XXXVI INTERNATIONAL CONFERENCE ON INTERACTION OF INTENSE ENERGY FLUXES WITH MATTER
MARCH 1-6, 2021, ELBRUS, KABARDINO-BALKARIA, RUSSIA

IIEFM 2021

Thermophysical properties of the phonon subsystem of gold in the region of the solid-liquid phase transition. Atomistic modeling.

V.I. Mazhukin, O.N. Koroleva, M.M. Demin, A.A. Aleksashkina
Keldysh Institute of Applied Mathematics of RAS, Russia

I. Introduction

Research in recent years has shown that gold nanoparticles exhibit excellent imitation of biological enzyme activity. Pulsed laser ablation (PLA) is one of the common methods for generating nanoparticles. The generation of gold nanoparticles by laser ablation is carried out in the temperature range where phase transitions play a decisive role: melting – crystallization, evaporation – condensation. Studies of the kinetics and dynamics of phase transformations are carried out by methods of mathematical modeling. PLA is accompanied by the phenomena of thermodynamic nonequilibrium, which leads to the need to consider the characteristics of two subsystems: electronic and phonon.

The article presents the results of atomistic modeling of the thermophysical properties of gold in the region of the solid-liquid phase transition. In the present work, we used the EAM potential for gold, developed and tested in [1]. The temperature dependences of the density, linear size of the sample, coefficient of linear expansion, enthalpy, and heat capacity are determined. The obtained dependences of the properties of gold are approximated by polynomials of low degrees. There is an acceptable agreement between the obtained characteristics of gold and the experimental data. Numerical and graphic information on the obtained properties and results of comparison with experimental data is presented.

[1] V.V. Zhakhovskii, N.A. Inogamov, Yu.V. Petrov, S.I. Ashitkov, K. Nishihara, "Molecular dynamics simulation of femtosecond ablation and spallation with different interatomic potentials", *Appl. Surf. Sci.,* 255, 9592-9596 (2009)

2.Equilibrium melting temperature of Au

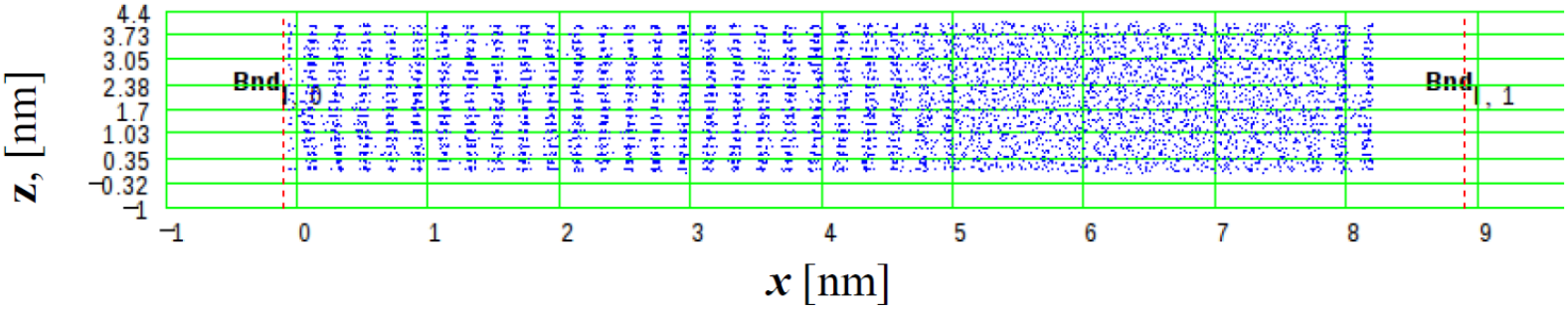

Fig: 1. Computational domain prepared for determining the melting point of gold.

The equilibrium melting temperature of gold T_m was determined within the framework of a computational experiment based on the simultaneous existence of solid and liquid phases in the computational domain. The computational domain was selected in the form of a parallelepiped with dimensions of 20×10×10 unit cells. In this case, half of the sample was presented in a solid crystalline form, and the other half was in the form of a liquid. Gold has a face-centered cubic lattice with a crystal lattice constant of 0.406 nm. The total number of particles in the given area was 8000. Periodic boundary conditions were set along all three axes. In this case, the temperature turned out to be equal to T_m = 1.332 kK. The reference value of the equilibrium melting point is T_m = 1.3334 kK [2]. Thus, the deviation of the obtained value from the reference value is 0.1%.

[2] Fizicheskie velichiny. Spravochnik. Red. I.S. Grigor`ev, E.Z. Melihov, Moskva, Energoatomizdat (1991)

3. Density of Au

The temperature dependence of density of gold in the temperature range 0.3 kK ≤ *T* ≤ 3.5 kK in this work was obtained from the MDM.

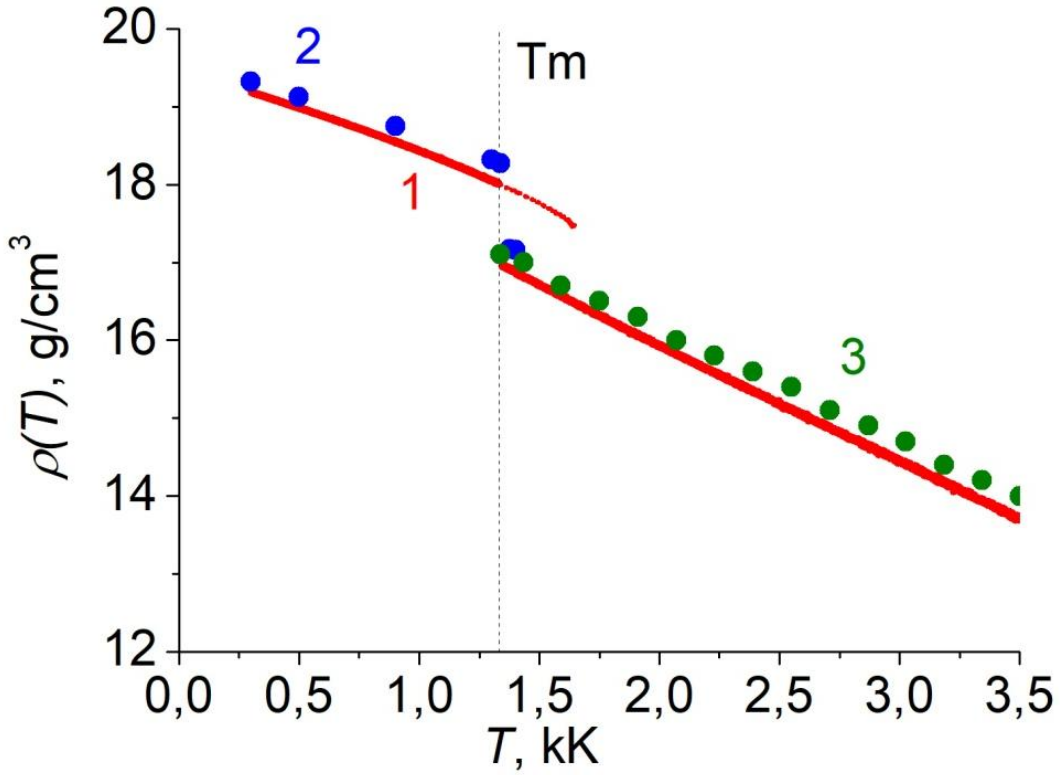

Fig. 2. Temperature dependence of Au density. (1) - results of MD calculations; (2), (3) - experimental data [3, 4].

[3] Zinoviev V.E. Teplofizicheskie svoi`stva metallov pri vysokikh temperaturakh // «Metallurgiia» (1989).

[4] G. Wilde, C. Mitsch, C.P. Gijrler, R. Willnecker. Specific heat and related thermodynamic functions of undercooled Cu-Ni and Au melts. Journal of Non-Crystalline Solids 205-207 (1996) 425-429

4. The sample linear size and coefficient of linear expansion

Figure 3 shows that L_{sol} (T) continues to increase upon overheating of the solid phase, which is $\Delta T \sim 1.24 T_m$. The increase in the linear size of the sample in the liquid phase at the equilibrium melting temperature $T = T_m$ in comparison with the solid state is 2.0%

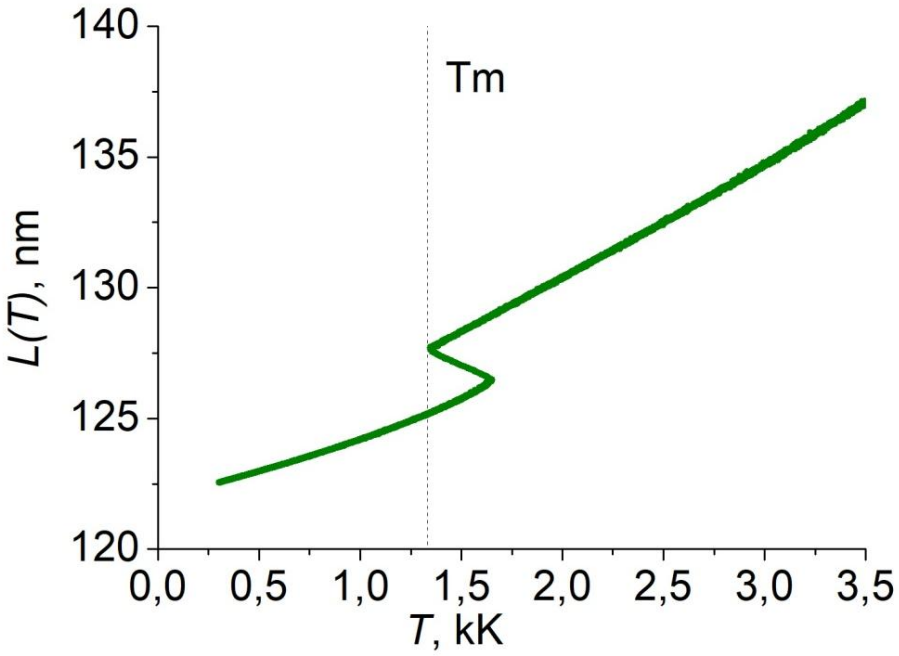

Fig. 3. Temperature dependence of the linear size of the gold sample according to the MDM results.

4. The sample linear size and coefficient of linear expansion

The temperature dependences $L(T)$ obtained from computational experiments were approximated by quadratic dependences for the solid and liquid phases. The coefficient of linear expansion $\alpha(T)$ at pressure P was calculated separately for the solid and liquid phases according to the relation

$$\alpha(T) = \frac{1}{\tilde{L}(T)} \left(\frac{\partial \tilde{L}(T)}{\partial T} \right)_P$$

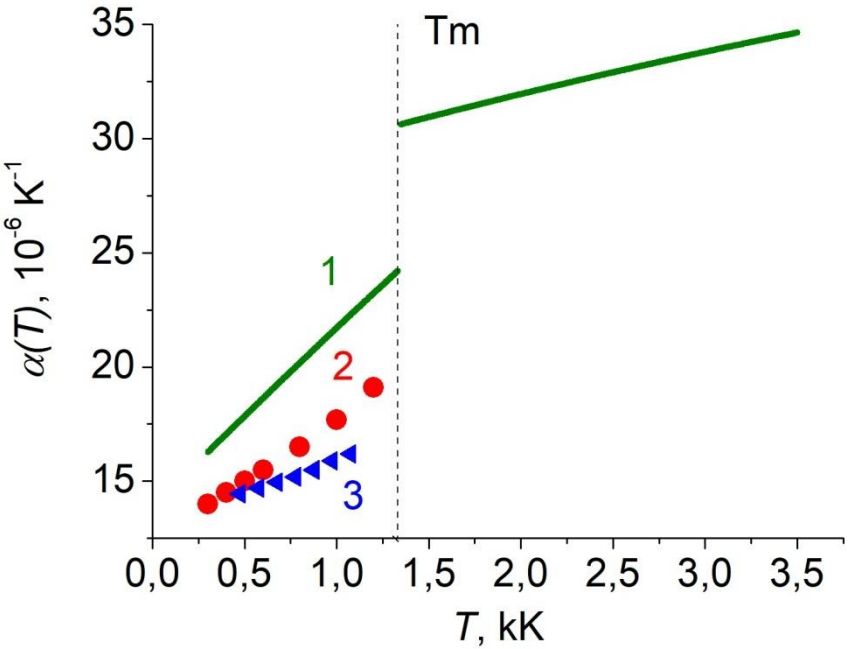

Fig. 4. Temperature dependence of the coefficient of linear expansion of Au. (1) - this work; (2) - experimental data [2]; (3) - experimental data [3].

5. Enthalpy and specific heat of Au

The temperature dependence of the enthalpy $H(T)$ was obtained as a result of MD calculations in the range 0.3 kK ≤ T ≤ 3.2 kK at constant pressure P. For better comparison with the experimental data, the results of MD calculations are presented by the values of the enthalpy increment $\Delta H(T) = H(T) - H(298°\ K)$.

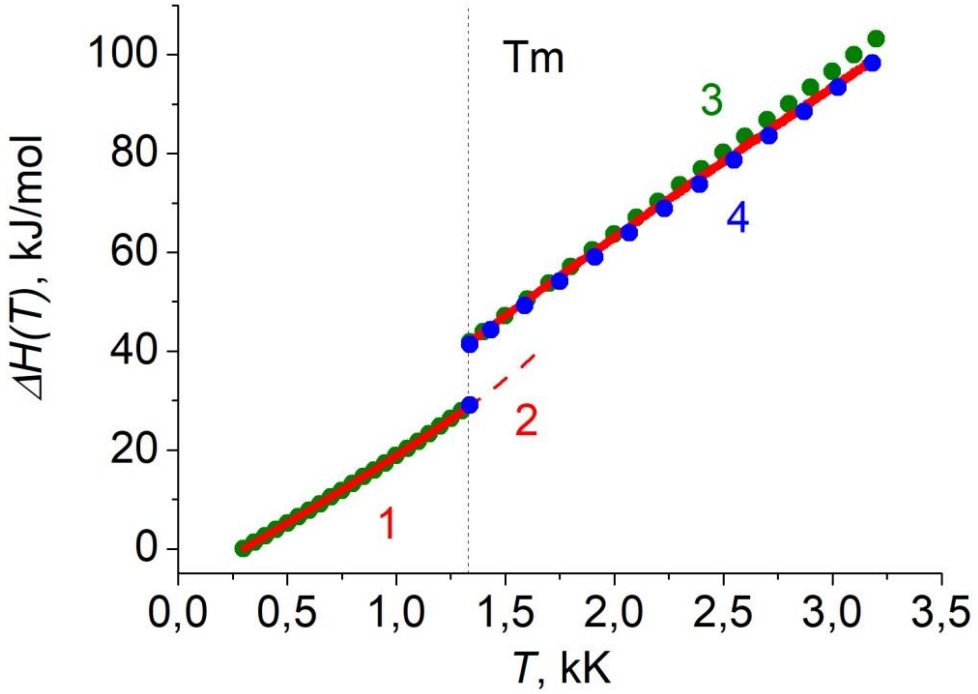

Fig. 5. Temperature dependence of the enthalpy increment Δ*H*(*T*): (1) - this work; (2) - when the solid phase is overheated; (3) - experimental data [5], (4) - experimental data [6]

[5] E. Kaschnitz, G. Pottlacher, and H. Jiiger. Microsecond-Resolution Measurements of the Thermophysical Properties of Liquid Gold. International Journal of Thermophysics, Vol. 14, No. 2, 1993

[6] J.W. Arblaster, Thermodynamic properties of gold, J. Phase Equilibria Diffusion 37 (2016) 229–245

5. Enthalpy and specific heat of Au

The temperature dependence of the lattice specific heat C_p(T) in the temperature range 0.3 kK ≤ T ≤ 3.2 kK at constant pressure P for each phase was determined by differentiating the corresponding dependence

$$C_p(T) = \left(\frac{\partial \tilde{H}(T)}{\partial T} \right)$$

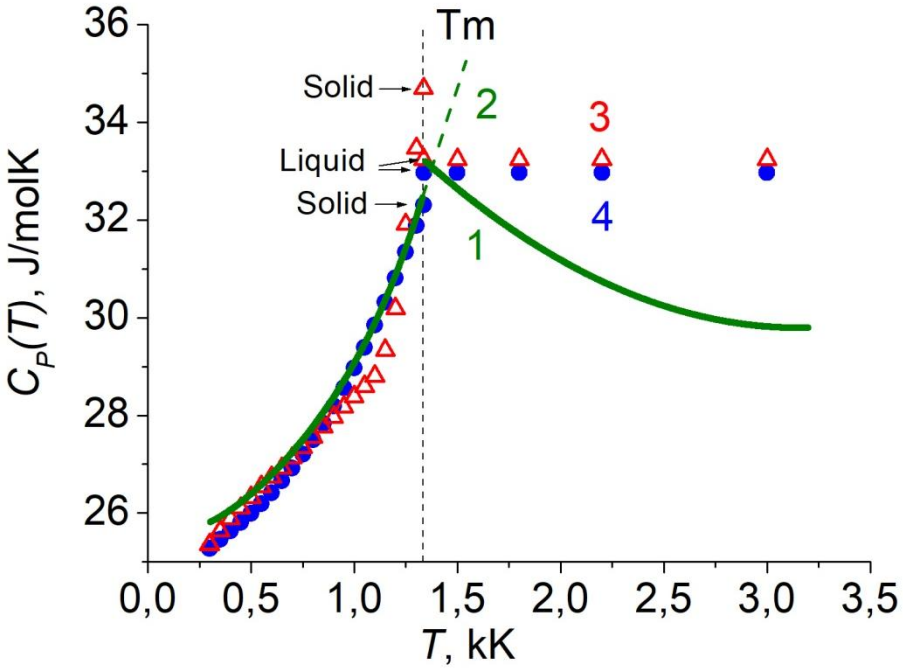

Fig. 6. Temperature dependence of the specific heat of gold (P = 0). (1) – specific heat according to the results of calculations; (2) - increase in specific heat capacity upon overheating of the solid phase (calculations); (3) - experimental data [7]; (4) - experimental data [6].

[7] J.W. Tester, R.C. Feber, C.C. Herrick, Calorimetric study of liquid gold, J. Chem. Eng. Data 13 (3) (1968) 419–421

6. Conclusion

As a result of molecular dynamics modeling in the range 0.3 kK ≤ T ≤ 3.2 kK, the temperature dependences with the transition through the melting point of such thermophysical characteristics of gold as phonon specific heat $C_p(T)$, linear expansion coefficient $\alpha(T)$, and density $\rho(T)$, were obtained. The equilibrium melting point of gold was obtained T_m = 1.332 kK at $P = 0$. The calculation results were approximated by polynomials of low degrees.

The determination of the equilibrium melting temperature of gold Tm was carried out within the framework of a computational experiment based on the simultaneous existence of two phases, solid and liquid, in the computational domain.

The temperature dependences of the density $\rho(T)$, specific heat $Cp(T)$, and the linear expansion coefficient of gold were determined from a series of molecular dynamics calculations within a single computational experiment.

The temperature dependence of the density of gold $\rho(T)$ was obtained in the range 0.3 kK ≤ T ≤ 3.2 kK. At the melting point, the density is calculated for two states of matter: solid and liquid. Based on the simulation results, the temperature range of overheating of the solid phase $T_m < T < 1.24T_m$ and the density values in this range were obtained. The results obtained show good agreement with the experimental results [3, 4].

6. Conclusion

The temperature dependence of the thermal expansion coefficient obtained from the MD calculations shows acceptable agreement with the experimental data [3]. At the solid-liquid phase transition, the thermal expansion coefficient increases abruptly by 26.5%.

The temperature dependence of the specific heat of gold $C_p(T)$ is obtained in the range $0.3\text{kK} \leq T \leq 3.2\text{kK}$. In the region of the solid-liquid phase transition at the equilibrium melting temperature T_m, there is a slight abrupt increase in the specific heat of gold, amounting to ~ 2.37% (according to the experimental data: [7] ~ - 4.46%, [6] ~ 2.046%,). In the temperature range of solid phase overheating $T_m < T < 1.24T_m$, the specific heat values are obtained. In the temperature range $T > 2.027T_m$ in the liquid phase, the specific heat is almost constant and amounts to $C_p(T) \approx 29.8$ J mol^{-1} K^{-1}, which shows good agreement with the results of [8].

Computational experiments carried out to determine the physical properties of gold show that the chosen potential [1] describes thermodynamic properties near the melting point with good accuracy.

[8] A.T. Dinsdale, SGTE data for pure substances, Calphad 15 (1991) 317–425.

XXXVI INTERNATIONAL CONFERENCE ON INTERACTION OF INTENSE ENERGY FLUXES WITH MATTER
MARCH 1-6, 2021, ELBRUS, KABARDINO-BALKARIA, RUSSIA

IIEFM 2021

THANK YOU FOR YOUR ATTENTION