On the role of heat flux in the non-stationary thermal problem

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Abstract. The paper reports on the analysis of experimental thermogram obtained in the process of instant cooling of a spherical solid-phase molybdenum sample by the method of electrostatic levitation. We show that the temperature gradient along the radius of the sample is absent during the cooling of the sample from the melting temperature of $T_{\text{melt}} = 2889$ K. Further, we describe a method for determining functional dependencies of local entropy rate of production, force and heat flux on time. It has appeared, that during cooling of the molybdenum solid sphere the local entropy rate of production and heat flux have identical dependence from time-aspire to a minimum with zero value at approach to ambient temperature (thermodynamic extremum principle). It has allowed draw a conclusion, that in the considered non-stationary problem the heat flux plays defining role unlike the stationary one-dimensional problem in which force is an original cause, and the heat flux results from action of force.

1. Introduction

One of the main notions of classical irreversible thermodynamics is the local entropy rate of production $p = \sum F_j J_i$, which is a bilinear function of forces $F_j$ and fluxes $J_i$, whereas in the linear regime it is assumed that the fluxes are linearly dependent on forces [1–3]. For steady-state one-dimensional heat problem ($dT/d\tau = 0$), where the temperature is only a function of a single spatial coordinate $T(x)$, it is known, that force $F_j(x)$ generates the corresponding in value heat flux. Consider a simple one-dimensional heat problem: if two different temperatures $T_1$ and $T_2$ on the two surfaces of a plane are held constant and the force arises $F_j(x) = \nabla \left(1/T(x)\right) = \text{const}$. The force leads to the generation of a heat flux which is constant $J_i(x) = -\lambda\nabla T(x)$ according to the Fourier’s law, where $\lambda$ is the coefficient of conductivity. As a consequence the local entropy rate of production is a constant $p = \text{const}$ as well. If force (gradient of temperature) equals zero, then the heat flux also obtains a zero value. In the given steady-state problem the force is the primary, and the heat flux is the consequence of the force.

In the current paper we consider an opposite case, namely one-dimensional non-stationary change of temperature ($dT/d\tau \neq 0$) with the absent gradient of temperature $T \neq f(x)$, where $T$ is only a function of the single time coordinate $T(\tau)$. Under these conditions, we assume to investigate the behavior of local entropy rate of production $p(\tau)$ and its components $F(\tau)$, $J(\tau)$ over time. Basis is the analysis of experimental thermogram obtained in the process of instant cooling of a spherical solid-phase molybdenum sample. We, firstly, show the results of computational modelling, proving that the isothermal approximation holds along the radius of the spherical sample: this proof is necessary to determine the entropy density $s = S/V$.
(where \( S \) is the entropy, \( V \) is the volume of a sphere). Then we describe the method for finding dependencies of local entropy rate of production, force and heat flux on time. The correctness of the method under consideration is verified by the fulfillment of the extremum principle for \( p(\tau) \). The extremum principle is fundamental and is satisfied in a wide class of problems [4,5]. Finally we compare the role of the heat flux in the steady-state and the non-stationary one-dimensional heat problems.

2. Proving that the isothermal approximation holds

We use the results of the experimental electrostatic levitation method. In the experiment a spherical sample with radius \( R \approx 1 \, \text{mm} \) was held by electrostatic field and spontaneously cooled down from the melting temperature \( T_{\text{melt}} \) to the ambient temperature \( T_{c} \). The advantages of electrostatic levitation method are: the absence of container and as a consequence the high purity of the investigated material of the sample, contact-free prior heating (laser), and usage of contact-free temperature diagnostics (pyrometer). From these researches [6–8], we choose \( p(\tau) \), \( F_{s}(\tau) \) and \( J_{s}(\tau) \), because molybdenum is a material with well studied properties. In this experiment the temperature is measured only on the outer surface of the spherical sample. However, to calculate the \( p(\tau) \), we need to have a sample with the equal temperature within the whole volume of the sphere. In given paper we have carried out numerical modelling of the process of cooling: we solve the non-stationary differential equation of conductivity in spherical coordinates, the dependence of properties on temperature is considered:

\[
\rho(T)C_{p}(T)\frac{\partial T(r, \tau)}{\partial \tau} = \lambda(T)\left(\frac{\partial^{2}T(r, \tau)}{\partial r^{2}} + \frac{2}{r}\frac{\partial T(r, \tau)}{\partial r}\right) + \frac{d\lambda(T)}{dT}\left(\frac{\partial T(r, \tau)}{\partial r}\right)^{2}, \tag{1}
\]

where \( \rho(T) = a_{2}T^{2} + a_{1}T + a_{0} \), where \( a_{0} = 1.0204 \times 10^{4} \, \text{kg/m}^{3}, \, a_{1} = -8.8336 \times 10^{-3} \, \text{kg/(m}^{3}\text{K}) \), \( a_{2} = -1.1104 \times 10^{-5} \, \text{kg/(m}^{3}\text{K}^{2}) \) is a density, \( C_{p}(T) = b_{3}T^{3} + b_{2}T^{2} + b_{1}T + b_{0} \), where \( b_{0} = 2.3221 \times 10^{2} \, \text{J/(kgK)} \), \( b_{1} = 9.4331 \times 10^{-2} \, \text{J/(kgK}^{2}) \), \( b_{2} = -9.6507 \times 10^{-5} \, \text{J/(kgK}^{3}) \), \( b_{3} = 4.0706 \times 10^{-8} \, \text{J/(kgK}^{4}) \) is the specific heat capacity of the material under the constant pressure, \( \lambda(T) = n_{2}T^{2} + n_{1}T + n_{0} \), where \( n_{0} = 1.58195 \times 10^{2} \, \text{W/(mK)} \), \( n_{1} = -4.88923 \times 10^{-2} \, \text{W/(mK}^{2}) \), \( n_{2} = 9.40393 \times 10^{-6} \, \text{W/(mK}^{3}) \), \( r \) is the current value of radius. The border condition and the entry condition are

\[
\lambda(T)\left(\frac{\partial T(r, \tau)}{\partial r}\right)_{r=R} = -\varepsilon(T)\sigma[T(R, \tau)^{4} - T_{c}^{4}], \tag{2}
\]

\[
T(r, 0) = T_{\text{melt}} = 2896 \, \text{K}, \tag{3}
\]

where \( \varepsilon(T) \) is a total hemi-spherical emissivity, and \( \sigma = 5.67 \times 10^{-8} \, \text{W/(m}^{2}\text{K}^{4}) \) is the Boltzmann constant, \( R = 1.1 \times 10^{-3} \, \text{m} \). The step on radius was equal \( \Delta r = 5 \times 10^{-5} \, \text{m} \), the minimum step on time \( \Delta \tau = 1.25 \times 10^{-5} \, \text{s} \). The numerical solution of equations (1)–(3) allows to obtain the change of temperature on the surface \( T(R, \tau) \) of the spherical sample with respect to time, which coincides with experimental function \( T_{R}(\tau) \). The change with respect to time of the difference between numerical temperatures in the center of sphere and on its surface \( T(0, \tau) - T(R, \tau) \) has also been calculated. The results of the calculations are presented in figure 1. Based on figure 1 we conclude, that the difference between the specified temperatures does not exceed 7 K (where \( (7 \, \text{K}/T_{\text{melt}})100 \approx 0.25\% \)), that allows to support the hypothesis about the uniform field of temperature within the whole volume of the sphere \( T = f(\tau) \neq f(r) \). As a result we are able to use the specific thermodynamic functions, in particular the entropy density \( s \).
3. Determining the local entropy rate of production

In the steady-state the full entropy of a system $S$ is constant and the production of the entropy equals zero:

$$\frac{dS}{d\tau} = \frac{d_1 S}{d\tau} + \frac{d_2 S}{d\tau} = 0.$$  \hspace{0.5cm} (4)

In the examined experiment the isothermal approach is fulfilled throughout the whole volume of the spherical sample, therefore it is possible to change here to the local entropy rate of production $p(\tau)$:

$$p(\tau) \equiv \frac{d_1 s}{d\tau} = -\frac{d_2 s}{d\tau} = 0,$$  \hspace{0.5cm} (5)

where $d_1 s$ is a change of entropy production, caused by irreversible processes within the system, $d_2 s$ is an incremental change of the entropy production of the system, responsible for the energy exchange with the environment. In the considered non-stationary experiments ([6–8]) equation 6 is used with the purpose of finding of the specific heat capacity $C_P$:

$$m C_P \frac{dT}{d\tau} = -\varepsilon f_{sph} \sigma (T_{R}^4(\tau) - T_{c}^4),$$  \hspace{0.5cm} (6)

where $T(\tau)$, $m$ and $f_{sph}$ are the true temperature of the sphere, mass and the surface area of the spherical sample accordingly. From the equation (6) follows, that the spherical sample exchanges energy with the environment, its mass and volume are remain constant ($m =$ const, $V_{sph} =$ const). Hence during cooling it is possible to consider the spherical sample as the thermodynamic “closed” system: $ds = d_1 s + d_2 s$, $d_1 s \geq 0$, $d_2 s = dQ/TV$, where $dQ$ is the quantity of heat which the system has exchanged with an environment during the period of time $d\tau$ [1]. Because of equation (6) is the instant thermal balance, we assume that equation (4) also holds instantly in the experimental conditions described above (denoted further
Figure 2. The entropy-production rate density as a function of time, which was obtained at cooling of the spherical sample of molybdenum in the solid phase: rhombs correspond to the results of calculations with equations (5), (7), (8) and experimental dependence $T_R(\tau)$; curve is the approximation $y(x)$ of the points (shown by rhombs) with the coefficient of determination $R^2$.

as assumption 1). Then, the $p(\tau)$ is derived by exchanging the differentials by infinitesimal final differences in equation (5) in the following way:

$$p(T, \tau) \equiv \frac{d_1 s(T, \tau)}{d\tau} = -\frac{d_2 s(T, \tau)}{d\tau} \approx -\frac{\Delta s_2(T, \tau)}{\Delta \tau}.$$  \hspace{1cm} (7)

Further $\Delta s_2(T, \tau)$ is calculated based on the equation from [9]:

$$\Delta s_2(T, \tau) = \rho C_P \ln \left( \frac{T_2(\tau_2)}{T_1(\tau_1)} \right),$$  \hspace{1cm} (8)

where $T_1(\tau_1)$, $T_2(\tau_2)$ are the values of temperature at the experimental cooling curve at the given time points. Note, that the use of equation (8) is justified in the analyzed experimental conditions as the specified temperatures hold within the volume of the sphere as a result of performance of isothermal approach. The equation (8) is deduced for a case $C_P = \text{const.}$ We believe, that its application is correct as infinitesimal changes of temperature are used, for each of which the specific heat capacity value remains constant. Using the thermogram, and equations (7) and (8), we calculate $p(\tau)$ and show that during the process of cooling of the solid-phase molybdenum sample the dependency of local entropy rate of production in the considered experimental conditions is justified.
Figure 3. The force as a function of time, which was obtained at cooling of the spherical sample of molybdenum in the solid phase: rhombs correspond to the results of calculations with equation (9) and experimental dependence $T_R(\tau)$; curve is the approximation $y(x)$ of the points (shown by rhombs) with the coefficient of determination $R^2$.

4. Dependence of a heat flux on time
Local entropy rate of production equals the product of force $F(\tau)$ and heat flux $J(\tau)$. For a spherical sample, force and heat flux can be found from equations (9), (10) in the following way:

$$F(\tau) = \frac{\ln \left( \frac{T_2(\tau_2)}{T_1(\tau_1)} \right)}{V_{sph}} = 3 \ln \left( \frac{(T_1 - \Delta T)/T_1}{R\Delta T} \right) < 0,$$

(9)

$$J(\tau) = R\rho C_P \frac{\Delta T}{\Delta \tau} < 0,$$

(10)

where $\Delta T = T_1(\tau_1) - T_2(\tau_2) > 0$, $\Delta \tau = \tau_1 - \tau_2 < 0$. Equation (10) allows to find the time dependences for a heat flux and to analyze its influence on the function $p(\tau)$. We find that the dependency of $p = f(\tau)$ is described by an exponential function with the fit of approximation with the coefficient of determination $R^2 \approx 0.84$ (figure 2) [10, 11].

In figures 3 and 4 we show the change of force and heat flux over time during the process of cooling of a spherical molybdenum sample.

In figure 3 we observe that force is characterized by a weak functional dependence as a time-linear function. When the temperature decreases to the room temperature ($dT/d\tau \rightarrow 0$, $T \rightarrow T_c$) the force tends not to zero (as in the steady-state case), but to a finite value: $\approx -3/(RT_1)$.

From figures 2 and 4 we conclude that the heat flux and the local entropy rate of production approaching to the exponential dependence on time.

5. Comparison of steady state and non-stationary state
In the steady-state problem the heat flux is the consequence of the force. However in a non-stationary case, the influence of a heat flux is predominating. Firstly, the heat flux and the local entropy rate of production follow the exponential dependency on time. Secondly, when approaching to the equilibrium state, the heat flux (not the force) tends to zero, which leads to $p(\tau) \rightarrow 0$. Thus during the process of cooling ($dT/d\tau < 10^3 \text{ K/s}$) and approaching
Figure 4. The heat-flux density as a function of time, which was obtained at cooling of the spherical sample of molybdenum in the solid phase: rhombs correspond to the results of calculations with equation (10) and experimental dependence $T_R(\tau)$; curve is the approximation $y(x)$ of the points (shown by rhombs) with the coefficient of determination $R^2$.

the equilibrium state ($dT/d\tau \to 0$), the heat flux has analogous dependency on time as the local entropy rate of production $p(\tau)$. Therefore, the heat flux (not force) is responsible for performance of the extremum principle. The given conclusion correlates with known proofs: in nonequilibrium stationary conditions when local entropy rate of production accepts the minimal value, the stream corresponding free force, accepts zero value [1]. It is important to mention here that the role of the heat flux becomes even more prominent in extended irreversible thermodynamics for processes which follow Maxwell–Cattaneo law (the gradient of temperature depends on the heat flux and the velocity of change of the heat flux), because there the heat flux is considered as well as the internal energy density to be an additional variable of entropy density [2, 12–14].

6. Conclusion
In non-stationary thermal problems the dependency of heat flux on time plays the defining role for the extremum principle to be fulfilled. Therefore for the studies carried out in the non-stationary conditions, researchers are advised to measure the heat flux as precisely as possible, analyze its dependence on time, make comparative analysis of the flux value and the velocity of its change over time. Such analyses would allow researchers to assign the results of the experiment to the concrete thermodynamic regime accurately.

References
[1] Kondepudi D and Prigogine I 1999 Modern Thermodynamics from Heat Engines to Dissipative Structures (Chichester: John Wiley & Sons)
[2] Serdyukov S I 2003 Phys. Lett. A 316 177–83
[3] Serdyukov S I 2013 Theor. Found. Chem. Eng. 47(2) 89–103
[4] Prigogine I 1967 Introduction to Thermodynamics of Irreversible Processes (New York: John Wiley)
[5] Glaeseroff P and Prigogine I 1971 Thermodynamics of Structure, Stability and Fluctuations (New York: Wiley)
[6] Rhim W K and Paradis P F 1999 Rev. Sci. Instrum. 70 4652–8
[7] Ishikawa T, Paradis P F and Yoda S 2001 Rev. Sci. Instrum. 72 2490–7
[8] Paradis P F, Ishikawa T and Yoda S 2002 Int. J. Thermophys. 23(2) 555–68
[9] Fogiel M (ed) 2004 The Thermodynamics Problem Solver (Piscataway, NJ: REA)
[10] Kostanovskiy A V and Kostanovskaya M E 2012 Meas. Tech. 55(9) 1043–8
[11] Kostanovskiy A V and Kostanovskaya M E 2013 Meas. Tech. 55(12) 1401–7
[12] Demirel Y and Sandler S I 2001 Int. J. Heat Mass Transfer 44 2439–51
[13] Jou D, Casas-Vázquez J and Lebon G 1996 Extended Irreversible Thermodynamics 2nd ed (Berlin: Springer-Verlag)
[14] Fort J and Llebot J E 1996 J. Phys. A: Math. Gen. 29 3427–36