Irreversible Processes in Nature and Technics

Equation of state and properties of fcc gold in macro and nano-sized state

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Abstract. An approach to studying the state equation and the thermodynamic properties of both a macrocrystal and a nanocrystal from a unified standpoint is proposed. The calculation of the state equation for gold showed good agreement with the experimental data. Graphs of pressure dependences were obtained for the following properties: bulk modulus, thermal expansion coefficient, isochoric and isobaric heat capacities, surface energy. An isobaric (at $P = 0$) size dependence of the distance between the centers of the nearest atoms and the melting temperature of a gold nanocrystal is obtained. It was shown that the size dependence of the melting temperature in the case of the isobaric conditions increases with the change in the nanocrystal size more rapidly compared with the isochoric conditions.

1. Introduction

Currently there are numerous investigations, both experimental and theoretical, devoted to the equation of state of gold [1-4]. However, the methods used to calculate the equation of state of a crystal at high pressures, both numerical (Monte Carlo, molecular dynamics) and analytical, contain in their formalism too many fitting constants that have no physical meaning. They are very difficult to recover from the experimental data, and predict their pressure dependence along a particular isotherm. This makes the results obtained by such methods inappropriate for further applications. In addition, these methods cannot be used to study the evolution of properties as the nanocrystal size decreases. To study the size dependencies, there are many both analytical and numerical methods [5-9]. However, most calculation methods do not clarify the conditions under which these size dependences were obtained: isochoric or isobaric process. In theoretical methods, due to the absence of the equation of state of a nanocrystal, the size dependences are calculated with the isochoric size reduction. But all experimental dependences are obtained for isobaric conditions.

Therefore, the present work utilizes an approach to investigate the equation of state and the thermodynamic properties of both macrocrystal and nanocrystal from a unified standpoint. Currently, this is the only approach that makes it possible to calculate both macroscopic and size properties of a substance within a single, relatively simple formalism.

Gold was chosen as the object of investigation because this metal does practically not oxidize, so it is well researched, both experimentally and theoretically. The technique can be tested in various conditions. In this regard, almost all known methods of calculating the size properties were tested on gold nanocrystals.

First we studied the properties of gold based on the method described in detail in [10] calculate both the equation of state of a macroscopic substance and the change in its lattice properties under...
various $P - T$ conditions, where $P$ is the pressure and $T$ is the temperature. Then the RP model from [11, 12] was used to study the change in the equation of state of a nanocrystal ($P$) as well as the isobaric (at $P = 0$) dependence of various properties, both on the size and on the surface shape of the gold nanocrystal.

2. Equation of state and baric properties of a macrocrystal

The gold crystal ($m$ (Au) = 196.967 a.m.u.) has a face-centered cubic structure (fcc), i.e. $k_B (N = \infty) = 12$, $k_B = 0.7405$. The pairwise interaction of gold atoms is represented in the form of the Mie-Lennard-Jones potential:

$$\phi(r) = \frac{D}{(b-a)} \left[ a \left( \frac{r_0}{r} \right)^b - b \left( \frac{r_0}{r} \right)^6 \right],$$

where $D$ and $r_0$ are the depth and the coordinate of the potential minimum, $b > a > 1$. The parameters of the Mie-Lennard-Jones pair interatomic potential for Au were defined as well as in [10], i.e. by fitting into the state equation $P(v/v_0, T = 300 \text{ K})$ and to the values of the thermal volumetric expansion coefficient $\alpha_p = [\partial \ln(v)/\partial T]_T$ and the bulk modulus $B_T = -[\partial P/\partial \ln(v)]_T$ at $T = 300 \text{ K}$ and $P = 0$ ($\alpha_p = 42.0 \cdot 10^{-5} \text{ K}^{-1}$ [13], $B_T = 166 \text{ GPa}$ [2]). Here, $v/v_0$ is the normalized value of the specific volume, $v_0 = (\pi/6k_B)r_0^3$. The following values were obtained by this method:

$$r_0 = 2.875 \cdot 10^{-10} \text{ m}, \quad a = 2.93, \quad b = 12.82, \quad D/k_B = 7411.5 \text{ K}.$$

Based on these values of the pair interatomic potential parameters, we calculated the lattice properties at $P = 0$: the Debye temperature ($\Theta$), the first, second and third Gruneisen parameters: $\gamma = [-\partial \ln(\Theta)/\partial \ln(v)]_T$, $\gamma_q = [-\partial \ln(\Theta)/\partial \ln(v)]_T$, $\gamma_z = [-\partial \ln(q)/\partial \ln(v)]_T$, the isothermal bulk modulus $B_T$ and its pressure derivative $B_T(P)$, volume expansion coefficient $\alpha_p$ and its pressure derivative $\alpha_p(P)$, the specific heat at constant volume and at constant pressure ($c_v = C_v/(Nk_B)$, $c_p = C_p/(Nk_B)$, where $k_B$ is the Boltzmann constant) and their pressure derivatives: $c_v'(P) = (\partial c_v/\partial P)_T$, $c_p'(P) = (\partial c_p/\partial P)_T$, specific (per unit area) surface energy of the face (100) $\sigma$ and its pressure and temperature derivatives $\sigma'(P) = (\partial \sigma/\partial P)_T$, $\sigma'(T) = (\partial \sigma/\partial T)_T$.

![Figure 1. Isotherms of the gold state equation. The solid curve – 300 K, the dashed curve – 1337 K.](image1)

![Figure 2. Pressure dependencies of the thermal expansion coefficient.](image2)

Figure 1 shows the isotherm of the equation of state for fcc Au. The solid curve represents our calculation performed for 300 K, dashed curve – for 1337 K. The symbols show experimental values:

- squares are from [1],
- open circles are from [2],
- crosses are from [3],
- triangles are from [4].

As seen in figure 1, our results are in good agreement with the results of other authors.

It should be noted that in [1] there are 10 fitting parameters, while in our model only $a$ and $b$ were fitted. In addition, the formalism that we use is much simpler than the formulas from [1].

Figure 2 shows the isotherms of the baric dependencies of the coefficient of thermal expansion of gold $(10^6 \text{ K}^{-1})$ for 300 K (solid curve) and 1337 K (dashed curve) in comparison with the data of other authors.
authors. Diamonds and circles are the theoretical calculations from [1] for 298 K and 1300 K correspondingly. Asterisks and triangles are the data from work [14] for 300 K and 1000 K correspondingly.

Figure 3 shows the isotherms of the pressure dependencies of $c_v = C_v/(Nk_B) = \text{isochoric (solid curve)}$ and $c_p = C_p/(Nk_B) = \text{isobaric (dashed curve)}$ specific heat capacities of gold. Diamonds and circles are calculated values from [1] for 298 K.

![Figure 3](image1.png)

**Figure 3.** The pressure dependences of the isochoric and isobaric specific heat capacities at 300 K.

Figure 4 shows the pressure dependences of the specific surface energy of the face (100) along two isotherms: 300 (solid curve) and 1337 K (dashed curve). As can be seen from the Figure 4, the dependence $\sigma(P)$ decreases with increasing temperature. These dependences can be useful in the study of thermodynamics and the kinetics of the formation of intergranular surfaces during crystal compression. There are no experimental or calculated data for gold $\sigma(P)$ in the literature. Therefore, there is nothing to compare the obtained dependencies with.

![Figure 4](image2.png)

**Figure 4.** Pressure dependences of the surface energy. The solid curve – 300 K, the dashed curve – 1337 K.

3. **Equation of state of a nanocrystal**

To determine the size dependencies we use a nanocrystal model in the form of a rectangular parallelepiped (RP-model). The shape of the model is varied using the shape parameter $f = N_{ps}/N_{po}$.

It is determined by the ratio of the atoms number on the side edge $N_{ps}$ to the atoms number on the base edge $N_{po}$ of the rectangular parallelepiped. Restricting the system by the surface will lead to the breakage of bonds on the border. Therefore, if the “only-nearest-neighbors interaction” approximation is used, then the value of the first coordination number $k_n$ will depend both on the size and the shape of a nanocrystal [11, 12]. The structure of a crystal is assumed to be unchanged: $k_p = \text{const}$, where $k_p$ is the packing coefficient. In terms of the RP model, the change in the normalized average value of the first coordination number with variations of $N$ and $f$ is determined according to [11, 12]:

$$k_n = \frac{k_p(N, f)}{k_p(x)} = 1 - Z_s(f) \left( \frac{\alpha}{N} \right)^{1/3},$$

where $k_p(\infty) = k_p(N=\infty)$ is the first coordination number for a macrocrystal, $\alpha = \pi/(6k_p)$ is the structure parameter. The function of the shape is determined as follows:

$$Z_s(f) = \frac{1 + 2f}{3f^{2/3}}.$$
Figure 5. The state equation of a macrocrystal (dashed line) and a nanocrystal (solid line) at 1337 K for a cubic shape.

Figure 6. The distance between the centers of the nearest atoms, normalized to the value for a macrocrystal at 1337 K.

Figure 5 shows the isothermal-isomorphous (at $T = 1337$ K, $f = 1$) dependence of the state equation on the normalized volume for the number of atoms $N = 11$ (i.e., $N_{po} = 2$) – solid curve, and $N = 14 \cdot 10^5$ (i.e., $N_{po} = 100$) – dashed curve. When the total number of atoms in a crystal is $14 \cdot 10^5$ or more, the size dependence disappears and the nanocrystal transforms into a macrocrystal. It can be seen that the smaller the number of atoms in the nanocrystal is, the more it stretches at $P = 0$. This is due to the presence of surface pressure in the system, which is determined by the difference $P_{macro} - P_{nano}$. Figure 5 shows that the state equation isotherms of the nanocrystal and the macrocrystal intersect at a certain point, so below this point the surface pressure will be compressive, and above this point it will stretch.

Figure 6 shows the size dependences of the distance between the centers of the nearest atoms, normalized to the value for a macrocrystal on $lg(N)$ for two shapes. The dependences are obtained at the melting temperature of a macrocrystal $T_m(Au) = 1337$ K. From the figure 6 it is clear that in order to maintain the isobaricity, we must increase the interatomic distance, because the surface pressure compresses the nanocrystal, and to achieve the condition $P = 0$, the nanocrystal will be stretched. This leads to a stronger dependence of the Debye temperature on the size than in the case of the isochoric process. Therefore, the calculated isobaric (at $P = 0$) dependence of the melting temperature of the nanocrystal on $N$ will be more noticeable than in the case of the isochoric process.

4. Size dependence of the melting and crystallization temperatures

The melting temperature was calculated by the formula obtained in [15], based on the Lindemann criterion:

$$T_m^* = \frac{T_m(N)}{T_m(\infty)} = \left( \frac{X_2(N) \Theta(N) c(N)}{X_2(\infty) \Theta(\infty) c(\infty)} \right)^{1/2} = (X_2^* \Theta^* c^*)^{1/2}.$$

Assuming that the Lindemann parameter $(X_2)$ does not depend on the size of the nanocrystal, we obtain $T_m^* = (\Theta^*)^{1/2}(c^*)^{1/2}$. Using the RP-model formalism, it is possible to calculate the dependence of $\Theta^*$ and $c^*$ on both the size and the shape of a nanocrystal of a simple substance, if the structure of the substance and the parameters of the interatomic potential are known.

The obtained isobaric dependence of the $T_m$ on $lg(N)$ is shown in figure 7 in comparison with the data provided by the other authors. Our isobars are calculated for two shapes of a nanocrystal ($f = 1$ and $f = 5$) in the isochoric ($c = r_0$) and isobaric ($P = 0$) processes.
As can be seen from figure 7, the size dependence is noticeably enhanced for transition from isochoric (dashed curve with open squares for \( f = 1, R = 1 \) and circles for \( f = 5, R = 1 \)) to isobaric (solid curve with closed squares for \( f = 1, P = 0 \) and circles for \( f = 5, P = 0 \)) process.

Symbols in figure 7 show theoretical estimates of other authors [6-9]. It can be seen that when the number of atoms in the system tends to infinity, the calculations of other authors deviate from the melting temperature of a macrocrystal that indicates low accuracy of their models at \( N = \infty \).

Dashed curve without symbols show the result of experimental studies of the gold melting temperature as function of size [5]. Our calculation of the distorted shape of a nanocrystal is closer to this curve than calculation of the optimal shape. This is due to the fact that the authors from [5] determined the dependence of \( T_m \) on the diameter of the nano-system, assuming that the nano-system has the shape of a sphere in both the liquid and solid state. Apparently, the shape of the nano-system deviated from the spherical one and an error appeared when expressed as the number of atoms.

The isobaric dependence of the \( T_m \) function on the \( N^{-1/3} \) argument for different shapes of a nanocrystal is shown in figure 8 for \( f > 1 \) and in figure 9 for \( f < 1 \). As figures 7–9 show, the \( T_m(N) \) dependence increases when a nanocrystal shape deviates from a cube. For the RP model, the \( T_m(N, P = 0) \) curves in figures 7–9 end at the minimum possible nanocrystal size: \( N_{cr} = 11 \) for the cube. The value of \( N_{cr} \) increases when the \( f \) value deviates from unity, i.e. at deformation of the cubic nanocrystal shape.

If we consider the end points of the melting temperature size dependence \( T_m(N_{cr}, P = 0) \) as the crystallization start points, then their approximation will give the dependence of the crystallization temperature \( (T_o) \) on the size, i.e. \( \text{MIN}[T_o(N_{cr}, P = 0)] = T_o(N, P = 0) \).

Figure 10 shows the approximation of the size dependence \( T_o(N^{-1/3}, P = 0) \) end points for plate-like and rod-like shapes that determines the crystallization start temperature: \( T_o(N^{-1/3}, P = 0) \). The symbols in figure 10 show the \( T_o(N^{-1/3}) \) estimates obtained in [7] by the Monte Carlo method. The extrapolation of the dependence \( T_o(N^{-1/3}, P = 0) \) on a macrocrystal (i.e. on \( N^{-1/3} = 0 \)) gave the value: \( T_o(N = \infty, P = 0) = 921 \) K (for rods) and 1146 K (for plates), as shown in figure 10. This agrees well with the Turnbull rule for the ratio of the crystallization start temperature to the melting temperature for a pure metal macrocrystal at \( P = 0 \): \( T_o / T_m = 0.7 - 0.867 \) [16], and also with estimates obtained using the classical nucleation theory: \( T_o / T_m = 0.76 - 0.83 \) [17].
5. Conclusion

Thus, we proposed a unique method to determine the parameters of the pair interatomic potential for fcc Au.

It was shown that using the correct functional dependence for the characteristic temperature $\Theta(V/V_0)$ and the self-consistently defined four parameters of the Mie-Lennard-Jones interatomic potential, both the equation of state and the baric dependence of the lattice properties of gold can be calculated using a relatively simple analytical model.

Graphs of baric dependences are obtained for the following properties: bulk modulus, coefficient of thermal expansion, heat capacities at constant volume and constant pressure, surface energy. The calculations performed along the isotherms of 300 K showed good agreement with the experimental data. For the gold, it is shown that as $P \to \infty$, the function $B_T(P)$ increases linearly. Therefore, as $P \to \infty$, the relation $B_T'(P) \to \text{const} > 0$ is satisfied. The function $\alpha_P(P)$ decreases as $P \to \infty$, tending to a constant. The function $\alpha_P'(P)$ tends to zero from the negative range of values.

It is shown that the pressure dependence of the surface energy $\sigma(P)$ with increasing pressure first increases to a maximum and then decreases sharply, transiting to the negative range at $P_{fr_{s}}$: $\sigma(P_{fr_{s}}) = 0$.

An isobaric (at $P = 0$) size dependence of the Debye temperature and the distance between the centers of the nearest atoms for an Au nanocrystal is obtained. The isobaric (at $P = 0$) size dependence $T_m(N)$ for an Au nanocrystal was calculated using the Lindemann criterion. The result is in better agreement with the experimental dependence from [5] than the calculated isochoric dependence.

It is shown that with decreasing of a nanocrystal size at $P = 0$, the distance between the centers of the nearest atom increases. This is due to the fact that the surface pressure compresses the nanocrystal with decreasing nanocrystal size, and in order to maintain the isobaric condition $P = 0$, we must increase the interatomic distance. In result the isobaric (at $P = 0$) size dependence of the Debye temperature decreases with the nanocrystal size more strongly than in the case of the isochoric process.

It is shown that the stronger the shape of the nanocrystal deviates from the most energetically optimal (for the RP model it is the shape of the cube), the more noticeable the isobaric (at $P = 0$) size dependence of the nanocrystal properties is.

It turned out that if we consider the end points of the size dependence of the melting temperature $T_m(N_{cr}, P = 0)$ as the crystallization start points, we can obtain the crystallization start temperature $T_{cr}$ dependence on the number of atoms in the nanodroplet from their dependence on $N$. The values obtained by this method for a macrocrystal coincided with the Turnbull rule.

If a drop is supercooled to $T < T_{min}$, then upon the transition to the solid phase a crystal structure will not be formed. The structure will be amorphous, i.e. have a melt structure. This is due to the fact...
that at $T < T_{\text{min}}$ crystal nuclei are not formed and solid nuclei will have a melt structure. The transition to the solid phase with $N < N_c = 11$ will be continuous.

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