=== **MECHANICS** ===

Molecular Dynamics Investigation of Heat Conduction in Crystals with Defects

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Descriptions of the process of heat exchange in periodic structures in terms of the classical heat conduction equations frequently encounter serious problems. For example, although the problem of heat conduction in a one-dimensional (1D) chain of particles has been investigated by various methods, including computer simulations [1–3] and the thermal processes occurring in real solids, liquids, and gases have been extensively studied [4, 5], questions concerning the adequate description of heat exchange processes [6, 7] both in 1D structures and in multidimensional systems still remain open. In this study, the process of heat conduction in perfect single-crystal lattices, as well as in those with defects, has been investigated by means of the molecular dynamics method. A mathematical model has been developed which, despite its simplicity, makes it possible to study heat exchange processes in great detail. In the course of our investigations, it has been established that heat conduction in a perfect single crystal cannot be adequately described by the classical equations. However, the classical relationships have proved to be applicable to crystals with defects, provided that the size of a sample is sufficiently large. In addition, in these cases, it is possible to calculate the thermal conductivity coefficient and investigate its dependence on the amount of defects, the sample size, and the space dimensionality.

Consider the classical heat conduction equation

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

where T is the temperature; β is the coefficient characterizing the heat conduction; and the upper dot and prime denote the derivatives with respect to time t and

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spatial coordinate x, respectively. Let an initial temperature distribution be set as follows:

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

where T_1 is the mean temperature and T_2 and L are the amplitude and spatial period of temperature variations, respectively. The exact solution to Eq. (1) under initial conditions (2) has the following form:

$$T = T_1 + T_2 e^{-2\beta k^2 t} \sin kx, \quad k = \frac{2\pi}{L}. \tag{3}$$

Consider the following integral expression

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

The value of $J(t)$ can easily be calculated from the data of computer experiments. On the other hand, an analytical expression of this integral for solution (3) is as follows:

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

Using expression (5) and two known values of the integral J, it is possible to calculate coefficient β as

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

where t_1 and t_2 are two arbitrarily chosen moments of time. This formula will be used to determine the coefficient β during molecular dynamics experiments.

We use the molecular dynamics method that is capable of effectively describing mechanical processes in solids [8–10]. Consider a material comprising a system of particles interacting according to the modified Len-
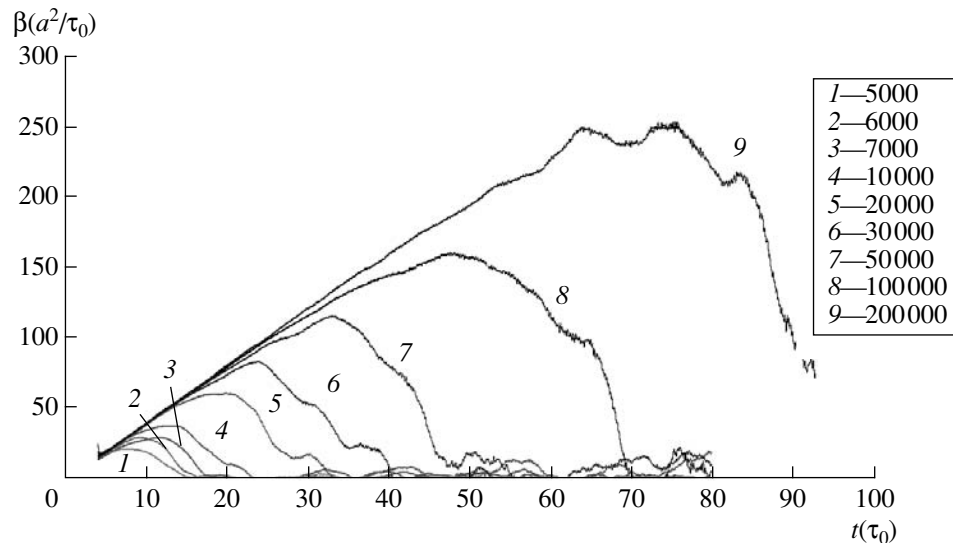
Fig. 1. Time dependence of the coefficient β for 2D perfect crystals with various sample sizes (numbers of particles).

nard-Jones law, for which the particle–particle interaction force is defined as

$$f(r) = \begin{cases} f_{LJ}(r), & 0 < r < b, \\ k(r)f_{LJ}(r), & b < r < a_{cut}. \end{cases} \quad (7)$$

Here, $f_{LJ}(r)$ is the interaction force for the Lennard-Jones potential and $k(r)$ is the modifying function, which are calculated as follows:

$$f_{LJ}(r) = \frac{12D}{a}\left[\left(\frac{a}{r}\right)^{13} - \left(\frac{a}{r}\right)^{7}\right],$$

$$k(r) = \left[1 - \left(\frac{r^2 - b^2}{a_{cut}^2 - b^2}\right)^2\right]^2, \quad (8)$$

where D is the binding energy, a is the equilibrium distance, $b = \sqrt[6]{\frac{13}{7}}\, a$ is the distance of bond breaking, and $a_{cut} = 1.4a$ is the distance of the force cut-off (retaining the interaction only between nearest neighbors in the close-packed lattice). The temperature is assumed to be proportional to the average kinetic energy of the system of particles (on the assumption that the average velocity for this system of particles is equal to zero).

Let us consider a sample of the material described above having the shape of a parallelepiped with temperature distribution (3), and introduce a coordinate system with the Ox axis directed along one edge of the parallelepiped. Let L be the length of the sample along this axis, let $L/4$ be the sample size in the orthogonal directions, and set periodic boundary conditions at all faces of the model crystal. The particles are situated at the sites of the close-packed lattice (triangular and face-centered cubic lattices in the two- (2D) and three-

dimensional (3D) cases, respectively). The mean temperature of the system is assumed to be $T_1 = 3.2 \times 10^{-6}T_d$ in the 2D case and $T_1 = 3.2 \times 10^{-5}T_d$ in the 3D case. Here, $T_d = \frac{v_d^2}{2}$, $v_d = \sqrt{\frac{2D}{m}}$ is the dissociation rate and m is the particle mass. The amplitude of temperature variations is taken equal to $T_2 = 2/3T_1$.

The coefficient β is calculated according to formula (6). For a better accuracy, $\beta(t)$ is taken as the average of β values calculated on the interval $[t - 4\tau_0, t + 4\tau_0]$, where τ_0 is the period of small-amplitude oscillations of a particle near the equilibrium position. Figure 1 shows the temporal variation of the coefficient β calculated using the above method for perfect 2D single crystals consisting of various numbers of particles. If Eq. (1) were valid for the model under consideration, the calculations would give approximately a constant value of β. However, as can be seen from Fig. 1, the coefficient β increases almost linearly and, after reaching a certain critical value, rapidly drops due to the fact that the temperature variations along the x coordinate become comparable with temperature fluctuations related to the discrete character of the system. The greater the sample, the longer the period of time during which the coefficient β exhibits linear growth.

Figure 2 shows the results of calculations for a 3D perfect single crystal and a similar single crystal with defects (homogeneously distributed vacancies). The number of particles in the sample was about 500 000. In the absence of defects or at their low density, it is clearly seen that the coefficient β initially increases, exhibits a maximum, and subsequently smoothly decreases virtually down to zero. If the defect density is high enough, the function $\beta(t)$ after a transient process tends to a certain constant value. This behavior leads us
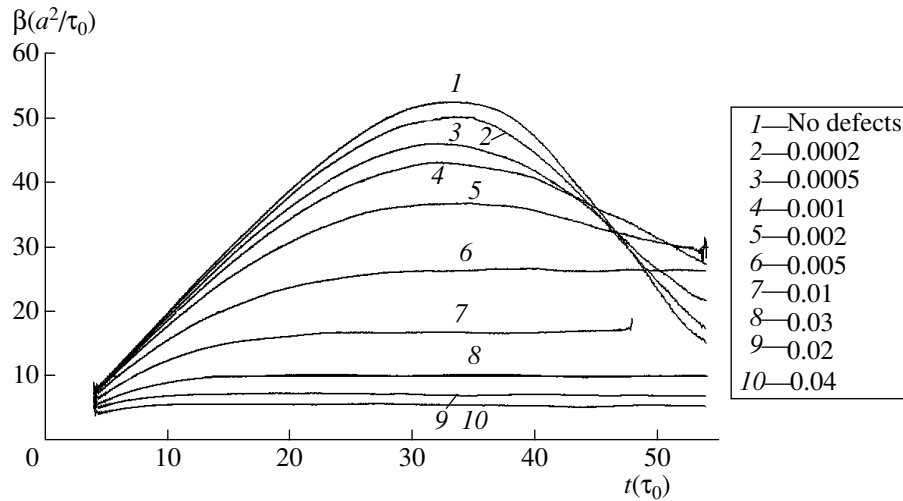
Fig. 2. Time dependence of the coefficient β for 3D perfect crystals with various densities of defects. The number of particles is $N = 500000$.

to conclude that, in such cases, classical heat conduction equation (1) adequately describes the heat transfer in the crystal.

Using the results of calculations, we have analyzed the dependence of β on the number of defects in the material. It is established that β is inversely proportional to the square root of the defect density p (Fig. 3) to within small deviations related to the insufficient statistical data. In the 3D case, these deviations are so small that the guide line connecting the points is visually indistinguishable from the graph itself.

Based on these results, the following approximate dependence of β on the defect density was obtained:

$$\beta = A(p^{-1/2} - p_0^{-1/2}), \qquad (9)$$

where A is a dimensional factor and p_0 is a critical value of the density of defects for which the effect of heat conduction completely disappears. Here, we present the values of these parameters found from computer experiments for the 2D and 3D crystals

	2D	3D
$A, a^2/t_0$	5.72	2.29
p_0	0.117	0.144

Figure 4 shows a comparison of the time dependences of β for the 1D, 2D, and 3D perfect crystal lattices. As can be seen, the coefficient β increases with time in all cases. However, in the 1D case, the growth proceeds with a positive second derivative; in the 2D case, the growth is almost linear; and in the 3D case, the second derivative is negative. When the amplitude of spatial variations of the temperature becomes comparable with the amplitude of thermal fluctuations, the coefficient β decreases down to zero. It should be noted that
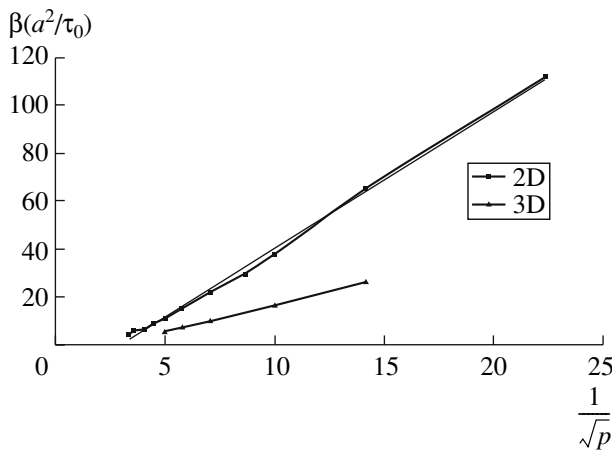

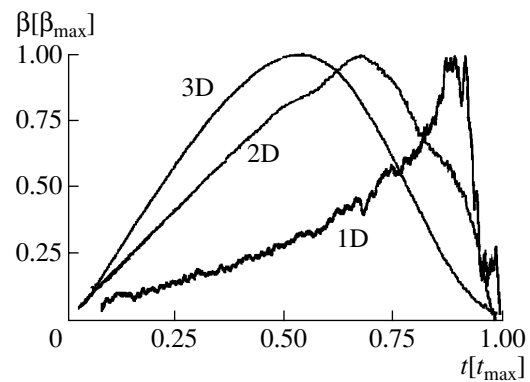**Fig. 3.** Dependence of the coefficient β on the defect density p in the 2D and 3D lattices.

Fig. 4. Temporal variation of the coefficient β for 1D, 2D, and 3D crystal lattices. The scales of the quantities β and t are normalized to the maximum value of β attained in the course of the experiments and the total time of heat exchange.

the lower the space dimension, the more sharply pronounced this effect.

Thus, we showed that the process of heat conduction in a perfect single crystal is not described by the classical equations. At least, this conclusion is valid for systems whose size is comparable with that considered in this study—in particular, for the majority of nanostructures with a perfect crystal lattice. For crystals with randomly distributed defects, we demonstrated that the process of heat exchange can be described by the classical equation of heat conduction and determined the dependence of heat conduction on the density of defects.

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