

ATOMISTIC MODELING OF THERMOPHYSICAL PROPERTIES OF COPPER IN THE REGION OF THE MELTING POINT

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Summary. The method of molecular dynamics is used for calculation of thermodynamic properties of copper: pressure dependence of melting temperature and latent heat of melting and temperature dependence of specific heat, linear expansion and density. The obtained dependences are compared with experiment. The dependences found can be further used as inputs to the continuum model of pulsed laser heating of matter.

1 INTRODUCTION

Technological operations of metal processing are carried out in a wide temperature range (from 300K to (3-4) 10^3 K), in which phase transitions of the first kind play a decisive role (melting-crystallization, evaporation-condensation). The approach to the high-temperature region is associated with a strong change in the thermophysical properties of the materials being treated. Studies of the kinetics and dynamics of phase transformations are carried out mainly by methods of mathematical modeling [1]. When constructing the appropriate mathematical models, it is necessary to take into account the temperature and pressure dependences of the materials. However, at temperatures above the melting point T_m , experimental data are usually absent.

Mathematical modeling based on atomistic models has become an indispensable tool for obtaining fundamental knowledge about processes [2-4] and material properties [5,6]. The obtained knowledge is often used to develop mesoscopic [7] and macroscopic [8,9] models of continuous media, in which the characteristics of materials, determined from atomistic modeling, serve as input parameters [10].

The aim of this work is to obtain the properties of copper near the melting point from the molecular dynamics using the EAM potential [2]. The investigated properties for solid and liquid phase include the temperature dependence of specific heat $C_p(T)$, coefficient of thermal expansion $\alpha(T)$, and the density $\rho(T)$ and the pressure dependence of melting temperature $T_m(p)$ and latent heat of melting $L_m(p)$.

The dependence of the melting point on the pressure for copper was previously obtained experimentally [12-14] and using molecular dynamics simulation [15-18]. To calculate the melting point by the molecular dynamics method, several methods are usually used: single-phase [15], two-phase (coexistence of solid and liquid phases) [17,19], free energy calculation method [20,21], hysteresis method [22], z-method [16,23].

The calculations were carried out using the LAMMPS package [20].

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Key words and Phrases: molecular dynamics, copper, EAM potential.

2 STATEMENT OF THE PROBLEM

2.1 System of equations of molecular dynamics

Molecular-dynamic modeling is based on the representation of the object in the form of a set of particles, each of which is regarded as a material point. A certain volume is allocated in which the particles are located. For each of them the mass, the radius vector and the velocity are given, i.e. $m_i, \vec{r}_i, \vec{v}_i$, where $i = 1..N$, N is the total number of particles.

The motion of particles is due to their interaction with each other with forces $\vec{F}_i = -\frac{\partial U(\vec{r}_1 \dots \vec{r}_N)}{\partial \vec{r}_i}$, and with the external field \vec{F}_i^{ext} . The function $U(\vec{r}_1, \dots, \vec{r}_N)$ describes the potential energy of the system. The interaction of the particles with each other and external fields is described by the Newton equations which is a set of $2N$ ordinary differential equations

$$\begin{cases} m_i \frac{d\vec{v}_i}{dt} = \vec{F}_i + F_i^{ext} \\ \frac{d\vec{r}_i}{dt} = \vec{v}_i \end{cases}, \quad i = 1 \dots N \quad (1)$$

To solve it, it is necessary to set the initial conditions.

2.2 Initial conditions

The peculiarity of setting the initial conditions in molecular dynamics is the formation, at the initial stage of the calculations, of the state of thermodynamic equilibrium for the entire ensemble of the particles.

The coordinates of the particles are given at lattice sites in accordance with the type of crystal lattice. The lattice constant a is used to determine them. The temperature dependence of the lattice constant a_T is determined from the virial theorem:

$$\frac{1}{2} \sum_{j=1}^N r_{0j} \frac{\partial u(r_{01} \dots r_{0j} \dots r_{0N})}{\partial r_{0j}} = 3k_B T, \quad r_{0j} = a_T \tilde{r}_{0j}, \quad (2)$$

where $\tilde{r}_{0j} = \sqrt{\tilde{x}_{0j}^2 + \tilde{y}_{0j}^2 + \tilde{z}_{0j}^2}$ is the distance from the coordinate origin to the particle j in the lattice site, k_B is the Boltzmann constant. The obtained value of a_T is underestimated since it does not consider deviations of the coordinates of the particles from the equilibrium positions. The refinement is performed by constructing an unperturbed crystal lattice with period a_T together with an increase in the kinetic energy of the ensemble of the particles. To achieve that, the particle velocities are given as random variables with the Maxwell distribution at the temperature $2T$, where T is the desired average initial temperature.

The obtained model corresponds to the fact that in the system all atoms are at lattice sites and have velocities corresponding to thermodynamic equilibrium. The entire energy of the

system consists only of the kinetic energy, so before the start of the computational experiments it is necessary to equilibrate the modeled object, at which part of the kinetic energy goes into the potential one and then practically does not change, the temperature of the object becomes equal to T .

Application of the corresponding relaxation procedure to the simulated ensemble of particles allows for a sufficiently short time to equalize the thermal and potential energy.

2.3 Boundary conditions

Since the system is sufficiently large, the periodic boundary conditions are set to accelerate the calculations, depending on the situation in two or three directions. In this paper we use periodic boundary conditions in all three directions. When we take a parallelepiped with dimensions a, b, c along the axes Ox, Oy, Oz respectively as a simulated object, we note special features of the formulation of the boundary conditions for the ODE system. When the periodic boundary conditions are set along Ox , that means that a particle leaving the domain through the right boundary is replaced with a particle with the same velocity but entering the domain through the left boundary. Thus the coordinate of the particle is changed in the following way: $x' = (x - a) \in [0, a)$, for $x' \in [a, 2a)$, where x' is the new coordinate, x is the old coordinate. At that, other coordinates and velocity does not change. Similar procedure is applied to the particles exiting through the left border of the domain.

Further the system of differential equations is solved using the Verlet scheme [25]. In this method, the particle coordinates are calculated on integer time layers, and the velocities on half-integer ones.

For the account of the interatomic interaction we used a semi-empirical EAM (embedded atom method) potential for copper from ref. [2]. The temperature and pressure were controlled by the thermostat [26] and barostat of Berendsen [27].

3 MODELING AND ANALYSIS OF RESULTS

In recent decades, molecular dynamics modeling has been used to determine the basic equilibrium [28-31] and nonequilibrium [32,33] properties of the solid-liquid interface. Melting / crystallization refers to phase transitions of the first kind and represents the process of transition of matter from a solid crystalline state to liquid and back with absorption / release of heat. The main properties of melting/crystallization is the melting temperature T_m and latent heat of melting L_m . The presence of a certain melting point is a sign of the crystalline structure of the solid phase. On this basis, crystalline substances easily differ from amorphous solids, which do not have a fixed melting point. The transition of amorphous solids to the liquid state occurs gradually over a certain temperature range. The both melting properties (temperature and latent heat) depend on the external pressure p : $T_m = T_m(p)$, $L_m = L_m(p)$. For pure substances, these dependences are curves of the coexistence of the solid and liquid phases.

3.1 Calculation of equilibrium melting temperature T_m

The equilibrium melting temperature was calculated using the method of coexistence of solid and liquid phases [19], according to which a region in the form of a parallelepiped is

first selected, with dimensions $20 \times 10 \times 10$ elementary cells, Fig. 1. In this case, half of the sample is presented in a solid crystalline form, and the other half in the form of a liquid. The copper has a face-centered cubic lattice, so there are 8,000 particles in this region. Periodic boundary conditions are set for all three axes. The time step was set to 2 fs.

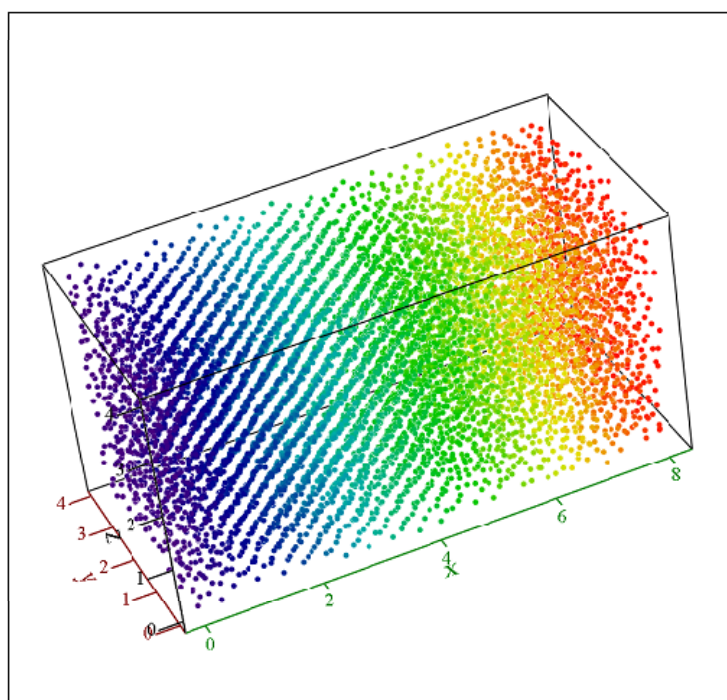


Figure 1. The sample for calculating the equilibrium melting point.

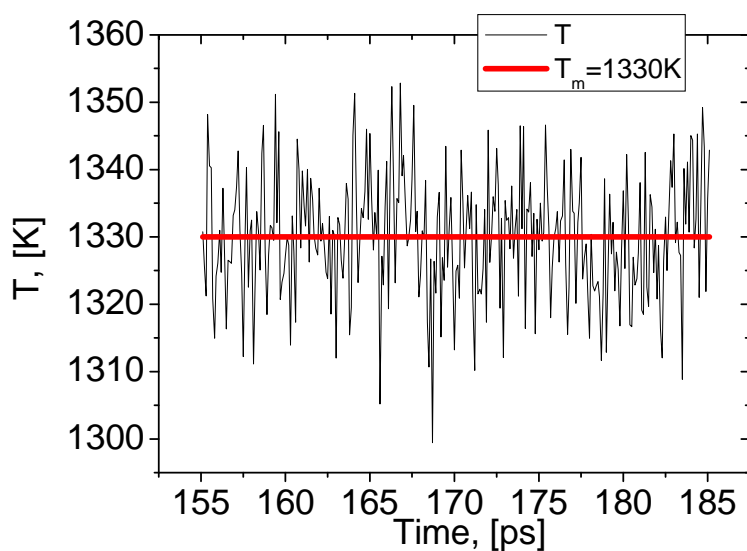


Figure 2. Determination of the melting point of copper

The establishment of thermodynamic equilibrium is carried out by means of the equilibration procedure. The particles are equilibrated at a certain temperature. To achieve equilibration at $T_0=300\text{K}$, the initial particle velocities are set corresponding to the Maxwell distribution at the temperature $2T_0=600\text{K}$. Molecular dynamic calculations are carried out at zero pressure, which is provided by Berendsen's barostat. After a few picoseconds, the equilibrium temperature of the sample is equal to 300K as a result of the redistribution of the initial kinetic energy, partially to the kinetic energy and partly to the potential one. Note that the relaxation methods used to establish equilibrium often require a time period, the duration of which may exceed the duration of the main simulation.

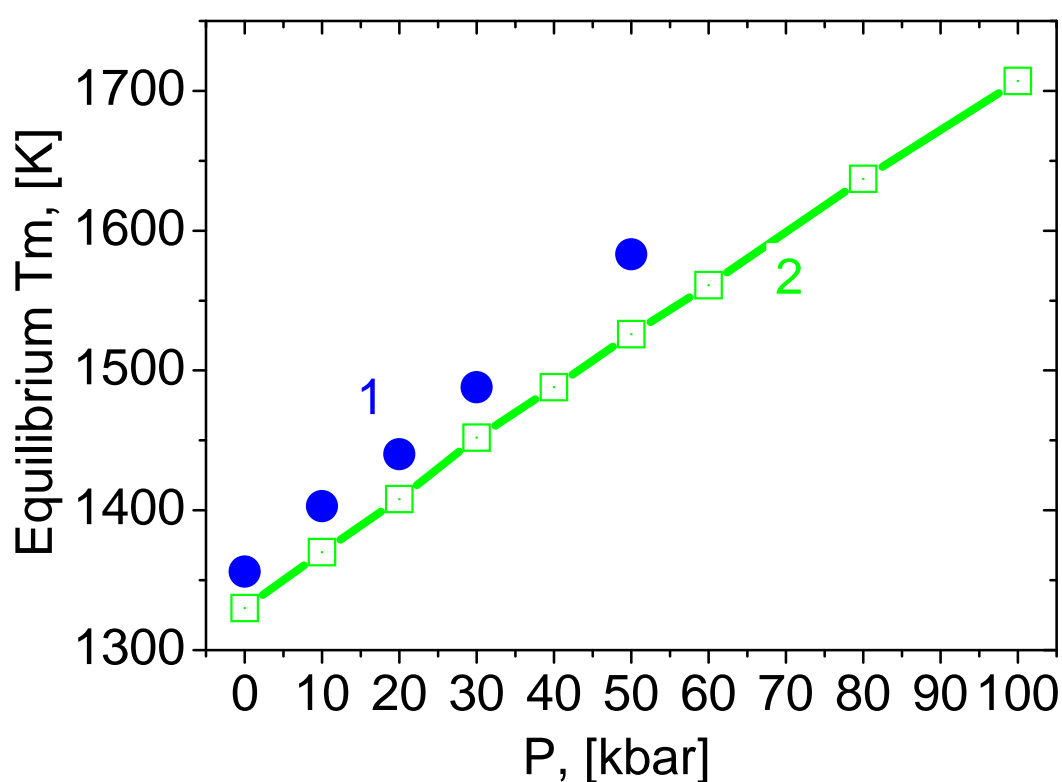


Figure 3. Pressure dependence of the equilibrium melting temperature of copper. 1- experiment, 2- modeling.

To determine the melting temperature T_m , several simulations of heating and melting of the sample are carried out to find the approximate temperature range where the sought value is located. Then the whole sample is heated to the temperature slightly below the melting temperature, 1325K . After that, one half of the sample is held at this temperature using a thermostat and the other is heated to 2200K . At this temperature, one can observe that, on the one side the crystal lattice of copper is visible, and on another side there is a chaotic arrangement of the molecules, which corresponds to the substance in the liquid phase. Also, the phase state can be monitored using the order parameter.

Then the heated part is cooled with a thermostat to a temperature of 1325 K. All this time the barostat is maintained at zero pressure. Then a relaxation calculation is initiated with the thermostat turned off at this temperature, and then the barostat is also turned off, and the calculation continues until phase equilibrium is established. At first, the sample will begin to crystallize slightly, and will therefore heat up. As soon as the phase equilibrium comes, the temperature will fluctuate near the equilibrium melting temperature, Fig. 2. In this case, the temperature was 1330K.

The reference value of the equilibrium melting temperature is 1356 K [34], i.e. the value obtained by modeling differs by 1.9% from the experimental one.

Then, the melting temperature was calculated in a similar manner as a function of the pressure, Fig. 3. In each calculation, the required pressure is set by the barostat. The studies were carried out in the range of values from 0 to 100 kbar.

Fig.3 shows pressure dependencies of $T_m(p)$, the simulated one (curve 2, $p=0-100$ kbar) and experimental one (curve 1, $p=0-50$ kbar). Comparison showed that the difference between dependencies 1 and 2 does not exceed several percent. The theoretical dependence of Z is approximated with sufficient accuracy by a linear function

$$T_m(p) = (3,775 * p[kbar] + 1330)[K]$$

The obtained results also indicate that the chosen potential [11] describes well the pressure dependence of the equilibrium melting point of copper.

3.2 Calculation of latent heat of melting

The specific heat of melting was calculated as the difference between the enthalpies of the solid and liquid parts at the same temperature and pressure. For calculation, two regions are taken, each of them has the form of a cube, the dimensions are $15*15*15$ elementary cells. Thus, in each region contains 13,500 particles and periodic boundary conditions are used in the calculations.

First, the sample is prepared at 300 K and zero pressure. Then it is heated by means of a thermostat (with the barostat turned on) to the melting point at zero pressure of 1330 K, and a relaxation calculation is performed with the barostat turned on, and the enthalpy of the system is calculated. The enthalpy oscillates around the mean value. Hence, the average value of the enthalpy of a solid is determined.

Then a sample with an initial temperature of 300 K is heated to 2200 K until a complete melt of the sample is achieved. The resulting liquid is cooled to a melting point of 1330 K. Then the relaxation calculation is started, the enthalpy of the system is calculated at each time, its average value is found.

Latent heat of melting will be equal to the difference in enthalpy for a solid and liquid, Fig. 4. The latent heat value at a zero pressure of 13010 J / mole is known from the experiment [34]. With the help of simulation at zero pressure, the value 11872 J / mol was obtained. The values differ by 8.7%, which indicates the adequacy of the potential used to determine the heat of melting.

The pressure dependence of the latent heat of melting, Fig. 4, was calculated according to the same scheme for other pressure values specified by the barostat. With the help of MD simulation, a linear dependence was constructed

$$L_m(p) = (25,83 * p[kbar] + 11872)[J / mole]$$

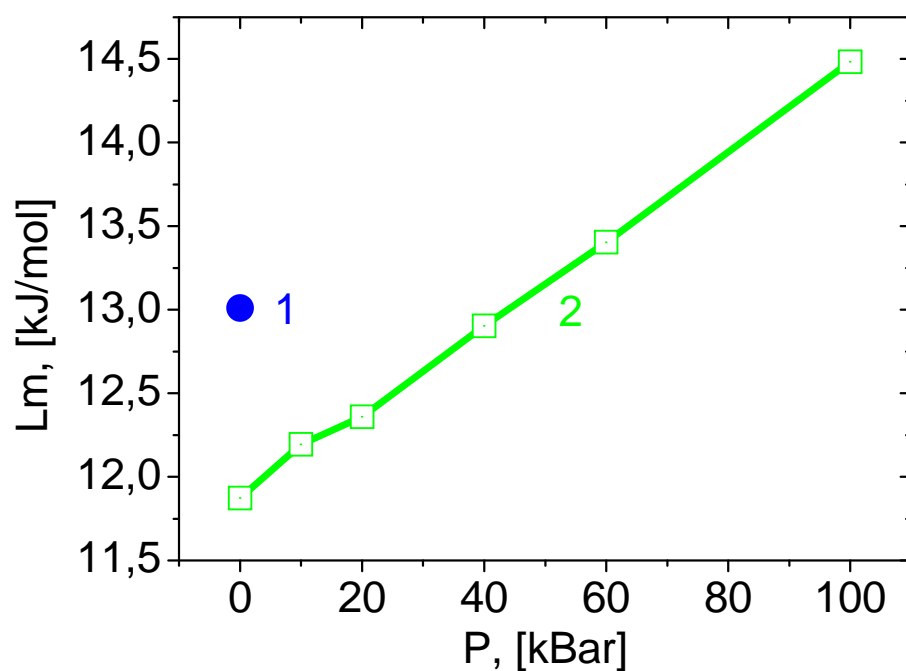


Figure 4. Pressure dependence of the latent melting heat of copper. 1- experiment, 2- modeling.

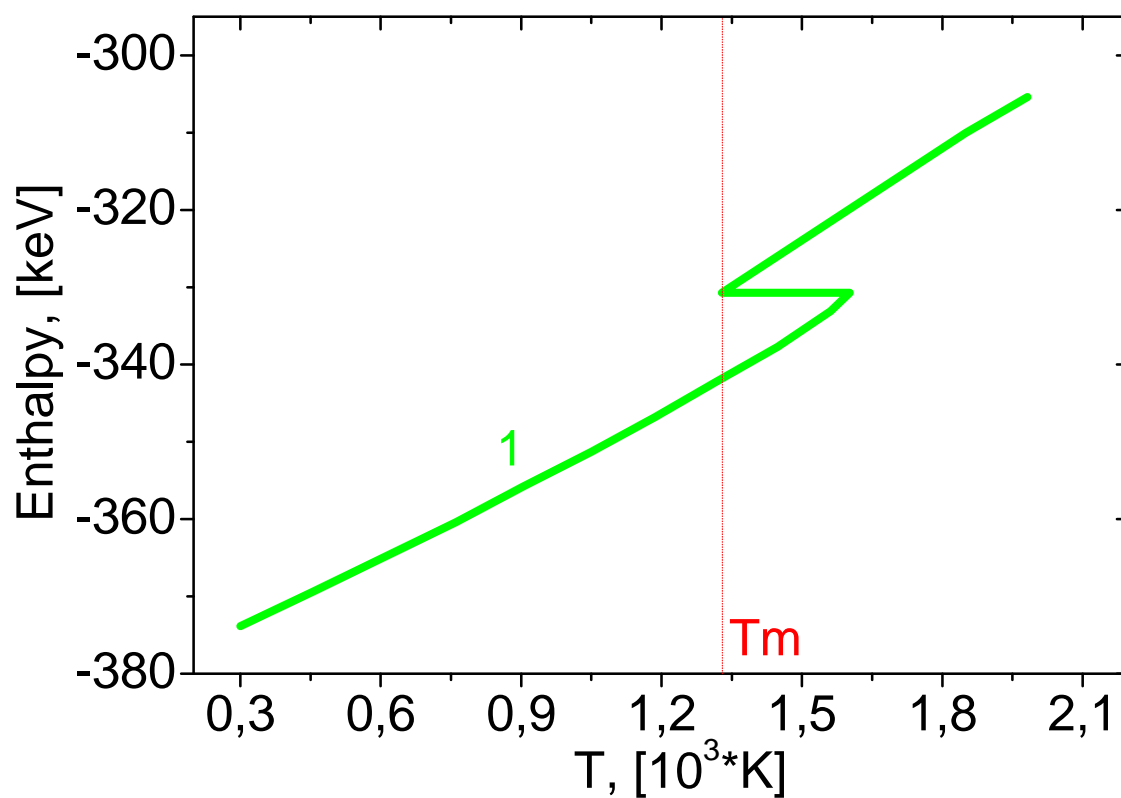


Figure 5. The temperature dependence of enthalpy.

3.3 Calculation of specific heat, linear expansion and density

Calculation of the specific heat, linear expansion and density is performed in the same computational experiment. The region is in the form of a cube, but larger than before, 30*30*30 elementary cells, which corresponds to 108,000 particles (with smaller dimensions, very large fluctuations arise). The equilibration of the sample is performed at 300 K and zero pressure.

Then the sample is heated very slowly at a constant heating rate. The heating rate is set to approximately 0.5 K/ps. Heating continues to the temperature of 2000K, since it is necessary that the entire sample is melted. When heated, the enthalpy is calculated (it is used to calculate the heat capacity later) as well as the linear dimensions of the region and the density.

On the graph of the enthalpy's dependence on temperature, Fig. 5, a jump is seen showing that at this temperature (the equilibrium melting point) the solid melts, and then the sample becomes a liquid.

The curves relating to the solid phase and liquid are separately approximated by polynomials, and then each of them is differentiated in temperature. Thus, we obtain a plot of the heat capacity versus temperature, Fig. 6.

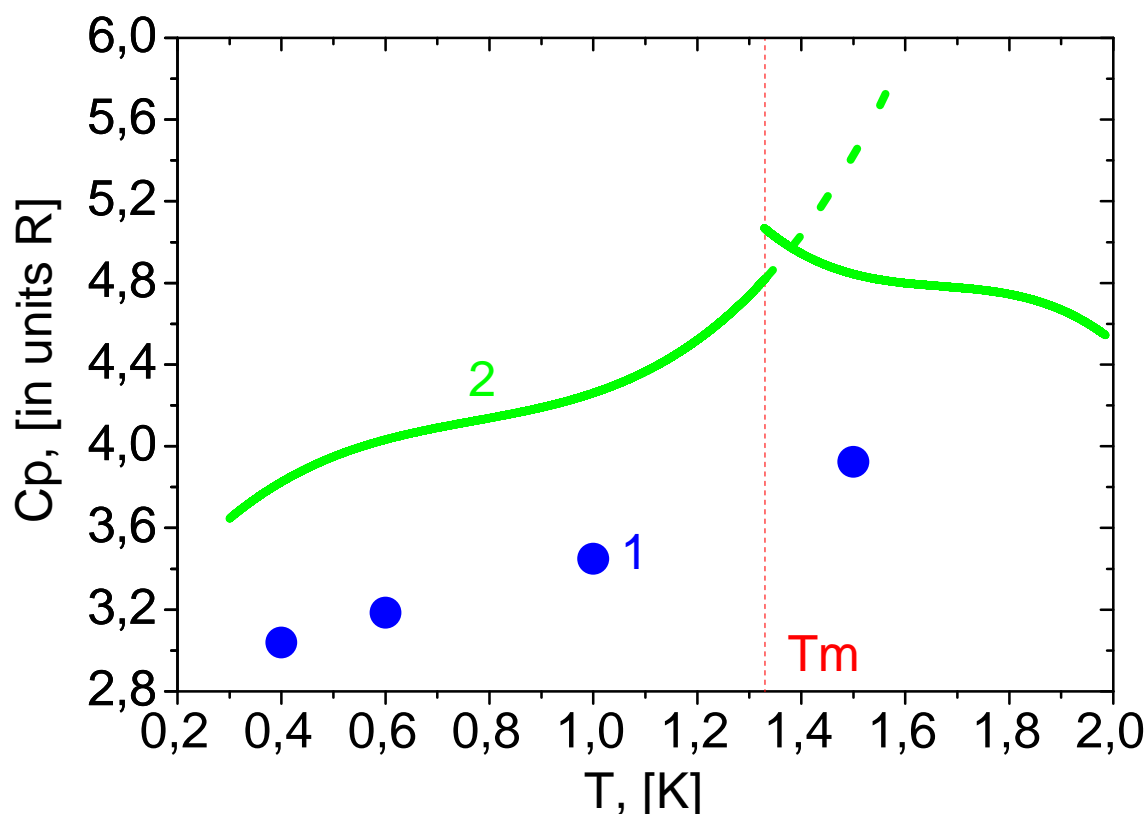


Figure 6. Temperature dependence of the specific heat at zero pressure. 1- experiment, 2- modeling

We obtained the following analytical expressions after approximation with polynomials, $C_p(T) = R(B_0 + B_1 * T + B_2 * T^2 + B_3 * T^3)_{s,l}$, where indexes s,l define solid and liquid phases, $R = 8,3145 J / (mole * K)$

	solid	liquid
$T_{min}, [K]$	300	1330
$T_{max}, [K]$	1330	2000
B_0	19,51313	229,46019
B_1	0,03626	0,034592
B_2	-4,25805E-5	2,06516E-4
B_3	1,8412E-8	-4,12756E-8

Table 1. Approximation parameters for specific heat

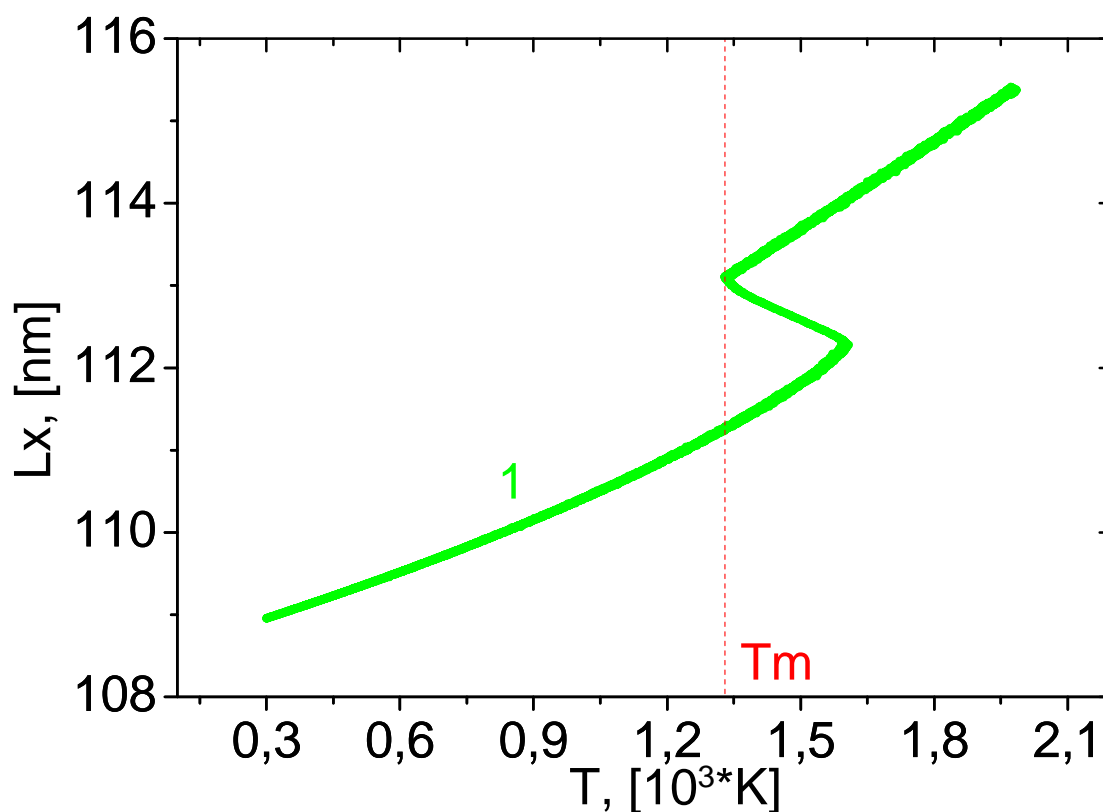


Figure 7. Temperature dependence of the sample size. 1-modeling.

Similarly, in the plot of the size of the region versus temperature, Fig. 7, a jump is seen that separates the solid and liquid. The curve relating to the solid phase is approximated by

polynomials and is differentiated in temperature. Then we obtain a graph of the linear expansion and compare it with experiment [34], Fig. 8.

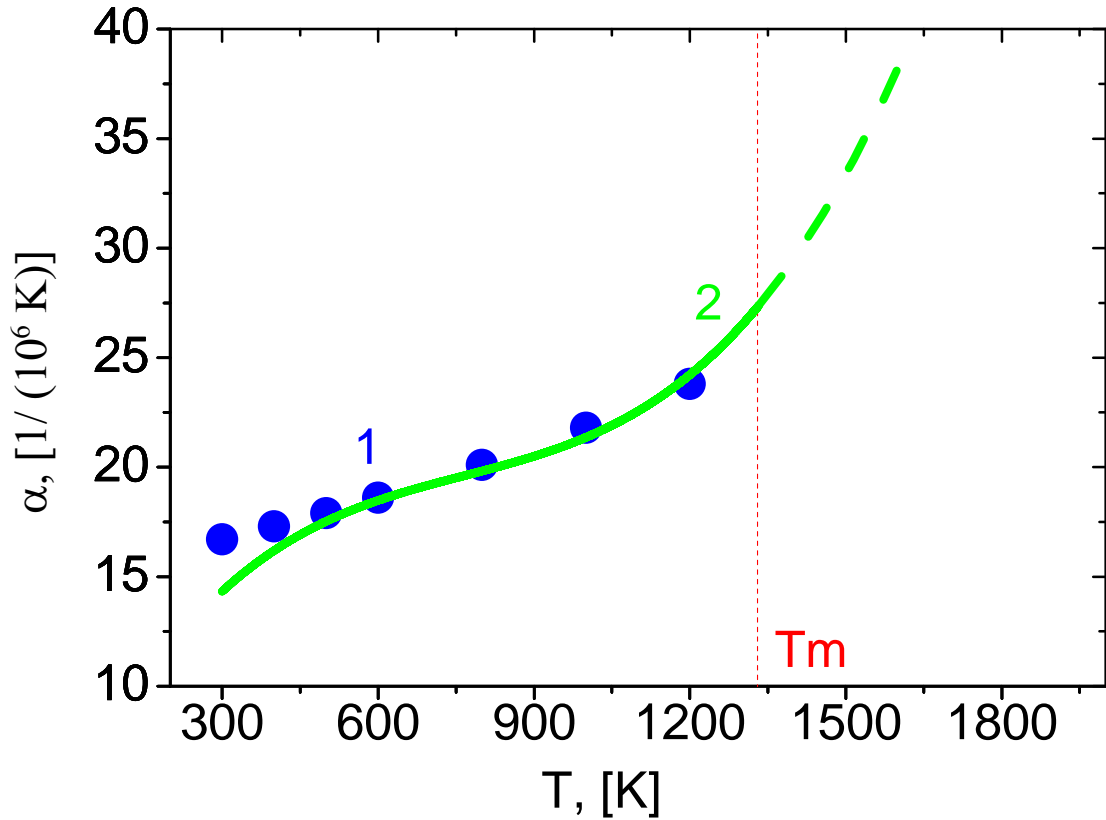


Figure 8. Temperature dependence of the linear expansion 1- experiment, 2- modeling

An analytical dependence can be written in the following form:

$$\alpha(T) = (B_0 + B_1 * T + B_2 * T^2 + B_3 * T^3) * 10^{-6} [K^{-1}]$$

$T_{\min}, [K]$	300
$T_{\max}, [K]$	1330
B_0	4,26131
B_1	0,04772
B_2	-5,41783E-5
B_3	2,35575E-8

Table 2. Approximation parameters for the coefficient of linear expansion.

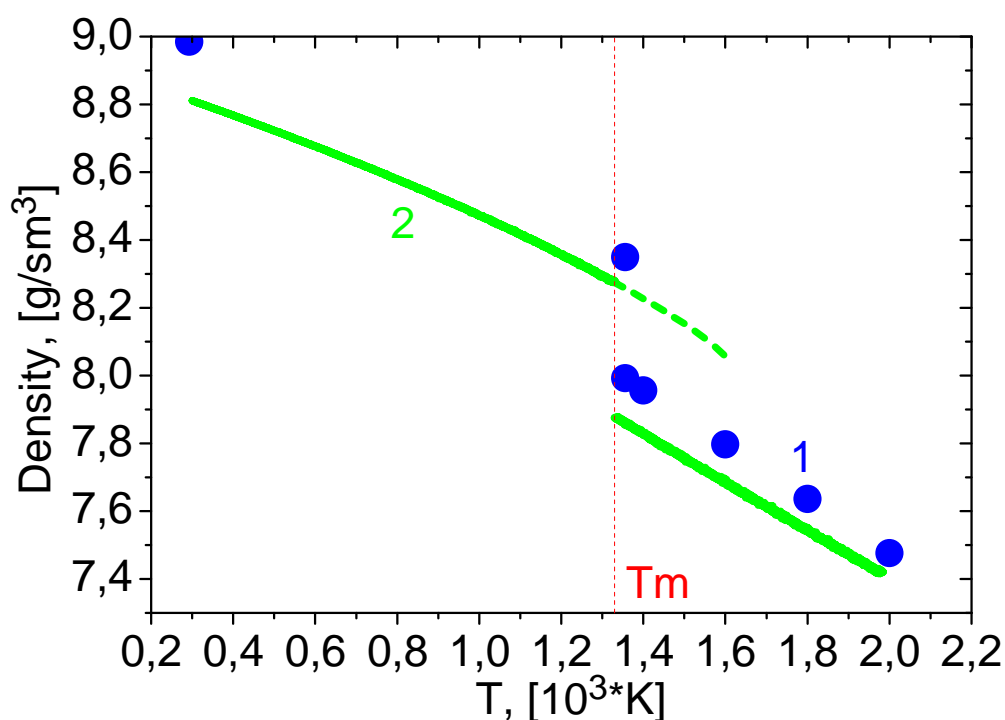


Figure 9. Temperature dependence of density. 1- experiment, 2- modeling.

The obtained temperature dependence is plotted at Fig. 9. One can see a jump separating solid and liquid. The difference of the values at the jump is about 5%. The difference in the experimental values [35] is 4,45%. After approximation of the obtained plot with polynomials one can obtain the following dependence: $\rho(T) = (B_0 + B_1 * T + B_2 * T^2 + B_3 * T^3)[g / cm^3]$

	solid	liquid
$T_{\min}, [K]$	300	1330
$T_{\max}, [K]$	1330	2000
B_0	8,94034	8,86038
B_1	-4,26695E-4	-7,37846E-4
B_2	4,23326E-9	-9,11223E-9
B_3	-4,47909E-11	6,92571E-12

Table 3. Approximation parameters for density.

4 CONCLUSION

As a result of molecular dynamic modeling, pressure dependences of such thermophysical characteristics of copper as equilibrium melting temperature and latent heat of melting as well as temperature dependences, with the transition through the melting point, of the specific heat $C_p(T)$, linear expansion coefficient $\alpha(T)$, and density $\rho(T)$ we determined.

The experiments carried out to determine the physical properties of copper show that the selected potential describes with good accuracy the thermodynamic properties of copper in the vicinity of the melting point. The order of accuracy for the equilibrium melting point is 3.7%; for specific heat 9.5%; for the coefficient of linear expansion of 16.6%; for a density of 2%.

Despite the fact that all the discussions in this paper are related to Cu, it can be hoped that a similar approach to simulating thermophysical properties can also be extended to most other metals.

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