

Calculation of the Thermodynamic Properties of Copper by Molecular Dynamics Simulation

O. V. Stepanyuk, D. B. Alekseev, and A. M. Saletskii

Department of General Physics, Faculty of Physics, Moscow State University, Moscow, 119991 Russia
e-mail: sam@phys.msu.ru

Abstract—It is shown that the thermodynamic characteristics of a system can be accurately described using many-body potentials of the interatomic interaction in molecular dynamics calculations.

Key words: molecular dynamics, thermodynamics, thermal, heat capacity, Cu.

DOI: 10.3103/S0027134909020271

There is much interest in using computer simulation of the physical properties of condensed matter for the fundamental and applied study of novel materials. The method of molecular dynamics (MD) is one of the most important approaches to the realistic description and prediction of the properties of large and small atomic systems [1]. The success in this direction is determined, to a great extent, by the possibility of the description of the interatomic interaction in a system [2]. Numerical calculation of the thermodynamic (TD) properties of condensed matter is of the most interest. In recent years, a number of interesting studies on simulation of the TD properties of clusters [3], nanowires [3, 4, and 5] and bulk materials [5, 6] have appeared.

Along with the problem of realistic description of the interatomic interactions, there are additional difficulties of high-accuracy determination of temperature fluctuations of such characteristics as total energy, mean-square atomic displacements, and free energy. In this study, we present an effective method of calculation of the TD characteristics on the basis of the MD simulation.

The interatomic interactions are described by the semiempirical potentials obtained by the tight-binding method [7]. In this approximation, the total energy of the system is a sum of two terms, which are the potential E_B^i describing interatomic attraction and the potential E_R^i describing interatomic repulsion:

$$E = \sum_i (E_R^i + E_B^i), \quad (1)$$

$$E_B^i = \left(\sum_j \xi_{\alpha\beta}^2 \exp[-2q_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta} - 1)] \right)^{1/2}, \quad (2)$$

$$E_R^i = \sum_j A_{\alpha\beta} [-P_{\alpha\beta}(r_{ij}/r_0^{\alpha\beta} - 1)], \quad (3)$$

where r_{ij} is the distance between the i -th and j -th atoms. The parameters from (2) and (3) are determined by fitting to the properties of a material (lattice parameter, modulus of elasticity, elastic constants, and cohesion energy) obtained experimentally. This approach and the potential parameters are described in detail in [7].

The key point of finding the TD characteristics is determination of the state function (partition sum Z) [8]:

$$Z = \frac{1}{h^{3N} N!} \int \exp\left(-\frac{H(p, q, T)}{kT}\right) d\Gamma, \quad (4)$$

where $H(p, q, T) = \sum_{i=1}^N \frac{p_i^2}{2m} + E(q_1, q_2, \dots, q_N)$ is the classical function of the Hamiltonian of the system, $d\Gamma = d^{3N}p d^{3N}q$ is the phase volume element ($d^{3N}p = \prod_{i=1}^N dp_{xi} dp_{yi} dp_{zi}$ and $d^{3N}q = \prod_{i=1}^N dx_i dy_i dz_i$), h is the Planck's constant, and k is the Boltzmann constant. In this study, we propose to calculate integral (4) using the MD method. The main idea of the calculation is to conduct a system of N atoms with temperature T consecutively through the points of a $6N$ -dimensional phase space. Total energy value $H(q_1, \dots, q_N, p_1, \dots, p_N)$ obtained in each point of the phase space ($q_1, \dots, q_N, p_1, \dots, p_N$) is used in calculation of integral (4).

Note that due to the huge number of elementary volumes in the phase space the system of N atoms cannot be conducted through all of its points. However, the following statement is valid: if integral (4) is calculated over a certain (sufficiently large) settled number of MD steps (or, in other words, if the system has been conducted through a sufficiently large number of elementary volumes in the phase space), then $Z_f = M\Delta VZ/V$, where Z_f is the calculated value of integral (4), V is the total volume of the system, and ΔV is the value of ele-

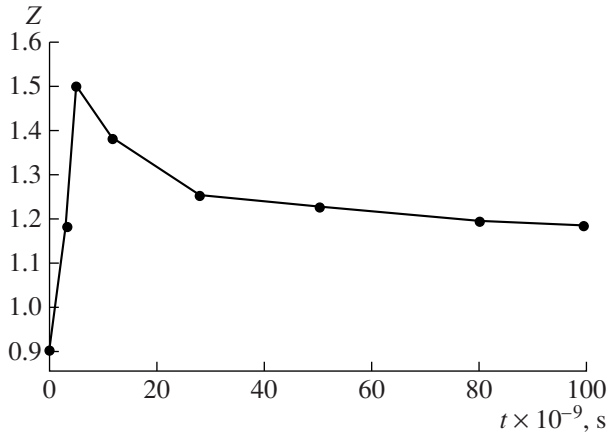


Fig. 1. Time dependence of the partition sum for the system of copper atoms.

mentary volume in the phase space. Thus, the MD method allows calculation of the partition sum accurate to the multiplicative constant; for this reason, it is impossible to calculate the TD characteristics dependent on Z and $\ln(Z)$ but, obviously, it is possible to find the characteristics determined by derivatives of $\ln(Z)$.

Figure 1 shows the results of calculation of partition sum Z_f normalized by a number of MD steps M for the system of $N = 3920$ copper atoms at $T = 300$ K. During calculation, one time step of the MD method was 2×10^{-15} s. First, the system was thermally stabilized for $M = 10^6$ MD steps. After that, the values of total energy $H(q_1, \dots, q_N, p_1, \dots, p_N)$ of the system were recorded and analyzed for $M = 10^8$ steps. One can see from Fig. 1 that fluctuations Z_f/M decay for 80–100 ns.

Now, using the calculation of specific heat of a system with constant volume C_v as an example, we demonstrate the calculation of the TD characteristics of the system by the MD method. According to [8], the mean energy of the system can be calculated if the partition sum is known:

$$\langle E \rangle = \frac{\partial \ln Z}{\partial \beta}, \quad (5)$$

where $\beta = kT$.

Specific heat C_v is determined by the energy fluctuations [8]:

$$C_v = \frac{\langle \langle E^2 \rangle - \langle E \rangle^2 \rangle}{k_B T^2}. \quad (6)$$

Taking into consideration that the energy fluctuations can be presented as

$$\langle (\delta E)^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}, \quad (7)$$

the final expression for C_v is

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2}. \quad (8)$$

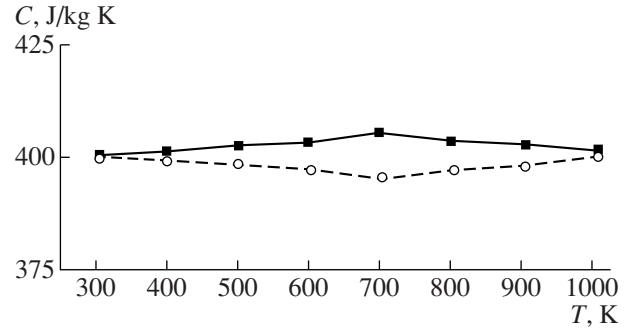


Fig. 2. Temperature dependence of specific heat of copper calculated using the first and second methods (black and grey curves, respectively).

The temperature dependence of C_v for copper calculated using formula (11) is presented in Fig. 2. The C_v value obtained from our calculation for $T = 300$ K is 395 J/kg K which is very close to the experimental value 380 J/kg K. This demonstrates that the proposed method allows high-accuracy calculation of C_v [5]. Interestingly, the obtained C_v value is close to $C_v = 3R = 392$ J/kg K [5] predicted by the empirical Dulong–Petit law. In the temperature interval of interest, C_v is nearly invariable with temperature, which is in agreement with the experimental data and results of other calculations [6].

There exists another way of C_v determination by the change in system energy with temperature, $C = \frac{\partial E(T)}{\partial T}$.

One can easily see (Fig. 2) that the temperature changes in C_v calculated using the two approaches are very close.

We presented the method for calculation of the MD characteristics of condensed matter on the basis of MD calculations. We showed that using the many-body potentials of the interatomic interaction specific heat of copper can be determined in good agreement with the experiment. The method can also be used for calculation of TD nanostructures at different temperatures.

REFERENCES

1. D. W. Heerman, *Computer Simulation Methods in Theoretical Physics* (Springer Verlag, 1990).
2. D. W. Brenner, *Phys. Stat. Sol. (b)* **217**, 23 (2000).
3. L. Miao, V. R. Bhetanabota, and B. Joseph, *Phys. Rev. B* **72**, 134109 (2005).
4. J. Wang, X. Chen, G. Wang, et.al, *Phys. Rev. B* **66**, 085408 (2002).
5. H. E. Aeper and P. Politzer, *Int. J. Quant. Chem.* **760**, 670 (2000).
6. H. E. Alper and P. Politzer, *J. Mol. Struct. (Theochem.)* **487**, 117 (1999).
7. F. Cleri and V. Rosato, *Phys. Rev. B* **48**, 22 (1993).
8. V. G. Levich, *Theoretical Physics Course*, Vol. 1 (Nauka, Moscow, 1969).