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PHONON GAS AND CHANGES OF SHAPE OF SECOND SOUND WAVE

T. RUGGERI (Bologna)

A generalized non linear Maxwell-Cattaneo equation is used to study shock waves propagating in a rigid heat conductor at low temperature.

Taking into account the experimental values for the second sound velocity, the existence of a critical temperature $\tilde{\theta}$ characteristic of the materials and separating two families of shocks, the "hot" and the "cold" ones, is proved both numerically and analytically. Finally a possible explanation of the distortion of the initial second sound thermal pulse during its propagation is proposed.

1. Introduction.

In 1947 Peshkow [1] suggested that heat could propagate in pure crystals as a true temperature wave, called second sound. In the following years a great work has been developed to understand the theoretical bases of this idea (see, in particular, the papers of Guyer and Krumhansl [2], [3]) and for finding experimentally the new wave. At the first time, second sound was observed in pure crystals of ^4He (1966) and then in high-purity crystals of ^3He (1969), NaF (1970) and Bi (1972).

To study the heat pulses in very pure crystals at low temperatures the starting point lies in considering the crystal as a phonon system. Here the normal processes (N-processes) in which phonon momentum is conserved are stronger, in certain temperature ranges, than the R-processes (dissipative processes not conserving momentum) and so the second sound can be identified. Two interesting features must be underlined: the first is the existence of a *critical temperature* such that the second sound is most clearly seen (for example, about $15^\circ K$ in NaF and $3.5^\circ K$ in Bi) and the second one concerns the modifications of the initial square wave form during its propagation according to the different temperatures of the crystal.

2. Generalized Maxwell-Cattaneo equation and second sound propagation.

The phenomenology previously illustrated cannot be interpreted by Fourier's theory because of the "paradox of instantaneous propagation" and so it is necessary to find a suitable set of hyperbolic field equations.

In the spirit of Extended Thermodynamics [4], [5], [6], let us now consider a general system of two balance laws writing, in correspondence to the state pair (θ, q)

$$\rho\dot{e} + \operatorname{div}\mathbf{q} = 0 \tag{2.1}$$

$$\dot{\mathrm{w}} + \operatorname{div}\mathbf{T} = -\mathrm{b}. \tag{2.2}$$

The first equation is the usual balance law of energy; ρ, e, q, are respectively the (constant) mass density, the internal energy and the heat flux vector. Moreover the superposed dot indicates the time derivative. Using representation theorems for w, T, b and supposing to be near the equilibrium state, the system (2.1)-(2.2) becomes [7], [8], [9], [10]

$$\rho\dot{e} + \operatorname{div}\mathbf{q} = 0 \tag{2.3}$$

$$(\alpha\mathrm{q})^{\bullet} + \nabla\nu = -\frac{\nu'}{\kappa}\mathrm{q} \tag{2.4}$$

Here $\kappa \equiv \kappa(\theta)$ represents the heat conductivity and the remaining functions α, ν together with e are constitutive quantities depending on the absolute temperature θ (the apex denotes the derivative with respect to θ and ∇ is the gradient operator). When α is equal to a constant, the Maxwell-Cattaneo equation

$$\tau\dot{\mathbf{q}} + \mathbf{q} = -\kappa\nabla\theta \tag{2.5}$$

is obtained ($\tau = \alpha\kappa/\nu'$) while, if $\alpha = 0$, we have the Fourier law.

The most important feature of (2.4) lies in the presence of the not constant factor α playing the role of thermal inertia. In fact, if $\alpha \equiv \alpha(\theta)$, the entropy principle as well as the hyperbolicity of the differential system (2.3)-(2.4) are satisfied without requiring the dependence of e on $\mathbf{q}$ in addition to temperature [11]. Besides the great generality due to the function $\alpha(\theta)$ allows us to recover the stability criterion of the maximum of entropy at equilibrium.

Let us impose now the compatibility of eqs. (2.3)-(2.4) with the entropy principle taken in the form

$$\dot{h}^o + \operatorname{div}\mathbf{h} \leq 0 \tag{2.6}$$

with

$$h^o = -\rho S, \qquad \mathbf{h} = -\frac{\mathbf{q}}{\theta} \tag{2.7}$$

(S is the specific entropy). Then we obtain [10]

$$\alpha = \gamma/(\nu'\theta^2), \quad \gamma = \text{const.}, \qquad \kappa > 0, \tag{2.8}$$

$$h^o = -\rho S = -\rho S_E(\theta) + \frac{\gamma q^2}{2(\nu'\theta^2)^2} \tag{2.9}$$

where S_E is the equilibrium entropy density.

Also the convexity condition for h^o, with respect to the field $\mathbf{u} \equiv (\rho e, \alpha\mathbf{q})^T$ is imposed and this implies our system is symmetric-hyperbolic (in the sense of Friedrichs)(1). If

$$\gamma > 0, \qquad c(\theta) = e'(\theta) > 0 \tag{2.10}$$

(1) For such systems a general theorem on the well-position of the Cauchy problem (locally) holds.

where c is the equilibrium specific heat.

Taking into account that $e = e(\theta)$ is known (for example, in the case of crystals at low temperature $e = \epsilon\theta^4/4$) and also $\kappa(\theta)$ is found through experimental data, we have at this step that the only arbitrary quantities are $\nu(\theta)$ and the constant γ. Besides the second sound velocity at equilibrium, $U_E \equiv U_E(\theta)$, can be identified with the characteristic velocities of the system (2.3)-(2.4) evaluated in an equilibrium state ($\mathbf{q} = 0$). The characteristic velocities in a generic state are given by the roots of the characteristic polynomial

$$\rho c \alpha \lambda^2 + \lambda \alpha' q_n - \nu' = 0, \tag{2.11}$$

where $q_n \equiv \mathbf{q} \cdot \mathbf{n}$ and $\mathbf{n}$ is the unit normal to the characteristic wave front.

Therefore from $(2.8)_1$ and (2.11), when $\mathbf{q} = 0$, the constitutive function ν in terms of U_E is obtained

$$\frac{\nu}{\sqrt{\rho\gamma}} = \int \frac{U_E(\theta)}{\theta} \sqrt{c(\theta)} d\theta. \tag{2.12}$$

Since it is possible to verify that γ is an inessential common factor we have no more free parameters: in other words all the constitutive functions are univocally determined knowing the equilibrium quantities $e \equiv e(\theta)$, $\kappa \equiv \kappa(\theta)$, $U_E \equiv U_E(\theta)$ [10].

3. Shock waves in high purity crystals.

As (2.3), (2.4) represent a system of balance laws (i.e. the first member is in the form of space-time divergence), it is possible to write it in an integral form and to study weak solutions and, in particular, shock waves [14]; then the Rankine-Hugoniot compatibility conditions across the shock front allow us to evaluate the shock velocity s in terms of the temperature θ_o, θ_1 respectively ahead and behind the shock surface.

In order to pick out the physically relevant shocks among all the mathematical solutions of the Rankine-Hugoniot equations, two selection rules are often used: i) *the entropy growth criterion* [15], [16] and ii) *the Lax shock conditions* [17], [18], [19], [20].

The first one consists in accepting only the shock wave solutions for which the entropy production η across the shock front is non-negative; the second one states that the admissible shocks are those satisfying the condition $U_1 > s > U_o$ (U_o and U_1 are the values of the characteristic velocities λ evaluated respectively in the states ahead and behind the shock front). From the mathematical theory of shock waves it is well known that the two criteria are equivalent for weak shocks, i.e. in a neighbourhood of the null shock, but we underline that, in general, this is not true for strong shocks as it will be showed in the following.

Let us apply now the present approach to the case of NaF and Bi crystals specifying in accordance with previous results, only the functions $U_E(\theta)$ and $e(\theta)$.

The values of U_E obtained from experiments by Jackson et al. (for NaF) [21] and by Narayanamurti-Dynes (for Bi) [22] are well described by the empirical equation [23]

$$U_E^{-2} = A + B\theta^n \tag{3.1}$$

in the temperature range $10^o K \leq \theta \leq 18.5^o K$ (for NaF) and $1.4^o K \leq \theta \leq 4^o K$ (for Bi), where heat pulses were observed with properties expected of second sound. Values of the parameters A, B, n giving an excellent fit are [23]

$$n = 3.10, \quad A = 9.09 \cdot 10^{-12}, \quad B = 2.22 \cdot 10^{-15} \quad \text{(NaF)}$$

$$n = 3.75, \quad A = 9.07 \cdot 10^{-11}, \quad B = 7.58 \cdot 10^{-13} \quad \text{(Bi)}$$

for U_E in centimeters per second and θ in Kelvin degrees. Furthermore we take the equilibrium specific heat $c = \epsilon\theta^3$, with $\epsilon = 23$ erg cm^{-3} $^oK^{-4}$ for NaF and $\epsilon = 550$ erg cm^{-3} $^oK^{-4}$ for Bi.

Considering a plane shock wave propagating in the x-direction ($\mathbf{n} \equiv (1,0,0)$), from the Rankine-Hugoniot equations it is possible to obtain $s = s(\theta_o, \theta_1)$ and $U_1 = U_1(\theta_o, \theta_1)$ where θ_o is the unperturbed temperature while θ_1 is the perturbed one (shock parameter).

Then, a numerical evaluation [14] allows us to plot s and U_1 vs. temperature θ_1, for a fixed value of θ_o, in both cases of NaF and Bi. Figures $1 \div 3$ refer to NaF case. We observe that when the

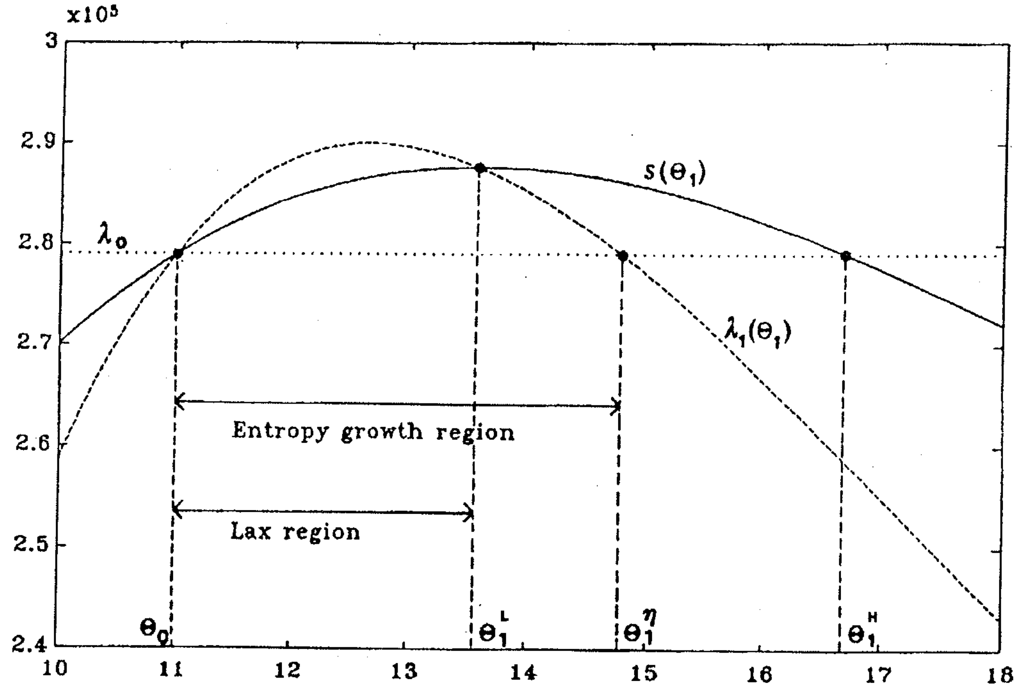

Fig. 1

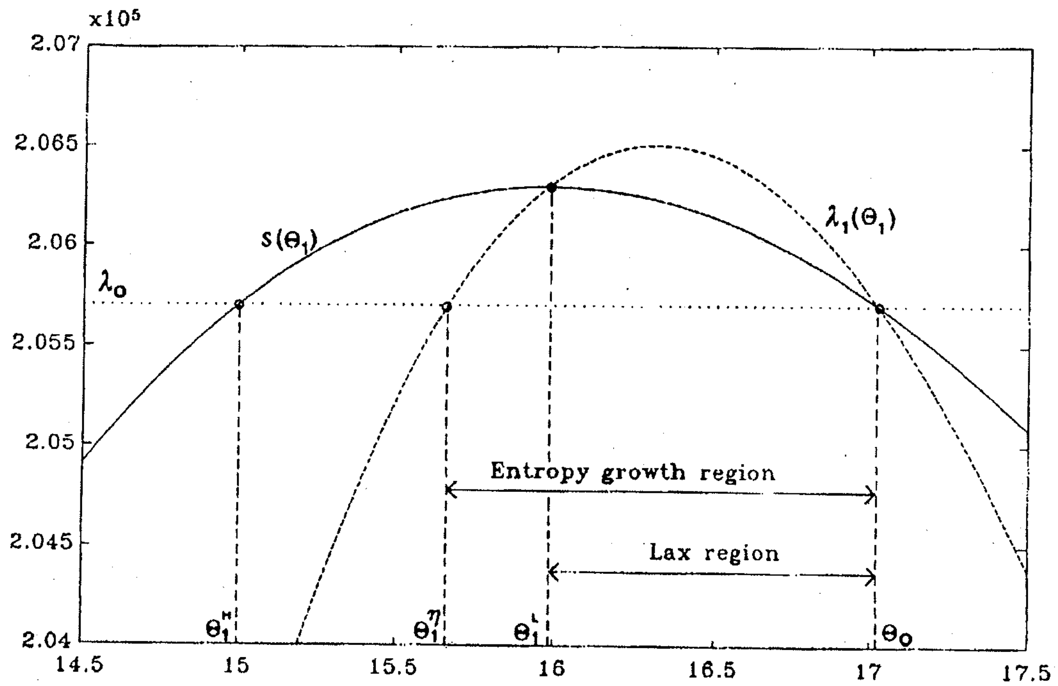

Fig. 2

temperature θ_o increases in the range $10^o K \sim 18.5^o K$ the plots are, at first, of type displayed in fig. 1 and then as in fig. 2.

Note that, in both figures, the Lax conditions impose that the possible shocks there exist only if $|\theta_1 - \theta_o|$ is bounded (unlike the usual shocks which occur, for example, in fluid dynamics). In particular in fig. 1 it is clearly seen that the Lax conditions are verified in the range $\theta_o < \theta_1 < \theta_1{}^L$ ($\theta_1{}^L$ depending on θ_o). The shock wave can then propagate through the material only if we generate a heat pulse with a positive jump of temperature not exceeding the maximum value of $\theta_1{}^L - \theta_o$. Let us call this shock a *hot shock*. In fig. 2 we note that there is a very different physical situation since the Lax conditions are verified in the range $\theta_1{}^L < \theta_1 < \theta_o$. The shock propagation takes place now if the initial temperature jump is negative and does not exceed in absolute value $|\theta_1{}^L - \theta_o|$ (*cold shock*).

The transition from a situation to the other one is shown in fig. 3 where it is pointed out the existence of a *critical temperature* $\tilde{\theta} = 15.36°K$ such that $\theta_o = \tilde{\theta} = \theta_1{}^L$. In this particular case, the Lax conditions are not satisfied and no shock is possible.

It turns out that $\tilde{\theta}$ is a structural temperature, i.e. characteristic of NaF, defining the boundary between two very different phenomena: for $\theta_o < \tilde{\theta}$ a hot shock is generated while the cold shock appears for $\theta_o > \tilde{\theta}$ and we point out that $\tilde{\theta}$ is the temperature for which the heat flux behind the front changes sign [14].

The same qualitative behaviour is observed in Bi in the range $1.4°K \sim 4°K$. In this case the critical temperature $\tilde{\theta} = 3.38°K$ is found.

The non usual *cold shock* might appear inconsistent with thermodynamics but the study of the function η characterizing the entropy growth across the shock surface shows that $\eta > 0$ in the Lax region. Furthermore note that the temperature range for which $\eta > 0$ is larger than the previous one: $\theta_1{}^\eta < \theta_1{}^L < \theta_1 < \theta_o$ (in fig. 4 η/ρ vs. θ_1 with a fixed $\theta_o > \tilde{\theta}$, i.e. in the case of cold shock, is plotted for NaF).

The explanation of this fact is that the density of entropy at non equilibrium depends not only on the temperature but also on the heat flux [10] and in the function η the heat flux q_1 plays a very important role. Therefore cold shocks are compatible with the thermodynamics principles (in a different context a similar situation was already noted by Nielsen and Shklovskii [24]).

The condition $\eta > 0$ provides the same qualitative results of the Lax conditions also for hot shocks with a $\theta_1{}^\eta > \theta_1{}^L$. Observing as

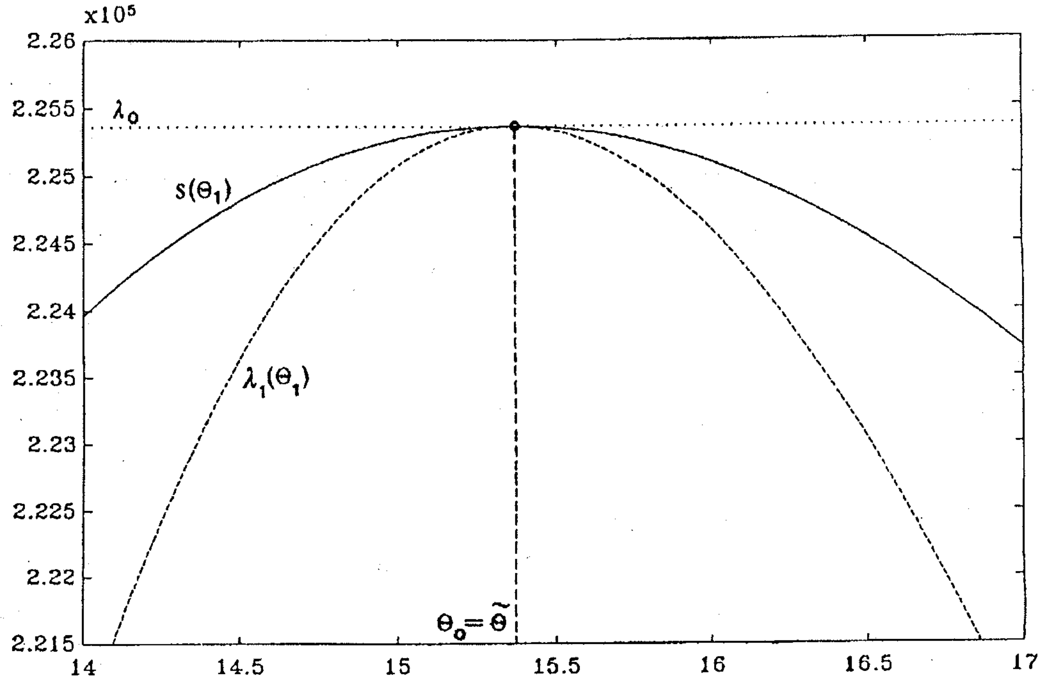

Fig. 3

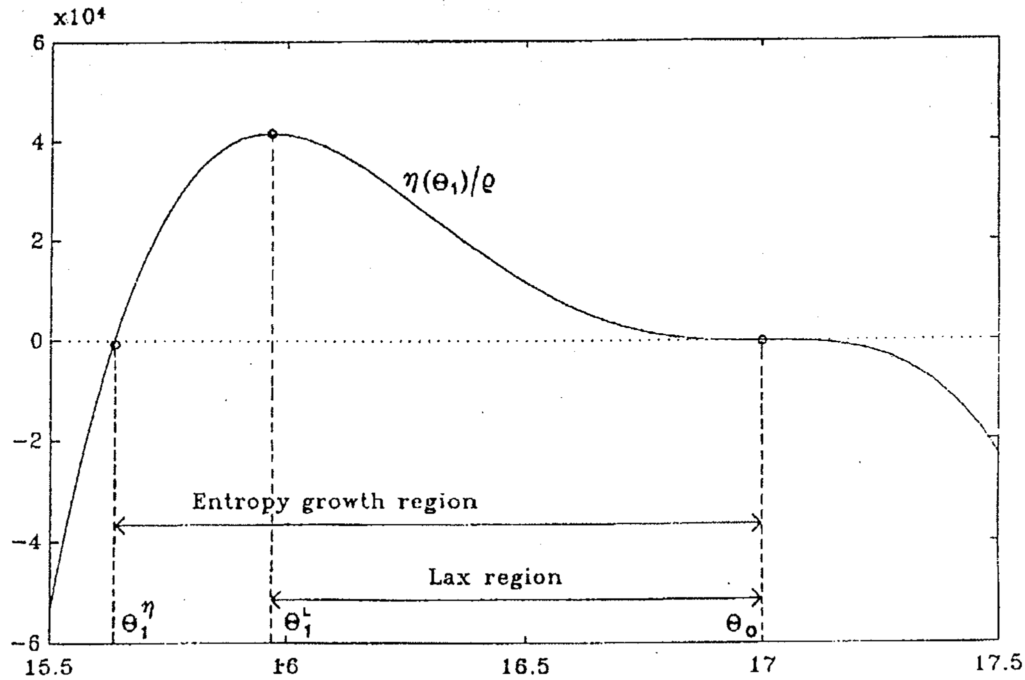

Fig. 4

the plot of the function η/ρ is modified changing the unperturbed temperature θ_o, it results that the value of the critical temperature $\tilde{\theta}$

remains unchanged.

So we want to remark that the present model shows unusual shocks characterized, from a macroscopic point of view, by the existence of a critical structural temperature $\tilde{\theta}$ for which the "state" of the material changes in a very unexpected way. In particular the value $\tilde{\theta} = 15.36^o K$ is found very close to the value ($\sim 15^o K$) at which a new pulse, identified as second sound, is clearly seen in a highly pure dielectric crystal of NaF. Also the value $\tilde{\theta} = 3.38^o K$ is practically coincident with the value ($\sim 3.5^o K$) at which the saturation of the velocity in the second sound regime has been observed in a pure crystal of the semimetal bismuth.

The value $\tilde{\theta}$ of the critical temperature was found by the plots of s and U_1 changing the value of θ_o. In fact, the presence of two very different shocks (hot and cold shocks) enables us to find numerically the transition temperature for which any shock at all is forbidden by the Lax conditions.

However using a bifurcation analysis of the Rankine Hugoniot equations, it is possible for a generic system to prove [25] that there exists a necessary analytical condition for the existence of a particular unperturbed state $\tilde{\mathrm{u}}_o$, such that the Lax conditions are violated also for weak shocks, i.e.

$$(\nabla\lambda \cdot \mathrm{d})_{\tilde{\mathrm{u}}_o} = 0 \tag{3.2}$$

where $\nabla \equiv \partial/\partial \mathrm{u}$, and λ, d are respectively an eigenvalue and the corresponding right eigenvector of the characteristic eigenvalue problem. Therefore in particular for the existence of $\tilde{\mathrm{u}}_o$ it is necessary that the system is not genuinely non linear.

In the present case (3.2) implies that $\tilde{\theta}$ is the value for which the function

$$\Phi(\theta) = U_E(\theta)\theta^{5/6} \tag{3.3}$$

has a maximum. Using for U_E the empirical relationship (3.1) it follows

$$\tilde{\theta} = \left\{ \frac{5A}{B(3n-5)} \right\}^{1/n} \tag{3.4}$$

and then also $\tilde{U}_E$ can be found analytically i.e.

$$\tilde{U}_E = \sqrt{\frac{3n-5}{3nA}}. \tag{3.5}$$

The relationships (3.4), (3.5) give

$$\tilde{\theta} = 15.36^o K, \qquad \tilde{U}_E = 2.26 \cdot 10^5 \text{cm/sec} \qquad (\text{for NaF}) \tag{3.6}$$

$$\tilde{\theta} = 3.38^o K, \qquad \tilde{U}_E = 7.83 \cdot 10^4 \text{cm/sec} \qquad (\text{for Bi}) \tag{3.7}$$

coincident with the values obtained numerically in our previous paper [14].

It is interesting to underline that using the function (3.3) it is possible to find $\tilde{\theta}$ also for the cases of ^3He and ^4He; as it will be reported in [25], the values so obtained are again very close to the values for which the second sound is clearly picked out in these crystals.

4. Changes of shape on second sound wave.

To conclude we present a possible explanation, based on the previous general results, of the distortion of the initial thermal pulse during its propagation in a rigid heat conductor. The results obtained could be a check for verifying experimentally the limits of validity of our model. Suppose we generate an heat pulse by some type of heater: usually, with a good approximation, the schematic shape of the initial pulse is rectangular. It is possible to imagine the rectangular profile of the initial wave as two successive shock fronts: the first one is generated when the heater is on and corresponds to the hot shock studied in the previous section; therefore this shock is stable and can be propagated if $\theta_o < \tilde{\theta}$ and $\theta_1 < \theta_1^L$. The second one (heater off), does not correspond to the cold shock, because at present the right side of the shock (unperturbed region) is the non equilibrium state $(\theta_1, q_1 \neq 0)$, while the left side (perturbed region) is the equilibrium state $(\theta_o, q_o = 0)$. Since in the previous shock analysis we have chosen always the right side coincident with the equilibrium state, then to study the second shock it is necessary to change the equilibrium state with the non equilibrium one and vice versa. However, it is a simple matter to show that the expressions of $s(\theta_o, \theta_1)$ and $U_1(\theta_o, \theta_1)$ remain unchanged, while the entropy production across the second shock coincides, except for the sign, with the entropy production of the first shock. The Lax conditions become now, the complementary ones:

$$U_1 < s < U_o; \tag{4.1}$$

and therefore it is possible to use all the previous figures by considering as admissible region for the Lax conditions the complementary set in which (4.1) holds. Moreover, the entropy growth condition differs by the sign with repsect the entropy growth condition of the first front.

Let's consider now the two cases: i) $\theta_o < \tilde{\theta}$; ii) $\theta_o \geq \tilde{\theta}$.

- Case i): $\theta_o < \tilde{\theta}$ (fig.1 for NaF)
  - i1) If $\theta_1 < \theta_1^L$, the Lax conditions are satisfied as regards the first front, but are violated for the second one and therefore the second front is unstable and the back part of the signal is regularised. This case corresponds, substantially, to *weak amplitude*.
  - i2) If $\theta_1 \geq \theta_1^L$ both the shocks violate the Lax conditions and the only possibility is a regularization of both sides of the wave (*strong amplitude*). Incidentally, we observe that when $\theta_1 > \theta_1^H$ the second front satisfies (4.1) but the proper Lax conditions are violated because the shock does not pass through the null shock.

- Case ii): $\theta_o \geq \tilde{\theta}$ (fig 2 for NaF)

  In this case, the first shock is always forbidden and the second one verifies, $\forall\theta_1 > \theta_o$, the Lax conditions (4.1): we have a shape change in which only the front part is regularizedas independently of the amplitude.

The same results arise by using the entropy growth criteria.

This behaviour seems in a good agreement with all the available experiments. In particular in all the materials under consideration there exists a temperature range in a neighbourhood of $\tilde{\theta}$ for which the wave appears regularised; the second sound shape described in the case i1) it is well supported by the oscilloscope traces in the case of ^4He and, moreover, in the case of NaF it can be deduced indirectly observing that the difference between the arrival times for leading edges and peaks increases with the temperature. On the other hand (unlike the case of superfluid Helium) the shape as described in ii) does not appear so evident in the experiments. In our opinions the reason, probably, could be that when $\theta_o > \tilde{\theta}$ we have the transition from the second sound range to the diffusion one and so our hyperbolic model loses its validity and it is necessary to add parabolic terms. If this is true the critical temperature $\tilde{\theta}$ becomes the transition temperature separating the hyperbolicity region (second sound wave) from the parabolic region (diffusion). From this point of view $\tilde{\theta}$ seems, somehow, to play the role of the lambda point in the superfluid Helium.

A detailed version of these results may be seen in the paper [25].

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Department of Mathematics
Research Center of Applied Mathematics
C.I.R.A.M. - University of Bologna
Via Saragozza 8, 40123 Bologna, Italy.