

THERMODYNAMIC PROPERTIES OF FREE STANDING THIN METAL FILMS: TEMPERATURE AND PRESSURE DEPENDENCES

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Abstract. *The moment method in the statistical dynamics (SMM) is used to study thermodynamic properties of free standing thin metal films with face-centered cubic structure (fcc) taking into account the anharmonicity effects of the lattice vibrations and hydrostatic pressures. The explicit expressions of the lattice constant, thermal expansion coefficient, and specific heats at the constant volume and those at the constant pressure, C_V and C_P of the metal thin films are derived in closed analytic forms in terms of the power moments of the atomic displacements. The thermodynamic quantities of Au, Ag, Cu and Al metal thin films are calculated as a function of the temperature and pressure, and they are in good agreement with the corresponding results obtained from other theoretical calculations and experimental values. The effective pair potentials work well for the calculations of fcc metal thin films.*

Keywords: moment method; thermodynamic properties; high pressure; equation of state; thin film..

I. INTRODUCTION

Films materials have become interesting for recent years. They have been found to show different physical, chemical, and mechanical properties comparing to bulk materials [1, 2]. Therefore, knowledge of the thermodynamic properties of thin films are important for their technological applications.

The dependence on pressure of the thermodynamic properties of thin film is of great interest not only from a fundamental point of view but also for technological applications [3-10]. In general, investigating for dependence on pressure of thin film almost at low-pressure and in deposition process of thin film on substrate [5, 7, 8]. Most of researches of thin films are mainly experimental work [3-10] but very few studies are theoretical ones. The influence of oxygen pressure on the growth of $(\text{Ba}_{0.02}\text{Sr}_{0.98})\text{TiO}_3$ thin film on MgO substrate by pulsed laser deposition techniques have been investigated in the oxygen pressure range from 40 to 10^{-3} Pa [7]. It is

revealed that the lattice parameter, film orientation, surface roughness, and deposition rate are dependent on the oxygen pressure. At lower oxygen pressure, more high energy particles will arrive to the substrate. Therefore, the deposition rate of $(\text{Ba}_{0.02}\text{Sr}_{0.98})\text{TiO}_3$ thin film increases with the decrease of oxygen pressure. A pressure dependent output current controlling thin film transistor was investigated [9]. The value of the contact length varies according to the external pressure. The pressure dependence of the capacitance - voltage curve for PbTiO thin films are prepared on SiO substrate was investigated by C. R. Cho [10]. A comparing the performance of the membrane of thin palladium films at high hydrogen partial pressure conditions with the numerous prior studies of these films characterized at low hydrogen partial pressure conditions was reported in [11]. Most previous studies of thin films have been done in non-metal thin films and not free-standing metal thin films.

In order to understand the pressure dependence of the thermodynamic properties of the metal thin films, it is highly desirable to establish an analytical method which enables us to evaluate the free energy of the system taking into account both the anharmonicity and quantum mechanical effect of the lattice vibration.

In this article, we present an analysis which can be used to extract the thermodynamic properties of the free-standing metal thin films, as a function of the pressure, using the moment method in the statistical dynamics [12-14] and derive the explicit expressions of the free energies of the system. In particular, the thermodynamic properties of the free-standing metal thin films with face-centered cubic (fcc) structure are investigated within the fourth order moment approximation of the atomic displacements. The explicit expressions of the lattice constant, thermal expansion coefficient, and specific heats at the constant volume and those at the constant pressure, C_V and C_P ... of the metal thin films are derived in terms of the hydrostatic pressure P and the temperature T . The numerical calculations are performed for fcc Au, Ag, Cu and Al metal thin films, using the effective pair potentials between the atoms. We will show that the theoretical calculations on the thermodynamic properties in good agreement with the corresponding experimental data and other results. The detailed formulation of the pressure dependence and temperature dependence of the thermodynamic quantities is presented in Sec. II. Some of the numerical examples will be given in Sec. III. Finally Sec. IV is devoted to the conclusions.

II. THEORY

II.1. Pressure versus volume relation

Let us consider a metal free standing thin film has n^* layers with the film thickness d . Suppose of the thin film has been consisting two atomic surface layers, two next surface atomic layers and $(n^* - 4)$ atomic internal layers, with N_{ng} surface layer atoms, N_{ng1} next surface layer atoms and N_{lr} internal layers atoms (see Fig. 1).

For the surface layer atoms of thin film, we will derive the pressure versus volume relation of crystals limiting only quadratic terms in the atomic displacements. The expression for the free energy in the harmonic approximation is determined as [15].

$$\psi_{ng} = 3N_{ng} \left\{ \frac{1}{6} u_0^{ng} + \theta [x_{ng} + \ln(1 - e^{-2x_{ng}})] \right\}, \quad u_0^{ng} = \sum_i \varphi_{i0}^{ng} (|a_{i,ng}|). \quad (1)$$

Where ψ_{ng} is the free energy in the harmonic approximation for surface layer atoms [15], u_0^{ng} is the sum of the effective pair interaction energies of the i^{th} atoms to the 0^{th} atom at the surface layer atoms; ($|a_{i,ng}|$) is the nearest neighbour distance of atoms at surface layer atoms.

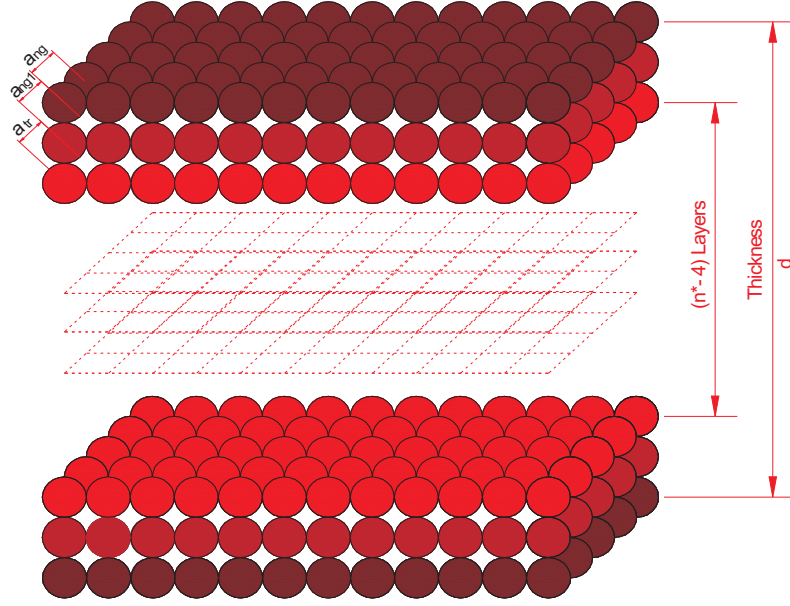


Fig. 1. The metallic free standing thin film

The hydrostatic pressure P is determined by [12, 16]

$$P = - \left(\frac{\partial \psi_{ng}}{\partial V_{ng}} \right)_T = - \frac{a_{ng}}{3V_{ng}} \left(\frac{\partial \psi_{ng}}{\partial a_{ng}} \right)_T. \quad (2)$$

From Eqs. (1) and (2), we obtain equation of state describes the dependence of the pressure on volume relation of the lattice as

$$Pv_{ng} = -a_{ng} \left[\frac{1}{6} \frac{\partial u_0^{ng}}{\partial a_{ng}} + \theta x_{ng} \coth x_{ng} \frac{1}{2k_{ng}} \frac{\partial k_{ng}}{\partial a_{ng}} \right], \quad (3)$$

where $\frac{\partial x_{ng}}{\partial a_{ng}} = \frac{x_{ng}}{2k_{ng}} \frac{\partial k_{ng}}{\partial a_{ng}}$, $x_{ng} = \frac{\hbar\omega_{ng}}{2\theta}$, $\theta = k_B T$ and ν_{ng} is the atomic volume $v_{ng} = \frac{V_{ng}}{N_{ng}}$ of the crystal, for the fcc lattice of the metal thin films $v_{ng} = \frac{1}{\sqrt{2}} a_{ng}^3$. Using Eq. (3), one can find the nearest neighbour distance a_{ng} at pressure P and temperature T . However, for numerical calculations, it is convenient to determine firstly the nearest neighbour distance $a_{ng}(P, 0)$ at pressure P and at absolute zero temperature $T = 0$. For $T = 0$ temperature, eq. (3) is reduced to

$$Pv_{ng} = -a_{ng} \left[\frac{1}{6} \frac{\partial u_0^{ng}}{\partial a_{ng}} + \frac{\hbar\omega_{ng}}{4k_{ng}} \frac{\partial k_{ng}}{\partial a_{ng}} \right]. \quad (4)$$

For simplicity, we take the effective pair interaction energy in metal systems as the power law, similar to the Lennard-Jones potential

$$\varphi(r) = \frac{D}{(n-m)} \left[m \left(\frac{r_0}{r} \right)^n - n \left(\frac{r_0}{r} \right)^m \right], \quad (5)$$

where D , m , n , r_0 are determined by fitting the experimental data (e.g., cohesive energy and elastic modulus). For fcc of the metal thin films we take into account the first nearest and second nearest neighbour interactions.

Using the effective pair potentials of Eq. (5), it is straitforward to get the interaction energy u_0^{ng} and the parameter k_{ng} in the crystal as [15]

$$u_0^{ng} = \frac{D}{(n-m)} \left[mA_{ng,n} \left(\frac{r_0}{a_{ng}} \right)^n - nA_{ng,m} \left(\frac{r_0}{a_{ng}} \right)^m \right]; \quad (6)$$

$$\begin{aligned} k_{ng} &= \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{ng}}{\partial u_{i\beta}^2} \right)_{eq} \\ &= \frac{Dnm}{2a_{ng}^2(n-m)} \left\{ [(n+2)A_{ng,n+4}^{a_{ix}^2} - A_{ng,n+2}] \left(\frac{r_0}{a_{ng}} \right)^n - [(m+2)A_{ng,m+4}^{a_{ix}^2}] \left(\frac{r_0}{a_{ng}} \right)^m \right\} \\ &= m_0 \omega_{ng}^2, \end{aligned} \quad (7)$$

where $A_{ng,n}$, $A_{ng,m}$, $A_{ng,n}^{a_{ix}^2}$, $A_{ng,m}^{a_{ix}^2}$, $A_{ng,n}^{a_{ix}^4}$, $A_{ng,m}^{a_{ix}^4}$, $A_{ng,n}^{a_{ix}^2 a_{iy}^2}$, $A_{ng,m}^{a_{ix}^2 a_{iy}^2}$, ... are the structural sums of surface layers atoms for the given crystal and given by [12, 13]

$$\begin{aligned} A_{ng,n} &= \sum_i \frac{Z_i^{ng}}{v_i^{ng,n}}; \quad A_{ng,m} = \sum_i \frac{Z_i^{ng}}{v_i^{ng,m}}; \\ A_{ng,n}^{a_{ix}^2} &= \frac{1}{a_{ng}^2} \sum_i \frac{Z_{i,x}^{ng} a_{ng,ix}^2}{v_i^{ng,n}}; \quad A_{ng,m}^{a_{ix}^2} = \frac{1}{a_{ng}^2} \sum_i \frac{Z_{i,x}^{ng} a_{ng,ix}^2}{v_i^{ng,m}}; \\ A_{ng,n}^{a_{ix}^4} &= \frac{1}{a_{ng}^4} \sum_i \frac{Z_{i,x}^{ng} a_{ng,ix}^4}{v_i^{ng,n}}; \quad A_{ng,m}^{a_{ix}^4} = \frac{1}{a_{ng}^4} \sum_i \frac{Z_{i,x}^{ng} a_{ng,ix}^4}{v_i^{ng,m}}; \\ A_{ng,n}^{a_{ix}^2 a_{iy}^2} &= \frac{1}{a_{ng}^4} \sum_i \frac{Z_{i,xy}^{ng} a_{ng,ix}^2 a_{ng,iy}^2}{v_i^{ng,n}}; \quad A_{ng,m}^{a_{ix}^2 a_{iy}^2} = \frac{1}{a_{ng}^4} \sum_i \frac{Z_{i,xy}^{ng} a_{ng,ix}^2 a_{ng,iy}^2}{v_i^{ng,m}}; \end{aligned} \quad (8)$$

here Z_i^{ng} is the coordination number of i -th nearest neighbour atoms of surface layers with radius r_i^{ng} (for fcc lattice of thin film) $r_k^{ng} = v_k^{ng} a_{ng}$.

Similar for next surface layers atoms and internal layers atoms of the system, we determined the interaction energy u_0^{ng1} , u_0^{tr} , the parameter (k_{ng1}, k_{tr}) , and structural sums

$$\begin{aligned} A_{ng1,n}, A_{ng1,m}, A_{ng1,n}^{a_{ix}^2}, A_{ng1,m}^{a_{ix}^2}, A_{ng1,n}^{a_{ix}^4}, A_{ng1,m}^{a_{ix}^4}, A_{ng1,n}^{a_{ix}^2 a_{iy}^2}, A_{ng1,m}^{a_{ix}^2 a_{iy}^2}, \\ A_{tr,n}, A_{tr,m}, A_{tr,n}^{a_{ix}^2}, A_{tr,m}^{a_{ix}^2}, A_{tr,n}^{a_{ix}^4}, A_{tr,m}^{a_{ix}^4}, A_{tr,n}^{a_{ix}^2 a_{iy}^2}, A_{tr,m}^{a_{ix}^2 a_{iy}^2}. \end{aligned} \quad (9)$$

For surface layers and next surface layers, we have considered to the surface effect - the defect on surface layers atoms and next surface layers atoms of the thin films. Using for two first coordination sphere, we obtained the structural sums as follows, respectively

$$\left\{ \begin{array}{l} A_{ng,n+2} = \sum_i \frac{Z_i^{ng}}{\nu_{ng,i}^{n+2}} = 8 + \frac{5}{(\sqrt{2})^{n+2}}; A_{ng,m+2} = \sum_i \frac{Z_i^{ng}}{\nu_{ng,i}^{m+2}} = 8 + \frac{5}{(\sqrt{2})^{m+2}} \\ A_{ng,n+4}^{2,ix} = \frac{1}{a_{ng}^2} \sum_i \frac{Z_{ix}^{ng}}{\nu_{ng,i}^{n+4}} a_{ng,ix}^2 = 3 + \frac{4}{(\sqrt{2})^{n+4}}; A_{ng,m+4}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{tr}}{\nu_{ng,i}^{m+4}} a_{ng,ix}^2 = 3 + \frac{4}{(\sqrt{2})^{m+4}} \\ A_{ng,n+6}^{2,kx} = \frac{1}{a_{ng}^2} \sum_i \frac{Z_{ix}^{ng}}{\nu_i^{n+6}} a_{ng,ix}^2 = 3 + \frac{4}{(\sqrt{2})^{n+6}}; A_{ng,m+6}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{tr}}{\nu_{ng,i}^{m+6}} a_{ng,ix}^2 = 3 + \frac{4}{(\sqrt{2})^{m+6}} \\ A_{ng,n+4} = \sum_i \frac{Z_i^{ng}}{\nu_{ng,i}^{n+4}} = 8 + \frac{5}{(\sqrt{2})^{n+4}}; A_{ng,m+4} = \sum_i \frac{Z_i^{ng}}{\nu_{ng,i}^{m+4}} = 8 + \frac{5}{(\sqrt{2})^{m+4}} \\ A_{ng,n+8}^4 = \frac{1}{a_{ng}^4} \sum_i \frac{Z_{ix}^{ng}}{\nu_{ng,i}^{n+8}} a_{ng,ix}^4 = \frac{3}{2} + \frac{8}{(\sqrt{2})^{n+8}}; A_{ng,m+8}^4 = \frac{1}{a_{ng}^4} \sum_i \frac{Z_{ix}^{ng}}{\nu_{ng,i}^{m+8}} a_{ng,ix}^4 = \frac{3}{2} + \frac{8}{(\sqrt{2})^{m+8}} \\ A_{ng,n+8}^{2,ix} a_{ng,iy}^2 = \frac{1}{a_{ng}^4} \sum_i \frac{Z_{i,xy}^{ng} a_{ng,ix}^2 a_{ng,iy}^2}{\nu_{ng,i}^{n+8}} = 1; A_{ng,m+8}^{2,ix} a_{ng,iy}^2 = \frac{1}{a_{ng}^4} \sum_i \frac{Z_{i,xy}^{ng} a_{ng,ix}^2 a_{ng,iy}^2}{\nu_{ng,i}^{m+8}} = 1, \end{array} \right. \quad (10)$$

$$\left\{ \begin{array}{l} A_{ng1,n+2} = \sum_i \frac{Z_i^{ng1}}{\nu_{ng1,i}^{n+2}} = 12 + \frac{5}{(\sqrt{2})^{n+2}}; A_{ng1,m+2} = \sum_i \frac{Z_i^{ng1}}{\nu_{ng1,i}^{m+2}} = 12 + \frac{5}{(\sqrt{2})^{m+2}} \\ A_{ng1,n+4}^{2,ix} = \frac{1}{a_{ng1}^2} \sum_i \frac{Z_{ix}^{ng1}}{\nu_{ng1,i}^{n+4}} a_{ng1,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{n+4}}; A_{ng1,m+4}^{2,ix} = \frac{1}{a_{ng1}^2} \sum_i \frac{Z_{ix}^{ng1}}{\nu_{ng1,i}^{m+4}} a_{ng1,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{m+4}} \\ A_{ng1,n+6}^{2,ix} = \frac{1}{a_{ng1}^2} \sum_i \frac{Z_{ix}^{ng1}}{\nu_{ng1,i}^{n+6}} a_{ng1,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{n+6}}; A_{ng1,m+6}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{ng1}}{\nu_{ng1,i}^{m+6}} a_{ng1,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{m+6}} \\ A_{ng1,n+4} = \sum_i \frac{Z_i^{ng1}}{\nu_{ng1,i}^{n+4}} = 12 + \frac{5}{(\sqrt{2})^{n+4}}; A_{ng1,m+4} = \sum_i \frac{Z_i^{ng1}}{\nu_{ng1,i}^{m+4}} = 12 + \frac{5}{(\sqrt{2})^{m+4}} \\ A_{ng1,n+8}^4 = \frac{1}{a_{ng1}^4} \sum_i \frac{Z_{ix}^{ng1}}{\nu_{ng1,i}^{n+8}} a_{ng1,ix}^4 = 2 + \frac{8}{(\sqrt{2})^{n+8}}; A_{ng1,m+8}^4 = \frac{1}{a_{ng1}^4} \sum_i \frac{Z_{ix}^{ng1}}{\nu_{ng1,i}^{m+8}} a_{ng1,ix}^4 = 2 + \frac{8}{(\sqrt{2})^{m+8}} \\ A_{ng1,n+8}^{2,ix} a_{ng1,iy}^2 = \frac{1}{a_{ng1}^4} \sum_i \frac{Z_{i,xy}^{ng1} a_{ng1,ix}^2 a_{ng1,iy}^2}{\nu_{ng1,i}^{n+8}} = 1; A_{ng1,m+8}^{2,ix} a_{ng1,iy}^2 = \frac{1}{a_{ng1}^4} \sum_i \frac{Z_{i,xy}^{ng1} a_{ng1,ix}^2 a_{ng1,iy}^2}{\nu_{ng1,i}^{m+8}} = 1, \end{array} \right. \quad (11)$$

$$\left\{ \begin{array}{l} A_{tr,n+2} = \sum_i \frac{Z_i^{tr}}{\nu_{tr,i}^{n+2}} = 12 + \frac{6}{(\sqrt{2})^{n+2}}; A_{tr,m+2} = \sum_i \frac{Z_i^{tr}}{\nu_{tr,i}^{m+2}} = 12 + \frac{6}{(\sqrt{2})^{m+2}} \\ A_{tr,n+6}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{tr}}{\nu_{tr,i}^{n+6}} a_{tr,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{n+6}}; A_{tr,m+6}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{tr}}{\nu_{tr,i}^{m+6}} a_{tr,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{m+6}} \\ A_{tr,n+4}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{tr}}{\nu_{tr,i}^{n+4}} a_{tr,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{n+4}}; A_{tr,m+4}^{2,ix} = \frac{1}{a_{tr}^2} \sum_i \frac{Z_{ix}^{tr}}{\nu_{tr,i}^{m+4}} a_{tr,ix}^2 = 4 + \frac{4}{(\sqrt{2})^{m+4}} \\ A_{tr,n+4} = \sum_i \frac{Z_i^{tr}}{\nu_{tr,i}^{n+4}} = 12 + \frac{6}{(\sqrt{2})^{n+4}}; A_{tr,m+4} = \sum_i \frac{Z_i^{tr}}{\nu_{tr,i}^{m+4}} = 12 + \frac{6}{(\sqrt{2})^{m+4}} \\ A_{tr,n+8}^4 = \frac{1}{a_{tr}^4} \sum_i \frac{Z_{ix}^{tr}}{\nu_{tr,i}^{n+8}} a_{tr,ix}^4 = 2 + \frac{8}{(\sqrt{2})^{n+8}}; A_{tr,m+8}^4 = \frac{1}{a_{tr}^4} \sum_i \frac{Z_{ix}^{tr}}{\nu_{tr,i}^{m+8}} a_{tr,ix}^4 = 2 + \frac{8}{(\sqrt{2})^{m+8}} \\ A_{tr,n+8}^{2,ix} a_{tr,iy}^2 = \frac{1}{a_{tr}^4} \sum_i \frac{Z_{i,xy}^{tr} a_{tr,ix}^2 a_{tr,iy}^2}{\nu_{tr,i}^{n+8}} = 1; A_{tr,m+8}^{2,ix} a_{tr,iy}^2 = \frac{1}{a_{tr}^4} \sum_i \frac{Z_{i,xy}^{tr} a_{tr,ix}^2 a_{tr,iy}^2}{\nu_{tr,i}^{m+8}} = 1. \end{array} \right. \quad (12)$$

From Eqs. (4), (6), and (8) we obtain equation of state for surface layers of the metal thin film with face-centered cubic structure at zero temperature

$$Pv_{ng} = \frac{Dnm}{6(n-m)} \left[A_{ng,n} \left(\frac{r_0}{a_{ng}} \right)^n - A_{ng,m} \left(\frac{r_0}{a_{ng}} \right)^m \right] + \frac{1}{a_{ng}} \frac{\hbar}{4\sqrt{m_0}} \sqrt{\frac{Dnm}{2(n-m)}} \\ \times \frac{\left\{ (n+2) \left[(n+2) A_{ng,n+4}^{a_{ng}^2, ix} - A_{ng,n+2} \right] \left(\frac{r_0}{a_{ng}} \right)^n - (m+2) \left[(m+2) A_{ng,m+4}^{a_{ng}^2, ix} - A_{ng,m+2} \right] \left(\frac{r_0}{a_{ng}} \right)^m \right\}}{\sqrt{\left[(n+2) A_{ng,n+4}^{a_{ng}^2, ix} - A_{ng,n+2} \right] \left(\frac{r_0}{a_{ng}} \right)^n - \left[(m+2) A_{ng,m+4}^{a_{ng}^2, ix} - A_{ng,m+2} \right] \left(\frac{r_0}{a_{ng}} \right)^m}} \quad (13)$$

Eq. (13) can be transformed to the form

$$P \frac{1}{\sqrt{2}} r_0^3 = c_{1ng} y_{ng}^{n+3} - c_{2ng} y_{ng}^{m+3} + \frac{c_{3ng} y_{ng}^{n+4} - c_{4ng} y_{ng}^{m+4}}{\sqrt{c_{5ng} y_{ng}^n - c_{6ng} y_{ng}^m}}. \quad (14)$$

where

$$y_{ng} = \frac{r_0}{a_{ng}(P, 0)}, \\ c_{1ng} = A_{ng,n} \frac{Dnm}{6(n-m)}, \\ c_{2ng} = A_{ng,m} \frac{Dnm}{6(n-m)}, \\ c_{3ng} = \frac{\hbar}{4\sqrt{m_0}} \sqrt{\frac{Dnm}{2(n-m)}} (n+2) \left[(n+2) A_{ng,n+4}^{a_{ng}^2, ix} - A_{ng,n+2} \right] \frac{1}{r_0}, \\ c_{4ng} = \frac{\hbar}{4\sqrt{m_0}} \sqrt{\frac{Dnm}{2(n-m)}} (m+2) \left[(m+2) A_{ng,m+4}^{a_{ng}^2, ix} - A_{ng,m+2} \right] \frac{1}{r_0}, \\ c_{5ng} = (n+2) A_{ng,n+4}^{a_{ng}^2, ix} - A_{ng,n+2}, \\ c_{6ng} = (m+2) A_{ng,m+4}^{a_{ng}^2, ix} - A_{ng,m+2}. \quad (15)$$

Similar derivation can be also done for next surface layers atoms and internal layers atoms of the equation of state as, respectively

$$P \frac{1}{\sqrt{2}} r_0^3 = c_{1ng1} y_{ng1}^{n+3} - c_{2ng1} y_{ng1}^{m+3} + \frac{c_{3ng1} y_{ng1}^{n+4} - c_{4ng1} y_{ng1}^{m+4}}{\sqrt{c_{5ng1} y_{ng1}^n - c_{6ng1} y_{ng1}^m}}, \quad (16)$$

$$P \frac{1}{\sqrt{2}} r_0^3 = c_{1tr} y_{tr}^{n+3} - c_{2tr} y_{tr}^{m+3} + \frac{c_{3tr} y_{tr}^{n+4} - c_{4tr} y_{tr}^{m+4}}{\sqrt{c_{5tr} y_{tr}^n - c_{6tr} y_{tr}^m}}. \quad (17)$$

In principle, Eqs. (14), (16) and (17) permit to find the nearest neighbour distance $a_{ng}(P, 0)$, $a_{ng1}(P, 0)$ and $a_{tr}(P, 0)$ for surface layers, next surface layers and internal layers atoms at zero temperature and pressure P , respectively.

II.2. Thermodynamic quantities of the metal thin film

For surface layers of the metal thin film, the calculation of the lattice spacing of the metal thin film at finite temperature and pressure P , the fourth order vibrational constants γ_{ng} and k_{ng} at pressure P and $T = 0\text{K}$ are defined by [12, 15]

$$\gamma_{ng} = \frac{1}{12} \sum_i \left[\left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\alpha}^4} \right)_{eq} + 6 \left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2} \right)_{eq} \right] = 4(\gamma_{1ng} + \gamma_{2ng}), \quad (18)$$

$$\gamma_{1ng} = \frac{1}{48} \sum_i \left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\alpha}^4} \right)_{eq}, \quad (19)$$

$$\gamma_{2ng} = \frac{6}{48} \sum_i \left(\frac{\partial^4 \varphi_{io}^{ng}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2} \right)_{eq}, \quad (20)$$

$$k_{ng} = \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{io}^{ng}}{\partial u_{i\alpha}^2} \right)_{eq} \equiv m_0 \omega_{ng}^2. \quad (21)$$

Using the effective pair potentials of eq. (5), the parameter $\gamma_{ng}, \gamma_{1ng}, \gamma_{2ng}, k_{ng}$ of the fcc metal thin film have the form

$$\begin{aligned} \gamma_{ng} = & \frac{1}{12} \frac{Dmn}{(n-m) a_{ng}^4} \left[\begin{array}{l} (n+2)(n+4)(n+6) \left(A_{ng,n+8}^{a_{ng,ix}^4} + 6A_{ng,n+8}^{a_{ng,ix}^2 a_{ng,iy}^2} \right) \\ -18(n+2)(n+4)A_{ng,n+6}^{a_{ng,ix}^2} + 9(n+2)A_{ng,n+4} \end{array} \right] \left(\frac{r_0}{a_{ng}} \right)^n \\ & - \frac{1}{12} \frac{Dmn}{(n-m) a_{ng}^4} \left[\begin{array}{l} (m+2)(m+4)(m+6) \left(A_{ng,m+8}^{a_{ng,ix}^4} + 6A_{ng,m+8}^{a_{ng,ix}^2 a_{ng,iy}^2} \right) \\ -18(m+2)(m+4)A_{ng,m+6}^{a_{ng,ix}^2} + 9(m+2)A_{ng,m+4} \end{array} \right] \left(\frac{r_0}{a_{ng}} \right)^m, \end{aligned} \quad (22)$$

$$\begin{aligned} \gamma_{1ng} = & \frac{1}{48} \frac{Dmn}{(n-m) a_{ng}^4} \left[\begin{array}{l} (n+2)(n+4)(n+6) A_{ng,n+8}^{a_{ng,ix}^4} \\ -6(n+2)(n+4) A_{ng,n+6}^{a_{ng,ix}^2} + 3(n+2)A_{ng,n+4} \end{array} \right] \left(\frac{r_0}{a_{ng}} \right)^n \\ & - \frac{1}{48} \frac{Dmn}{(n-m) a_{ng}^4} \left[\begin{array}{l} (m+2)(m+4)(m+6) A_{ng,n+8}^{a_{ng,ix}^4} \\ -6(m+2)(m+4) A_{ng,n+6}^{a_{ng,ix}^2} + 3(n+2)A_{ng,n+4} \end{array} \right] \left(\frac{r_0}{a_{ng}} \right)^m, \end{aligned} \quad (23)$$

$$\begin{aligned} \gamma_{2ng} = & \frac{1}{8} \frac{Dmn}{(n-m) a_{ng}^4} \left[\begin{array}{l} (n+2)(n+4)(n+6) A_{ng,n+8}^{a_{ng,ix}^2 a_{ng,iy}^2} \\ -2(n+2)(n+4) A_{ng,n+6}^{a_{ng,ix}^2} + (n+2)A_{ng,n+4} \end{array} \right] \left(\frac{r_0}{a_{ng}} \right)^n \\ & - \frac{1}{8} \frac{Dmn}{(n-m) a_{ng}^4} \left[\begin{array}{l} (m+2)(m+4)(m+6) A_{ng,n+8}^{a_{ng,ix}^2 a_{ng,iy}^2} \\ -2(m+2)(m+4) A_{ng,m+6}^{a_{ng,ix}^2} + (n+2)A_{ng,m+4} \end{array} \right] \left(\frac{r_0}{a_{ng}} \right)^m, \end{aligned} \quad (24)$$

$$k_{ng} = \frac{Dmn}{2(n-m)a_{ng}^2} \left\{ \left[(n+2)A_{ng,n+4}^{a_{ng}^2,ix} - A_{ng,n+2} \right] \left(\frac{r_0}{a_{ng}} \right)^n - \left[(m+2)A_{ng,m+4}^{a_{ng}^2,ix} - A_{ng,m+2} \right] \left(\frac{r_0}{a_{ng}} \right)^m \right\}. \quad (25)$$

Similar derivation can be also done for next surface layers atoms and internal layers atoms, we obtain the values of $\gamma_{ng1}, \gamma_{1ng1}, \gamma_{2ng1}, k_{ng1}, \gamma_{tr}, \gamma_{1tr}, \gamma_{2tr}, k_{tr}$, respectively.

Using the obtained results of nearest neighbour distance for surface layers atoms $a_{ng}(P, 0)$ and Eqs. (25), (22) and (10), we find the values of parameters $k_{ng}(P, 0)$, and $\gamma_{ng}(P, 0)$ at pressure P and $T = 0$ K.

Similar derivation can be also done for next surface layers atoms and internal layers atoms, we find the values of parameters $k_{ng1}(P, 0), k_{tr}(P, 0)$, and $\gamma_{ng1}(P, 0), \gamma_{tr}(P, 0)$, at pressure P and $T = 0$ K.

For surface layers of the metal thin film, the thermally induced lattice expansion $y_0^{ng}(P, T)$ at pressure P , temperature T is given in a closed formula using the force balance criterion of the fourth order moment approximation as [12, 15]

$$y_0^{ng}(P, T) = \sqrt{\frac{2\gamma_{ng}(P, 0)\theta^2}{3k_{ng}^3(P, 0)}A_{ng}(P, T)}, \quad (26)$$

where

$$A_{ng}(P, T) = a_1^{ng} + \frac{\gamma_{ng}^2(P, 0)\theta^2}{k_{ng}^4(P, 0)}a_2^{ng} + \frac{\gamma_{ng}^3(P, 0)\theta^3}{k_{ng}^6(P, 0)}a_3^{ng} + \frac{\gamma_{ng}^4(P, 0)\theta^4}{k_{ng}^8(P, 0)}a_4^{ng} + \frac{\gamma_{ng}^5(P, 0)\theta^5}{k_{ng}^{10}(P, 0)}a_5^{ng} + \frac{\gamma_{ng}^6(P, 0)\theta^6}{k_{ng}^{12}(P, 0)}a_6^{ng}. \quad (27)$$

In Eq. (27), using $X_{ng} = x_{ng} \coth x_{ng}$, one can find the values of parameters as [13]

$$\begin{aligned} a_1^{ng} &= 1 + \frac{X_{ng}}{2}; & a_2^{ng} &= \frac{13}{3} + \frac{47}{6}X_{ng} + \frac{23}{6}X_{ng}^2 + \frac{1}{2}X_{ng}^3, \\ a_3^{ng} &= - \left(\frac{25}{3} + \frac{121}{6}X_{ng} + \frac{50}{3}X_{ng}^2 + \frac{16}{3}X_{ng}^3 + \frac{1}{2}X_{ng}^4 \right), \\ a_4^{ng} &= \frac{43}{3} + \frac{93}{2}X_{ng} + \frac{169}{3}X_{ng}^2 + \frac{83}{3}X_{ng}^3 + \frac{22}{3}X_{ng}^4 + \frac{1}{2}X_{ng}^5, \\ a_5^{ng} &= - \left(\frac{103}{3} + \frac{749}{6}X_{ng} + \frac{363}{2}X_{ng}^2 + \frac{391}{3}X_{ng}^3 + \frac{148}{3}X_{ng}^4 + \frac{53}{6}X_{ng}^5 + \frac{1}{2}X_{ng}^6 \right), \\ a_6^{ng} &= 65 + \frac{561}{2}X_{ng} + \frac{1489}{3}X_{ng}^2 + \frac{927}{2}X_{ng}^3 + \frac{733}{3}X_{ng}^4 + \frac{145}{2}X_{ng}^5 + \frac{31}{3}X_{ng}^6 + \frac{1}{2}X_{ng}^7, \\ x_{ng} &= \frac{\hbar\omega_{ng}(P, 0)}{2\theta}, & \omega_{ng}(P, 0) &= \sqrt{\frac{k_{ng}(P, 0)}{m_0}}. \end{aligned} \quad (28)$$

Similar derivation can be also done for next surface layers atoms and internal layers atoms of the average atomic displacement, respectively

$$y_0^{ng1}(P, T) = \sqrt{\frac{2\gamma_{ng1}(P, 0)\theta^2}{3k_{ng1}^3(P, 0)}A_{ng1}(P, T)}, \quad (29)$$

$$y_0^{tr}(P, T) = \sqrt{\frac{2\gamma_{tr}(P, 0)\theta^2}{3k_{tr}^3(P, 0)}A_{tr}(P, T)}. \quad (30)$$

So, for surface layers atoms we can find the nearest neighbour distance $a_{ng}(P, T)$ at pressure P and temperature T as

$$a_{ng}(P, T) = a_{ng}(P, 0) + y_0^{ng}(P, T). \quad (31)$$

Thus, for next surface layers atoms and internal layers atoms the nearest neighbour distance are determined as, respectively

$$a_{ng1}(P, T) = a_{ng1}(P, 0) + y_0^{ng1}(P, T) \quad (32)$$

$$a_{tr}(P, T) = a_{tr}(P, 0) + y_0^{tr}(P, T). \quad (33)$$

The average nearest neighbor distance of thin film at pressure P , temperature T and zero temperature are determined as [15]

$$\bar{a}(P, T) = \frac{2a_{ng}(P, T) + 2a_{ng1}(P, T) + (n^* - 5)a_{tr}(P, T)}{n^* - 1}. \quad (34)$$

$$\bar{a}(P, 0) = \frac{2a_{ng}(P, 0) + 2a_{ng1}(P, 0) + (n^* - 5)a_{tr}(P, 0)}{n^* - 1}. \quad (35)$$

The average lattice constant \bar{a}_c , we can be calculated in [15]

$$\bar{a}_c = \sqrt{2\bar{a}}(P, T). \quad (36)$$

Using the above formula $\bar{a}(P, T)$, we can find the change of the crystal volume under pressure P at a given temperature T as

$$\frac{V}{V_0} = \left(\frac{\bar{a}(P, T)}{\bar{a}(0, T)}\right)^3 \quad (37)$$

with

$$\bar{a}(0, T) = \frac{2a_{ng}(0, T) + 2a_{ng1}(0, T) + (n^* - 5)a_{tr}(0, T)}{n^* - 1}. \quad (38)$$

The average thermal expansion coefficient of metal thin film can be calculated as [12, 15]

$$\alpha = \frac{k_B}{\bar{a}(P, 0)} \frac{\partial \bar{a}(P, T)}{\partial \theta} = \frac{d_{ng}\alpha_{ng} + d_{ng1}\alpha_{ng1} + (d - d_{ng} - d_{ng1})\alpha_{tr}}{d}, \quad (39)$$

where

$$\alpha_{tr} = \frac{k_B}{a_{tr}(P, 0)} \frac{\partial y_0^{tr}(P, T)}{\partial \theta}; \alpha_{ng} = \frac{k_B}{a_{ng}(P, 0)} \frac{\partial y_0^{ng}(P, T)}{\partial \theta}; \alpha_{ng1} = \frac{k_B}{a_{ng1}(P, 0)} \frac{\partial y_0^{ng1}(P, T)}{\partial \theta} \quad (40)$$

here d_{ng} and d_{ng1} are the surface layers and next surface layers thickness, respectively.

For surface layers of the metal thin film, we find also the free energy Ψ_{ng} of the crystal using the statistical moment method as [15]

$$\Psi_{ng} = \left\{ U_0^{ng} + 3N_{ng}\theta[x_{ng} + \ln(1 - e^{-2x_{ng}})] \right\} + \frac{3N_{ng}\theta^2}{k_{ng}^2} \left\{ \gamma_{2ng}X_{ng}^2 - \frac{2\gamma_{1ng}}{3} \left(1 + \frac{X_{ng}}{2} \right) \right\} + \frac{6N_{ng}\theta^3}{k_{ng}^4} \left\{ \frac{4}{3}\gamma_{2ng}^2 \left(1 + \frac{X_{ng}}{2} \right) X_{ng} - 2(\gamma_{1ng}^2 + 2\gamma_{1ng}\gamma_{2ng}) \left(1 + \frac{X_{ng}}{2} \right) (1 + X_{ng}) \right\}. \quad (41)$$

On the other hand, we obtain the expression of the free energy as [15]

$$\frac{\psi}{N} = \frac{d\sqrt{2} - 3\bar{a}(P, T)}{d\sqrt{2} + \bar{a}(P, T)} \psi_{tr} + \frac{2\bar{a}(P, T)}{d\sqrt{2} + \bar{a}(P, T)} \psi_{ng} + \frac{2\bar{a}(P, T)}{d\sqrt{2} + \bar{a}(P, T)} \psi_{ng1}. \quad (42)$$

With the aid of the free energy formula $\Psi = E - TS$, we can find the thermodynamic quantities of the system. The specific heats at temperature T are directly derived from the free energy of the system.

The specific heat at constant volume C_V is

$$C_V = \left[\frac{\partial E}{\partial T} \right]_V = -T \frac{\partial^2 \psi}{\partial T^2} = \frac{d\sqrt{2} - 3\bar{a}(P, T)}{d\sqrt{2} + \bar{a}(P, T)} C_V^{tr} + \frac{2\bar{a}(P, T)}{d\sqrt{2} + \bar{a}(P, T)} C_V^{ng} + \frac{2\bar{a}(P, T)}{d\sqrt{2} + \bar{a}(P, T)} C_V^{ng1}, \quad (43)$$

where

$$C_V^{tr} = 3k_B N \left\{ \frac{x_{tr}^2}{\sinh^2 x_{tr}} + \frac{2\theta}{k_{tr}^2} \left[\left(2\gamma_{2tr} + \frac{\gamma_{1tr}}{3} \right) \frac{x_{tr}^3 \coth x_{tr}}{\sinh^2 x_{tr}} + \frac{2\gamma_{1tr}}{3} - \gamma_{2tr} \left(\frac{x_{tr}^4}{\sinh^4 x_{tr}} + 2 \frac{x_{tr}^4 \coth^2 x_{tr}}{\sinh^2 x_{tr}} \right) \right] \right\}, \quad (44)$$

$$C_V^{ng} = 3k_B N \left\{ \frac{x_{ng}^2}{\sinh^2 x_{ng}} + \frac{2\theta}{k_{ng}^2} \left[\left(2\gamma_{2ng} + \frac{\gamma_{1ng}}{3} \right) \frac{x_{ng}^3 \coth x_{ng}}{\sinh^2 x_{ng}} + \frac{2\gamma_{1ng}}{3} - \gamma_{2ng} \left(\frac{x_{ng}^4}{\sinh^4 x_{ng}} + 2 \frac{x_{ng}^4 \coth^2 x_{ng}}{\sinh^2 x_{ng}} \right) \right] \right\}, \quad (45)$$

$$C_V^{ng1} = 3k_B N \left\{ \frac{x_{ng1}^2}{\sinh^2 x_{ng1}} + \frac{2\theta}{k_{ng1}^2} \left[\left(2\gamma_{2ng1} + \frac{\gamma_{1ng1}}{3} \right) \frac{x_{ng1}^3 \coth x_{ng1}}{\sinh^2 x_{ng1}} + \frac{2\gamma_{1ng1}}{3} - \gamma_{2ng1} \left(\frac{x_{ng1}^4}{\sinh^4 x_{ng1}} + 2 \frac{x_{ng1}^4 \coth^2 x_{ng1}}{\sinh^2 x_{ng1}} \right) \right] \right\}. \quad (46)$$

The isothermal compressibility λ_T is given by

$$\begin{aligned} \lambda_T &= -\frac{1}{V_0} \left(\frac{\partial V}{\partial P} \right)_T \\ &= \frac{3 \left(\frac{\bar{a}(P,T)}{\bar{a}(P,0)} \right)^3}{2P + \frac{\bar{a}^2(P,T)}{3V} \left(\frac{d\sqrt{2}-3\bar{a}(P,T)}{d\sqrt{2}+\bar{a}(P,T)} \frac{\partial^2 \psi_{tr}}{\partial a_{tr}^2} + \frac{2\bar{a}(P,T)}{d\sqrt{2}+\bar{a}(P,T)} \frac{\partial^2 \psi_{ng}}{\partial a_{ng}^2} + \frac{2\bar{a}(P,T)}{d\sqrt{2}+\bar{a}(P,T)} \frac{\partial^2 \psi_{ng1}}{\partial a_{ng1}^2} \right)_T} = \frac{1}{B_T}, \end{aligned} \quad (47)$$

where B_T denotes the isothermal elastic modulus of the thin film.

The specific heat at constant pressure C_P is determined from the thermodynamic relations

$$C_P = C_V - T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T = C_V + 9TV\alpha^2 B_T. \quad (48)$$

One can now apply the above formular to study the thermodynamic properties of fcc metal thin films under hydrostatic pressures. The pressure dependences of the crystal volume, specific heats and the linear thermal expansion coefficient are calculated self-consistently with the lattice spacing of the given fcc crystals.

III. NUMERICAL RESULTS AND DISCUSSION

In order to check the validity of the present moment method for the study of the thermodynamic properties of the metal thin films systems described herein, we performed calculations for pure metal thin films Au, Ag, Cu and Al. Using the experimental data of the parameters D and r_0 (Table 1), and the MAPLE XIII program, Eqs. (14), (16) and (17) can be solved, we find the values of the nearest neighbour distance $a_{ng}(P, 0)$, $a_{ng1}(P, 0)$, $a_{tr}(P, 0)$ at absolute temperature $T=0$ and pressure P for Au, Ag, Cu and Al metal thin films. Using the obtained results of the nearest neighbor distance $a_{ng}(P, 0)$, $a_{ng1}(P, 0)$, $a_{tr}(P, 0)$ and Eqs. (22), and (25), we find the values of parameters $k_{ng}(P, 0)$, $k_{ng1}(P, 0)$, $k_{tr}(P, 0)$, and $\gamma_{ng}(P, 0)$, $\gamma_{ng1}(P, 0)$, $\gamma_{tr}(P, 0)$ at pressure P and absolute temperature $T = 0$ K, respectively.

Table 1. Lennars-Jones potential parameters for Au, Ag, Cu and Al of metal thin films [17].

| Metals | n | m | $r_0, (A^0)$ | $D/k_B, (K)$ |
|--------|------|-----|--------------|--------------|
| Au | 10.5 | 5.5 | 2.8751 | 4683.0 |
| Ag | 11.5 | 5.5 | 2.8760 | 3325.6 |
| Cu | 10.5 | 5.5 | 2.5487 | 3401.1 |
| Al | 12.5 | 5.5 | 2.8541 | 2995.6 |

With the use of the expressions obtained in Section 2, we calculate the values of the everage lattice constant, \bar{a}_c , the thickness, d , and thermodynamic properties: the specific heats at constant volume and constant pressure, C_V and C_P , and the linear thermal expansion coefficient, α , for Al, Au, Cu and Ag metal thin films at various temperatures and pressures. The calculated results are presented in Figs. 2- 8.

In Table 2, we show the average lattice constant for Au metal thin film with various pressure at room temperature $T=300$ K. The calculated values of the average lattice constant by the present SMM have been compared with the calculated values reported by Z. Kolska et al. [2]. Our results calculations of the average lattice constant for Au thin film, it is decrease with the increasing of thickness. These results are in good agreement with the results presented by Z. Kolska et al. in [2]. Furthermore, we realize that the average lattice constant decrease with the increasing of pressure. When pressure increases, it impede the movement down of atoms at surface layers and next surface layers but surface layers and next surface layers atoms fluctuate more strongly than the internal layers atoms leading to the atom-atom distance at external layers is larger than that of the internal layers. Therefore, the average lattice constants decrease with the increasing of thickness. In Fig. 2, we present the pressure dependence of the average lattice constant of metal thin film for Au as a function of the pressure. In Fig. 3, we present the temperature dependence of the average lattice constant of metal thin films for Al, Au and Ag as a function of the temperature, it is increase with absolute temperature T . On the other hand, we consider with difference the thicknesses for the metal thin films with fcc structure as Au, Ag, Cu and Al ... also show temperature and pressure dependence of the average lattice parameters are similar.

Table 2. Calculated results for the average lattice constant of Au thin film, \bar{a}_c , at $T = 300$ K and various pressures, comparing with the Z. Kolska *et al.*'s calculated results [2].

| Thickness (nm) | $\bar{a}_c (\times 10^{-10} m)$ | P (GPa) | | |
|-------------------|---------------------------------|-----------|--------|--------|
| | | 0 | 0.5 | 0.9 |
| 14 | SMM | 4.0243 | 4.0233 | 4.0193 |
| | Ref. [2] | 4.0835 | — | — |
| 45 | SMM | 4.0241 | 4.0232 | 4.0192 |
| | Ref. [2] | 4.0738 | — | — |
| 72 | SMM | 4.0240 | 4.0231 | 4.0191 |
| | Ref. [2] | 4.0732 | — | — |

The changes in volume of metal thin films under hydrostatic pressure P are calculated for metal thin films Ag and Cu, the calculated results are presented in Figs. 4 and 5. We show the ratio volume $V/V_0 = \frac{V}{V_0} = \left(\frac{\bar{a}(P,T)}{\bar{a}(0,T)}\right)^3$, for Ag metal thin film with the thickness 55 nm and Cu metal thin film with the thickness 80 nm as the functions of the pressure P at room temperature $T=300$ K. The present SMM calculations for the ratio V/V_0 are compared corresponding to Ag nanomaterials with the thickness 55 nm and Cu nanomaterials with the thickness 80 nm in [18] showing the good agreement. Our calculation results of the ratio V/V_0 for Au and Al realize also that, it is decrease with the pressure P . These results are in agreement with the laws of other authors [19, 20] for nanomaterials and materials of metals bulk [21].

The thermodynamic properties in the metal thin film dependence on the average nearest neighbor (or the average lattice constant) at pressure P and temperature T therefore, the thermodynamic properties also dependence size, pressure and temperature effect for the metal thin films.

In Fig. 6, we present the temperature dependence of the thermal expansion coefficients under various pressure of metal thin film Al with thin film thickness 720 nm. One can be seen that

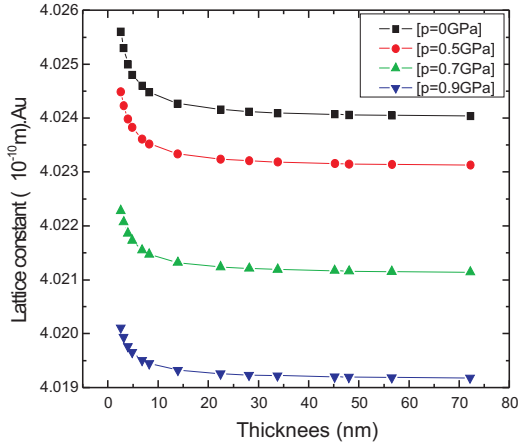


Fig. 2. Dependence on thickness of the lattice constant for Au thin film at $T = 300\text{K}$

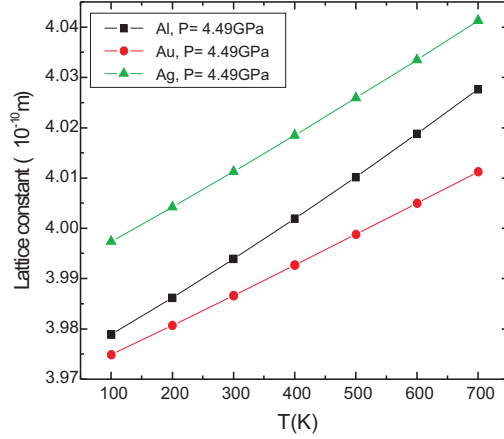


Fig. 3. Dependence on temperature of the lattice constant for Al, Au and Ag with thickness 50 layers

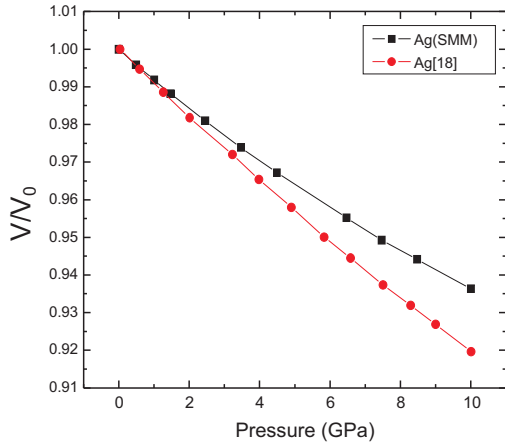


Fig. 4. Volume expansion (V/V_0) as a function of pressure P for Ag thin film

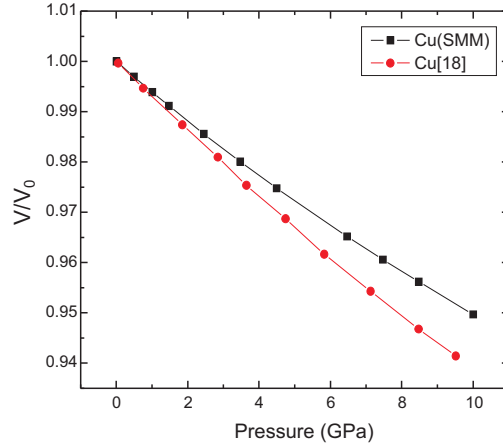


Fig. 5. Volume expansion (V/V_0) as a function of pressure P for Cu thin film

the thermal expansion coefficients increase with absolute temperature T with various pressure. Our calculation results have been compared with the results presented in [22] for Al thin film also as the same thickness 720 nm , and Al bulk [23] under zero pressure showing the excellent agreement. We realize that the thermal expansion coefficients of the thin film is smaller than that of the bulk. Furthermore, we also realize that the thermal expansion coefficients of metal thin films change with the fluctuation of absolute temperature and the pressure, when the pressure increases then the thermal expansion coefficients decrease. Results obtained from our calculations of the thermal expansion coefficients for Cu, Au and Ag thin films, they are decrease aslo with the increasing of pressure. On the other hand, when the thickness increases then the thermal expansion coefficients approach the bulk value in agreement with the results presented in [15, 24].

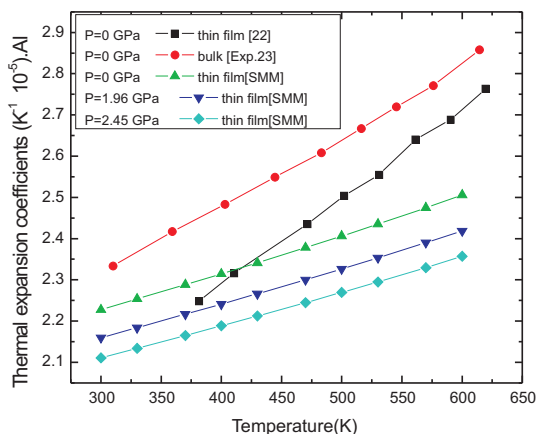


Fig. 6. Temperature dependence of the thermal expansion coefficients for Al

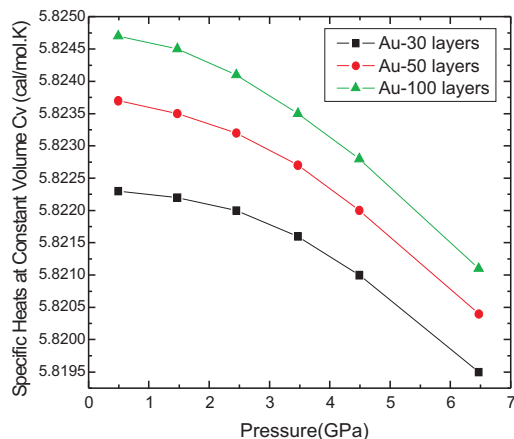


Fig. 7. Pressure dependence of specific heats at the constant volume of Au thin film

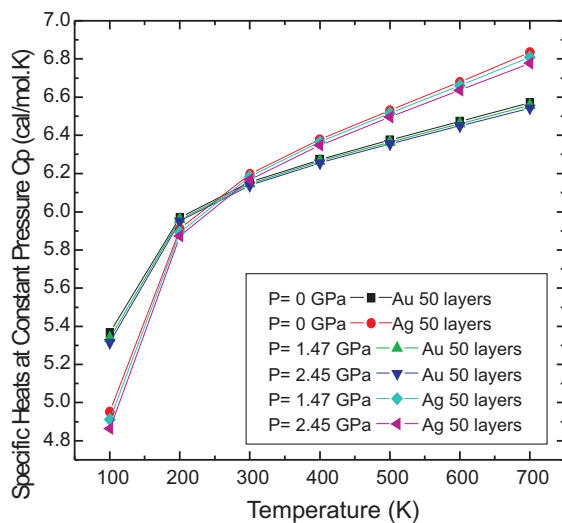


Fig. 8. Temperature dependence of specific heats at constant pressure of Au and Ag thin film

In Fig. 7, we present the pressure dependence of the specific heats at constant volume of Au metal thin film as a function of the pressure. The specific heats at constant volume decrease with the increasing of pressure. Let us consider with various thickness we also realize that the the specific heats at constant volume of metal thin film change with the fluctuation of pressure and the thickness, when the thickness increases then the specific heats at constant volume approach the bulk value in agreement with the results presented in [15, 24]. In Fig. 8, we present the temperature dependence of the specific heat at constant pressure with various pressure for the thickness 50 layer of Au and Ag metal thin films. When the pressure increases then the specific heats at constant pressure decrease, our calculation results have been compared with the results

presented in [15] at zero pressure showing in good agreement. The calculated results for the metal thin films with face-centered cubic structure as Cu and Al . . . also show temperature and pressure dependence of the specific heat at constant pressure is similar.

IV. CONCLUSIONS

The SMM calculations are performed by using the effective pair potential for the Au, Ag, Cu and Al metal thin films. The use of the simple potentials is due to the fact that the purpose of the present study is to gain a general understanding of the effects of the anharmonicity of the lattice vibration temperature and pressure on the thermodynamic properties for the FCC metal thin films.

In the present study, we have used effective pair potentials for metal thin films atoms to demonstrate the utility of the present theoretical scheme based on the moment method in the statistical dynamics. The method is simple and physically transparent, and thermodynamic quantities of metal thin films with FCC structures can be expressed in closed forms within the fourth order moment approximation of the atomic displacements. In general, we have obtained good agreement in the thermodynamic quantities between our theoretical calculations and other theoretical results, and experimental values.

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