Transition to thermal equilibrium in a deformed crystal

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We study transient thermal process in infinite nonlinear crystal after initial deformation. Initially particles have random displacements and random velocities corresponding to a uniform initial temperature. After homogeneous deformation the crystal is in the nonequilibrium state. As a result of the transient process the crystal transfers to a new equilibrium state. Analytical expressions describing the crystal temperature at an arbitrary moment of time are obtained. These results are supported by numerical simulation of the crystal dynamics and they are in accordance with the virial theorem.

I. INTRODUCTION

Nonequilibrium thermal processes in solids are the subject of intensive research in physics, especially in connection with the active development of Nanotechnologies [1–5]. Initialization of such processes can be achieved, for example, by exposure to an ultrashort laser pulse [6–12]. The rapid heating of crystals can also be caused by adiabatic processes, for example, by the fast loading or by the passing shock waves through the material [13–16]. At the micro level, the state of the liner system, after the transition process is characterized by the equalization of the kinetic and potential energies of the atomic motion according to the virial theorem [17–20]. However, the virial theorem does not allow to describe the processes that occur during transients. At the macro level, the process of a crystal transition from a nonequilibrium state to a state of thermodynamic equilibrium is described by the equations relating deformation and temperature. The relationship between the descriptions of transients at the micro and macro levels of the crystal is still not clear.

Crystals with simple lattices are convenient for studying nonequilibrium processes in solid. It is known from the results of numerical simulations [21] that the process of energies equalization in molecular systems is accompanied by high-frequency oscillations. In the paper by Klein and Prigogine [22], the equations for atoms motion of a one-dimensional harmonic crystal are solved directly and it is shown that the energies oscillations after an instantaneous thermal perturbation are described by the Bessel function of the first kind. In [23], this problem is solved by analyzing the covariances, which allowed to generalize the results to the case of non-equilibrium processes in multidimensional crystals [24–29]. In this paper, we study an analogy non-equilibrium process that occurs in a nonlinear one-dimensional crystal after fast heating caused by an instant deformation.

In the work the analytical expressions describing the crystal temperature as a function of time are obtained. Analytically it is shown that the system transfers into a state of equilibrium in accordance with the virial theorem.

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II. MATHEMATICAL MODEL

In this section the model of an infinitive one-dimensional crystal subjected to instant deformation ε is presented. It is assumed that the crystal consists of identical particles, which interact only with their neighbours. The equation of motion for the crystal particles is

$$\begin{gathered} m\dot{v}_n = \Delta F_n\,, \\ F_n \overset{\text{def}}{=} -F(\varepsilon+\varepsilon_n)\,, \qquad \varepsilon_n \overset{\text{def}}{=} \Delta u_n, \end{gathered} \tag{1}$$

where $v_n \overset{\text{def}}{=} \dot{u}_n$ is the velocity of the particle n, u_n is the displacement of the particle n from its equilibrium position, deformation is separated to stochastic deformation ε_n due to the thermal motion of particles and homogeneous deformation ε, m is the particle mass, $\Delta f_n = f_{n+\frac{1}{2}} - f_{n-\frac{1}{2}}$ is the difference operator. Indexes of particles are integers $n = 1, 2, 3, ...$, and indexes of bonds are half the sum of interacting particles, F_n is the force acting on the particle $n-1$ from the particle n, and function F is the force of elastic interaction of two particles. The elastic force between the lattice particles can be expressed in the following way:

$$\begin{aligned} F_n &= \Pi'(\varepsilon+\varepsilon_n) = C(\varepsilon+\varepsilon_n) + \alpha(\varepsilon+\varepsilon_n)^2, \\ \Pi(\varepsilon+\varepsilon_n) &= \frac{C}{2}(\varepsilon+\varepsilon_n)^2 + \frac{\alpha}{3}(\varepsilon+\varepsilon_n)^3, \end{aligned} \tag{2}$$

where C and α are stiffnesses of the interparticle bonds, Π is the interparticle potential, and the prime marks the differentiation with respect to the coordinate. The right part of equation of motion (1) for the particles of the considered crystal is determined using first one of equations (2). Homogeneous deformation ε is applied instantaneously to the crystal at the initial moment of time:

$$\varepsilon(t) = \begin{cases} 0, & \text{if } t < 0 \\ \varepsilon, & \text{if } t \geq 0, \end{cases} \tag{3}$$

where ε is a constant and t is time. The crystal is in thermodynamic equilibrium before the homogeneous deformation, and it transits into a non-equilibrium state

after applying homogeneous deformation ε (3). After the transition process is completed the crystal is in equilibrium state again. The following sections provide an analytical description of this process.

III. STATISTICAL CHARACTERISTICS

The total energy of this system is the sum of kinetic and potential energies. To describe the statistical characteristics of the system, mathematical expectations of the corresponding energy quantities are introduced:

$$\begin{aligned} &K \stackrel{\text{def}}{=} \frac{1}{2} m\langle v_n^2\rangle\,, \qquad U(\varepsilon+\varepsilon_n) \stackrel{\text{def}}{=} \langle \Pi(\varepsilon+\varepsilon_n)\rangle\,, \\ &E \stackrel{\text{def}}{=} K+U\,, \qquad T \stackrel{\text{def}}{=} \frac{2K}{k_B}, \end{aligned} \tag{4}$$

where $\langle ...\rangle$ is the operator of the mathematical expectation, k_B is the Boltzmann constant, T is the kinetic temperature, K, U, and E are mathematical expectations of the kinetic, potential, and total energies respectively. Since only the mathematical expectations of energies are considered, the words "mathematical expectation" are omitted below.

The virial theorem [17, 18] allows to link the kinetic energy in the equilibrium state and the macroscale deformation through the following relation (see Appendix A):

$$K = -\frac{1}{2}\langle \varepsilon_n F_n\rangle. \tag{5}$$

The next section gives expressions for the kinetic temperature of the crystal before and after the instantaneous deformation.

IV. CRYSTAL IN THE THERMODYNAMIC EQUILIBRIUM

A. Crystal before loading

For $t < 0$ homogeneous deformation ε is equal to zero (3). In this case the energies are

$$\begin{aligned} &K = \frac{1}{2} m\langle v_n^2\rangle\,, \qquad U = \frac{C}{2}\langle \varepsilon_n^2\rangle + \frac{\alpha}{3}\langle \varepsilon_n^3\rangle\,, \\ &E = K+U, \end{aligned} \tag{6}$$

and the crystal is assumed to be in thermodynamic equilibrium. According to virial relation (5) the following expression holds:

$$\frac{1}{2} m\langle v_n^2\rangle = -\frac{1}{2}\langle \varepsilon_n F_n\rangle = \frac{C}{2}\langle \varepsilon_n^2\rangle + \frac{\alpha}{3}\langle \varepsilon_n^3\rangle. \tag{7}$$

Term $\alpha\langle \varepsilon_n^3\rangle/3$ of equation (7) is assumed to be small and then the kinetic temperature of the crystal before loading is

$$T_0 = \frac{m}{k_B}\langle v_n^2\rangle = \frac{C}{k_B}\langle \varepsilon_n^2\rangle. \tag{8}$$

B. Crystal after loading

For $t \geqslant 0$ homogeneous deformation ε is a nonzero constant. Then for the kinetic and potential energies of the crystal the following expressions are satisfied:

$$\begin{aligned} &K = \frac{1}{2} m\langle v_n^2\rangle\,, \qquad U = \Pi(\varepsilon) + U_T\,, \\ &U_T = \frac{1}{2}\left(C+2\alpha\varepsilon\right)\langle \varepsilon_n^2\rangle + \frac{1}{3}\alpha\langle \varepsilon_n^3\rangle, \end{aligned} \tag{9}$$

where U_T is the thermal part of the potential energy. In order to obtain formula (9) relation $\langle \varepsilon_n\rangle = 0$ is taken into account. Note that at the moment of loading $t = 0$, kinetic energy K does not change, however, a jump of potential energy U is realized due to the homogeneous deformation. Let us introduce thermal energy E_T and thermal Lagrangian L_T:

$$E_T \stackrel{\text{def}}{=} K + U_T\,, \qquad L_T \stackrel{\text{def}}{=} K - U_T. \tag{10}$$

Note that thermal energy E_T is constant in the transient process

$$E_T = E_T|_{t=0}\,. \tag{11}$$

According to equation (8) the expression

$$\frac{m}{k_B}\langle v_n^2\rangle = \frac{C}{k_B}\langle \varepsilon_n^2\rangle = T_0, \tag{12}$$

is performed for initial moment of time. The energy initial conditions are obtained by substituting (12) to (9)-(10) and omitting the term $\alpha\langle \varepsilon_n^3\rangle/3$:

$$E_T|_{t=0} = T_0 k_B\left(1+\frac{\alpha\varepsilon}{C}\right)\,, \qquad L_T|_{t=0} = -\frac{\varepsilon k_B \alpha}{C} T_0. \tag{13}$$

Using the virial theorem [17, 18] let us find the crystal kinetic temperature after the transition process for $t \to \infty$. The kinetic energy can be found using relations (2) and (5) and by omitting the term proportional to $\langle \varepsilon_n^3\rangle$:

$$K = \frac{1}{2}(C+2\alpha\varepsilon)\langle \varepsilon_n^2\rangle. \tag{14}$$

Substitution expressions for K (14) and for U_T (9) to the first one of formulas (10) gives us the following formula for the thermal energy:

$$E_T = (C+2\alpha\varepsilon)\langle \varepsilon_n^2\rangle. \tag{15}$$

From equations (13) and (15) and relation (11) the following identity is obtained:

$$E_T = (C+2\alpha\varepsilon)\langle \varepsilon_n^2\rangle = T_0 k_B\left(1+\frac{\alpha\varepsilon}{C}\right). \tag{16}$$

Let us note that equation (15) is doubled the kinetic energy (14) which is associated with the temperature by the last one of relations (4). Thus, from equation (16)

we obtain the crystal temperature after the completion of the transition process:

$$T|_{t\to\infty} = T_0\left(1+\frac{\alpha\varepsilon}{C}\right). \tag{17}$$

From expression (17) follows that the change in kinetic temperature T in a first approximation is proportional to deformation ε. In the next section we obtain an expression for temperature as function of time.

V. DYNAMIC OF THE TRANSITION PROCESS

Substituting expression (2) into (1) we obtain the following equation of motion:

$$m\dot{v}_n = C\Delta\varepsilon_n + 2\alpha\varepsilon\Delta\varepsilon_n + \alpha\Delta\varepsilon_n^2\,, \qquad \dot{\varepsilon}_n = \Delta v_n. \tag{18}$$

Term $\alpha\Delta\varepsilon_n^2$ is negligibly small in the case of small deformation. Thus equations (18) become linear:

$$\dot{v}_n = \omega_e^2\Delta\varepsilon_n\,, \qquad \dot{\varepsilon}_n = \Delta v_n, \tag{19}$$

where $\omega_e = \sqrt{(C+2\alpha\varepsilon)/m}$ is the frequency of particle oscillation. The initial conditions for system (19) are determined by equation (12):

$$v_n|_{t=0} = \sqrt{\frac{k_BT_0}{m}}\rho_n\,, \qquad \varepsilon_n|_{t=0} = \sqrt{\frac{k_BT_0}{C}}\varrho_n\,, \tag{20}$$

where ρ_n and ϱ_n are independent random numbers with zero mathematical expectation and unit variance. The initial problem (19)-(20) describes the stochastic dynamics of the crystal particles. The kinetic temperature of the crystal can be found from analysis of statistic characteristics dynamics. Let us consider the particle velocities covariance κ_k and the bond deformations covariance μ_k [23, 26, 30]:

$$\kappa_k = \langle v_n v_{n+k}\rangle\,, \qquad \mu_k = \langle\varepsilon_n\varepsilon_{n+k}\rangle. \tag{21}$$

Following [23] these covariances allow us to define generalized kinetic K_k and potential U_k energies and generalized Lagrangian $\mathcal{L}_k$:

$$K_k = \frac{1}{2}m\kappa_k\,, \qquad U_k = \frac{1}{2}m\omega_e^2\mu_k\,, \qquad \mathcal{L}_k = K_k - U_k. \tag{22}$$

Differentiation of energies (22) leads to the initial problem for the generalized Lagrangian [23]:

$$\begin{aligned} &\ddot{\mathcal{L}}_k = 4\omega_e^2(\mathcal{L}_{k-1} - 2\mathcal{L}_k + \mathcal{L}_{k+1})\,,\\ &t=0: \quad \mathcal{L}_k = -\frac{T_0k_B\varepsilon\alpha}{C}\delta_k\,, \qquad \dot{\mathcal{L}}_k = 0, \end{aligned} \tag{23}$$

where δ_k is the Kronecker symbol: $\delta_k = 1$ for $k = 0$ and $\delta_k = 0$ otherwise. The solution of an initial problem similar to (23) is obtained in [23]. According to that solution, generalized Lagrangian oscillates with a monotonically decreasing amplitude:

$$\mathcal{L}_k = -\frac{T_0k_B\varepsilon\alpha}{C}J_{2k}(4\omega_et), \tag{24}$$

where $J_k(x)$ is the Bessel function of k-th order [31].

Note, that kinetic energy K and thermal part of the potential energy U_T are equal to the generalized kinetic and potential energies with zero indexes. Therefore, from formulas (10) and (22) the equality of thermal Lagrangian L_T and generalized Lagrangian $\mathcal{L}_k$ with zero index is obtained:

$$L_T = \mathcal{L}_0. \tag{25}$$

After solving equation (23) temperature T can be expressed through thermal energy E_T (11) and thermal Lagrangian L_T (25) in the following way:

$$T = \frac{1}{k_B}(L_T + E_T). \tag{26}$$

The kinetic temperature of the crystal as a function of time can be found using formulas (16) and (24)-(26):

$$T = T_0 + \frac{T_0\alpha\varepsilon}{C}\Big(1 - J_0(4\omega_et)\Big). \tag{27}$$

Note, that according to the asymptotic representation for the Bessel function [31]

$$\begin{aligned} &x \gg \mu+1:\\ &J_\mu(x) = \sqrt{\frac{2}{\pi x}}\cos\left(x - \frac{\pi\mu}{2} - \frac{\pi}{4}\right) + O(x^{-3/2}), \end{aligned} \tag{28}$$

the amplitude of the kinetic temperature oscillations decreases as the inverse root of time.

Fig. 1 shows comparison of the analytical solution (solid line), describing by formula (27) and the numerical solution obtained by computer simulation of the crystal dynamics (circle). In computer simulation the crystal consists of $N = 200$ particles under periodic boundary conditions. The computer simulation uses the method of central differences and integration step $0.01/\omega_e$. The result is averaged over 5000 realizations. Analytical solution (27) practically coincides with results of numerical integration of lattice dynamics equations.

Equation (17) gives us the value around which the kinetic temperature oscillates after crystal deformation. For $t \to \infty$ expression (27) consistents with expression (17) which is obtained from the virial theorem. However, formulas obtained in this section, based on the correlation analysis, allow us to describe the nonequilibrium transient process. Such description is impossible within the framework of equilibrium thermodynamics or statistical mechanics.

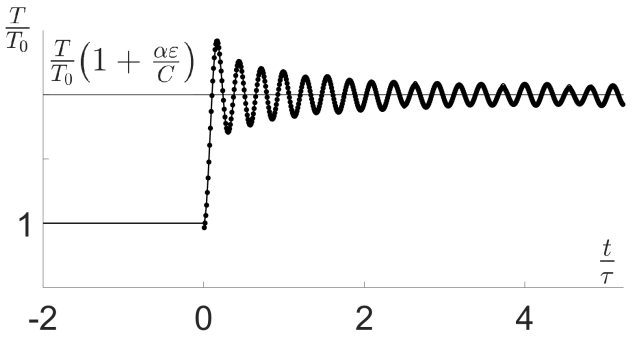

FIG. 1. Oscillations of kinetic temperature T in the infinite crystal after loading in zero moment of time. Numerical (dots) and analytical (solid line) solutions are presented. The averaging is performed using 5000 numerical experiments. The number of particles $N = 200$, constant $\tau = 2\pi/\omega_e$, stiffnesses $C = 1$, $\alpha = 1$ and homogeneous deformation $\varepsilon = 0.1$.

VI. CONCLUSIONS

The paper presents an analytical analysis of the transition process in a one-dimensional nonlinear crystal subjected to instantaneous homogeneous deformation. It is established that the transition process is high-frequency energy oscillations. These oscillations are similar to those realized during instantaneous thermal perturbation of the crystal [23]. For the initially deformed crystal the energy oscillations process is described by the Bessel function of the first kind. Relaxation of the transition process is inversely proportional to the square root of time. After the completion transition process, the well-known solution corresponding to adiabatic heating [19, 20] is established. It is shown that the presented analytical solution practically coincides with results of numerical simulation.

The obtained results can be generalized for the two- and three-dimensional cases[24, 26]. Also the results may be taken into account in future investigations of nanostructures.

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APPENDIXES

Appendix A: The virial relation

Following [19] the mathematical expectation of kinetic energy (4) of the system can be represented by

$$K = \frac{m}{2}\langle u_n v_n\rangle^{\cdot} + \frac{1}{2}\langle u_n \Delta F_n\rangle, \tag{A1}$$

where expression (1) is used. The second term (A1) is

$$\langle u_n \Delta F_n\rangle = -\langle \varepsilon_n F_n\rangle + \langle F_{n+1} u_n\rangle - \langle F_n u_{n-1}\rangle. \tag{A2}$$

Let us define function $g_n \stackrel{\text{def}}{=} \langle F_n u_{n-1}\rangle$, then equation (A1) is

$$K = -\frac{1}{2}\langle \varepsilon_n F_n\rangle + \frac{1}{2} g_n' + \frac{m}{2}\langle u_n v_n\rangle^{\cdot}. \tag{A3}$$

Values g_n and $\langle u_n v_n\rangle$ are constant in the thermodynamical equilibrium state and their derivatives are zero. Therefore the expression for the kinetic energy is

$$K = -\frac{1}{2}\langle \varepsilon_n F_n\rangle. \tag{A4}$$

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