

Molecular dynamics investigation of heat conductivity in monocrystal materials with defects

Anton M. Krivtsov, Alexander A. Le-Zakharov

bosiakov@bsu.by

Abstract

The heat transfer processes in ideal monocrystals and monocrystals with predefined distribution of defects are studied using molecular dynamics technique. Space dimensions 1, 2, 3 are considered. A simple model to study the heat conductivity processes is suggested. It is shown that in ideal monocrystals the heat conductivity is not described by the classical conductivity theory. For the crystals with defects for the big enough specimens the conductivity obeys the classical relations and the coefficient describing the heat conductivity is calculated. The dependence of the heat conductivity on the defect density, number of particles in the specimen, and dimension of the space is investigated.

1 Introduction

Rational description of heat conductivity processes in media with microstructure remains a serious challenge for the modern science. For one-dimensional case it is known that the classical heat conductivity is not valid for perfect crystals [1, 2, 3] at least with a weak nonlinearity. In one-dimensional case the equations of thermoelasticity can be derived in adiabatic approximation [4, 5], however account of the heat conductivity does not allow obtaining a closed system of equations. In the presented work the heat conductivity process is studied in 2D and 3D cases using molecular dynamics technique [5, 6, 7].

2 Problem statement

Let us consider the classical heat conductivity equation

$$\dot{T} - \beta T'' = 0, \tag{1}$$

where β is coefficient, characterizing the heat conductivity. Suppose the initial temperature distribution has the form

$$T|_{t=0} = T_1 + T_2 \sin kx, \quad k = 2\pi/L, \quad (2)$$

where T_1 is the average temperature, T_2 is the amplitude of the temperature variation, L is the space period of the temperature variation. It is easy to obtain that the exact L -periodical solution of Eq. (1) with initial conditions (2) is

$$T = T_1 + T_2 e^{-\beta k^2 t} \sin kx. \quad (3)$$

This solution will be used to obtain the coefficient β from the MD (molecular dynamics) computer experiments. Let us introduce integral

$$J(t) = \int_0^L (T(x, t) - T_1)^2 dx. \quad (4)$$

This integral can be easily computed using MD. From the other hand, calculation of this integral for the solution (3) gives

$$J(t) = \frac{T_2^2 L}{2} e^{-2\beta k^2 t}. \quad (5)$$

Using Eq. (5) the coefficient β can be calculated from the known values of integral J as

$$\beta = \frac{1}{2k^2(t_2 - t_1)} \ln \frac{J(t_1)}{J(t_2)}, \quad (6)$$

where t_1 and t_2 are some selected moments of time.

3 Simulation technique

The simulation procedure applied in this work is a standard molecular dynamics technique, for more details the references [5, 6, 7] can be followed. The material is represented by a set of particles interacting through a pair potential $\Pi(r)$. The equations of particle motion have the form

$$m\ddot{\mathbf{r}}_k = \sum_{n=1}^N \frac{f(|\mathbf{r}_k - \mathbf{r}_n|)}{|\mathbf{r}_k - \mathbf{r}_n|} (\mathbf{r}_k - \mathbf{r}_n), \quad (7)$$

where \mathbf{r}_k is the radius vector of the k -th particle, m is the particle mass, N is the total number of particles, and $f(r) = -\Pi'(r)$ is the interparticle interaction force. Main notations: a is the equilibrium distance between two particles, $D = |\Pi(a)|$ is binding energy, $C = \Pi''(a) \equiv -f'(a)$ is the stiffness of the interatomic bond at equilibrium, and $T_0 = 2\pi\sqrt{m/C}$ is the period of vibrations of the mass m under the action of a linear force with stiffness C , $v_d = \sqrt{2D/m}$ is dissociation velocity (the minimum velocity required to escape from the potential field). The temperature is

taken to be proportional to an average of the kinetic energy of a set of particles (supposing that the average velocity of this set is zero)

$$T = \tilde{k} \left\langle \frac{mv^2}{2} \right\rangle = \tilde{k} \frac{m}{2} \langle v^2 \rangle, \quad (8)$$

where \tilde{k} is Boltzmann constant, $\langle \dots \rangle$ stands for averaging over the selected set of particles. In this work, we will consider close packed crystals: 2D material with triangular lattice and 3D material with FCC (face-centered cubic) crystal lattice. Let us consider the classical Lennard–Jones potential:

$$\begin{aligned} \Pi_{LJ}(r) &= D \left[\left(\frac{a}{r} \right)^{12} - 2 \left(\frac{a}{r} \right)^6 \right], \\ f_{LJ}(r) &= -\Pi'_{LJ}(r) = \frac{12D}{a} \left[\left(\frac{a}{r} \right)^{13} - \left(\frac{a}{r} \right)^7 \right], \end{aligned} \quad (9)$$

where D and a are the binding energy and the equilibrium interatomic distances, introduced earlier. In the case of the Lennard–Jones potential, the stiffness C and the binding energy D obey the relation $C = 72D/a^2$; the force (4) reaches its minimum value (the bond strength) at $r = b = \sqrt[6]{13/7}$, where b is the break distance. For calculations we will consider modification of the Lennard–Jones interaction, set by formula

$$f(r) = \begin{cases} f_{LJ}(r), & 0 < r \leq b, \\ k(r)f_{LJ}(r), & b < r \leq a_{\text{cut}}; \end{cases} \quad (10)$$

where b is the break distance for Lennard-Jones potential, a_{cut} is the cut-off distance (for $r > a_{\text{cut}}$ the interaction vanishes). The coefficient $k(r)$ is the shape function

$$k(r) = \left[1 - \left(\frac{r^2 - b^2}{a_{\text{cut}}^2 - b^2} \right)^2 \right]^2. \quad (11)$$

The cut-off distance will be set as $a_{\text{cut}} = 1.4a$, in this case only the first neighbors are interacting for the close-packed structures. This simplifies comparison with analytical considerations where only the first neighbors are taken into account and also allows to speed-up the calculations. In the current paper we study the principal possibility of describing the heat transfer rather than simulate the behavior of a certain material; therefore, the proposed simplified potential is sufficient.

4 Results of 2D Simulations

The results of calculation of β coefficient for 2D monocrystal are shown in Fig.1. A square specimen with ideal triangular lattice and periodic boundary conditions was used. The initial random velocity of the particles was set to have the temperature distribution according to Eq. (2), where x is one of the basic directions of the lattice, and T_1, T_2 are equal to

$$T_1 = 3.2 \times 10^{-6} T_d, \quad T_2 = 2.133 \times 10^{-6} T_d, \quad T_d = v_d^2/2. \quad (12)$$

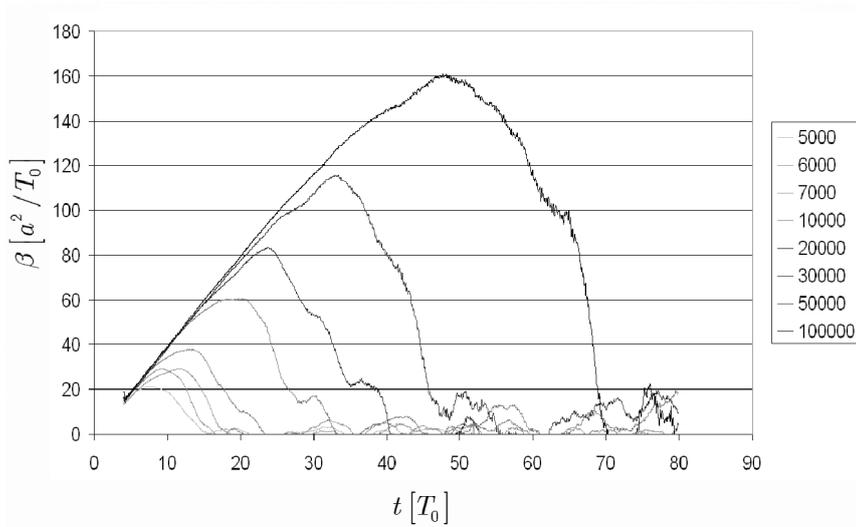


Figure 1: *Time dependence of β for 2D monocrystal with different number of particles.*

During the simulation the value of β was calculated using Eq. (6). For better accuracy each value of $\beta(t)$ was obtained as average from the values calculated using t_1 and t_2 uniformly distributed in the interval $[t - 4T_0, t + 4T_0]$. If the equation Eq.(1) is valid for the considered model, then the calculations should give approximately constant value for $\beta(t)$. However, the graphs show nearly linear increasing with time up to some specified value, after each they rapidly drop down. The greater is the number of particles N , the higher is the maximum value of $\beta(t)$. The explanation of the drop down of the dependence $\beta(t)$ is that the temperature variation along x coordinate became comparable with the temperature fluctuations due to discreteness of the considered system. The greater is the number of particles the longer time is needed for this. It is much more difficult to give an explanation for the linear increase of the β coefficient. Probably it means that the classical equation of heat conductivity is not valid for the considered system.

The next set of computer experiments correspond to ideal 2D monocrystal, same as before, but with predefined distribution of defects. The defects are vacancies — the randomly selected atoms are removed from the lattice — see Fig.2. The density of defects is characterized by porosity p , which is calculated as ratio of the number of defects to the number of particles. In this case the situation is different — see Fig.3 (the graphs are calculated for $N = 100\,000$). If the porosity p is high enough, then the dependence $\beta(t)$ is constant with small fluctuations. The lower is porosity, the longer time is needed for $\beta(t)$ to increase up to its constant value, and sooner the dependence drops down due to the thermal fluctuations. The average values of β as a function of porosity obtained from graphs Fig.3 are shown in Fig.4. From Fig.4 it follows that the heat conductivity falls down with the increase of porosity. Analysis of graphs in Fig.3 shows that some time is needed for β to reach its equilibrium value. The lower is the value of porosity the higher is equilibrium value and the more time is needed. But since the heat conductivity increases, the faster the temperature variation falls down to the value where it is lost in the random noise. Therefore the

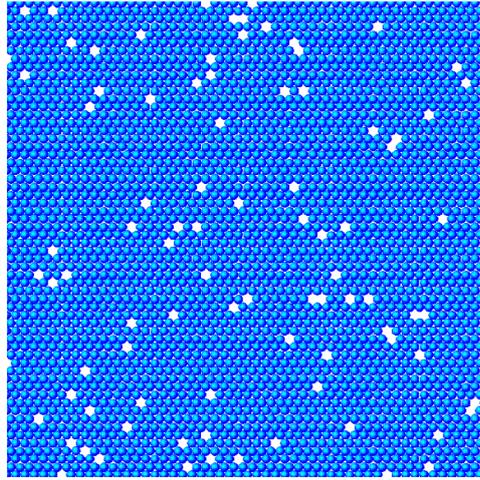


Figure 2: An element of 2D monocrystal with predefined distribution of defects.

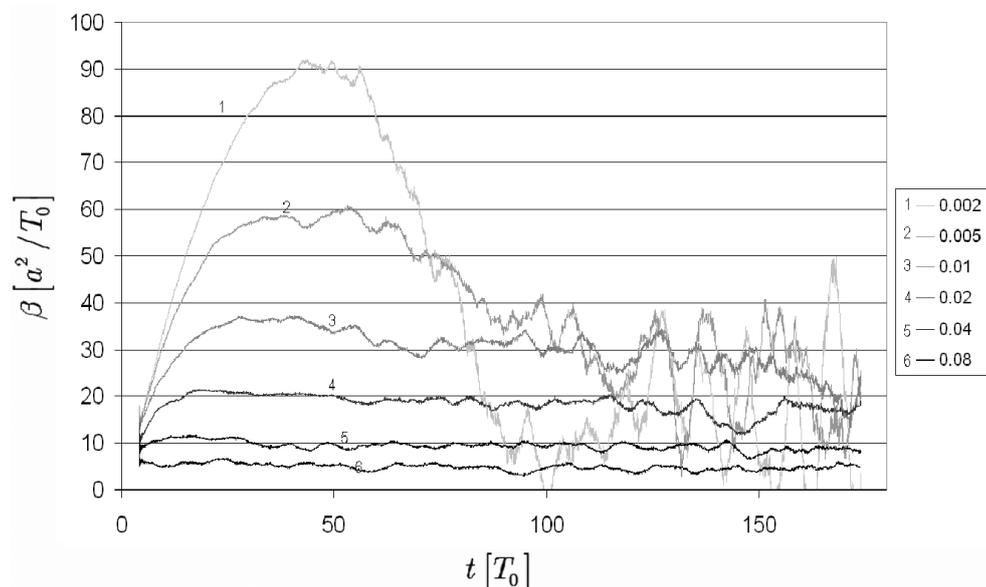


Figure 3: Time dependence of β for 2D monocrystal with different porosity p .

less is porosity the more particles is needed to get to the state where $\beta(t)$ is constant. Maybe for a big enough specimen the constant behavior of $\beta(t)$ can be observed even for the perfect crystal. However more likely is that the heat conductivity for the perfect crystal tends to infinity.

The dependence of β on the number of particles for two different values of porosity is shown in Fig.5. From the graphs it follows, that for the higher porosity the coefficient β does not depend much on the number of particles, but for the lower porosity this dependence is significant — much greater number of particles is needed to get close to the limit value, corresponding to the infinite crystal.

To make the results more clear let us consider in more details the process of heat conductivity in the crystal with defects. The change of temperature distribution with time is shown in Fig.6. The number of particles is 70 000, porosity is 0.03. It is seen that the temperature variation is decreasing its magnitude more or less preserving

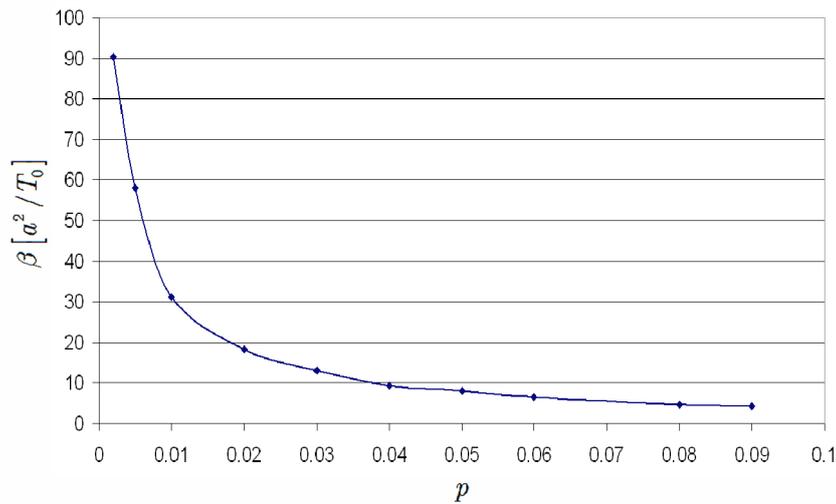


Figure 4: Heat transfer coefficient β depending on porosity of material p for 2D monocrystal.

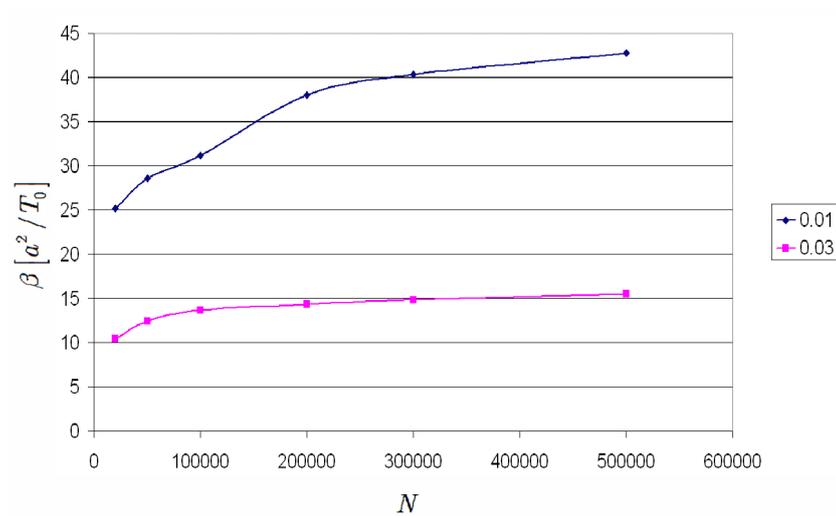


Figure 5: Heat transfer coefficient β depending on number of particles in specimen N for 2D monocrystal.

its shape. However some short-wave oscillations are visible, caused by randomness of the initial velocity distribution (the curve is averages along x direction). The time-dependence of integral $J(t)$ calculated from temperature distribution Fig.6 is shown in Fig.7. The graph clearly shows an exponential behavior. To verify the exponential character of $J(t)$ the time-dependence of logarithm of the integral is shown in Fig.8. The dependence is close to linear, but with additional noise, which becomes higher for higher values of t . The corresponding time-dependence of β is shown in Fig.9. The graph demonstrates much more irregular behavior than the previous one. In fact this graph is a derivative of the dependence $\lg(J/J_0)$, and the derivation always adds an additional noise to the system. Nevertheless it allows obtaining the average value for the β coefficient.

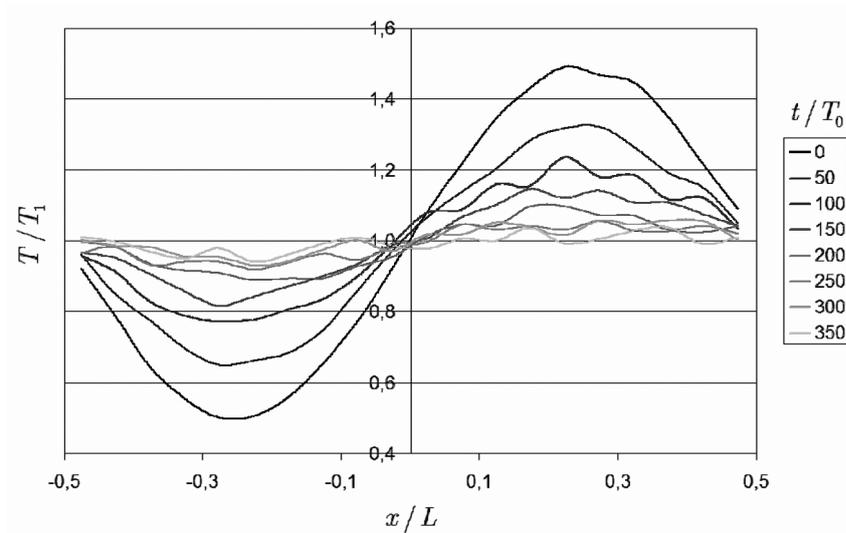


Figure 6: *Change of temperature distribution with time in crystal with defects.*

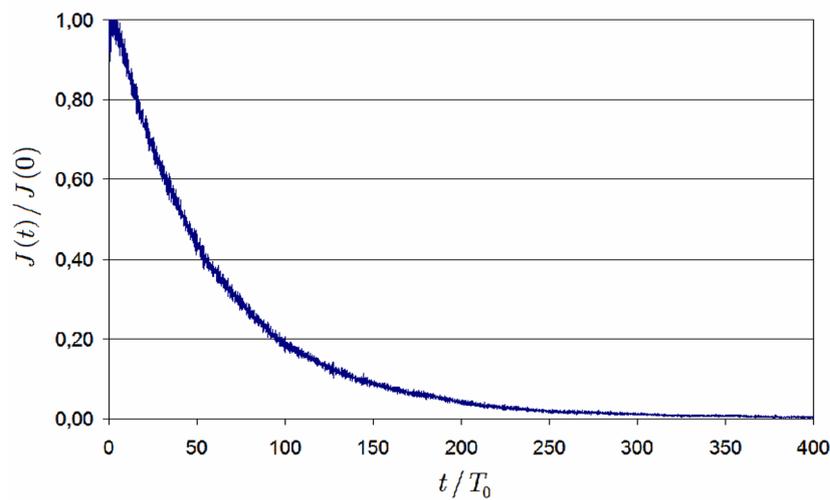


Figure 7: *Decreasing of integral $J(t)$ with time.*

5 Results of 3D simulations

In 3D case, as before, a rectangular specimen with the temperature distribution

$$T|_{t=0} = T_1 + T_2 \sin kx, \quad k = 2\pi/L, \quad (13)$$

was used where x is direction along one of the sides of the rectangle, L is length of the specimen in x direction. The width of the specimen in orthogonal directions is chosen to be $L/4$. Periodic boundary conditions are used at all boundaries. The particles are arranged in an ideal face centered cubic (FCC) lattice. Mean temperature of the system is equal to

$$T_1 = 3.2 \cdot 10^{-5} T_d, \quad T_d = v_d^2/2 \quad (14)$$

with v_d being the dissociation velocity. Amplitude of temperature deviation T_2 is taken equal to $\frac{2}{3} T_1$ in the first series of experiments and $\frac{1}{15} T_1$ (ten times smaller)

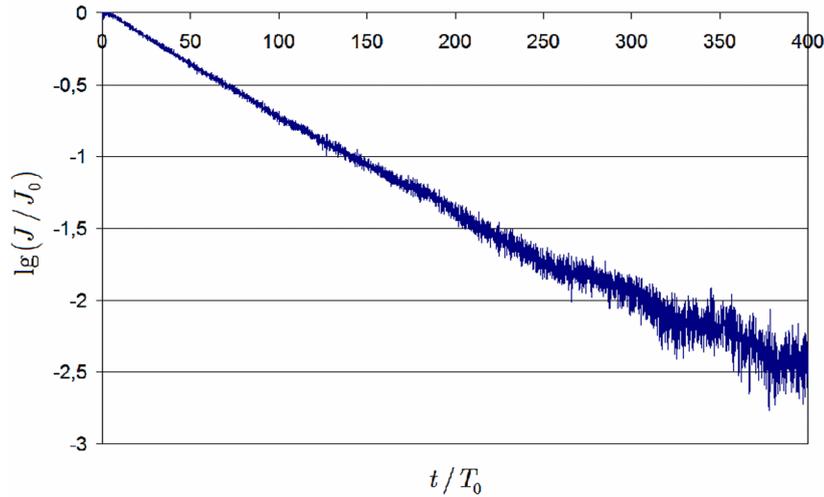


Figure 8: *Time-dependence of logarithm of integral $J(t)$.*

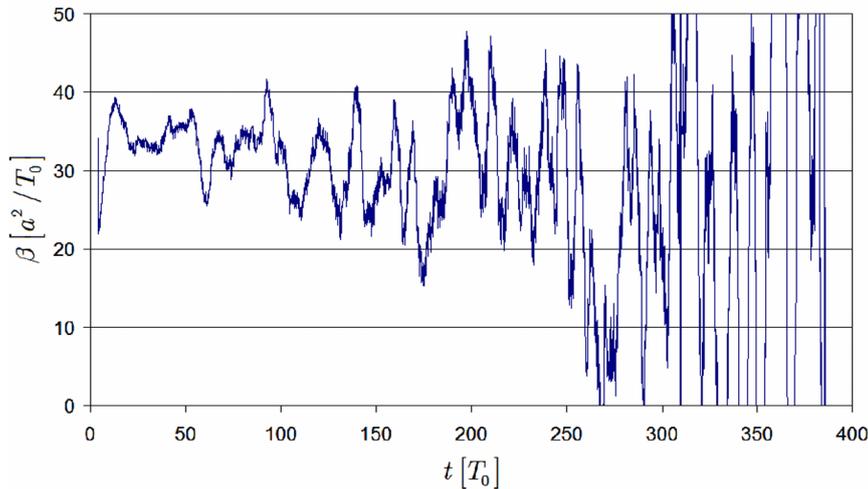


Figure 9: *Time-dependence of β .*

in the second one. The same technique for determination of heat conductivity coefficient as in 2D case is used. Fig.10 shows the time dependence of β for the systems containing 15 000 and 100 000 particles. Deviation of temperature T_2 is related to its mean value T_1 as $\frac{T_2}{T_1} = \frac{2}{3}$. As in 2D case the graphs also have well pronounced maximums but they are much smoother then in 2D case. For 3D case the increase of the dependence $\beta(t)$ probably is not linear, like it was in 2D. However the 3D calculations are in contradiction with the classical equation of heat conductivity as it was for 2D case.

In figures 11 and 12 the time dependencies of heat conductivity coefficient β for the cases of different porosity and temperature deviation are shown. Half of a million particles are used in these simulations. On the base of these results the graph 13 for dependence of β on porosity was constructed. This dependence is similar to the one obtained in 2D case, however the values of β in 3D are much lower. Comparison of dependencies of β on porosity in 2D and 3D is given in Fig. 14. The horizontal axis

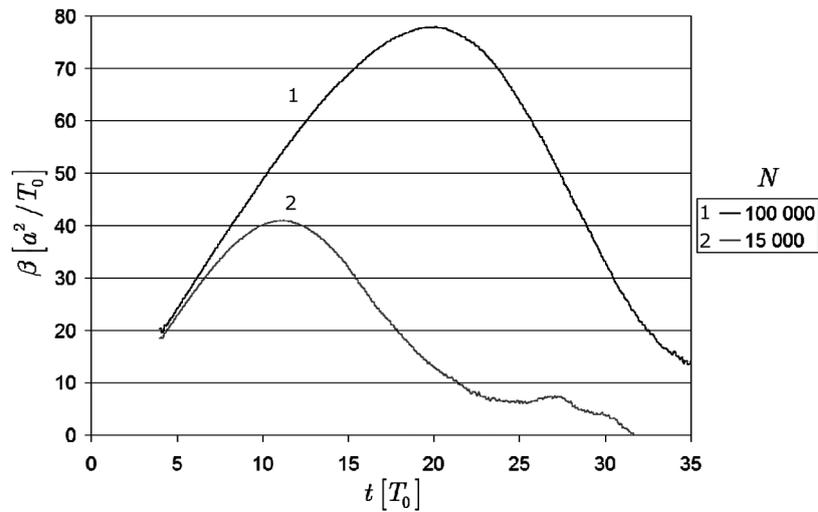


Figure 10: Time dependence of β for 3D monocrystal with different number of particles.

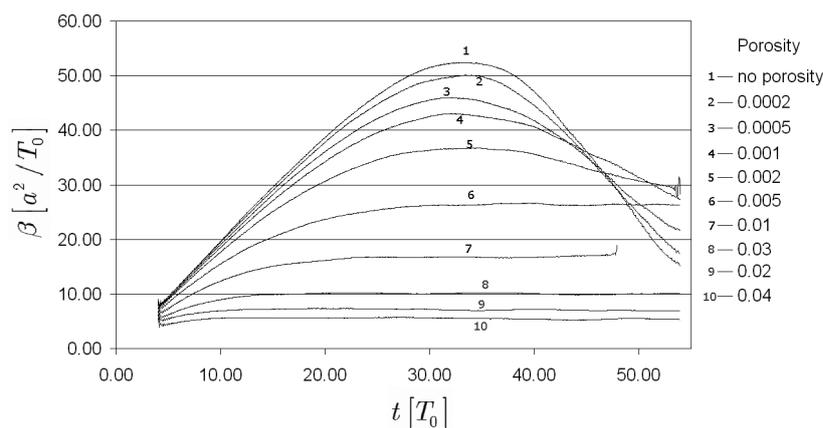


Figure 11: Time dependence of parameter β for 3D monocrystal with different porosity; $T_2/T_1 = 2/3$.

corresponds to $p^{-1/2}$ and in this case both graphs are almost linear. The trend lines are also shown in the figure. For 2D case the linear fit is so precise that the trend line can not be distinguished from the real graph. From the graphs the following approximation can be obtained for the β dependence on porosity

$$\beta = A(p^{-1/2} - p_0^{-1/2}), \quad (15)$$

where A is dimensional coefficient, p_0 is the value of porosity for which the heat conductivity vanishes. The values of these parameters obtained from the above computer experiments for 2D and 3D cases are summarized in Table 1.

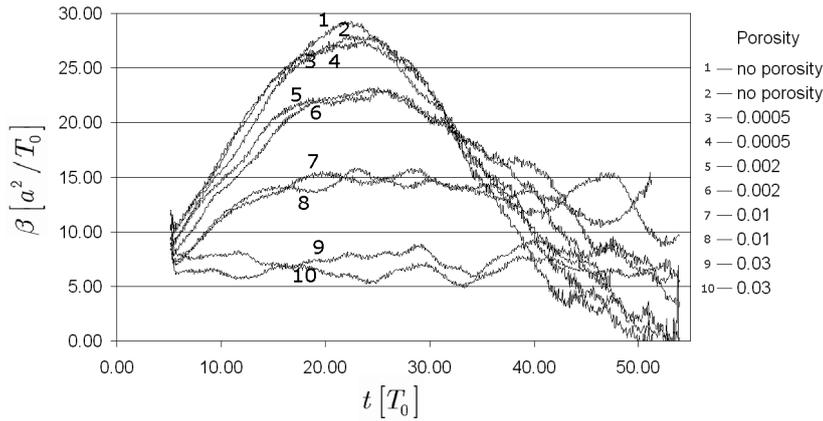


Figure 12: Time dependence of parameter β for 3D monocrystal with different porosity; $T_2/T_1 = 1/15$.

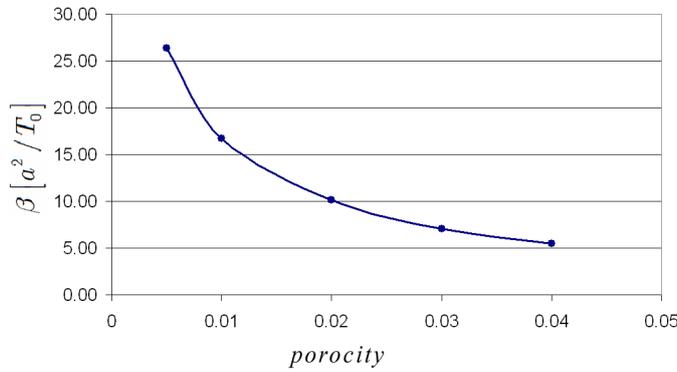


Figure 13: β depending on different porosity according to the results presented on the figure 11.

Table 1: Coefficients for β dependence on porosity

	2D	3D
A, s^{-1}	4.67	2.29
p_0	0.131	0.144

As it follows from the table the value of A for 2D is approximately twice higher than in 3D, the values of p_0 in 2D and 3D are almost the same.

Thus the main features of the heat transfer process obtained for 2D case also remain in 3D case. The presented experiments suggest that the heat conductivity process does not satisfy the classical equations in the case of ideal lattice and agrees with the classical conductivity theory only in the case of crystal with porosity.

6 Concluding remarks

In the presented paper the heat conductivity process was studied for ideal 2D and 3D monocrystals, and for 2D crystal with predefined distribution of defects. It was

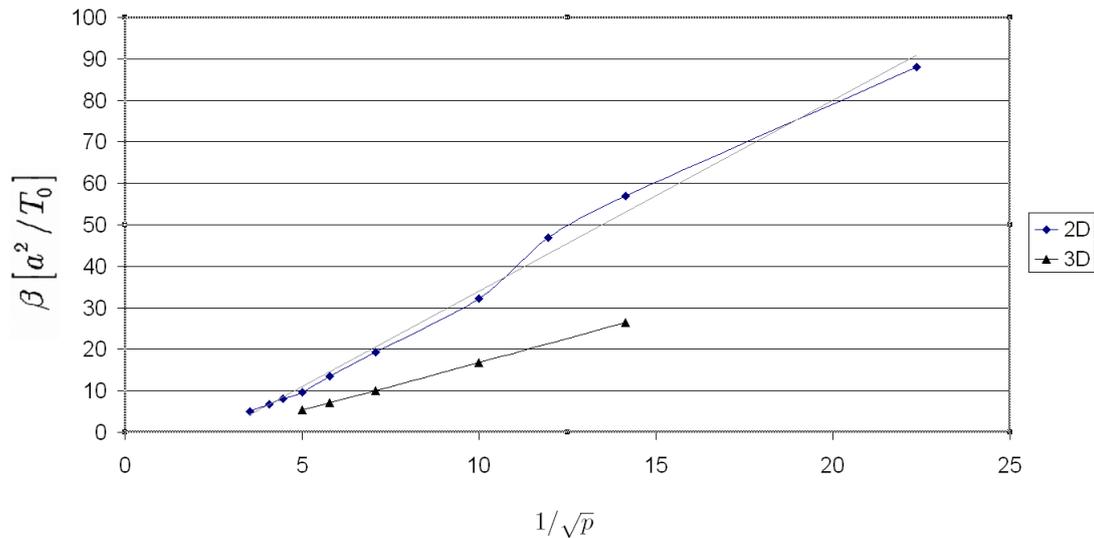


Figure 14: Heat conductivity coefficient β depending on $1/\sqrt{p}$.

shown that in the crystal with defects the heat conductivity process is described by the classical heat conductivity equation and the values of the coefficient β , characterizing the heat conductivity where obtained. It was shown that the heat conductivity increases with decreasing the number of defects. The less is the number of defects the bigger specimen (e.g. containing more particles) is needed to calculate the β coefficient. If the defects are absent at all then the heat conductivity process can not be described by the classical equation, at list for the sizes of specimens, which where considered.

In figures 15 comparison of the time dependencies for the coefficient characterizing the heat conductivity in 1D, 2D, and 3D are shown. According to the classical theory these dependencies should be constant. However, the obtained dependencies increase with time: almost linear in 2D case, and nonlinear in 1D an 3D (with positive time derivative in 1D case, and with negative time derivative in 3D case). This behavior can be observed until the long scale temperature variations decreasing with time due to the heat conductivity are not lost in the thermal noise. In principle it can happen that for much greater monocrystal specimens the classical heat conductivity equation fulfils, but from the presented investigations it follows that at least for monocrystal nanostructures it is not valid.

Acknowledgements

This work was partially supported by Sandia National Laboratories.

References

- [1] H. A. Posch, Wm. G. Hoover. Heat conduction in one-dimensional chains and nonequilibrium Lyapunov spectrum. 1998. *Phys. Rev. E* **58**, p. 4344.

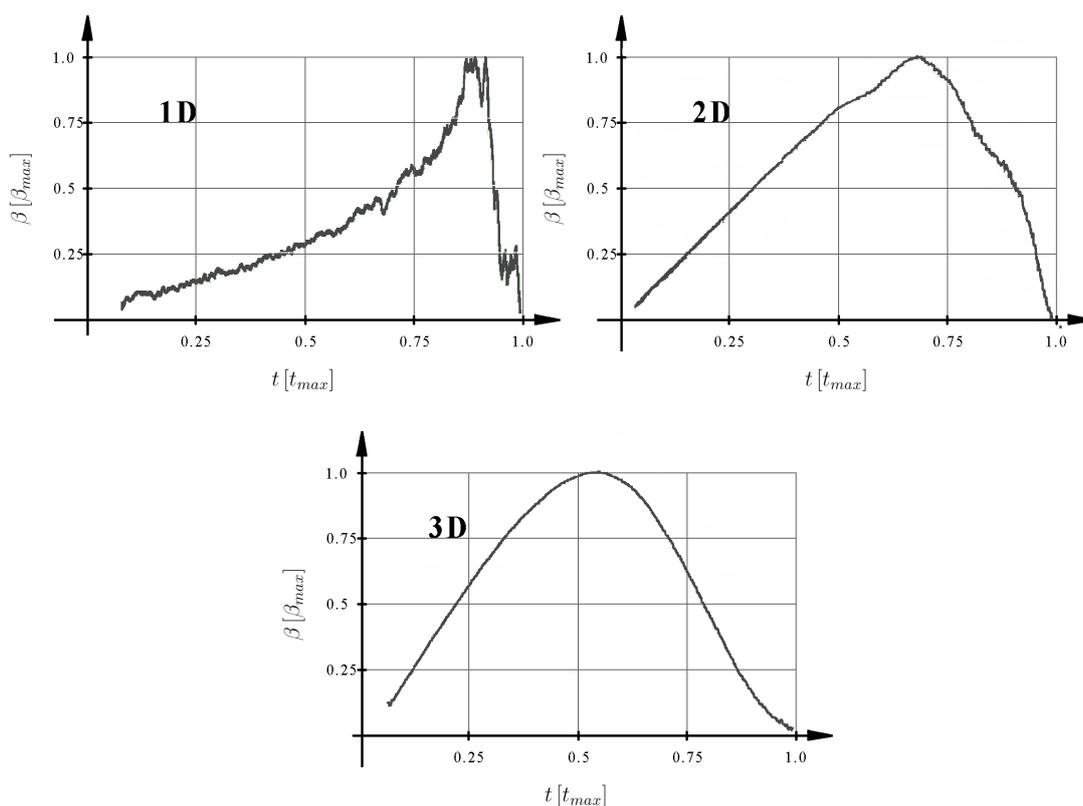


Figure 15: Comparison of forms of diagrams for β for different dimensions of crystal lattice. Scales for β and t are normalized relative to the maximum of heat transfer coefficient obtained in the course of particular experiment and process life time respectively.

- [2] O. V. Gendelman, A. V. Savin. Normal Heat Conductivity of the One-Dimensional Lattice with Periodic Potential of Nearest-Neighbor Interaction. 2000. *Phys. Rev. Lett.* **84**, p. 2381.
- [3] T. Mai, O. Narayan. Universality of one-dimensional heat conductivity. 2006. *Phys. Rev. E.* **73**, p. 061202.
- [4] Krivtsov A. M. From nonlinear oscillations to equation of state in simple discrete systems. *Chaos, Solitons & Fractals*. 2003. V. 17. No 1. P. 79–87.
- [5] A. M. Krivtsov. Deformation and fracture of solids with microstructure. Moscow, Fizmatlit. 2007. 304 p. (In Russian).
- [6] A.M. Krivtsov, V. P. Myasnikov. Modelling using particles of the transformation of the inner structure and stress state in material subjected to strong thermal action. *Mechanics of Solids*. 2005, **1**, 87–102.
- [7] A.M. Krivtsov. Molecular Dynamics Simulation of Plastic Effects upon Spalling. *Phys. Solid State* **46**, 6 (2004).

Anton M. Krivtsov, IPME RAS, St.-Petersburg, Russia

Alexander A. Le-Zakharov, IPME RAS, St.-Petersburg, Russia