

Transport processes and traveling waves in systems with local nonequilibrium

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Transport equations are studied for two types of media exhibiting properties of local nonequilibrium: media with thermal memory and media with a discrete structure. A hyperbolic transport equation that is a special case of these local-nonequilibrium equations is used for the analysis of traveling waves having high velocities. These waves have certain important properties: there can be a temperature discontinuity at the wave front; there exist thermal shock waves; the temperature at the wave front exceeds the equilibrium adiabatic value; there exist stationary autowave regimes in addition to those corresponding to the classical local-equilibrium case, and the velocities of these regimes are bounded by the velocity of propagation of a thermal signal. The approach developed here may be useful for the study of transport processes for short times or high fluxes in systems near critical points, in heterogeneous systems, and in other extremal situations.

INTRODUCTION

In recent years interest has increased in the study of various kinds of systems exhibiting local nonequilibrium properties and the transport processes in them (transport of energy, mass, momentum, or their analogs). This interest is related, on the one hand, to the natural evolution of science—from systems in equilibrium as a whole to systems in local equilibrium, and then to systems with local nonequilibrium. On the other hand, the intensification of technological processes, the use of materials with complicated structures (polymers, liquid crystals, capillary-porous and other disperse systems), as well as the widespread use of laser technology and the possibility of reaching ultrahigh or ultralow temperatures and pressures explain from the practical point of view the interest in systems in extremal, locally nonequilibrium conditions.

The study of such systems can be based on various versions of local-nonequilibrium thermodynamics,^{1–7} kinetics,^{8–12} molecular dynamics,^{13,14} and phenomenological and other methods (see the literature cited in Refs. 3–5, 28, 29, 44, 45, and 52). Experimentally, the effects of local nonequilibrium are observed most often at low temperatures,^{3–5,15} in the irradiation of matter with ultrashort pulses of energy,^{16,20} in shock waves,^{13,21} and disperse systems,^{22–26} since it is in these cases that the time for the relaxation of the system into local equilibrium is commensurate with the characteristic time of the process itself. In this paper two models of local-nonequilibrium systems are examined—systems with memory and discrete systems, with the greatest attention paid to the corresponding transport equations and their various limiting cases. Later, on the basis of a hyperbolic transport equation, which may be derived both from a generalized transport equation for systems with memory and from a discrete transport equation, an analysis will be made of a number of general properties of travelling waves in local-nonequilibrium systems, and specific examples will be presented.

1. LIMITS OF APPLICATION OF LOCAL-NONEQUILIBRIUM THEORIES OF TRANSPORT PROCESSES

The classical theory of transport processes is based on the approximation of local thermodynamic equilibrium and a continuous medium. The approximation of local thermodynamic equilibrium means that in each small element of the medium there exists a state of local equilibrium for which the local entropy is the same function of the macroscopic variables as for an equilibrium system. Local thermodynamic equilibrium can be established in a system if the rate at which its macroparameters change because of external influences, that is, the rate of disruption of equilibrium, is much lower than the rate at which equilibrium is established. Moreover, the approximation of local thermodynamic equilibrium is valid for times t_0 that exceed substantially the characteristic time τ required for the system to relax to local equilibrium.^{2,3,52} The approximation of a continuous medium, which implies the absence of any internal structure in the medium, means that in the integral representations of the conservation laws for this medium it is possible to take the limit as the volume of integration goes to zero. This transition to the limit makes it possible to obtain the equation for the conservation of energy (mass, etc.) in differential form. From the physical point of view this procedure is not correct, since the medium always consists of discrete elements (atoms, molecules, cells, separate entities, etc.) and has its own internal discrete structure. However, if the characteristic macroscopic scale L of the system is much larger than the characteristic dimension h of its microstructure, then it is possible to neglect the discreteness of the material and study the system in the approximation of a continuous medium. Thus, the condition for the validity of the approximation of local thermodynamic equilibrium and of a continuous medium (that is, spatial localization) can be written in the form

$$t_0 \sim \Psi \left(\frac{\partial \Psi}{\partial t} \right)^{-1} \gg \tau, \tag{1.1}$$

$$L \sim \Psi \left(\frac{\partial \Psi}{\partial x} \right)^{-1} \gg h, \quad (1.2)$$

where Ψ is the transport potential (temperature, concentration, etc.) and x is the coordinate. In the propagation of a travelling wave with a constant velocity V the characteristic dimension of its front is $L = a/V$, and the characteristic time is $t_0 = a/V^2$, where a is the transport coefficient (thermal diffusivity, diffusion constant and so forth). Assuming that the relaxation time τ is related to the velocity of propagation of the disturbance¹⁾ by $v = (a/\tau)^{1/2}$ (Refs. 3,4), and to the characteristic microscopic length scale by $h = \tau v$, one finds that (1.1) and (1.2) are equivalent to the following inequality

$$v \gg V. \quad (1.3)$$

Consequently, classical transport theory is valid if the characteristic rate of the given process is much lower than the speed of propagation of the disturbance in these media.²⁾ In this case the transport process is described by parabolic partial differential equations with an infinitely large speed of propagation of the disturbance from an instantaneous point source,^{3,4,5,2} which, from the physical point of view is not tenable. However, for sufficiently slow processes, where an infinite speed of propagation of the disturbance is understood in the sense of inequality (1.3), this approximation may be considered quite correct. Otherwise, i.e., for fast processes where inequalities (1.1)–(1.3) do not hold, the classical local-equilibrium theory of the transport processes are no longer valid, and methods involving local nonequilibrium are required to describe these systems. This topic is the subject of the following section.

2. TRANSPORT EQUATIONS IN LOCAL-NONEQUILIBRIUM SYSTEMS

A variety of thermodynamic, kinetic, phenomenological, and other methods can be used to describe local-nonequilibrium systems.^{1–12} Rational thermodynamics, giving up the principle of local thermodynamic equilibrium, introduces the concept of thermal memory.^{1,2} Media with internal degrees of freedom, high-speed media, and media with memory have been analyzed within the framework of rational thermodynamics. Extended irreversible thermodynamics,³ the wave theory of Gyarmati,^{6,7} and a number of other versions of local-nonequilibrium theories^{3–5} have been based on the assumption that the specific entropy is simultaneously a function of the equilibrium extensive parameters and of their fluxes (“velocity variables”), which describe the inertial properties of a system as local equilibrium is established.²⁷ The transport equations in local-nonequilibrium media may also be derived from the Boltzmann equation, by molecular kinetics methods, with the use of random walk theory and others methods.^{1–12,28,29,44,45,52}

In the study of local-nonequilibrium systems the question arises as to the meaning of the temperature of a local-nonequilibrium state. In classical thermodynamics the temperature is defined only for a system in equilibrium or local equilibrium. Various versions of nonequilibrium thermodynamics introduce the concept of the local-nonequilibrium entropy η and internal energy E , thus giving a basis within these theories for defining the local-nonequilibrium temperature as $T^{-1} = \partial \eta / \partial E$ (Ref. 3). For high-velocity me-

dia, where the state of the system depends on the rate of change of the temperature, the absolute temperature can be replaced by the thermodynamic temperature.² The thermodynamic temperature is a function of the absolute temperature and its rate of change. These two temperatures coincide when the rate of change of the absolute temperature is zero. Therefore, the thermodynamic temperature can be represented as an expansion in a Taylor series in powers of the absolute temperature and its rate of change.² The amount that the thermodynamic temperature deviates from the absolute temperature is proportional to the rate of change of the latter, and it characterizes the degree of local nonequilibrium of the system. This interpretation of the thermodynamic temperature can also be used for media of other types. In molecular dynamics the notion of the “kinetic” temperature is introduced as a measure of the mean kinetic energy of the molecules, which can be defined in terms of the local-nonequilibrium distribution function.^{13,14} The results of molecular dynamics calculations of the propagation of thermal pulses in solids with the use of the kinetic temperature¹⁴ shows a remarkable agreement with theoretical and experimental data obtained on the basis of the ordinary ideas of the absolute temperature.⁴ Moreover, it has been shown¹² that for small deviations from local equilibrium, where the absolute value of the difference between the local-nonequilibrium and local-equilibrium distribution functions is much less than the latter, the energy of the system at each instant of time and at each point of space is determined by the local-equilibrium distribution function, and, consequently, the local-equilibrium absolute temperature. The degree of nonequilibrium of the system in this case has an effect only on the heat flux, which in this case is not determined by the Fourier law, but depends on the relaxation time of the system to local thermodynamic equilibrium.

2.1. Transport equation in media with memory

If a system is not in local thermodynamic equilibrium, the relation between the heat flux q and the temperature gradient, as well as between the internal energy of the system and the temperature T has an integral form:^{28,29}

$$q = - \int_0^{\infty} K(z) \nabla T(t-z) dz, \quad (2.1)$$

$$E = C_p T + \int_0^{\infty} \beta(z) T(t-z) dz, \quad (2.2)$$

where $K(z)$ and $\beta(z)$ are the relaxation functions of the heat flux and the internal energy, respectively. Expressions (2.1) and (2.2) take into account that far from local equilibrium the heat flux and the internal energy do not depend just on the instantaneous values of the temperature gradient and the temperature, but are determined by the entire previous history of the heat transport process in the element of space being considered. Such media are called “media with memory.”^{1,2} From expressions (2.1) and (2.2) and the law of conservation of energy one can derive the transport equation in a medium with memory:^{5,30,31}

$$\begin{aligned} & (\tau \beta'(0) + C_p) \frac{\partial T}{\partial t} + \tau C_p \frac{\partial^2 T}{\partial t^2} + \int_0^{\infty} (\tau K'(z) + K(z)) \Delta T(t-z) dz \\ & = \tau K(0) \Delta T + \int_0^{\infty} (\tau \beta'(z) + \beta(z)) \frac{\partial T(t-z)}{\partial t} dz + W + \tau \frac{\partial W}{\partial t}, \end{aligned} \quad (2.3)$$

where τ is a constant whose physical meaning will be defined below, $W(x,t)$ is the intensity of the energy sources distributed in the system, C is the specific heat, and ρ is the density. The transport equation in an active medium with memory (2.3) is of the hyperbolic type, which implies that the propagation of heat in such systems is wavelike.^{4,28} Equation (2.3) contains both the intensity function W of the distributed sources of energy, which corresponds to classical transport theory, and also its time derivative $\partial W/\partial t$, the latter a consequence of the inertial nature of the heat transport process in local-nonequilibrium systems. Let us consider the case where the integrand on the left-hand side of (2.3) vanishes:

$$\tau K'(z) + K(z) = 0.$$

The relaxation function for the heat flux now has an exponential form

$$K(z) = K(0) \exp\left(-\frac{z}{\tau}\right). \quad (2.4)$$

It follows from (2.4) that τ can be regarded as the characteristic time of relaxation of the system to local equilibrium. Substituting (2.4) into (2.1) we obtain

$$q + \tau \frac{\partial q}{\partial t} = -\tau K(0) \nabla T.$$

For $\tau K(0) = \lambda$ this relation is equivalent to the Maxwell-Cattaneo equation:^{3,4,8}

$$q + \tau \frac{\partial q}{\partial t} = -\lambda \nabla T. \quad (2.5)$$

The Maxwell-Cattaneo equation (2.5), which relates the heat flux to the temperature gradient in a medium with thermal relaxation, is a generalization of the classical Fourier law $q = -\lambda \nabla T$, which is valid under the assumption of local equilibrium, i.e., for $\tau = 0$. The physical meaning of expression (2.5) is that heat transport in local-nonequilibrium media has inertial properties: such a system does not react to a thermal influence (nor does the heat flux respond to a change in the temperature gradient) just at the instant of time t , as in the classical local-equilibrium case, but later, after a relaxation time τ :

$$q(t + \tau) = -\lambda \nabla T(t). \quad (2.6)$$

Expanding the left-hand side of (2.6) in a Taylor series in powers of τ we obtain in the zero-order approximation the classical Fourier law, and in the first-order approximation the Maxwell-Cattaneo equation (2.5).

From the law of conservation of energy and the Maxwell-Cattaneo equation follows the equation of heat transport of the "telegraph" type^{3,4} with distributed sources.^{5,31-34}

$$C\rho\tau \frac{\partial^2 T}{\partial t^2} + C\rho \frac{\partial T}{\partial t} = \lambda \Delta T + W + \tau \frac{\partial W}{\partial t}. \quad (2.7)$$

The transport equation (2.7) is a hyperbolic equation with a finite velocity of propagation, $v = (a/\tau)^{1/2}$, of the thermal signal (a thermal wave), where $a = \lambda/C\rho$. It combines the properties of a wave equation that describes the propagation of undamped waves of constant amplitude (the first term on the left side of (2.7)) with a diffusion equation that corresponds to the dissipative mode of energy transmission. It follows from the solution of (2.7) in an inert medium

($W = 0$) that a thermal pulse propagates with constant velocity v , and its amplitude decays exponentially with time.^{33,35-37} Such a pulse is totally reflected from a thermally insulated boundary,^{33,36} while if it is incident on the interface between two media it is partially reflected and partially transmitted into the other medium.³⁷ It should be expected that in systems with relaxation a thermal pulse will also have other wave properties, such as being refracted when incident at an angle on the boundary of two media, where the refractive index would be $n = v_1/v_2$, where v_1 and v_2 are the velocities of propagation of the thermal pulse in these media.

In a similar way one can derive an equation for the heat flux in a medium with relaxation, and like (2.7) this equation will be hyperbolic with a finite velocity of propagation of the thermal signal:

$$\tau \frac{\partial^2 q}{\partial t^2} + \frac{\partial q}{\partial t} = a \nabla \operatorname{div} q - a \nabla W. \quad (2.8)$$

The processes that propagate in the form of traveling waves (autowaves, phase-transition waves, detonation waves, fracture waves etc.) are usually studied with the use of the self-similar variable $x \rightarrow x - Vt$, where V is the velocity of propagation of the traveling wave.³⁸⁻⁴¹ In this case Eqs. (2.7) and (2.8) reduce to the ordinary differential equations^{5,34}

$$\lambda \left(1 - \frac{V^2}{v^2}\right) \frac{d^2 T}{dx^2} - C\rho V \frac{dT}{dx} + W + \tau V \frac{dW}{dx} = 0, \quad (2.9)$$

$$a \left(1 - \frac{V^2}{v^2}\right) \frac{dq}{dx} - Vq = W. \quad (2.10)$$

For $\tau \rightarrow 0$, when $v \rightarrow \infty$ Eqs. (2.9) and (2.10) reduce to the classical transport equation for traveling waves in local-equilibrium systems, while for $\tau > 0$ they have significant characteristic features. First, (2.9) contains the derivative of the source function with respect to the coordinate, which can be regarded as a positive source of heat, or more accurately, as a "pseudosource," with an intensity that depends not only on the form of the heat source function W , but also on the magnitude (and direction) of the velocity V of the wave. Second, the amount and direction of the heat transmitted by diffusion in the wave (see the first term in (2.9) and in (2.10)) depend on the relation between the velocity V of the traveling wave and the velocity v of the thermal signal.^{5,34,56} If $V < v$, then the diffusion of heat in the traveling wave goes in the same direction as in the classical local-equilibrium case, in the direction of motion of the wave, and thus this diffusion heats the medium ahead of the wave front. As V increases the diffusion of heat in the traveling wave decreases, and when $V = v$ the direction of the diffusion of heat changes sign—the heat propagates in the direction opposite to the motion of the wave. Therefore, for $V > v$ the medium ahead of the traveling wave front remains unheated.

Let us turn now to a discussion of the generalized transport equation in a medium with thermal memory, (2.3). As mentioned above, Eq. (2.3) is a hyperbolic equation, which reflects the wave nature of the propagation of heat in local-nonequilibrium media. In the limit, (2.3) reduces to well-known special cases. If the relaxation function for the heat flux is of the exponential form (2.4), which for $\tau K(0) = \lambda$ corresponds to the Maxwell-Cattaneo equation (2.5), and, further, if $\beta(z) \equiv 0$, then (2.4) is equivalent to the transport equation of the telegraph type (2.7). It should be noted that

in this case the values of τ and $K(0)$ are finite. If $\tau \rightarrow 0$ and $K(0) \rightarrow \infty$ in such a way that $\tau K(0) = \lambda$, then the relaxation function for the heat flux is $K(z) = \lambda \tau^{-1} \exp(-z/\tau) \rightarrow \lambda \delta(z)$, where $\delta(z)$ is the Dirac delta function. In this case the Maxwell-Cattaneo equation (2.5) and the integral relation (2.1) reduce to the classical Fourier law, while the generalized transport equation (2.3) reduces to the classical parabolic transport equation (with $\beta(z) \equiv 0$). This fact, in my opinion, argues in favor of Eq. (2.3) over other types of transport equations in media with memory, which do not give the well-known simple limiting cases.^{28,29}

2.2. Media with a discrete structure

One of the variants of the local-nonequilibrium approach to the study of transport processes may be based on the random-walk model.^{5,44,45} This model assumes that the transport process has a discrete space-time structure. For simplicity we shall consider a one-dimensional medium composed of particles carrying out random walks to the left or to the right (Fig. 1). The distance h that a particle (phonon) carries the energy in one transition is of a microscopic scale that characterizes the discrete spatial structure of the heat transport process. The time 2τ between two consecutive transitions corresponds to the scale of the temporal discreteness (below it will be shown that the quantity τ can be considered as the relaxation time of the system to local equilibrium). Let us denote by P_1 the probability of the transition of a particle along the positive x direction, and by P_2 the probability for a transition in the negative x direction, with $P_1 + P_2 = 1$. If the probability that a particle at some instant of time $t + 2\tau$ is located within some element x of the medium is denoted by $u(x, t + 2\tau)$, then⁴⁴

$$u(x, t + 2\tau) = P_1 u(x - h, t) + P_2 u(x + h, t). \quad (2.11)$$

Then, assuming that the local internal energy of the medium is proportional to the number of particles (phonons) in a given discrete element of the medium⁴⁴ and to the intensity of the sources distributed in the medium,⁵ we obtain from Eq. (2.11)

$$\begin{aligned} T(x, t + 2\tau) \\ = P_1 T(x - h, t) + P_2 T(x + h, t) + \frac{2\tau}{C\rho} W(x, t + \tau). \end{aligned} \quad (2.12)$$

We shall consider a source intensity function W that is sufficiently smooth so that

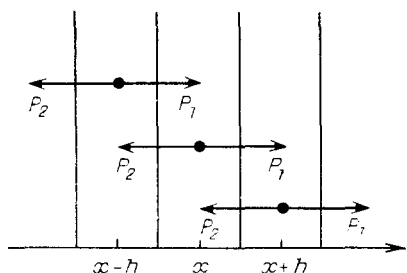


FIG. 1. A model of random walks. P_1 and P_2 are the probabilities of a transition of a particle (energy transport) to the adjacent element of the medium.

$$\int_t^{t+2\tau} W(x, t) dt = 2\tau W(x, t + \tau).$$

In this way, expression (2.12) becomes a heat transport equation in a medium that is discrete in space and time, with energy sources distributed in it. The structure of Eq. (2.12) specifies a finite propagation velocity $v = h/2\tau$ for thermal perturbations. In a similar way one can obtain for such systems a relation between the heat flux and the temperature (the analog of the Fourier law) in discrete form:

$$q(x, t + \tau) = -\frac{hC\rho}{8\tau} (T(x + h, t) - T(x - h, t)). \quad (2.13)$$

Here and henceforth it will be assumed that the medium is isotropic; i.e., $P_1 = P_2 = 1/2$. In (2.12) and (2.13) the intensity W of the heat source and the heat flux q are taken at time $t + \tau$, halfway between two consecutive events of heat exchange at times t and $t + 2\tau$, in keeping with the integral nature of these quantities.

In discrete media the transport equation (2.12) and the relation between the heat flux and the temperature (2.13) (the generalized Fourier law) are nonlocal; that is, they specify the relation between the thermodynamic variables not at a point, but in some region of space-time. The spatial nonlocality is symmetrical—if h is replaced by $-h$, the form of these equations is unchanged. The temporal nonlocality of these equations has no such symmetry, a reflection of the irreversible nature of the relaxation processes. The transport equation (2.12) and the relation between the heat flux and the temperature (2.13) can be used for analyzing local-nonequilibrium systems directly in discrete form. This is particularly convenient for numerical calculations (since (2.12) and (2.13) do not require translation to the language of discrete mathematics) for the analysis of random dynamics of various objects, for the study of systems with a complex structure, and so forth.

In order to convert the equations that are in discrete form, (2.12) and (2.13), into partial differential equations, it is necessary to expand the functions T , q , and W in Taylor series in powers of τ and h . These expansions contain an infinite number of terms with two small parameters. To obtain equations with a finite number of terms one must specify the limiting behavior, i.e., the relation between τ and h as $\tau, h \rightarrow 0$. This limiting behavior is determined by the nature of the processes occurring in the given system. The two most typical cases will be considered.⁵

2.2.1. Diffusion form of limiting behavior

In the expansion of the discrete transport equation in the random walk model Weyman⁴⁴ assumed that the transport (diffusion) coefficient $a = h^2/\tau$ remains finite as $\tau, h \rightarrow 0$. This form of limiting behavior will be called the "diffusion" form. It should be pointed out at once that the "diffusion" form of limiting behavior implies that the velocity v of propagation of perturbations is infinite, since $v = h/2\tau = 2a/h \rightarrow \infty$.

In the zero order approximation in τ for the diffusion form of limiting behavior the classical relations of local-equilibrium thermodynamics follow from (2.12) and (2.13)—the parabolic transport equation and the Fourier law.

In the first approximation in τ (2.12) and (2.13) yield⁵

$$\frac{\partial T}{\partial t} + \tau \frac{\partial^2 T}{\partial t^2} = a \frac{\partial^2 T}{\partial x^2} + \frac{a^2 \tau}{3} \frac{\partial^4 T}{\partial x^4} + \frac{W}{C\rho} + \frac{\tau}{C\rho} \frac{\partial W}{\partial t}, \quad (2.14)$$

$$q + \tau \frac{\partial q}{\partial t} = -\lambda \frac{\partial T}{\partial x} - \frac{\lambda a \tau}{6} \frac{\partial^3 T}{\partial x^3}. \quad (2.15)$$

Here the transport equation (2.14) and the analog of the Fourier law (2.15), as in the classical approximation, are parabolic partial differential equations with an infinite propagation velocity of the perturbations. The subsequent approximations of the discrete equations (2.12) and (2.13), containing terms of the expansion with higher powers of τ , in accordance with the diffusion form of limiting behavior, will also be parabolic differential equations with an infinite propagation velocity of the perturbations (thermal signal).

2.2.2. Wave mode of limiting behavior

Let us now consider the case where the velocity of propagation of perturbations, $v = \hbar/2\tau$, remains finite when $\hbar, \tau \rightarrow 0$. This form of limiting behavior will be called the "wave" form.

In the first approximation in τ for the wave form of limiting behavior we obtain from the discrete equations (2.12) and (2.13)

$$\frac{\partial T}{\partial t} + \tau \frac{\partial^2 T}{\partial t^2} = v^2 \tau \frac{\partial^2 T}{\partial x^2} + \frac{W}{C\rho} + \frac{\tau}{C\rho} \frac{\partial W}{\partial t}, \quad (2.16)$$

$$q + \tau \frac{\partial q}{\partial t} = -C\rho v^2 \tau \frac{\partial T}{\partial x}. \quad (2.17)$$

The transport equation and the analog of the Fourier law (2.17) are partial differential equations with a finite speed of propagation of perturbations, which corresponds to the wave form of limiting behavior. For $\lambda = C\rho v^2 \tau$ Eq. (2.16) coincides with the transport equation in a medium with exponential relaxation (memory) of a heat flux (2.7), and (2.17) coincides with the Maxwell-Cattaneo equation (2.5). Subsequent approximations of the discrete equations Eqs. (2.12) and (2.13) for the case of the wave form of limiting behavior will also yield partial differential equations with a finite speed of propagation of a thermal signal.

In going from the discrete transport equations to their approximations of various accuracy in the form of partial differential equations it is necessary to specify the form of the limiting behavior, i.e., the relation between the space and time scales, and the internal structure of the system. The limiting form determines the type of partial differential equations and some of the fundamental properties of their solutions. Strictly speaking, the wave-type limiting form is more correct, since it gives a finite speed of propagation of perturbations, which corresponds to the properties of the random walk model and to the physical meaning of transport processes. However, if the process is so slow that its characteristic velocity is much less than the speed of propagation of perturbations, then one can also use the diffusion-type limiting form. The space-time nonlocality of the discrete transport equation (2.12) and the discrete analog of the Fourier law (2.13) have a clear physical meaning: the energy (mass, etc.) in one region of space and at some instant of time is transferred to another region of space and arrives there at another instant of time. As mentioned above, it is more convenient for an analysis of transport processes in a number of cases to use Eqs. (2.12) and (2.13) directly in their discrete form.

2.3. Two-component systems

The transport equation in media in local nonequilibrium, considered in the preceding sections, may be used for the analysis of complex multicomponent systems consisting of two or several interacting subsystems with different properties. In this case the mathematical model consists of the corresponding number of transport equations, written for each separately selected subsystem, with allowance for the exchange of energy, mass, etc., between them. The type of transport equation is determined by the relation between the characteristic times of the processes and the relaxation times to local equilibrium in the subsystems. Let us consider two examples.

2.3.1. Two-temperature model

At the present time wide use is made of the two-temperature model of the diffusion type, which is a system of two parabolic heat-conduction equations.^{16,46-48} These models describe heat transport in systems with a complex structure consisting of subsystems, each of which can be assigned its own temperature. The introduction of the two-temperature model is necessary if the time to establish equilibrium among the subsystems is comparable to the characteristic time of the transport process as a whole. Such conditions are realized, for example, in the irradiation of metals with ultrashort energy pulses, where at some stage of the process the temperature of the electron gas can be considerably higher than the temperature of the lattice.¹⁶⁻²⁰ In shock waves the role of the subsystems with their own temperature is taken by the various degrees of freedom of the molecules.²¹ In heterogeneous systems the gaseous and solid phases can have different temperatures.^{22,46-48} The two-temperature (or multitemperature) model of transport processes may also be applicable to other systems with a complex structure, consisting of various subsystems between which the exchange of energy (matter, etc.) is hindered.

Existing two-temperature models of the diffusion type are valid under conditions such that the time to establish equilibrium within each subsystem is much less than the time to establish equilibrium between them.¹⁶ In the most general case, where the relaxation within each subsystem is taken into account, the two-temperature model will consist of a system of hyperbolic transport equations

$$C_1 \rho_1 \tau_1 \frac{\partial^2 T_1}{\partial t^2} + C_1 \rho_1 \frac{\partial T_1}{\partial t} = \lambda_1 \Delta T_1 + W_1 + \tau_1 \frac{\partial W_1}{\partial t} + g(T_2 - T_1) + g\tau_1 \frac{\partial (T_2 - T_1)}{\partial t}, \quad (2.18)$$

$$C_2 \rho_2 \tau_2 \frac{\partial^2 T_2}{\partial t^2} + C_2 \rho_2 \frac{\partial T_2}{\partial t} = \lambda_2 \Delta T_2 + W_2 + \tau_2 \frac{\partial W_2}{\partial t} + g(T_1 - T_2) + g\tau_2 \frac{\partial (T_1 - T_2)}{\partial t}, \quad (2.19)$$

where T_1 and T_2 are the temperatures of the subsystems, g is the coefficient of heat transfer between them, and τ_1 and τ_2 are the relaxation times to local equilibrium for systems 1 and 2, respectively. As mentioned above, it follows from the solution of a hyperbolic equation that the thermal wave (the thermal signal) propagates with a finite velocity $v = (a/\tau)^{1/2}$, where $a = \lambda/C\rho$. In the two-component sys-

tem (2.18)–(2.19) the thermal wave will propagate through each of the subsystems with a velocity characteristic of that subsystem: $v_1 = (a_1/\tau_1)^{1/2}$ and $v_2 = (a_2/\tau_2)^{1/2}$.

Let us consider the two-temperature model (2.18)–(2.19) as applied to heat exchange between the electron gas and the lattice as a metal surface is irradiated with ultrashort energy pulses. For this situation it is usually assumed that the energy of the laser pulse is absorbed only by the electron gas, while the transfer of heat to the lattice can be neglected.^{16–20} With these assumptions Eqs. (2.18)–(2.19) take the form (here the index 1 refers to the electron gas, index 2 to the lattice, and W denotes the intensity of the energy absorbed by the electron gas):

$$\frac{a_1}{v_F^2} \frac{\partial^2 T_1}{\partial t^2} + \frac{\partial T_1}{\partial t} = a_1 \Delta T_1 + W + \tau_1 \frac{\partial W}{\partial t} + g(T_2 - T_1) + g\tau_1 \frac{\partial(T_2 - T_1)}{\partial t}, \quad (2.20)$$

$$\frac{a_2}{v_s^2} \frac{\partial^2 T_2}{\partial t^2} + \frac{\partial T_2}{\partial t} = g(T_1 - T_2) + g\tau_2 \frac{\partial(T_1 - T_2)}{\partial t}. \quad (2.21)$$

It is assumed that the electrons in the metal, which play the major role in the transport of heat, move with a velocity of the order of the Fermi velocity v_F , i.e., $v_1 = (a_1/\tau_1)^{1/2} \approx v_F$, while $v_2 = (a_2/\tau_2)^{1/2} \approx v_s$, where v_s is the speed of sound in the metal. It follows from (2.20) that the thermal wave propagates through the electron gas with a velocity v_F [see the first term on the right in Eq. (2.20)]. This conclusion agrees with the experimental results of Brorson *et al.*,¹⁷ who studied heat transport in thin metal films. In general, heat is transported in thick metal samples with the velocity $v = v_F$, but because of dissipative effects [see the second term on the left of Eq. (2.20)] the amplitude of a thermal signal is exponentially damped, so that it is difficult to observe experimentally. Although the presence of the time derivative of the intensity of the radiation source, $\partial W/\partial t$ in (2.20), does not affect the total energy balance of the system, it does significantly influence the shape of the pulse of energy absorbed by the electron gas i.e., the shape becomes $W + \tau \partial W/\partial t$. This effect may lead at the initial instant of time to a discontinuous jump in the electron gas temperature that is more abrupt than that calculated by the classical diffusion model. A more detailed analysis of the system of equations (2.20)–(2.21) or of the special cases of this system will permit a more thorough study of the mechanism of interaction between the electron gas and the lattice in metals and provide a reliable interpretation of existing experimental results.

In the analysis of fast processes, whose characteristic time is comparable to the time of relaxation to local equilibrium in the subsystems, the two-temperature model of the hyperbolic type, (2.18)–(2.19) should be used. The solutions of this model may differ not only quantitatively, but also qualitatively from the solutions of the parabolic two-temperature model.

2.3.2. Systems with heat conduction and diffusion

There exist a large number of systems in which energy and mass can be transported simultaneously. If the process occurs under conditions of local equilibrium, then parabolic equations of heat conduction and diffusion can be used to describe it. Otherwise, when the approximation of local

equilibrium is not satisfied either for heat transport or mass transport, i.e., when the characteristic time of the process is comparable to the times τ_T and τ_Y , required for the temperature and concentration, respectively, to relax to their local-equilibrium values, the mathematical model will consist of a system of hyperbolic equations (Section 2):

$$C\rho \frac{\partial T}{\partial t} + C\rho\tau_T \frac{\partial^2 T}{\partial t^2} = \lambda\Delta T + W_1(T, Y) + \tau_T \frac{\partial W_1}{\partial t},$$

$$\rho \frac{\partial Y}{\partial t} + \rho\tau_Y \frac{\partial^2 Y}{\partial t^2} = D\Delta Y + W_2(T, Y) + \tau_Y \frac{\partial W_2}{\partial t},$$

where Y is the concentration, $W_1(T, Y)$ and $W_2(T, Y)$ are the heat and mass sources, respectively, and D is the diffusion coefficient. This system of equations determines both the finite velocity of propagation of a heat wave (temperature perturbations), $v_T = (a/\tau_T)^{1/2}$, and also the finite velocity of propagation of a concentration wave (concentration perturbations), $v_Y = (D/\tau_Y)^{1/2}$. For the cases of gases, for example, $v_T \approx v_Y$, and for capillary-porous media $v_T \gg v_Y$.²³ In the latter case, if the characteristic rate of the transport process is comparable in order of magnitude to v_Y , the effects of local nonequilibrium will have a significant effect only on the mass transport, while the heat transport will proceed under conditions of local equilibrium. In this case the system of equations of heat and mass transport will consist of the classical parabolic heat conduction equation and a hyperbolic mass transport equation^{5,23}

$$C\rho \frac{\partial T}{\partial t} = \lambda\Delta T + W_1(T, Y),$$

$$\rho \frac{\partial Y}{\partial t} + \rho\tau_Y \frac{\partial^2 Y}{\partial t^2} = D\Delta Y + W_2(T, Y) + \tau_Y \frac{\partial W_2}{\partial t}.$$

This system of equations may be useful for the analysis of very intense heat and mass transport processes in capillary-porous media, in heterogeneous catalysis, in chemical reactions, in filtration combustion, and so forth.

3. GENERAL PROPERTIES OF TRAVELING WAVES IN LOCAL-NONEQUILIBRIUM SYSTEMS

3.1. Conditions at the wave front

If relaxation processes are taken into account, the temperature and heat fluxes in a traveling wave are described by the law of conservation of energy and the Maxwell–Cattaneo equation (2.5), which in the coordinate system attached to the wave front, have the following form:

$$C\rho V \frac{\partial T}{\partial x} = -\frac{\partial q}{\partial x} + W, \quad (3.1)$$

$$\tau V \frac{\partial q}{\partial x} + q = -\lambda \frac{\partial T}{\partial x}, \quad (3.2)$$

where V is the velocity of propagation of the traveling wave. By integrating (3.1) and (3.2) within the limits of an infinitely narrow zone that includes the wave front, one can obtain the difference in the values of T and q ahead of and behind the front (i.e., the temperature and heat flux discontinuities at the wave front); these differences will be denoted by square brackets: $[T]$ and $[q]$.

3.1.1.

If the latent heat of the phase transition is zero at the wave front and the thermophysical parameters of the system are constant, then it follows from (3.1) and (3.2) that $[q] = [T] = 0$ for $V \neq v$, where $v = (a/\tau)^{1/2}$ is the velocity

of propagation of a thermal signal in the relaxing medium. The temperature gradient behaves in accordance with the heat generation function W : if $[W] = 0$, then the temperature gradient is continuous, while if the heat generation function at the wave front changes discontinuously, i.e., if $[W] \neq 0$, then the temperature gradient also changes discontinuously. In the latter case the wave front is a surface of weak discontinuity. If $v = V$, then it follows from (3.1) and (3.2) that $[q] \sim [T] \sim [W]$, and if $[W] \neq 0$, the wave front is a surface of strong discontinuity.

3.1.2.

If the latent heat of the phase transition at the wave front is nonzero, then it follows from (3.1) and (3.2) that

$$[T] = -\tau V Q \lambda^{-1} \left(1 - \frac{V^2}{v^2}\right)^{-1}, \quad [q] = Q \left(1 - \frac{V^2}{v^2}\right)^{-1}.$$

The wave front in a relaxing medium with a phase transition (or an infinitely narrow zone of heat generation) is thus a surface of strong discontinuity. The jumps in the temperature and the heat flux at the wave front are proportional to the heat of the phase transition and change sign for $V = v$. The presence of a jump in the temperature at the wave front should be taken into account also in the analysis of the Stefan problem for relaxing media: the classical condition of continuity of the temperature in the region of the phase transition is not applicable in this situation.

3.1.3.

In some cases the wave front may be a boundary surface between states of the medium with different thermophysical properties.^{5,49,50} For example, for the He I to He II phase transition the thermal conductivity changes discontinuously at the front.^{49,51} Then, from (3.1) and (3.2) we have

$$\begin{aligned} \tau V [q] &= -[\lambda T], \\ C \rho V [T] &= -[q]. \end{aligned} \quad (3.3)$$

It then follows for a given value of V that $[T] \sim [\lambda]$; i.e., the wave front is a surface of strong discontinuity.

Taking into account the fact that the thermal conductivity in He II is much greater than in He I,⁵¹ and using relation (3.3), we obtain the approximation $[T] \sim [q^2]$; that is, the temperature jump at the He I–He II phase transition front is proportional to the square of the heat flux density through the surface of the front, a conclusion that is in qualitative agreement with experimental results.⁴⁹

In a similar way one can show that the strong discontinuity in the temperature field at the front of a traveling wave in a relaxing medium can be caused by a discontinuous change in the relaxation time or the power-law temperature dependence of the thermophysical parameters (τ, λ, C).^{5,34,52}

The relaxation processes in some cases thus lead to the formation of strong or weak discontinuities at the front of a traveling wave—thermal shock waves. We might expect such discontinuities in the propagation of waves of switching between the superconductor and the normal metal,^{40,50,57,63} in waves of explosive crystallization of an amorphous material,⁴¹ in waves of low-temperature chemical reactions,⁵³ in combustion waves,^{5,30,38} in systems that are described by the Stefan problem,^{54,55} and others.

3.2. Distribution of temperature and heat flux in traveling waves

In relaxing media the temperature and the heat flux in a traveling wave are described by Eqs. (2.9) and (2.10), which in dimensionless variables have the form

$$(1 - \varphi^2) \frac{d^2 \theta}{dx^2} - \varphi \frac{d\theta}{dx} + \omega + \varphi \frac{d\omega}{dx} = 0, \quad (3.4)$$

$$(1 - \varphi^2) \frac{dj}{dx} - \varphi j - \omega = 0, \quad (3.5)$$

where $\theta = (T - T_0)(T_m - T_0)^{-1}$ is the dimensionless temperature, T_0 and T_m are the initial and scaled temperature, respectively, $\varphi = V/v$ is the dimensionless velocity of propagation of the traveling waves, $j = q/C\rho v(T_m - T_0)$, and $\omega = W\tau/C\rho(T_m - T_0)$. The solutions of (3.4) and (3.5) can be obtained by the Fourier transform method:^{31,34}

$$\theta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{(1 - iu\varphi) \exp(-iux)}{(1 - \varphi^2)u^2 - iu\varphi} \mu(u) du, \quad (3.6)$$

$$j(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\exp(-iux)}{(1 - \varphi^2)iu + \varphi} \mu(u) du, \quad (3.7)$$

where

$$\mu(u) = \int_{-\infty}^{\infty} \omega(x) \exp(iux) dx.$$

Expressions (3.6) and (3.7) give the distribution of the temperature and of the heat flux in the wave for an arbitrary type of source ω if the latter is a function of only the coordinate x . Models of this sort are widely used for describing the various types of autowave phenomena,^{5,38-41} individual examples of which will be considered below. Transforming (3.6) and (3.7) with the use of the convolution theorem, one can easily show that if $\varphi \geq 1$ then $\theta(x) = 0$ and $j(x) = 0$ for $x < 0$; i.e., the medium ahead of the wave front remains unheated. This property of traveling waves is related to the finite velocity of propagation of a thermal signal (thermal perturbation) and is the reason for the upper limit ($\varphi < 1$) of the propagation velocities of autowaves of the processes.^{34,56,57} This fact will be discussed in more detail below.

3.3. The mechanism of propagation of autowaves in relaxing media

Autowaves are ordinarily considered to be stable wave processes in nonlinear nonequilibrium systems that are self-sustaining because of energy sources distributed in the system.^{5,38-41} The velocity of propagation of an autowave, as well as its shape and amplitude, do not depend on the initial conditions over a wide range of those initial conditions, but are determined by the local properties of the medium itself. An autowave mechanism for the propagation of any process implies that there is a coupling (e.g., by diffusion) between adjacent elements of the medium. This coupling provides for a layer-by-layer initiation of the sources distributed in the system, and thereby sustains the propagation of the autowave process. This propagation mechanism distinguishes autowaves from other types of traveling waves such as detonation waves, where the layer-by-layer initiation is accomplished by the shock compression of the material. The characteristic length scale of the coupling between adjacent elements of the medium, required for the existence of the autowave regime, will be denoted as l^* . The value of l^* is

determined by the mechanism of initiation of the sources distributed in the system and has a specific meaning for each particular system. For example, in a wave of transition between the normal and superconducting state of a metal^{40,50} the quantity l^* can be the smallest dimension of a superconducting region surrounded by the normal zone, i.e., the coherence length. In gases, l^* depends on the kinetic features of the autowave process, but in any case it cannot be smaller than the mean free path of a molecule.

In discrete media l^* is bounded from below by the characteristic length scale h of the medium (Sec. 2.2). It is clear that autowaves for which the characteristic depth l of heating ahead of the wave front is less than l^* cannot exist, since in such a case there could be no coupling between adjacent elements of the medium, as is necessary for sustaining the autowave regime. It follows from this discussion that since for $\varphi \gg 1$ the medium ahead of the wave front remains unheated, i.e., $l = 0$ (see the previous section), and the spectrum of possible autowave velocities is bounded from above by the velocity of propagation of the perturbations, $\varphi = 1$ (Refs. 5,56,57) It should be emphasized that this property is characteristic only of autowave processes. Other types of traveling waves, for example, detonation waves, phase waves, or combustion waves can propagate with any velocity.^{5,38,52}

4. STRUCTURE OF TRAVELING WAVES IN LOCAL-NONEQUILIBRIUM SYSTEMS

4.1. Infinitely thin region of heat generation

In the propagation of phase-transition waves,^{39,41} certain types of combustion waves,³⁸ in the Stephan problem,^{54,55} and others, it is assumed that the zone of heat generation is infinitely thin, and thus can be written as a Dirac delta function: $\omega(x) = \bar{\omega}\delta(x)$, where $\bar{\omega}$ is a constant. From (3.6) one can then find the temperature distribution in a traveling wave in a relaxing medium with an infinitely thin zone of heat generation^{5,30}

$$\theta(x) = \frac{\bar{\omega}}{(1-\varphi^2)(\gamma_1-\gamma_2)} \times (1 + \gamma_1\varphi)\exp(\gamma_1x), \quad x < 0, \\ \varphi < 1 \quad \times (1 + \gamma_2\varphi)\exp(\gamma_2x), \quad x > 0, \quad (4.1)$$

$$\theta(x) = \frac{\bar{\omega}}{(1-\varphi^2)(\gamma_1-\gamma_2)} \times 0, \quad x < 0, \\ \varphi > 1 \quad \times (1 + \gamma_1\varphi)\exp(\gamma_1x) - (1 + \gamma_2\varphi)\exp(\gamma_2x), \quad x > 0, \quad (4.2)$$

where

$$2\gamma_{1,2} = \varphi(1+B)(1-\varphi^2)^{-1} \pm [\varphi^2(1+B)^2(1-\varphi^2)^{-2} + 4B(1-\varphi^2)^{-1}]^{1/2},$$

$B = \tau/t_\alpha$ is a dimensionless criterion—the ratio of the relaxation time τ to the characteristic time t_α of heat transfer to the surrounding medium.^{5,31,56,57} Curves of (4.1) and (4.2) are shown in Fig. 2 (curves 1 and 2). The temperature in the zone of heat generation, $x = 0$, in accordance with the general conclusions of Sec. 3.1.2, changes discontinuously, i.e., the wave front is a surface of strong discontinuity. Near the zone of heat generation the temperature $\theta(x)$ can considerably exceed the adiabatic temperature $\theta_a = 1$ (Fig. 2). This effect is due to the fact that for $\varphi \sim 1$ the system is in a local-nonequilibrium state, whose temperature, maintained by the distributed energy sources, can be higher than the equilibrium adiabatic temperature.³¹ In other words, when the velocity V of the wave is comparable to the velocity v of propagation of thermal perturbations, the heat from the source cannot travel very far, and therefore the temperature near it can exceed the adiabatic temperature.

If $\varphi > 1$, the temperature ahead of the wave front is zero, since the heat diffuses in the direction opposite to the motion of the front, while behind the front the temperature steadily relaxes to the adiabatic temperature for $B = 0$ or to the temperature of the surrounding medium if $B > 0$. By virtue of the structure of the wave for $\varphi > 1$ (Fig. 2b) we can consider it a thermal shock wave.^{5,30,34} A similar result, i.e., the formation of a thermal shock wave in the motion of a point source of heat, was obtained in the work of Refs. 42 and 43 in the case of a two-dimensional temperature field.

For the case $\varphi < 1$ the characteristic dimension l of the heated layer ahead of the wave front is determined by the following relation [(4.1)]:

$$l = \frac{1}{\gamma_1}. \quad (4.3)$$

It follows from (4.3) that $l \rightarrow 0$ as $\varphi \rightarrow 1$. This result differs fundamentally from the classical local-equilibrium case, where $l \rightarrow 0$ only when $\varphi \rightarrow \infty$.

The heat flux density $j(x)$ and the temperature gradient $d\theta/dx$ are not mutually equal aside from a sign, as they are for the classical Fourier law, but can be quite different (Fig. 2).

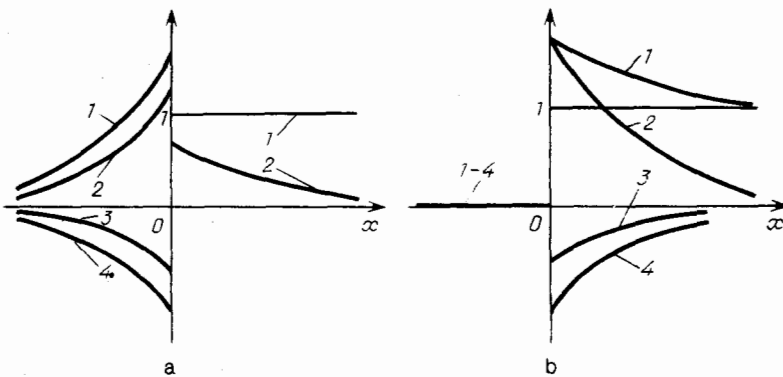


FIG. 2. Temperature $\theta(x)$ (curves 1 and 2), heat flux $j(x)$ (curve 3), and temperature gradient $d\theta/dx$ (curve 4) in a wave with an infinitely thin zone of heat generation. Curves 1,3,4 are for the adiabatic case ($B = 0$), curve 2: $B > 0$; a) $\varphi < 1$; b) $\varphi > 1$.

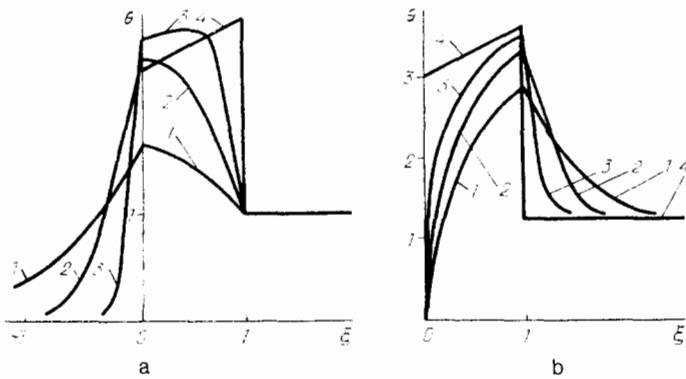


FIG. 3. Distribution of the temperature, $\theta(\xi)$ in a wave for various values of the dimensionless velocity of φ of propagation of the wave for $\bar{\omega} = 3$. a) Curve 1: $\varphi = 0.8$; curve 2: $\varphi = 0.95$; curve 3: $\varphi = 0.98$; curve 4: $\varphi = 1$. b) Curve 1: $\varphi = 1.1$; curve 2: $\varphi = 1.05$; curve 3: $\varphi = 1.02$; curve 4: $\varphi = 1$.

4.2. Π -shaped source of heat generation

In a number of cases one may use a source function of finite width x_0 and constant intensity $\bar{\omega}$ to simulate the propagation of traveling waves (Refs. 5, 53)

$$\omega(x) = \bar{\omega} = \text{const}, \quad 0 < x < x_0, \\ = 0, \quad x < 0, \quad x > x_0. \quad (4.4)$$

Substituting (4.4) into (3.6) one can easily obtain the temperature distribution in a traveling wave with such a Π -shaped heat generation function. Such distributions are shown in Fig. 3. As in the previous case, the temperature in the zone of heat generation ($0 < \xi < 1$, where $\xi = x/x_0$ is the new dimensionless variable) and near it can considerably exceed the adiabatic equilibrium temperature. For $\varphi < 1$ the relaxation processes take place within and ahead of the zone of heat generation ($\xi < 1$), while behind the zone, $\theta(\xi) = \theta_a = 1$. If $\varphi > 1$, then the medium ahead of the wave front remains unheated, while behind the front the temperature relaxes to the adiabatic value, i.e., $\theta(\xi) \rightarrow \theta_a$ as $\xi \rightarrow \infty$ (Fig. 3b).⁴⁾

Figure 4 shows curves of the heat flux $j(\xi)$ and the temperature gradient $d\theta/d\xi$. The discontinuous change in the temperature gradient at the points $\xi = 0$ and $\xi = 1$ is due to relaxation processes in the system and to the form of the heat generation function (4.4) The heat flux in this case remains continuous (Fig. 4). For $\varphi = 1$ not only the gradient, but also the temperature and the heat flux at the wave front

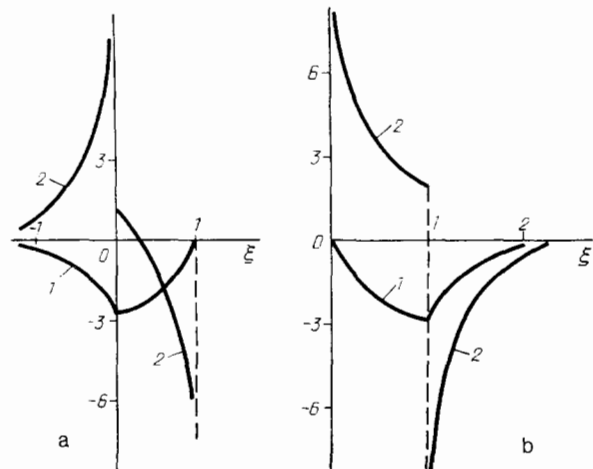


FIG. 4. Heat flux $j(\xi)$ and temperature gradient $d\theta/d\xi$ for $\bar{\omega} = 3$. a: $\varphi < 1$; b: $\varphi > 1$.

change discontinuously. In the wave there is no heat diffusion, which, for $\varphi \neq 1$, smooths out the variations of the temperature and the heat flux.

4.3. Heat generation step function

Let us consider a source of heat generation of the following form:

$$\omega(x) = \bar{\omega} = \text{const}, \quad x > 0, \\ = 0, \quad x < 0. \quad (4.5)$$

This step function of heat generation is used for the analysis of the propagation of switching waves of homogeneous stationary states of a system, for example, a superconductor/normal metal transition wave,^{40,50} a semiconductor/metal transition wave,⁵⁸ a wave of transition between the diffusion and kinetic regimes in heterogeneous catalysis,⁵⁹ and others. Substituting (4.5) into (3.6) we obtain the temperature distribution in a switching wave with allowance for relaxation processes.^{5,31,56,57}

$$\theta(x) = B\kappa_1 \exp(\gamma_1 x), \quad x < 0, \\ \theta(x) = 1 - B\kappa_2 \exp(\gamma_2 x), \quad x > 0, \quad (4.6)$$

$$\theta(x) = 0, \quad x < 0, \\ \theta(x) = 1, \quad x > 0, \quad (4.7)$$

$$\theta(x) = 0, \quad x < 0, \\ \theta(x) = 1 + B\kappa_2 \exp(\gamma_2 x) - B\kappa_1 \exp(\gamma_1 x), \quad x > 0, \quad (4.8)$$

where

$$\kappa_{1,2} = \bar{\omega} (1 + \varphi\gamma_{1,2}) [(1 - \varphi^2)(\gamma_1 - \gamma_2)\gamma_{1,2}]^{-1}.$$

Curves of $\theta(x)$ representing expressions (4.6)–(4.8) are shown in Fig. 5. For $x \rightarrow \pm \infty$ the temperature of the system is determined by its homogeneous stable states with $\theta_1 = 1$

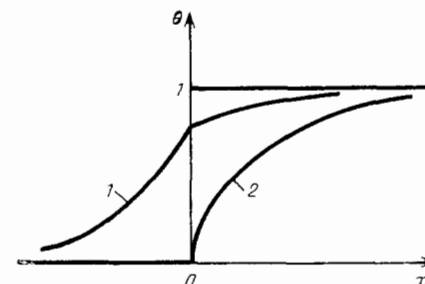


FIG. 5. Temperature $\theta(x)$ in a switching wave for various values of φ : 1) $\varphi < 1$; 2) $\varphi > 1$.

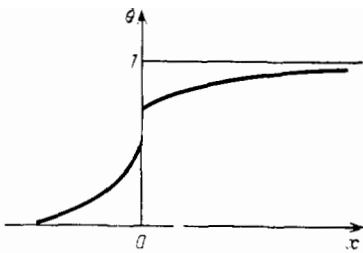


FIG. 6. Temperature $\theta(x)$ in a switching wave with a phase transition ($\varphi < 1, \omega_1 < 0$).

and $\theta_0 = 0$. As in the previous cases, the heated layer ahead of the wave front exists only for $\varphi < 1$ (curve 1 in Fig. 5), while if $\varphi > 1$, then $\theta(x) = 0$ for $x < 0$ (curve 2 in Fig. 5). For $\varphi = 1$ there is no diffusion of heat in the wave, and the temperature of the wave is determined by the balance between the heat input from the heat sources and the heat output into the surrounding medium. If the heat output obeys Newton's law $\alpha(T - T_0)$, as assumed previously, and if the heat source function is a step function (4.5), then the temperature behaves in a corresponding way: it changes discontinuously at the wave front (4.7).

If there is a phase transition at a switching wave front, for example, in a superconductor/normal metal wave,⁵⁰ then the heat source can be represented as a sum of a delta function (Sec. 4.1) plus the source (4.4). Then the temperature distribution is also determined by the integral relation (3.6). Figure 6 shows the curve of $\theta(x)$ for $\varphi < 1$. The presence of a phase transition at the wave front causes a temperature jump at the front (Sec. 3.1.2 and 4.1). This effect, which is due to the relaxation properties of the system, must be taken into account in the determination of the velocity of propagation of traveling waves. If $\varphi > 1$ there will also be a temperature jump at the wave front, while ahead of the front the medium remains unheated; therefore this wave can also be considered a thermal shock wave.

As a result of the relaxation processes the temperature field in traveling waves exhibits important properties that are distinct from those of the classical case of local equilibrium. First, the temperature in and near the zone of heat generation can considerably exceed the equilibrium adiabatic temperature. Second, if the velocity of a traveling wave is higher than the velocity of propagation of perturbations (a thermal signal), the medium ahead of the front remains unheated. Third, if there is an infinitely narrow heat source in the wave (e.g., in the case of phase transitions), the temperature in the wave front changes discontinuously, i.e., the wave front is a surface of strong discontinuity.

5. VELOCITY AND CRITICAL CONDITIONS FOR THE PROPAGATION OF AUTOWAVES IN LOCAL-NONEQUILIBRIUM MEDIA

5.1. Combustion waves

In the approximation of an infinitely thin zone of chemical reaction the velocity of a combustion wave is determined by the temperature T^* of the front in the following way:³⁸

$$V = A \exp\left(-\frac{E^*}{2RT^*}\right), \quad (5.1)$$

where A is a constant, E^* is the activation energy, and R is the universal gas constant. In turn, the temperature in the

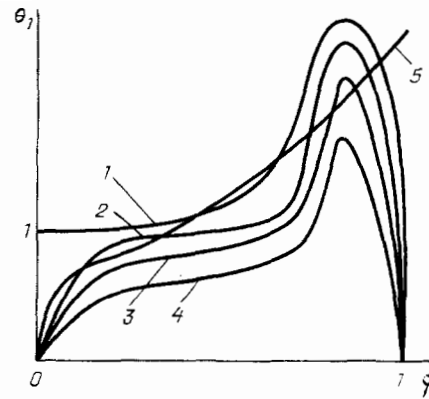


FIG. 7. Left-hand side (curves 1-4) and right-hand side (curve 5) of Eq. (5.2) as functions of φ . 1) $B_1 = 0$; 2) $B_2 > 0$; 3) $B_3 > B_2$; 4) $B_4 > B_3$.

reaction zone depends on the velocity of the wave (formula (4.1)). Therefore, the steady-state velocity of propagation of a combustion wave is determined by the following transcendental equation:^{5,30}

$$\frac{\varphi(1 + \gamma_1\varphi) \exp(-\gamma_1 l^*)}{(1 - \varphi^2)(\gamma_1 - \gamma_2)} = \theta_E \left(\frac{\ln \bar{A}}{\varphi}\right)^{-1}, \quad (5.2)$$

where $\theta_E = E^*/(2R(T_a - T_0))$ and $\bar{A} = A/v$. Graphs of the left-hand side of Eq. (5.2) (curves 1-4) and of the right hand side (curve 5) are shown in Fig. 7. The horizontal coordinates of their intersection points are equal to the velocities φ of the autowave regimes of combustion. As mentioned previously, these velocities are bounded from above by the velocity of propagation of thermal perturbations, $\varphi = 1$. It follows from Eq. (5.2) that the parameter B , which is equal to the ratio of the relaxation time to the characteristic time of heat transfer into the surrounding medium, determines not only the velocity φ of the wave, but also the number of autowave regimes. For $B = B_1 = 0$ (curve 1 of Fig. 6), where there is no heat loss into the surrounding medium, there can be three autowave regimes of combustion, with different propagation velocities. For $B = B_2 > 0$ (curve 2), there are four, for $B = B_3 > B_2$ (curve 3) there are two, and for $B = B_4 > B_3$ (curve 4), there is no autowave regime. The solutions with the lower velocities (one on curve 1 and two on curve 2) correspond to the classical solutions of the parabolic equation,³⁸ when the relaxation processes can be neglected. The autowave regimes with high velocities are possible only in media with relaxation. Thus relaxation effects lead to the existence of additional autowave regimes. Moreover, autowave regimes can exist in relaxing media under conditions where there are no classical (local-equilibrium) solutions at all (curve 3 of Fig. 7). In this case the equilibrium temperature ahead of the wave front, which is determined by the initial heat content of the system, does not reach values necessary for chemical reaction of combustion to take place, and consequently there will be no layer-by-layer initiation of distributed sources. Therefore the classical autowave regimes with $\varphi \ll 1$, where the temperature in the reaction zone does not exceed the adiabatic (equilibrium) value, will not propagate. However, at high wave velocities ($\varphi \sim 1$) the local-nonequilibrium temperature at the wave front is considerably above the equilibrium temperature

(Fig. 2) and can be high enough to activate the combustion reaction so as to sustain the autowave mode of propagation of the wave. The analogous effect, i.e., the existence of autowaves in relaxing systems, where classical local-equilibrium solutions do not exist, evidently is also possible for other types of autowave processes.

On curve 2 the regime with the lowest velocity is unstable;³⁸ its velocity increases with an increase in the heat loss. From this discussion one should expect that of the pair of relaxation solutions (curves 1-3 in Fig. 7) the regime with the lower velocity should be unstable. However, this issue requires further study.

It is possible by the same means to take into account the effect of relaxation processes on autowave regimes of propagation of phase transitions of various kinds, for example, the front of explosive crystallization of amorphous material.⁴¹ To do so one must use, instead of (5.1), the corresponding macrokinetic equation.

This section has examined the effect of local nonequilibrium on autowave regimes of combustion in terms of the transport processes. At the same time, the high temperatures and temperature gradients at the combustion wave front can cause the chemical reactions to proceed under nonequilibrium conditions, i.e., conditions of kinetic nonequilibrium.⁶⁰ In the general case, it is necessary to take into account both of these effects, both for combustion waves, and for other types of waves that propagate in relaxing media.

5.2. Superconductor/normal metal transition waves

Some of the most common types of autowave processes are waves of switching between homogeneous states in bistable systems.^{39,40,50,59} Switching waves describe superconductor/normal metal (S/N) transitions,^{40,50} transitions between kinetic and diffusion regimes in heterogeneous catalysis,⁵⁹ as well as wave processes in thermoelectric systems⁶¹ and neuristors.⁶² The last of these can be used to make logic circuits, delay lines, memory elements for computer technology, etc.^{62,63} In addition, neuristors that are made on the basis of superconducting systems simulate nerve fibers.^{62,64} Interest in component elements whose operation is based on the switching of homogeneous states of a bistable system in the autowave regime is due to their "bio-similarity" and their simplicity and high speed of operation. For example, the velocity of a transition wave can reach 10^6 cm/s.^{50,63} The theory of propagation of switching waves based on the classical parabolic transport equations⁴⁰ is inapplicable for these velocities.⁵⁰ Instead it is necessary to use transport equations that take into account relaxation of the system to local equilibrium (Sec. 2). This treatment will consider S/N transition waves in relaxing media,^{5,31,56,57} although the generality of the mathematical model allows the results to be extended to other types of switching waves.

5.2.1. The intensity of heat generation in a S/N transition wave can be represented by a step function (4.5) (Refs. 40,50,63). In this case the velocity of propagation of the S/N transition wave obeys the following equation:^{5,31,56,57}

$$\theta^* = \frac{B(1 + \gamma_1 \varphi) \exp(-\gamma_1 \bar{\zeta}_0)}{(1 - \varphi^2)(\gamma_1 - \gamma_2)\gamma_1} \equiv f(\varphi), \quad (5.3)$$

where θ^* , the temperature of the intermediate unstable state

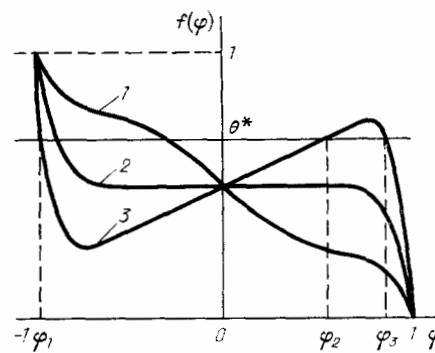


FIG. 8. Temperature at a switching wave front for various values of B . 1) $B < 1$; 2) $B = 1$; 3) $B > 1$.

of the system ($0 < \theta^* < 1$), determines the transition from one stable state to the other, and $\bar{\zeta}_0$ is the dimensionless coherence length. The right-hand side of (5.3), denoted by $f(\varphi)$, is the temperature at the wave front. Curves of $f(\varphi)$ for various values of the parameter B are shown in Fig. 8. If $B < 1$ (curve 1 of Fig. 8), then $f(\varphi)$ is a monotonically decreasing function. Then there is only one point of intersection of $f(\varphi)$ with the line $\theta^* = \text{const}$, and, consequently, a single autowave regime of the S/N transition. For $B > 1$ the curve $f(\varphi)$ has a local minimum f_{\min} and maximum f_{\max} (curve 3, Fig. 8). If $\theta^* > f_{\max}$ or $\theta^* < f_{\min}$, then as in the previous case the S/N transition in the autowave regime is possible with only one velocity. If $f_{\min} < \theta^* < f_{\max}$ there are three points of intersection of $f(\varphi)$ with $\theta^* = \text{const}$. They correspond to autowaves regimes with different velocities of propagation $\varphi_1 < \varphi_2 < \varphi_3$ (Fig. 8). The nonuniqueness of the autowave regimes of switching waves for $B > 1$ is due to relaxation processes in the system. The bifurcation value of the parameter B , which determines the rearrangement of the qualitative structure of the solution, is unity. At that value, $f_{\min} = f_{\max}$ (curve 2, Fig. 8). The velocity of propagation of the S/N transitions, as in all other types of autowaves, is bounded by $|\varphi| = 1$ (Fig. 8). In addition to this general constraint, there is another, which is related to the properties of the S/N transition. Since the depth of heating l of the system ahead of the wave front goes to zero as $|\varphi| \rightarrow 1$, and since l is bounded from below by the minimum width of the transition zone, that is, the coherence length $\bar{\zeta}_0$, the velocity of autowave regimes of the S/N transition will be limited by $\varphi_{\text{cr}} < 1$, the value of which is determined from the condition

$$\gamma_1(\varphi_{\text{cr}}) \bar{\zeta}_0 = 1.$$

5.2.2. In some cases the latent heat of the S/N transition may exert a considerable influence on the autowave regimes of its propagation.⁵⁰ If it is assumed that the zone of the S/N transition is infinitely thin, its front will be a surface of strong discontinuity (Fig. 6). In a more detailed analysis of S/N waves it is necessary to take into account the fact that the thickness of the S/N transition zone cannot be less than the coherence length $\bar{\zeta}_0$. Therefore, a change in the temperature at the wave front, equal to the temperature jump for the case of an infinitely thin S/N transition zone, takes place over a distance of the order of $\bar{\zeta}_0$. The velocity of propagation of the S/N transition wave in this case is given by the relation:⁵

$$\theta^* = \frac{(1 + \gamma_1 \varphi) \exp(-\gamma_1 \bar{\zeta}_0)}{(1 - \varphi^2)(\gamma_1 - \gamma_2)} (B\gamma_1^{-1} - \varphi\omega_1) \equiv f_1(\varphi), \quad (5.4)$$

where ω_1 is the dimensionless latent heat of the phase transition. As in the previous case, there exists a bifurcation value $B = B^*$ of the parameter B such that for $B < B^*$ there is a unique autowave regime, while for $B > B^*$ there are three (Fig. 8). The value $B = B^*$ is given by the equality (5.4) and the condition

$$f_{1\min}(B^*) = f_{1\max}(B^*).$$

From formula (5.4) it follows that for $\theta^* \rightarrow 0$ the velocity of the S/N wave approaches the maximum possible value φ_{\max} , the value of which depends on, among other things, the latent heat of the phase transition, ω_1 , and is given by the formula

$$B = \omega_1 \varphi_{\max} \gamma_1(\varphi_{\max}).$$

The latent heat of the phase transition and its finite width is the cause of the limiting velocities φ_{cr} and φ_{\max} , whose values are less than the velocity of propagation of a thermal wave, $\varphi = 1$. In the general case the velocity of a S/N wave will be limited by the lower of the velocities corresponding to these effects

$$|\varphi| \leq \min(\varphi_{cr}, \varphi_{\max}).$$

If the intensity of heat generation in a S/N wave is not a step function but has a piecewise linear form,⁴⁰ then the temperature distribution and the velocity of propagation of the switching wave can be determined by the methods outlined above. If the linear part of the heat generation function is small, the expression for the velocity of the S/N wave is the same as (5.2), where $\bar{\zeta}_0$ is understood to mean the dimensionless width of this linear part.⁶⁵

Thus, the local nonequilibrium nature of a system has a significant effect on autowave processes of various types. First, it limits the spectrum of possible velocities of the autowave regimes to the velocity of propagation of perturbations (footnote 1). In each specific case there may be stronger limitations. Second, it leads to the formation of a surface of strong or weak discontinuity at the wave front. Third, it allows for the possibility of a superadiabatic temperature at the wave front and for other autowave regimes of propagation in addition to those corresponding to the classical local-equilibrium case.

CONCLUSIONS

The purpose of this paper was to show that the properties of traveling waves propagating with high velocities under conditions of local nonequilibrium, where it is necessary to take into account relaxation processes, differ considerably from the properties of slow traveling waves that are described by classical local-equilibrium transport equations. Basic to this analysis are the various theoretical methods of describing the dynamics of systems, which do not rest on the principle of local equilibrium. Random-walk models and models of media with memory are the clearest examples of such methods. The necessity for such investigations is due not only to their theoretical interest, but also to the ubiquitous nature of local-nonequilibrium systems and their application in practice.

Extremal conditions—low temperatures, high gradi-

ents and fluxes, ultrashort energy pulses, high characteristic velocities or short characteristic times of processes—are responsible for the local-nonequilibrium nature of various processes.

Already the first results obtained with allowance for relaxation effects show that traveling waves, propagating under local-nonequilibrium conditions, have a number of important special properties. At the wave front there can exist surfaces of strong or weak discontinuity, while for wave velocities greater than the velocity of propagation of perturbations (a thermal signal), thermal shock waves are formed. In and near the zone of heat generation the temperature may be considerably above the equilibrium adiabatic temperature. In local-nonequilibrium systems, as compared to the classical local-equilibrium case, there exist additional autowave regimes of propagation of various processes, with the velocities of all the autowaves being bounded from above by the velocity of propagation of perturbations.

In my opinion, further investigations of transport processes in extremal situations will not only take into detailed account relaxation of the system to local equilibrium, i.e., temporal nonlocality, but will also allow for spatial nonlocality, which is a characteristic feature of transport processes in complex discrete systems. The relation between the space and time scales of the system defines certain fundamental properties of transport processes, such as the velocity of propagation of perturbations corresponding to the transport potential, and it determines the type of transport equation (Sec. 2.2). It is to be expected that the use of nonlocal equations for the analysis of various physical, physicochemical, biological, ecological, and other nonequilibrium systems with a complex structure will in the near future lead to new and interesting results.

¹ The velocity of propagation of a perturbation will be understood to mean the velocity of propagation of perturbations of the transport potential corresponding to the given process. In the case of heat transport it is the propagation velocity of a thermal wave (thermal signal).^{3,4}

² In this sense local-nonequilibrium theories of transport processes can be regarded as "relativistic" as compared to classical local-equilibrium theories.

³ The overall energy balance is, of course, conserved: the elevation of the temperature near the zone of heat generation is compensated by a narrower heated region ahead of it.

⁴ Analogous phenomena of superequilibrium temperatures at a wave front and the relaxation of the temperature to the equilibrium value behind the front have been observed in filtration combustion^{46,47} and in the accompanying motion of thermal waves in a catalyst layer.⁴⁸ The two-temperature model (Sec. 2 and 3) used in the work of Refs. 46–48 has been taken to apply to the different temperatures of the gaseous and solid phases. The similitude of these effects affords a basis for applying the relaxation model to similar kinds of systems where the relaxation time is taken to mean the characteristic time of interphase heat exchange.²²

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