Addendum to the paper "Heat waves" [Rev. Mod. Phys. 61, 41(1989)]

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Since the appearance of our paper on heat waves [Rev. Mod. Phys. **61**, 41 (1989)], certain papers that should have been cited have come to our attention. It appears that our effort to write a relatively complete chronology of thought about heat waves fell somewhat short of the mark. We thought it would be useful to correct the more serious omissions in that chronology in this addendum, and not to try to list all the papers that bear on one or another aspect of the subject. The literature on heat waves is still a manageable one; the subject is still active, but not explosively so. It seems to us that nearly the whole of the literature is covered in our review, in the various summaries of results on propagation of waves in liquid helium, and in the recent review of Jou, Casas-Vázquez, and Lebon (1988), which gives some references missed by us and thoroughly reviews the literature coming from the special school of thought about thermodynamics called extended thermodynamics. We did not think it useful to try to add something to the already complete review of the literature on liquid helium, and we confined our remarks to signal events in the development of equations leading to wave propagation of heat. The fascinating story of the nonlinear evolution of shock waves in helium II can be found in Chap. 16 of *Fluid Mechanics* by Landau and Lifshitz (1959) and especially in the book by Khalatnikov (1965). These topics and others that arise in the study of liquid helium are thoroughly reported in the works of Donnelly (1967), Putterman (1974), Roberts and Donnelly (1974), Tilley and Tilley (1986), and Wilks and Betts (1987).

Our paper and the references cited in the above paragraph do not quite cover all the lines of thought about heat waves that we now think ought to be listed in our chronology. In particular it is important to draw attention to the notion of the nonlocal theory of transport of heat, which emerges from nonequilibrium statistical mechanics and thermodynamics. Another problem that needs to be addressed is the question of how to regard the heat flux and what types of invariance ought to be imposed. The origin of the relation between the heat flux and the temperature can be regarded either as a constitutive problem, whose solution is independent of the frame of the observer, or as a manifestation of dynamics governing the random motions of small particles satisfying the weaker conditions of invariance associated with the equations of motion. There is a small number of interesting approaches to nonlinear problems of heat transmission. The theory of "thermal waves" is generated out of the nonlinear dependence of conductivity on temperature arising, say, in the diffusion theory of thermal radiation (see the review of Zel'dovich and Razier, 1966). Parabolic waves are possible when the conductivity vanishes with temperature. The whole theory is based on similarity solutions and is fully nonlinear. An interesting generalization of thermal waves to a hyperbolic problem was achieved by Wilhelm and Choi (1975), who used a Cattaneo law with temperature-dependent conductivity and relaxation time. This theory also can be treated by similarity solutions. The mathematical and physical relationship between these two solutions is far from fully resolved. Other nonlinear approaches based on thermodynamics have been developed for application to the problem of second sound in dielectric crystals. Recent experiments on ultrafast thermal excitation of metals using femtosecond, high-intensity laser pulses may be good for testing ideas about heat wave propagation at high temperatures. At present, the theory is based on the two-temperature diffusion model of Anisimov *et al.* (1974), even though the relaxation times involved are well within the range where wave propagation could be dominant. The times of transit across thin gold films of heat pulses measured by Brorson, Fujimoto, and Ippen (1987) are linear in the sample thickness, consistent with wave propagation.

This addendum follows the strictly chronological sequence of our annotated bibliography. At various points, however, we felt obliged to give some further explanations so that the text is composed of an annotated bibliography interspersed with clearly identified commentaries.

1948, Carlo Cattaneo, Atti Semin. Mat. Fis. Univ. Modena **3**, 3.

We wrote a summary of this important paper in "Heat waves," but we missed an important point that has been made forcefully by I. Müller (1987), who notes that Cattaneo first proposed that the heat flux depends on the history of the temperature gradient, writing

$$q=-\kappa_1\frac{\partial T}{\partial x}+\kappa_2\frac{d}{dt}\left[\frac{\partial T}{\partial X}\right] . \tag{1}$$

The heat flux at a point (x,t) is not only proportional to the temperature gradient there, but also remembers faintly the temperature gradient that the particle at x had at an earlier time. When this is combined with the energy equation

$$\rho c \frac{dT}{dt} + \frac{\partial q}{\partial x} = 0 , \tag{2}$$

we get a parabolic equation

$$\frac{dT}{dt} = \frac{\kappa_1}{\rho c} \frac{\partial^2 T}{\partial x^2} - \frac{\kappa_2}{\rho c} \frac{d}{dt} \frac{\partial^2 T}{\partial x^2} \tag{3}$$

predicting the spreading of pulses with infinite speed. Müller notes that Cattaneo must have noticed this, because he proceeded to the equation

$$q + \sigma \frac{dq}{dt} = -\kappa_1 \frac{\partial T}{\partial x} \tag{4}$$

through a sequence of steps

$$\mathbf{q} = -\kappa_1 \left[1 - \sigma \frac{d}{dt} \right] \frac{\partial T}{\partial x}, \quad \sigma = \kappa_1 / \kappa_2 , \tag{5}$$

$$\frac{1}{1 - \sigma \frac{d}{dt}} q = -\kappa_1 \frac{\partial T}{\partial x} , \tag{6}$$

$$\left[1 + \sigma \frac{d}{dt} \right] q = -\kappa_1 \frac{\partial T}{\partial x} . \tag{7}$$

Müller notes that this sequence is difficult to justify. Before the sequence we get diffusion, after the sequence we get hyperbolicity and waves.

If a term dq/dt were added on the right-hand side of Eq. (1), we would arrive at a heat conductor of the Jeffreys type (see "Heat waves," p. 44), which has a diffusive response, singularly perturbing waves when σ is small.

1956, Harry Jones, "Theory of electrical and thermal conductivity in metals," in *Handbuch der Physik XIX: Electrical Conductivity I* (Springer, Berlin), p. 227.

It is argued that conduction in metals can be modeled by an electron gas satisfying Fermi statistics in which collisions between electrons can be neglected. An electron in a space periodic field behaves like a free particle, justifying the use of the kinetic theory of gases to study conduction, except that quantum statistics are used and that the steady state arises from lattice irregularities or motions and not from collisions. This is to say that electron interactions with phonons and singularities are what is important. Jones shows that, when scattering alone is considered, an arbitrary initial probability distribution will relax to the equilibrium with a $\tau(\mathbf{k})$ time of relaxation, which depends on the wave vector $\mathbf{k}$. He concludes that there is a time of relaxation in pure metals at high temperatures, and in sufficiently impure metals at all temperatures. The analysis is for weak temperature gradients in the sense that the heat current is proportional to the temperature gradient at equilibrium. This gives rise to a Cattaneo type of equation (cf. Wilhelm and Choi, 1975). The Wiedemann-Franz relation can be used to relate a relaxation time to the thermal conductivity. Empirical formulas for the temperature dependence of the thermal conductivity of metals lead then to nonlinear laws of heat propagation in metals.

1960, J. M. Richardson, J. Math. Anal. Appl. **1**, 12.

Richardson derives general hydrodynamic equations for a system of identical structureless particles under the action of central forces and conservative external forces, using methods of nonequilibrium statistical mechanics. He extends the work of Irving and Kirkwood (1950) by advancing arguments about the nature of the underlying ensemble to obtain a closed set of equations with a partially implicit prescription for calculating irreversible terms. He does not use Boltzmann's transport equation and gives criticisms of approaches that do. The irreversible terms in Richardson's theory are nonlocal in space and time [Eqs. (18) and (19) under Piccirelli, 1968]. He says that he expects the nonlocal dependence to have a spatial extension of the order of the range of interaction forces. He remarks that the time sequence of mean observables almost never can be the solution of a set of first-order differential equations, but it can be the solution of sets of equations in which the present rates of change of mean observables depend not only upon the present values but also on their past values.

Richardson's work appears to be the first in which the transport of heat is expressed by an integral whose kernel is influenced by values far from the point of observation.

It may be useful at this point to make precise what is meant by a spatially nonlocal material; it may have many different forms. A spatially nonlocal theory in continuum mechanics is not a simple material. The reader should not confuse simple materials in statistical mechanics with simple materials in continuum mechanics; they have nothing to do with one another. A simple liquid in statistical mechanics would be a liquid of featureless molecules acted on by potential forces whose action need not be short range. A simple material in isothermal continuum mechanics is one whose stress is determined by the history of the first spatial gradient of the deformation, short range. A simple heat conductor is one in which the heat flux is determined by the history of the first gradient of the temperature, as in the theories of Cattaneo, Gurtin and Pipkin, and Nunziato. But the equations of Richardson are obviously not simple in this sense.

1964, R. J. von Gutfeld and A. H. Nethercot, Jr., Phys. Rev. Lett. **12**, 641.

von Gutfeld and Nethercot were the first to observe the ballistic propagation of heat in cold crystal of quartz (SiO_2) and sapphire (Al_2O_3). Ballistic propagation takes place when the temperature of the crystal is colder than that at which heat waves (second sound) propagate. The speed of the ballistic phonons induced by heat pulsing is the first, rather than the second, sound speed.

1966, Y. B. Zel'dovich and Y. P. Razier, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena,* Vol. II, Chap. X, "Thermal Waves" (Academic, New York/London).

The theory of parabolic wave propagation arises in the theory of thermal waves, which was developed in the paper by Zel'dovich and Kompaneets (1959). Chapter X of the book by Zel'dovich and Razier (1966) contains a thorough, detailed, and clear account of the whole subject. Here we shall define thermal waves in a formal way, then go a little deeper into the physical underpinning. The diffusive propagation of heat is governed by a diffusion equation

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot k \nabla T \ , \tag{8}$$

where ρ, c, and k are density, specific heat, and thermal conductivity. Now suppose that the conductivity $k(T)=aT^n$ depends on temperature, $n \geq 0$, and it is possible to support a plane propagating wave

$$T=\Theta(x-vt) \ . \tag{9}$$

Any such wave necessarily satisfies

$$-\rho c v \frac{d\Theta}{dx} = \frac{d}{dx}\left[a\Theta^n \frac{d\Theta}{dx} \right] \ . \tag{10}$$

This can be integrated once if $\rho c v$ is independent of Θ. We can find a solution for this problem with $\Theta=0$ at $x=x_f$

$$\Theta = \left[\frac{n\rho c v}{a} |x_f - x| \right]^{1/n} \ . \tag{11}$$

This solution is locally valid near the front coordinate $x=x_f$; the front velocity $v=dx_f/dt$ and position may be determined from the spatial solution as functions of the time. Some similarity solutions for different problems are given in the book. The wave velocity v is not a constant in time. For example, in the problem of heat release from an instantaneous plane source, the heat release parameter

$$Q=\int_{-\infty}^{\infty} T\,dx \tag{12}$$

is a constant and

$$x_f \sim (aQ^n)^{1/(n+1)} t^{1/(n+2)} \ , \tag{13}$$

$$v \sim \frac{dx_f}{dt} \sim \frac{x_f}{t} \sim (aQ^n)^{1/(n+1)} t^{1/(n+2)-1} \ . \tag{14}$$

When $n=1$, the front moves as $t^{1/3}$ and the front velocity decreases to zero as $1/t^{2/3}$. Similar results hold for instantaneous release of heat from a point source, as in explosions.

Now we consider some properties of the thermal conductivity $k=aT^n$, the gradient $T'=dT/dx$ at the front, and the flux kT',

$$k=aT^n \begin{cases} n>0, & k \text{ vanishes at the front} \ , \\ n=0, & k=a \text{ for all } T \ , \\ n<0, & k\to\infty \text{ as } x\to x_f \ . \end{cases}$$

The conductivity does not go to zero with T when $n \leq 0$, and there are no solutions with $T=0$ at any finite x. This case, $n \leq 0$, corresponds to the instantaneous propagation of heat to infinity, "infinite wave speeds."

We also have $T' \sim |x_f - x|^{1/n-1}$, which is infinite at $x=x_f$ when $n>1$. The solution here violates the small gradient hypothesis of the diffusion theory of radiation. Thus when $n>1$ we have a sharp discontinuity, rather too sharp. When $0<n\leq 1$, T' tends to zero at the fronts. The flux $q \sim T^n T' \sim |x_f - x|^{1/n}$ vanishes at the front for all $n>0$.

The propagation just described of a heat pulse into a region of zero temperature is what we understood by *parabolic propagation* of heat.

The theory of thermal waves can never be achieved in nature if T is the absolute temperature, because $T=0$ is then impossible to attain. In fact, T is the absolute temperature because the theory of thermal waves arises out of the theory of radiation for optically dense materials in local equilibrium (see Sec. 12 in Zel'dovich and Razier, Vol. 1). Photons arriving at any point in space are born in the vicinity of that point at distances of not more than several mean free paths; photons born farther away are absorbed in transit. Consequently, only the immediate vicinity of the point "participates" in establishing the equilibrium intensity. The necessary condition for local equilibrium—small gradients in an extended, optically thick medium—serves simultaneously as a justification for the use of the diffusion approximation when considering radiative heat transfer. The heat flux transported by radiation can be written

$$k=\frac{16\sigma T^3 l}{3} \ , \tag{15}$$

where T^3 arises from differentiation of the T^4 radiation law, σ is the Stefan-Boltzmann constant, and l is the radiation mean free path, which also depends on temperature.

Suppose we have a real explosion in which hot gas is radiating into the ambient air with, say, $T_0=300$ K. Can we use the similarity solution for the instantaneous release of energy from a point source, which assumes that $T_0=0$ K, to model the real problem? At early times the interior temperature will be enormously larger than the 300 K ambient. One may then expect that the real problem could be modeled by the self-similar problem, but nonuniformly and certainly not near x_f. As Zel'dovich and Razier state, "self-similar solutions are of interest not so much as particular solutions of a specific narrow class of problem, but mainly as limits which are asymptotically approached by solutions of more general problems that are not self similar."

The following citation from Israel and Stewart (1979), p. 341, motivates a brief discussion of heat waves and extended thermodynamics:

> One of the most annoying paradoxes which have plagued thermodynamical theory has been the parabolic character of the differential equations of heat flow. Even in classical theory, instantaneous propagation of heat is an offense to intuition, which expects propagation at about the mean molecular speed; in a consistent relativistic theory it ought to be completely prohibited.
>
> Although it was recognized that the origin of this problem must reside in some deficiency of conventional thermodynamics when applied to the description of transient effects, the nature of this deficiency was not pinpointed for a long time. In 1949, Grad showed how transient effects could be effectively treated within the framework of classical kinetic theory by employing a method of moments instead of the Chapman-Enskog normal solution. Suitable truncation of the moment equations gave a closed system of differential equations which turned out to be hyperbolic, with propagation speeds of the order of the speed of sound. . . .
>
> In the context of phenomenological theory, instantaneous propagation remained for many years a puzzle that makeshift devices, like the addition of *ad hoc* relaxation terms to Fourier's law (Cattaneo, 1948), could not resolve in a logically satisfying way. However . . . Müller (1967a) showed that the difficulty lies in the conventional theory's neglect of terms of second order in heat flow and viscosity in the expression for the entropy. Restoring these terms, Müller derived a modified system of phenomenological equations which was consistent with the linearized form of Grad's kinetic equations.

1967, I. Müller, Z. Phys. **198**, 329.

Müller's paper is the first to use irreversible thermodynamics to replace the parabolic, diffusive propagation heat with hyperbolic wave propagation. To do this, Müller had to extend the idea of local equilibrium, introducing a new state variable. From the author's summary,

> It is shown that the paradox of Fourier's heat conduction theory (propagation of temperature disturbances with infinite velocity) is a consequence of an insufficient description of the thermodynamical state in nonequilibrium. Taking heat flow and flow of momentum as additional state variables and thoroughly investigating the equation of entropy balance, we derive an extended theory of thermodynamics of irreversible processes, which can be shown to remove the paradox of heat conduction theory for materials with appropriate equations of state. The velocity of temperature propagation is calculated explicitly for a one atomic ideal gas using an approximate solution of the Boltzmann equation.

Some observations and modifications of Müller's theory are presented by Ruggeri (1983).

Extended thermodynamics is one of a few thermodynamic theories far from equilibrium. The classical theory of irreversible processes rests on the assumption that although globally the system is in a state of nonequilibrium, each small element of the system remains in a state of local equilibrium, and the equations of thermostatics are valid in such elements. In particular, the local entropy has the same functional dependence on the local macroscopic variables as at equilibrium. This enables one to calculate the entropy production in systems, which in such cases is a bilinear expression of thermodynamical forces and fluxes. In fast irreversible processes or when inertial and relaxation phenomena in the continuum are strong, the system no longer remains in the state of local equilibrium. To define the nonequilibrium state of the system, new variables that vanish at equilibrium must be introduced. The entropy flux is treated as a constitutive quantity different from the quotient of the heat flux and absolute temperature. The history of the generalizations of Gibb's equation for entropy production is given by Jou *et al.* (1988).

Other papers that confront the problem of infinite speed of propagation with extensions of irreversible thermodynamics are those of Lambermont and Lebon (1973), Gyarmati (1977), and Lebon (1978).

Recent theories of extended thermodynamics are represented in the proceedings volume edited by Müller and Ruggier (1987). Most of the papers there and elsewhere deal with the thermodynamics of gases and are inspired by the kinetic theory of gases. Müller (1987) and Ruggeri (1987) offer thirteen quasilinear equations of evolution type to determine the density, internal energy, velocity, heat flux, and stress fields, with a fourteenth equation showing that the stress is traceless. Five of the equations come from balance laws for mass, momentum, and energy; the other nine are called balance laws for fluxes. We could regard the other nine equations as constitutive equations of the rate type, in that the form of these nine rate equations is not known without making constitutive assumptions. The thirteen equations just mentioned can also be regarded as arising as moments of the Boltzmann equations, following Grad (1949). The number thirteen of moment equations is then the simplest possible truncation number, with the same number of equations and unknowns. As is usual in mathematical physics, the closure leaves some unknown terms, which can be determined by constitutive modeling, by some kind of guessing about how these terms should look, or else by higher-order moments, postponing the guessing to yet higher-order terms.

Since the thirteen equations are quasilinear, it is possible to consider the possibility of arranging the modeling to give rise to a strictly hyperbolic system, avoiding diffusion and infinite wave speeds. This procedure has been elevated to a principle in extended thermodynamics. Grad's method of dealing with Boltzmann's equation leads to strict hyperbolicity and finite wave speeds, but Enskog's procedure leads to Burnett's equations, which are diffusive. [Another example of this appears in the work of Carrassi (1978).] What you get depends on what you assume, with different physical problems requiring different assumptions.

A problem of extended thermodynamics is that each rate equation gives rise to only one time of relaxation [see Eq. (44)], though different times of relaxation may be needed to describe responses to different frequencies. We have discussed this problem in "Heat waves," Sec. VI.

1968, R. A. Piccirelli, Phys. Rev. **175**, 77.

Piccirelli uses methods of statistical mechanics (that is, an application of probability theory to mechanics) to derive expressions adding to the results of Richardson (1960). The two papers of Richardson and Piccirelli treat simple liquids and obtain expressions for the stress heat flux that are nonlocal in time and space. Piccirelli adds explicit molecular expressions to the general dynamical theory given by Richardson. Though these expressions are explicit, they are very idealized and depend on a number of unverifiable assumptions. Piccirelli himself remarks that his "... present results are not directly useful as they stand." The value of his results is to give an example of how a nonlocal theory might look. His results are perhaps also of interest in that his effort is to derive constitutive equations from dynamics, using statistical mechanics rather than, say, kinetic theory or molecular modeling.

Let

$$\mathbf{T}=\mathbf{P}_0+\boldsymbol{\tau} \tag{16}$$

be the stress tensor, $\mathbf{P}_0$ is the reversible part and τ is the irreversible part. Piccirelli finds that $\mathbf{P}_0$ is a functional determined by the present values of the temperature [rather, by the inverse temperature $\beta=(kT)^{-1}$] and the Helmholtz free energy f. Though $\mathbf{P}_0$ depends on present values and not on the history of β and f, it is not local in space; a distant point $\mathbf{x}'$ affects the value of $\mathbf{P}_0$ at the observation point $\mathbf{x}$. The tensor $\mathbf{P}_0$ reduces to the thermodynamic pressure times the unit tensor in the classical case. In Piccirelli's theory, $\mathbf{P}_0$ is not diagonal, but it is reversible in the sense that it does not appear in the equation governing the evolution of the entropy. (The reader may recall that the balance equation governing the evolution of the specific internal energy contains a dilatational work term, pressure times the divergence of the velocity, but no such term appears in the equation for the entropy.) The caloric equation is also generalized into a nonlocal (in space) law.

The heat-flux vector

$$\mathbf{q}=\mathbf{q}_0+\hat{\mathbf{q}} \tag{17}$$

is determined in a decomposed form in which $\mathbf{q}_0$, the reversible heat flux, does not appear in the evolution equation expressing the balance of entropy. There is no counterpart for $\mathbf{q}_0$ in classical theory; it reduces to zero in the classical limit. Like $\mathbf{P}_0$, $\mathbf{q}_0$ depends on the present values of β and f and, in addition, on $\mathbf{v}$, the velocity, but the dependence is nonlocal in space. Piccirelli's equation (57) for $\mathbf{q}_0$ depends explicitly on local and distant values of $\nabla\mathbf{v}$, and not on $\mathbf{v}$ itself.

The irreversible parts of the stress and heat flux are given by Piccirelli as

$$\tau(\mathbf{x},t)=-\int_0^t dt'\int_\Omega d\mathbf{x}'[\,\boldsymbol{\kappa}^{(4)}(\mathbf{x},t;\mathbf{x}',t'):\nabla\mathbf{v}(\mathbf{x}',t') +\boldsymbol{\kappa}^{(3)}(\mathbf{x},t;\mathbf{x}',t')\cdot\nabla\ln\beta(x',t')]\ , \tag{18}$$

$$\hat{\mathbf{q}}(\mathbf{x},t)=-\int_0^t dt'\int_\Omega d\mathbf{x}'[\,\boldsymbol{\kappa}^{(3)}(\mathbf{x},t;\mathbf{x}',t')\cdot\nabla\mathbf{v}(\mathbf{x}',t') +\boldsymbol{\kappa}^{(2)}(x,t;\mathbf{x}',t')\cdot\nabla\ln\beta(\mathbf{x}',t')]\ . \tag{19}$$

Here $\boldsymbol{\kappa}^{(4)}$, the *viscosity kernel,* is a fourth-order tensor, $\boldsymbol{\kappa}^{(2)}$, the *thermal conductivity kernel,* is a second-order tensor, and the *cross-effects* tensor $\boldsymbol{\kappa}^{(3)}$ is of third order and is not present in classical theory. These kernels are actually worse than they look; they are functionals of the spatially nonlocal history of β, f, and $\mathbf{v}$ in Ω and $[0,t]$. "Somewhat less sweeping generalizations have also been suggested in which the transport kernels ... depend only on the local values of β, f, and $\mathbf{v}$, and are functions only of space and time differences." The forms given in Eqs. (18) and (19) are actually special cases of the forms derived by Piccirelli, which have additional terms that depend on initial values. He notes that there are no indications that the initial-value terms relax faster than the kernels. To get rid of these terms it is necessary that one select initial values so that the extra terms vanish. The assumption necessary for this is called "constrained equilibrium," and Eqs. (18) and (19) are supposed to hold only for constrained equilibrium. Actually, it seems to us that initial values are a somewhat ambiguous concept for problems that depend on history. Surely the materials remember things that happen when $t<0$.

1969, T. André-Talamon, C. R. Acad. Sci. Paris **269B**, 101.

André-Talamon studied Cattaneo's equation in a solid when the thermal conductivity depends on the temperature. He also let the density and specific heat in the energy equation depend on the temperature. He found a general solution in three dimensions without taking special cases for the dependence of material parameters on the temperature. He noted that because of the possibly strong variation of the temperature-dependent coefficient at early times, linearization might not be valid. He treated only early times under the condition that the first derivative in the nonlinear telegraph equation arising from combining the heat law and entropy equation be much smaller than the second derivative. Under these conditions he was able to solve the equation generally with a functional equation of the D'Alembert type.

We turn next to engineering applications, thinking of ordinary materials at temperatures above super cool. For such materials heat waves could be important when the imposed change of temperature takes place in a time, the process time, not too much longer than the relaxation times for thermal waves. The relaxation times for these materials of engineering interest are much smaller than the process time. This is why heat waves are not important in most engineering applications. For engineering applications, Fourier's law and diffusion give an easier and better description. We have already argued in "Heat waves" that even in cases where the relaxation and process times were comparable it would be desirable to allow for both diffusion and relaxation by adopting constitutive models like Jeffreys', which have both a thermal conductivity and a relaxation time or relaxation spectra.

The engineering literature on heat waves suffers from a lack of observational data that could establish the applications in which they are important and the theoretical approximations appropriate to these applications. There are a few good discussions of areas of application in which heat waves may be important in the engineering literature, but the discussions are usually perfunctory and shallow, and the literature is more or less dedicated to comparing results from numerical calculations of traditional theories and those based on the telegraph equation. For applications to common materials it is necessary to do experiments with process times in the window $10^{-13}-10^{-8}$ sec, where hyperbolic phenomena and relaxation effects can be important. The recent literature on laser pulse experiments in metal, reviewed later, is of interest here.

The problem of sintering of catalysts is interesting because the process time has been estimated by Luss (1970) as 10^{-13} sec, a domain in which relaxation effects and heat waves ought to be important. The problem has been studied by Chan, Low, and Mueller (1971) and Ruckenstein and Petty (1972). Some numerical calculations for this problem when the thermal conductivity grows linearly have been performed by Glass, Özisik, and McRae (1986), who also mention possible applications to pulsed lasers, and by Glass, Özisik, and Vick (1987). Some numerical calculations that include the effects of surface radiation are given in the paper last mentioned and by the same authors in 1985. Frankel, Vick, and Özisik (1987) have analyzed the formulation of hyperbolic conduction for composite materials.

The engineering literature on "hyperbolic conduction" is collected each year in "Reviews of the Heat Transfer Literature" in the *International Journal of Heat and Mass Transfer.*

1971, S. H. Chan, M. J. Low, and W. K. Mueller, Am. Inst. Chem. Eng. J. **17**, 1499.

In exothermic reactions the maximum temperature may occur in times of the order 10^{-13} sec, and the hyperbolic transport of heat should be important. Chan *et al.* imagine periodic pulses of heat entering the sample from one face. If the waves travel at the speed of sound and the relaxation time is 10^{-14} sec, then the rise in temperature of the platinum sample is 1600 °C according to Fourier's law and 1800 °C according to Cattaneo's law. Experiments exhibit temperature rises between 2000 and 3000 °C. Chan *et al.* note that the higher temperatures would be generated from the Cattaneo law with lower wave speeds and the same time of relaxation.

1972, E. Ruckenstein and C. A. Petty, Chem. Eng. Sci. **27**, 937.

This paper contains a good physical description of the possible effects of finite propagation speeds on the aging of platinum (metal) catalysts supported on aluminica or silica. Sintering and agglomeration of crystallites is by hot spots generated by exothermic reactions on the catalyst. The magnitude of the heat rise depends on how fast the heat is carried to the support. The finite propagation speed, in addition to being responsible for high temperatures close to the surface of platinum clusters, also possibly conducts heat to the support. The generation (process) time is 10^{-13} sec and is smaller or of the same order as the relaxation time for the heat flux. The finite speed of propagation could be important. For example, an estimate of the time taken to cool a crystallite on a platinum slab 10 Å thick with a prescribed temperature at the support is less than the process time t_R for Fourier's law, but it will take $5t_R$ for heat to travel 10 Å with a speed $c=2$ Å$/t_R$. The conclusion is reached that the temperature achieved near the reaction surface is much higher than that resulting from Fourier's law and that the cooling of the hot spot after the completion of a reaction is so hindered that the high temperature lasts sufficiently long for detachments of clusters of atoms to take place.

We shall next consider a group of papers on the theory of constitutive equations for the heat flux. Some of these are reviewed below. It is generally thought that constitutive equations characterize materials, and the description of material response should be independent of the observer; two observers on different planets, or on different turntables on the same planet, should come up with, say, the same equation relating stress and deformation or the heat flux and temperature gradient, and their equation should not depend on the frame. There are two requirements stated here: the first is that constitutive equations be form invariant, and the second is that their form be independent of the frame. The first requirement means that different observers agree about the form of the governing equations. This need not imply that the equations are independent of the frame. In fact the equations of motion, which depend on the frame, are form invariant. Form invariance means that equations should transform like tensors under a change of frame. They are then said to be "indifferent" or "objective" tensors. Vector-valued equations should transform like vectors $\mathbf{a}^*=\mathbf{Q}\mathbf{a}$ under the change of frame $\mathbf{x}\rightarrow\mathbf{x}^*$,

$$\mathbf{x}^*=\mathbf{Q}(t)\mathbf{x}+\mathbf{b}(t) \ ,$$

where $\mathbf{Q}(t)$ is an arbitrary time-dependent orthogonal matrix $\mathbf{Q}\mathbf{Q}^T=\mathbf{1}$, and $\mathbf{b}(t)$ is a time-dependent spatially constant vector. Similarly second-order tensor-valued equations $\mathbf{A}=0$ transform like tensors,

$$\mathbf{A}^* = \mathbf{Q}\,\mathbf{A}\mathbf{Q}^T ,$$

under a change of frame. The velocity $\mathbf{u}-\mathring{\mathbf{b}}$ and velocity gradient $\mathbf{L}=\nabla\mathbf{u}=\partial\mathbf{u}/\partial\mathbf{x}$ are not indifferent,

$$\begin{aligned} \mathbf{u}^* - \mathring{\mathbf{b}} &= \mathbf{Q}(t)\mathbf{u}(\mathbf{x},t) + \mathring{\mathbf{Q}}(t)\mathbf{x} , \\ \partial\mathbf{u}^*/\partial\mathbf{x}^* &= \mathbf{L}^*(\mathbf{x}^*,t) = \mathbf{Q}(t)\mathbf{L}(\mathbf{x},t)\mathbf{Q}^T + \mathring{\mathbf{Q}}\mathbf{Q}^T . \end{aligned} \tag{20}$$

The second requirement for constitutive equations is that form-invariant expressions describing material response depend on the material and not on the frame in which the material is observed. This is obvious on the one hand and deeply mysterious on the other. There is of course no more mystery in the "principle" of material frame indifferences than in the idea of an inertial frame, which seems to work well. Certainly the requirement that constitutive equations not depend on the frame does not follow from first principles, and frame-dependent expressions often arise for the stress tensor and heat-flux vector when they are derived from statistical mechanics, as in the work of Richardson (1960) and Piccirelli (1968), from studies in the kinetic theory of gases, which were analyzed in the papers of I. Müller (1972) and Edelen and McLennan (1973), or from molecular dynamic simulations, as in the work of Hoover, Moran, More, and Ladd (1981).

A different interpretation of the second requirement of invariance has been presented by Murdoch (1983), who would let constitutive equations depend on the frame, but only through the intrinsic spin, an indifferent tensor expressing the spin of the body relative to an inertial frame. When interpreted this way, the constitutive equations coming from the kinetic theory also satisfy the revised second requirement of invariance. There are two separate questions answered in the two requirements of invariance. The first is whether a material knows if the observer is rotating. The answer is obviously no. The second is whether a material knows about its own rotation, and the answer may depend on the material. It seems to us that the exact circumstances under which dynamics gives rise to constitutive equations that are independent of frame is largely an unexplored topic at the foundation of continuum mechanics.

1972, I. Müller, Arch. Ration. Mech. Anal. **45**, 241.

From the author's summary, ". . . However, a careful study of the kinetic theory shows that the constitutive equations for stress and heat flux should be dependent on the frame of the observer, although such a dependence is normally excluded in thermodynamics. The purpose of this paper is to substantiate the remark above and to illustrate it. The results imply that the field equation for the temperature in a gas at rest in the observer frame depends on that frame and, in particular, on whether or not the frame is an inertial one." In the paper, Müller considers the Boltzmann equation for Maxwellian molecules using expressions for the second, third, and fourth moments derived by Ikenberry and Truesdell (1956). Truesdell has influenced people to believe that constitutive equations ought to be independent of the frame, and at the time of this article Müller worked as an assistant professor in a department and milieu strongly controlled by Truesdell. Müller derives expressions for the stress deviator and the heat flux from these moment equations whose right-hand sides contain terms, some of which depend on the frame, that are separately not objective, but when these terms are added, the added expression is objective and form invariant, but still depends on the frame. There is a second paper by Müller (1987), in which this problem is treated. There he cites an equation of Grad (1949) for the heat flux $\mathbf{q}$,

$$q_i + \frac{\kappa_2}{\kappa_1}\left[\frac{dq_i}{dt} + \frac{\partial v_i}{\partial x_j}q_j - 2W_{ij}q_j\right] = \kappa_1\frac{\partial T}{\partial xi} \quad \cdots , \tag{21}$$

in which he notes that the bracketed term depends on the frame through the angular velocity tensor W_{ij} of the frame, but is objective; nonobjective contributions of the separate terms sum to zero. Müller shows that the same feature, a frame-dependent objective sum of nonobjective terms, arises in Burnett's (1935) equation for the heat flux and arises also in the equations for the stress derived by Burnett and Grad.

To illustrate Müller's point and to make one of our own, recall that invariant rates were discussed in our summary of the paper by Fox (1969a) in "Heat waves," where we showed that the derivative s,

$$\overset{\nabla}{\mathbf{q}} = \mathring{\mathbf{q}} - \mathbf{L}\mathbf{q}, \quad \mathbf{L}=\nabla\mathbf{u}, \quad \mathring{\mathbf{q}} = d\mathbf{q}/dt \tag{22}$$

and

$$\overset{\Delta}{\mathbf{q}} = \mathring{\mathbf{q}} + \mathbf{L}^T\mathbf{q} , \tag{23}$$

are objective. Linear combinations of these are also objective, and any one of these combinations may be used to form nonlinear equations of the Cattaneo type, which do not depend on the frame.

Müller showed that $\mathring{\mathbf{q}}+\mathbf{L}\mathbf{q}$ is not objective because $\mathring{\mathbf{q}}^* = \mathring{\overline{\mathbf{Q}\mathbf{q}}} = \mathring{\mathbf{Q}}\mathbf{q} + \mathbf{Q}\mathring{\mathbf{q}}$ and

$$\mathbf{L}^*\mathbf{q}^* = (\mathbf{Q}\mathbf{L}\mathbf{Q}^T + \mathring{\mathbf{Q}}\mathbf{Q}^T)(\mathbf{Q}\mathbf{q}) = \mathbf{Q}\mathbf{L}\mathbf{q} + \mathring{\mathbf{Q}}\mathbf{q}$$

do not transform as tensors. He also observed that

$$\mathring{\mathbf{q}} + \mathbf{L}\mathbf{q} - 2\mathbf{W}\mathbf{q} \tag{24}$$

is objective. Here

$$W_{ik} = -\varepsilon_{ijk}\omega_j \tag{25}$$

is the angular velocity tensor in $\mathbf{x}$ corresponding to the angular velocity vector $\boldsymbol{\omega}$, relative to an inertial frame with position vector $\mathbf{x}^I$, so that $\mathbf{W}=\mathring{\mathbf{P}}\mathbf{P}^T$ where $\mathbf{x}=\mathbf{P}\mathbf{x}^I+\mathbf{b}$, $\mathbf{x}^*=\mathbf{P}^*\mathbf{x}^I+\mathbf{b}^*$ relate $\mathbf{x}$, $\mathbf{x}^*$ to $\mathbf{x}^I$ in the inertial frame and

$$\mathbf{W}^* = \mathbf{Q}\mathbf{W}\mathbf{Q}^T + \mathring{\mathbf{Q}}\mathbf{Q}^T . \tag{26}$$

The orthogonal matrices are related to $\mathbf{Q}=\mathbf{P}^*\mathbf{P}^T$. All the linear algebra is nicely set out in the beginning of Müller's paper. Now we compute

$$\frac{d^*\mathbf{q}^*}{dt^*}=\left[\frac{\partial}{\partial t}+\mathbf{u}^*\frac{\partial}{\partial \mathbf{x}^*}\right]\mathbf{Q}\mathbf{q}$$

$$=\left[\frac{\partial}{\partial t}+\mathbf{u}\frac{\partial}{\partial \mathbf{x}}\right]\mathbf{Q}\mathbf{q}=\mathbf{Q}\frac{d\mathbf{q}}{dt}+\mathring{\mathbf{Q}}\mathbf{q}\ . \tag{27}$$

This, together with the transformation formulas for $\mathbf{L}^*\mathbf{q}^*$ and $\mathbf{W}^*$, gives

$$\mathring{\mathbf{q}}^*+\mathbf{L}^*\mathbf{q}^*-\mathbf{W}^*\mathbf{q}^*=\mathbf{Q}(\mathring{\mathbf{q}}+\mathbf{L}\mathbf{q}-2\mathbf{W}\mathbf{q})\ , \tag{28}$$

proving the objectivity of this frame-dependent quantity.

It follows now that Eqs. (22) and (23) are independent, objective, frame-independent rates and that Eq. (24) is another objective, but frame-dependent rate. Any linear combination of these three is again objective.

Müller reports a calculation in his paper that is very important, though Müller and subsequent authors make no reference to it. He notes (p. 242) that ". . . By a long but straightforward calculation it can be proved . . . that

$$\mathring{v}_i-\mathring{\mathring{b}}_i-2W_{ik}(v_k-\dot{b}_k)+W_{ik}^2(x_k-b_k)-\mathring{W}_{ik}(x_k-b_k) \qquad [(29)]$$

is an objective tensor; the dot derivative of a function (of $\mathbf{x}$) denotes the material time derivative . . ." Müller's expression (29) is the acceleration relative to an inertial frame seen by an observer in $\mathbf{x}$, and there is the same expression with $*$ seen in $\mathbf{x}^*$. Together with the usual assumptions about body forces and the stress tensors, Müller's equation (29) shows that the equations of motion are objective, though of course they are frame dependent. People working in continuum mechanics frequently note that ". . . the laws of motion themselves do not enjoy invariance with respect to the observer" (Truesdell and Toupin, 1960), proving that $\mathring{\mathbf{v}}$ does not transform like a tensor, taking no notice of the invariance of the acceleration relative to an inertial frame embodied in Eq. 29.

1973, J. Lambermont and G. Lebon, Phys. Lett. **42A**, 499.

These authors derive a generalized Fourier law

$$\mathbf{q}+\tau\dot{\mathbf{q}}=L\nabla T^{-1},\quad L>0 \tag{30}$$

by extending the local equilibrium hypothesis for isotropic solids. Their result is a special case of the theory of Müller (1967a) if the choice $L=\lambda T^2$, corresponding to Cattaneo's law, is made. A further generalization of these ideas for elastic bodies is given by Lebon and Lambermont (1976).

1973, D. G. B. Edelen and J. A. McLennan, Int. J. Eng. Sci. **11**, 813.

This apparently independent work carries the same message as Müller (1972) (the submission dates are January 1972 for Müller and October 1972 for Edelen and McLennan), but the conclusion is expressed more forcefully. "If there is one instance above all others in which extreme care has to be exercised it is in the elevation of a known convenience to the peerage of a Fundamental Principle. A case in point is the principle of material frame indifference . . ." From the authors' summary, "Constitutive relations for stress and energy flux, derived from the Boltzmann equation by the Chapman-Enskog procedure, are shown to violate the principle of material indifference while exhibiting invariance under Galilei transformations."

Other references on frame indifference are by Wang (1975) and Truesdell (1976), who argue for frame indifference, and Söderholm (1976, 1981), Hoover, Moran, More, and Ladd (1981), and Ryskin (1985), who argue against it. Hoover *et al.* did a molecular dynamics simulation for a fluid in two-dimensional rotating disks and found an azimuthal component of the heat flux, violating frame indifference.

Some recent points of view on whether or not the heat flux and stress tensor should satisfy objective constitutive equations that are frame indifferent develop on an idea of Bressan (1982), who notes that in the various extensions of thermodynamics beyond local equilibrium, rate equations are introduced for the heat flux and the other system variables. He then suggests that these rate equations ought to be regarded as balance laws, on the same footing as the balance of mass, momentum, and energy. The inertial part of these balance laws then need not be independent of frame, any more than the inertial terms in the momentum balance. In this case the angular velocity matrix W_{ij} of the frame that appears in Eq. (29) is in the inertial term, and the remaining relations that need constitutive modeling can be made frame different. The problem is resolved by declaring that it is not a problem. This is the point of view presently advocated by Müller (1987) and Ruggeri (1987), and it seems closely related to the extended notion of frame independence advanced by Murdoch (1983).

1974, P. H. Roberts and R. J. Donnelly, Ann. Rev. Fluid Mech. **6**, 179.

In this review of superfluid mechanics many topics are discussed. Of interest for discussions of invariance of constitutive equations is a discussion in Sec. 3 of a phenomenological theory of rapidly rotating helium II, where it is shown that the force terms in the superfluid, which depend on the superfluid vorticity (the body spin), are not indifferent. Invariance questions for superfluids are considered in greater detail by Hills and Roberts (1977).

1975, H. E. Wilhelm and S. H. Choi, J. Chem. Phys. **63**(5), 2119.

Wilhelm and Choi develop a quasilinear hyperbolic theory of heat transmission in metals using a generalization of Cattaneo's law,

$$\mathbf{q}_t = -\frac{1}{\tau}\mathbf{q} - \frac{\mathbf{k}}{\tau}\nabla T , \tag{31}$$

with a temperature-dependent conductivity $k(T)$ proportional to T^n and relaxation time $\tau(T)$ proportional to T^m. They justify using this law with the relaxation results for metals based on Boltzmann's equation that are given by Jones (1956). Values for m and n for different ranges of temperature given by Jones are used in this paper. Wilhelm and Choi give an explicit similarity solution for cylindrical thermal waves in metals, showing that the heat released from a line source propagates a discontinuous wave front radially outward with a finite, time-dependent wave speed determined by m and n. For constant k, $n=0$, and $m=-1$, they get

$$\frac{dR(t)}{dt} = \sqrt{2}\left[\frac{k_0}{\rho c}\right]^{1/2} t^{-1/2} , \tag{32}$$

the speed of the radially spreading wave decreasing with time. Unique nonlinear hyperbolic thermal wave solutions exist up to a critical amount of driving energy. For larger energy releases, the flow becomes multivalued, indicating the development of shock waves.

Wilhelm and Choi also calculate and compare the parabolic theory to their hyperbolic theory. They say that "... the parabolic thermal wave theory gives in general a misleading picture of the profile and propagation of thermal waves, and leads to physical (infinite speed of heat propagation) and mathematical (divergent energy integrals) difficulties. Attention is drawn to the importance of temporal heat-flux relaxation for the physical understanding of fast, transient processes, such as thermal waves, and more general explosions and implosions."

This paper of Wilhelm and Choi is very interesting because it generalizes nonlinear heat conduction to the hyperbolic case in such a way that similarity solutions may be used in both cases. There are many interesting questions left open; for example, we expect that when the relaxation times of the hyperbolic theory are much shorter than any characteristic time for the parabolic theory, then the parabolic theory will dominate at later times, with the already relaxed hyperbolic modes perturbing the conductivity (see Sec. VI of "Heat waves").

1975, C. C. Wang, Arch. Ration. Mech. Anal. **58**, 381.

Wang seems to have been encouraged by Truesdell to have a critical look at the papers of Müller (1972) and Edelen and McLennan (1973), which raise doubts about the principle of frame indifference. He is only slightly critical, remarking that "... it seems to me that there is no rigorous proof to substantiate the claims of ... I believe that there are four major gaps in their arguments:

(a) There is no proof that the formal expansions of the iterative procedures are convergent so as to justify the leading terms as approximations of the limits.

(b) There is no proof that the limits of the expansions share the same properties as the leading terms, especially with regard to frame indifference.

(c) There is no proof that the approximate constitutive relations given by the leading terms of the expansions can be applied to macroscopic processes which do not satisfy the [macroscopic energy balance].

(d) There is no proof that the iterative procedures are valid for any 'real materials.' "

1976, G. Lebon and J. Casas-Vázquez, Phys. Lett. A **55**, 393.

Lebon and Casas-Vázquez extend an earlier analysis of Glansdorff and Prigogine (1971, Chap. VII) for Fourier's law to the generalized Cattaneo law. They study the stability of heat conduction with prescribed temperatures of heat flux in rigid bodies in the context of linearized theory, using Liapunov's theory, and find that "... contrary to what happens in the classical situation investigated by Glansdorff and Prigogine, it cannot be concluded that heat conduction is always stable."

1976, C. Truesdell, Meccanica **11**, 196.

Truesdell states strongly that the criticism of material frame indifference coming from the kinetic theory is wrong.

> SUMMARY: Certain results of formal processes of "approximation" in the kinetic theory are similar in form to constitutive relations of continuum mechanics. It is wrong to regard them as such. Continuum mechanics takes the variables entering constitutive functions as being independent. Thus it is possible to ask whether or not those functions be frame indifferent. In the kinetic theory, on the contrary, all solutions automatically satisfy the principle of linear momentum. In order even to ask whether gross relations satisfied by solutions be frame indifferent, it would be necessary to show first that those relations pertain to a class of solutions that correspond to velocity fields which differ from one another by arbitrary time-dependent orthogonal transformations of the motion. It is not presently known whether any such classes of solutions exist in the kinetic theory. Indeed, as the constraint imposed by the principle of linear momentum is frame dependent, the existence of any such class is implausible. Be that as it may, to claim that the kinetic theory can bear in any way whatever upon the principle of material frame indifference is presently ridiculous.

One can assume that materials satisfy constitutive equations as is done in continuum mechanics, but it is also valid to enquire if constitutive equations can be derived from the laws of dynamics at a microscopic level. The second line of inquiry should not be suppressed. Actually it is not hard to enter into a frame of mind in which it is the concept of a constitutive equation that appears ridiculous. For example, the idea that a certain material must satisfy Fourier's law under all conditions is not just astonishing, it is also incorrect. The best that can be expected is that a constitutive equation is some form of "approximation" in a restricted class of conditions, and the determination of the conditions is the main point at issue.

1976, Lars H. Söderholm, Int. J. Eng. Sci. **14**, 523.

From the author's summary, "It is shown from simple physical arguments that the material equations of a gas should have frame-dependent terms of the kind appearing in the Burnett equations. This indicates severe limitations of the range of validity of the Principle of Material Frame Indifference."

1976, S. H. Choi and H. E. Wilhelm, Phys. Rev. A **14**, 1825.

This paper is about explosions in a fully ionized electron-ion plasma governed by a generalization of Cattaneo's law based on the application of the moment method to Boltzmann's equation. Let $\mathbf{q}$, $\mathbf{v}$, m, p, T, and τ be the heat flux, the mass-averaged velocity, the mass, partial pressure, temperature, and relaxation time. Then the heat equation reduces to

$$\dot{\mathbf{q}}+(\mathbf{q}\cdot\nabla)\mathbf{v}+\mathbf{q}\,\mathrm{div}\mathbf{v}+\tfrac{2}{5}[(\mathbf{q}\cdot\nabla)\mathbf{v}+\mathbf{q}\,\mathrm{div}\mathbf{v}+(\nabla\mathbf{v})\cdot\mathbf{q}] +\frac{5}{2}\frac{k}{m}p\nabla T=-\mathbf{q}/\tau\ , \quad (33)$$

when inhomogeneous terms of the third order in the Boltzmann equation are neglected. One and the same equation applies to the electrons and the ions; m_e, p_e, τ_e, etc. are for electrons, m_i, p_i, etc. for ions. Equation (33) reduces to Cattaneo's law under linearization. Equation (33) may be written as

$$\dot{\mathbf{q}}+\mathbf{L}\mathbf{q}+\mathbf{q}\,\mathrm{tr}\mathbf{L}+\tfrac{2}{5}(\mathbf{L}\mathbf{q}+\mathbf{q}\,\mathrm{tr}\mathbf{L}+\mathbf{L}^T\mathbf{q})+\frac{5}{2}\frac{k}{m}p\nabla T=\frac{-\mathbf{q}}{\tau}\ , \quad (34)$$

where $\mathbf{L}=\nabla\mathbf{v}$. Assuming now that the velocity and mass-averaged velocity have the same form under a change of frame, we may use Eq. (20) to show that Eq. (34) is not objective.

From the authors' summary,

> The nonlinear partial differential equations describing plane, cylindrical, and spherical explosions in a fully ionized electron-ion plasma with heat-flux relaxation and thermal relaxation are reduced to ordinary differential equations by means of novel similarity transformations. The resulting ordinary boundary-value problem for the plasma explosion, with the strong shock conditions as boundary values at the moving shock front, is formulated mathematically. The scaling laws for the plasma fields are presented, which show how the plasma properties change with time during the course of the explosion. The importance of electron and ion heat-flux relaxation, which enhances the concentration of thermal energy behind the shock front, is stressed for the understanding of the shock-heating mechanism in fast processes. It is concluded that heat-flux relaxation is an important process for short-time plasma explosions, which determines the discontinuity of the electron and ion temperature fields at the shock front.

1977, S. Sienuitycz, Int. J. Heat Mass Transfer **20**, 1221.

Sienuitycz derives a functional with a stationary point corresponding to a hyperbolic equation for heat transport. There is no claim made that the stationary point is extremalizing, so that the variational results given in the paper may not be very useful.

1977, L. Gyarmati, J. Non-Equil. Thermodyn. **2**, 233.

When the imposed changes in state variables are sufficiently rapid, the kinetic energy of the currents contributes to the entropy. The entropy is decomposed into an equilibrium and a kinetic part $S=S_{\mathrm{eq}}+S_{\mathrm{kin}}$, where

$$S_{\mathrm{eq}}=\sum_{i=1}^{n}a_i\Gamma_i\ , \quad (35)$$

a_i are generalized coordinates, Γ_i are generalized conjugated thermostatic forces,

$$S_{\mathrm{kin}}=\tfrac{1}{2}\sum_{i,k=1}^{n}m_{ik}\mathbf{J}_i\mathbf{J}_k\ , \quad (36)$$

J_k are fluxes, and m_{ik} is a positive-definite matrix of inductivities. The generalized Gibbs equation for solids is

$$\frac{\partial S}{\partial t}+\sum_{i=1}^{n}\mathrm{div}(\Gamma_i\mathbf{J}_i)=\sum_{k=1}^{n}\mathbf{J}_1\cdot\left[\nabla\Gamma_i+\sum m_{ik}\frac{\partial\mathbf{J}_k}{\partial t}\right] =\sum^{n}\mathbf{J}_i\cdot\mathbf{E}_i=\sigma\geq 0\ . \quad (37)$$

Here $\mathbf{E}_i=\nabla\Gamma_i+\sum m_{ik}\partial\mathbf{J}_k/\partial t$ is the new thermodynamic force incorporating both dissipative and inertial effects. If a linear relation between $\mathbf{E}_i$ and $\mathbf{J}_i$ is valid, then

$$\mathbf{J}_i=\sum_{k=1}^{n}L_{ik}\mathbf{E}_k\ ,\qquad \mathbf{J}_i=\sum_{k=1}^{n}L_{ik}\nabla\Gamma_k-\sum_{k=1}^{n}\tau_{ik}\frac{\partial\mathbf{J}_k}{\partial t}\ , \quad (38)$$

where

$$[\tau_{ik}]=-\sum_{\ell=1}^{n}L_{i\ell}m_{\ell k}$$

is a matrix of relaxation times from nonlocal to local equilibrium. Equation (38) generalizes Cattaneo's equations, and it leads to hyperbolic transfer equations $(j=1,2,\ldots,n)$,

$$\sum_{\ell=1}^{n}\left[\mathring{\tau}_{j\ell}\frac{\partial^2\Gamma_\ell}{\partial t^2}+\delta_{j\ell}\frac{\partial\Gamma_\ell}{\partial t}-\mathring{k}_{j\ell}\nabla^2\Gamma_\ell\right]=0\ .$$

With appropriate choices of Γ_ℓ, this equation can account for thermal waves in solids, waves in thermodiffusion systems.

1978, M. Carrassi, Nuovo Cimento **46**, 363.

This paper shows that the kind of heat propagation you get from the kinetic theory of gases depends strongly on the approximation scheme used to derive the equation. Probably the different types of approximation correspond to physical processes arising in different situations.

SUMMARY: Various forms of the linear heat equation which can be deduced from the kinetic theory of gases are analyzed. It is shown that, if one uses a perturbative procedure based on a power-series expansion in the viscosity coefficient μ (or in the mean free path λ), the resulting equations are of the "parabolic" type, which means that the propagation velocity of the thermal disturbance is always infinite. Conversely, both the equations derived by using the Cattaneo procedure and those which are directly derived from the thirteen-moment approximation introduced by Grad to solve the Boltzmann equation are all of the "hyperbolic" type with well-defined propagation velocity. The theoretical interest of the direct measurement of the propagation velocity of a thermal disturbance is also pointed out.

1981, W. G. Hoover, B. Moran, R. M. More, and A. J. C. Ladd, Phys. Rev. A **24**, 2109.

Hoover *et al.* present a molecular dynamics simulation of the problem of heat conduction in a two-dimensional rotating disk of dense fluid. The calculation addresses the issue of whether or not the heat flux should be frame indifferent with a purely radial component of flux, corresponding to an axially symmetric prescription of the prescribed temperature difference. In molecular dynamic simulations the equations of motion of N particles with a given interaction potential are solved numerically. The calculation is of interest because it is an independent method for seeing if the flux remains radial in a rotating system, as is required by frame indifference. They find an angular part of the heat flux that contains nearly equal potential and kinetic parts. It fluctuates wildly with time and is considerably smaller than the radial flux. According to an approximate theory using Boltzmann's equation, worked in the paper, the angular flux equals $-2q_r\omega\tau$, where q_r is the radial flux, ω the angular frequency, and τ the relaxation time. The molecular dynamic simulation confirms this order of magnitude estimate.

"We conclude that the approximate kinetic theory and Enskog's dense-fluid modification of Boltzmann's equation correctly predicts a violation of Fourier's law. In dense media a radial temperature gradient induces an angular heat flux in a comoving frame."

1981, S. Sienuitycz, J. Non-Equil. Thermodyn. **6**, 79.

Sienuitycz generalizes the analysis of Lebon and Casas-Vázquez (1976) using another approach. "... The unsteady-state coupled heat and mass transfer, occurring in an isobaric unreacting fluid, is considered. Using the second (direct) method of Liapunov the stability of the stationary state, approached by the wave solution, is proven, providing that the well-known thermostatic matrix c, characterizing the stable equilibrium of every macroscopic system is negative."

1983, A. I. Murdoch, Arch. Ration. Mech. Anal. **83**, 186.

Murdoch enunciates a different principle of frame indifference under which Müller's (1972) relations are frame indifferent. He notes also that there are two kinds of invariance. The first is that physical quantities that characterize the behavior of a given material are intrinsic. He defines this to mean that the constitutive equations for the heat flux and stress tensor should be indifferent. The second assumption is that all observers should agree upon the nature of any given material.

Various interpretations of the second assumption are possible. The usual interpretation is that the constitutive equation should be independent of frame. Murdoch suggests a new interpretation of the second assumption; constitutive equations may depend on the frame, but only through an indifferent tensor called the intrinsic spin and defined as $\mathbf{\Omega}-\mathbf{W}$, where $\mathbf{\Omega}$ is the skew-symmetric part of the velocity gradient, the spin of the body, and $\mathbf{W}=\mathring{\mathbf{P}}\mathbf{P}^T$ [defined under Eq. (25)] is the spin of the frame of the observer relative to an inertial frame (Murdoch's intrinsic spin is $\mathbf{W}+\mathbf{S}$, where his $\mathbf{W}$ is our $\mathbf{\Omega}$, and his $\mathbf{S}$ is our $-\mathbf{W}$). The spin of the body relative to an inertial frame is the intrinsic spin. Murdoch shows that the intrinsic spin is indifferent and that it is just this spin which exhibits the dependence of frame found in the various works of Müller (1972), Edelen and McLennan (1973), Roberts and Donnelly (1974) and Söderholm (1976).

The intrinsic spin enters into the formula for the acceleration in a frame rotating relative to an inertial frame,

$$\mathbf{\Omega}_{ij}-W_{ij}=\varepsilon_{jil}(\tfrac{1}{2}\zeta_l-\omega_l)\ ,$$

where ω is the angular velocity of the frame relative to an inertial frame and ζ is the vorticity of a material element. Since this acceleration is indifferent, it splits into two indifferent parts.

We already remarked in "Heat waves" (p. 67) that molecular dynamic simulations of heat propagation suggest a kind of time-temperature equivalence in which slowly propagating pulses at ultralow temperatures are in some sense equivalent to fast pulses at high temperatures. The advent of high-intensity fentosecond (10^{-15} sec) laser pulsing and high-resolution detection methods have made it possible to probe thermal response in metals at high temperatures. One of the main goals in this effort has been to detect nonequilibrium electron and lattice temperatures suggested by the physics of rapid pulsed heating and by the two-temperature diffusive theory of heat transport [see Eq. (39) below] of Anisimov, Kapeliovich, and Perel'man (1974). There has been some success in this effort. At the same time, it might be argued that no diffusive theory could be correct in the femtosecond range where waves following hyperbolic models rather than diffusion should dominate. In fact, the experiments of Brorson, Fujimoto, and Ippen (1987) do appear to give rise to a heat wave with a speed $\approx 10^8$ cm/sec together with pulse spreading of a type seen in the literature on second sound in cold dielectric crystals.

1984, J. G. Fujimoto, J. M. Liu, E. P. Ippen, and N. Bloembergen, Phys. Rev. Lett. **53**, 1837.

This paper is the first to probe nonequilibrium between electrons and phonons at time scales shorter than or comparable to, the relaxation time of electron to phonon temperatures. From the authors' summary,

> High-intensity, 75-fs optical pulses have been applied to observe multiphoton and thermally enhanced photoemission from a tungsten metal surface. Experimental results suggest the presence of anomalous heating, a transient nonequilibrium temperature difference between the electrons and lattice. Pump-probe measurements indicate an electron-phonon energy relaxation time of several hundred femtoseconds.

The application of intense optical pulses of short duration may heat electrons more than phonons because of the smaller heat capacity of the electron gas. The energy of a short pulse is first absorbed by the electrons, which thermalize rapidly through electron-electron scattering. The electrons then transfer energy to the crystal lattice through electron-phonon coupling. If the laser pulse duration is comparable to, or shorter than, the electron-phonon energy-transfer time, then the electrons and lattice temperatures T_e and T_i are universally assumed to satisfy the two-temperature diffusive model of Anisimov *et al.* (1974):

$$\begin{aligned} C_e(T_e)\frac{\partial T_e}{\partial t} &= k\nabla^2 T_e - g(T_e - T_i) + A(r,t) , \\ C_p\frac{\partial T_i}{\partial t} &= g(T_e - T_i) , \end{aligned} \tag{39}$$

where $A(r,t)$ represents internal heating due to the laser pulse and g is a coupling constant whose values could be determined from pulse experiments. In fact, the experimental determination of g seems still to be controversial (see Corkum *et al.*, 1988). The two-temperature theory itself may be flawed. The physical phenomena involved depend essentially at least on the time of relaxation of nonequilibrium temperatures, but the existence and relaxation of thermal inertia is not acknowledged in the theory; all the relaxation effects are subsumed in the coupling constant g. Moreover, thermal relaxation can be expected to give rise to wave propagation rather than diffusion at the time scale of hundreds of femtoseconds reported in this paper or the 2–3 picoseconds (10^{-12} sec) reported by Schoenlein *et al.* (1987).

In general, diffusion theories will generate smaller rises of temperature than hyperbolic theories for which the wave speed is finite. Some possibly relevant comparisons have been calculated by Vick and Özisik (1983; see "Heat waves") and by Glass, Özisik, and Vick (1987).

1985, G. Ryskin, Phys. Rev. A **32**, 1239.

Ryskin's short essay gives some criticisms of the principle of material frame indifference. He adopts a point of view close to that expressed in this review concerning two different kinds of invariance under a change of frame (see discussion under Ruckenstein and Petty, 1972):

> The confusion over the nature of the useful restriction on the allowable forms of constitutive relations ("material frame indifference," or "objectivity") is due to the vague language of its formulation. In the final analysis, the confusion arises because the concept of general covariance of physical laws is applied in the inappropriate setting of the three-dimensional space instead of the four-dimensional space-time.

He notes further that the only ways to check material frame indifference (MFI) are ". . . by experiments or derivation of a constitutive equation from macroscopic physics. The latter approach shows that the MFI cannot be exactly true (because the microscopic physics obeys Newton's laws . . .), but is a very good approximation for ordinary materials and circumstances (because the absolute acceleration due to the rigid body motion are usually much smaller than the accelerations at the molecular scale)."

Truesdell and Muncaster (1980) and Spezialle (1987) have argued that constitutive equations can represent only special solutions of the microscopic dynamics and, as such, can have a larger invariance group than the Galilean group. This possibility seems not to be realized in the special cases so far considered, e.g., Piccirelli (1968), Hoover *et al.* (1981), and other references mentioned in Ryskin's paper.

1987, S. D. Brorson, J. G. Fujimoto, and E. P. Ippen, Phys. Rev. Lett. **59**, 1962.

This paper reports an experiment that lends itself to interpretation in terms of wave propagation, though the authors do not so interpret their results. From the authors' summary,

> We have observed ultrafast heat transport in thin gold films under fentosecond laser irradiation. Time-of-flight (front-pump back-probe) measurements indicate that the heat transit time scales linearly with the sample thickness, and that heat transport is very rapid, occurring at a velocity close to the Fermi velocity of electrons in Au.

Their Fig. 3 shows that there is a linear relation between the transit time and the distance traveled by a heat pulse. This is characteristic of wave propagation and not of diffusion. Brorson *et al.* note that ". . . the measured delays are much shorter than would be expected if the heat were carried by the diffusion of electrons in equilibrium with the lattice (tens of picoseconds). This suggests that heat is transported via the electron gas alone, and that electrons are out of equilibrium with the lattice on this time scale. Second, since the delay increases approximately linearly with sample thickness (see Fig. 3), we may extract a heat-transport velocity $\approx 10^8$ cm/s."

They note further that "the rise time of the signal increases slightly with increasing thickness. This indicates spreading in the front edge of the electron-velocity distribution, which propagates through the sample. At present, the origin of this phenomenon is unknown, although it may be related to small-angle scattering." The hyperbolic spreading could be due to dispersion, say, the first derivative term in a telegrapher's equation. This is the type of spreading induced by umklapp processes in cold dielectric crystals (also due in part to scattering). The broadening of pulses could also occur as a diffusive effect associated with an effective thermal conductivity arising from the relaxation of the electronic mode of heat transport. This is an effect of the third derivative of the diffusion equation [Eq. (4.3) in "Heat waves"] of the Jeffreys type. This type of pulse broadening is due to the viscosity of the phonon gas in dielectric crystals, associated with normal processes.

1987, D. E. Glass, M. N. Özisik, and B. Vick, Int. J. Heat Mass Transfer **30**, 1623.

From the authors' summary,

> The transient temperatures resulting from a periodic on-off heat flux boundary condition have many applications, including, among others, the sintering of catalysts frequently found during coke burn-off and the use of laser pulses for annealing of semiconductors. In such situations, the duration of the pulses is so small (i.e., picosecond–nanosecond) that the classical heat diffusion phenomenon breaks down and the wave nature of energy propagation characterized by the hyperbolic heat conduction equation governs the temperature distribution in the medium. In this work, an explicit analytic solution is presented for a linear transient heat conduction problem in a semi-infinite medium subjected to a periodic on-off type heat flux at the boundary $x=0$ by solving the hyperbolic heat conduction equation. The nonlinear case allowing for the added effect of surface radiation into an external ambient is studied numerically.

1988, D. K. Bhattacharya, Acta Mechanica **47**, 87.

Bhattacharya studies the stability of stationary states in the context of the hyperbolic transfer equations proposed by Gyarmati (1977). He finds that a monotonic transition from nonequilibrium states to stationary states is insured only when dissipative processes are dominant over relaxation phenomena. The possibility of oscillating transitions to stationary states is left open. These results differ from those of Sienuitycz, who shows that in the linear case the generalized excess entropy source would decrease along trajectories of the governing generalized telegraph equation. Some conjectures about the reasons for the discrepancy are given in Bhattacharya's paper.

1988, A. Morro and T. Ruggeri, J. Phys. C: Solid State Phys. **21**, 1743

Morro and Ruggeri have proposed a general nonlinear model for heat conduction in solids which they believe corrects certain defects in the model based on a generalization of Cattaneo's law by Coleman, Fabrizio, and Owen (1982). They note that in the theory of Coleman *et al.* the internal energy is given by $e=e_\theta(\theta)+a(\theta)q^2$, where θ is the temperature and q is the heat flux. Comparison of this theory with second-sound propagation in dielectric crystals shows that $a'<0$, and this implies that the specific heat will go negative when $q^2>c/|a'|$; moreover, the entropy is a minimum instead of a maximum at equilibrium. Presumably the Cattaneo-based theory either breaks down for large q or is not a valid theory. Adopting this second view, Morro and Ruggeri propose to replace the Cattaneo law with

$$(\dot{\alpha\mathbf{q}})+\nabla\cdot(\gamma\mathbf{1}+\beta\mathbf{q}\otimes\mathbf{q})=-\nu\mathbf{q}\ ,$$

where α, γ, β, and ν are scalars and $\otimes$ is a dyadic product. This gives back the Cattaneo law when $\beta=0$, $\alpha=$const, and γ and ν are functions of θ. In their theory they assume that the internal energy e, entropy α, γ, β, and ν depend on θ and q; finally they put $\beta=0$. They make their theory consistent with thermodynamics using an entropy inequality and derive the governing equations

$$\begin{aligned}&e_\theta\mathring{\theta}+e_w\mathbf{q}\cdot\mathring{\mathbf{q}}+\nabla\cdot\mathbf{q}=0\ ,\\&\alpha_0'\mathbf{q}\mathring{\theta}+\alpha_0\mathring{\mathbf{q}}+\Psi_0'\nabla\theta+\nu\mathbf{q}=0\ ,\end{aligned}\tag{40}$$

where $w=\frac{1}{2}q^2$. The first equation is for the balance of energy. This is a hyperbolic system. They claim that this model fits data on sound speeds and bears evidence of the need for a thermal inertiaa. The essential difference between Eq. (40) and Cattaneo's equation is in the nonlinear term $\alpha_0'\mathbf{q}\mathring{\theta}$, which is not zero only if $\alpha_0'=0$, α cannot be constant.

1988, D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **51**, 1105.

This is a review paper that deals with the formulation of nonequilibrium thermodynamics known as extended irreversible thermodynamics. In Sec. 4 of this paper the equations of hydrodynamic transport of phonons, the equations of Guyer and Krumhansl, are derived from the equations of extended thermodynamics. Jou *et al.* work with a generalized Gibbs equation

$$\rho\dot{s}+\mathrm{div}\mathbf{J}_s=\sigma\ ,\tag{41}$$

where s is the entropy, the overdot is the substantial derivative, $\rho=1/v$ is the density, $\mathbf{J}_s$ is the entropy flux, and σ is the entropy production. They take the specific volume v, the internal energy u, the heat flux $\mathbf{q}$, the mean normal stress $\Theta=\frac{1}{3}\mathrm{tr}F$, and the stress deviator $\boldsymbol{\zeta}=\mathbf{P}-\Theta\mathbf{1}$ as the canonical variables of s. The temperature T and pressure p are obtained as derivatives of s in the usual way. They assume that the entropy flux depends on all dissipative fluxes,

$$\mathbf{J}_s=\beta_0\mathbf{q}+\beta_1\tau\mathbf{q}+\beta_2\tau^2\mathbf{q}\ ,\tag{42}$$

where the β's depend on u, v, and Θ, and algebraic invariants of functions arising from derivatives of s. This determines the left-hand side of Eq. (41). For the entropy production on the right-hand side they write

$$\sigma = \mathbf{q}\cdot\mathbf{x}_1 + \Theta x_0 + \tau{:}\mathbf{x}_2 , \tag{43}$$

where the $\mathbf{x}_i$'s are taken as functions of the fluxes and their first gradients. The coefficients of $\mathbf{q}$, τ, and Θ in Eq. (41) are now put to zero, giving rise to evolution equations for $\mathbf{q}$, Θ, and τ.

The above sketch of the theory shows that it is for a simple material, one that depends on the system variables and their first derivatives locally; the system variables are related as point functions; their derivatives at $\mathbf{x},t$ are determined by the values of these variables at $\mathbf{x},t$.

The identification of the coefficients of $\mathbf{q}$, τ, and Θ leads, after many simplifications, to evolution equations, a first-order quasilinear system:

$$\begin{aligned} \tau_1\dot{\mathbf{q}} &= -(\mathbf{q}+\lambda\nabla T)+\beta\lambda T^2 \operatorname{div}\tau + \beta'\lambda T^2\nabla\Theta , \\ \tau_0\dot{\theta} &= -(\theta+\xi \operatorname{div}\mathbf{u})+\beta'\zeta T \operatorname{div}\mathbf{q} , \\ \tau_2\dot{\tau} &= -(\dot{\tau}+2\eta\mathbf{D}[\mathbf{u}])+2\beta\eta T\mathbf{sLq} , \end{aligned} \tag{44}$$

where $\mathbf{u}$ is the velocity, $\mathbf{D}[\mathbf{u}]$ is the rate of strain, and $\mathbf{sLq}$ is the symmetric part of

$$\mathbf{Lq} = \nabla\otimes\mathbf{q} - \tfrac{1}{3}\operatorname{tr}(\nabla\otimes\mathbf{q})\mathbf{1} , \tag{45}$$

the deviatoric part of the dyadic gradient of $\mathbf{q}$. It seems desirable to choose the coefficients of the quasilinear system so that catastrophic short-wave instabilities do not occur. These instabilities are associated with ill-posedness of the Cauchy problems. Evidently this system gives rise to real roots if the coefficients are well chosen, and it can be made hyperbolic. Complex roots can be avoided. The idea that the system should be hyperbolic has been elevated to a principle in extended thermodynamics, but it depends on assumptions already made at the beginning. We could get a well-posed evolutionary system with other assumptions that do not lead to hyperbolic system, for examples with assumptions, like the one leading to conductors of the Jeffreys type.

Another point to be made about the evolution equations is that they have only one time of relaxation for each flux. This is certainly an incorrect physical approimation, though it may work well for problems that can be defined over a limited range of frequencies.

To get the equations of Guyer and Krumhansl, Jou *et al.* put $\mathbf{u}=0$ for a rigid conductor and they also set τ_0 and τ_2 to zero. Then, there is still a stress that is induced by the heat-flux gradient

$$\Theta = \beta'\zeta T \operatorname{div}\mathbf{q} , \tag{46}$$

$$\tau = 2\beta\eta T\mathbf{sLq} , \tag{47}$$

and

$$\mathbf{sLq} = \tfrac{1}{2}(\nabla\mathbf{q}+\nabla\mathbf{q}^T) - \tfrac{1}{3}\operatorname{div}\mathbf{q} .$$

We now substitute Eqs. (46) and (47) into (44). Then, after linearizing around $\mathbf{q}$, we get

$$\begin{aligned} \tau_1\dot{\mathbf{q}} = &-(\mathbf{q}+\lambda\nabla T)+\beta^2\lambda\eta T^3\nabla^2\mathbf{q} \\ &+(\tfrac{1}{3}\beta^2\lambda\eta T^3+\beta'^2\lambda T^3\zeta)\nabla \operatorname{div}\mathbf{q} . \end{aligned} \tag{48}$$

This may be compared with the Guyer-Krumhansl equation (4.2a) in "Heat waves." The coefficients of the two equations can be identified [the identification (4.10) of Jou *et al.* is incorrect; several minor errors appear in their derivation]. In this way, the unknown coefficients in the thermodynamic theory may be expressed in terms of the known coefficients of the Guyer-Krumhansl theory.

The derivation just given is interesting because it shows how the hydrodynamic theory, which contains second derivatives, arises by elimination from a locally determined system of partial differential equations. Therefore these second derivatives should not be regarded as arising from a nonlocal theory.

1988, D. Brandon and W. J. Hrusa, J. Integral Eqs. Appl. **1**, 175-201.

Brandon and Hrusa construct nonlinear models of heat conductors of the integral type introduced by Gurtin and Pipkin (1968; see "Heat waves"). They let the internal energy and the heat flux depend on history and make this dependence consistent with the Clausius-Duhem inequality. They derive constitutive equations for the heat flux and the internal energy $e(\theta)$, where $\theta>0$ is the absolute temperature. When these expressions are substituted into the equation expressing the balance of energy in a one-dimensional homogeneous rigid heat conductor of unit density, Brandon (1989) finds that

$$\left[\hat{e}'(\theta(x,t))+\frac{2}{\theta(x,t)^2}\int_0^\infty a'(s)F(\bar{\theta}_x^t(x,s))ds\right]\theta_t(x,t)$$
$$-\frac{2}{\theta(x,t)}\int_0^\infty a'(s)F'(\theta_x^t(x,s))[\theta_x(x,t)-\theta_x(x,t-s)]ds+\int_0^\infty a'(s)F''(\bar{\theta}_x^t(x,s))\bar{\theta}_{xx}^t(x,s)ds = r(x,t), \quad x\in I, \quad t\geq 0 , \tag{49}$$

where the coefficient of $\theta_t(x,t)$ is the specific heat, $\hat{e}(\theta(x,t))$ is the present value of the heat capacity, $r(x,t)$ is the external heat supply, $F(\bar{\theta}_x^t)$ and $a(s)$ are scalar functions required by thermodynamics to satisfy

$$F(0)=F'(0)=0,\quad F''(0)>0,\quad F(\gamma)\geq 0 \quad \forall\gamma\in\mathbb{R}\ ,$$

$$a''(s)\geq 0\forall s\geq 0,\quad a(s) \text{ positive definite }, $$

and

$$\bar{\theta}^t(x,s)=\int_{t-s}^{t}\theta_x(x,z)dz \quad \forall s\geq 0$$

is the summed history up to time t of $\theta_x(x,\cdot)$. Equation (49) was analyzed by Brandon (1989).

1989, D. Brandon, CMS Technical Summary Report No. 89-37, University of Wisconsin.

Nonlinear models of heat conductors should lead to well-posed initial-value problems for the propagation of heat. Ill-posed problems are catastrophically unstable to short waves, with growth rates that tend to infinity as the wavelength tends to zero. This stability problem is tied to the classification of type of the equation governing the flow of heat. Hyperbolic and parabolic equations are well posed in this sense and elliptic problems are ill posed. Ill-posed problems cannot be integrated numerically; the finer the mesh the worse the instability. The classification of quasilinear equations depends on the solutions because the coefficients of the highest derivatives are not constants but are defined on the unknown system variables. There are "forbidden" values of the solutions for which the equation becomes elliptic and loses stability. Ill-posedness, catastrophic instability to short waves, may be studied by freezing coefficients and discarding lower-order terms (Joseph and Saut, 1990). Brandon's paper deals with this problem of change of type for the integral models derived by Brandon and Hrusa (1988). Differentiation of Eq. (49) leads to

$$A(x,t)\theta_{tt}(x,t)+B(x,t)\theta_{xt}(x,t) + c(x,t)\theta_{xx}(x,t)=R(x,t)\ , \qquad (50)$$

where

$$A(x,t)=\hat{e}(\theta(x,t))+\frac{2}{\theta(x,t)^2}\int_0^\infty a'(s)F(\bar{\theta}_x^t(x,s))ds\ , \qquad (51)$$

$$B(x,t)=-\frac{2}{\theta(x,t)}\int_0^\infty a'(s)F'(\bar{\theta}_x^t(x,s))ds\ , \qquad (52)$$

$$C(x,t)=\int_0^\infty a'(s)F''(\bar{\theta}_x^t(x,s))ds\ , \qquad (53)$$

and R consists of lower order terms in addition to the forcing term r_t.

It is now easy to see that, near equilibrium (i.e., near a state where θ is a constant and $\theta_x\equiv 0$), Eq. (49) is of hyperbolic type (since for $|\theta_x|$ sufficiently small $A>0$ and $C<0$. However, we observe that the second term on the right-hand side of Eq. (51) is negative and hence, far enough from equilibrium, Eq. (49) may become elliptic.

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