One-Dimensional Heat Conduction and Entropy Production

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Abstract This review paper analyzes the entropy concept and the second law of thermodynamics in the context of one-dimensional media. For simplicity, only thermal processes are taken into account and mechanical motions are neglected. The relation between entropy and temperature and the constraints on the direction of the heat flux are discussed. A comparison with the approach of P. A. Zhilin and the approach based on statistical mechanics is presented. The obtained conclusions are applied to three models: classical, hyperbolic and ballistic heat conduction. It is shown that the concept according to which heat flows from hot to cold is consistent only with the classical model. The peculiarities of the entropy definition and the second law of thermodynamics formulation for non-classical systems are discussed.

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1   Introduction

The concept of entropy is one of the most ambiguous in connection with the description of thermal processes. The reason for this is that there is no unique approach for analysis of non-equilibrium thermal processes. Therefore in this work we analyze thermal processes by using one of the simplest models: a homogeneous one-dimensional medium without mechanical motions. In this case, the equation of the energy balance can be written in the form

$$\rho\dot{U} = -h', \tag{1}$$

where ρ is the density, U is the (specific) internal (in the present case purely thermal) energy, h is the heat flux, the dot and the prime denote the time and spatial derivatives, respectively. In our case the thermal energy depends only on temperature T, thus

$$\dot{U} = c_V\dot{T}, \tag{2}$$

where c_V is the specific heat capacity at constant volume. If the temperature deviations are small, then the heat capacity can be treated as a constant. The relation between the heat flux and the temperature is usually described by Fourier's law [1, 2]:

$$h = -\kappa T' \quad \Rightarrow \quad \dot{T} = \beta T'' \tag{3}$$

As a result, we obtain the classical heat conduction equation, where κ is the thermal conductivity coefficient and $\beta = \kappa/(\rho c_V)$ is the thermal diffusivity coefficient. The equation is obtained by substituting Fourier's law together with relation (2) into the energy balance equation (1). The heat equation (3) describes the diffusive propagation of heat. It is widely used, but it has a number of drawbacks, such as an absence of a thermal front and an infinite speed of a signal propagation. This problem can be avoided by modification of Fourier's law, which leads to the equation of hyperbolic heat conduction (Maxwell, Cattaneo, Veronotte, Lykov) [3, 4]

$$\dot{h} + \frac{1}{\tau}h = -\frac{\kappa}{\tau}T' \quad \Rightarrow \quad \ddot{T} + \frac{1}{\tau}\dot{T} = \frac{\beta}{\tau}T''. \tag{4}$$

However, in this equation, another problem arises. It is difficult to provide an accurate physical interpretation and calculation of the relaxation time τ. Another alternative to Fourier's law leads to the equation of ballistic heat propagation [5]:

$$\dot{h} + \frac{1}{t}h = -\rho c_V c^2 T' \quad \Rightarrow \quad \ddot{T} + \frac{1}{t}\dot{T} = c^2 T'', \tag{5}$$

where the constant c is the speed of sound in the media. Equation (5) contains the variable physical time t instead of the constant relaxation time τ. The ballistic heat equation (5) describes the evolution of an instantaneous thermal perturbation at $t = 0$

in the most simple model of a one-dimensional harmonic crystal. Such a perturbation can be realized by an ultrafast laser heating [6].

Fourier's law (3) represents the intuitive idea that the heat must flow from hot to cold. Equations (4) and (5) allow for the reverse situation—when the heat flows from cold to hot. The reason for this is that these equations have inertial terms (due to the term $\ddot{T}$). In inertial processes, the direction of the media's reaction does not necessarily coincide with the direction of the external perturbation. However, in this case a serious question arises: does this behavior of the system contradict the second law of thermodynamics? This question is analyzed in the current work.

2 The Simplest Thermodynamics of a One-Dimensional Medium

2.1 Energy Balance Equations

Let us consider the simplest theory for a one-dimensional continuous medium. We only consider the process of heat propagation, neglecting mechanical motions. In this case, the energy balance equation for a certain material volume can be written in the form:

$$\dot{\mathscr{U}} = \mathscr{Q}, \tag{6}$$

where $\mathscr{U}$ is the internal energy of the considered volume, $\mathscr{Q}$ is the rate of heat supply to the system, the dot denotes the time derivative. These quantities can be written in the form:

$$\mathscr{U} = \int_V \rho U \, dV, \qquad \mathscr{Q} = -\int_\Gamma vh \, d\Gamma + \int_V \rho r \, dV, \tag{7}$$

where ρ is the density (related to the number of particles per unit volume or length), U is the specific energy (per particle), h is the heat flux, r is the volumetric heat supply, V is the one-dimensional volume (length) of the media, Γ is the boundary, $v = \pm 1$ is the one-dimensional normal (the direction indication coefficient).

Since there are no mechanical motions, the volume V does not change and the density ρ is constant. For the one-dimensional crystal it is fulfilled that $\rho = 1/a$, where a is the initial distance between neighboring particles. Following [7] notations V, Γ and v are used that are analogues of the corresponding quantities for a three-dimensional continuous medium. For a one-dimensional medium the volume V is some interval of the spatial coordinate $x \in [x_1, x_2]$, the boundary Γ are the points x_1 and x_2. The coefficient v has the values $v = -1$ for $x = x_1$ and $v = +1$ for $x = x_2$ and is an analogue of the normal vector of the three-dimensional case. Thus, the integrals used in (7) can be written in the form

$$\int_V f \, dV = d \int_{x_1}^{x_2} f(x) \, dx, \qquad \int_\Gamma vf \, d\Gamma = f(x)\Big|_{x_1}^{x_2} = \int_{x_1}^{x_2} f'(x) \, dx. \tag{8}$$

Here the volume integration is replaced by the boundary integration. This replacement is an analogue of the Gauss-Ostrogradsky formula but for the one-dimensional case. Substitution of the quantities (7) to the balance equation (6) with the use of (8) after contracting the domain of integration into a point ($x_1 \to x_2$) yields the differential form for the energy balance equation:

$$\rho \dot{U} = -h' + \rho r, \tag{9}$$

where the prime denotes the derivative with respect to the spatial coordinate x.

2.2 Entropy and the Second Law of Thermodynamics

Entropy is introduced as an additive function of volume:

$$\mathscr{S} = \int_V \rho S \, dV, \tag{10}$$

where S is the specific entropy (per particle). The rate of entropy change has two components:

$$\dot{\mathscr{S}} = \dot{\mathscr{S}}^i + \dot{\mathscr{S}}^e, \tag{11}$$

where the index i denotes the entropy production due to internal processes in the system, and the index e is related to the change of entropy due to the heat transfer across the boundary. The second term in (11) is defined by the relation

$$\dot{\mathscr{S}}^e = -\int_\Gamma v \frac{h}{T} \, d\Gamma + \int_V \rho \frac{r}{T} \, dV, \tag{12}$$

where T is the temperature. Formula (12) is based on the principle that an elementary increment of the entropy caused by an external heat supply is equal to an elementary heat transfer to the system divided by the temperature at the considered point: $\delta S^e = \delta Q/T$. For the entropy production due to internal processes in the system there is no analogous definition. The following inequality for the entropy production is postulated instead:

$$\dot{\mathscr{S}}^i \geq 0, \tag{13}$$

which is one of the forms of *the second law of thermodynamics*.

Inequality (13) can also be formulated as [8]:

$$\dot{\mathscr{S}} \geq \dot{\mathscr{S}}^e. \tag{14}$$

According to [8], this relation is the *Clausius-Duhem inequality*. Its formulation reads [8]: The rate of change of the entropy of a material body is not less than the rate of entropy supplied to this body from the outside.[1] Obviously, this formulation is equivalent to formulation (13): the internal production of entropy is non-negative. The formulation (13) is shorter and contains only one concept, so it may be preferable from a methodical point of view.

Substitution of the relations (10)–(12) into the inequalities (13) and (14) with the use of (8) yields

$$\mathscr{S}^i = \int_V \left(\rho \dot{S} + \left(\frac{h}{T} \right)' - \rho \frac{r}{T} \right) dV \geq 0. \tag{15}$$

Since the volume is arbitrary, we obtain the local form of the Clausius-Duhem inequality:

$$\rho \dot{S} + \left(\frac{h}{T} \right)' - \rho \frac{r}{T} \geq 0 \qquad \Longleftrightarrow \qquad \rho T \dot{S} + h' - \rho r - \frac{h T'}{T} \geq 0. \tag{16}$$

2.3 Dissipative Inequality

By using the energy balance equation (9), we transform the inequality (16) to

$$\rho(T\dot{S} - \dot{U}) - \frac{h T'}{T} \geq 0. \tag{17}$$

This inequality can be written in the form of the *universal dissipative inequality* [8]:

$$\Phi - \frac{h T'}{T} \geq 0, \tag{18}$$

where

$$\Phi \stackrel{\text{def}}{=} \rho(T\dot{S} - \dot{U}) = -\rho(S\dot{T} + \dot{\Psi}) \tag{19}$$

is called dissipative function. The second form of expression (19) contains the (Helmholtz) free energy Ψ:

$$\Psi \stackrel{\text{def}}{=} U - TS. \tag{20}$$

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[1]Literally it is said in [8]: "the rate of change of internal entropy...". However, the word "internal" is used only as an antithesis to entropy coming from outside. Therefore, this notation of "internal entropy" is equivalent to the notation of "entropy" used in the current work. Moreover, one cannot divide the entropy into internal and external. Entropy supply is different—it can be associated with a transfer from outside or with an internal processes. After entropy has entered the system, it "mixes," and it is impossible to divide it into internal and external.

The free energy is widely used in continuum mechanics [8], but in this paper we use the internal energy U, since it enables a clearer physical interpretation in context with the considered problem. Let us consider the universal dissipative inequality (18). It contains the dissipative function Φ and the term hT'/T. When mechanical motions are also taken into account, the dissipative function contains one more term, describing the dissipation of the mechanical energy. The second term characterizes the relation between the direction of the heat flux and the temperature gradient. As it will be shown later, in our case the inequality (18) splits in two relations:

$$\Phi = 0, \qquad hT' \leq 0. \tag{21}$$

The first of them demonstrates the absence of dissipation in the system. The second one is the the so-called *Fourier's inequality* [8]. According to *Fourier's inequality* [8] the direction of the heat flux is opposite to the temperature gradient.

2.4 Constitutive Equation

Let the internal energy be a function of the entropy. Then we have:

$$U = U(S) \quad \Rightarrow \quad \dot{U} = \frac{dU}{dS} \dot{S}. \tag{22}$$

Substituting of this expression to inequality (17) yields

$$\rho \left(T - \frac{dU}{dS} \right) \dot{S} - \frac{hT'}{T} \geq 0. \tag{23}$$

Assuming that T and U do not depend on $\dot{S}$, and that $\dot{S}$ can take arbitrary values,[2] we obtain from (23):

$$T = \frac{dU}{dS}, \qquad hT' \leq 0. \tag{24}$$

The first expression gives the relation between the internal energy, entropy and temperature, the second inequality (Fourier's inequality) means that heat flows in the direction opposite to the temperature gradient.

Let us suppose that the temperature deviations are small so that the heat capacity can assumed to be a constant. Postulating further that the internal energy is a function of temperature, we obtain:

$$dU = c_V dT, \tag{25}$$

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[2]Due to external heat supply (12) any value for quantity $\dot{S}$ can be realized.

where c_V is a constant: the heat capacity of the medium at a constant volume.[3] Furthermore we will show later in (43) that in the case of a harmonic crystal $c_V \equiv k_B$. Substituting (25) into (24), we obtain that:

$$T = c_V \frac{dT}{dS} \quad \Rightarrow \quad \dot{S} = c_V \frac{\dot{T}}{T} \quad \Rightarrow \quad S = S_0 + c_V \ln\left(\frac{T}{T_0}\right), \tag{26}$$

where S_0 and T_0 are the initial values of the corresponding quantities in the given spatial point.

Using that $T - T_0 \ll T_0$ and the third equation from (26), we obtain the approximate formula

$$S \approx S_0 + c_V \frac{T - T_0}{T_0}. \tag{27}$$

Note that (26) formally contradicts the third law of thermodynamics [8], which claims that as the absolute temperature tends to zero the entropy should also tend to zero. In our case it is not fulfilled. The reason for this contradiction is that only small deviations of the temperature are considered, so that the heat capacity is treated as a constant. In the general case the heat capacity will tend to zero as the temperature decreases, which allows to fulfill the third law of thermodynamics. However, the specific heat capacity of a harmonic crystal is constant at all temperatures, so this question requires additional analysis.

Let us now consider the second consequence of the second law of thermodynamics, Fourier's inequality: $hT' \leq 0$. If Fourier's law (3) is fulfilled we have

$$h = -\kappa T' \quad \Rightarrow \quad hT' = -\frac{1}{\kappa} h^2 \leq 0. \tag{28}$$

Thus, to fulfill the second law of thermodynamics the thermal conductivity should be nonnegative. However, for the hyperbolic and for the ballistic heat conduction, Eqs. (4) and (5), respectively, we obtain

$$\dot{h} + \frac{1}{\tau} h = -\frac{\kappa}{\tau} T' \quad \Rightarrow \quad hT' = -\frac{1}{\kappa}\left(h^2 + \frac{\tau}{2}\left(h^2\right)^{\cdot}\right); \tag{29}$$

$$\dot{h} + \frac{1}{t} h = -\rho c_V c^2 T' \quad \Rightarrow \quad hT' = -\frac{1}{\rho c_V c^2}\left(h^2 + \frac{t}{2}\left(h^2\right)^{\cdot}\right). \tag{30}$$

In both cases, Fourier's inequality will be satisfied if the absolute value of the heat flux increases. If, however, the absolute value of the heat flux decreases rapidly enough, then the inequality can be violated, and, consequently, heat can flow in the opposite direction: from cold to hot. Thus, the formulation of the second law of thermodynamics in the form presented above is not valid for the hyperbolic and the ballistic heat conduction.

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[3]Since there are no mechanical motions, the volume remains unchanged.

2.5 *Modification of the Constitutive Equation*

The relations (29) and (30) show that Fourier's inequality can be violated for the hyperbolic and ballistic heat conduction. Does this mean a violation of the second law of thermodynamics? Non-equilibrium thermodynamics has possible solutions for this contradiction. Following [9, 10] it can be accepted that the entropy is a function of the internal energy and the heat flux:

$$S = S(U, h^2) \quad \Rightarrow \quad \dot{S} = \frac{\partial S}{\partial U} \dot{U} + 2 \frac{\partial S}{\partial h^2} \dot{h} h. \tag{31}$$

Here h^2 is used since the entropy does not depend on the heat flux direction (according to the principal of material objectivity). Substituting this relation to the inequality (17) we obtain the following form of the Clausius-Duhem inequality:

$$\rho \left(T \frac{\partial S}{\partial U} - 1 \right) \dot{U} + h \left(2\rho T \frac{\partial S}{\partial h^2} \dot{h} - \frac{T'}{T} \right) \geq 0. \tag{32}$$

Applying the approach used in derivation of (24) and assuming that S and T are independent of $\dot{U}$, one obtains

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \qquad h \left(2\rho T^2 \frac{\partial S}{\partial h^2} \dot{h} - T' \right) \geq 0. \tag{33}$$

In accordance with (33), the following constitutive equation for the heat flux can be formulated based on a linear thermodynamic approach:

$$h = \kappa \left(2\rho T^2 \frac{\partial S}{\partial h^2} \dot{h} - T' \right). \tag{34}$$

Following [9, 10] let us assume that

$$\frac{\partial S}{\partial h^2} = -\frac{\tau}{2\kappa \rho T^2}, \tag{35}$$

where τ is the relaxation time. Then (34) yields the differential relation between the heat flux and the temperature:

$$\dot{h} + \frac{1}{\tau} h = -\frac{\kappa}{\tau} T', \tag{36}$$

which corresponds to the equation of hyperbolic heat conduction. Substitution of (35) and the first equality from (33) to (31) gives the following equation for the entropy:

$$\dot{S}(U, h) = \frac{1}{T} \dot{U} - \frac{\tau}{\kappa \rho T^2} \dot{h} h. \tag{37}$$

Thus, the second law of thermodynamics (13) and its consequence—the Clausius-Duhem inequality in the form (16)—were used. Then two assumptions were made: (1) the entropy is a function of the internal energy and the heat flux, (2) relation (35), the form of which was chosen to satisfy the hyperbolic heat equation. This allows to obtain the equation of hyperbolic heat conduction (36) in consistence with the second law of thermodynamics (13).

3 The Approach of P. A. Zhilin

Let us represent the approach of Pavel A. Zhilin [11] to the definition of the entropy in the context of the considered problem. The proposed interpretation of P. A. Zhilin's approach is a personal interpretation of one of the authors of this work (A. M. Krivtsov) and it may differ from other interpretations. Let us consider the energy balance equation (9)

$$\rho \dot{U} = -h' + \rho r. \tag{38}$$

The peculiarity of P. A. Zhilin's approach is that in the general case the arguments of the internal energy are not specified a priori. Instead they should be determined from the energy balance equation. However, this primarily concerns the tensor parameters of state corresponding to the mechanical motion: it is difficult to choose an appropriate form of these parameters without the energy balance equation analysis. In the considered case the mechanical motion is absent, and there is the only one scalar state parameter. Therefore it should be assumed that the internal energy is a function of specific entropy S, then

$$U = U(S) \quad \Rightarrow \quad \dot{U} = T\dot{S}, \qquad T \overset{\text{def}}{=} \frac{\mathrm{d}U}{\mathrm{d}S}. \tag{39}$$

The entropy characterizes the dependence of the internal energy on the ignored degrees of freedom. Temperature is introduced as a coefficient at the entropy time-derivative in the representation of the internal energy time-derivative. Temperature characterizes the energy of the motion via the ignored degrees of freedom. The entropy is the parameter conjugate to the temperature. The temperature is considered as a measurable parameter and the entropy is not. Measurability necessitates the existence of a device (e.g., a thermometer), allowing to measure the considered physical quantity directly.

Thus relation (39)

$$T = \frac{\mathrm{d}U}{\mathrm{d}S} \tag{40}$$

is a consequence of two statements (a) internal energy depends on entropy, (b) temperature is the coefficient at the entropy time-derivative. This is the important difference between P. A. Zhilin's approach and the approaches considered in the previous

sections, where the relation (40) is a consequence of the second law of thermodynamics.

In the approach of P. A. Zhilin the second law of thermodynamics is not considered as a general law of nature. It is replaced by a number of particular laws. The following inequalities are used:

$$\boldsymbol{\Phi} \geq 0, \qquad hT' \leq 0. \tag{41}$$

The first inequality (the dissipative function is not negative)[4] means that dissipation always leads to a loss of energy. The second inequality is Fourier's inequality, which represents the experimental fact that the heat always flows from hot to cold—*the zeroth law of thermodynamics*.[5] In the approach presented above, two inequalities are combined in one (18)

$$\boldsymbol{\Phi} - \frac{hT'}{T} \geq 0, \tag{42}$$

—*the universal dissipative inequality* [8], which represents the second law of thermodynamics in the form of Clausius-Duhem.

It is obvious that inequality (42) is a consequence of the inequalities (41), but the reverse is not true. In Ref. [11] the inequality (42) is said to be too weak for practical applications. If we demand that the inequality (41) is the basic assumption, then we need to prove that there are cases when (42) is fulfilled and (41) is not. If this cannot be shown, then the fundamental nature of the universal dissipative inequality (41) may be in doubt.

In the considered problem the mechanical motion is absent and consequently $\boldsymbol{\Phi} \equiv 0$ and the both approaches lead to Fourier's inequality. This inequality, as it was shown above, is not fulfilled for the systems where the heat propagation is inertial. Resolving this contradiction will be different for each approach. From the point of view of P. A. Zhilin's approach, nothing crucial happens if Fourier's inequality is not fulfilled. From this point of view that it is a particular law, its non-fullfillment does not affect any further derivations. Fourier's inequality can be replaced by some other inequality, and maybe even discarded. From the point of view of the approaches based on the second law of thermodynamics, the situation is more complicated. The violation of Fourier's inequality requires modification of the derivation of the universal dissipative inequality. This modification can be obtained either by changing the formulation of the second law, or by introducing additional state variables.

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[4]This inequality is sometimes called the Planck inequality or the Clausius-Planck inequality, however, in monograph [11] these terms are not used.

[5]In monograph [11] the term "Fourier's inequality" is not mentioned, instead the term "zeroth law of thermodynamics" is used.

4 Harmonic Crystal

Simple lattice models provide an attractive playground to investigate thermomechanical processes at the microscale [2, 5, 12, 13]. Let us consider the application of the equations obtained above for the model of a one-dimensional harmonic crystal. By considering this model it is possible to derive equations which describe the distribution of heat (5) from the dynamic equations of the lattice [5]. The derivation of these equations does not require the concept of entropy and the second law of thermodynamics. However, this model can be used for testing thermodynamical concepts in the case of nonequilibrium processes.

4.1 Kinetic Temperature

The heat motions in a harmonic crystal are the chaotic oscillations of atoms near their equilibrium positions. The internal energy is the mechanical energy of these oscillations, which can be divided into kinetic and potential parts. The following equations holds:

$$U = K + \Pi \,, \qquad \Pi = K = \frac{d}{2}\, k_B T \,, \qquad d = 1 \quad \Rightarrow \quad U = k_B T. \qquad (43)$$

The potential and kinetic energies, Π and K, are equal because: (1) the crystal is harmonic [14], and (2) the process of heat propagation is much slower than the process of energy equalization [15]. Therefore the potential and kinetic energies satisfy the conditions of the virial theorem [16], according to which in a sufficiently long time for a harmonic system these energies should became equal. The relation (43) between the kinetic energy and the temperature is valid because we consider *the kinetic temperature* of the crystal. Comparing relations (43) and (25) we see that the heat capacity for the harmonic crystal is equal to Boltzmann's constant: $c_V = k_B$. Let us note that expression (25) was obtained under the assumption that the temperature has small deviations comparing to it's absolute value. For the harmonic crystal these conditions are not obligatory: there is an explicit relation between the internal energy and the temperature. Therefore, for the harmonic crystal expression (43) has a wider range of applicability than expression (25) for an arbitrary medium.

Substitution of relation (43) between the internal energy and the temperature into Eq. (9) and inequality (17) gives

$$\rho k_B \dot{T} = -h' + \rho r \,, \qquad \rho T \dot{S} - \rho k_B \dot{T} - \frac{h T'}{T} \geq 0. \qquad (44)$$

By using the constitutive equations for h and r the first expression yields a closed equation for the heat propagation. In particular, expression (5) for the heat flux in

the harmonic crystal in the absence of volumetric heat input ($r = 0$) [5] results in the equation of the ballistic heat conduction (5):

$$\ddot{T} + \frac{1}{t}\,\dot{T} = c^2 T''. \tag{45}$$

The inequality in (44) allows to derive an entropy formula in a way similar to (26). It is sufficient to assume that the entropy is a function of the temperature $S = S(T)$. Then the inequality from (44) takes the form

$$\rho\left(T\,\frac{dS}{dT} - k_B\right)\dot{T} - \frac{hT'}{T} \geq 0. \tag{46}$$

Since $\dot{T}$ is arbitrary we obtain

$$T\,\frac{dS}{dT} = k_B\,, \qquad hT' \leq 0. \tag{47}$$

Exactly the same result is obtained if we assume that the temperature is a function of the entropy: $T = T(S)$. The first expression in (47) gives the relation between entropy and the temperature which was considered above. In the case of the harmonic crystal it takes the form

$$S = S_0 + k_B \ln\left(\frac{T}{T_0}\right), \tag{48}$$

where S_0 and T_0 are the initial values of temperature and entropy at a given point in space. Thus, we obtain an explicit relation between temperature and the entropy for each point of the media. The second relation from (47) is Fourier's inequality. In the next section it will be shown that this inequality can be violated for the harmonic crystal. If we limit our consideration to small deviations of temperature T from its initial value T_0 then an approximate formula similar to (27) can be obtained:

$$S \approx S_0 + k_B\,\frac{T - T_0}{T_0}. \tag{49}$$

In the case considered above, both the logarithmic and the linear equations, (26) and (27), respectively, are approximate. For the harmonic crystal, however, the logarithmic dependence (48) is exact, while the linear relation (49) is valid only for small temperature deviations.

4.2 Direction of the Heat Flux

From the thermodynamic analysis presented above it follows that for a harmonic crystal Fourier's inequality should be fulfilled:

$$hT' \leq 0. \tag{50}$$

This means that the direction of the heat flux should be opposite to the temperature gradient. In other words, the heat should flow from hot to cold. However, for a harmonic crystal this condition can either be satisfied or not, depending on the considered initial problem. In [5] it was shown that in the case of instantaneous thermal perturbation the heat propagation in the harmonic crystal is described by equation

$$\dot{h} + \frac{1}{t} h = -k_B \rho c^2 \, T'. \tag{51}$$

Then we have

$$hT' = -\frac{1}{k_B \rho c^2} \left(h^2 + \frac{t}{2} \left(h^2 \right)^{\cdot} \right). \tag{52}$$

From this formula, as well as from formula (30), it follows that for a sufficiently fast decrease of the heat flux Fourier's inequality may be violated. This happens due to the inertial nature of the heat propagation in harmonic crystals, for example, if we solve the ballistic heat equation for a localized temperature distribution (e.g., a rectangular one) [17].

4.3 Entropy for the Harmonic Crystal

For a harmonic crystal the propagation of heat is ballistic—the heat flux can be represented as a superposition of harmonic waves. In addition, the equation of the ballistic heat conduction (45) can be interpreted as reversible in the following sense: it is invariant with respect to replacement of t by $-t$. Let us show, however, that the entropy in the harmonic crystal is not constant. The first of the inequalities shown in Eq. (16) takes the following form in the case of constant entropy ($\dot{S} = 0$) and zero volumetric heat supply ($r = 0$)

$$\left(\frac{h}{T} \right)' \geq 0. \tag{53}$$

This means that the ratio h/T is not decreasing with x. But this is in contradiction with the problem symmetry: both positive and negative directions of x axis are equivalent from the symmetry point of view.

Let us show the violation of the inequality (53) in a particular case, a sinusoidal initial temperature field, $T_0(x) = A \sin \kappa x + B$, where A and B are positive constants with the dimension of temperature, κ is the wave number. In this case the inequality (53) can be satisfied only if h/T is constant. However, according to [5] the solution for the sinusoidal initial temperature distribution has the form:

$$T(t, x) = A J_0(\kappa c t) \sin \kappa x + B, \qquad h(t, x) = -A k_B \rho c J_1(\kappa c t) \cos \kappa x. \tag{54}$$

Substitution of these formulae to (53) yields

$$\frac{h}{T} = -\frac{Ak_B\rho cJ_1(\kappa ct)\cos\kappa x}{AJ_0(\kappa ct)\sin\kappa x + B} \neq \text{const.} \tag{55}$$

Here c is the speed of sound in the harmonic crystal, J_n is the Bessel function. Thus, these contradictions prove that the entropy of the harmonic crystal generally is not constant.

5 Statistical Mechanics

Further above the relation (48) between the entropy and the temperature for a harmonic crystal and Fourier's inequality $hT' \leq 0$ were obtained. In general, Fourier's inequality is not satisfied for the harmonic crystal. This questions the applicability of the formula (45) for the entropy. However, this formula can also be obtained from statistical mechanics [18]:

$$S = k_B \ln\left(\frac{2\pi eU}{h_P\,\omega_e}\right), \tag{56}$$

where S is the specific entropy, U is the specific heat energy, e is Euler's number, h_P is Planck's constant, and ω_e is the elementary frequency.[6] This formula was obtained on the basis of the Boltzmann principle, which relates entropy to the logarithm of the number of possible microstates of the macroscopic system. Equation (56) is derived analytically for a one-dimensional thermodynamically equilibrated harmonic crystal with fixed boundary conditions. By assuming in accordance with (43) that $U = k_BT$ we obtain from (56)

$$S = k_B \ln T + C, \qquad C \overset{\text{def}}{=} \ln\left(\frac{2\pi ek_B}{h_P\,\omega_e}\right). \tag{57}$$

This formula is obtained from statistical mechanics. From a thermodynamical approach the similar formula (48) can be obtained:

$$S = k_B \ln T + C, \qquad C \overset{\text{def}}{=} S_0 - k_B \ln T_0. \tag{58}$$

Formulae (57) and (58) are equal if the initial entropy and temperature are related by (57). Then the initial entropy can be defined as

$$S_0 = k_B \ln\left(\frac{2\pi ek_BT_0}{h_P\,\omega_e}\right). \tag{59}$$

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[6]$\omega_e = \sqrt{C/m}$: the frequency of a particle with the mass m on a spring with the stiffness C, which is $C = \Pi''(a)$, where Π is the potential of the atomic interaction, a is the lattice step.

Thus, statistical mechanics confirms the relation between the entropy and the temperature, Eq. (26), which was obtained above by the thermodynamical approach.

6 Conclusions and Closing Remarks

In the paper, three approaches to the definition of the entropy are considered:

1. The classical thermodynamics approach based on the Clausius-Duhem inequality [8].
2. The approach by P. A. Zhilin [11].
3. The approach of classical statistical mechanics [18].

For the considered system, all three approaches lead to the same differential relation connecting the temperature T, the specific internal energy U, and the specific entropy S:

$$T = \frac{\mathrm{d}U}{\mathrm{d}S}. \tag{60}$$

If the heat capacity c_V is constant, the relation (60) between entropy and temperature is:

$$S = c_V \ln T + C, \tag{61}$$

where C is a constant determined by the initial values S and T at a given point in space. Furthermore, the first approach leads to Fourier's inequality:

$$hT' \leq 0, \tag{62}$$

which means that the heat flux h has the direction in which the temperature decreases. This inequality holds for the classical model of heat conduction (3), but it is in contradiction with models that describe inertial heat transport, such as the hyperbolic (4) or the ballistic (5) heat conduction. In these models the heat can flow in the direction of the temperature increase (form cold to hot). This could be an argument against these models. On principle this could question Eq. (4), which is empirical. But Eq. (5) is analytically derived from the dynamics of the crystal lattice and it is a strict mathematical consequence of the equations of the lattice dynamics.

There are two possible solutions to avoid this contradiction, namely, a change of the formulation of the second law of thermodynamics or consideration of additional state variables. Another explanation, according to P. A. Zhilin, is that the second law of thermodynamics is not a general law. Instead of it, he formulates a set of particular laws, such as Fourier's inequality (61). If this inequality is not fullfilled for specific systems, it is not crucial and shows the peculiarity of such systems. However, for the classical approach, the violation of (61) is critical, since it questions the second law of thermodynamics, which is fundamental for this approach.

Let us introduce possible ways of eliminating this contradiction. It can be made by introduction of additional state variables.

- In Sect. 2.5 it was shown that if the entropy is a function of the fluxes, second law of thermodynamics in the formulation (13) is satisfied. This approach, by choosing the expression for $\partial S/\partial h^2$ (relation (35)), allows to obtain different models of heat conduction. In book [9] the mentioned above variant is analysed, which leads to the hyperbolic heat conduction equation.
- It was shown in [5] that a full description of the thermal processes in a harmonic crystal requires the consideration of an infinite number of generalized (nonlocal) temperatures, in addition to the kinetic temperature. So it makes sense to assume that the entropy of a harmonic crystal also depends on generalized temperatures.
- When we consider slow motions (which are associated with heat propagation), fast processes are neglected. This leads to equalization of kinetic and potential energies. This is also an irreversible process, which leads to the entropy increase.

One of these approaches can be possible solution in order to fulfill the second law of thermodynamics in the considered models of heat conduction.

In conclusion, we want to discuss the concept of irreversibility. The equations of the classical and the hyperbolic heat conduction, Eqs. (4) and (5), respectively, are not invariant with respect to reversing time (the substitution of t by $-t$). This makes them different from, for example, the wave equation. It is usually accepted that this is directly connected with irreversibility of these equations. However, the equation of the ballistic heat conduction

$$\ddot{T} + \frac{1}{t}\,\dot{T} = c^2 T'' \tag{63}$$

is invariant with respect to time reversal: its form remains unchanged when t is substituted by $-t$. On the other hand, it describes irreversible processes: for example, damping of the sinusoidal initial temperature perturbation. Moreover, it was shown in Sect. 4.3 that the entropy for this process is not constant. Therefore, it turns out that the process reversibility is not directly related to the equation invariance with respect to time reversal.

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