=== **MECHANICS** ===

High-Frequency Thermal Processes in Harmonic Crystals[1]

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Abstract—We consider two high frequency thermal processes in uniformly heated harmonic crystals relaxing towards equilibrium: (i) equilibration of kinetic and potential energies and (ii) redistribution of energy among spatial directions. Equation describing these processes with deterministic initial conditions is derived. Solution of the equation shows that characteristic time of these processes is of the order of ten periods of atomic vibrations. After that time the system practically reaches the stationary state. It is shown analytically that in harmonic crystals temperature tensor is not isotropic even in the stationary state. As an example, harmonic triangular lattice is considered. Simple formula relating the stationary value of the temperature tensor and initial conditions is derived. The function describing equilibration of kinetic and potential energies is obtained. It is shown that the difference between the energies (Lagrangian) oscillates around zero. Amplitude of these oscillations decays inversely proportional to time. Analytical results are in a good agreement with numerical simulations.

Description of nonequilibrium thermal processes is a challenging problem for modern mechanics and physics of solids. The problem is particularly important due to recent advances in nanotechnologies [1]. In the present paper, fast thermal processes [2−4] accompanying the transition of the system from nonequilibrium state towards thermodynamic equilibrium are considered [5]. Initial nonequilibrium state is caused, for example, by fempto- or attosecond laser excitation [6] or by shock waves [7]. In this state kinetic and potential energies are not equal. Also kinetic temperatures corresponding to thermal motion of atoms in different spatial directions may be different [7].[2] Computer simulations show that in harmonic crystals there are two thermal processes accompanying the transition to equilibrium: (i) equilibration of kinetic and potential energies [2, 3, 8] and (ii) redistribution of energy among spatial directions. Characteristic time of these processes is of the order of ten periods of atomic vibrations.[3]

The present paper focuses on the analytical description of the above mentioned thermal processes. The approach described in papers [2, 4] is generalized for the multidimensional case. Two- and three-dimensional harmonic crystals with random initial velocities and displacements of particles[4] are considered. Thermal processes in the crystal are described using the correlation analysis [2, 4, 9−11]. Deterministic problem for the generalized energies [2−4, 10, 11] is formulated. Solution of the deterministic problem yields the function describing equilibration of kinetic and potential energies and the relation between temperatures in different spatial directions in the stationary state.

We consider an infinite simple crystal lattice consisting of particles with equal masses. The nearest neighbors interact via linearized (harmonic) forces. Particles are identified by their radius-vectors in the undeformed state. Motion of particles is described by differential-difference equation:[5]

$$\dot{\mathbf{v}}(\mathbf{r}) = \mathcal{D} \cdot \mathbf{u}(\mathbf{r}), \qquad \mathcal{D} = \omega_*^2 \sum_\alpha \mathbf{e}_\alpha \mathbf{e}_\alpha \Delta_\alpha^2,$$

$$\Delta_\alpha^2 \mathbf{u}(\mathbf{r}) = \mathbf{u}(\mathbf{r} + \mathbf{a}_\alpha) - 2\mathbf{u}(\mathbf{r}) + \mathbf{u}(\mathbf{r} - \mathbf{a}_\alpha), \tag{1}$$

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[1] The article was translated by the authors.

[2] Here and below, kinetic temperature proportional to kinetic energy of thermal motion is considered.

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[3] We define the period as $\tau_* = 2\pi\sqrt{m/C}$, where m is the mass of the atom, C is the bond stiffness.

[4] The randomness is introduced with initial conditions.

[5] This equation is equivalent to the infinite system of ordinary differential equations of the second order.

where $\mathbf{u}(\mathbf{r})$, $\mathbf{v}(\mathbf{r})$ are displacement and velocity of the particle with radius-vector $\mathbf{r}$; $\mathcal{D}$ is the tensor difference operator; $\mathbf{a}_\alpha$ is the vector connecting two neighboring particles; $\mathbf{e}_\alpha = \mathbf{a}_\alpha / |\mathbf{a}_\alpha|$; $\omega_* = \sqrt{C/m}$; C is the bond stiffness; m is the particle's mass. The summation is carried out over noncollinear bond directions α. In particular, $\alpha = 1, 2$ for a square lattice and $\alpha = 1, 2, 3$ for a triangular lattice. Initial displacements and velocities of the particles have the form:

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}_0(\mathbf{r}), \quad \mathbf{v}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}), \tag{2}$$

where $\mathbf{u}_0$, $\mathbf{v}_0$ are independent random vectors with zero mean.

Equation (1) with initial conditions (2) completely determines the dynamics of the crystal. In principle, it can be solved analytically. The resulting solution yields stochastic displacements and velocities of all particles. In contrast, description of macroscopic thermal processes usually focuses on statistical characteristics such as temperature.

In papers [2, 3, 10, 11] it is shown that kinetic temperature is insufficient for obtaining closed system of equations. A closed system can be derived for the generalized energies. We define the generalized (two-particle) kinetic $\mathbf{K}$ and potential Π energies for particles i and j with radius-vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ as:

$$\mathbf{K}(\mathbf{r}_i, \mathbf{r}_j) = \frac{m}{2}\langle \mathbf{v}_i \mathbf{v}_j \rangle,$$
$$\Pi(\mathbf{r}_i, \mathbf{r}_j) = -\frac{m}{4}(\mathcal{D} \cdot \langle \mathbf{u}_i \mathbf{u}_j \rangle + \langle \mathbf{u}_i \mathbf{u}_j \rangle \cdot \mathcal{D}). \tag{3}$$

Here, $\mathbf{v}_i = \mathbf{v}(\mathbf{r}_i)$; brackets $\langle\ \rangle$ denote the expected value of a random variable. For $i = j$, the traces of tensors $\mathbf{K}$, Π correspond to conventional kinetic and potential energies per particle. We also define the *tensor temperature* $\mathbf{T}$ [7] as

$$\frac{1}{2}k_B\mathbf{T}(\mathbf{r}_i) = \frac{m}{2}\langle \mathbf{v}_i \mathbf{v}_j \rangle = \mathbf{K}|_{i=j}, \tag{4}$$

where k_B is Boltzmann's constant, d is the space dimensionality. The kinetic temperature T is associated with the tensor $\mathbf{T}$ by the relation $T = (1/d)\mathrm{tr}\mathbf{T}$. The generalized total energy $\mathbf{H}$ and the generalized Lagrangian $\mathbf{L}$ are defined as

$$\mathbf{H} = \mathbf{K} + \Pi, \quad \mathbf{L} = \mathbf{K} - \Pi. \tag{5}$$

We consider only processes in uniformly heated crystals. In this case the generalized energies satisfy the relations

$$\mathbf{K}(\mathbf{r}_i, \mathbf{r}_j) = \mathbf{K}(\mathbf{r}_i - \mathbf{r}_j), \quad \Pi(\mathbf{r}_i, \mathbf{r}_j) = \Pi(\mathbf{r}_i - \mathbf{r}_j).$$

Argument $\mathbf{r}_i - \mathbf{r}_j$ is omitted below for brevity. Note that the points defined by vectors $\mathbf{r}_i - \mathbf{r}_j$ form the same lattice as vectors $\mathbf{r}_i$.

We show that the generalized total energy $\mathbf{H}$ satisfies several conservation laws. Computing the time

derivative of $\mathbf{H}$ and using equations of motion (1) yields:

$$\dot{\mathbf{H}} = \mathcal{D} \cdot \mathbf{q} - \mathbf{q} \cdot \mathcal{D}, \quad \mathbf{q} = \frac{m}{4}\langle \mathbf{u}_i \mathbf{v}_j - \mathbf{v}_i \mathbf{u}_j \rangle. \tag{6}$$

Multiplying equation (6) by $\mathcal{D}^n$, we obtain the conservation laws

$$\mathcal{D}^n \cdot \mathbf{H} = \mathrm{const}, \quad n = 0, 1, 2, \dots . \tag{7}$$

In the case $n = 0$ and $i = j$ formula (7) coincides with the conventional law of energy conservation. From the Cayley–Hamilton theorem it follows that the number of independent conservation laws (7) is equal to space dimensionality.

We derive the dynamic equations for generalized energies. Differentiating the generalized Lagrangian $\mathbf{L}$ with respect to time and taking equations of motion (1) into account yields:

$$\ddot{\mathbf{L}} - 2(\mathcal{D} \cdot \ddot{\mathbf{L}} + \ddot{\mathbf{L}} \cdot \mathcal{D})$$
$$+ \mathcal{D}^2 \cdot \mathbf{L} - 2\mathcal{D} \cdot \mathbf{L} \cdot \mathcal{D} + \mathbf{L} \cdot \mathcal{D}^2 = 0, \tag{8}$$

where $\mathcal{D}^2 = \mathcal{D} \cdot \mathcal{D}$. It can be shown that quantities $\mathbf{K}$, Π, $\mathbf{H}$ also satisfy Eq. (8). Corresponding initial conditions are uniquely determined by initial displacements and velocities of the particles (2). Thus dynamics of the generalized energies is described by Eq. (8) with deterministic initial conditions.

Computer simulations show that after a short transient process the system practically reaches the *stationary state*.[6] Consider the relation between stationary values of the generalized energies and the initial conditions. Using Eq. (8) for $\mathbf{H}$ and conservation laws (7) yields the closed system of equations for stationary values of the generalized energies:

$$\mathrm{tr}\mathbf{H} = \mathrm{tr}\mathbf{H}_0, \quad \mathcal{D} \cdot \mathbf{H} = \mathcal{D} \cdot \mathbf{H}_0, \quad \mathcal{D}^2 \cdot \mathbf{H} = \mathcal{D}^2 \cdot \mathbf{H}_0,$$
$$\mathcal{D}^2 \cdot \mathbf{H} - 2\mathcal{D} \cdot \mathbf{H} \cdot \mathcal{D} + \mathbf{H} \cdot \mathcal{D}^2 = 0, \tag{9}$$

where $\mathbf{H}_0$ is the initial value of the generalized total energy. The relation between the generalized kinetic and potential energies follows from the identity $\frac{m}{4}\langle \mathbf{u}_i \mathbf{u}_j \rangle^{..} = \mathbf{L}$. In the stationary state, the left hand side of this equation is equal to zero, then

$$\mathbf{K} = \Pi = \frac{1}{2}\mathbf{H}. \tag{10}$$

Equation (10) and the first of Eq. (9) lead to the following expression for traces of the generalized energies: $\mathrm{tr}\mathbf{K} = = \mathrm{tr}\Pi = \frac{1}{2}\mathrm{tr}\mathbf{H}_0$. In the particular case $i = j$, the given expression follows from the virial theorem. Deviators of the generalized energies are determined by solution of Eqs. (9), (10).

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[6] The stationary state is defined so that the second time derivatives of the generalized energies are equal to zero.
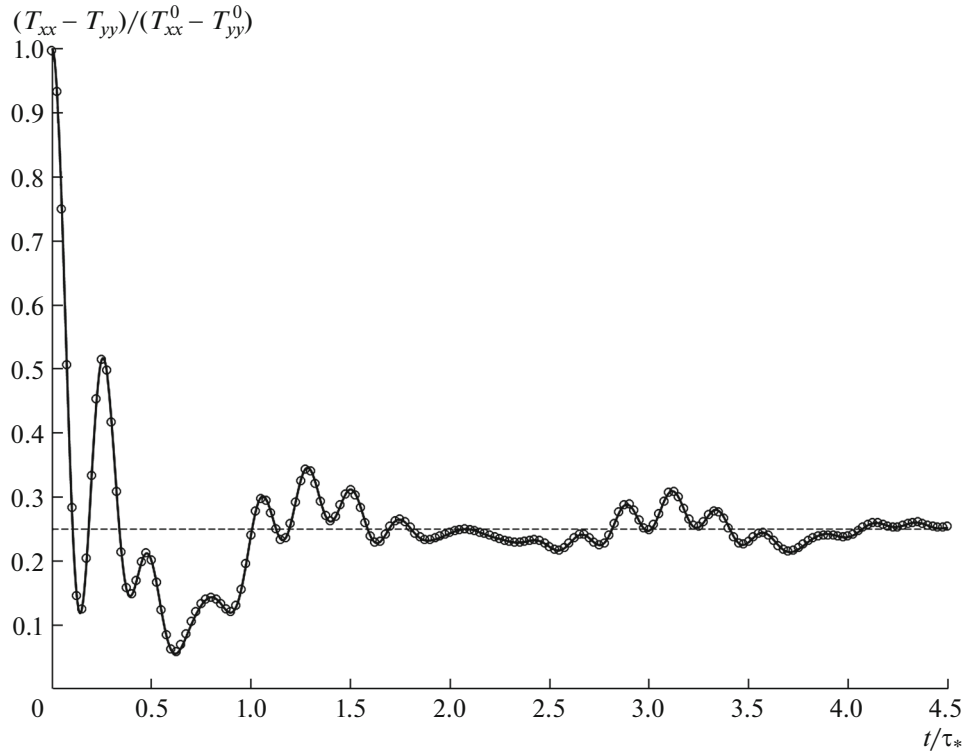
Fig. 1. Time-dependence of the difference of temperatures corresponding to x and y directions (triangular lattice). Circles—numerical solution of lattice dynamics Eqs. (1) (1.6×10^4 particles; periodic boundary conditions). Solid line—numerical solution of the differential-difference Eq. (8) for the generalized kinetic energy. Dashed line—analytical solution (12) of the stationary problem.

The derivations presented above are valid in two- and three-dimensional cases. As an example, consider transition to the stationary state in the two-dimensional harmonic triangular lattice. Initial velocities of the particles are independent random vectors with zero mean; initial displacements are equal to zero. In this case initial conditions for the Lagrangian $\mathbf{L}$ have the form:

$$\mathbf{L} = \mathbf{H} = \mathbf{K}_0 \delta(\mathbf{r}_i - \mathbf{r}_j),$$
$$\mathbf{K}_0 = \frac{m}{2} \langle \mathbf{v}_i \mathbf{v}_i \rangle, \quad \dot{\mathbf{L}} = 0, \quad (11)$$
$$\ddot{\mathbf{L}} = 2(\mathcal{D} \cdot \mathbf{L} + \mathbf{L} \cdot \mathcal{D}), \quad \dddot{\mathbf{L}} = 0,$$

where $\delta(\mathbf{r}_i - \mathbf{r}_j) = 0$ for $i \neq j$; $\delta(0) = 1$.

Consider the stationary value of the tensor temperature (4). Equations (9) with initial conditions (11) are solved with respect to $\mathbf{H}$ using the discrete Fourier transform. After that the tensor temperature is calculated using formulas (4), (10). For an infinite triangular lattice the following relation between the temperature tensor (4) and initial conditions is obtained:

$$k_\mathrm{B} \mathrm{dev}\mathbf{T} = \frac{1}{2} \mathrm{dev}\mathbf{K}_0. \quad (12)$$

Therefore, the temperature tensor in the stationary state, in general, is not isotropic.

We compare the results given by formula (12) with numerical solution of lattice dynamics Eqs. (1). Verlet integration scheme with the time step $10^{-3}\tau_*$ is used. Here and below, $\tau_* = 2\pi/\omega_*$. Initial displacements of particles are equal to zero. Initial velocities have random magnitude and directed along one of the lattice directions (x axis). Time dependence of the difference between temperatures in x and y directions is shown in Fig. 1. Numerical solution of Eq. (8) for $\mathbf{K}$ is also given for comparison. It is seen that the system practically reaches the stationary state after several periods τ_*. In the stationary state, the relation (12) is satisfied. Transition to the stationary state is exactly described by Eq. (8).

Consider equilibration of kinetic and potential energies in the triangular lattice. The process is described by Eq. (8). Initial particle velocities are independent random vectors, uniformly distributed among spatial directions. In this case $\mathbf{K}_0 = \dfrac{K_0}{2}\mathbf{E}$, where $\mathbf{E}$ is the unit tensor. The following assumption
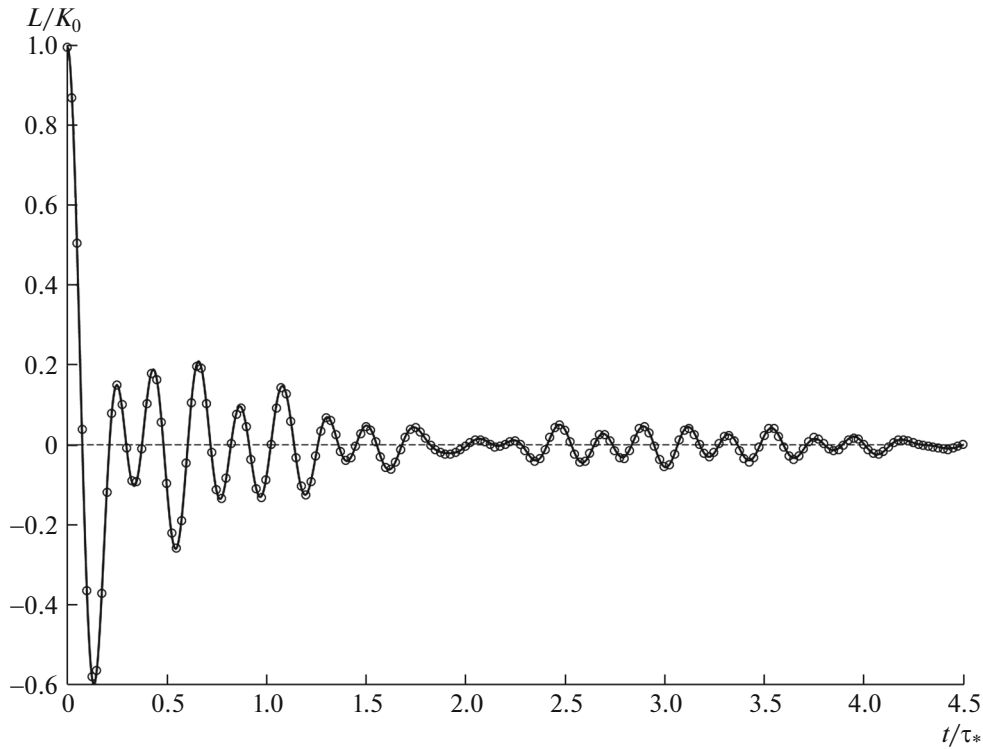
Fig. 2. Oscillations of the Lagrangian in the triangular lattice with random initial velocities. Solid line—analytical solution (14); circles—numerical solution of lattice dynamics Eqs. (1).

is used for solution of Eq. (8) with initial conditions (11)[7] $\mathcal{D} \cdot \mathbf{L} = \mathbf{L} \cdot \mathcal{D}$. Then Eq. (8) takes the form

$$\ddot{\mathbf{L}} = 4\mathcal{D} \cdot \mathbf{L}. \tag{13}$$

Note that Eq. (13) is similar to the equation of motion (1). Equation (13) is solved using the discrete Fourier transform. In the case of infinite crystal the solution gives the following expression for Lagrangian $L = \mathrm{tr}\mathbf{L}\,|_{i=j}$:

$$L(t) = \frac{K_0}{2\pi^2} \int_0^\pi \int_0^\pi \left(\cos(2\Omega_1(s, p)t) \right.$$
$$+ \cos(2\Omega_2(s, p)t) \big) \, \mathrm{d}s \mathrm{d}p,$$
$$\Omega_k^4 - 4\omega_*^2 \Omega_k^2 (\sin^2 s + \sin^2 p + \sin^2(s + p))$$
$$+ 12\omega_*^4 \big(\sin^2 s \sin^2 p \tag{14}$$
$$+ \sin^2(s + p)(\sin^2 s + \sin^2 p) \big) = 0, \quad k = 1, 2.$$

The second formula from (14) corresponds to the dispersion relation for the triangular lattice.

Formula (14) shows that the difference between kinetic and potential energies oscillates with the

amplitude inversely proportional to time. It decays by two orders of magnitude in $10\tau_*$. In the one-dimensional case, similar oscillations are described by the Bessel function of the first order, which decays inversely proportional to the square root of time [2].

Analytical solution (14) is compared with numerical solution of lattice dynamics Eqs. (1) (see Fig. 2). It is seen that solutions practically coincide.

Thus in the present paper the analytical description of two nonequilibrium thermal processes, notably (i) equilibration of kinetic and potential energies and (ii) redistribution of energy among spatial directions, was proposed. Equation (8) with deterministic initial conditions describing both processes in two- and tree-dimensional cases was derived. Stationary values of the generalized energies are related with the initial conditions by Eqs. (9), (10). It was shown that in the triangular lattice the temperature tensor is not isotropic. Its deviator in the stationary state is determined by formula (12):

$$T_{xx} - T_{yy} = \frac{1}{4}\left(T_{xx}^0 - T_{yy}^0\right), \tag{15}$$

where T_{xx}^0, T_{yy}^0 are initial temperatures in x and y directions. Also it was shown that equilibration of kinetic and potential energies is described by formula (14).

The results obtained in the present paper can be used for description of fast thermal processes in weakly

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[7] This assumption significantly simplifies Eq. (8). Comparison with numerical solution of the lattice dynamics Eqs. (1) shows that Eq. (13) correctly describes behavior of Lagrangian $L = \mathrm{tr}\mathbf{L}\,|_{i=j}$ (see Fig. 2). Therefore the assumption is acceptable.

anharmonic crystals (at low temperatures). In paper [12] it is shown that small nonlinearity leads to slow energy exchange between the normal modes. As a result, at short times considered above the effect of nonlinearity is weak.

Also the results may serve for description of anomalous heat transfer. This process in defect-free crystals, in general, is not described by the Fourier law [3, 9−11, 13−15].

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