INFLUENCE OF PRESSURE ON STRUCTURAL PROPERTIES OF AG: A MOLECULAR DYNAMICS SIMULATION

Mai Van Dung⁽¹⁾, Truong Duc Quynh⁽¹⁾

(1) Thu Dau Mot University; (2) Ho Chi Minh city University of Transport Corresponding author: dungmv@tdmu.edu.vn

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Article Info	Abstract
Volume: 7 Issue: 2 Jun: 2025 Received: May. 13 th , 2025 Accepted: Jun. 4 th , 2025 Page No: 527-535	In this study, molecular dynamics simulations were employed to investigate the influence of pressure on the structural properties of silver (Ag) at 300K. The results reveal that an increase in pressure leads to a reduction in nearest-neighbor distance, a promotion of local ordering, and a transition from a largely disordered state to a predominantly face-centered cubic FCC crystalline structure. At intermediate pressures, both hexagonal close-packed HCP and body- centered cubic BCC phases are observed; however, these phases diminish as pressure rises, with FCC becoming the prevailing phase at higher pressures. These findings demonstrate that pressure is a key factor in driving phase transitions and improving crystallinity in metallic systems.
Keywords: molecular, pres	ssure, simulation, structure, properties

1. Introduction

Silver (Ag) is a noble metal with exceptional electrical, thermal, and optical properties, which makes it widely used in electronics, catalysis, coatings, and medical applications (Glavan et al., 2015; Jiang et al., 2004). At the nanoscale, Ag exhibits unique size- and shape-dependent behaviors, such as modified melting temperatures, altered mechanical strength, and distinct phase transitions, which have been the focus of numerous experimental and theoretical studies (Ao et al., 2007; Fu et al., 2017; Kuzmin et al., 2008).

Molecular dynamics (MD) simulations have become an indispensable method for investigating the structural and thermodynamic properties of metallic systems at the atomic level. Earlier studies have applied MD to study the thermal behavior of graphite-supported Ag nanoclusters (Akbarzadeh et al., 2014), the size effects on the thermodynamic stability of Ag nanoparticles (Luo et al., 2008), and the melting and crystallization mechanisms under various conditions (Ding et al., 2006; Ji et al., 2014). However, while the effects of temperature and size on Ag systems have been well explored, the influence of external pressure on the structural evolution of bulk Ag has received comparatively little attention.

Understanding how pressure affects the atomic structure, and phase composition of Ag is critical for applications in high-pressure environments and for tuning material properties.

In this study, we use molecular dynamics simulations to investigate the influence of pressure on the structural properties of bulk silver at 300K. We analyze key parameters such as nearest-neighbor distances, radial distribution functions, and the distribution of FCC, HCP, BCC, and other local structures under pressures ranging from 0 to 15GPa. Our goal is to provide a detailed understanding of how increasing pressure drives structural ordering and phase transitions in Ag, offering insights into the pressure-dependent behavior of metallic systems.

2. Computational method

The models of Ag bulks with FCC structure, consisting of 4000, 13500, 23238, and 32000 atoms, are illustrated in Figure.1



Figure 1. Models of Ag bulks: a) 4000, b) 13500, c) 23238 and d) 32000 atoms

In this work, we investigate the structural properties and the influence of pressure on the Ag system by applying molecular dynamics (MD) simulations of atomic displacement cascades. Ag models consisting of 4000, 13500, 23238, and 32000 atoms are subjected to periodic boundary conditions in all three spatial directions x, y, and z. The simulations are performed using the LAMMPS software, which has been successfully applied in numerous MD studies (Plimpton, 1995). To numerically solve the equations of motion, we employ the Verlet algorithm with a time step of 1.0 fs.

The accuracy of the simulation results depends on the interatomic potential. In this study, the interactions between Ag atoms are modeled using the embedded atom method (EAM) potential, which was successfully developed by Johnson for investigating the properties of FCC-based noble metals (Johnson, 1989):

$$E = \sum_{i} \{F_i(\overline{\rho_i}) + \frac{1}{2} \sum_{i \neq j} V_{ij}(r_{ij})\}$$
(2.1)

F is a function of electron density $\overline{\rho}_i$ and $V_{ij}(r_{ij})$ is the pairwise interaction between *i* and *j* atoms at a distance r_{ij} . To compute the coordination number distribution, we use a cutoff radius of 3.95Å, corresponding to the first minimum after the first peak in the radial distribution function of the equilibrium model at 300K, is selected. Initially, the systems are equilibrated at 4000K for 10⁵MD steps until they reach a stable state at zero pressure. These models are then cooled down to 300K. Configurations under 5GPa, 10GPa, and 15GPa are generated by compressing the equilibrated 0GPa models. Temperature control is achieved using the Nosé–Hoover thermostat, while pressure is maintained at 0GPa using a barostat, as described in Refs (Nosé, 1984; Hoover, 1985). The OVITO software is used to visualize the atomic configurations and identify structural units using the Common Neighbor Analysis (CNA) method (Stukowski, 2009).

3. Results and discussions

3.1. Structure of Ag at 300K và 0GPa

Table 1 presents the structural characteristics of silver (Ag) bulk systems with varying numbers of atoms: 4000, 13500, 23238, and 32000 atoms at T = 300K. The data include the nearest-neighbor distance r, the height of the first peak in the radial distribution function g(r), the distribution of structural units (FCC, HCP, BCC, and Other), the system length l, and the total potential energy E_{tot} .

As the system size increases, the nearest-neighbor distance r slightly decreases from 2.87Å for the 4000-atom system to 2.80Å for larger systems, indicating a subtle contraction of the lattice, likely due to surface effects diminishing in larger models. Concurrently, the peak value of g(r) increases progressively from 4.85 to 5.32, reflecting enhanced structural ordering and more pronounced short-range correlations.

TABLE 1. The structural characteristics of Ag bulks at 300K—including the nearestneighbor distance r, the radial distribution function peak g(r), the number of structural units FCC, HCP, BCC, and Other, the system size l, and the total energy E_{tot} at different atomic numbers.

Ag	4000	13500	23238	32000
r(Å)	2.87	2.80	2.80	2.80
g(r)	4.85	5.10	5.29	5.32
FCC	155 (3.9%)	2106 (15.6%)	5551 (23.8%)	7640 (23.9%)
HCP	142 (3.5%)	1600 (11.9%)	3523 (15.1%)	4943 (15.4%)
BCC	99 (2.5%)	1004 (7.4%)	1943 (8.3%)	2549 (8%)
Other	3596 (89.9%)	8784 (65.1%)	12311 (52.8%)	16864 (52.7%)
l(Å)	40.855	61.2825	73.539	81.71
Etot (eV)	-9875.33	-33285.27744	-57526.56476	-78917.51867

A significant trend is observed in the distribution of structural units. In the smallest system of 4000 atoms, over 89.9% of atoms fall into the Other category, indicating a high of disorder. As the system size increases, the proportion of atoms in ordered structures FCC, HCP, BCC rises substantially. In the 32000-atom system, FCC units dominate (23.9%), followed by HCP (15.4%) and BCC (8.0%), with only 52.7% remaining as Other. This

transition suggests that increased system size facilitates atomic rearrangement toward more energetically favorable crystalline phases, particularly FCC, which is the equilibrium structure of Ag.

Additionally, the total energy E_{tot} becomes more negative with increasing system size, consistent with the expectation that larger systems with greater crystallinity possess lower energy states. The system length l also increases accordingly, matching the volume expansion with the number of atoms while maintaining a constant average atomic density.

These results collectively indicate that structural ordering in silver bulk systems improves with increasing number of atoms, promoting the formation of stable FCC domains and reducing amorphous or disordered regions.



Figure 2. The dependence of the size (l) on the number of atoms (N)

Figure 2 presents the relationships between the number of atoms (N), system size (l), and total energy E_{tot} . Specifically, Figure 2a depicts a linear correlation between the system size l and the inverse cubic root of the number of atoms N^{-1/3}, following the equation $l = -123.92N^{-1/3} + 11.747$. This result indicates a predictable scaling behavior, consistent with theoretical expectations for finite systems, where the size is inversely proportional to N^{-1/3} due to geometric and packing considerations. The observed linear trend suggests that the system maintains a nearly constant atomic density as N increases.

Figure 2b shows the dependence of the total energy E_{tot} on the number of atoms N. The relationship between the total energy E_{tot} and the number of atoms N is described by the formula E = -2.4659N + 5.1607. A clear linear relationship is observed, indicating that E_{tot} increases proportionally with N. This implies that the average energy per atom remains approximately constant, further confirming bulk-like behavior in the simulated systems. Such trends are characteristic of crystalline structures, where per-atom energy contributions stabilize with increasing system size. These findings align with prior studies, which have reported that properties such as glass transition temperature T_g and particle size (*D*) scale proportionally with N^{-1/3} (Qi et al., 2001) for metallic nanoparticles, including Ni (Nguyen, 2017; Nguyen et al., 2017; Trong et al., 2020).



Figure 3. a) Total energy per atom and b) Number of atoms at different temperatures of Ag with 4000 atoms

Figure 3a shows the variation of total energy per atom during the cooling process of silver (Ag). Initially, at high temperatures, the total energy decreases linearly, reflecting the gradual cooling of the liquid state. At $T_g = 446K$, a notable change in the slope of the energy curve is observed, corresponds to the glass transition temperature. Below T_g , the system enters a more ordered state, likely transitioning from a supercooled liquid to an amorphous or glassy phase. This distinct change in slope confirms the phase transition during the cooling process. This value of $T_g = 446K$ is in good agreement with the experimental data (Wang et al., 2015) and simulated results (Ji, Wang, Li & Kim, 2014).

Figure 3b shows the variation in the number of Other atoms within the temperature range surrounding the phase transition temperature. To determine the number of these atoms, the system was equilibrated for 500ps at specific temperatures: 300K, 400K, 420K, 430K, 440K, 450K, 500K, 550K, and 600K. The results, presented in Figure 3b, reveal that the phase transition temperature lies between 430K and 500K. A distinct peak at 446K identifies the phase transition temperature of the system ($T_g = 446$ K). This finding aligns well with the analysis shown in Figure 3a.

Figure 4a shows the atomic configuration of silver (Ag) at a temperature of 300K and a pressure of 0GPa. The cubic simulation box contains densely packed atoms, characteristic of the crystalline or stable solid phase of silver at low temperatures. The uniform arrangement and close atomic packing suggest that the system has a face-centered cubic (FCC) structure, typical for silver in its solid phase at this temperature.

Figure 4b compares the radial distribution function (RDF), g(r), of Ag at 300K from this study (red line) with the results reported by Celik et al. (blue points). The first prominent peak at approximately 2.81Å corresponds to the nearest-neighbor distance in the FCC lattice of silver, confirming the short-range order of the crystalline structure. The position and height of this peak align closely with the results of Celik et al. (Celik et al., 2008), demonstrating good agreement between the two studies. The subsequent peaks represent higher coordination shells, reflecting the long-range periodicity of the crystalline structure. The gradual damping of these peaks indicates the loss of long-range correlation due to thermal vibrations. These findings underline the reliability of the simulation methodology and its effectiveness in studying structural properties.



Figure 4. The atomic configuration (a) and the radial distribution function (b) of Ag at temperature of 300K and pressure of 0GPa

3.2. The effects of pressure

Table 2 presents the structural characteristics of silver (Ag) bulk systems under varying pressures (0, 5, 10, and 15GPa) at a constant temperature of 300K. This dataset provides critical insights into how external pressure affects the local atomic arrangements and phase characteristics of Ag bulk materials. At ambient pressure (0GPa), the nearest-neighbor distance r is 2.87Å, which slightly decreases with increasing pressure, namely, r = 2.85Å at 5GPa, 2.78Å at 10GPa, and 2.75Å at 15GPa.

Pressure (GPa)	0 GPa	5 GPa	10 GPa	15 GPa	
r(Å)	2.87	2.85	2.78	2.75	
g(r)	4.85	5.14	5.25	7.06	
FCC	155 (3.9%)	748 (18.7%)	833 (20.8%)	3482 (87.0%)	
НСР	142 (3.5%)	500 (12.5%)	475 (11.9%)	144 (3.6%)	
BCC	99 (2.5%)	229 (5.7%)	412 (10.3%)	53 (1.3%)	
Other	3596 (89.9%)	2522 (63.0%)	2280 (57.0%)	321 (8.0%)	

Table 2. The structural characteristics as r, g(r), the number of structural units FCC, HCP, BCC, Other of Ag bulks at different pressures (T=300K)

This reduction indicates lattice compression as expected under applied pressure. The corresponding g(r), representing the first peak of the radial distribution function (and thus the degree of short-range order), increases progressively from 4.85 at 0GPa to 5.14 at 5GPa, then to 5.25 at 10GPa, and sharply to 7.06 at 15GPa. This trend suggests that under high pressure, the local ordering becomes significantly more pronounced, possibly due to densification and structural transitions favoring more ordered phases.



Figure 5. The shape (a), the number of structural units of Ag (T=300 K)

The evolution of structural units shows how the populations of different structural units (given both as counts and percentages) change under pressure. FCC units increase remarkably with pressure: Only 155 atoms (3.9%) at 0GPa, growing to 748 (18.7%) at 5GPa, 833 (20.8%) at 10GPa, and surging to 3482 atoms (87.0%) at 15GPa. This indicates that dominant FCC ordering occurs at high pressure, consistent with the known bulk crystal phase of Ag under dense conditions. HCP units also increase initially, peaking at intermediate pressures: 142 atoms (3.5%) at 0GPa, 500 (12.5%) at 5GPa, 475 (11.9%) at 10GPa, but sharply decreasing to 144 (3.6%) at 15GPa. This suggests that HCP serves as an intermediate or transient phase under moderate compression but becomes less favorable at very high pressures where FCC dominates. BCC units follow a similar pattern: Starting from 99 atoms (2.5%) at 0GPa, rising to 229 (5.7%) at 5GPa, 412 (10.3%) at 10GPa, and dropping dramatically to just 53 atoms (1.3%) at 15GPa. Again, BCC may form under intermediate pressure but is largely replaced by FCC under higher compression. Other units dominate at ambient conditions: 3596 atoms (89.9%) at 0 GPa, falling to 2522 (63.0%) at 5 GPa, 2280 (57.0%) at 10 GPa, and sharply reduced to 321 (8.0%) at 15GPa. This sharp reduction in disordered structures under pressure confirms the system's trend toward crystallization and ordering, particularly toward the stable FCC phase. Thus, the data in Table 2 illustrate that increasing pressure at room temperature leads to: compression of interatomic distances, enhancement of local atomic ordering, and structural phase transition where the system shifts from largely disordered or mixed local environments to a predominantly FCC crystalline state. This behavior aligns well with the known thermodynamic stability of FCC silver under high-pressure conditions and suggests that pressure can be an effective external control parameter to induce crystallization and phase purification in metallic systems.

Figure 5 presents the structural configuration of the Ag system at 5GPa, corresponding to the data shown in Table 2. Under this condition, the numbers of FCC, HCP, BCC, and Other structural units are 748 (18.7%), 500 (12.5%), 229 (5.7%), and 2522 (63.0%), respectively. This indicates that although the crystalline phases FCC, HCP, and BCC are clearly present, the majority of the structure remains disordered Other, which is consistent with the trend of increasing structural order with pressure observed in Table 2.

4. Conclusion

This study investigated the structural evolution of silver (Ag) bulk systems at 300K under varying numbers of atoms and applied pressures. The results demonstrated that increasing the number of atoms significantly enhances structural ordering, with a clear transition from disordered atomic arrangements to dominant face-centered cubic FCC structures. The nearest-neighbor distance slightly decreases, while the radial distribution function peak height increases with system size, indicating improved short-range order. The total potential energy scales linearly with the number of atoms, affirming bulk-like behavior with a consistent energy contribution per atom.

Under increasing pressure from 0 to 15GPa, the systems exhibited further structural refinement. The interatomic distance decreased, and the g(r) peak height increased notably, reflecting compression and densification. A pronounced transformation toward the FCC structure was observed, particularly at 15Gpa, where FCC units constituted 87% of the system, and disordered Other atoms dropped sharply to 8%. HCP and BCC structures appeared transiently at intermediate pressures but were largely suppressed at higher compression levels. These trends underline the role of pressure in promoting crystallization and phase purification in metallic systems.

Overall, the findings highlight that both system size and external pressure are critical parameters in controlling the atomic structure of silver, enabling the transition from disordered states to thermodynamically stable crystalline phases, especially FCC, which is characteristic of bulk silver.

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