulation provides insight into understanding and describing the structural and thermomechanical properties of the amalgam on the microscopic scale, being supportive for developing a new scheme and controlling internal structure during the fabrication of this material.



## 1. Introduction

Mercury is a polyvalent metallic element being liquid at room temperature which represents thermoelectric power and various other peculiar properties [1]. Mercury can dissolve nearly all metals, forming liquid or solid solutions known as amalgams. One of the well-admired compounds of this element is the dental amalgam, which has been found useful over the last 150 years for dental filling. The dental amalgam is a combination of mercury with a specially prepared silver alloy, which is used as a restorative material. Silver, copper and mercury are the amalgam constituents, where silver is the main component and mercury usually forms more than 50% (w/w%) [2–7].

In spite of the potential toxicity of mercury from mercury amalgam, silver amalgam is popularly used as a direct restorative filler material available due to its high strength, durability, and low cost as well as long-term satisfactory clinical performance [8–10], while other filing materials such as dental composites have poor performance of the dental restoration [11]. On the other hand, amalgams have been reported to be capable of sealing tooth-restoration margins with corrosion products [12]. Importantly, the modulus of elasticity of the typical dental filler amalgam was found to be very close to the teeth enamel [12].

Under such circumstances, the properties and behaviors of such product continue to be explored in various areas of science and technology. A number of researches have aimed determining properties of mercury amalgams such as phase diagrams and thermodynamic properties for Ag–Hg and Cu–Hg binary systems [13,14]. Also, several experimental literatures have addressed properties such as mechanical, modulus of elasticity, hardness, compression strength, dimensional changes, thermal expansion coefficient, and creeps as well as chemical behavior like electrochemical corrosion in mercury amalgam [8,15–19].

Recently, quantum-mechanical-based quantitative structure–activity relationship (QSAR) from AM1 semi-empirical method was used to study the effect of chemical nature and structure of the monomer on the flexural modulus of dental restorative polymer [20].

The molecular simulation has been of great utility to increase the knowledge about structural and thermophysical behaviors of materials. Molecular simulation can greatly supplement experimental information for these materials. However, throughout the history of dental amalgam, no simulation work have been done to date to investigate the microscopic structural information such as pair correlation function, configuration of the nearest-neighboring shell, thermodynamics assessment, heat capacity and isothermal compressibility of these products.

In this study Monte Carlo (MC) simulation techniques were carried out to characterize structural and thermodynamic properties of mercury amalgam (with composition near dental amalgam) at atomic level.

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To manifest the amalgamation mechanism, a solvation process of (Ag–Cu) alloy in Hg was simulated. Thermodynamic and thermomechanical properties such as heat capacity, isothermal compressibility and bulk modulus of elasticity were calculated and discussed. Evaluation and comparison with isothermal compressibility by various theories lead to interesting outcome. The present work turns out to be a comprehensive simulation study of the silver amalgam.

## 2. Canonical Monte Carlo

The simulations were carried out in canonical (*NVT*) ensemble [21,22] by means of Monte Carlo algorithm. The positions of the atoms are allowed to change between the old and new state with the probability as prescribed by Metropolis algorithm:

$$P_{acc.} = \mathrm{Min}\{1, \exp(-\Delta E/k_B T)\} \quad (1)$$

where $\Delta E$ is the difference between the total internal energies of new and the old configurations, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. This procedure is continued until equilibration is attained by the state of constant energy.

The simulation ensemble was consisted of a cubic box with side length of 22.8 Å containing 557 atoms (64 Cu, 192 Ag, and 301 Hg), under periodic boundary condition in three directions. The cut-off radius was close to one half of the box side length. The interactions between atoms are modeled by the LJ potential function:

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (2)$$

where $r$ is the distance between two interacting fluid particle, $\sigma$ denotes the LJ fluid–fluid collision diameter, and $\varepsilon$ is the LJ fluid–fluid potential well-depth. The potential parameters for Hg…Hg, Ag…Ag and Cu…Cu are listed in Table 1 [23,24]. Lorentz–Berthelot combining rules were used for interactions between unlike pair of atoms:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad (3)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}. \quad (4)$$

Of $10^9$ configurations simulated at 293 K, the first half were propagated to reach equilibrium and the rest were used for statistical analysis and calculation of ensemble average.

## 3. Results and discussion

### 3.1. Structural study

The structure featuring the noncrystalline solid and liquid, consistent with thermodynamic and mechanical stable state, can be studied by simulation of the pair correlation function, $g(r)$. Basically for solid state crystalline materials, $g(r)$ shows peaks in all ranges with appreciable amplitude indication of strong correlation at long range. However, in the case of liquids and amorphous materials, $g(r)$ represents oscillations decaying rapidly at long range indicating weak correlation at large atomic distances [25]. This feature is very helpful and was pursued to establish the mechanism of amalgam formation from solid alloy.

**Table 1**
Lennard-Jones potential parameters for Ag–Cu amalgam [23,24].

| species | $\varepsilon/k$ (K) | $\sigma$ (Å) |
|---|---|---|
| Cu | 4755.51 | 2.338 |
| Ag | 4005.43 | 2.664 |
| Hg | 750 | 2.989 |

The partial correlation function is defined by the probability of finding particle $i$ in the spherical shell at the distance $r$ from particle $j$ taken to be at the origin [26,27]:

$$g_{\alpha\beta}(r, \Delta r) = \frac{V}{N_\alpha N_\beta} \sum_{i=1}^{N_\alpha} \sum_{j>i}^{N_\beta} \frac{\langle N_{ij}(r, \Delta r)\rangle}{4\pi r^2 \Delta r}. \quad (5)$$

Here $N_{ij}(r, \Delta r)$ is the number of $j$ atom around $i$ atom within the spherical shell of thickness $\Delta r$ and volume of $4\pi r^2\Delta r$, *V is the volume, and* $\alpha$ *and* $\beta$ *represent the atom type*. Also, the total partial correlation function is defined as [27]:

$$g(r, \Delta r) = \frac{V}{N} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{\langle N_{ij}(r, \Delta r)\rangle}{4\pi r^2 \Delta r} \quad (6)$$

where $N$ is the total number of atoms present in the system.

The pair correlation function was calculated and visualized in VMD (V. 1.8.7) environment [28].

### 3.2. Simulation of Hg/Ag–Cu amalgamation

Initially, the accuracy of employed interaction potential and the corresponding parameters was verified by simulation of heat capacity at constant volume, $C_v$, of mercury which is estimated from energy fluctuation in ensemble (shall see in subsection 3.5). The value of 24.48 J/mol · K at 293 K is in good agreement (within 1.2%) with the experimental value of 24.18 J/mol · K [29]. Further verification of the method and potential parameters were done by simulation of heat capacities for Cu and Ag. These plus the first peak position of simulated $g(r)$ for pure Hg, Cu, and Ag metal are compared with the corresponding experimental values in Table 2. The well consistency with the experimental result [30–32], as can be seen from Table 2, qualifies the model potential for simulation of properties of the Ag–Cu amalgam filler.

The MC simulation was started from an initial configuration with FCC structure of Ag–Cu alloy. The number of atoms chosen nearly corresponds to the weight percent of the Ag–Cu alloy used very often in the dental fillers amalgam (Cu, 25% and Ag, 75%). The calculation of pair correlation function for Ag and Cu was followed after optimization and achievement of equilibrium by performing MC simulation at 293 K. A snapshot of the initial and final ensembles is shown in Fig. 1.

For Ag···Ag, Cu···Cu and Ag···Cu, the $g(r)$'s are displayed in Fig. 2. It can be seen that $g(r)$ for each case is nearly a periodic function, spanning the interatomic distance across the simulation box. The $g(r)$ shows high sharp peaks at the positions corresponding to the distances between lattice points, and vanishes for other domains. This pattern characterizes the crystalline structure of alloys simulated.

Also, since the composition percentage of Cu in this alloy is relatively low, the structure of Ag in Ag–Cu can be comparable with Ag crystal. The structure of Ag in this alloy compares well with the available data of pure Ag crystal (supplied by Rojas et al. [33], from their molecular dynamic simulation). A comparison of pair correlation function of Ag in MC simulation is made with that of FCC Ag crystal nanoparticle resulted by MD simulation at 300 K. Due to large number of Ag (2869) atoms, this nanoparticle assumes bulk Ag, which can be understood by

**Table 2**
Comparison of heat capacity ($C_v$) and first peak position of pair correlation function with experiment.

| Metal | $T$ (K) | Heat capacity (J/mol) | | First peak position of $g(r)$ (Å) | |
|---|---|---|---|---|---|
| | | This study | Experiment | This study | Experimental |
| Cu | 1423 | 24.69 | 26.82 (1300 K) [32] | 2.55 | 2.55 [30,31] |
| Ag | 1273 | 25.90 | – | 2.85 | 2.90 [30,31] |
| Hg | 293 | 24.48 | 24.18 [29] | 3.15 | 3.10 [30,31] |