M. Fabrizio
Dipartimento di Matematica, Piazza di Porta S. Donato 5, 40127 Bologna, Italy

C. Giorgi
Dipartimento di Matematica, Via Valotti 9, 25133 Brescia, Italy

A. Morro
DIBE, Via Opera Pia 11a, 16145 Genova, Italy

Running title: Non-isothermal phase field and second sound

Abstract
Stationary and non-stationary models of heat conduction in solids are associated with two different phases of the solid. The passage between the two regimes is then viewed as a phase transition of the second kind. The order parameter of the transition is modelled as a phase field which changes smoothly in space. A thermodynamic approach is developed by regarding the phase field as an internal variable and the kinetic or evolution equation is regarded as a constitutive equation. Along with the other constitutive equations, the unknown evolution equation is required to satisfy the second law of thermodynamics. Necessary and sufficient restrictions placed by thermodynamics are derived for the constitutive equations. This provides a unified model of heat conduction which simplifies in the pertinent models for the two phases. The generality of the scheme allows previous models to be recovered as particular cases.

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1 Introduction

The phase-field model is applied to describe phase transitions which occur in a finite or unbounded region rather than at a sharp surface. The order parameter, or phase field, is then allowed to vary smoothly within the pertinent region. The literature on the subject shows how the phase field model is widely applied in different contexts such as solidification processes, microstructure evolution in solids, isothermal or non-isothermal phase transitions, in pure substances and in alloys. In this regard we mention [1-4] and references therein.

To our mind the order parameter can be regarded quite naturally as an internal variable which is governed by an evolution equation to be characterized within the whole set of constitutive assumptions and the thermodynamic restrictions. Lately we have applied this viewpoint to quite a general model of phase transition and hence, in particular, to the solid-fluid transition in water [5].

Though the pertinent details are deferred to the next section, here we say that, according to conditions, heat conduction in solids may be well modelled as a stationary phenomenon, through the Fourier law, and a non-stationary phenomenon through one of the variants, or improvements, of the Maxwell-Cattaneo equation. For the benefit of the reader, the main ideas and equations about the modelling of heat conduction are outlined in §2.

The purpose of this paper is to frame the passage between the two regimes as a phase transition, of the second kind, which spatially occurs in a finite region and is induced by the temperature. Framing this passage as a phase transition is suggested e.g. by the phase transition of Helium II. Below the critical temperature $\theta_0 = 2.2^\circ$ K, Helium II is a superfluid with a small value of heat conductivity [6] and viscosity coefficient [7, 8]. Second sound, and hence the Maxwell-Cattaneo regime, occurs below the critical temperature θ_0. We regard the second sound as a phenomenon strictly related to a state of matter and that is why we model the two regimes as two phases of heat conduction as different phases.

To obtain a description of the phase transition we ascribe a phase field to the heat conduction and develop a thermodynamic theory for heat conduction with an evolution equation to be characterized for the order parameter. As a result, we set up a general thermodynamic scheme which provides known models for heat conduction as particular cases. Moreover, the pertinent equations simplify to stationary (Fourier-like) models or unstationary models depending on whether the order parameter approaches the limit values associated with the two phases.

Notation. Functions of $\mathbf{x}$ and t are considered in the space-time domain $\Omega \times \mathbb{R}$, $\Omega \subset \mathbb{R}^3$. ∇ denotes the gradient relative to the position vector $\mathbf{x} \in \Omega$, a superposed dot stands for time differentiation. Lower case boldface letters denote vectors, capital boldface letters denote second-order tensors. Partial differentiations are denoted by subscripts; for example, ψ_θ stands for $\partial\psi/\partial\theta$.

2 Modelling of heat conduction

For almost-stationary problems, where the temperature θ varies slowly in time, the classical Fourier law of heat conduction

$$\mathbf{q} = -k\nabla\theta \tag{2.1}$$

is commonly accepted and widely applied. In general, the *thermal conductivity* k depends on the temperature and on the nature of the material. In the pioneering work [9], Cattaneo proposed an improvement of (2.1) so that the non-equilibrium properties, involved in non stationary problems, are incorporated. Using some arguments from the kinetic theory of gases and disregarding higher-order terms, he derived the so called Cattaneo–Maxwell equation

$$\tau\dot{\mathbf{q}} + \mathbf{q} = -k\nabla\theta \tag{2.2}$$

which reduces to (2.1) when the relaxation time τ vanishes.

By (2.2) and replacing ρe with $C\theta$ into the energy balance, it follows that the temperature θ obeys the evolution equation

$$\tau C\ddot{\theta} + C\dot{\theta} - k\Delta\theta = 0$$

and hence waves propagate with finite speed $v = \sqrt{k/\tau C}$ (*second sound* effect), C being the heat capacity. As pointed out in [10], in dielectric solids at low temperatures heat conduction is well described by the Cattaneo–Maxwell equation where, though, the relaxation time τ and the heat conductivity k are allowed to depend on the temperature θ. Incidentally, k, C and τ, are usually regarded as related by

$$k/\tau \simeq C\,V^2\,, \tag{2.3}$$

where V is the root-mean-square phonon speed.

Later, second sound was observed also in solids at very low temperatures, for instance in NaF and Bi. In experiments performed by Jackson *et al* [11] the speed of second sound pulses have been measured over an appreciable range of temperature. To account for non-isotropic phenomena, which are a typical feature of solids, a generalization of the Cattaneo–Maxwell equation was set up by Pao & Banerjee [12] in the form

$$\mathbf{T}(\theta)\dot{\mathbf{q}} + \mathbf{q} = -\boldsymbol{\mathcal{K}}(\theta)\nabla\theta\,. \tag{2.4}$$

Here $\mathbf{T}$ and $\boldsymbol{\mathcal{K}}$ are symmetric, second-order tensors. In a set of papers by Coleman *et al* [13, 14, 15, 16] a general thermodynamic approach is developed assuming that the internal energy depends on θ but also on $\mathbf{q}$ through a quadratic form. This assumption implies that the heat flux enters into the thermodynamic potentials as a state variable. As pointed out in [16], experimental results seem to fit quite well with equation (2.4).

Models of this kind are consistent with the second law but hold for small values of $|\mathbf{q}|^2$ (see, for instance, [15]). The smallness is consistent with the fact that, as it happens in He II, the phase transition to second sound regime occurs at small values of $\mathbf{q}$. This feature is made formal in §5.

Following the lines of extended thermodynamics, Morro and Ruggeri [19, 20] elaborate a model, which holds for each value of $\mathbf{q}$, by assuming an evolution equation for $\mathbf{a} = \boldsymbol{\mathcal{A}}(\theta)\mathbf{q}$ rather than $\mathbf{q}$, namely

$$\rho\dot{\mathbf{a}} = -\mathbf{N}(\theta)\mathbf{a} - m(\theta)\nabla\theta\,. \tag{2.5}$$

This equation is compatible with thermodynamics provided that the *thermal inertia* tensor $\boldsymbol{\mathcal{A}}$ is related to m by

$$\boldsymbol{\mathcal{A}}(\theta) = \frac{1}{m(\theta)\theta^2}\mathbf{B}^{-1}$$

where $\mathbf{B}$ is constant and positive definite. Of course, when $\boldsymbol{\mathcal{A}}$ is constant (namely, $m(\theta) = \theta^{-2}$) equation (2.4) is recovered by setting

$$\mathbf{T}(\theta) = \rho\mathbf{N}^{-1}(\theta) \qquad \text{and} \qquad \boldsymbol{\mathcal{K}}(\theta) = m(\theta)\mathbf{N}^{-1}(\theta)\boldsymbol{\mathcal{A}}^{-1}$$

whereas Fourier law (2.1) follows when $\rho = 0$. In general, when $\boldsymbol{\mathcal{A}}$ is not constant the internal energy e is allowed to be independent of $\mathbf{q}$. If this is the case, the specific heat is positive however large $|\mathbf{q}|^2$ may be and (see [20]) the non-equilibrium terms are fully determined by measurable functions of the temperature.

These investigations suggested that non-equilibrium properties could be directly related to the wave speed at equilibrium. In this sense, Ruggeri *et al* [22, 23] studied the propagation of shock waves in an isotropic rigid heat conductor obeying a simplified version of (2.5), namely

$$\frac{d}{dt}(\alpha(\theta)\mathbf{q}) + \nabla\nu(\theta) = -\frac{\nu'(\theta)}{\kappa(\theta)}\mathbf{q} \tag{2.6}$$

They proved the existence of a critical temperature θ_0 which is typical of the material and very close to the values at which the second sound was experimentally identified.

2.1 Physical evidence of the transition

It is apparent that the Fourier law (2.1) is recovered from (2.2) as the relaxation time τ vanishes. According to (2.3), the averaged phonon velocity V and the thermal wave speed v approach infinity as $\tau \to 0$, as expected in the parabolic Fourier regime. However, from the physical point of view, the two regimes of heat conduction are due to completely different material properties. Indeed, in the Fourier regime the heat conduction is mainly due to the vibrations of the crystal lattice whereas, at very low temperatures, the Maxwell-Cattaneo regime is mainly due to quantum effects and phonons transportation with negligible interaction of the lattice.

Since for metals and semimetals the heat conductivity k is proportional to the electric conductivity through the so-called Wiedemann-Franz law, we may argue on the Fourier law by analogy with the Ohm law. In the normal state, phonons are accelerated by the temperature gradient (the driving force) and retarded by the interaction with the crystal lattice. Below a fixed (low) temperature the phonons enter the Maxwell-Cattaneo regime and at very low temperatures they become thermally-superconducting, in the sense that they are carried without any resistance (perfect conduction). This analogy cannot be complete because electromagnetic superconducting materials exhibit the Meissner effect which has no counterpart in perfect heat conductors. Nevertheless, taking into account some results on non-linear wave propagation which seems to be absent in other models, a more stringent similarity between the present theory and superfluidity could be possible (see [23, 24]).

In addition, in defect–free crystals a (low) temperature value θ_0 occurs such that some physical quantities change abruptly across it (see [22, 23]) and below it the second sound property appears (see, for instance, [11] for NaF and [21] for Bi). For instance, in a pure crystal of NaF $\theta_0 \approx 15^\circ$ K and in the semimetal bismuth $\theta_0 \approx 3.5^\circ$ K. It is worth noting that these values yield approximately the same temperature ratio $\theta_0/\theta_D \approx 0.03$, where θ_D is the Debye temperature (491°K for NaF and 120°K for Bi).

All these arguments suggest that we model the passage between the two regimes of heat conduction as a thermally–induced phase transition. If we look at the heat flux as a flow produced by two populations of phonons as thermal carriers with finite speed, this approach looks very close to the non isothermal Ginzburg–Landau theory for superconductors. However, because of the smallness of the temperature ratio ($\theta_0/\theta_D \ll 1$), the specific heat is assumed here to be proportional to θ^3.

All these arguments suggest that we model the passage between the two regimes of heat conduction as a thermally–induced phase transition.

3 Balance laws and thermodynamic restrictions

Let $\Omega \subset \mathbb{R}^3$ be the region occupied by the conductor and $\mathbf{x}$ is a point in Ω. The conductor is regarded as a rigid body and hence we let the mass density ρ be constant and the velocity gradient be zero. To describe a phase transition we allow for the conductor to occur in two phases. The interface between the two phases is diffuse (not sharp) in that the pertinent fields do not jump across a surface but change smoothly on a transition layer. The order parameter or phase field φ varies smoothly across the transition layer. Though φ, or a function of φ, is the concentration of one phase, we model the material, at any point $\mathbf{x}$ of the body, as a continuum without any internal structure. Hence we say that the balance of energy is the only significant balance law and takes the standard form

$$\rho\dot{e} = -\nabla \cdot \mathbf{q} + \rho r) \tag{3.1}$$

where e is the (internal) energy density per unit mass, $\mathbf{q}$ is the heat flux vector and r is the heat supply.

The transition layer, rather than a sharp interface, accounts for nonlocal effects. This suggests that the entropy flux is not merely the ratio $\mathbf{q}/\theta$. Accordingly we state the second law of thermodynamics (in differential form) as follows.

Second law. *The inequality*

$$\rho\dot{\eta} \geq -\nabla \cdot (\frac{\mathbf{q}}{\theta} + \mathbf{k}) + \frac{\rho r}{\theta} \tag{3.2}$$

must hold, at each point $\mathbf{x} \in \Omega$ *and time* $t \in \mathbb{R}$ *for all fields* $e, \mathbf{q}, \theta, r,$ *of* $\mathbf{x}$ *and* t*, compatible with the balance of energy.*

The extra-flux $\mathbf{k}$ is regarded as unknown and has to be determined so that the second law holds. Integration of (3.2) over the whole region Ω provides

$$\frac{d}{dt}\int_\Omega \rho\eta\, dv \geq -\int_{\partial\Omega} (\frac{\mathbf{q}}{\theta} + \mathbf{k}) \cdot \mathbf{n}\, da + \int_\Omega \frac{\rho r}{\theta}\, dv.$$

To let the second law for the whole body take the standard form

$$\frac{d}{dt}\int_\Omega \rho\eta\, dv \geq -\int_{\partial\Omega} \frac{\mathbf{q}}{\theta} \cdot \mathbf{n}\, da + \int_\Omega \frac{\rho r}{\theta}\, dv$$

we assume the boundary condition

$$\mathbf{k} \cdot \mathbf{n}|_{\partial\Omega} = 0. \tag{3.3}$$

With the purpose we have in mind, it is convenient to describe heat conduction through the vector

$$\boldsymbol{\omega} = \alpha(\theta, \varphi)\mathbf{Q}^{-1}\mathbf{q} \tag{3.4}$$

where $\mathbf{Q}$ is a non-singular constant tensor and

$$\alpha > 0, \qquad \lim_{\varphi \to 0_+} \alpha(\theta, \varphi) = 0 \quad \forall\theta > 0, \tag{3.5}$$

so that, as $\varphi > 0$, we can invert to obtain

$$\mathbf{q} = \mathbf{Q}\boldsymbol{\omega}/\alpha(\theta, \varphi).$$

We then assume that

$$\Gamma = (\theta, \nabla\theta, \nabla\nabla\theta, \varphi, \nabla\varphi, \nabla\nabla\varphi, \boldsymbol{\omega})$$

is the set of independent variables. By assumption, as $\varphi \to 0$ the vector $\boldsymbol{\omega}$ approaches zero and hence $\varphi = 0$ describes the model where $\theta, \nabla\theta, \nabla\nabla\theta$ is the whole set of independent variables.

The dependence of φ and $\boldsymbol{\omega}$ on the time t is governed by the evolution laws

$$\dot{\varphi} = f(\Gamma), \qquad \dot{\boldsymbol{\omega}} = \mathbf{w}(\Gamma). \tag{3.6}$$

The functions f and $\mathbf{w}$ are so far unknown and we look for the restrictions placed on them by the second law. In this sense we regard φ and $\boldsymbol{\omega}$ as internal variables.

Letting $\psi = e - \theta\eta$ we can write the inequality (3.2) in the form

$$-\rho(\dot{\psi} + \eta\dot{\theta}) - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \theta\nabla \cdot \mathbf{k} \geq 0. \tag{3.7}$$

The constitutive properties of the material are expressed by letting $e, \eta, \mathbf{k}$, as well as $f, \mathbf{w}$, be functions of Γ. Hence (3.7) becomes

$$-\rho(\psi_\theta+\eta)\dot{\theta}-\rho\psi_{\nabla\theta}\cdot\nabla\dot{\theta}-\rho\psi_{\nabla\nabla\theta}\cdot\nabla\nabla\dot{\theta}-\rho\psi_\varphi f-\rho\psi_{\nabla\varphi}\cdot\nabla f-\rho\psi_{\nabla\nabla\varphi}\cdot\nabla\nabla f-\rho\psi_{\boldsymbol{\omega}}\cdot\mathbf{w}-\frac{1}{\theta}\mathbf{q}\cdot\nabla\theta+\theta\nabla\cdot\mathbf{k} \geq 0.$$

The arbitrariness of $\dot{\theta}$, $\nabla\dot{\theta}$ and $\nabla\nabla\dot{\theta}$, at any point $\mathbf{x}$ and time t, implies that

$$\eta = -\psi_\theta, \qquad \psi_{\nabla\theta} = 0, \qquad \psi_{\nabla\nabla\theta} = 0. \tag{3.8}$$

We can write the remaining inequality as

$$\rho(\psi_\varphi - \nabla \cdot \psi_{\nabla\varphi})f + \rho\psi_{\nabla\nabla\varphi} \cdot \nabla\nabla f + \mathbf{k} \cdot \nabla\theta + \rho\psi_{\boldsymbol{\omega}} \cdot \mathbf{w} + \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta - \nabla \cdot (\theta\mathbf{k} - \rho\psi_{\nabla\varphi}f) \leq 0. \tag{3.9}$$

We now examine the consequences of (3.9).

Because

$$\nabla\nabla f = \nabla(f_\theta\nabla\theta + f_{\nabla\theta}\nabla\nabla\theta + f_{\nabla\nabla\theta}\nabla\nabla\nabla\theta + f_\varphi\nabla\varphi + f_{\nabla\varphi}\nabla\nabla\varphi + f_{\nabla\nabla\varphi}\nabla\nabla\nabla\varphi + f_{\boldsymbol{\omega}}\nabla\boldsymbol{\omega}),$$

the left-hand side of (3.9) is linear in $\nabla\nabla\nabla\nabla\theta, \nabla\nabla\nabla\nabla\varphi, \nabla\nabla\boldsymbol{\omega}$ with coefficients $-\rho\psi_{\nabla\nabla\varphi}f_{\nabla\nabla\theta}$, $-\rho\psi_{\nabla\nabla\varphi}f_{\nabla\nabla\varphi}$, $-\rho\psi_{\nabla\nabla\varphi}f_{\boldsymbol{\omega}}$. The arbitrariness of $\nabla\nabla\nabla\nabla\theta, \nabla\nabla\nabla\nabla\varphi, \nabla\nabla\boldsymbol{\omega}$ and the assumption that either $f_{\nabla\nabla\theta}$ or $f_{\nabla\nabla\varphi}$ or $f_{\boldsymbol{\omega}}$ does not vanish imply that (3.9) holds only if

$$\psi_{\nabla\nabla\varphi} = 0. \tag{3.10}$$

Now let

$$\mathbf{h} = \theta\mathbf{k} - \rho\psi_{\nabla\varphi}f \tag{3.11}$$

which then is a function of Γ. Upon evaluation of $\nabla \cdot \mathbf{h}$, in view of (3.10), the left-hand side of (3.9) contains

$$\zeta := \mathbf{h}_{\nabla\nabla\theta} \cdot \nabla\nabla\nabla\theta + \mathbf{h}_{\nabla\nabla\varphi} \cdot \nabla\nabla\nabla\varphi + \mathbf{h}_{\boldsymbol{\omega}} \cdot \nabla\boldsymbol{\omega}.$$

The arbitrariness of $\nabla\nabla\nabla\theta$, $\nabla\nabla\nabla\varphi$, $\nabla\boldsymbol{\omega}$ requires that (3.9) holds only if $\zeta = 0$ which means that $\mathbf{h}$ may depend only on $\theta, \varphi, \nabla\theta, \nabla\varphi$. Hence (3.11) and (3.6) give

$$\theta\mathbf{k}(\Gamma) = \rho\psi_{\nabla\varphi}(\theta, \varphi, \nabla\varphi, \boldsymbol{\omega})\dot{\varphi} + \mathbf{h}(\theta, \varphi, \nabla\theta, \nabla\varphi).$$

By analogy with the requirement that fluxes be factorized by $\dot{\varphi}$ (see [3]) we let $\mathbf{h} = 0$. This motivates the assumption

$$\theta \mathbf{k} = \rho \psi_{\nabla\varphi} f. \tag{3.12}$$

As a consequence (3.9) reduces to

$$\theta[\rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta)]f + \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta + \rho\psi_{\boldsymbol{\omega}}\cdot\mathbf{w} \le 0. \tag{3.13}$$

Let $\varphi > 0$ so that we can replace $\mathbf{q}$ with $\mathbf{Q}\boldsymbol{\omega}/\alpha$. Hence, dividing throughout by θ we have

$$f[\rho\psi_\varphi/\theta - \nabla \cdot (\rho\psi_{\nabla\varphi}/\theta)] + \frac{1}{\theta^2\alpha}\mathbf{Q}\boldsymbol{\omega}\cdot\nabla\theta + \mathbf{w}\cdot(\rho\psi_{\boldsymbol{\omega}}/\theta) \le 0.$$

It is reasonable to require that the separate inequalities

$$f[\psi_\varphi/\theta - \nabla \cdot (\psi_{\nabla\varphi}/\theta)] \le 0, \tag{3.14}$$

$$\frac{1}{\theta\alpha}\boldsymbol{\omega}\cdot\mathbf{Q}^T\nabla\theta + \mathbf{w}\cdot\rho\psi_{\boldsymbol{\omega}} \le 0 \tag{3.15}$$

hold. Indeed, in an adiabatic process (that is when $\mathbf{q}$ is zero in the time interval), by (3.5) and (3.6) it follows that $\boldsymbol{\omega}$ and $\mathbf{w}$ vanish identically and (3.13) reduces to (3.14).

While (3.8) is necessary for the validity of the second law, it is evident that the whole set of restrictions so established is sufficient. This is stated as follows.

Proposition 1. *The functions* $f, \mathbf{q}, \psi, \eta, \mathbf{k}$, *of* Γ, *are compatible with the second law of thermodynamics, in the form (3.7), if (3.8), (3.12), (3.10), (3.14) and (3.15) hold.*

4 Models and evolution equations

The simplest way to satisfy (3.14) is to let f be given by

$$f(\Gamma) = -\nu[\psi_\varphi/\theta - \nabla\cdot(\psi_{\nabla\varphi}/\theta)], \qquad \nu > 0. \tag{4.1}$$

The coefficient ν may be a positive constant but also a positive-valued function of Γ.

In connection with (3.15), restrict attention to a free energy ψ which depends quadratically on $\boldsymbol{\omega}$ in the form

$$\rho\psi = \rho\psi^*(\theta, \varphi, \nabla\varphi) + \frac{1}{2}\boldsymbol{\omega}\cdot\mathbf{M}(\theta,\varphi)\boldsymbol{\omega}, \tag{4.2}$$

where $\mathbf{M}$ is a (symmetric and) positive definite matrix for every θ and φ. The inequality (3.15) then becomes

$$\Big[\frac{1}{\theta\alpha(\theta,\varphi)}\mathbf{Q}^T\nabla\theta + \mathbf{M}(\theta,\varphi)\mathbf{w}\Big]\cdot\boldsymbol{\omega} \le 0. \tag{4.3}$$

Regard the inequality (4.3) in the variable $\boldsymbol{\omega}$ with $\theta, \varphi, \nabla\theta, \nabla\varphi$ as parameters. Since $\mathbf{w}$ is allowed to depend on $\boldsymbol{\omega}$ then we can write

$$[\mathbf{g}_0 + \mathbf{g}(\boldsymbol{\omega})]\cdot\boldsymbol{\omega} \le 0 \tag{4.4}$$

where, of course,

$$\mathbf{g}_0 = \frac{1}{\theta\alpha}\mathbf{Q}^T\nabla\theta, \qquad \mathbf{g}(\boldsymbol{\omega}) = \mathbf{M}\mathbf{w}(\cdot, \boldsymbol{\omega})$$

and $\mathbf{g}$ is assumed to be a C^1 function. The following property allows us to exploit the inequality (4.4).

Lemma 1. *Let V be a finite-dimensional vector space, $\mathbf{g}_0 \in V$ and $\mathbf{g} \in C^1(V,V)$. If (4.4) holds for every $\boldsymbol{\omega} \in V$ then $\mathbf{g}(\boldsymbol{\omega}) = -\mathbf{g}_0 + \mathbf{G}(\boldsymbol{\omega})\boldsymbol{\omega}$ and*

$$\mathbf{g}(\mathbf{0}) = -\mathbf{g}_0, \qquad \boldsymbol{\omega} \cdot \mathbf{G}(\boldsymbol{\omega})\boldsymbol{\omega} \leq 0 \quad \forall \boldsymbol{\omega} \in V.$$

Proof. By analogy with [18], we start from (4.4) in the form

$$[\mathbf{g}_0 + \mathbf{g}(\mathbf{0}) + \hat{\mathbf{g}}(\boldsymbol{\omega})] \cdot \boldsymbol{\omega} \leq 0$$

where $\hat{\mathbf{g}}(\boldsymbol{\omega}) = \mathbf{g}(\boldsymbol{\omega}) - \mathbf{g}(\mathbf{0})$. Since $\mathbf{g}$ is continuous then $|\hat{\mathbf{g}}(\boldsymbol{\omega})| \to 0$ as $|\boldsymbol{\omega}| \to 0$. Hence, for a suitably small $|\boldsymbol{\omega}|$ we can make $\hat{\mathbf{g}}(\boldsymbol{\omega})$ as small as we please and hence the inequality holds only if

$$[\mathbf{g}_0 + \mathbf{g}(\mathbf{0})] \cdot \boldsymbol{\omega} \leq 0.$$

The arbitrariness of the direction of $\boldsymbol{\omega}$ implies that $\mathbf{g}_0 + \mathbf{g}(\mathbf{0}) = \mathbf{0}$. Hence we are left with

$$\hat{\mathbf{g}}(\boldsymbol{\omega}) \cdot \boldsymbol{\omega} \leq 0.$$

Because $\hat{\mathbf{g}} \in C^1(V,V)$ and $\hat{\mathbf{g}}(\mathbf{0}) = \mathbf{0}$ then

$$\hat{\mathbf{g}}(\boldsymbol{\omega}) = \mathbf{G}(\boldsymbol{\omega})\boldsymbol{\omega}$$

where $\mathbf{G}(\boldsymbol{\omega}) = \mathbf{G}_0' + O(\boldsymbol{\omega})$ and $\mathbf{G}_0'$ is the derivative of $\hat{\mathbf{g}}$ at $\boldsymbol{\omega} = \mathbf{0}$. The conclusion then follows. □

As a consequence of Lemma 1 we have

$$\mathbf{g}_0 + \mathbf{g}(\boldsymbol{\omega}) = \hat{\mathbf{g}}(\boldsymbol{\omega}) = \mathbf{G}(\boldsymbol{\omega})\boldsymbol{\omega}.$$

Accordingly, in the present case we can write

$$\mathbf{M}(\theta,\varphi)\mathbf{w}(\cdot,\boldsymbol{\omega}) = -\frac{1}{\theta\alpha(\theta,\varphi)}\mathbf{Q}^T\nabla\theta + \mathbf{G}(\cdot,\boldsymbol{\omega})\boldsymbol{\omega}$$

whence

$$\dot{\boldsymbol{\omega}} = -\mathbf{R}\boldsymbol{\omega} - \mathbf{P}\nabla\theta \tag{4.5}$$

where

$$\mathbf{P}(\theta,\varphi) = \frac{1}{\theta\alpha(\theta,\varphi)}\mathbf{M}^{-1}(\theta,\varphi)\mathbf{Q}^T,$$
$$\mathbf{R}(\cdot,\boldsymbol{\omega}) = -\mathbf{M}^{-1}(\theta,\varphi)\mathbf{G}(\cdot,\boldsymbol{\omega}).$$

The evolution equation (4.5) for $\boldsymbol{\omega}$ has the Cattaneo-Maxwell form and, as we see in a moment, generalizes (2.4), (2.5) and (2.6). By the model equations (4.1) and (4.2) the evolution of φ is governed by

$$\dot{\varphi} = -\nu\Big[\frac{\psi^*_\varphi}{\theta} - \nabla \cdot (\frac{\psi^*_{\nabla\varphi}}{\theta}) - \frac{1}{2\theta}\boldsymbol{\omega} \cdot \mathbf{M}_\varphi\boldsymbol{\omega}\Big]. \tag{4.6}$$

To model the phase transition we require that the evolution equation (4.5) reduce to the standard Fourier law as $\varphi \to 0_+$. To this end we observe that upon the assumptions

$$\lim_{\varphi\to 0_+} \alpha(\theta,\varphi) = 0, \qquad \lim_{\varphi\to 0_+} \mathbf{M}(\theta,\varphi) = 0$$

the variable (3.4) vanishes as $\varphi \to 0_+$. Hence within the state $\sigma = (\theta, \varphi, \boldsymbol{\omega})$ only the pair (θ, φ) is significant and the free energy ψ approaches ψ^*, a function of (θ, φ) only. For simplicity we let $\mathbf{M}$ approach zero as well as $\boldsymbol{\omega}$ does and hence we assume

$$\mathbf{M}(\theta, \varphi) = \alpha(\theta, \varphi)\mathbf{A}(\theta) \tag{4.7}$$

where $\mathbf{A}$ is positive definite for every temperature θ. In addition we let $\mathbf{G}$ be a function of $\theta, \varphi, \boldsymbol{\omega}$ in the form

$$\mathbf{G}(\theta, \varphi, \boldsymbol{\omega}) = -\gamma^2(\theta, \varphi)\mathbf{K}^{-1}(\boldsymbol{\omega}) \tag{4.8}$$

where $\mathbf{K}$ is positive definite for every $\boldsymbol{\omega}$. Upon substitution of (4.7) and (4.8) in (4.5) and (4.6) we have

$$\dot{\boldsymbol{\omega}} = -\frac{\gamma^2(\theta, \varphi)}{\alpha(\theta, \varphi)}\mathbf{A}^{-1}(\theta)\mathbf{K}^{-1}(\boldsymbol{\omega})\boldsymbol{\omega} - \frac{1}{\theta\alpha^2(\theta, \varphi)}\mathbf{A}^{-1}(\theta)\mathbf{Q}^T\nabla\theta, \tag{4.9}$$

$$\dot{\varphi} = -\nu\Big[\frac{1}{\theta}\psi^*_\varphi(\theta, \varphi, \nabla\varphi) - \nabla\cdot(\frac{\psi^*_{\nabla\varphi}(\theta, \varphi, \nabla\varphi)}{\theta}) - \frac{\alpha_\varphi(\theta, \varphi)}{2\theta}\boldsymbol{\omega}\cdot\mathbf{A}(\theta)\boldsymbol{\omega}\Big]. \tag{4.10}$$

We assume that the product $\alpha\gamma$ has a nonzero limit as $\varphi \to 0_+$ and then we let

$$\lim_{\varphi\to 0_+} \alpha^2(\theta, \varphi)\gamma^2(\theta, \varphi) = \lambda(\theta) > 0 \tag{4.11}$$

for each value of θ. Also, let $\mathbf{K}_0 = \mathbf{K}(\mathbf{0})$ and

$$\mathcal{K}(\theta) = \frac{1}{\theta\lambda(\theta)}\mathbf{Q}\mathbf{K}_0\mathbf{Q}^T.$$

Hence we can prove how the Fourier law follows from (4.9) as $\varphi \to 0_+$.

Proposition 2. *The evolution equation (4.9) reduces to the Fourier law in the form*

$$\mathbf{q} = -\mathcal{K}(\theta)\nabla\theta \tag{4.12}$$

as $\varphi \to 0_+$.

Proof. Substitution of $\boldsymbol{\omega}$ from (3.4) into (4.9) and multiplication by $\theta\alpha^2\mathbf{A}$ give

$$\theta\alpha^2(\theta, \varphi)\mathbf{A}(\theta)\dot{\boldsymbol{\omega}} = -\theta\alpha^2(\theta, \varphi)\gamma^2(\theta, \varphi)\mathbf{K}^{-1}(\alpha\mathbf{Q}^{-1}\mathbf{q})\mathbf{Q}^{-1}\mathbf{q} - \mathbf{Q}^T\nabla\theta.$$

The limit as $\varphi \to 0_+$ and the conditions (3.5) and (4.11) provide

$$0 = -\theta\lambda(\theta)\mathbf{K}_0^{-1}\mathbf{Q}^{-1}\mathbf{q} - \mathbf{Q}^T\nabla\theta.$$

Hence it follows the Fourier law (4.12) for $\mathbf{q}$. □

If λ is positive, the positive definiteness of $\mathbf{K}_0$ implies that of $\mathcal{K}(\theta)$ for all θ. In addition, if λ has a nonzero limit then $\mathcal{K}$ has a singularity at $\theta = 0$ so that the heat conductivity approaches infinity as $\theta \to 0$.

Remark 1. The tensor $\mathcal{K}$ is independent of θ, and hence is constant, if

$$\lambda(\theta) = \frac{\lambda_0}{\theta}$$

λ_0 being a positive constant. Also, $\mathcal{K}$ is isotropic if

$$\mathbf{K} = \mathbf{1}, \qquad \mathbf{Q}^T = \mathbf{Q}^{-1}.$$

We now show that, for any value of $\varphi \in (0,1)$, the evolution equation (4.9) generalizes a set of non-stationary heat-conduction models appeared in the literature.

Remark 2. For any value $\varphi = \varphi_0 \in (0,1)$, the heat-conduction model of Morro and Ruggeri [19] follows from (4.9) as a particular case by letting $\mathbf{a} = \boldsymbol{\omega}$, $\mathbf{B} = \mathbf{Q}$, $m^{-1}(\theta) = \alpha(\theta, \varphi_0)\theta^2$ and

$$\mathbf{R}(\theta, \varphi_0) = \mathbf{N}(\theta)/\rho, \qquad \mathbf{P}(\theta, \varphi_0) = m(\theta)\mathbf{1}/\rho.$$

and requiring the positive definiteness of $\mathbf{Q}$. In addition,

$$\mathbf{A}(\theta) = \frac{\rho\theta}{\alpha(\theta, \varphi_0)}\mathbf{Q}^T, \qquad \lambda(\theta) = \alpha^2(\theta, \varphi_0)\gamma^2(\theta, \varphi_0).$$

By replacing $\boldsymbol{\omega}$ with $\alpha\mathbf{Q}^{-1}\mathbf{q}$ via (3.4) we can write the evolution equation (4.9) in the form

$$\dot{\mathbf{q}} = -\mathbf{Q}\Big[\frac{\dot{\alpha}(\theta, \varphi)}{\alpha(\theta, \varphi)}\mathbf{1} + \mathbf{R}(\theta, \varphi)\Big]\mathbf{Q}^{-1}\mathbf{q} - \mathbf{Q}\frac{\mathbf{P}(\theta, \varphi)}{\alpha(\theta, \varphi)}\nabla\theta. \tag{4.13}$$

This form is appropriate for the following

Remark 3. The model set up by Pao and Banerjee [12] is obtained, for any value $\varphi = \varphi_0 \in (0,1)$ by letting α be independent of θ, namely $\alpha(\theta, \varphi_0) = \alpha_0$, so that (4.13) becomes

$$\mathbf{Q}\mathbf{R}^{-1}(\theta, \varphi_0)\mathbf{Q}^{-1}\dot{\mathbf{q}} = -\mathbf{q} - \frac{1}{\alpha_0}\mathbf{Q}\mathbf{R}^{-1}(\theta, \varphi_0)\mathbf{P}(\theta, \varphi_0)\mathbf{P}(\theta, \varphi_0)\nabla\theta.$$

Hence (2.4) follows by making the identifications

$$\mathbf{T}(\theta) = \mathbf{Q}\mathbf{R}^{-1}(\theta, \varphi_0)\mathbf{Q}^{-1}, \qquad \boldsymbol{\mathcal{K}}(\theta) = \frac{1}{\alpha_0}\mathbf{Q}\mathbf{R}^{-1}(\theta, \varphi_0)\mathbf{P}(\theta, \varphi_0).$$

This in turn means that (2.4) is a special case of the present model provided only that $\lambda(\theta) = \alpha_0^2\gamma^2(\theta, \varphi_0)$.

5 A special form of the evolution equations

By analogy with [20] for heat conduction and having in mind applications to superconductivity we now look for a model such that the internal energy e is independent of $\boldsymbol{\omega}$. Let $\alpha_0, \gamma_0, \gamma_1$ and β be positive functions such that

$$\alpha_0, \gamma_0 : \mathbb{R}^+ \to \mathbb{R}^+, \qquad \lim_{\theta\to 0_+} \alpha_0(\theta) = \bar{\alpha}, \qquad \lim_{\theta\to 0_+} \gamma_0(\theta) = \bar{\gamma},$$

$$\gamma_1 : \mathbb{R}^+ \to (0,1], \qquad \lim_{\theta\to 0_+} \gamma_1(\theta) = 1,$$

$$\beta : (0,1] \to (0,1], \qquad \lim_{\varphi\to 0_+} \beta(\varphi) = 0.$$

For simplicity we assume $\mathbf{Q} = \mathbf{1}$ and

$$\alpha(\theta, \varphi) = \alpha_0(\theta)\beta(\varphi) \qquad \forall\theta \in \mathbb{R}^+, \varphi \in [0,1]$$

and

$$\gamma(\theta, \varphi) = \beta^{-1}(\varphi)\gamma_0(\theta)\sqrt{1 - \gamma_1^2(\theta)\beta^2(\varphi)} \qquad \forall\theta \in \mathbb{R}^+, \varphi \in [0,1].$$

Accordingly,

$$\lim \varphi \to 0_+ \alpha^2(\theta,\varphi)\gamma^2(\theta,\varphi) = \alpha_0^2(\theta)\gamma_0^2(\theta)$$

and the condition (4.7) is satisfied by letting

$$\lambda(\theta) = \alpha_0^2(\theta)\gamma_0^2(\theta).$$

In addition we let $\mathbf{A}$ and $\mathbf{K}$ be isotropic, namely

$$\mathbf{A}(\theta) = \mu(\theta)\mathbf{1}, \qquad \mathbf{K}(\boldsymbol{\omega}) = k_0\mathbf{1}$$

where $k_0 > 0$ and $\mu(\theta) > 0$ for all θ. As a consequence, letting

$$d(\theta) = \alpha_0(\theta)\mu(\theta)$$

we can write the free energy in the form

$$\rho\psi = \rho\psi^*(\theta,\varphi,\nabla\varphi) + \frac{1}{2}\beta(\varphi)d(\theta)|\boldsymbol{\omega}|^2.$$

Hence, by (4.1) and (4.9) the evolution of φ and $\boldsymbol{\omega}$ is governed by

$$\dot\varphi = -\nu\Big[\frac{\psi^*_\varphi}{\theta} - \nabla\cdot(\frac{\psi^*_{\nabla\varphi}}{\theta}) + \frac{1}{2\theta}\beta'(\varphi)d(\theta)|\boldsymbol{\omega}|^2\Big], \tag{5.1}$$

$$\dot{\boldsymbol{\omega}} = -\frac{\gamma_0^2(\theta)[1-\beta^2(\varphi)\gamma_1^2(\theta)]}{k_0\beta^3(\varphi)d(\theta)}\boldsymbol{\omega} - \frac{1}{\beta^2(\varphi)d(\theta)\alpha_0(\theta)\theta}\nabla\theta. \tag{5.2}$$

The internal energy e is given by

$$\rho e = \rho(\psi^* - \theta\psi^*_\theta)(\theta,\varphi,\nabla\varphi) + \frac{1}{2}\beta^{1/2}(\varphi)[d(\theta) - \theta d'(\theta)]|\boldsymbol{\omega}|^2.$$

By (3.1) we find that

$$-\rho\theta[\psi^*_{\theta\theta} + \frac{1}{2}\beta^{1/2}(\varphi)d''|\boldsymbol{\omega}|^2]\dot\theta = -\rho e_\varphi\dot\varphi - \rho e_{\nabla\varphi}\nabla\dot\varphi - e_{\boldsymbol{\omega}}\cdot\dot{\boldsymbol{\omega}} - \nabla\cdot\frac{\boldsymbol{\omega}}{\alpha_0(\theta)\beta(\varphi)} + \rho r \tag{5.3}$$

where $\dot\varphi$ and $\dot{\boldsymbol{\omega}}$ in the right-hand side of (5.3) have to be replaced with the right-hand sides of (5.1) and (5.2). In this sense, eqs (5.1)-(5.3) are the evolution equations for $\varphi, \boldsymbol{\omega}, \theta$.

The internal energy e is independent of $\boldsymbol{\omega}$ if and only if $d(\theta)$ is linear, that is $d(\theta) = \theta d_0$, $d_0 > 0$. This in turn implies that $\mu(\theta) = \theta d_0/\alpha_0(\theta)$. In such a case the specific heat,

$$e_\theta = -\theta\psi^*_{\theta\theta}$$

is non-negative provided only that

$$\psi^*_{\theta\theta} \le 0.$$

We now consider two possible functions ψ^* which are suggested by the theory of superconductivity and differ from each other by a temperature-dependent term only. If ψ^* is given by

$$\rho\psi^* = -\frac{1}{12}c\theta^4 - \frac{1}{2}a\varphi^2(1-\theta/\theta_0) + \frac{1}{4}a\varphi^4 + \frac{1}{2}b\theta|\nabla\varphi|^2$$

we obtain

$$-\rho\theta\psi^*_{\theta\theta} = c\theta^3$$

and hence $c\theta^3$ is the specific heat as is the case for the Debye theory at low temperatures. The internal energy becomes

$$\rho e(\theta,\varphi) = \frac{1}{4}c\theta^4 - \frac{1}{2}a\varphi^2 + \frac{1}{4}a\varphi^4.$$

Another function ψ^* can be taken in the form

$$\rho\psi^* = -c\theta\ln(\theta/\theta_0) - \frac{1}{2}a\varphi^2(1-\theta/\theta_0) + \frac{1}{4}a\varphi^4 + \frac{1}{2}b\theta|\nabla\varphi|^2.$$

It follows that

$$-\rho\theta\psi^*_{\theta\theta} = c$$

whence c is the specific heat. Moreover the internal energy is given by

$$\rho e(\theta,\varphi) = c\theta - \frac{1}{2}a\varphi^2 + \frac{1}{4}a\varphi^4.$$

Let now $\beta(\varphi) = \varphi^2$. The evolution equations become

$$\dot{\varphi} = -\nu\varphi\frac{a}{\theta}(\varphi^2 - 1 + \theta/\theta_0) - \nu b\Delta\varphi - \nu\varphi d_0|\boldsymbol{\omega}|^2, \tag{5.4}$$

$$\varphi^4 d_0\dot{\boldsymbol{\omega}} = -\frac{\gamma_0^2(\theta)[1-\gamma_1^2(\theta)\varphi^4]}{k_0\theta\varphi^2}\boldsymbol{\omega} - \frac{1}{\theta^2\alpha_0(\theta)}\nabla\theta. \tag{5.5}$$

To derive the model equation as $\varphi \to 0$ we replace $\boldsymbol{\omega}$ with $\varphi^2\alpha_0(\theta)\mathbf{q}$ in (5.5). Hence we have

$$\varphi^4 d_0\frac{d}{dt}[\varphi^2\alpha_0(\theta)\mathbf{q}] = -\frac{\gamma_0^2(\theta)[1-\gamma_1^2(\theta)\varphi^4]}{k_0\theta}\alpha_0(\theta)\mathbf{q} - \frac{1}{\theta^2\alpha_0(\theta)}\nabla\theta.$$

The limit as $\varphi \to 0$ is now trivial and gives

$$0 = -\frac{\gamma_0^2(\theta)\alpha_0(\theta)}{k_0\theta}\mathbf{q} - \frac{1}{\theta^2\alpha_0(\theta)}\nabla\theta$$

whence we have the Fourier law in the form

$$\mathbf{q} = -\frac{k_0}{\theta\lambda(\theta)}\nabla\theta$$

with a temperature-dependent heat conductivity $k(\theta)$,

$$k(\theta) = \frac{k_0}{\theta\lambda(\theta)}.$$

On the other side, as $\varphi \to 1$ eq. (5.5) gives

$$d_0\dot{\boldsymbol{\omega}} = -\frac{\gamma_0^2(\theta)[1-\gamma_1^2(\theta)]}{k_0\theta}\boldsymbol{\omega} - \frac{1}{\theta^2\alpha_0(\theta)}\nabla\theta. \tag{5.6}$$

Now, time differentiation of (3.4) gives

$$\dot{\boldsymbol{\omega}} = \alpha_0(\theta)\Big[\dot{\mathbf{q}} + \frac{\alpha_0'(\theta)}{\alpha_0(\theta)}\dot{\theta}\mathbf{q}\Big].$$

Substitution of $\dot{\boldsymbol{\omega}}$ in (5.6) provides

$$d_0\dot{\mathbf{q}} = -\Big[\frac{d_0\alpha_0'}{\alpha_0}\dot{\theta} + \frac{\gamma_0^2(1-\gamma_1^2)}{k_0\theta}\Big]\mathbf{q} - \frac{1}{\theta^2\alpha_0^2}\nabla\theta, \tag{5.7}$$

which is an evolution equation for $\mathbf{q}$ of the Cattaneo-Maxwell form. Indeed, (2.6) is recovered through the identifications

$$\alpha(\theta) = \alpha_0(\theta), \qquad \nu' = \frac{1}{d_0 \theta^2 \alpha_0(\theta)}, \qquad \kappa = \frac{k_0}{\lambda(\theta)\theta(1-\gamma_1^2)}.$$

If $\gamma_1 = 1$ then eq. (5.7) reduces to

$$d_0 \dot{\mathbf{q}} = -\frac{d_0 \alpha_0'}{\alpha_0} \dot{\theta} \mathbf{q} - \frac{1}{\theta^2 \alpha_0^2} \nabla \theta,$$

which has still the Cattaneo-Maxwell form but has a peculiar factor $\dot{\theta}$ in the coefficient of $\mathbf{q}$.

The evolution equation (5.4) shows that the transition can be induced by θ or $|\mathbf{q}|^2$. In this regard, for the sake of definiteness we express (5.4) in the form

$$\dot{\varphi} = -\nu \varphi \frac{a}{\theta} [\varphi^2 - 1 + \frac{\theta}{\theta_0} + \frac{d_0}{a} \theta |\mathbf{q}|^2] - \nu b \Delta \varphi.$$

The stationary solutions $\varphi = \bar{\varphi}$ then are given by

$$\bar{\varphi} [\bar{\varphi}^2 - 1 + \frac{\theta}{\theta_0} + \frac{d_0}{a} \theta |\mathbf{q}|^2] = 0.$$

Hence, for any pair of values θ and $|\mathbf{q}|^2$ we have the two solutions

$$\bar{\varphi}_1 = 0, \qquad \bar{\varphi}_2 = \sqrt{1 - \frac{\theta}{\theta_0} - \frac{d_0}{a} \theta |\mathbf{q}|^2}.$$

Of course the solution $\bar{\varphi}_2$ holds provided that

$$1 - \frac{\theta}{\theta_0} - \frac{d_0}{a} \theta |\mathbf{q}|^2 \geq 0. \tag{5.8}$$

In the domain $\mathbb{R}^+ \times \mathbb{R}^+$ for the variables θ, $|\mathbf{q}|$, the inequality (5.8) holds below the curve given by

$$|\mathbf{q}| = \sqrt{\frac{a(\theta_0 - \theta)}{d_0 \theta_0 \theta}}.$$

Hence for any value $\hat{\mathbf{q}}$ of the heat flux the solution $\hat{\varphi}_2$ holds, and the transition occurs, if the temperature is small enough in the sense that

$$\theta \leq \frac{a\theta_0}{a + d_0 \theta_0 |\hat{\mathbf{q}}|^2} \leq \theta_0.$$

Instead, for a fixed value $\hat{\theta}$ of the temperature, $0 < \hat{\theta} < \theta_0$, the transition occurs if $\mathbf{q}$ satisfies the bound

$$|\mathbf{q}|^2 \leq \frac{a}{d_0} [\frac{1}{\hat{\theta}} - \frac{1}{\theta_0}].$$

As a comment, the fact that the transition occurs for suitably small values of $\mathbf{q}$ is the analogue of phase transition in superfluids in which the small valuedness is required for the velocity.

Remark 4. A Cattaneo-Maxwell equation is regarded to provide a hyperbolic equation for the temperature θ whose wave solution is the second sound. Really, depending on the form of the equation, it merely gives a system of equations in $\theta, \mathbf{q}$. For definiteness, let $e = e(\theta)$. Hence (5.7) and (3.1), namely

$$\rho e_\theta \dot{\theta} + \nabla \cdot \mathbf{q} = \rho r,$$

constitute the first-order system of differential equations for θ and $\mathbf{q}$. Usually the equations are not decoupled. In this regard we observe that the divergence of (5.7) and the replacement of $\nabla \cdot \mathbf{q}, \nabla \cdot \dot{\mathbf{q}}$ with $-\rho \dot{e} - \rho r, -\rho \ddot{e} - \rho \dot{r}$ yield

$$\rho d_0 e_\theta \ddot{\theta} - \frac{1}{\theta^2 \alpha_0^2} \Delta\theta - \frac{\rho d_0 \alpha_0'}{\alpha_0} \mathbf{q} \cdot \nabla\dot{\theta} - \Big[d_0 (\alpha_0'/\alpha_0)_\theta + [\gamma_0^2 (1 - \gamma_1^2)/k_0 \theta]_\theta \Big] \mathbf{q} \cdot \nabla\theta + g(\theta, \dot{\theta}, \nabla\theta) = 0, \quad (5.9)$$

where g is a function of the indicated variables. If $\alpha_0' = 0$ and $\gamma_1 = 1$ then eq. (5.9) is a decoupled hyperbolic equation in θ. For discontinuity waves propagating in a state with $\mathbf{q} = 0$ (see [20]), eq. (5.9) implies that the speed of propagation U is given by

$$U^2 = \frac{1}{\rho d_0 e_\theta \theta^2 \alpha_0^2}.$$

6 Conclusions

The transition between different regimes of heat conduction is modelled, as a phase transition of the second kind, through the order parameter φ and the vector field $\boldsymbol{\omega}$ which are regarded as internal variables. Their evolution is then subject to the restrictions placed by thermodynamics.

The phase transition is framed within a phase-field model. Consistent with the nonlocal character of the model, the second law of thermodynamics allows for an entropy extra flux. Upon a standard analysis, the thermodynamic scheme is made complete through a set of sufficient conditions for the entropy flux (see (3.12)) and the evolution functions (see (3.14)-(3.15)).

A free energy in the form (4.2) allows known models to be recovered as particular cases of the evolution equation $\dot{\boldsymbol{\omega}} = \mathbf{w}(\theta, \nabla\theta, \nabla\nabla\theta, \varphi, \nabla\varphi, \nabla\nabla\varphi, \boldsymbol{\omega})$. In addition, further simplifications in §5 provide the transition from the Maxwell-Cattaneo regime, as $\varphi = 1$, to the Fourier regime, as $\varphi = 0$.

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