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Local non-equilibrium transport models

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Contents

Abstract. Local non-equilibrium models of heat and mass transport processes are considered and shown to form a hierarchy of parabolic and hyperbolic equations whose order increases with deviation from local equilibrium. The basic features of these models, in particular their relationship to generalized irreversible thermodynamics, are discussed.

1. Introduction

The processes of energy and mass transport are widespread in nature and technology. That is why the development of transport theory and effective techniques to solve transport problems are of great importance for science and industry.

As any other thermodynamic theory, the classical thermodynamics of irreversible processes and the related theory of transport [1, 2], are based on a number of main concepts (axioms). The axioms help to establish clarity in the formulation of basic theoretical foundations. On the other hand the axioms considerably restrict the application of theory. The concept of local thermodynamic equilibrium and the concept of locality are the main limitations of classical transport theory.

The concept of local thermodynamic equilibrium implies that while the system as a whole is in a non-equilibrium state and gradients of temperature or concentration exist, a state of local equilibrium exists in each small element of medium. For local equilibrium, entropy is a function of the same macroscopic variables as for a system in equilibrium. This means that the state of a non-equilibrium system is described by the local thermodynamic potentials. In turn these potentials only depend on spatial coordinates and time through thermodynamic parameters and follow the equations of thermostatics. For example, if one chooses as independent variables the local density of internal energy $U(x,t)$, the specific volume $v(x,t)$, and the local concentration of different components $C_i(x,t)$ then the state of a physically small volume in the vicinity of point x in the instant of time t is described by the local entropy:

$$S = S\big(U(x,t),\ v(x,t),\ C_1(x,t),\ \ldots,\ C_i(x,t),\ \ldots\big)\,, \quad (1.1)$$

for which Gibbs' law is valid:

$$T\,\mathrm{d}S = \mathrm{d}U + P\,\mathrm{d}v - \sum \mu_i\,\mathrm{d}C_i\,, \quad (1.2)$$

where T, P, μ are the local temperature, pressure and chemical potential respectively. Physically, the approximation of local equilibrium is correct if the relaxation time τ (the time for the establishment of equilibrium in the macroscopically small domains, although containing a large number of particles) is considerably smaller than characteristic time of the process t_0, that is

$$\tau \ll t_0\,. \quad (1.3)$$

In other words, the state of local thermodynamic equilibrium can be established in the system if the speed of deviation of macroparameters due to external stimuli (the speed of equilibrium disruption) is much smaller than the speed of system relaxation into the state of local equilibrium. The concept of locality, used in the development of either the classical thermodynamics of irreversible processes or other thermodynamic theories, assumes that the basic laws of mechanics are valid not only for the system as a whole, but for any part, however small the part may be. It follows that a limit transition is possible in the integral conservation laws for such systems, when the volume of integration tends to zero. The equivalent conservation laws in the form of partial differential equations can be obtained. Physically, such a procedure is not correct as the medium consists of micro-objects (atoms, molecules, clusters, etc.) with qualitatively new properties. The properties of micro-objects are incompatible with the classical knowledge of the mechanics of a

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continuous medium. However, if the characteristic microscale of the process L is much larger than characteristic scale of the medium microstructure h, that is

$$L \gg h\,, \tag{1.4}$$

then such a process is local and complies with the transport equations in the local form. For example, the law of conservation of density of any quantity A in the integral form (substantive balance equation) is [2]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_v \rho A\,\mathrm{d}v = -\int_\Omega J_A\,\mathrm{d}\Omega + \int_v \sigma_A\,\mathrm{d}v\,, \tag{1.5}$$

where ρ is the density, J_A is the flux of A, σ_A is the production of A, v is the volume, and Ω is the surface of the system. From the concept of locality it follows that Eqn (1.5) is valid when $v \to 0$ and $\Omega \to 0$. A differential form of the balance equation can be obtained using the Gauss theorem:

$$\rho\,\frac{\mathrm{d}A}{\mathrm{d}t} + \nabla J_A = \sigma_A\,. \tag{1.6}$$

Equation (1.6) is local because the form of the equation is independent of the characteristic scales of the system. This equation can be applied to any part of the system, however small the part may be.

On the grounds of the concept of local thermodynamic equilibrium and the concept of locality the classical thermodynamics of irreversible processes leads to a parabolic equation of heat transport (and a similar diffusion equation) [1, 2]:

$$\frac{\partial T}{\partial t} = a\nabla^2 T + W\,, \tag{1.7}$$

where a is the thermal diffusivity and W is the heat source. As expected, the classical transport equation (1.7) is local, that is it does not contain the characteristic scale of these systems and, consequently, is valid for any part of the system, however small it may be. Besides, the approximation of local thermodynamic equilibrium [see inequality (1.3)] leads to a transport equation which also does not contain the characteristic time scale (relaxation time). This means that Eqn (1.7) is local with respect to time. Thus, the classical parabolic transport equations are local with respect to time and space.

The characteristic space – time scales L, h, t_0, and τ determine the two characteristic speeds:

$$V = \frac{L}{t_0}\,, \tag{1.8}$$

$$V^* = \frac{h}{\tau}\,. \tag{1.9}$$

The speed (1.8) represents the ratio of microscales of the process and characterizes the linear speed of parameter deviation forced by the external influence. For example, this may be the speed of isotherm movement upon movement of the heat source in the thermoconducting medium. The ratio of microparameters V^* in Eqn (1.9) is an internal characteristic of the system and independent of the external conditions. The value of V^* is the speed of propagation of transport potential perturbations, in other words, the speed of propagation of heat and diffusion waves. For example, in gases, the characteristic microparameters of the medium, for both the processes of heat transport or mass transport, consist of an average free path h and an interval of time between two subsequent collisions of molecules τ. Therefore, V^* is the average velocity of gas molecules, and, because in gases $a = D$, then $V^* = 3D/h = 3a/h$ (where D is the diffusion coefficient). In more complicated systems the diffusion coefficient and thermal conductivity may differ considerably. Thus, for example, in molten metals the diffusion coefficient of an impurity $D \sim 10^{-9} - 10^{-8}\ \mathrm{m^2\,s^{-1}}$ is considerably smaller than thermal conductivity $a \sim 10^{-5} - 10^{-4}\ \mathrm{m^2\,s^{-1}}$. Consequently, the speed of propagation of concentration perturbations (diffusion speed) $V_\mathrm{D} \sim 1-20\ \mathrm{m\ s^{-1}}$ is much smaller than the speed of propagation of heat perturbations $V_T \sim 10^{-3} - 10^4\ \mathrm{m\ s^{-1}}$. In this case the characteristic time of diffusion relaxation $\tau_\mathrm{D} \sim h/V_\mathrm{D}$ is much greater than the time of heat relaxation $\tau_T \sim h/V_T$. In other words, in such system the thermal local equilibrium is established at the time τ_T and only thereafter at the time τ_D are the local equilibrium values of concentration achieved. The situation with diffusion equilibrium following heat equilibrium may arise in other systems with complicated structure, for example in polymers and capillary-porous media.

In the case of propagation of traveling waves the concepts of local equilibrium and space locality are valid subject to $V \ll V^*$ [3].

Note that a transport process is essentially non-local as a particle transports energy and mass from one point in space to another not instantaneously, but over a finite interval of time τ. If the approximation of local equilibrium (1.3) and the concept of space locality (1.4) are satisfied then these effects can be neglected and the transport processes can be described by the classical (local) parabolic equations of type (1.7). These processes are local in space and time and will be called local below. Otherwise, when $t_0 \sim \tau$ or $L \sim h$ the transport process is not local and cannot be correctly described by the classical (local) parabolic transport equation of type (1.7). In order to describe transport in the latter case one should use a non-local transport model, which is not based on the approximation of local thermodynamic equilibrium and the concept of space locality. In the case of the propagation of traveling waves a criterion of the absence of local equilibrium is $V \sim V^*$ [3].

As indicated earlier the propagation velocity of diffusion perturbations V_D may be several orders of magnitude lower than the speed of heat perturbations V_T. Consequently, it is not improbable that the characteristic speed of a transport process can be such that $V_\mathrm{D} \sim V \ll V_T$. In this case the heat transport process occurs in local equilibrium conditions and can be described by the classical parabolic heat conduction equation, while the mass transport process is in local non-equilibrium and does not obey the classical diffusion equation [3 – 6].

2. Extended irreversible thermodynamics

2.1 Basic principles

The so called 'extended irreversible thermodynamics' (EIT) [3, 7 – 13] is one of the most consistent and comprehensive thermodynamic theories, based on the space non-locality of the transport processes and not on the concept of local equilibrium. Apart from classical independent variables, used by the local equilibrium thermodynamics of irreversible processes to describe the state of system far from the local equilibrium, EIT introduces dissipative fluxes (heat flux q, mass flux J, and pressure tensor P) as new independent variables. Thus, in a local non-equilibrium system the

entropy S is a function of not only classical variables [see Eqn (1.1)], but of dissipating fluxes as well (we consider one component diffusion for simplicity):

$$S = S\big(U(x,t),\, v(x,t),\, C(x,t),\, q(x,t),\, J(x,t),\, P(x,t)\big)\,. \tag{2.1}$$

Notice that physically new variables differ significantly from the classical ones. If classical variables obey the conservation laws and change relatively slowly in the process of system evolution, the fluxes, generally, do not obey the conservation laws and are relatively 'fast' variables. The speed of change of these variables upon system relaxation may be high. The introduction of fluxes as independent variables is justified from the physical point of view. Really, any flux in the system means a directional movement of heat and mass carriers, that suggests such a system to be more ordered than a system without fluxes. The entropy is known as a measure of 'disorder'. Consequently, the entropy should be smaller in the systems with fluxes. EIT uses an extended set of independent variables in the description of local non-equilibrium entropy (2.1) and the classical formulation of the second law of thermodynamics with new local non-equilibrium terms in the equations for an entropy production and entropy flux. This leads to evolutionary (relaxation) differential equations for the dissipative fluxes in the form [7–13]:

$$q + \tau_T \frac{\partial q}{\partial t} = -\lambda \nabla T\,, \tag{2.2}$$

$$J + \tau_{\mathrm{D}} \frac{\partial J}{\partial t} = -D \nabla C\,, \tag{2.3}$$

$$p + \tau_0 \frac{\partial p}{\partial t} = -\zeta \nabla V\,, \tag{2.4}$$

$$P^v + \tau_{2p} \frac{\partial P^v}{\partial t} = -2\eta \mathring{V}, \tag{2.5}$$

where $P = p\delta + P^v$, δ is the unit tensor, p is the pressure viscosity (one third of the tensor trace P), P^v is the part of tensor P with trace equal to zero, λ is the thermal conductivity, D the diffusion coefficient, ζ the bulk viscosity, η the dynamic viscosity, $\mathring{V}$ is the symmetrical part of the gradient of speed, and τ_T, τ_{D}, τ_0 and τ_{2p} are the relaxation times for the corresponding dissipating fluxes. In contrast to the classical local equilibrium case, the inclusion of the dissipating fluxes into the independent variables leads to a situation, where the dissipative fluxes are not determined by the respective transport potential gradients, but are the solutions to the evolutionary equations. For instance, in a system with zero temperature gradient the relaxation of the initial value of heat flux q_0 to the equilibrium value $q = 0$ obeys the exponential law:

$$q(t) = q_0 \exp\left(-\frac{t}{\tau_T}\right).$$

It should be emphasized that the equations of dissipative fluxes (2.2)–(2.5) describe the simplest case of a one-step (or one-stage) relaxation. This case does not take into consideration either crossover or spatial non-local effects. Generally, the system can approach local equilibrium through several subsequent stages with different relaxation times and such a process can be spatially non-local.

Furthermore, we consider for simplicity only the process of heat conduction. One should bear in mind that similar considerations and calculations can be applied to other transport processes [7]. In this case the local non-equilibrium entropy $S(U, v, q)$ takes the form

$$S = S_{\mathrm{eq}} - \frac{\tau_T}{2\lambda\rho T^2}\,(\mathbf{q}\cdot\mathbf{q})\,, \tag{2.6}$$

where S_{eq} is the local equilibrium entropy. Taking into consideration that local equilibrium absolute temperature T, determined by the expression $T^{-1} = (\partial S_{\mathrm{eq}}/\partial U)_v$, the local non-equilibrium temperature Θ can be obtained by the differentiation of (2.6) with respect to U:

$$\frac{1}{\Theta} = \left(\frac{\partial S}{\partial U}\right)_{v,q} = \frac{1}{T} + \alpha(\mathbf{q}\cdot\mathbf{q})\,, \tag{2.7}$$

where α is a positive constant. For example, for an ideal monatomic gas expression (2.7) takes the form [11, 12]

$$\frac{1}{\Theta} = \frac{1}{T} + \frac{2}{5}\,\frac{m}{n^2k^3T^4}\,(\mathbf{q}\cdot\mathbf{q})\,, \tag{2.8}$$

where m is the molecular mass, k is the Boltzmann constant, and n is the number of gas molecules in the unit of volume. From equations (2.7) and (2.8) it follows that $\Theta < T$. It is known from molecular kinetic theory that

$$\frac{kT}{m} = \langle V_x^2\rangle = \langle V_y^2\rangle = \langle V_z^2\rangle\,,$$

where V_x, V_y, and V_z are the components of the velocity of a gas molecule. In the local non-equilibrium case the existence of heat flux q leads to the violation of the concept of a uniform distribution of energy by degrees of freedom [12]. Let us assume that the heat flux is directed along the y axis and $q_x = q_z = 0$. In such situation the uniform distribution of energy by degrees of freedom does not hold, that is $\Theta_x = \Theta_z = \Theta < T$ and $\Theta_y = 3T - 2\Theta > T$, where

$$\Theta_x = \frac{m}{k}\langle V_x^2\rangle, \quad \Theta_y = \frac{m}{k}\langle V_y^2\rangle, \quad \Theta_z = \frac{m}{k}\langle V_z^2\rangle$$

[12]. It follows that on deviation of the system from local equilibrium due to the existence of a heat flux, the mean square molecular velocity in the direction of the heat flux exceeds the equilibrium value. In contrast, the mean square velocity along other directions is smaller than the equilibrium value and is determined by the local temperature Θ [see Eqns (2.7) and (2.8)].

It should be emphasized that in strict terms, in the heat flux equation (2.2), one should use a gradient of local non-equilibrium temperature, that is $\nabla\Theta$, instead of ∇T. In practice the difference between Θ and T is small [11, 12]. However, from the conceptual point of view the appearance of $\nabla\Theta$ in the heat flux equation means the existence of a local non-equilibrium stationary state with $q = -\lambda\nabla\Theta$ [7, 11, 12]. This state may differ significantly from the local equilibrium stationary state with $q = -\lambda\nabla T$.

2.2 High order fluxes

The inclusion of dissipative fluxes into the independent variables describing the local non-equilibrium state of system, results in evolutionary equations for these fluxes. Without considering cross effects this leads to the so called Maxwell–Cattaneo equations (2.2)–(2.5). However, these equations can not be represented as complete conservation

laws, where a change in any quantity in a given point of space is attributed to the flux of this quantity (divergence term) and the source of this quantity. Really, the Maxwell – Cattaneo equation (2.2) can be represented as

$$\rho \frac{\partial q}{\partial t} = -\frac{\rho}{\tau_T}(q + \lambda \nabla T)\,.$$

From the phenomenological point of view the right hand side of this equation can be considered as a source. In order to obtain the equation in the form of a complete conservation law the EIT introduces an additional divergence

$$\rho \frac{\partial q}{\partial t} = -\frac{\rho}{\tau_T}(q + \lambda \nabla T) - \nabla q_2\,, \tag{2.9}$$

where q_2 is the flux of heat flux or the second order flux represented by a tensor of second rank. The last term in Eqn (2.9) describes non-local spatial effects. A comparison with the kinetic theory demonstrates that the flux q_2 is related to the fourth moment of non-equilibrium function of the distribution by speeds. Fundamentally, the procedure of introduction of fluxes should be continued, because in the general case, the local non-equilibrium entropy may depend on fluxes of all orders [7].

A rational question at this point is: which order fluxes have to be considered for the description of any system relaxation to the local equilibrium? The answer depends on the range of relaxation times τ_n. If the relaxation time of flux q_n is much bigger than the relaxation time of fluxes $q_{n+1}, q_{n+2}, \ldots$ then, subject to the condition that the characteristic time of the process $t_0 \gg \tau_{n+1}$, it is sufficient to introduce fluxes up to order n. If all the characteristic times t_n are of the same order of magnitude and $t_0 \sim \tau_n$ then one should take into consideration the fluxes of all orders. Let us take the simplest case, when $\tau_T \gg \tau_2, \tau_3, \ldots$ Then the evolutionary equation for heat flux takes the form

$$q + \tau_T \frac{\partial q}{\partial t} = -\lambda \nabla T - l^2 \nabla^2 q\,. \tag{2.10}$$

Taking into account the second order flux q_2 with zero relaxation time $\tau_2 = 0$ leads to the appearance of an additional term $l^2\nabla^2 q$, which describes the non-local spatial effect of the heat transport. Here l is the characteristic scale of non-locality (correlation length).

Thus, a subsequent introduction of high order fluxes results in a hierarchy of heat flux equations, which consider different deviations of the system from local thermodynamic equilibrium and non-local spatial effects. For instance, to describe heat waves and other peculiarities of the transport process in a solid state at low temperature one needs to take into consideration only the second order flux with zero relaxation time, that is limited by equation (2.10) [7]. For ideal gases, fundamentally, all relaxation times τ_n are of the same order of magnitude. Consequently, all relaxation times must be taken into account while describing the system far from local equilibrium [13]. However, in practice, it is usually sufficient to consider only several extra fluxes.

2.3 Transport equation

In previous chapters we considered the heat flux equations. A conservation law is another relationship, which bounds q and T. From the Maxwell – Cattaneo law (2.2) and the law of energy conservation one can derive the equations:

$$\frac{\partial T}{\partial t} + \tau_T \frac{\partial^2 T}{\partial t^2} = a\nabla^2 T + \frac{W}{c_p\rho} + \frac{\tau_T}{c_p\rho}\frac{\partial W}{\partial t}\,, \tag{2.11}$$

$$\frac{\partial q}{\partial t} + \tau_T \frac{\partial^2 q}{\partial t^2} = a\nabla(\nabla q) - a\nabla W\,, \tag{2.12}$$

where $a = \lambda/c_p\rho$ is the temperature conductivity. These equations describe the space and time evolution of temperature and heat fluxes in local non-equilibrium conditions. Thus, the introduction of a heat flux q among the independent variables results in the appearance of relaxation term in the Maxwell – Cattaneo law. This in turn leads to the hyperbolic heat conduction equation (2.11). In such a formulation, when the heat flux is independent variable, in order to determine the time – space evolution of flux a new equation (2.12) is derived (which is also a hyperbolic partial differential equation). The hyperbolic heat conduction equation (2.11) and the related heat flux equation (2.12) possess two groups of parameters $x \pm V_T t = \text{const}$. This means that a heat signal (or high frequency heat perturbation) propagates in the local non-equilibrium conditions with a finite speed $V_T = (a/\tau_T)^{1/2}$. In other words, Eqns (2.11) and (2.12) predict that the temperature deviation on the surface of a semi-infinite body will propagate into the bulk of the body with finite speed V_T. This feature of solutions of the hyperbolic equations differs drastically from the solutions of the classical parabolic equations (1.9) or (1.10). According to these equations the effect of any heat perturbation propagates instantaneously into all space. That means that after application of a heat source the heat from point x propagates so that at the next instant of time the heat perturbations already approach zero asymptotically only at $x \to \infty$ [26]. This 'paradox of the infinite speed of propagation of perturbations' is not correct from the physical point of view as it violates the concept of causality. Thus, the hyperbolic local non-equilibrium equations resolve this paradox.

The hyperbolic heat conduction equation (2.11) possesses the properties of both the classical heat conduction equation, describing a purely dissipative energy transport, and the wave equation (the second derivative with respect to time), describing the propagation of undamped waves. This explains the experimentally observed wave properties of the heat transport process at low temperature, namely the propagation of heat waves with finite speed [14, 15]; the reflection of a heat wave from a thermo-isolating boundary, and the partial reflection and transmission from and into another medium upon arrival of a heat wave on the boundary between two media [16]; the interference of heat waves [17].

Note that, in contrast to the classical local equilibrium case, a definition of the boundary problem for Eqns (2.11) and (2.12) demands specifying an initial value of not only of the temperature, but of $\partial T/\partial t$, q, and $\partial q/\partial t$. The reason is that Eqns (2.11) and (2.12) are equations of the second order and the heat flux q is an independent variable.

Let us consider now the influence of spatial non-local effects on the process of heat transport. In such a case the heat flux q and the temperature gradient are bound by relationship (2.10). From the conservation law and Eqn (2.10) one can derive the heat transport equation, describing the space-time evolution of the temperature of the system T:

$$\frac{\partial T}{\partial t} + \tau_T \frac{\partial^2 T}{\partial t^2} = a\nabla^2 T + l^2 \frac{\partial \nabla^2 T}{\partial t} + \frac{\tau}{c_p\rho}\frac{\partial W}{\partial t} + \frac{W}{c_p\rho} - \frac{l^2}{c_p\rho}\nabla^2 W. \tag{2.13}$$

It follows from Eqn (2.13) that a consideration of spatial non-locality in the heat flux equation (2.10) results in the appearance of new term in the temperature equation as well. The presence of the mixed derivative $\partial\nabla^2 T/\partial t$ in Eqn (2.13) returns the equation from hyperbolic to parabolic. Thus, without accounting for spatial non-locality the hyperbolic transport equation (2.11) predicts that a temperature jump propagates as a surface of a strong discontinuity with constant speed V_T. In contrast, the non-local term $\partial\nabla^2 T/\partial t$ smooths the temperature jump and leads to the occurrence of a front with a continuous change of temperature instead of a strong discontinuity. The thickness of this front increases gradually as $t^{1/2}$. The smoothing action of non-local effects is similar to the smoothing action of the viscosity in gas dynamics. Therefore, the mixed derivative $\partial\nabla^2 T/\partial t$ in the heat transport equation (2.13) may be associated with 'temperature viscosity'.

Note that the method of dummy viscosity, that is the introduction of a dummy viscous term into the equation of gas dynamics, is used to overcome difficulties arising in the numerical analysis of breakup solutions. In this case it is not necessary to specify the boundary conditions for breakup in the computation. At the end of the computation the dummy viscosity tends to zero and the gas return to a non-viscous state. Such a technique, that is the introduction of dummy 'temperature viscosity' may find application in numerical modeling of heat shock waves as well.

If $\tau_2 > 0$ then

$$(\tau_T + \tau_2)\frac{\partial q}{\partial t} + \tau_T\tau_2\frac{\partial^2 q}{\partial t^2} = -\lambda\nabla T - q + l^2\nabla q - \tau_2\lambda\frac{\partial\nabla T}{\partial t}\,. \tag{2.14}$$

Thus at $\tau_2 > 0$ and $\tau_n = 0$ $(n > 2)$ the heat flux equation (2.14) is a second order hyperbolic equation. Corresponding the temperature equation takes the form

$$\frac{\partial T}{\partial t} + (\tau_T + \tau_2)\frac{\partial^2 T}{\partial t^2} + \tau_T\tau_2\frac{\partial^3 T}{\partial t^3} = a\nabla T^2 + (a\tau_2 + l^2)\frac{\partial\nabla^2 T}{\partial t} + \frac{1}{c_p\rho}\left[W + (\tau_T + \tau_2)\frac{\partial W}{\partial t} + \tau_T\tau_2\frac{\partial^2 W}{\partial t^2} - l^2\nabla^2 W\right]. \tag{2.15}$$

Equation (2.15) is also hyperbolic with a finite speed of propagation of perturbations V_2^*:

$$V_2^* = \left(\frac{a}{\tau_T} + \frac{l^2}{\tau_T\tau_2}\right)^{1/2}. \tag{2.16}$$

From equation (2.16) it is clear that $V_2^* > V_T = (a/\tau_T)^{1/2}$, that is the heat wave corresponding to the heat transport equation (2.15), propagates with a higher speed than the heat wave described by Eqn (2.11) (without consideration of the high order fluxes).

Fundamentally, the procedure of introduction of higher order fluxes can be continued. This will lead to a sequence of partial differential transport equations. The equation will be parabolic in the case of zero relaxation time and hyperbolic in the case of non-zero relaxation time. The speed of propagation of the heat wave, corresponding to the series of hyperbolic equations, will increase and approach a finite limit [13].

One of the distinctions of non-local transport equations (2.11), (2.13), and (2.15) is the existence in the right hand side of not only the function of source W, but also its derivatives with respect to both time and space. Formally, these terms can be considered as additional sources of heat, or more precisely as 'quasi-sources'. Of course, the existence of such 'quasi-sources' does not change the overall specific heat of the system, determined by the initial specific heat and the function of real source W. However, 'quasi-sources' can significantly distort the space – time propagation of the temperature and heat flux in the system. Note that the Maxwell–Cattaneo equation (2.2) can be represented as a first order approximation under expansion of a more general relationship $q(t + \tau_T) = -\lambda\nabla T$ into a Fourier series as τ_T. This expression means that a time shift, equal to the time of relaxation, exists between heat fluxes and the temperature gradient. In the context of molecular kinetic theory such a time delay can be considered as the time between two subsequent collisions of molecules, because the molecules need about this interval of time to reach the allocated surface used for the determination of the heat flux. An extra term $\tau\partial q/\partial t$ in the Maxwell–Cattaneo law (2.2) can be considered as a manifestation of the inertial properties of heat transport. Really, writing Eqn (2.2) in the form

$$\tau_T\frac{\partial q}{\partial t} + q = \lambda T^2\nabla\left(\frac{1}{T}\right), \tag{2.17}$$

we can easily find an analogy between Eqn (2.17) and the equation of a movement of a mechanical body induced by a force $\lambda T^2\nabla(1/T)$ and the force of viscosity [second term in the left hand side of Eqn (2.17)]. The heat flux q plays the role of the velocity of movement and the relaxation time τ_T plays the role of mass. Remember that in thermodynamics the quantity $\nabla(1/T)$ is called a thermodynamic force.

3. Two-temperature model

One of the simplest and at the same time quite effective models, describing the process of heat transport in the local non-equilibrium conditions, is the so called two-temperature ($2T$) model [3, 10, 18–30]. It is assumed that the system consists of two interacting subsystems and the characteristic energy exchange (relaxation) time between them is much higher than the relaxation time to the local equilibrium of an individual subsystem. In this case an individual temperature can be assigned to each subsystem. Then the thermal problem in the system can be reduced to the determination of the space – time evolution of these two temperatures taking into the consideration the energy exchange between subsystems.

The $2T$-model was first used to analyze the process of heat transport in metals, where electrons and a lattice played the roles of interacting subsystems [18]. The $2T$-model happened to be rather effective for the description of energy relaxation between different degrees of freedom for molecules in gases and between light and heavy fraction in the mixture of two gases [19]. The $2T$-approximation was used for the description of heat exchange between gaseous and solid phases in capillary-porous media [20–22]. Besides, the $2T$-model showed good performance in the analysis of the interaction of a high energy source with polymeric materials, when the energy from the source is first transmitted to a phonon subsystem and then from phonons to vibrational degrees of freedom of polymer molecules. In the last case an individual temperature can be assigned to each subsystem and the relaxation energy between them plays the most significant role near the point of glass transition [23]. In addition, the $2T$-model can be applied to analyze the process of heat transport

in a plasma, where electrons and ions play the roles of interacting subsystems; in a turbulent flux, where heat exchange occurs between turbulent patches and an inert sublayer [25].

In a number of publications [31 – 33], for the investigation of heat conduction in inhomogeneous media, it was suggested to use the hyperbolic equation accounting for system relaxation to the local equilibrium. Using this approach, estimates of the relaxation times in inhomogeneous systems were obtained. It was shown that these values are several orders of magnitude higher than the relaxation times to local equilibrium in gases, liquids and solids. Consequently, the relaxation time for heat transport in inhomogeneous systems has another physical meaning. The same is applied to other thermophysical parameters of the inhomogeneous system.

First let us consider the case when equilibrium in the system as a whole is absent and there is an energy exchange between subsystems. That is the subsystems have different temperatures T_1 and T_2, but inside each system local equilibrium exists. Then the space – time evolution of the temperatures T_1 and T_2 is described by a pair of related parabolic equations (that is by the classical local equilibrium transport equations) [23, 34]:

$$c_i \frac{\partial T_i}{\partial t} = \lambda_i \nabla^2 T_i \pm g(T_2 - T_1) + W_i \,, \tag{3.1}$$

where $i = 1, 2$; g is the coefficient of heat exchange between the subsystems; a sign plus corresponds to $i = 1$, a minus corresponds to $i = 2$, and W_i is the intensity of the heat evolution sources. Note that all coefficients in Eqn (3.1) are related to the volume unit of the inhomogeneous medium.

In the majority of cases it is, in practice, more convenient to use a mean temperature, which is a measure of heat energy for a volume unit of the inhomogeneous system. For the two component system the mean temperature takes the form

$$\bar{T} = \frac{c_1 T_1 + c_2 T_2}{c_1 + c_2} \,.$$

From equation (3.1) one can obtain the equations, describing the space – time evolution of both subsystem temperatures $T_i\,(i = 1, 2)$ and the mean temperature $\bar{T}$:

$$\frac{\partial T_i}{\partial t} + \tau_1 \frac{\partial^2 T_i}{\partial t^2} - l_{\mathrm{a}}^2 \frac{\partial}{\partial t} \nabla^2 T_i = a^* \nabla^2 T_i - a_{\mathrm{g}} l_{\mathrm{g}}^2 \nabla^4 T_i + \frac{W_1 + W_2}{c_1 + c_2} + \tau_1 \frac{\partial}{\partial t} \frac{W_i}{c_i} - \frac{l_{\mathrm{g}}^4}{c_i} \nabla^2 \frac{W_i}{h_i^2} \,, \tag{3.2}$$

$$\frac{\partial \bar{T}}{\partial t} + \tau_1 \frac{\partial^2 \bar{T}}{\partial t^2} - l_{\mathrm{a}}^2 \frac{\partial}{\partial t} \nabla^2 \bar{T} = a^* \nabla^2 \bar{T} - a_{\mathrm{g}} l_{\mathrm{g}}^2 \nabla^4 \bar{T} + \frac{W_1 + W_2}{c_1 + c_2} + \tau_1 \frac{\partial}{\partial t} \frac{W_1 + W_2}{c_1 + c_2} - \frac{l_{\mathrm{g}}^4}{c_1 + c_2} \nabla^2 \left(\frac{W_1}{h_1^2} + \frac{W_2}{h_2^2} \right) , \tag{3.3}$$

where $\tau_1 = c_1 c_2 / g(c_1 + c_2)$; $h_i^2 = \tau_1 a_i$; $a_i = \lambda_i / c_i$; $l_{\mathrm{a}}^2 = h_1^2 + h_2^2$; $l_{\mathrm{g}}^2 = h_1 h_2$; $a^* = (\lambda_1 + \lambda_2)/(c_1 + c_2)$; $a_{\mathrm{g}} = l_{\mathrm{g}}^2 / \tau_1$.

The heat conduction equations for inhomogeneous media (3.2), (3.3) differ significantly from either the parabolic or hyperbolic thermal conductivity equations. Equations (3.2) and (3.3) contain the parameters of time τ_1 and space l non-locality. This means that if the characteristic space – time scales of the transport process in an inhomogeneous system t_0 and L are such that $t_0 \sim \tau_1$ and $L \sim l$, then parabolic local transport equation becomes invalid and non-local equations (3.2), (3.3) should be used instead.

Let us consider a particular case of equations (3.2) and (3.3) and the physical meaning of the parameters in these equations. In dissipative processes, when heat is transported only by diffusion, the macroscales of such a process L and t_0 are bound as follows: $L^2 = a^* t_0$. Then in zero approximation Eqns (3.2) and (3.3) are resolved into the classical parabolic local equations (the diffusion equations). In the next approximation all terms in Eqns (3.2) and (3.3) should be taken into consideration and the process of heat transport is non-local. The spatial non-locality is characterized by the constants l_{a} and l_{g}, which are the arithmetic and geometric means of characteristic depths of the warming-up of subsystems h_1 and h_2 over the time τ_1, respectively. Parameter τ_1 characterizes the time non-locality of transport process and represents the relaxation time for the temperature difference between subsystems (the time to equalize the temperature or the characteristic time of heat exchange between subsystems). Both these approximations result in parabolic partial differential equations with an infinite speed for the propagation of perturbations.

If the characteristic speed of a process, for example the speed of heat source movement and the speed of propagation of the warm zone $V \sim L/t_0$, is similar in order of magnitude to the characteristic speed $V_T \sim l/\tau$, determined by the relationship between the scales of space and time non-locality, then from Eqns (3.2) and (3.3) a hyperbolic equation (in the one dimensional case) follows:

$$\frac{\partial \bar{T}}{\partial t} + \tau_1 \frac{\partial^2 \bar{T}}{\partial t^2} = a^* \frac{\partial^2 \bar{T}}{\partial x^2} + \frac{W_1 + W_2}{c_1 + c_2} + \tau_1 \frac{\partial}{\partial t} \frac{W_1 + W_2}{c_1 + c_2} \,. \tag{3.4}$$

In this case a spatial non-locality of the heat transport process is absent and the parameter τ_1 characterizes the inertial properties of heat conduction and determines the speed of propagation of heat perturbations:

$$V_T = \left(\frac{a^*}{\tau_1} \right)^{1/2} = \left[\frac{(\lambda_1 + \lambda_2) g}{c_1 c_2} \right]^{1/2} .$$

The inertial properties of heat conduction in inhomogeneous media is related to the presence of a derivative of the source function with respect to time in Eqns (3.2) and (3.3). That is, an external heat stimulus is received by the system with characteristic time delay τ. In a number of cases [31] the application of the hyperbolic thermal conductivity equation to analyze processes in media with inhomogeneous internal structures gives the best fit with experimental data.

Thus, the analysis of heat transport in a two-temperature medium, which obeys the set of bound local heat conduction equations (3.1), showed that this process is non-local both in time and in space. The characteristic scales of non-locality are represented by the time of energy relaxation between subsystems τ_1 and spatial scale l. The latter is equal in order of magnitude to the depth of warming-up of the system for the time τ_1. We should emphasize that these parameters, τ_1 and l, are internal characteristics of the system, similar to specific heat and thermal conductivity. They can be obtained experimentally. The value of these parameters determines when and at which stage of the heat transport process space and/or time non-locality should be taken into consideration. Moreover, as was shown earlier, the relationship between the scales of non-locality and the characteristic macroscales of the transport process determine the type (hyperbolic or parabolic) of the partial differential transport equations for a given process.

Let us consider now a practically important specific case, when the heat conduction and the heat evolution in one of the subsystems can be neglected, for example, $\lambda_1 = 0$ and $W_1 = 0$. Then equation (3.2) takes the form

$$\frac{\partial T_i}{\partial t} + \tau_1 \frac{\partial^2 T_i}{\partial t^2} - l^2 \frac{\partial^3 T_i}{\partial t\, \partial x^2} = a^* \frac{\partial^2 T_i}{\partial x^2} + \frac{W}{c_1 + c_2} + \chi_i \frac{\tau_1}{c_1} \frac{\partial W}{\partial t}\,, \tag{3.5}$$

where $\chi_1 = 0$ and $\chi_2 = 1$. As a consequence of the assumption that $\lambda_1 = 0$, the heat flux through the allocated area in a $2T$-system is determined by the gradient of temperature only in the second subsystem: $q = -\lambda_2 \partial T_2/\partial x$. However, the Fourier law for a $2T$-system as a whole, represented by the interconnection between the heat flux q and temperature gradient $\partial \bar{T}/\partial x$, takes the non-local form:

$$q + \tau_1 \frac{\partial q}{\partial t} = -\lambda \frac{\partial \bar{T}}{\partial x} - l^2 \frac{\partial^2 q}{\partial x^2}\,. \tag{3.6}$$

The modified Fourier law (3.6) and the law of energy conservation, written for the mean temperature, lead to a non-local transport equation for the mean temperature $\bar{T}$, similar to Eqn (3.5).

Notice that the equation for heat flux (3.6) in the $2T$-system coincides with Eqn (2.13), obtained in the frameworks of EIT by the introduction of high order dissipating fluxes as extra independent variables (see Section 2). This means that the presence of high order fluxes in the system is equivalent to a multistage process of energy relaxation between the interacting subsystems with different temperatures $T_1, T_2, \ldots, T_n, \ldots$.

The $2T$-model (3.1), with the corresponding heat transport equations (3.2) and (3.3), and the equation for the heat flux (3.6), is obtained with an assumption of local equilibrium inside each subsystem. The $2T$-system, where the process of relaxation to the local equilibrium takes place in one of the subsystems, is a natural generalization of this model:

$$c_1 \frac{\partial T_1}{\partial t} = g(T_2 - T_1)\,, \tag{3.7}$$

$$c_2 \frac{\partial T_2}{\partial t} + \tau_2 c_2 \frac{\partial^2 T_2}{\partial t^2} = \lambda \frac{\partial^2 T_2}{\partial x^2} + g(T_1 - T_2)\,, \tag{3.8}$$

where τ_2 is the relaxation time to local equilibrium for subsystem 2. It is assumed for simplicity that $W = 0$. After simple transformations from Eqns (3.7) and (3.8) one obtains the heat conduction equation for each temperature T_1 and T_2:

$$\frac{\partial T_i}{\partial t} + \tau_1 \left(1 + \frac{\tau_2 g}{c_2}\right) \frac{\partial^2 T_i}{\partial t^2} + \tau_1 \tau_2 \frac{\partial^3 T_i}{\partial t^3} = a^* \frac{\partial^2 T_i}{\partial x^2} + l^2 \frac{\partial^3 T_i}{\partial t\, \partial x^2}\,. \tag{3.9}$$

As should be expected, accounting for the relaxation process in the subsystem 2 [see Eqn (3.8)] leads to a hyperbolic heat conduction equation (3.9). Both (3.8) and (3.9) determine the finite speed of propagation of heat perturbations $V_2 = (a_2/\tau_2)^{1/2}$.

Equation (3.9) contains three additional parameters (compared with the classical parabolic equation of heat conduction): two times τ_1 and τ_2 ($\tau_1 > \tau_2$) and one space parameter l. The relationship between these microparameters, which characterize the internal properties of the system, and the characteristic parameters (macroparameters) t_0 and L of the transport process, determine the type of transport process and the type of corresponding heat conduction equation.

1. The local limit. If $t_0 \gg \tau_1$ and $L \gg l$ then Eqn (3.9) is resolved to the classical local equilibrium equation of parabolic type. In this case the transport process is local in time and space and independent of the characteristic scales of non-locality τ_1, τ_2, and l. A temperature profile in a semi-infinite body, $x > 0$, at $T = \text{const}$ on the surface $x = 0$, is shown in Fig. 1a. As was already noted, the temperature variation on the surface $x = 0$ is affected by the finite interval of time even at the infinity point $x \to 0$. This means that the parabolic local heat conduction equation predicts an infinite speed of propagation for heat perturbations.

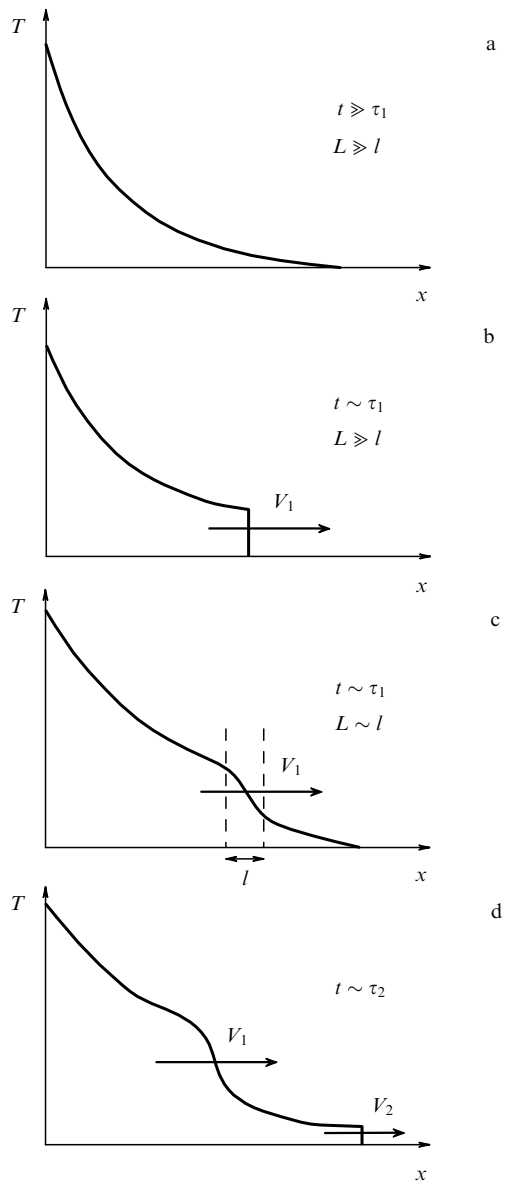

Figure 1. Temperature profiles in a semi-infinite body at $x > 0$ after the temperature jump on the boundary ($x = 0$), at the initial time instant: (a) in the locally equilibrium approximation, corresponding to the solution of the classical parabolic heat conduction equation; (b) in the locally non-equilibrium approximation, corresponding to the solution of the hyperbolic heat conduction equation (2.11) ['telegraph' equation]; (c) in the local approximation, corresponding to the solution of the $2T$-model; (d) in the local approximation, corresponding to the solution of the $2T$-model of hyperbolic type (3.5).

2. In the local spatial limit ($L \gg l$), taking into account local non-equilibrium (that is time non-locality) $t_0 \sim \tau_1$, the transport equation (3.9) is resolved into a hyperbolic one. This equation predicts that the heat perturbations in the local non-equilibrium system propagate with finite speed $V_1 = (a^*/\tau_1)^{1/2}$. In other words, the temperature jump on the boundary of a semi-infinite body propagates as a surface of strong discontinuity with finite speed V_1 (Fig. 1b).

3. In the next approximation, when both the spatial, $L \sim l$, and temporal, $t_0 \sim \tau_1$, non-locality of the process are taken into consideration, Eqn (3.9) takes the form (3.5). The spatial non-locality again results in an infinite speed of propagation of perturbations (Fig. 1c). The spatial non-locality also smooths the surface of strong breakup, transforming the surface into a wave structure with continuous variation of temperature. The speed of propagation of this front is of the same order of magnitude as V_1 and the front width increases with $x^{1/2}$. The presence of this front is attributed to the energy relaxation process between subsystems.

4. Taking into account all the non-local terms in equation (3.6) we obtain two characteristic fronts in the temperature profile for a semi-infinite body (Fig. 1). The first, propagating with a higher speed $V_2 = (a_2/\tau_2)^{1/2}$, corresponds to relaxation to local equilibrium inside subsystem 2 and does not depend on the heat exchange with subsystem 1 as $\tau_1 < \tau_2$. This front represents the surface of strong breakup. The second front, propagating with a lower speed $V_1 < V_2$, is related to the process of energy relaxation between subsystems. This front was discussed in some detail in case 3.

The choice of heat transport model depends on the problem to be solved. For example, if one needs to obtain the speed of the heat wave front, corresponding to the energy relaxation between subsystems, and the distance from the front to the surface of body, but the structure of front is not important, the approximation described in case 2 should be used. In this case the distance L between the body surface and the wave front is a characteristic macroscale, and $L \gg l$. If the structure of the wave front is also important, that is $L \sim l$, the spatial non-locality should be considered (case 3).

The presence of a large number of interacting subsystems will lead to the appearance of new wave fronts in the temperature profile. The speed and form of these fronts will correspond to the stage of energy relaxation between subsystems.

Example. The $2T$-model (3.7) and (3.8) and the corresponding transport equation (3.9) can be applied to the analysis of the heat transport process upon irradiation of a metal surface with super-short laser pulses. Such experiments revealed the wave propagation of heat pulses with speed $V \sim V_{\mathrm{F}}$, where V_{F} is the Fermi speed [35]. The set of equations (3.7) and (3.8) predict the propagation of a heat wave through an electron gas with a speed V_2 (see Fig. 1). Taking into account that the electrons make the main contribution to the heat transport and their speed is of the order of V_{F}, it is possible to estimate that $V_2 \sim V_{\mathrm{F}}$. This estimate corresponds to the experimental results.

4. Discrete model

Currently the interest in discrete type models is increasing. Contrary to the classical continuous approach these models assume that space and time are not continuous, but discrete variables. In other words, it is assumed that the system consists of interacting discrete objects and the state of these objects changes in discrete intervals of time. This approach is used in mechanics, hydrodynamics, magnitohydrodynamics, the theory of crystal growth, biology, etc. [27–29, 35–41].

An axiom of the discrete approach to the modeling of transport processes is based on the idea of a random walk [3, 7, 27, 39–41]. Let us consider for the simplicity the one-dimensional case. It is assumed that a particle, which follows a random walk and transfers energy or mass, undergoes a jump of equal probability along positive or negative x direction with length h. These jumps occur in equal time intervals τ. Then taking into consideration that the transport potential Θ (temperature or concentration) is proportional to the number of particles in the considered element of medium, we can write the following discrete transport equation [27, 39–41]

$$\Theta(x, t+\tau) = \frac{1}{2}\left[\Theta(x+h, t) + \Theta(x-h, t)\right] + F\big(\Theta(x, t)\big)\,, \tag{4.1}$$

where $F\big(\Theta(x, t)\big)$ is the discrete analogue of a heat or mass source. Equation (4.1) means that the number of particles in an element of medium x for the time $t+\tau$ is equal to the sum of particles, arriving from the nearest neighboring elements of the medium with coordinates $x+h$ and $x-h$ (where these particles were on the previous time step t) and the number of particles, determined by an external source (not related to the transport process). Note that it has been assumed in Eqn (4.1) that the probability of a particle jump along the positive and negative x directions is 1/2. The function F is the solution of the semigroup of the ordinary differential equation [38]

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t} = W\big(\Theta(t)\big)\,. \tag{4.2}$$

It follows that the function of source $F(\Theta)$ in the discrete transport equation (4.1) and the function of source $W(\Theta)$ in the differential equation (4.2) are interrelated as follows

$$F(\Theta) = \int_t^{t+\tau} W\big(\Theta(t)\big)\,\mathrm{d}t\,.$$

As was discussed earlier, in the local non-equilibrium situation either the temperature or the heat flux is an independent variable. Consequently, the value of the heat flux is not accessible through differentiation of a temperature distribution in the system as in the local equilibrium case. This value should be found from a solution to the independent equation describing the space-time evolution of flux . Therefore, to describe the heat transport process we have to formulate a discrete equation for the heat flux along with the discrete temperature equation (4.1). By definition, the heat flux q is the energy transferred through unit area per unit time. In the discrete model the heat flux through a discrete element of medium with coordinate x can be described in the form

$$q\left(x, t+\frac{\tau}{2}\right) = -\frac{c_p \rho h}{2\tau}\left[\Theta(x+h, t) - \Theta(x-h, t)\right]\,. \tag{4.3}$$

One considers an average instant of time $t+\tau/2$, that is the time between two states of the discrete element in the instants of time t and $t+\tau$. An energy exchange between discrete elements occurs exactly in the intermediate moment

between stationary states of the system. In expression (4.3) the heat flux is described at this average time. Notice that one generally needs only a single discrete equation (4.1) to describe the system dynamics and expression (4.3) may be considered as a definition of the heat flux.

The discrete transport equations (4.1) and (4.3) are particularly convenient for computer modeling of non-local mass or heat transport processes as a translation to a the language of discrete mathematics is not necessary. Examples of numerical modeling based on the discrete equation (4.1) can be found in Ref. [40].

Furthermore, we shall express the discrete equations (4.1) and (4.3) in operator form:

$$\left[\exp(\tau\partial_t) - \cosh(h\partial_x)\right]\Theta(x,t) = F(\Theta)\,, \tag{4.4}$$

$$\exp\left(\frac{\tau}{2}\,\partial_t\right)\left[q(t,x)\right] = -\sinh(h\partial_x)\left[\Theta(x,t)\right]\frac{c_p h}{\tau}\,. \tag{4.5}$$

Now one can make a limit transition from the discrete equations (4.1) and (4.3) to continuous partial differential equations. For that we should take the limits $\tau \to 0$ and $h \to 0$ in the Eqns (4.4) and (4.5). Such a limit is expanded as an infinite number of terms of the Tailor series with two small parameters τ and h.

To derive an equation with finite number of terms the law of limit transition has to be formulated. That means one has to describe the relationships between τ and h at $\tau, h \to 0$. The law of limit transition is determined by a character of processes occurring in the system. Let us consider two basic cases.

4.1 Diffusion law of limit transition

In the random walk theory it is usually assumed that the transport coefficient $D = h^2/2\tau$ remains finite when h and τ tend to zero, that is

$$\lim_{n,\tau\to 0}\frac{h^2}{2\tau} = D = \text{const} > 0\,. \tag{4.6}$$

In this case a zero approximation with respect to τ of the discrete equation (4.1) takes the form of the classical parabolic transport equation:

$$\frac{\partial\Theta}{\partial t} = D\,\frac{\partial^2\Theta}{\partial x^2} + W. \tag{4.7}$$

In a similar approximation of equation (4.6) we obtain the classical Fourier law (or the Fick law in the case of mass transport):

$$q = -\lambda\,\frac{\partial\Theta}{\partial x}\,, \tag{4.8}$$

where $\lambda = D\rho c_p$ is the thermal conductivity.

It should be emphasized that expansions of any accuracy for the discrete equation are parabolic equations in the sense that they determine an infinite speed for the propagation of perturbations $V^* \to \infty$. This feature is a consequence of the diffusion law of limit transition (4.6), because $V = h/\tau = 2D/h \to \infty$ when $h \to 0$.

4.2 Wave law of limit transition

In the previous section we considered the diffusion law of limit transition which determines the infinite speed of propagation of perturbations V^* . Let us consider now such a law of limit transition which results in a finite value for V^*. Consequently, we shall assume that

$$\lim_{h,\tau\to 0}\frac{h}{\tau} = V^* < \infty\,. \tag{4.9}$$

Let us call this law of limit transition 'the wave law'. In a first approximation with respect to τ from Eqns (4.4) and (4.5) and using the wave law of limit transition (4.9) we obtain

$$\frac{\partial\Theta}{\partial t} + \frac{\tau}{2}\frac{\partial^2\Theta}{\partial t^2} = \frac{V^{*2}}{2}\tau\,\frac{\partial^2\Theta}{\partial x^2} + W + \frac{\tau}{2}\frac{\partial W}{\partial t}\,,$$

$$q + \frac{\tau}{2}\frac{\partial q}{\partial t} = -\frac{V^{*2}}{2}\tau c_p\rho\,\frac{\partial\Theta}{\partial x}\,. \tag{4.10}$$

As expected, Eqns (4.10) are the hyperbolic equations with finite speed of propagation of perturbations V^* which corresponds to the wave law of limit transition (4.9). These equations coincide with the hyperbolic transport equation (2.11) and the law of Maxwell – Cattaneo (2.2), respectively, which were obtained in the EIT by the introduction of heat flux into the independent variables describing local non-equilibrium systems.

Thus, the law of limit transition has to be specified while going from the discrete transport equation to an approximation of any accuracy in the form of partial differential equations. This means that the relationship between the characteristic time and space microscales has to be specified. The law of limit transition determines the type (hyperbolic or parabolic) of transport equations and, consequently, determines the main qualitative properties of their solutions. The choice of law of limit transition is determined by the speed of transport process. For relatively slow processes of 'diffusion' type, with characteristic speed V much smaller than the speed of propagation of perturbations V^*, the diffusion law of limit transition (4.6) has to be used. The high speed regime of transport processes, when $V \sim V^*$, corresponds to the wave law of limit transition (4.9).

The two-temperature discrete model, which unites the principal features of the discrete model (Section 4) and the $2T$-model (Section 3), was considered and analyzed in Refs [27, 29].

5. The integral model

As already noted, the extended irreversible thermodynamics and other thermodynamic statistical theories lead to the space – time non-locality of the equations for dissipating fluxes (mass and heat fluxes). These equations, complemented with the corresponding conservation laws, lead to non-local transport equations for temperature and concentration. Notice that this treatment usually involves conservation laws in the form of local partial differential equation. Strictly speaking, a correct derivation of the transport equations has to be based on the non-local form of the conservation laws, containing the same number of non-local terms as in the equations for dissipating fluxes. We shall show in this section that an assumption of the space – time non-locality of the conservation laws simultaneously leads to an non-local transport equation and a non-local equation for dissipating fluxes.

Let us consider a set of classical (local) equations, which are the basis of the locally reversible thermodynamics of irreversible processes and, consequently, the locally reversi-

ble theory of transport processes. The set consists of the energy conservation law, the Gibbs law and the equation of entropy balance. In the case of solid state the equations take the form

$$\rho \frac{\mathrm{d}U}{\mathrm{d}t} = -\nabla q\,, \tag{5.1}$$

$$\mathrm{d}S = T^{-1}\,\mathrm{d}U\,, \tag{5.2}$$

$$\rho \frac{\mathrm{d}S}{\mathrm{d}t} + \nabla J_S = \sigma_S\,, \tag{5.3}$$

where J_S and σ_S are the flux and production of entropy, respectively. As already noted, the differential form of Eqns (5.1) – (5.3) is a consequence of the assumption of space – time locality, when the volume of integration in the conservation laws tends to zero. In the general case, the integral equations, corresponding to Eqns (5.1) – (5.3), take the form:

$$\rho\big[U(x,t+\tau) - U(x,t)\big] = \frac{1}{\Omega}\int_t^{t+\tau}\oint_\eta q(x,t)\,\mathrm{d}\eta\,\mathrm{d}t\,, \tag{5.4}$$

$$S(x,t+\tau) - S(x,t) = T^{-1}\big[U(x,t+\tau) - U(x,t)\big]\,, \tag{5.5}$$

$$\rho\big[S(x,t+\tau) - S(x,t)\big] + \frac{1}{\Omega}\int_t^{t+\tau}\oint_\eta J_S(x,t)\,\mathrm{d}\eta\,\mathrm{d}t = \int_t^{t+\tau}\int \sigma_S(x,t)\,\mathrm{d}\Omega\,\mathrm{d}t\,, \tag{5.6}$$

where τ is the time scale of non-locality, Ω is the volume, and η is the area, corresponding to the linear scale of non-locality h, that is $\Omega \sim h^3$ and $\eta \sim h^2$.

Let us underline that Eqns (5.4) – (5.6) are non-local in space and time, because the speeds of variation of energy and entropy (first derivatives by respect to time), representing local members, are substituted with the finite differences of the characteristic scale of non-locality τ. In the one-dimensional case Eqn (5.4) can be rewritten

$$\rho\big[U(x,t+\tau) - U(x,t)\big] = -\frac{\tau}{2h}\left[q\left(x+h,t+\frac{\tau}{2}\right) - q\left(x-h,t+\frac{\tau}{2}\right)\right]. \tag{5.7}$$

In equation (5.7) an integration with respect to time is substituted by some approximate value q in an average instant of time $t+\tau/2$. Substituting Eqn (5.7) into (5.5) we obtain the expression for the flux and entropy production, corresponding to the integral formulation (5.4) – (5.6). According to the second law of thermodynamics the entropy production should be positive. From this requirement the relationships, represented in the form of a Fourier series with the small parameter τ and h, become:

$$\frac{\partial T}{\partial t} + \frac{\tau}{2}\frac{\partial^2 T}{\partial t^2} + \ldots = a\left(\frac{\partial^2 T}{\partial x^2} + \frac{h^2}{12}\frac{\partial^4 T}{\partial x^4} + \ldots\right), \tag{5.8}$$

$$q + \tau\frac{\partial q}{\partial t} + \frac{h^2}{2}\frac{\partial^2 q}{\partial t^2} + \ldots = -\lambda\left(\frac{\partial T}{\partial x} + \frac{h^2}{6}\frac{\partial^3 T}{\partial x^3} + \ldots\right). \tag{5.9}$$

The heat conduction (5.8) and the flux (5.9) equations in the corresponding approximations, and with the corresponding law of limit transition, contain the classical parabolic transport equation and the Fourier law, the hyperbolic transport equation (telegraph equation) and the Maxwell – Cattaneo law.

Thus, the integral formulation of Eqns (5.4) – (5.6) and the corresponding second law of thermodynamics lead to the appearance of non-local terms in the transport equations, coinciding with (or equal in order of magnitude) the terms in the transport equations, obtained in the framework of EIT or other thermodynamic and statistical methods based on the local formulation of conservation laws. This signifies that a strict approach to the study of the dynamics of non-local systems has to be grounded on the conservation laws in the integral or other non-local form.

6. Conclusions

Mathematical models, describing locally non-equilibrium transport processes, form a hierarchical sequence, corresponding to the degree of deviation of the system from local equilibrium. The degree of deviation of the system from local equilibrium and, consequently, the adequate choice of a transport model depend on the relationships between the characteristic space – time scale of transport process (macroscales) and the microscales, characterizing the relaxation of the system to local equilibrium. Notice that the characteristic scale of the transport process depends on external factors, such as boundary and initial conditions, heat and mass sources, and also on the system parameters, e.g. the diffusion coefficient, thermal conductivity, etc. The characteristic relaxation times and the scale of space non-locality are internal system parameters, independent of external conditions.

The hierarchy of mathematical models, describing locally non-equilibrium transport processes, consists of a sequence of parabolic and hyperbolic partial differential equations. The order of these equations increases with an increase of the degree of system deviation from local equilibrium. The type of equation depends on the law of limit transition, which is in turn determined by the character of the transport process. It should be noted that the problem of a small parameter (or several parameters) often occurs in thermodynamic and statistical theories, e.g. the Navier – Stokes theory, the Grad method, the Chapman – Enskog method, etc. Consequently, the idea of the introduction of the different laws of limit transition, which determine the mutual behavior of the distribution parameters when they tend to zero, appears to be useful in these cases.

On the one hand the locally non-equilibrium models of transport processes discussed above are in agreement with the existent versions of local non-equilibrium thermodynamics. On the other hand they expand the range of possible objects for investigation. These models possess a relatively simple form, allowing them to be used for the analysis of specific physical situations.

Discrete models of transport processes are particularly convenient for computer simulation as they do not require a transition to the language of discrete mathematics. Discrete models are already represented in a recurrence form.

The investigations based on these models revealed that locally non-equilibrium effects exert a primary control over the mechanism and principal behavior of the propagation of high speed traveling waves in active media [3 – 6, 28, 40, 42 – 50]. Among the examples of such waves are the combustion waves, waves of superconductor – normal metal, fusing and solidification waves, etc. In conditions far from local equilibrium the transport potential distribution (e.g. temperature and component concentrations) differ significantly from the classical locally irreversible conditions. This leads to qualitatively new properties of traveling waves in locally

irreversible conditions. These problems will be discussed in some detail elsewhere.

The methods developed are sufficiently general and may serve as the basis for construction of locally irreversible models of transport processes, occuring in different physical systems. For instance, this approach may appear to be useful in the analysis of a transition from combustion to detonation, in the study of anomalous diffusion in polymer materials near the point of glass transition, in the investigation of the interaction of supershort laser pulses with plasma, in the study of conditions of fabrication of amorphous alloys upon superfast hardening, etc.

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