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A continuum theory for first-order phase transitions based on the balance of structure order

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SUMMARY

First-order phase transitions are modelled by a non-homogeneous, time-dependent scalar-valued order parameter or phase field. The time dependence of the order parameter is viewed as arising from a balance law of the structure order. The gross motion is disregarded and hence the body is regarded merely as a heat conductor. Compatibility of the constitutive functions with thermodynamics is exploited by expressing the second law through the classical Clausius–Duhem inequality. First, a model for conductors without memory is set up and the order parameter is shown to satisfy a maximum theorem. Next, heat conductors with memory are considered. Different evolution problems are established through a system of differential equations whose form is related to the manner in which the memory property is represented. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS: phase changes; evolution equation; structure order; heat conductor

1. INTRODUCTION

In any phase transition, the states of the two phases are endowed with different structures or symmetries. Indeed, for a number of materials, the structure order below a critical temperature is greater than above the temperature. In the solid-fluid transition, the solid phase has a greater structure order due to the crystal symmetry group. In ferromagnetism below the critical temperature, the magnetic moments are aligned, and in superconductivity and superfluidity, the order is associated with the structure of the velocity. Following Landau and Ginzburg [1], we characterize the structure order through an order parameter which is a scalar quantity $\varphi \in [0, 1]$.

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In order to establish ideas, we let φ increase with the structure order so that $\varphi = 0$ in the less-ordered phase. Often φ is identified with the concentration. Hence, for example, in the ice-water transition, φ is the ice concentration and $\varphi = 0$ and 1 in the fluid and solid phases, respectively.

The aim of this paper is to model the evolution of φ as a non-equilibrium phase transition induced by temperature or pressure variations. The evolution is allowed to be non-homogeneous and hence the order parameter φ is a time-dependent field, currently named the phase field.

In this paper, we follow the view that the evolution of φ is a balance law for the structure order. This view may appear reminiscent of those of Fried and Gurtin [2, 3] and Frémond *et al.* (see, e.g. [4, 5]) in which the phase transition is based on a balance equation of microforces. The difference mainly lies in our view of the structure order as a macroscopic and observable quantity that enters a balance equation. Upon appropriate characterizations, the balance law eventually results in the pertinent Ginzburg–Landau equation.

The approaches to the modelling of phase transitions can be characterized through the corresponding framework for compatibility with thermodynamics. In [6], the phase field is viewed as an internal variable and an entropy extra-flux is allowed to enter the second law. The model so established is shown to involve the free energy in the rescaled form (see [7]). In [2, 3], the crucial step is the introduction of microforces and the associated power in the balance of energy, whereas the second law is kept in the classical Clauius–Duhem form. In [5], the modelling equations are established through the principle of virtual power involving the microscopic velocities and the virtual power of acceleration.

In essence, the present approach is based on a further balance law that of the structure order. Such an equation may also be viewed as the evolution equation for the phase field and involves a vector structure flux. Such a vector field is associated with an appropriate power in the energy balance. Compatibility with thermodynamics is proved by expressing the second law in the classical Clausius–Duhem inequality. Preliminarily, we set up a model for materials without memory; next, we insert memory properties for the dependence on the temperature gradient. It is a remarkable result that the evolution equation, for the order parameter, allows us to establish a maximum theorem.

Notation: A superposed dot and ∂_t stand for time differentiation. Also, ∇ is the gradient operator, ∇ is the divergence and Δ is the Laplacian. A prime denotes the derivative with respect to the pertinent variable.

2. BALANCE LAW FOR THE STRUCTURE ORDER

We consider a body \mathscr{B} . The formulation of the balance equations for a material with a structure order, undergoing phase transitions, is established by analogy with the standard balance laws, in continuum mechanics, which may be viewed as the equality among internal and external actions for any part of a body.

Following the general scheme of continua, for any part $S \subset \mathscr{B}$ we let the external structure-order action $\mathscr{A}^{e}(S)$, on the material system in S, consist of a volume part and a surface part, namely

$$\mathscr{A}^{\mathbf{e}}(S) = \int_{\partial S} \mathbf{p} \cdot \mathbf{n} \, \mathrm{d}a + \int_{S} \rho \sigma \, \mathrm{d}v$$

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where **p** is the structure-order flux and σ is the structure-order supply. Let $\mathscr{A}^i(S)$ be the internal structure-order action with density κ per unit mass:

$$\mathscr{A}^{\mathbf{i}}(S) = \int_{S} \rho \kappa \, \mathrm{d}v \tag{1}$$

The balance of structure order is expressed by the equality of the two actions whence, for any $S \subset \mathcal{B}$,

$$\int_{S} \rho \kappa \, \mathrm{d}v = \int_{\partial S} \mathbf{p} \cdot \mathbf{n} \, \mathrm{d}a + \int_{S} \rho \sigma \, \mathrm{d}v$$

The divergence theorem and the arbitrariness of S give the local form

$$\rho \kappa = \nabla \cdot \mathbf{p} + \rho \sigma \tag{2}$$

Multiplying (2) by $\dot{\varphi}$, we obtain

$$\rho \kappa \dot{\phi} + \mathbf{p} \cdot \nabla \dot{\phi} = \nabla \cdot (\mathbf{p} \dot{\phi}) + \rho \sigma \dot{\phi} \tag{3}$$

This suggests that we consider the left-hand side of (3) as the internal power (density) and the right-hand side as the external power:

$$\mathscr{P}^{1} = \rho \kappa \dot{\phi} + \mathbf{p} \cdot \nabla \dot{\phi}, \quad \mathscr{P}^{e} = \nabla \cdot (\mathbf{p} \dot{\phi}) + \rho \sigma \dot{\phi}$$
(4)

The density κ of internal action is allowed to depend on φ and $\dot{\varphi}$ in the form

$$\rho \kappa = \gamma \dot{\varphi} + f(\varphi) + ug(\varphi) \tag{5}$$

where γ is a positive constant, f and g are functions so far unrestricted and u is a parameter controling the transition.

For definiteness, the parameter u may represent the temperature and the pressure in solid-fluid and fluid-vapour transitions, the temperature and the magnetic field in conducting-superconducting transitions, and, possibly, the square of the velocity in turbulence.

Since the structure flux **p** arises because of the inhomogeneity of φ , it is natural to let **p**, be given by the constitutive equation:

$$\mathbf{p} = v\nabla\varphi \tag{6}$$

where v is a positive constant. Also, for simplicity we let $\sigma = 0$.

Owing to (2), (5) and (6), we obtain

$$\gamma \dot{\varphi} + f(\varphi) + ug(\varphi) = v \Delta \varphi \tag{7}$$

which may be viewed as the Ginzburg–Landau equation for the transition. Since we disregard the gross motion, henceforth we look only at phase transitions induced by the temperature. It is then natural to identify u with the ratio of the absolute temperature θ over the (absolute) transition temperature θ_c . Hence, we write

$$\gamma \dot{\varphi} + f(\varphi) + \frac{\theta}{\theta_c} g(\varphi) = v \Delta \varphi \tag{8}$$

Upon the choice (5), Equation (2) may be viewed as the evolution equation for φ . We now need a further differential equation involving θ so that, along with (7), a system of equations for φ and θ is available. That is why we now examine the balance of energy.

3. BALANCE OF ENERGY

Having in mind a thermally induced phase transition, we express the balance of energy by assuming that the external heat action \mathscr{H}^{e} results from a heat flux vector **q** and a heat supply *r*:

$$\mathscr{H}^{\mathbf{e}}(S) = -\int_{\partial S} \mathbf{q} \cdot \mathbf{n} \, \mathrm{d}a + \int_{S} \rho r \, \mathrm{d}v$$

Denote by h the specific internal heat action and

$$\mathscr{H}^{i}(S) = \int_{S} \rho h \, \mathrm{d} v$$

Equality of internal and external actions

$$\int_{S} \rho h \, \mathrm{d}v = -\int_{\partial S} \mathbf{q} \cdot \mathbf{n} \, \mathrm{d}a + \int_{S} \rho r \, \mathrm{d}v$$

for any sub-body S results in

$$\rho h = -\nabla \cdot \mathbf{q} + \rho r \tag{9}$$

The heat flux \mathbf{q} is denoted by the form

$$\mathbf{q} = -k(\theta)\nabla\theta \tag{10}$$

where k is a temperature-dependent conductivity. In the classical Fourier law for heat conductors k is a constant, whereas for insulators, and hence for water [8], k is often assumed to be linear, $k(\theta) = k_0 \theta$.

The internal structure-order density \mathcal{P}^i is viewed as an internal action power and then, by the first law of thermodynamics, we write

$$\rho \dot{e} = \rho h + \mathscr{P}^{i}$$

It then follows from (9) that

$$\rho(\dot{e} - \kappa \dot{\phi}) - \mathbf{p} \cdot \nabla \dot{\phi} = k' |\nabla \theta|^2 + k\Delta \theta + \rho r$$

the prime denoting the derivative.

Let F and G be the integrals of f and g. Upon substitution for κ and **p**, we obtain

$$\rho \dot{e} - \dot{F} - \frac{\theta}{\theta_c} \dot{G} - \gamma \dot{\phi}^2 - \frac{1}{2} v \partial_t |\nabla \phi|^2 = k' |\nabla \theta|^2 + k\Delta \theta + \rho r \tag{11}$$

For convenience we let

$$F(0) = 0, \quad G(0) = 0$$

Also, henceforth we will regard ρ as a constant and hence we let $\rho = 1$.

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4. THERMODYNAMIC RESTRICTIONS

Let η be the entropy density. The second law of thermodynamics is taken in the form of the Clausius–Duhem inequality

$$\dot{\eta}{\geqslant}{-}\nabla\cdot\frac{\mathbf{q}}{\theta}+\frac{\rho r}{\theta}$$

to hold for all functions compatible with (7) and (11).

By replacing $-\nabla \cdot \mathbf{q} + r$ with $\dot{e} - \mathscr{P}^i$ (see (9)) and using the free energy $\psi = e - \theta \eta$, we have

$$\dot{\psi} + \eta \dot{\theta} - \kappa \dot{\phi} - \mathbf{p} \cdot \nabla \dot{\phi} + \frac{1}{\theta} \mathbf{q} \cdot \nabla \theta \leqslant 0$$
(12)

The free energy ψ and the entropy η are assumed to depend on θ , φ , $\nabla \varphi$. Hence upon substitution of \mathscr{P}^i , we obtain

$$(\psi_{\theta} + \eta)\dot{\theta} - \gamma\dot{\phi}^{2} + \left(\psi_{\varphi} - f - \frac{\theta}{\theta_{c}}g\right)\dot{\phi} + (\psi_{\nabla\varphi} - \nu\nabla\varphi) \cdot \nabla\dot{\phi} - \frac{1}{\theta}k|\nabla\theta|^{2} \leqslant 0$$
(13)

We now evaluate the restrictions placed by the second law through (13). The arbitrariness of $\dot{\theta}$ and the linearity in $\dot{\theta}$ imply that

$$\eta = -\psi_{\theta} \tag{14}$$

Now, $\dot{\phi}$ is subject to (7) and hence may be chosen arbitrarily because $\Delta \phi$ does so. The arbitrariness of $\nabla \dot{\phi}$ implies that

$$\psi_{\nabla \phi} = v \nabla \phi \tag{15}$$

Now, letting $\nabla \theta = 0$ we have

$$-\gamma \dot{\phi}^2 + \left(\psi_{\varphi} - f - \frac{\theta}{\theta_c}g\right) \dot{\phi} \leqslant 0$$

If $\psi_{\phi} - f - g\theta/\theta_c \neq 0$, then by letting $|\dot{\phi}|$ be sufficiently small, we conclude that the linear term predominates and hence the inequality is contradicted. Hence, it follows that

$$f + \frac{\theta}{\theta_c}g = \psi_{\varphi} \tag{16}$$

The reduced inequality

$$-\theta\gamma\dot{\phi}^2 - k|\nabla\theta|^2 \leqslant 0$$

holds if and only if

$$\gamma \geqslant 0, \quad k \geqslant 0 \tag{17}$$

Conversely, it is obvious that the restrictions (14)–(17) are sufficient for the validity of the Clausius– Duhem inequality (13), subject to (7) and (11).

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Remark

In other approaches (see [6]), the phase field φ is found to satisfy the differential equation:

$$\dot{\varphi} = -\frac{1}{\gamma} \left[\frac{\psi_{\varphi}}{\theta} - \nabla \cdot \left(\frac{1}{\theta} \psi_{\nabla \varphi} \right) \right]$$

In such a case, the evolution equation (7) follows by letting γ be a constant and

$$\psi = \theta \left[H(\theta) + F(\varphi) + \frac{\theta}{\theta_c} G(\varphi) + \frac{1}{2} \nu |\nabla \varphi|^2 \right]$$

5. SOLID-FLUID TRANSITION

For the sake of definiteness, we have to choose a form of the free energy function ψ . Let

$$B(\theta) = c\theta(\ln \theta - 1)$$

Having in mind the description of the ice-water transition, we mention that the Penrose-Fife model [9] is based on the free energy:

$$\psi_{\rm s}(\theta) = L \frac{\theta - \theta_c}{\theta_c} - B(\theta)$$

for the solid phase and the free energy

$$\psi_{\rm l}(\theta) = -B(\theta)$$

for the liquid phase. This model is corroborated by the feature that the corresponding internal energies e_s , e_l satisfy

$$e_1 = e_s + L$$
, $e_1 = -B(\theta) + \theta B'(\theta)$

L playing the role of latent heat, consistent with the description of first-order transitions. As $\varphi \in [0, 1]$, the free energy is taken as

$$\psi(\theta, \phi) = L \left[h(\phi) \frac{\theta - \theta_c}{\theta_c} + w(\phi) \right] - B(\theta)$$

where h(0) = 0, h(1) = 1 and w(0) = w(1) = 0.

Here, we set up a more detailed model by generalizing the dependence on θ and φ . In view of non-uniform configurations, we define ψ in the form:

$$\psi(\theta, \varphi, \nabla \varphi) = -B(\theta) + F(\varphi) + \frac{\theta}{\theta_c} G(\varphi) + \frac{1}{2} \nu |\nabla \varphi|^2$$

whence the Penrose–Fife model follows by letting $G(\varphi) = Lh(\varphi)$, $F(\varphi) = Lw(\varphi) - G(\varphi)$ and v = 0. By (14), we have

$$\eta(\theta, \varphi) = B'(\theta) - \frac{1}{\theta_c} G(\varphi)$$

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The ice–water transition suggests that we choose (see [6, 10])

$$F(\varphi) = 12L(\frac{1}{4}\varphi^4 - \frac{1}{3}\varphi^3), \quad G(\varphi) = 12L(\frac{1}{4}\varphi^4 - \frac{2}{3}\varphi^3 + \frac{1}{2}\varphi^2)$$
(18)

so that

$$W(\varphi) := F(\varphi) + G(\varphi) = 6L\varphi^2(1-\varphi)^2$$

is the double-well potential with 3L/8 as the maximum value, at $\varphi = \frac{1}{2}$. Hence, we can write the free energy in the form:

$$\psi(\theta, \varphi, \nabla \varphi) = -B(\theta) + W(\varphi) + \frac{\theta - \theta_c}{\theta_c} G(\varphi) + \frac{1}{2} \nu |\nabla \varphi|^2$$

By (14), we have

$$\eta = B'(\theta) - \frac{1}{\theta_c}G(\varphi)$$

and hence, because

$$-B(\theta) + \theta B'(\theta) = c\theta$$

$$e = c\theta + \theta B'(\theta) + F(\varphi) + \frac{1}{2}v|\nabla\varphi|^2$$
(19)

5.1. Latent heat

It is customary to define the latent heat as the minimum energy released or absorbed during a homogeneous and quasi-static change of state. The phase transition occurs at the transition temperature θ_c . Let L be the specific latent heat, per unit mass, and let the phase transition, φ from 1 to 0, occur in the time interval $[t_1, t_2]$, $\varphi(t_1) = 1$, $\varphi(t_2) = 0$. In a uniform configuration, by (19) and (11) we have

$$-\dot{G} - \gamma \dot{\phi}^2 = r$$

Integration over $[t_1, t_2]$ gives

$$\int_{t_1}^{t_2} r \, \mathrm{d}t = -G(0) + G(1) - \gamma \int_{t_1}^{t_2} \dot{\phi}^2 \, \mathrm{d}t$$

For quasi-static processes, the integral of $\dot{\phi}^2$ is as small as we please and, accordingly, we have

$$L = G(1) - G(0)$$

This result is consistent with the definition of L as

$$L = \theta_c [\eta(\theta_c, 0) - \eta(\theta_c, 1)]$$

5.2. Thermal potential

To select the function $C(\theta) = -B(\theta) + \theta B'(\theta)$, we observe that $c(\theta) = C'(\theta)$ is the specific heat. Now, according to the Debye theory the specific heat is a function of the ratio θ/θ_D , θ_D being the

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Debye temperature, namely

$$c(\theta) = \bar{c}D(\theta/\theta_{\rm D}), \quad \bar{c} > 0$$

the function D being defined by

$$D(\xi) = \xi^3 \int_0^{1/\xi} \frac{x^3}{\exp(x) - 1} \, \mathrm{d}x - \frac{1}{4\xi [\exp(1/\xi) - 1]}$$

As θ is much smaller than θ_D , we may use the approximation

$$c(\theta) = c_0 \theta^3, \quad c_0 > 0$$

Correspondingly e, ψ and η take the form

$$e(\theta, \varphi, \nabla\varphi) = \frac{1}{4}c_0\theta^4 + F(\varphi) + \frac{1}{2}\nu|\nabla\varphi|^2$$

$$\psi(\theta, \varphi, \nabla\varphi) = -\frac{1}{12}c_0\theta^4 + F(\varphi) + \frac{\theta}{\theta_c}G(\varphi) + \frac{1}{2}\nu|\nabla\varphi|^2$$

$$\eta(\theta, \varphi) = \frac{1}{3}c_0\theta^3 - \frac{1}{\theta_c}G(\varphi)$$
(20)

At very low temperatures, the electronic contribution to the specific heat is significant and results in a linear term so that

$$c(\theta) = c_0 \theta^3 + c_1 \theta, \quad c_0, c_1 > 0$$

When the linear term becomes predominant, the internal energy and the free energy are quadratic in θ , whereas the entropy is linear.

In the limit of high temperatures, $\theta \gg \theta_D$, the specific heat becomes a constant (Dulong–Petit law) and

$$c(\theta) = \hat{c} > 0, \quad \hat{c} = \frac{1}{3}\bar{c}$$

In such a case

$$e(\theta, \varphi, \nabla \varphi) = \hat{c}\theta + F(\varphi) + \frac{1}{2}\nu|\nabla \varphi|^2$$

$$\psi(\theta, \varphi, \nabla \varphi) = -\hat{c}\theta \ln \theta + F(\varphi) + \frac{\theta}{\theta_c}G(\varphi) + \frac{1}{2}\nu|\nabla \varphi|^2$$

$$\eta(\theta, \varphi) = \hat{c}(1 + \ln \theta) - \frac{1}{\theta}G(\varphi)$$

6. EVOLUTION PROBLEM

We now investigate the evolution problem associated with the phase transition. To this end, we observe that the balance of energy in the form (11) and the choice (20) of *e* give

$$\hat{c}\dot{\theta} - \frac{\theta}{\theta_c}g\dot{\phi} - \gamma\dot{\phi}^2 - k'|\nabla\theta|^2 - k\theta\Delta\theta - r = 0$$
⁽²¹⁾

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Also, by (18) we have $f(\varphi) = \varphi^2(1 - \varphi)$, $g(\varphi) = \varphi(\varphi - 1)^2$. Hence, we can write (8) as

$$\gamma \dot{\varphi} + \varphi(\varphi - 1) \left(\varphi + (\varphi - 1) \frac{\theta}{\theta_c} \right) - v \Delta \varphi = 0$$
⁽²²⁾

Equations (21) and (22) constitute the system of evolution equations for the variables θ , φ .

The *evolution problem* for θ and φ in the domain $\Omega \times [0, T]$ consists of the differential equations (21), (22) and the boundary conditions

 $\theta_{\partial\Omega_1} = \hat{\theta}, \quad \nabla\theta \cdot \mathbf{n}|_{\partial\Omega_2} = 0, \quad \nabla\varphi \cdot \mathbf{n}|_{\partial\Omega} = 0$ (23)

where $\partial \Omega_1$ and $\partial \Omega_2$ are a partition of $\partial \Omega$ such that $\overline{\partial \Omega_1 \cup \partial \Omega_2} = \partial \Omega$ and $\partial \Omega_1 \cap \partial \Omega_2 = \emptyset$.

Theorem 1

Every solution (φ, θ) , $\theta > 0$, to the evolution problem, subject to the initial condition $\varphi(\mathbf{x}, 0) = \varphi_0(\mathbf{x}) \in [0, 1]$, satisfies $\varphi(\mathbf{x}, t) \in [0, 1]$ almost everywhere in $\Omega \times [0, T]$.

Proof

First we show that $\varphi \ge 0$ and next that $\varphi \le 1$. Let

$$\varphi_{-} := \max(-\varphi, 0)$$

Multiply (22) by φ_{-} to obtain

$$\gamma \varphi_{-} \dot{\varphi} = v \nabla \cdot (\varphi_{-} \nabla \varphi) - v \nabla \varphi_{-} \cdot \nabla \varphi + \varphi_{-} \varphi (1 - \varphi) (\varphi + (\varphi - 1)\theta/\theta_{c})$$
(24)

Now,

$$\varphi_{-}\varphi(1-\varphi)(\varphi-1)\theta/\theta_{c} = \begin{cases} 0, & \varphi > 0\\ \varphi^{2}(1-\varphi)^{2}\theta/\theta_{c}, & \varphi < 0 \end{cases}$$

Hence,

$$\psi \varphi_{-} \dot{\varphi} \ge v \nabla \cdot (\varphi_{-} \nabla \varphi) - v \nabla \varphi_{-} \cdot \nabla \varphi + \varphi_{-} \varphi^{2} (1 - \varphi)$$
(25)

Since

$$\dot{\varphi}_{-} = \begin{cases} 0, & \varphi > 0 \\ -\dot{\varphi}, & \varphi < 0 \end{cases}$$

then

 $\varphi_- \dot{\varphi}_- = - \varphi_- \dot{\varphi}$

Likewise

$$\nabla \varphi_{-} \cdot \nabla \varphi_{-} = - \nabla \varphi_{-} \cdot \nabla \varphi$$

Consequently, integration of (25) over Ω and the boundary conditions (23) yield

$$\frac{1}{2} \int_{\Omega} \gamma(\varphi_{-}^2) \, \mathrm{d}\upsilon = -\int_{\Omega} \nu |\nabla \varphi_{-}|^2 \, \mathrm{d}\upsilon - \int_{\Omega} \varphi_{-} \varphi^2 (1-\varphi) \, \mathrm{d}\upsilon$$

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For any $\mathbf{x} \in \Omega$, the initial condition $\varphi(\mathbf{x}, 0) \in [0, 1]$ implies that

$$\varphi_{-}(\mathbf{x}, 0) = 0$$

Integration in time over [0, t] then provides

$$\frac{1}{2} \int_{\Omega} \gamma \varphi_{-}^{2}(\mathbf{x}, t) \, \mathrm{d}v + \int_{0}^{t} \int_{\Omega} [v |\nabla \varphi_{-}|^{2} + \varphi_{-} \varphi^{2} (1 - \varphi)](\mathbf{x}, \tau) \, \mathrm{d}v \, \mathrm{d}\tau \leqslant 0$$

By definition, we have

$$\varphi_{-}(1-\varphi) \ge 0$$

As a consequence, it follows that

$$\int_{\Omega} \gamma \varphi_{-}^{2}(\mathbf{x},t) \, \mathrm{d} v \leqslant 0$$

whence

$$\varphi_{-}(\mathbf{x},t) = 0 \quad \forall \mathbf{x} \in \Omega \ \forall t > 0$$

and then $\phi \ge 0 \forall t > 0$ in Ω . We now show that $\phi \le 1 \forall t > 0$. To this end, multiply (22) by

$$(\varphi - 1)_+ := \max(\varphi - 1, 0)$$

to obtain

$$\gamma(\varphi-1)_{+}\dot{\varphi} = \nu(\varphi-1)_{+}\Delta\varphi + (\varphi-1)_{+}\varphi(1-\varphi)(\varphi+(\varphi-1)\theta/\theta_{c})$$

By paralleling the previous procedure, we have

$$\frac{1}{2}\gamma \int_{\Omega} ((\varphi - 1)_{+}^{2}) \, \mathrm{d}v \leqslant -\nu \int_{\Omega} |\nabla(\varphi - 1)_{+}|^{2} \, \mathrm{d}v - \int_{\Omega} \varphi^{2} (\varphi - 1)_{+}^{2} \, \mathrm{d}v$$

The initial condition $\varphi(\mathbf{x}, 0) \in [0, 1]$ implies that

$$(\varphi - 1)_+(\mathbf{x}, 0) = 0$$

Consequently, integration in time over [0, t] leads to

$$(\varphi - 1)_+(\mathbf{x}, t) = 0 \quad \forall \mathbf{x} \in \Omega \ \forall t > 0$$

and hence $\phi \leq 1 \forall t > 0$ in Ω .

Based upon the approximation that $\gamma \dot{\phi}^2$ and $k |\nabla \theta|^2$ are neglected in (21) and dividing by θ , the balance of energy (21) reduces to

$$\hat{c}\,\partial_t \ln\theta - \frac{1}{\theta_c}g\dot{\phi} - k_0\Delta\theta - \frac{r}{\theta} = 0$$
⁽²⁶⁾

By applying Theorem 1, well posedness of the resulting system of equations (22), (26), with the conditions (23), may be established (see [11]).

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7. HEAT CONDUCTORS WITH MEMORY

We now look at a model of phase transition in rigid heat conductors with memory. A Jeffreys-type conductor (see [12]) obeys the differential equation

$$\dot{\mathbf{q}} + \varepsilon \mathbf{q} = -k_0 \nabla \dot{\theta} - \varepsilon k_1 \nabla \theta \tag{27}$$

This equation provides a Fourier law both in the fast limit, i.e. $\varepsilon \to 0$, and in the slow limit, i.e. $\varepsilon \to \infty$,

$$\mathbf{q} \rightarrow -k_0 \nabla \theta$$
, $\mathbf{q} \rightarrow -k_1 \nabla \theta$

Integration of (27) over $(-\infty, t)$ yields

$$\mathbf{q}(t) = -k_0 \nabla \theta(t) - \int_0^\infty k_\varepsilon(s) \nabla \theta(t-s) \, \mathrm{d}s$$

where

$$k_{\varepsilon}(s) = \varepsilon(k_0 - k_1) \exp(-\varepsilon s), \quad s \in \mathbb{R}^+$$

By paralleling non-linear generalizations of the Maxwell–Cattaneo model (see [13, 14]), we consider the vector variable

$$\mathbf{v} = \alpha(\theta) \mathbf{q}$$

and let \mathbf{v} be given by the evolution equation:

$$\dot{\mathbf{v}} + \varepsilon \mathbf{v} = -k_0 \nabla \theta - \varepsilon k_1 \nabla \theta$$

Upon integration over $(-\infty, t]$, we have

$$\mathbf{q}(t) = -\frac{1}{\alpha(\theta(t))} \left[k_0 \nabla \theta(t) + \int_0^\infty k_\varepsilon(s) \nabla \theta(t-s) \, \mathrm{d}s \right]$$

The identifications

$$k(\theta) = \frac{k_0}{\alpha(\theta)}, \quad h(s) = \frac{k_{\varepsilon}(s)}{k_0}$$

allow **q** to be given by

$$\mathbf{q}(t) = -k(\theta(t)) \left[\nabla \theta(t) + \int_0^\infty h(s) \nabla \theta(t-s) \,\mathrm{d}s \right]$$
(28)

The constitutive equation (28) shows that **q** depends on the actual value $\nabla \theta(t)$ and on the history of $\nabla \theta$ through the same conductivity coefficient $k(\theta)$. As a comment, the linear model by Coleman and Gurtin [15] is recovered by letting the conductivity *k* be a constant.

We assume $h \in W^{2,1}(\mathbb{R}^+) \cap H^1(\mathbb{R}^+)$. Also, to simplify the notation, henceforth we let $\mathbf{g} = \nabla \theta$ and denote by \mathbf{g}^t the history up to the time *t*, i.e.

$$\mathbf{g}^t(\mathbf{x},s) := \mathbf{g}(\mathbf{x},t-s), \quad s \in \mathbb{R}^+$$

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For later developments, it is convenient to consider

$$\tilde{\mathbf{g}}^{t}(s) = \int_{0}^{s} \mathbf{g}(t-\xi) \,\mathrm{d}\xi = \int_{t-s}^{t} \mathbf{g}(\tau) \,\mathrm{d}\tau$$

we call \tilde{g} the summed history of **g**. By definition,

$$\partial_s \tilde{\mathbf{g}}^t(s) = \mathbf{g}^t(s), \quad \partial_t \tilde{\mathbf{g}}^t(s) = \mathbf{g}(t) - \mathbf{g}^t(s)$$

An integration by parts gives

$$\int_0^\infty h(s)\mathbf{g}^t(s)\,\mathrm{d}s = -\int_0^\infty h'(s)\tilde{\mathbf{g}}^t(s)\,\mathrm{d}s$$

Hence, we can write (28) as

$$\mathbf{q}(t) = -k(\theta(t)) \left[\mathbf{g}(t) - \int_0^\infty h'(s) \tilde{\mathbf{g}}^t(s) \,\mathrm{d}s \right]$$
(29)

The balance of energy (9) then becomes

$$\dot{e} - \dot{F}(\varphi) - \frac{\theta}{\theta_c} \dot{G}(\varphi) - \gamma \dot{\varphi}^2 - v \partial_t \frac{1}{2} |\nabla \varphi|^2$$
$$= k\Delta \theta + k' |\mathbf{g}|^2 - k\nabla \cdot \int_0^\infty h'(s) \tilde{\mathbf{g}}^t(s) \, \mathrm{d}s - k' \mathbf{g} \cdot \int_0^\infty h'(s) \tilde{\mathbf{g}}^t(s) \, \mathrm{d}s + r \tag{30}$$

the dependence on the present time t being understood. Once we specify the form of the internal energy e, Equation (30) results in an evolution equation coupled with the Ginzburg-Landau equation (8).

7.1. Thermodynamic potentials

By (29) we can write

$$\mathbf{q}(t) = -k(\theta(t))[\mathbf{g}(t) + \mathbf{w}(\tilde{\mathbf{g}}^t)]$$
(31)

where the functional $\mathbf{w}(\tilde{\mathbf{g}}^t)$ is defined by

$$\mathbf{w}(\tilde{\mathbf{g}}^t) = -\int_0^\infty h'(s)\tilde{\mathbf{g}}^t(s)\,\mathrm{d}s$$

For definiteness, we now choose particular forms of the free energy and examine the corresponding thermodynamic restrictions associated with the functional dependence (31).

Let the free energy depend on the present value of θ , φ , $\nabla \varphi$ and on the summed history $\tilde{\mathbf{g}}^t$, which means that we regard $s = (\theta, \varphi, \nabla \varphi, \tilde{\mathbf{g}})$ as the state. The dependence on *s* is assumed in the additive form:

$$\psi(t) = \overline{\psi}(\theta(t), \varphi(t), \nabla \varphi(t)) + \Psi(\widetilde{\mathbf{g}}^t)$$

where $\bar{\psi}$ and Ψ are non-negative and subject to

$$\psi(0, 0, 0) = 0, \quad \Psi(0) = 0$$

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If $\mathbf{g}(\cdot)$ is a zero function, then (12) becomes

$$\dot{\bar{\psi}} + \eta \dot{\theta} - \kappa \dot{\phi} - \mathbf{p} \cdot \nabla \dot{\phi} \leqslant 0$$

Accordingly, the relations

$$\eta = -\bar{\psi}_{\theta}, \quad v\nabla \varphi = \bar{\psi}_{\nabla \varphi}, \quad f + \frac{\theta}{\theta_c}g = \bar{\psi}_{\varphi}$$

are required to hold. As a consequence, (12) reduces to

$$\partial_t \Psi(\tilde{\mathbf{g}}^t) + \frac{1}{\theta(t)} \mathbf{q}(t) \cdot \mathbf{g}(t) \leqslant 0$$
(32)

If Ψ is differentiable, then

$$\partial_t \Psi(\tilde{\mathbf{g}}^t) = \delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}(t) - \mathbf{g}^t)$$

 δ denoting the Fréchet differential. By the linearity of the differential, we can write

$$\partial_t \Psi(\tilde{\mathbf{g}}^t) = \mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t) - \delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}^t)$$

where J_g is the operator defined by

$$\mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t) = \delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}(t))$$

Hence, (32) gives

$$\left[\mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^{t}) - \frac{k}{\theta}(t)\mathbf{w}(\tilde{\mathbf{g}}^{t})\right] \cdot \mathbf{g}(t) - \delta \Psi(\tilde{\mathbf{g}}^{t}|\mathbf{g}^{t}) - \frac{k}{\theta}(t)\mathbf{g}^{2}(t) \leqslant 0$$
(33)

Let $\mathbf{J}_{\mathbf{g}}$ and $\delta \Psi$ be continuous functionals. We can arbitrarily change $\mathbf{g}(t)$ and meanwhile the change of $\mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^t)$, $\delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}^t)$ and $\mathbf{w}(\tilde{\mathbf{g}}^t)$ can be as small as we choose. This implies that (33) holds only if

$$\left[\mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^{t}) - \frac{k}{\theta}(t)\mathbf{w}(\tilde{\mathbf{g}}^{t})\right] \cdot \mathbf{g}(t) - \frac{k}{\theta}(t)\mathbf{g}^{2}(t) \leqslant 0, \quad \delta \Psi(\tilde{\mathbf{g}}^{t}|\mathbf{g}^{t}) \geqslant 0$$

Moreover, the arbitrariness of $\mathbf{g}(t)$ implies that

$$\mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^{t}) - \frac{k}{\theta}(t)\mathbf{w}(\tilde{\mathbf{g}}^{t}) = 0, \quad k \ge 0$$
(34)

Conversely, (34) and

$$\delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}^t) \ge 0 \tag{35}$$

are sufficient for the validity of (33) and hence of (32).

It follows from (34) that k/θ has to be independent of θ . As a consequence, assuming that Ψ is a functional on $\tilde{\mathbf{g}}^t$ only amounts to letting k/θ be a constant, namely

$$k(\theta) = k_0 \theta$$

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By (34), we have

$$\mathbf{w}(\tilde{\mathbf{g}}^t) = \frac{1}{k_0} \mathbf{J}_{\mathbf{g}}(\tilde{\mathbf{g}}^t)$$

which shows that the history-dependent heat flux is determined by $\delta \Psi$. The inequality in (35) is a restriction on the dissipation part.

If the transition temperature is much smaller than θ_D , then it is reasonable to assume that

$$e_{\theta} = c\theta, \quad c > 0$$

We can then represent the functionals for free energy, entropy and internal energy in the form:

$$\begin{split} \psi &= -\frac{1}{2}c\theta^2 + F(\varphi) + \frac{\theta}{\theta_c}G(\varphi) + \frac{1}{2}v|\nabla\varphi|^2 + \Psi(\tilde{\mathbf{g}}^t)\\ \eta &= c\theta - \frac{1}{\theta_c}G(\varphi)\\ e &= F(\varphi) + \frac{1}{2}v|\nabla\varphi|^2 + \frac{1}{2}c\theta^2 + \Psi(\tilde{\mathbf{g}}^t) \end{split}$$

If, instead, the transition temperature is larger than θ_D , then we regard the specific heat as a constant, c. Accordingly, we take the free energy in the form

$$\psi = -c\theta \ln \theta + F(\varphi) + \frac{\theta}{\theta_c}G(\varphi) + \frac{1}{2}\nu|\nabla\varphi|^2 + \Psi(\tilde{\mathbf{g}}^t)$$

whence we have

$$\eta = c(1 + \ln \theta)\theta - \frac{1}{\theta_c}G(\varphi)$$

$$e = F(\varphi) + \frac{1}{2}v|\nabla\varphi|^2 + c\theta + \Psi(\tilde{\mathbf{g}}^t)$$
(36)

8. FREE ENERGIES FOR THE SUMMED HISTORIES

We look again at the constitutive equation (29) for **q**. Since

$$\frac{\mathrm{d}}{\mathrm{d}t}\Psi(\tilde{\mathbf{g}}^t) = k_0 \mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t) - \delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}^t)$$
(37)

by (35) it follows that

$$\frac{\mathrm{d}}{\mathrm{d}t}\Psi(\tilde{\mathbf{g}}^t) \leqslant k_0 \mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t)$$
(38)

We now ascertain that there are functionals satisfying (38).

First, we consider the maximum free energy Ψ_M , analogous to that for linear viscoelasticity [16], in the form:

$$\Psi_{\rm M}(\tilde{\mathbf{g}}^t) = \frac{1}{2} k_0 \int_0^\infty \int_0^\infty h''(|s_1 - s_2|) \tilde{\mathbf{g}}^t(s_1) \cdot \tilde{\mathbf{g}}^t(s_2) \, \mathrm{d}s_1 \, \mathrm{d}s_2$$

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where h is subject to

$$\int_0^\infty h(\xi) \cos \omega \xi \, \mathrm{d}\xi \ge 0 \tag{39}$$

Hence, Ψ_M proves to be non-negative. We denote by D_M the domain of Ψ_M namely

$$D_{\mathrm{M}} = \{ \tilde{\mathbf{g}}^{t} : \Psi_{\mathrm{M}}(\tilde{\mathbf{g}}^{t}) < \infty \}$$

A direct calculation shows that (38) holds as an equality:

$$\partial_t \Psi_{\mathbf{M}}(\tilde{\mathbf{g}}^t) = k_0 \mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t)$$

The maximum property of Ψ_M is characterized by

$$\Psi_{\mathrm{M}}(\tilde{\mathbf{g}}^{t}) \geqslant \Psi(\tilde{\mathbf{g}}^{t}) \quad \forall \tilde{\mathbf{g}}^{t} \in D_{\mathrm{M}}$$

A second functional, Ψ_G , is the analogue of the Graffi–Volterra free energy in linear viscoelasticity. It is given by

$$\Psi_{\rm G}(\tilde{\mathbf{g}}^t) = -\frac{k_0}{2} \int_0^\infty h'(s) \tilde{\mathbf{g}}^t(s) \cdot \tilde{\mathbf{g}}^t(s) \,\mathrm{d}s$$

where $h \in C^2(\mathbb{R}^+)$ is subject to

$$h'(s) < 0, \quad h''(s) \ge 0 \tag{40}$$

and hence satisfies (39). We denote by $D_{\rm G}$ the domain of definition:

$$D_{\mathrm{G}} = \{ \tilde{\mathbf{g}}^t : \Psi_{\mathrm{G}}(\tilde{\mathbf{g}}^t) < \infty \}$$

As proved in [17], along the lines of [18], if

$$\alpha h'(s) + h''(s) \ge 0, \quad s \in \mathbb{R}^+ \tag{41}$$

for some $\alpha \ge 0$, then

$$\partial_t \Psi_{\mathcal{G}}(\tilde{\mathbf{g}}^t) \leqslant -\alpha \Psi_{\mathcal{G}}(\tilde{\mathbf{g}}^t) + k_0 \mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t)$$
(42)

It is easy to check that

$$\delta \Psi_{\mathbf{G}}(\tilde{\mathbf{g}}^t|\mathbf{g}^t) = -k_0 \int_0^\infty h'(s)\tilde{\mathbf{g}}^t(s) \cdot \mathbf{g}^t(s) \,\mathrm{d}s = \frac{k_0}{2} \int_0^\infty h''(s)\tilde{\mathbf{g}}^t(s) \cdot \tilde{\mathbf{g}}^t(s) \,\mathrm{d}s \ge 0$$

whence (38) holds.

A further free energy, which is the minimum one, Ψ_m is considered in [19] borrowing from the Golden representation of the free energy for viscoelastic materials [20] (see [21]).

A free energy functional, which proves convenient for applications, arises from a different description of the fading memory. Hence, we let $t = t_0 + \tau$, regard t_0 as an initial time, possibly $t_0 = 0$. Based upon an integration by parts, we can write

$$\mathbf{w}(\tilde{\mathbf{g}}^{t_0+\tau}) = \int_0^\infty h(s) \mathbf{g}^{t_0+\tau}(s) \,\mathrm{d}s$$

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Now,

$$\int_0^\infty h(s) \mathbf{g}^{t_0 + \tau}(s) \, \mathrm{d}s = \int_0^\tau h(s) \mathbf{g}^{t_0 + \tau}(s) \, \mathrm{d}s + \int_\tau^\infty h(s) \mathbf{g}^{t_0 + \tau}(s) \, \mathrm{d}s$$
$$= \int_0^\tau h(s) \mathbf{g}^{t_0 + \tau}(s) \, \mathrm{d}s + \int_0^\infty h(\tau + \xi) \mathbf{g}^{t_0}(\xi) \, \mathrm{d}\xi$$

and hence a further integration by parts gives

$$\mathbf{w}(\tilde{\mathbf{g}}^{t_0+\tau}) = \int_0^\tau h(s) \mathbf{g}^{t_0+\tau}(s) \,\mathrm{d}s - \mathbf{I}^{t_0}(\tau) \tag{43}$$

where

$$\mathbf{I}^{t_0}(\tau) := \int_0^\infty h'(\tau + \xi) \tilde{\mathbf{g}}^{t_0}(\xi) \,\mathrm{d}\xi$$

The conceptual and operative meaning of (43) is apparent. For any function **g**, we have

$$\mathbf{w}(\tilde{\mathbf{g}}^{t_0}) = -\mathbf{I}^{t_0}(0)$$

Also, if $\mathbf{g} = 0$ in $(t_0, t_0 + \tau)$ then

$$\mathbf{w}(\tilde{\mathbf{g}}^{t_0+\tau}) = -\mathbf{I}^{t_0}(\tau)$$

This means that $-\mathbf{I}^{t_0}(0)$ is the initial value of **w** at time t_0 and, moreover, $-\mathbf{I}^{t_0}(\tau)$ is the value of **w** at time $t_0 + \tau$ if **g** vanishes in $(t_0, t_0 + \tau)$. By (43) the response of the material, at $t_0 + \tau$, is given by $\mathbf{I}^{t_0}(\tau)$ and the function **g** on $[t_0, t_0 + \tau)$. Hence, following the lines of [22-24], we regard the state at time $t_0 + \tau$ as the pair of $\mathbf{I}^t(\tau)$ and the process **g** on $[t_0, t_0 + \tau)$. This is because the state is required for determining a unique response of the material to a given process.

By

$$\mathbf{I}^{t}(\tau) = \int_{0}^{\infty} h'(\tau + \xi) \tilde{\mathbf{g}}^{t}(\xi) \, \mathrm{d}\xi = -\int_{0}^{\infty} h(\tau + \xi) \mathbf{g}^{t}(\xi) \, \mathrm{d}\xi$$

we can view \mathbf{I}^t as determined by the summed history $\tilde{\mathbf{g}}^t$ or by \mathbf{g}^t . Moreover, we have

$$\mathbf{w}(\tilde{\mathbf{g}}^t) = -\mathbf{I}^t(0)$$

Also we can define the functional Ψ_{I} on I^{t} in the form

$$\Psi_{\mathbf{I}}(\mathbf{I}^{t}) = -\frac{k_{0}}{2} \int_{0}^{\infty} [h'(\tau)]^{-1} \partial_{\tau} \mathbf{I}^{t}(\tau) \cdot \partial_{\tau} \mathbf{I}^{t}(\tau) \,\mathrm{d}\tau \tag{44}$$

We now show that Ψ_{I} is a free energy.

A direct evaluation shows that

$$\partial_t \mathbf{I}^t(\tau) = -h(\tau)\mathbf{g}(t) + \partial_\tau \mathbf{I}^t(\tau)$$
(45)

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By using the exchange of the order of differentiation, identity (45) and an integration by parts we obtain

$$\dot{\psi}_{\mathbf{I}}(\mathbf{I}^{t}) = k_{0}\mathbf{g}(t) \cdot \mathbf{w}(\tilde{\mathbf{g}}^{t}) - \frac{k_{0}}{2} \left[\frac{1}{h'(\tau)} \partial_{\tau} \mathbf{I}^{t}(\tau) \cdot \partial_{\tau} \mathbf{I}^{t}(\tau) \right]_{0}^{\infty} - \Phi_{\mathbf{I}}(\mathbf{I}^{t})$$

where

$$\Phi_{\mathbf{I}}(\mathbf{I}^{t}) = \frac{k_{0}}{2} \int_{0}^{\infty} \frac{h''(\tau)}{[h'(\tau)]^{2}} \partial_{\tau} \mathbf{I}^{t}(\tau) \cdot \partial_{\tau} \mathbf{I}^{t}(\tau) \, \mathrm{d}\tau$$

Because of the assumption $h'' \ge 0$, we have

$$\Phi_{\mathrm{I}}(\mathbf{I}^t) \geqslant 0 \tag{46}$$

Let $\mu = -h'$ and hence $\mu > 0$. Since

$$\partial_{\tau} \mathbf{I}^{t}(\tau) = \int_{0}^{\infty} \mu(\tau + \xi) \mathbf{g}(t - \xi) \,\mathrm{d}\xi$$

we can write

$$\begin{bmatrix} \frac{1}{h'(\tau)} \partial_{\tau} \mathbf{I}^{t}(\tau) \cdot \partial_{\tau} \mathbf{I}^{t}(\tau) \end{bmatrix}_{0}^{\infty} = -\lim_{\tau \to \infty} \left[\int_{0}^{\infty} \frac{\mu(\tau+\xi)}{\sqrt{\mu(\tau)}} \mathbf{g}^{t}(\xi) \, \mathrm{d}\xi \right]^{2} + \frac{1}{\mu(0)} \left[\int_{0}^{\infty} \mu(\xi) \mathbf{g}^{t}(\xi) \, \mathrm{d}\xi \right]^{2}$$
$$\geqslant -\lim_{\tau \to \infty} \left[\int_{0}^{\infty} \frac{\mu^{2}(\tau+\xi)}{\mu(\tau)\mu(\xi)} \, \mathrm{d}\xi \right] \int_{0}^{\infty} \mu(\xi) |\mathbf{g}^{t}(\xi)|^{2} \, \mathrm{d}\xi$$

Provided that

$$\int_0^\infty \mu(\xi) |\mathbf{g}^t(\xi)|^2 \,\mathrm{d}\xi < \infty$$

and

$$\lim_{\tau \to \infty} \int_0^\infty \frac{\mu^2(\tau + \xi)}{\mu(\tau)\mu(\xi)} \, \mathrm{d}\xi = 0 \tag{47}$$

we conclude that

$$\left[\frac{1}{h'(\tau)}\partial_{\tau}\mathbf{I}^{t}(\tau)\cdot\partial_{\tau}\mathbf{I}^{t}(\tau)\right]_{0}^{\infty} \ge 0$$
(48)

By (46) and (48) we find that

 $\dot{\psi}_{\mathbf{I}}(\mathbf{I}^t) \leqslant k_0 \mathbf{g}(t) \cdot \mathbf{w}(\tilde{\mathbf{g}}^t)$

and hence conclude that Ψ_I is a free-energy functional.

To ascertain that (47) may hold, we consider a function μ such that

$$\mu(\tau + \xi) \leqslant f(\tau)\mu(\xi) \quad \forall \tau, \xi \ge 0 \tag{49}$$

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where f is subject to

$$f(\tau) > 0, \quad f(0) \ge 1, \quad \lim_{\tau \to \infty} f(\tau) = 0, \quad \int_0^\infty f(\xi) \, \mathrm{d}\xi = F < \infty$$

The trivial integration gives

$$\int_0^\infty \frac{\mu^2(\tau+\xi)}{\mu(\tau)\mu(\xi)} \,\mathrm{d}\xi \leqslant \int_0^\infty f(\tau)f(\xi) \,\mathrm{d}\xi = Ff(\tau)$$

whence (47) follows. In particular, $f(\tau) = \exp(-\alpha\tau)$ may be considered and, in such a case, the condition (49) is equivalent to (41).

By (48), we can write

$$\dot{\psi}_{\mathbf{I}}(\mathbf{I}^t) \leqslant k_0 \mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t) - \Phi_{\mathbf{I}}(\mathbf{I}^t)$$

If (41), we have

$$0 \leqslant \frac{h''}{[h']^2} + \alpha \frac{h'}{[h']^2} = \frac{h''}{[h']^2} + \alpha [h']^{-1}$$

Hence, we have

 $\Phi_I{\geqslant}\alpha\Psi_I$

whence

$$\dot{\psi}_{\mathbf{I}}(\mathbf{I}^t) \leq k_0 \mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t) - \alpha \Psi_{\mathbf{I}}(\mathbf{I}^t)$$

The set of free energies is convex and the domains of the free-energy functionals $\mathscr{D}\Psi$ depend on the functional under consideration. Indeed, we can show that

$$\mathscr{D}\Psi_M \subset \mathscr{D}\Psi_G \subset \mathscr{D}\Psi_I \subset \mathscr{D}\Psi_m$$

and the values of the functionals are related by

$$\Psi_{\mathrm{m}}(\tilde{\mathbf{g}}^{t}) \leqslant \Psi_{\mathrm{I}}(\mathbf{I}^{t}) \leqslant \Psi_{\mathrm{G}}(\tilde{\mathbf{g}}^{t}) \leqslant \Psi_{\mathrm{M}}(\tilde{\mathbf{g}}^{t})$$

With any free energy Ψ , we can associate a seminorm in \mathscr{D}_{Ψ} by

$$\|\tilde{\mathbf{g}}^t\|^2 = \frac{2}{k_0} \Psi(\tilde{\mathbf{g}}^t) \tag{50}$$

Moreover, the constitutive functional (29) for **q** is continuous relative to the seminorm (50).

As with any system with memory, the state is infinite dimensional and the associated stability properties may depend on the selected norm. It follows from definition (50) that if

$$\Psi_a(\tilde{\mathbf{g}}^t) \leqslant \Psi_b(\tilde{\mathbf{g}}^t)$$

then

$$\mathscr{D}\Psi_b \subseteq \mathscr{D}\Psi_a$$

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Hence, if the system is stable relative to the Ψ_b -norm then it is stable also relative to the Ψ_a -norm. The converse is not true.

With this in mind, proving stability properties relative to Ψ_I is convenient in two respects. First, stability holds in a domain, \mathscr{D}_I , which is larger than those for Ψ_G and Ψ_M . Secondly, Ψ_I is defined on \mathbf{I}^t , which is the minimal state of the system.

9. EVOLUTION PROBLEMS IN CONDUCTORS WITH MEMORY

In this section, we investigate the system of differential equations, for a first-order phase transition, for a heat conductor with memory modelled by (28), in a smooth three-dimensional region Ω . Upon substitution of *e* from (36) into the balance equation (30), and observing that

$$\frac{\mathrm{d}}{\mathrm{d}t}\Psi(\tilde{\mathbf{g}}^t) = \frac{k}{\theta}(t)\mathbf{w}(\tilde{\mathbf{g}}^t) \cdot \mathbf{g}(t) - \delta\Psi(\tilde{\mathbf{g}}^t|\mathbf{g}^t)$$

we have

$$c\dot{\theta} - \delta\Psi(\tilde{\mathbf{g}}^{t}|\mathbf{g}^{t}) - \frac{\theta}{\theta_{c}}g(\varphi)\dot{\varphi} - \gamma\dot{\varphi}^{2} = k(\theta)\Delta\theta + k'(\theta)|\mathbf{g}|^{2} + k(\theta)\nabla\cdot\mathbf{w}(\tilde{\mathbf{g}}^{t}) + r$$
(51)

Again we let k/θ be a constant, k_0 . Moreover, having in mind evolutions near equilibrium $(\mathbf{g}=0, \dot{\phi}=0)$, we make the approximation that $\dot{\phi}^2$ and $|\nabla \theta|^2$ are negligible. With appropriate assumptions on h, at least for Ψ_M , Ψ_G , Ψ_I , we can show that

$$\delta \Psi(\tilde{\mathbf{g}}^t | \mathbf{g}^t) \leqslant C(h) \sup_{s \in [0,\infty)} |\mathbf{g}^t(s)|^2$$

thus proving that $\delta \Psi$ is negligible if so is $|\mathbf{g}(t)|^2$ at any time t > 0. Hence, upon dividing throughout by θ , we can write the approximate version of (55) as

$$\frac{c}{\theta}\dot{\theta} - \frac{1}{\theta_c}g(\phi)\dot{\phi} = k_0\Delta\theta + k_0\nabla\cdot\mathbf{w}(\tilde{\mathbf{g}}^t) + \frac{r}{\theta}$$
(52)

whence

$$\partial_t \left[c \ln \theta - \frac{1}{\theta_c} G(\varphi) \right] = k_0 \Delta \theta + k_0 \nabla \cdot \int_0^\infty h(s) \nabla \theta(t-s) \, \mathrm{d}s + \frac{r}{\theta}$$
(53)

where g = G'. In the terminology of, e.g. [4] (see also [25]), Equation (59) would be referred to as the entropy equation. It has to be associated with the Ginzburg–Landau equation (7), within the evolution problem, as follows.

Problem 1

The past history of θ up to t = 0 is known, $\theta(-s) = \hat{\theta}(s)$, s > 0. We denote the known function by R

$$R(t) = \frac{r(t)}{\theta(t)} + k_0 \nabla \cdot \int_0^\infty h(t+\xi) \nabla \hat{\theta}(\xi) \,\mathrm{d}\xi$$

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The state of the material at time t is given by the pair $(\theta(t), \varphi(t))$. The state evolution is governed by the system of differential equations

$$\partial_t \left[c \ln \theta - \frac{1}{\theta_c} G(\varphi) \right] = k_0 \Delta \theta + k_0 \nabla \cdot \int_0^t \nabla \theta(t - s) \, \mathrm{d}s + R$$
$$\gamma \partial_t \varphi + f(\varphi) + \frac{\theta}{\theta_c} g(\varphi) = v \Delta \varphi$$

subject to the boundary and initial conditions

$$\theta = \theta_{\partial\Omega}, \quad \nabla \varphi \cdot \mathbf{n} = 0 \text{ on } \partial\Omega$$
$$\theta(0) = \theta_0, \quad \varphi(0) = \varphi_0 \text{ in } \Omega$$

Heretofore, the dependence on the position $\mathbf{x} \in \Omega$ is understood and not written.

9.1. Evolution equations in the history-space setting

We now set up a different scheme by viewing $\tilde{\mathbf{g}}^t$ as a part of the state that accounts for the history of \mathbf{g} up to time t. This is made possible by the feature that different summed histories $\tilde{\mathbf{g}}^t$ produce different response functions \mathbf{I}^t .

The summed history $\tilde{\mathbf{g}}^t$ satisfies a differential equation of the transport type,

$$\partial_t \tilde{\mathbf{g}}^t(s) + \partial_s \tilde{\mathbf{g}}^t(s) = \mathbf{g}(t) \tag{54}$$

and the boundary condition

 $\tilde{\mathbf{g}}^t(0) = 0$

Since (52) can be written in the form

$$\nabla \cdot \mathbf{w}(\tilde{\mathbf{g}}^t) = k_0 \nabla \cdot \int_0^\infty \mu(s) \tilde{\mathbf{g}}^t(s) \, \mathrm{d}s$$

in view of (52), (7) and (62), we can state the evolution problem as follows.

Problem 2

Represent the state of the material, at time t, by the triplet $(\theta(t), \varphi(t), \tilde{g}^t)$. Hence, the evolution of the state is governed by the system of differential equations:

$$\partial_t \left[c \ln \theta - \frac{1}{\theta_c} G(\varphi) \right] = k_0 \Delta \theta + k_0 \nabla \cdot \int_0^\infty \mu(s) \tilde{\mathbf{g}}^t(s) \, \mathrm{d}s + \frac{r}{\theta}$$
$$\gamma \partial_t \varphi + f(\varphi) + \frac{\theta}{\theta_c} g(\varphi) = v \Delta \varphi$$
$$\partial_t \tilde{\mathbf{g}}^t(s) = \nabla \theta(t) - \partial_s \tilde{\mathbf{g}}^t(s)$$

subject to the boundary conditions

$$\theta = \theta_{\partial\Omega}, \quad \nabla \varphi \cdot \mathbf{n} = 0 \text{ on } \partial\Omega, \quad \tilde{\mathbf{g}}^t(0) = 0 \text{ in } \Omega$$

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and the initial conditions

$$\theta(0) = \theta_0, \quad \varphi(0) = \varphi_0, \quad \tilde{\mathbf{g}}^0(s) = \mathbf{f}_0(s) \quad s > 0 \text{ in } \Omega$$

In this setting, the history space is $L^2_{\mu}(\mathbb{R}, L^2(\Omega))$ endowed with the natural norm:

$$\|\tilde{\mathbf{g}}^t\|_{\mu}^2 = \frac{2}{k_0} \int_{\Omega} \Psi_{\mathrm{G}}(\tilde{\mathbf{g}}^t) \,\mathrm{d}v = \int_0^\infty \mu(s) \int_{\Omega} |\tilde{\mathbf{g}}^t|^2 \,\mathrm{d}v \,\mathrm{d}s$$

If r/θ is a known function of the position **x** only then well posedness leads to the existence of a continuous semigroup of solutions.

9.2. Evolution equations in the minimal-state space setting

We now regard the material state component, which accounts for the past history of **g** up to time t, as represented by a class of different but equivalent functions $\tilde{\mathbf{g}}^t$ which does not reduce to a singleton. Indeed, different summed history functions $\tilde{\mathbf{g}}^t$ are defined to be equivalent if they produce the same response function \mathbf{I}^t . As a consequence, \mathbf{I}^t is taken to represent all of the history functions in the same class, which realizes the minimal state representation. Hence, we write the constitutive equation (29) for **q**, in terms of $\mathbf{I}^t(0)$, **g** and θ , in the form

$$\mathbf{q}(t) = -k_0 \theta(t) [\mathbf{g}(t) - \mathbf{I}^t(0)]$$

and the free energy in the form (44). For later convenience, we observe that

$$\mathbf{I}^{t}(\tau) = \int_{0}^{\infty} h'(\tau + \xi) \tilde{\mathbf{g}}^{t}(\xi) \,\mathrm{d}\xi$$

satisfies the transport-like equation

$$\partial_t \mathbf{I}^t(\tau) = -h(\tau)\mathbf{g}(t) + \partial_\tau \mathbf{I}^t(\tau)$$

Unlike the previous case, we now cannot say that $\mathbf{I}^{t}(0) = 0$. Indeed,

$$\mathbf{I}^t(0) = -\mathbf{w}(\tilde{\mathbf{g}}^t)$$

provides \mathbf{w} in terms of the minimal state representation \mathbf{I}^t .

The free energy Ψ_I in (44) is a quadratic functional of $\partial_{\tau} \mathbf{I}^t$, not of \mathbf{I}^t . Hence, to set up a natural norm, we look at

$$\mathbf{J}^{t}(\tau) := \partial_{\tau} \mathbf{I}^{t}(\tau) = -\int_{0}^{\infty} \mu'(\tau + \xi) \tilde{\mathbf{g}}^{t}(\xi) \, \mathrm{d}\xi = \int_{0}^{\infty} \mu(\tau + \xi) \mathbf{g}^{t}(\xi) \, \mathrm{d}\xi$$

The free energy Ψ_I then takes the form

$$\Psi_{\mathbf{I}}(\mathbf{J}^t) = \frac{k_0}{2} \int_0^\infty [\mu(\tau)]^{-1} |\mathbf{J}^t(\tau)|^2 d\tau$$

The function \mathbf{J}^t satisfies the differential equation

$$\partial_t \mathbf{J}^t(\tau) = \mu(\tau) \mathbf{g}(t) + \partial_\tau \mathbf{J}^t(\tau)$$

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while

$$\mathbf{J}^{t}(0) = \int_{0}^{\infty} \mu(\xi) \mathbf{g}^{t}(\xi) \,\mathrm{d}\xi$$

Because

$$\mathbf{I}^{t}(0) = -\int_{0}^{\infty} \int_{0}^{\infty} \mu(s) \tilde{\mathbf{g}}^{t}(s) \, \mathrm{d}s = \int_{0}^{\infty} \int_{0}^{\infty} \mu'(\tau+s) \, \mathrm{d}\tau \, \tilde{\mathbf{g}}^{t}(s) \, \mathrm{d}s$$

and

$$\mathbf{I}^{t}(0) = -\mathbf{w}(\tilde{\mathbf{g}}^{t}) = -\int_{0}^{\infty} \mathbf{J}^{t}(\tau) \, \mathrm{d}\tau$$

it follows that the constitutive equation (28) for \mathbf{q} can be given the form

$$\mathbf{q}(t) = -k_0\theta(t) \left[\mathbf{g}(t) + \int_0^\infty \mathbf{J}^t(\tau) \,\mathrm{d}\tau \right]$$

A direct calculation provides

$$\dot{\psi}_{\mathrm{I}}(\mathbf{J}^{t}) = k_{0}\tilde{\mathbf{w}}(\mathbf{J}^{t}) \cdot \mathbf{g}(t) - \delta \Psi_{\mathrm{I}}(\mathbf{J}^{t}|\mathbf{g}^{t})$$

which is the analogue of (37). Indeed, provided $\mu' \leq 0$, $\mu > 0$, we find that

$$\delta \Psi_{\mathbf{I}}(\mathbf{J}^{t}|\mathbf{g}^{t}) = -\frac{k_{0}}{2} \int_{0}^{\infty} [\mu(\tau)]^{-2} \mu'(\tau) |\mathbf{J}^{t}(\tau)|^{2} \,\mathrm{d}\tau + \frac{1}{\mu(0)} \left[\int_{0}^{\infty} \mu(\xi) \mathbf{g}^{t}(\xi) \,\mathrm{d}\xi \right]^{2} \ge 0$$

and hence

$$\dot{\psi}_{\mathrm{I}}(\mathbf{J}^{t}) \leqslant k_{0} \tilde{\mathbf{w}}(\mathbf{J}^{t}) \cdot \mathbf{g}(t)$$

These relations allow us to state the evolution problem as follows.

Problem 3

The state of the material at time t is the triplet $(\theta(t), \varphi(t), \mathbf{J}^t)$. The state evolution is governed by the system of differential equations

$$\partial_t \left[c \ln \theta - \frac{1}{\theta_c} G(\varphi) \right] = k_0 \Delta \theta + k_0 \nabla \cdot \int_0^\infty \mathbf{J}^t(\tau) \, \mathrm{d}\tau + \frac{r}{\theta}$$
$$\gamma \partial_t \varphi + f(\varphi) + \frac{\theta}{\theta_c} g(\varphi) = v \Delta \varphi$$
$$\partial_t \mathbf{J}^t(\tau) = \mu(\tau) \nabla \theta(t) + \partial_\tau \mathbf{J}^t(\tau)$$

subject to the boundary conditions

$$\theta = \theta_{\partial \Omega}, \quad \nabla \varphi \cdot \mathbf{n} = 0 \quad \text{on } \partial \Omega$$

and the initial conditions

$$\theta(0) = \theta_0, \quad \varphi(0) = \varphi_0, \quad \mathbf{J}^0(s) = \mathbf{J}_0(s), \quad s > 0 \text{ in } \Omega$$

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Let $\zeta = 1/\mu$. In the present minimal-state setting, the underlying function space is $L^2_{\zeta}(\mathbb{R}^+, L^2(\Omega))$ endowed with the natural norm

$$\|\mathbf{J}^t\|_{\zeta}^2 = \frac{2}{k_0} \int_{\Omega} \Psi_{\mathbf{I}}(\mathbf{J}^t) \, \mathrm{d}v = \int_0^\infty \zeta(s) \int_{\Omega} |\mathbf{J}^t(s)|^2 \, \mathrm{d}v \, \mathrm{d}s$$

If the source term r/θ is a known function, independent of t, then well posedness leads to the existence of a continuous semigroup of solutions.

9.3. Stability

As remarked at the end of Section 8, it is convenient to prove stability with respect to the minimalstate space (Problem 3). To this end, we assume existence and uniqueness of the solution with positive temperature and enough regularity to guarantee the required *a priori* estimates. Well posedness of Problems 1-3 will be investigated in a future paper.

To investigate the stability of the solution to Problem 3 *via* standard methods, we need a more convenient formulation. First, we give evidence of the gradient form of the minimal-state variable J^t by means of the summed past history of the temperature,

$$\tilde{\theta}^t(\tau) = \int_0^\tau \theta(t-s) \,\mathrm{d}s$$

and the integral

$$j^{t}(\tau) = -\int_{0}^{\infty} \mu'(\tau+s)\tilde{\theta}^{t}(s) \,\mathrm{d}s = \int_{0}^{\infty} \mu(\tau+s)\theta^{t}(s) \,\mathrm{d}s$$

Hence,

$$\tilde{\mathbf{g}}^{t}(\tau) = \nabla \tilde{\theta}^{t}(\tau), \quad \mathbf{J}^{t}(\tau) = \nabla j^{t}(\tau)$$

To make the boundary conditions homogeneous, we consider the function $\theta_{\mathscr{H}} \in H^1(\Omega)$ subject to

$$\Delta \theta_{\mathscr{H}} = 0 \quad \text{in } \Omega$$
$$\theta_{\mathscr{H}} = \theta_{\partial \Omega} \quad \text{on } \partial \Omega$$

Let $\theta_{\partial\Omega}$ be time independent such that

$$\theta_{\partial\Omega} \in H^{1/2}(\partial\Omega) \cap L^{\infty}(\partial\Omega), \quad 0 < \theta_* \leq \theta_{\partial\Omega} \leq \theta^*$$

Hence, $\theta_{\mathscr{H}}$ satisfies the inequalities

$$\theta_* \leqslant \theta_{\mathscr{H}} \leqslant \theta^*$$
 a.e. in $\Omega \times (0, T)$ (55)

and

$$\|\theta_{\mathscr{H}}\|_{H^{1}(\Omega)} \leqslant c \|\theta_{\partial\Omega}\|_{H^{1/2}(\partial\Omega)}$$

The difference

$$u = \theta - \theta_{\mathscr{H}}$$

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satisfies a homogeneous Dirichlet boundary condition. Moreover, $\Delta u = \Delta \theta$ identically. Accordingly, we introduce the new variable:

$$\xi^{t}(\tau) = \int_{0}^{\infty} \mu(\tau + s)u^{t}(s) \,\mathrm{d}s = j^{t}(\tau) - h(\tau)\theta_{\mathscr{H}}, \quad h(\tau) = \int_{0}^{\infty} \mu(\tau + s) \,\mathrm{d}s$$

It is easy to check that ξ^t satisfies a homogeneous Dirichlet boundary condition and the identity $\Delta \xi^t = \Delta j^t$.

By means of the new scalar state variables $(u(t), \varphi(t), \xi^t)$, we can express Problem 3 by the evolution equations

$$\partial_t \left[c \ln(u + \theta_{\mathscr{H}}) - \frac{1}{\theta_c} G(\varphi) \right] = k_0 \Delta u + k_0 \nabla \cdot \int_0^\infty \nabla \xi^t(s) \, \mathrm{d}s + \frac{r}{u + \theta_{\mathscr{H}}} \tag{56}$$

$$\gamma \partial_t \varphi + f(\varphi) + \frac{u + \theta_{\mathscr{H}}}{\theta_c} g(\varphi) = v \Delta \varphi$$
(57)

$$\partial_t \xi^t(\tau) = \mu(\tau) u(t) + \partial_\tau \xi^t(\tau)$$
(58)

the homogeneous boundary conditions

$$u(t) = 0, \quad \nabla \varphi(t) \cdot \mathbf{n} = 0, \quad \xi^t = 0 \text{ on } \partial \Omega$$

and the initial conditions

$$u(0) = \theta_0 - \theta_{\mathscr{H}}, \quad \varphi(0) = \varphi_0, \quad \xi^0(\tau) = \xi_0(\tau), \quad \tau > 0 \text{ in } \Omega$$

Also in view of (41), the data are required to satisfy the following assumptions.

 $\begin{array}{l} H_1: \ c, \gamma, v, \theta_c, k_0 > 0; \\ H_2: \ \mu, \mu' \in L^1(\mathbb{R}^+), \mu > 0 \ \text{and} \ \mu' + \alpha \mu \leqslant 0 \ \text{a.e. in} \ \mathbb{R}^+; \\ H_3: \ \varphi_0 \in H^1(\Omega), 0 \leqslant \varphi_0 \leqslant 1 \ \text{a.e. in} \ \Omega, \ \theta_0 \in L^\infty(\Omega), \ \xi_0 \in L^2_{\zeta}(\mathbb{R}^+, H^1(\Omega)); \\ H_4: \ r \in L^1(\mathbb{R}^+, L^\infty(\Omega)); \\ H_5: \ \text{there exist two positive constants} \ \theta_* \ \text{and} \ \theta^* \ \text{such that} \ \theta_* \leqslant \theta_0 \leqslant \theta^*. \end{array}$

As usual, let $\|\cdot\|$ and $\langle\cdot,\cdot\rangle$ be the norm and the inner product of $L^2(\Omega)$. In addition, since $\zeta = 1/\mu$, let $\langle\cdot,\cdot\rangle_{\zeta}$ denote the inner product of $L^2_{\zeta}(\mathbb{R}^+, H^1(\Omega))$. Also, Ω is assumed to be bounded and $|\Omega|$ denotes the volume. Assume the existence of a unique solution $(u(t), \varphi(t), \zeta^t) \in L^1(\Omega) \times H^1(\Omega) \times L^2_{\zeta}(\mathbb{R}^+, H^1(\Omega))$ and take the energy norm of the system as

$$\mathscr{E}(t) = \|u\|_{L^{1}(\Omega)} + \|\varphi\|_{H^{1}(\Omega)}^{2} + \|\xi^{t}\|_{\zeta}^{2}$$

We now multiply (56), (57) by $u, \partial_t \varphi \in L^2(\Omega)$ and evaluate their inner products in $L^2(\Omega)$. Also, multiply (58) by $k_0\xi^t$ and evaluate the inner product in $L^2_{\zeta}(\mathbb{R}, H^1(\Omega))$. Summation and the

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observation that f = F', g = G' yield

$$\gamma \|\partial_t \varphi\|^2 + k_0 \|\nabla u\|^2 + c \langle \partial_t \theta, 1 \rangle - c \langle \partial_t \ln \theta, \theta \mathscr{H} \rangle + \langle \partial_t F(\varphi), 1 \rangle + v \langle \nabla \varphi, \partial_t \nabla \varphi \rangle + \frac{1}{\theta_c} \langle \partial_t G(\varphi), \theta_{\mathscr{H}} \rangle + k_0 \langle \xi^t, \partial_t \xi^t \rangle_{\zeta} = k_0 \langle \partial_\tau \xi^t, \xi^t \rangle_{\zeta} + \langle r, 1 \rangle - \left\langle r, \frac{\theta_{\mathscr{H}}}{\theta} \right\rangle$$
(59)

Since

$$\langle \partial_{\tau} \xi^{t}, \xi^{t} \rangle_{\zeta} = -\frac{1}{2} \int_{0}^{\infty} \zeta'(\tau) \|\nabla \xi^{t}(\tau)\|^{2} \, \mathrm{d}\tau = \frac{1}{2} \int_{0}^{\infty} \frac{\mu'(\tau)}{\mu^{2}(\tau)} \|\nabla \xi^{t}(\tau)\|^{2} \, \mathrm{d}\tau \leqslant 0$$

by means of the properties H_1 and H_2 , we obtain the estimate

$$\partial_t (c\langle\theta,1\rangle - c\langle \ln\theta,\theta_{\mathscr{H}}\rangle + \langle F(\varphi),1\rangle + \frac{1}{\theta_c} \langle G(\varphi),\theta_{\mathscr{H}}\rangle + \frac{\nu}{2} \|\nabla\varphi\|^2 + \frac{k_0}{2} \|\xi^t\|_{\zeta}^2) \leqslant \left\langle r,1 - \frac{\theta_{\mathscr{H}}}{\theta} \right\rangle \tag{60}$$

In view of (18) for F and G, we consider the functions

$$\begin{split} \Phi_0(t) &= c \|\theta\|_{L^1(\Omega)} + 3L \|\varphi\|_{L^4(\Omega)}^4 + \frac{v}{2} \|\nabla\varphi\|^2 + \frac{k_0}{2} \|\xi^t\|_{\zeta}^2 \\ \Phi_1(t) &= L \int_{\Omega} \left[3\varphi^4 - 4\left(1 + \frac{2\theta_{\mathscr{H}}}{\theta_c}\right)\varphi^3 + \alpha_1 \right] \mathrm{d}v \\ \Phi_2(t) &= c \int_{\Omega} (\alpha_2 - \theta_{\mathscr{H}} \ln \theta) \,\mathrm{d}v \end{split}$$

where α_1, α_2 are positive constants. By (60) the function

$$\Phi(t) = \Phi_0(t) + \Phi_1(t) + \Phi_2(t)$$

satisfies

$$\dot{\Phi}(t) \leqslant \left\langle r, \frac{\theta - \theta_{\mathscr{H}}}{\theta} \right\rangle$$
 (61)

Incidentally, if r = 0 we have $\dot{\Phi}(t) \leq 0$ and hence $\Phi(t) \leq \Phi(0)$.

We now assume that the initial value θ_0 allows the temperature $\theta(t)$ to remain close to $\theta_{\mathscr{H}}$ in Ω for all times. This assumption is reasonable because $\theta(t) = \theta_{\mathscr{H}}$ on $\partial\Omega$ for all t>0. As a consequence, we make the approximation

$$\left\langle \frac{r}{\theta}, \theta - \theta_{\mathscr{H}} \right\rangle \simeq \left\langle \frac{r}{\theta_{\mathscr{H}}}, \theta - \theta_{\mathscr{H}} \right\rangle$$

Moreover, by means of (55) we can establish the estimate

$$\left\langle \frac{r}{\theta_{\mathscr{H}}}, \theta - \theta_{\mathscr{H}} \right\rangle \leqslant \frac{1}{\theta_{*}} \|r(t)\|_{L^{\infty}(\Omega)} [\|\theta(t)\|_{L^{1}(\Omega)} + \theta^{*}|\Omega|] \leqslant \rho(t) [\Phi_{0}(t) + C]$$

where

$$C = c\theta^* |\Omega|, \quad \rho = \frac{1}{c\theta_*} ||r||_{L^{\infty}(\Omega)} \in L^1(\mathbb{R}^+)$$

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Hence, by (61) we have

$$\Phi(t) \leqslant \rho(t) [\Phi_0(t) + C] \tag{62}$$

To establish the boundedness of Φ_0 , we need a relation between Φ and Φ_0 . Provided we let α_1 be sufficiently large and α_0 be sufficiently small, we can write

$$\int_{\Omega} \left[3\varphi^4 - 4\left(1 + \frac{2\theta_{\mathscr{H}}}{\theta_c}\right)\varphi^3 + \alpha_1 \right] \mathrm{d}v \geq 3\alpha_0 \int_{\Omega} \frac{\theta_{\mathscr{H}}}{\theta_c} \varphi^2(\varphi^2 + 2) \,\mathrm{d}v > 0$$

Moreover, the inequality $\ln \theta \leq \sqrt{\theta}$ and the bounds (55) imply that, for a sufficiently large α_2 and a sufficiently small $c_0 < 1$,

$$\int_{\Omega} (\theta - \theta_{\mathscr{H}} \ln \theta + \alpha_2) \, \mathrm{d}v \ge \int_{\Omega} (\theta - \theta^* \sqrt{\theta} + \alpha_2) \, \mathrm{d}v \ge c_0 \int_{\Omega} \theta \, \mathrm{d}v$$

Collecting these results, we can write

$$\Phi \ge \Phi_0 + \Phi_2 \ge c_0 c \|\theta\|_{L^1(\Omega)} + 3L \|\varphi\|_{L^4(\Omega)}^4 + \frac{v}{2} \|\nabla\varphi\|^2$$

Hence, Φ is positive valued and satisfies

$$c_0\Phi_0 \leqslant \Phi \leqslant c_1\Phi_0 + c_2$$

for some positive constants c_1, c_2 . As a consequence, by Gronwall's lemma (62) implies that

$$\Phi(t) \leq M_1 \Phi(0) + M_2$$

where

$$M_1 = \exp(m/c_0), \quad M_2 = \exp(Cm), \quad m = \int_0^\infty \rho(t) \, dt$$

Since

$$\|\varphi\| \leq |\Omega|^{1/4} \|\varphi\|_{L^4(\Omega)}, \quad \|u(t)\|_{L^1(\Omega)} \leq \|\theta\|_{L^1(\Omega)} + \|\theta_{\mathscr{H}}\|_{L^1(\Omega)}$$

the boundedness of $\Phi_0(t)$ implies that of the energy norm $\mathscr{E}(t)$. This concludes the proof of the stability of the solution to (56)–(58) relative to the norm $\mathscr{E}(t)$.

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